

RHODIUM-CATALYSED [2+2+2] CYCLOADDITION REACTIONS FOR THE PREPARATION OF HIGHLY FUNCTIONALISED CYCLIC COMPOUNDS

Daniel Cassú Ponsatí

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Doctoral Thesis

**Rhodium-catalysed [2+2+2] cycloaddition
reactions for the preparation of highly
functionalised cyclic compounds**

Daniel Cassú Ponsatí

2018

Doctoral Programme in Chemistry

Supervised by: Prof. Anna Roglans Ribas, Prof. Miquel Solà Puig and
Dr. Anna Pla Quintana

Tutor: Prof. Anna Roglans Ribas

Presented in partial fulfilment of the requirements for a **doctoral
degree** from the **Universitat de Girona**



Prof. Anna Roglans Ribas, Prof. Miquel Solà Puig and Dr. Anna Pla Quintana, from the Universitat de Girona,

WE DECLARE:

That the thesis entitled “Rhodium-catalysed [2+2+2] cycloaddition reactions for the preparation of highly functionalised cyclic compounds” presented by **Daniel Cassú Ponsatí** to obtain the doctoral degree has been completed under our supervision.

For all intents and purposes, we hereby sign this document.

Prof. Anna Roglans Ribas

Prof. Miquel Solà Puig

Dr. Anna Pla Quintana

Girona, 8th of January, 2018

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PUBLICATIONS

This doctoral thesis has resulted in the following publication:

- Rhodium-catalyzed [2+2+2] cycloaddition reactions of linear allene-ene-ynes to afford fused tricyclic scaffolds: Insights into the mechanism. Cassú, D.; Parella, T.; Solà, M.; Pla-Quintana, A.; Roglans, A. *Chem. Eur. J.* **2017**, 23, 14889.

Contributions in other publications not included in this thesis:

- A new mild synthetic route to *N*-arylated pyridazinones from aryldiazonium salts. El Bakouri, O.; Cassú, D.; Solà, M.; Parella, T.; Pla-Quintana, A.; Roglans, A. *Chem. Commun.* **2014**, 50, 8073.

ABBREVIATIONS

Å	Angstrom
a.u.	atomic units
Ac	acetyl
AcOEt	ethyl acetate
anh.	anhydrous
Ar	aryl
ATR	Attenuated Total Reflectance
B3LYP	Becke, three parameter, Lee-Yang-Parr method
Bn	benzyl
BO	Born-Oppenheimer
Boc	<i>tert</i> -butyloxycarbonyl
Bu	butyl
Bz	benzoyl
cc-pVDZ	correlation consistent polarized valence-only double-zeta basis set
cc-pVTZ	correlation consistent polarized valence-only triple-zeta basis set
CID	Collision-Induced Dissociation
CNT	Carbon Nanotube
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethyl- η^5 -cyclopentadienyl
Cy	cyclohexyl
d.r.	diastereoisomeric ratio
DCE	1,2-dichloroethane
DFT	Density Functional Theory
E.A.	Elemental analysis
ECP	Effective Core Potentials
ee	enantiomeric excess
eq.	equivalent
ESI	Electrospray Ionization
Et	ethyl
EtOH	ethanol
FLCC	Finite-Length Clar Cells

FT	Fourier Transform
g	grams
GGA	Generalized Gradient Approximation
GTO	Gaussian-Type Orbitals
h	hours
Hex	hexyl
HF	Hartree-Fock
HK	Hohenberg-Kohn
HOMO	Highest Occupied Molecular Orbital
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
Ind	Indenyl
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
<i>i</i> Pr	<i>iso</i> -propyl
IR	Infrared spectroscopy
K	Kelvin degrees
kcal	Kilocalories
KS	Kohn-Sham
L	ligand
LCAO	Linear Combination of Atomic Orbitals
LDA	Local Density Approximation
lit.	literature
LSD	Local Spin Density
LUMO	Lowest Unoccupied Molecular Orbital
<i>m</i>	meta
M	molar
m.p.	melting point
<i>m/z</i>	mass to charge ratio
mCPBA	<i>meta</i> -chloroperoxybenzoic acid
Me	methyl
mg	milligrams
min.	minutes
mL	milliliter
mol%	molar percentage
MOM	methoxymethyl
MS	Mass Spectrometry

Ms	mesyl, methanesulfonyl
MW	Molecular Weight
MWCNT	Multi-Walled Carbon Nanotube
NBO	Natural Bond Orbital
Ns	nosyl, 4-nitrobenzenesulfonyl
∅	diameter
<i>o</i>	ortho
°C	Celsius degrees
oct	octane
<i>p</i>	para
PCM	Polarized Continuum Model
PES	Potential Energy Surface
Ph	phenyl
PNSO	<i>N</i> -phosphino- <i>tert</i> -butylsulfonamide
PP	pseudopotential
PW86	Perdew and Wang method (1986)
Q-TOF	Quadrupole-Time-of-Flight
R.T.	room temperature
<i>rac</i>	racemic
SCF	Self-Consistent Field
STO	Slater-Type Orbitals
SWCNT	Single-Walled Carbon Nanotube
T	temperature
TBS	<i>tert</i> -butyldimethylsilyl
^t Bu	<i>tert</i> -butyl
Tf	triflate, trifluoromethylsulfonyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	tetramethylsilane
Tol	tolyl
Tripp	2,4,6-triisopropylphenyl
Ts	tosyl, 4-methylphenylsulfonyl
TS	Transition State
ZPE	Zero-Point Energy
ΔE	Relative electronic energy
ΔG	Relative Gibbs free energy

μW

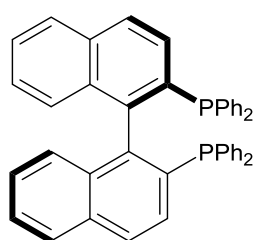
microwave

Abbreviations used in Nuclear Magnetic Resonance (NMR)

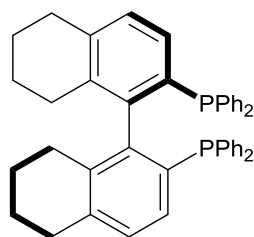
^{13}C NMR	13-Carbon Nuclear Magnetic Resonance
^1H NMR	Proton Nuclear Magnetic Resonance
^1H - ^{13}C HMBC	Proton-13-Carbon Heteronuclear Multiple-Bond Correlation Spectroscopy
^1H - ^{13}C HSQC	Proton-13-Carbon Heteronuclear Single-Quantum Correlation Spectroscopy
^1H - ^1H COSY	Proton-Proton Correlation Spectroscopy
^1H - ^{31}P HMBC	Proton-31-Phosphorous Heteronuclear Multiple-Bond Correlation Spectroscopy
$^{31}\text{P}\{^1\text{H}\}$ NMR	Proton decoupled 31-Phosphorous Nuclear Magnetic Resonance
ba	broad band
CDCl_3	deuterated chloroform
d	doublet
dd	double doublet
DOSY	Diffusion-Ordered Spectroscopy
dq	double quartet
hept.	heptuplet
Hz	Hertz
J	coupling constant
m	multiplet
MHz	Mega-Hertz
NOESY	Nuclear Overhauser Effect Spectroscopy
ppm	parts per million
q	quadruplet
qd	quadruple doublet
qt	quadruple triplet
quint.	quintuplet
s	singlet
t	triplet
td	triple doublet
Toluene- D_8	deuterated toluene
δ	chemical shift (units: ppm)

Biphosphines

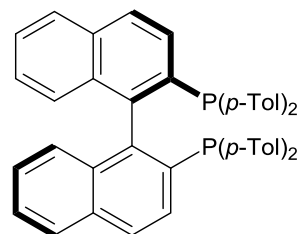
binap	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Biphep	2,2'-bis(diphenylphosphino)biphenyl
dppe	1,2-bis(diphenylphosphino)ethane
DTBM-SegPhos	5,5'-bis[di(3,5-di- <i>tert</i> -butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole
H ₈ -binap	2,2'-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl
SegPhos	5,5'-bis(diphenylphosphine)-4,4'-bi-1,3-benzodioxole
Tol-binap	2,2'-bis(di- <i>para</i> -tolylphosphino)-1,1'-binaphthyl



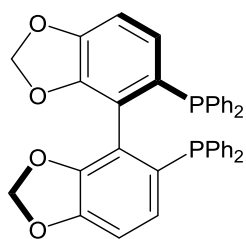
(*R*)-BINAP



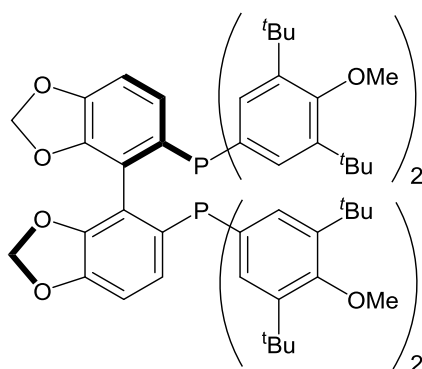
(*R*)-H₈-BINAP



(*R*)-tol-BINAP



(*R*)-SegPhos



(*R*)-DTBM-SegPhos

GRAPHICAL SUMMARY

Summary (Page 1)

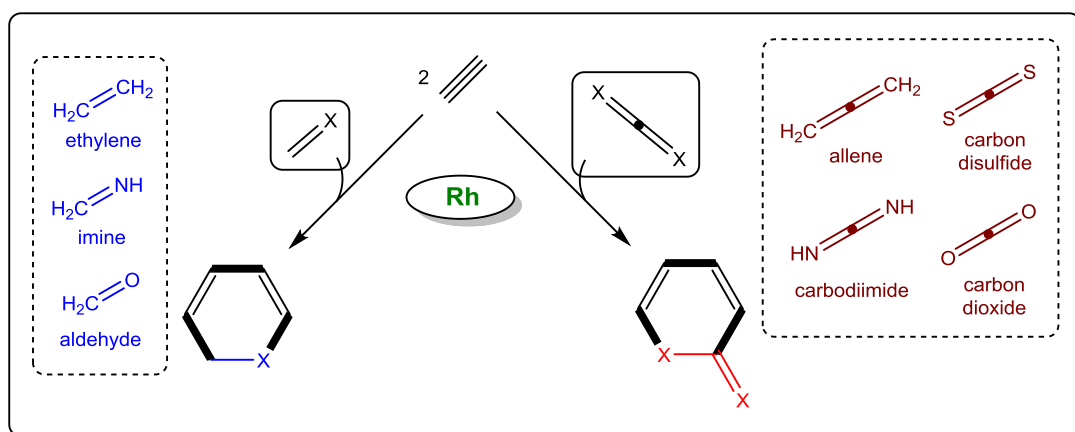
Resumen (Page 2)

Resum (Page 3)

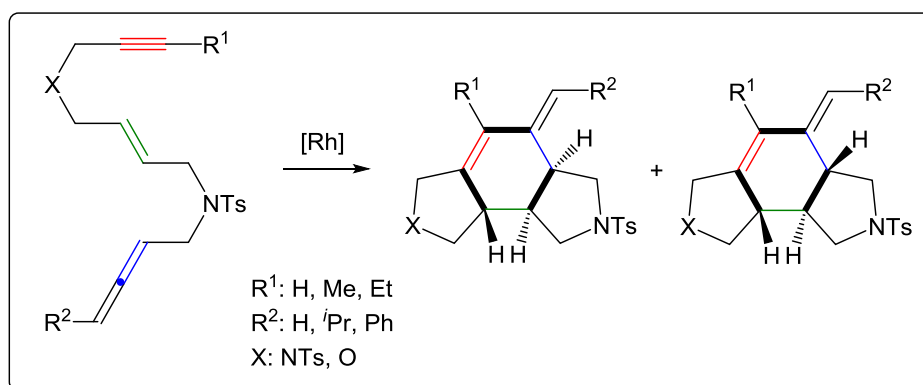
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Chapter 2. General objectives (Page 43)

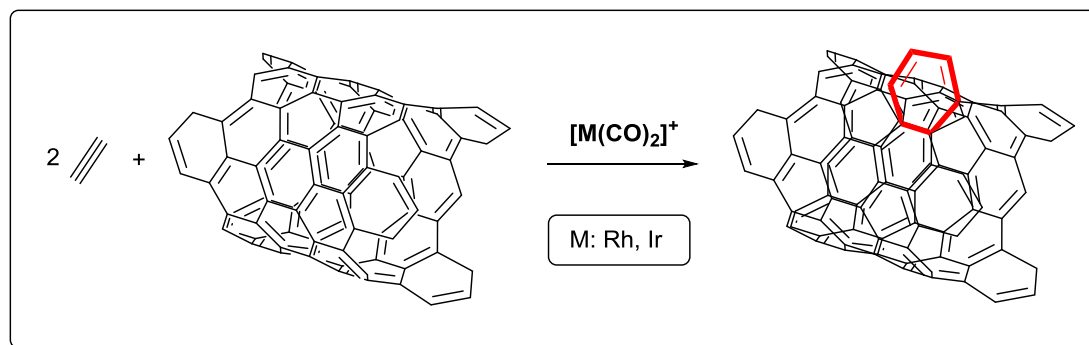
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(Page 123)



Chapter 6. General conclusions (Page 153)

Chapter 7. Methods (Page 157)

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SUPPLEMENTARY DATA

The material listed below is attached as supplementary data on the CD included in this thesis:

- **Thesis:** Memory of the thesis (thesis.pdf)
- **Chapter 3:**

XYZ coordinates of the catalytic intermediates found by DFT calculations (annex 1.pdf)
- **Chapter 4:**

Spectra for the synthetic intermediates, allene-ene-yne substrates, cycloisomerised products and detected catalytic intermediates (annex2.pdf)

XYZ coordinates of the catalytic intermediates found by DFT calculations (annex 3.pdf)
- **Chapter 5:**

XYZ coordinates of the catalytic intermediates found by DFT calculations (annex 4.pdf)
- **Publication:** publication resulting from this thesis (publication_chapter4.pdf)

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Summary

Transition metal-catalysed [2+2+2] cycloaddition reactions of unsaturated substrates represent one of the most elegant and versatile methods in organic chemistry for the preparation of highly functionalised cyclic compounds. In these processes three carbon-carbon or carbon-heteroatom bonds are generated in a single reaction step in a high atom economy process.

One of the objectives of our research group is the development of transition metal-catalysed cycloadditions, especially using rhodium catalysts, to obtain highly functionalised polycyclic systems which would be difficult to obtain through other synthetic routes. In this respect, this doctoral thesis, which is divided in seven chapters, is aimed to provide with a deeper insight into the versatility of transition metal-catalysed [2+2+2] cycloaddition reactions and, at the same time, to better understand the mechanistic principles that govern these processes.

Chapter 1 of this thesis contains a general introduction to the reactivity of several unsaturations that can serve as substrate partners to perform [2+2+2] cycloaddition reactions, making reference to the main examples found in the literature. Chapter 2 sets out the general objectives of the present thesis. In Chapter 3, the efficiency of several rhodium-based catalysts is evaluated, from the theoretical point of view, to perform the [2+2+2] cycloaddition of two acetylenes and various $C(sp^2)$ unsaturations, at the time that the main aspects of each mechanistic route are analysed. Chapter 4 focuses on the study of the reactivity of lineal allene-ene-yne substrates in totally intramolecular rhodium-catalysed [2+2+2] cycloaddition both from the experimental and theoretical perspectives. In Chapter 5, the feasibility of the transition metal-catalysed [2+2+2] cycloaddition reaction involving single-walled carbon nanotubes is computationally evaluated. Chapter 6 draws the general conclusions extracted from the results of these studies. Finally, Chapter 7 contains the experimental procedures, the characterisation data and an explanation of the theoretical bases employed to perform the computational calculations.

Resumen

Las reacciones de cicloadición [2+2+2] de sustratos insaturados catalizadas por metales de transición representan uno de los métodos más elegantes y versátiles en química orgánica para la preparación de compuestos cíclicos altamente funcionalizados. En los susodichos procesos se generan tres enlaces carbono-carbono o carbono-heteroátomo en un solo paso de reacción y en un proceso de elevada economía atómica.

Uno de los objetivos de nuestro grupo de investigación es el desarrollo de cicloadiciones catalizadas por metales de transición, especialmente usando catalizadores de rodio, para obtener sistemas policíclicos altamente funcionalizados que serían difíciles de obtener mediante otras rutas sintéticas. En este sentido, la presente tesis doctoral, la cual se encuentra dividida en siete capítulos, pretende lograr un mejor entendimiento sobre la versatilidad de las reacciones de cicloadición [2+2+2] catalizadas por metales de transición y, asimismo, comprender mejor los principios mecanísticos que gobiernan estos procesos.

El Capítulo 1 de esta tesis contiene una introducción general sobre la reactividad de varias insaturaciones que pueden ser empleadas como sustratos para llevar a cabo reacciones de cicloadición [2+2+2], haciendo referencia a los principales ejemplos hallados en la bibliografía. El Capítulo 2 presenta los objetivos generales de la tesis. En el Capítulo 3, se evalúa, desde el punto de vista teórico, la eficacia de varios catalizadores de rodio para producir la cicloadición [2+2+2] de dos acetilenos con varias insaturaciones C(sp²), al mismo tiempo que se analizan los principales aspectos de cada ruta mecanística. El Capítulo 4 se centra en el estudio de la reactividad de sustratos lineales aleno-alqueno-alquino en cicloadiciones [2+2+2] intramolecular catalizadas por rodio, tanto desde el punto de vista experimental como teórico. En el Capítulo 5, se estudia la viabilidad de la reacción de cicloadición [2+2+2] al involucrar nanotubos de carbono monocapa. El Capítulo 6 detalla las conclusiones generales extraídas a partir de los resultados de estos estudios. Finalmente, el Capítulo 7 contiene los procedimientos experimentales, los datos de caracterización y una descripción de los fundamentos teóricos empleados para llevar a cabo los cálculos computacionales.

Resum

Les reaccions de cicloadició [2+2+2] de substrats insaturats catalitzades per metalls de transició representen un dels mètodes més elegants i versàtils en química orgànica per a la preparació de compostos cíclics altament funcionalitzats. En els processos esmentats es generen tres enllaços carboni-carboni o carboni-heteroàtom en un sol pas de reacció i en un procés d'elevada economia atòmica.

Un dels objectius del nostre grup d'investigació és el desenvolupament de cicloadicions catalitzades per metalls de transició, especialment utilitzant catalitzadors de rodi, per tal d'obtenir sistemes policíclics altament funcionalitzats que serien difícils d'obtenir mitjançant altres rutes sintètiques. En aquest sentit, la present tesi doctoral, la qual es troba dividida en set capítols, pretén aconseguir una millor comprensió sobre la versatilitat de les reaccions de cicloadició [2+2+2] catalitzades per metalls de transició i, així mateix, comprendre millor els principis mecanístics que governen aquests processos.

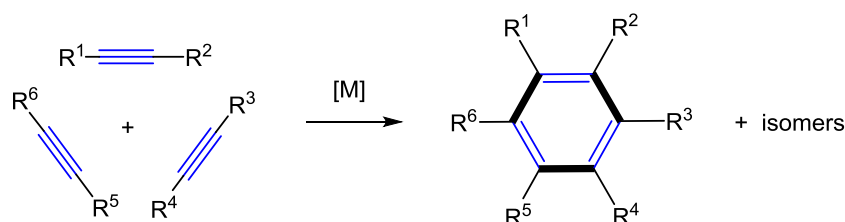
El Capítol 1 d'aquesta tesi conté una introducció general sobre la reactivitat de diverses insaturacions que poden ser usades com a substrats per dur a terme reaccions de cicloadició [2+2+2], tot fent referència als principals exemples trobats a la bibliografia. El Capítol 2 presenta els objectius generals de la tesi. En el Capítol 3, s'evalua, des d'un punt de vista teòric, l'eficàcia de diversos catalitzadors de rodi per produir la cicloadició [2+2+2] de dos acetilens amb diverses insaturacions C(sp²), al mateix temps que s'analitzen els principals aspectes de cada ruta mecanística. El Capítol 4 se centra en l'estudi de la reactivitat de substrats lineals al·lè-alquè-alquí en cicloadicions [2+2+2] intramolecular catalitzades per rodi, tant des del punt de vista experimental com teòric. En el Capítol 5, s'estudia la viabilitat de la reacció de cicloadició [2+2+2] al involucrar nanotubs de carboni monocapa. El Capítol 6 detalla les conclusions generals extretes a partir dels resultats d'aquests estudis. Finalment, el Capítol 7 conté els procediments experimentals, les dades de caracterització i una descripció sobre els fonaments teòrics utilitzats per dur a terme els càlculs computacionals.

Chapter 1. General introduction

1.1. Transition metal-catalysed [2+2+2] cycloaddition reactions

The development of new chemical processes and efficient catalysts to allow the formation of carbon-carbon bonds is an important topic in organic chemistry. More specifically, the use of simple precursors to attain cyclic systems bearing high structural complexity is of great importance. One of these processes is the metal-catalysed [2+2+2] cycloaddition reaction, in which a wide variety of six-membered carbon and heterocyclic compounds with different functionalities can be prepared.

In 1948, Reppe and Schweckendiek¹ described the first transition metal-catalysed version of this process. This consisted in the use of alkynes to obtain substituted benzene derivatives under nickel catalysis. Nowadays, this reaction represents one of the most elegant methods for the construction of six-membered rings, as three carbon-carbon bonds are generated in a single reaction step through an atom economy process (**Scheme 1**).



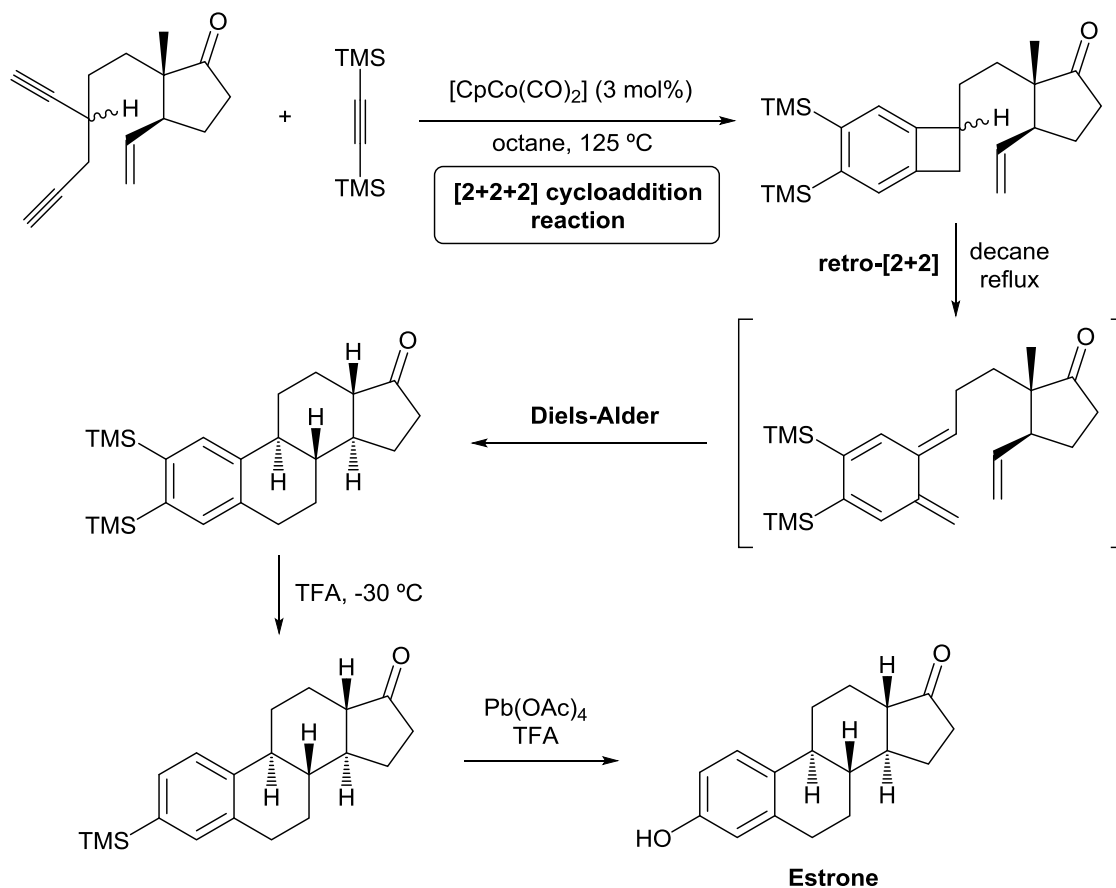
Scheme 1. Transition metal-catalysed [2+2+2] cycloaddition reaction of three alkynes

Since this first study, many cases involving alkyne cycloaddition catalysed by different transition metals have been reported. The most commonly used metals are Ni, Co, Pd, Rh, Ru, Zr and Ir.² Over the last few years, this reaction, which originally demanded stoichiometric amounts of the transition metal and extreme reaction conditions, has become a highly efficient catalytic process which can be carried out under mild conditions requiring only low catalytic loads.

Due to the high structural complexity that can be attained in a single reaction step, [2+2+2] cycloaddition reactions have been used as a straightforward strategy to prepare natural products. Some of the most relevant synthesis involving the assembly of benzenes through the reaction of three alkynes are shown below.

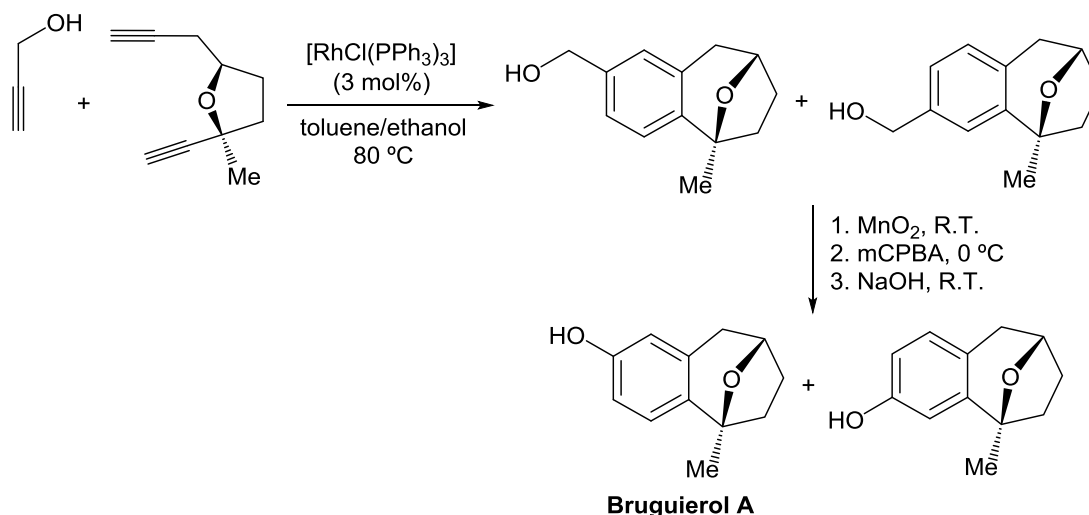
An example of the potential of [2+2+2] cycloaddition reactions was reported by Vollhardt and co-workers in 1977,³ who managed to prepare Estrone by means of this process. Their work consisted in performing a partially intermolecular [2+2+2] cycloaddition, using a cobalt catalyst to generate a benzocyclobutane, which could

undergo a subsequent 4π electrocyclic ring opening to afford a diene through a retro-[2+2] process. Later on, a Diels-Alder reaction was performed with the tethered alkene. The last steps of the synthesis entailed the removal of the TMS groups under acidic conditions. Remarkably, this transformation took place in a single synthetic manipulation (**Scheme 2**).



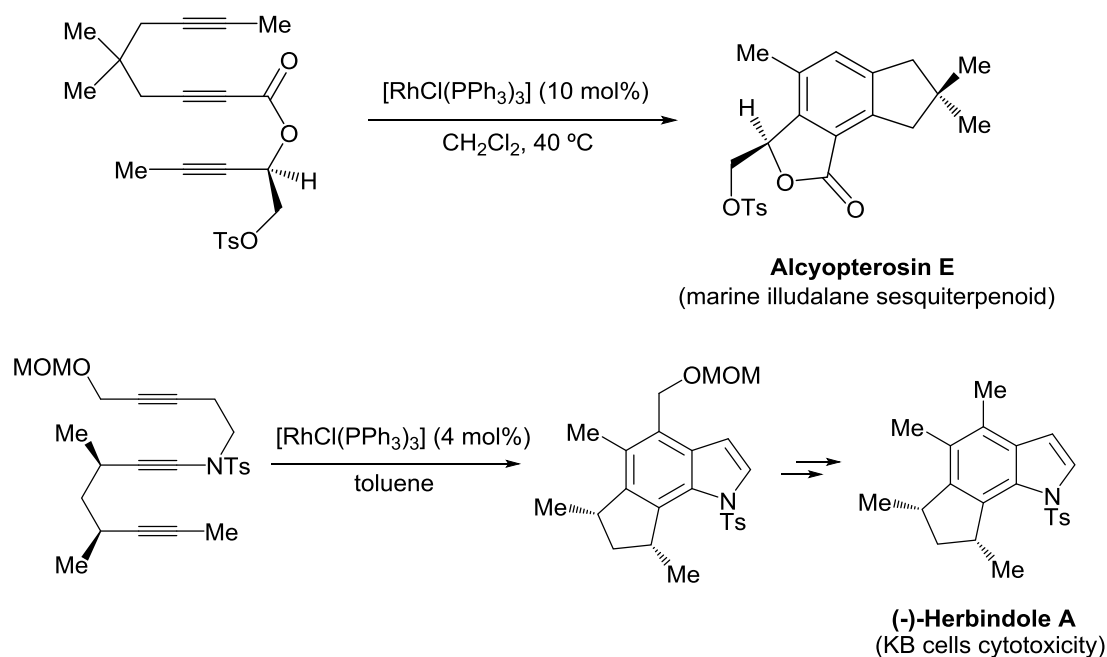
Scheme 2. Vollhardt's synthesis of Estrone based on a $[2+2+2]$ cycloaddition reaction

A more recent work related to the preparation of natural products is the synthesis of Bruguierol A, which can act against gram-positive and gram-negative bacteria. Following a partially intermolecular approach, Ramana and co-workers⁴ performed a rhodium-catalysed $[2+2+2]$ cycloaddition reaction of a diyne with propargylic alcohol (**Scheme 3**). Since neither the diyne nor the alkyne was symmetrically substituted, two regioisomers were obtained. The resulting compounds were oxidized with MnO_2 to obtain a benzaldehyde group, which could later be turned into an ester group through a Baeyer-Villiger oxidation with mCPBA. Lastly, the addition of aqueous NaOH could finally lead to Bruguierol A by means of a saponification reaction.



Scheme 3. Synthesis of Bruguierol A by means of a rhodium-catalysed [2+2+2] cycloaddition reaction

In contrast to the previous partially intermolecular cases, totally intramolecular reactions allow an easier control of the chemo- and regioselectivity of the process. A particular case of intramolecular cycloadditions is the use of macrocyclic structures to efficiently build polycyclic systems, though the preparation of starting materials that possess the necessary substituents or functional groups at the desired positions can be quite complex. Our group has contributed to the development of [2+2+2] cycloaddition reactions on macrocycles.^{2g,5} On the other hand, completely intramolecular reactions on open-chain substrates have been used for the preparation of natural products.⁶ As an example of this, the synthesis of Alcyopterosin E⁷ and Herbindole A⁸ that make use of the Wilkinson's catalyst are shown below (**Scheme 4**).



Scheme 4. Synthesis of Alcyopterosin E and (-)-Herbindole A by totally intramolecular [2+2+2] cycloaddition reaction

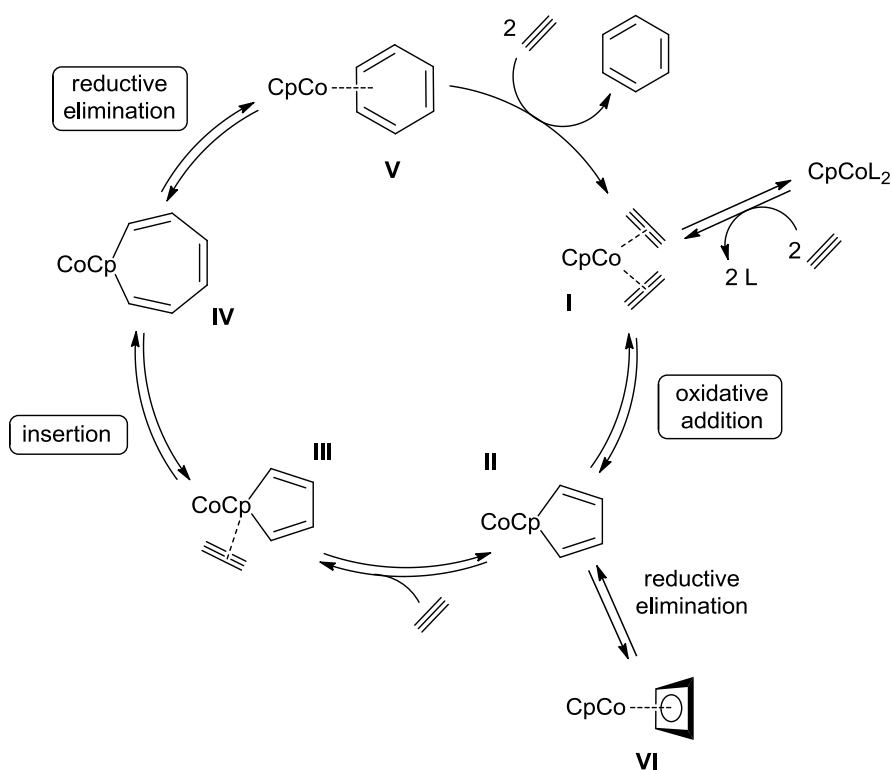
Aside from the applications that [2+2+2] cycloaddition reactions have, many other aspects related to them are worthy of study. These include the search for highly-active catalytic species, to broaden the type of unsaturated substrates that can participate in the cycloaddition and the control of the chemo- and regioselectivity, and at times the enantioselectivity. All these aspects can be tackled more efficiently if the mechanistic aspects that govern these processes are known in detail. Thanks to the advancements of computational chemistry, a deep understanding of the mechanistic rationale of the transition metal-catalysed [2+2+2] cycloaddition reaction has been achieved.⁹

The first attempt to fully rationalise the mechanism of the [2+2+2] cycloaddition reaction was reported by Albright and co-workers¹⁰ in 1999. More concretely, the whole mechanism for the trimerization of acetylene promoted by [CpCo]-based catalysts was explored by means of DFT calculations (**Scheme 5**).

The mechanistic proposal entails the initial generation of a coordination bisacetylene intermediate **I** from $[\text{CpCoL}_2]$ complex by undergoing a pair of ligand-substitution reactions. The oxidative addition of the two acetylenes affords cobaltacyclopentadiene **II**, which is unsaturated from the coordination point of view. This fact facilitates that a third acetylene unit coordinates to the cobalt centre, which gives rise to intermediate **III**. At this point, the coordinated acetylene can be inserted into a $\text{Co-C}(sp^2)$ σ -bond to give cobaltacycloheptatriene intermediate **IV** through the so-called Schore mechanism.¹¹

Finally, a reductive elimination process can yield η^4 -benzene complex **V**, which is able to release benzene and coordinate to a new pair of acetylene units to recover **I**, thus completing the catalytic cycle.

In their publication, the authors remarked the possibility that cobaltacyclopentadiene **II** suffers a secondary reaction in which η^4 -cyclobutadiene complex **VI** is generated through a reductive elimination process. Due to the high strength of the cobalt-cyclobutadiene binding, the stability of **VI** creates a thermodynamic trap and can therefore provoke the deactivation of the catalyst.



Scheme 5. Catalytic cycle for the cobalt-mediated [2+2+2] cycloaddition reaction of three acetylenes

On the basis of Albright's work, Koga's group¹² studied more rigorously the oxidative addition step by considering that singlet- and triplet-state intermediates can be both present along the catalytic pathway. They concluded that, when [CpCo]-based catalysts are involved, the most favourable pathway entails a spin state change along the reaction coordinate, thus leading to a cobaltacyclopentadiene intermediate that is more stable in triplet than in singlet state. These observations are in accordance with

the fact that 18-electron cobalt species usually exist as singlet states, while 16-electron species present triplet ground states.¹³

In the same study,^{12b} the authors also evaluated the regioselectivity of the oxidative addition step when mono- and disubstituted alkynes are involved. Their results showed that a higher stability is associated to the symmetry and steric hindrance of the intermediates (**Figure 1**). Furthermore, the analysis also revealed a clear influence of the electronic nature of the studied substituents on the energy barriers associated to the formation of the cobaltacyclopentadiene intermediates and on their stability. Such conclusion was extracted from the fact that the methyl group tends to destabilise and the methoxycarbonyl group to stabilise the structures with respect to the unsubstituted intermediate.

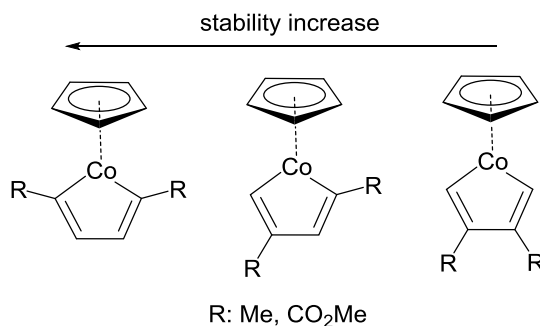
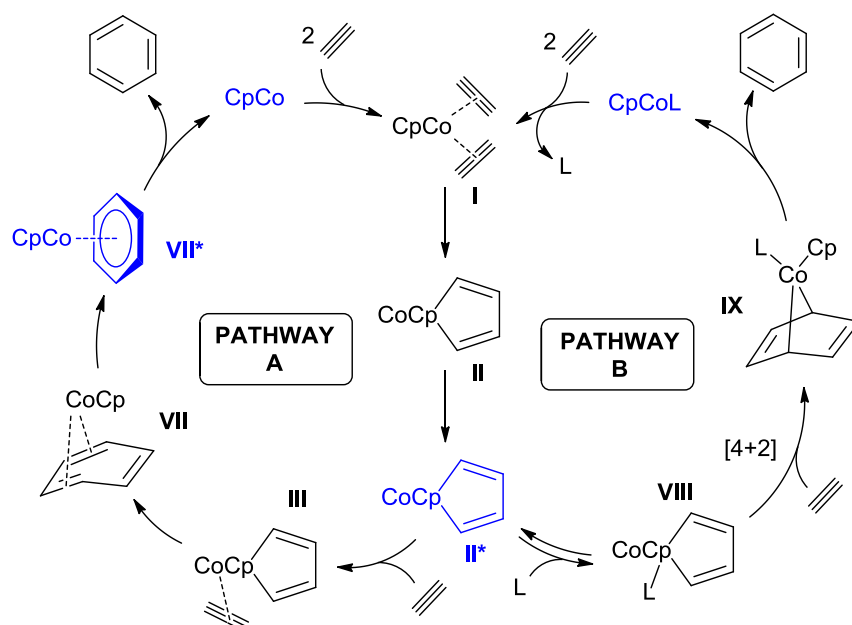


Figure 1. Stability increase of mono- and disubstituted cobaltacyclopentadiene intermediates

In a later work, Gandon, Vollhardt and co-workers¹⁴ reported another mechanistic study of the cyclotrimerisation of acetylenes catalysed by CpCo-based catalysts (**Scheme 6**). This study complemented the mechanistic proposal previously reported by Koga by taking into account key alternative intermediates. Their proposal begins with the oxidative addition on the bisacetylene complex **I** to form the cobaltacyclopentadiene intermediate **II**, which spontaneously relaxes to the triplet state (**II***). At this point, intermediate **II*** can coordinate to another acetylene unit, thus affording intermediate **III** preferably in the singlet state, and suffer a metal-assisted concerted [4+2] cycloaddition followed by a reductive elimination process. The resulting intermediate **VII** tends to turn into the excited form **VII*** and finally release benzene to close the catalytic cycle (pathway **A**). For this mechanism, and contrary to Koga's route in which the formation of cobaltacycloheptatriene was proposed, a [4+2] process was observed to take place more easily and thus generate norbornadiene intermediate **VII** instead.

These authors also studied the mechanism of the reaction in the presence of a strong σ -donor ligand (PR_3 , CO, THF, etc.) and involving electronically-poor alkynes. In this

case, cobaltacyclopentadiene **II*** preferably coordinates to one unit of such ligands and affords **VIII** species in the singlet state (pathway **B**). Intermediate **VIII** can undergo a [4+2] process by incorporating a third acetylene unit and yield the bicyclic complex **IX**. Contrary to pathway **A** where **VII** evolved to **VII***, **IX** species is more stable in the singlet state and can finally release benzene as the product by reductive elimination.



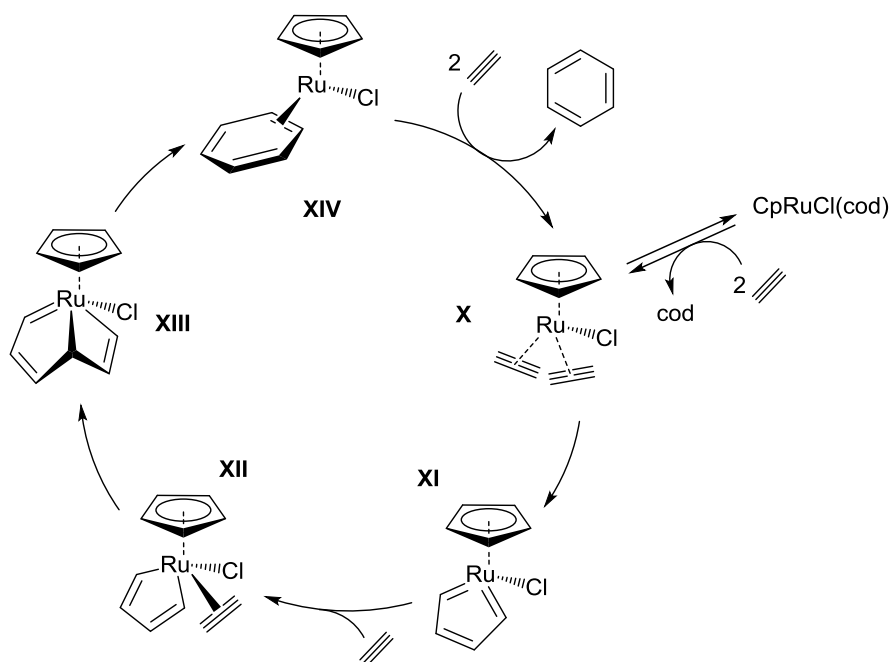
Scheme 6. Catalytic cycle for the cobalt-mediated [2+2+2] cycloaddition reaction of three alkynes. Singlet states are represented in black. Triplet states are represented in blue and marked with a *

The theoretical analysis of the mechanism has been extended to the use of other metals as well. Kirchner and co-workers¹⁵ studied, from the mechanistic point of view, the catalytic cycle of the [2+2+2] cycloaddition reaction of three acetylenes assisted by [CpRuCl]-based catalysts (**Scheme 7**).

The initial step of their proposal consists in the oxidative addition on the bisacetylene ruthenium complex **X**, which generates ruthenacyclopentatriene **XI**. Contrary to Albright's work in which a metallacyclopentadiene is proposed, the biscarbenic metallacyclopentatriene structure presented by Kirchner seems to be more accurate when looking at the bond distances that the optimised geometry displays.

Another remarkable difference with respect to Albright's work is found in the next step of the cycle, since the generation of ruthenabicyclo[3.2.0]heptatriene **XIII** is significantly more favourable than the insertion step to afford a ruthenacycloheptatriene. The reason for the preferential formation of species **XIII** is that no bonds are formally broken and the acetylene triple bond becomes weaker tending toward a double bond, which is

probably more feasible in this case for the higher metallic radius that ruthenium (1.33 Å) presents compared to cobalt (1.25 Å).

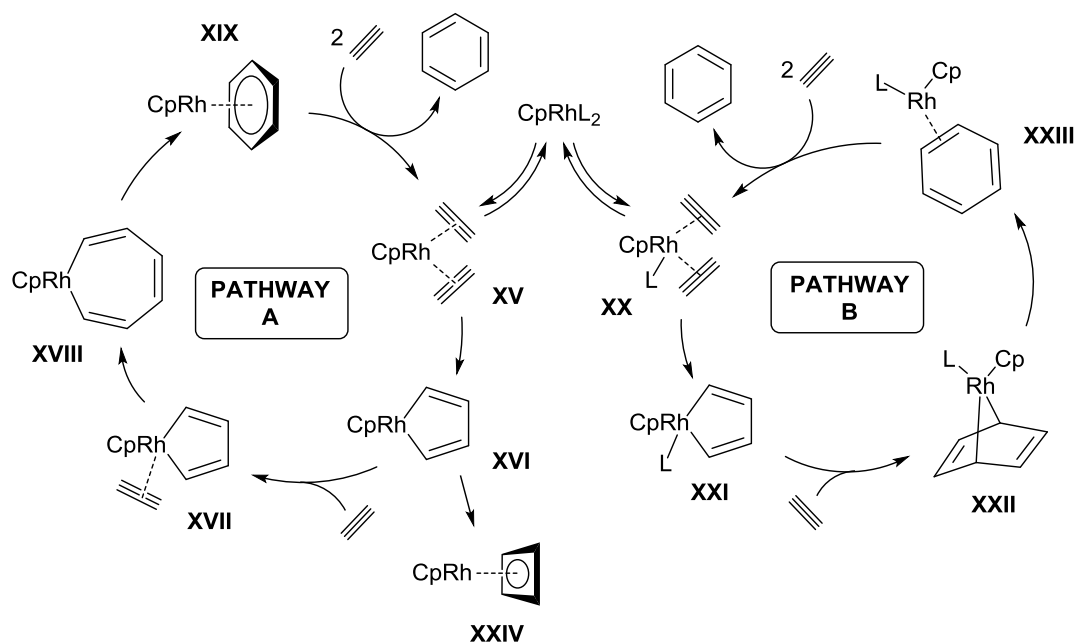


Scheme 7. Catalytic cycle for the ruthenium-mediated [2+2+2] cycloaddition reaction of three alkynes

Bickelhaupt and co-workers^{9f} reported the first work in which the mechanism of [2+2+2] cycloaddition reactions catalysed by rhodium complexes was studied. Their study consisted in the analysis of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}]$ -mediated cyclisation of three acetylenes to afford benzene (**Scheme 8**). Bickelhaupt's group found that the mechanism follows two different pathways depending on the presence or not of σ -donor ligands similarly to Gandon and Vollhardt's proposal, though the routes are not so energetically favourable when $[\text{CpRh}]$ -based catalyst is involved.

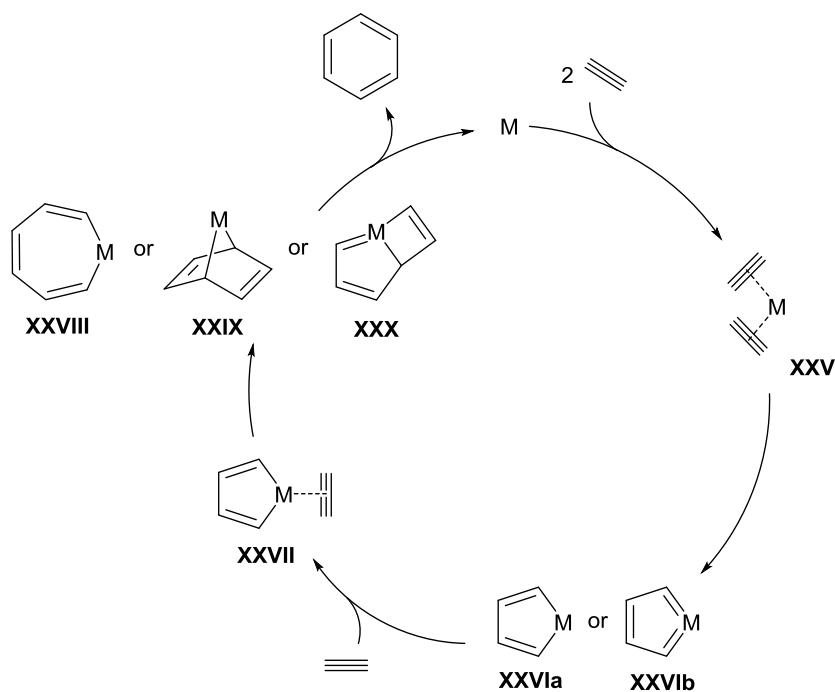
More concretely, the system in which no σ -donor ligands are involved (pathway **A**) entails the formation of rhodacycloheptatriene **XVIII** insertion intermediate following the analogous steps proposed by Albright and co-workers (**Scheme 5**). On the other hand, the presence of σ -donor ligands (pathway **B**) favours the system to evolve through the generation of norbornadiene intermediate **XXII** similarly to the one proposed by Gandon and Vollhardt's group (**Scheme 6**).

Bickelhaupt and co-workers concluded that the rate-determining step of the studied process resides on the oxidative addition step and that the electronic structure of the metal core influences more on the mechanistic stages of the $[\text{CpM}]$ -catalysed process than the size of the metal.



Scheme 8. Catalytic cycle for the rhodium-mediated [2+2+2] cycloaddition reaction of three alkynes

As a result of the theoretical works carried out, the mechanism of the transition metal-catalysed [2+2+2] cycloaddition reaction involving three alkynes can be generalised as **Scheme 9** depicts.



Scheme 9. Postulated general mechanism of the transition metal-catalysed [2+2+2] cycloaddition reaction involving three alkynes (M = transition metal catalyst)

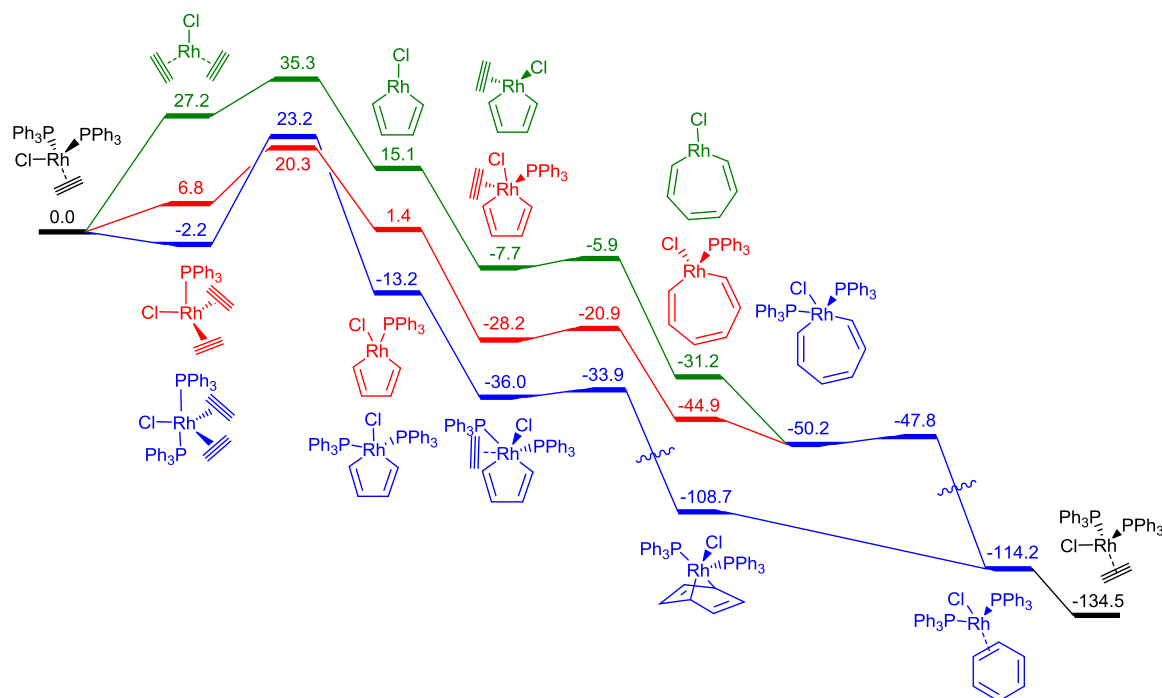
In a first step, the coordination of two alkyne partners to the metal takes place leading to species **XXV**. After that, the oxidative addition of the metal is generated, thus producing the metallacyclopentadiene **XXVIa** or the metallacyclopentatriene **XXVIb** with a biscarbene type structure (when $M = Ru$) in which the oxidation state of the metal becomes two units higher than its precursor **XXV**. This has been often established as the rate-determining step.^{9i-o} The subsequent coordination of the third alkyne to intermediates **XXVIa** or **XXVIb** results in the formation of metallacyclopentadiene(alkyne) **XXVII**, the generation of which has been experimentally confirmed by means of X-ray.¹⁶ The system can later proceed to either an alkyne insertion to form the metallacycloheptatriene **XXVIII** or by a metal-mediated [4+2] cycloaddition to afford the bicyclic complex **XXIX**, or by a formal [2+2] cycloaddition giving rise to metallabicyclo[3.2.0]heptatriene **XXX**. Finally, a ring closure through a reductive elimination of the metal occurs, thus yielding the benzene ring and allows the catalyst (M) to be recovered.

The whole process is highly exothermic as the thermodynamic driving force is provided by the new σ bonds formed and the aromaticity that is gained. Unlike the uncatalysed [2+2+2] cycloaddition of acetylenes, which presents a prohibitive energy barrier,¹⁷ the barriers for the transition metal-catalysed [2+2+2] cycloaddition are relatively low. This agrees with the fact that this reaction typically occurs under mild conditions.

Given the extensive use of $[RhCl(PPh_3)_3]$ complex from the synthetic perspective, our group has deeply analysed its catalytic activity to promote [2+2+2] cycloaddition reactions and has also analysed the mechanistic particularities of the reactions catalysed with this complex. To attain such goal, several theoretical and mechanistic studies have been undertaken in our group to postulate the mechanistic pathways through which the system can evolve.

With the aim of contributing to the understanding of the mechanism of the [2+2+2] cycloaddition of acetylenes, the most favourable pathways were unravelled when $[RhCl(PPh_3)_3]$ catalyst is employed by performing DFT calculations.^{9m} The analysis entailed the evaluation of reaction pathways bearing two, one or no triphenylphosphine ligands coordinated to the rhodium centre. As a result of that, a complete overview of the potential energy surface could be obtained (**Scheme 10**), which shows that the most favourable pathway is featured by the presence of two triphenylphosphine ligands, whereas the presence of only one or no triphenylphosphine is associated to less stable intermediates. Furthermore, the rate-determining step was observed to be the oxidative addition in the three cases.

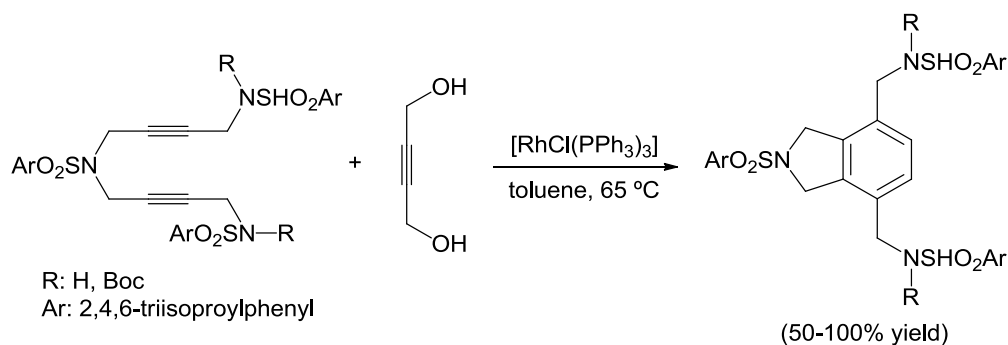
Remarkably, when two triphenylphosphine ligands are coordinated to the metal, a [4+2] process is more likely to produce a norbornadiene intermediate, similar to the one proposed by Gandon and Vollhardt (**Scheme 6**), whereas the presence of only one or no phosphines provokes that the system preferably evolves through an insertion step, as proposed by Albright's group (**Scheme 5**).



Scheme 10. Gibbs free energy profile (kcal·mol⁻¹) at 298K for the [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition of acetylenes. Intermediates with two PPh₃ ligands are represented in blue, with one PPh₃ in red and with none in green.

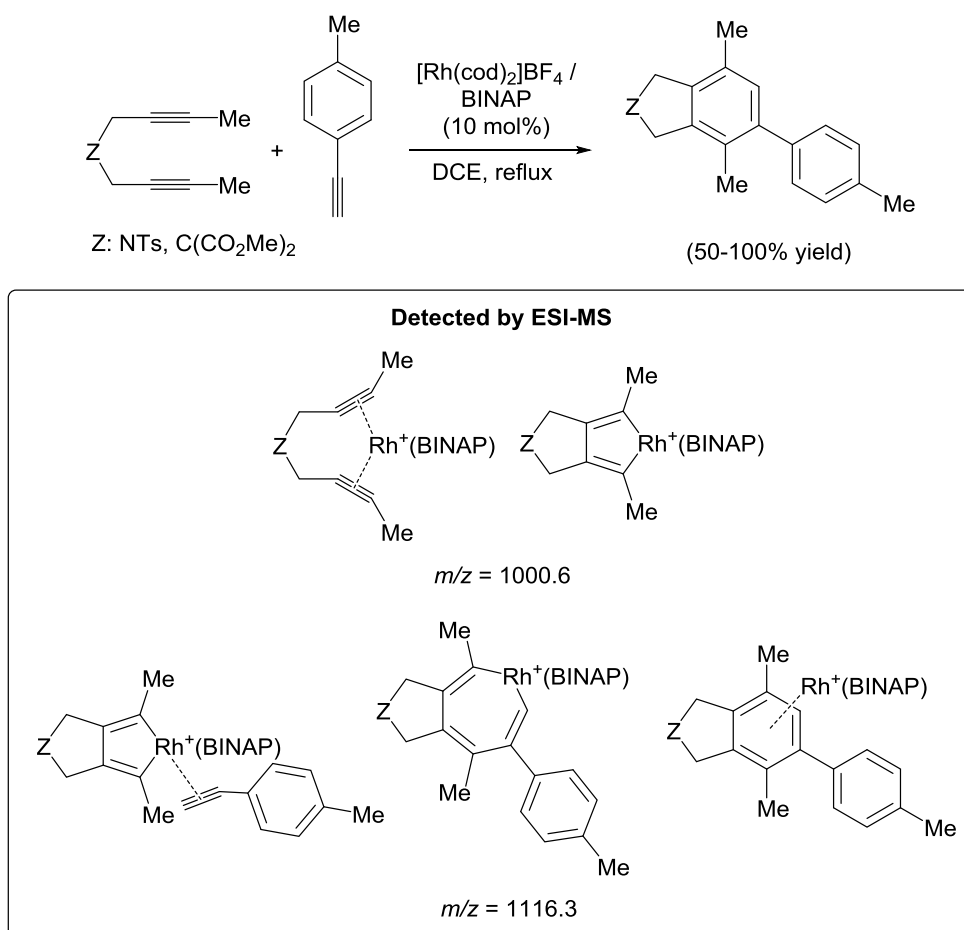
Moreover, our group has also published several works aimed to empirically corroborate the generation of the intermediates predicted in the theoretical studies.⁹¹⁻⁹

As a piece of example, in a collaboration with Prof. A. Jutand, our research group described for the first time kinetic data for the catalytic cycle of the [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition of a 1,6-diyne and 2-butyne-1,4-diol.⁹⁰ The oxidative addition and the insertion of the third alkyne were kinetically characterized by electrochemically monitoring the formation and further reaction of the oxidative addition intermediate (**Scheme 11**). As a result of that, it could be concluded that the oxidative addition to form a rhodacyclopentadiene constitutes the rate-determining step of the transformation when a bulky diyne is employed (R = Boc). However, when a less bulky diyne is used (R = H), the rate-determining step turns out to be the subsequent incorporation of the monoyne on the rhodacyclopentadiene generated.



Scheme 11. [2+2+2] cycloaddition reaction between a diyne and 2-butyn-1,4-diol

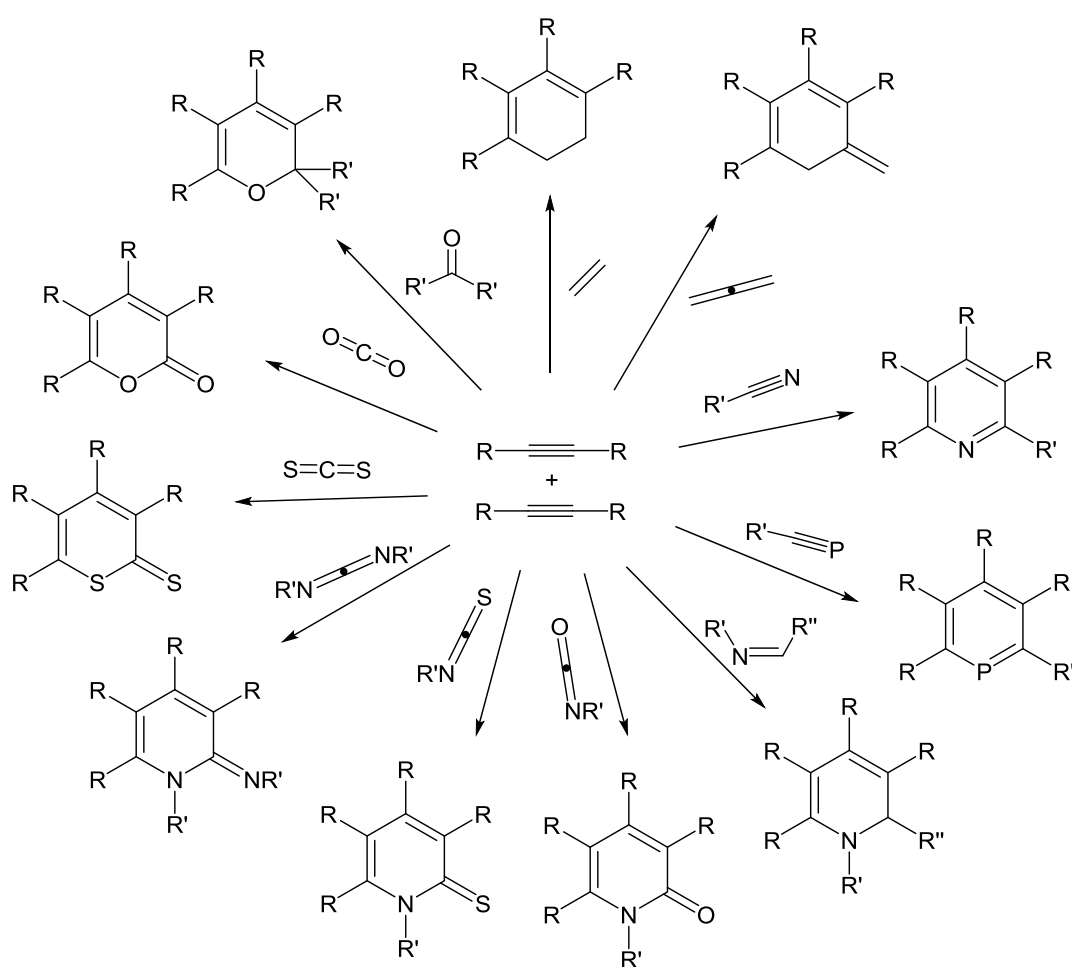
Although there are numerous examples on the use of $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst in the [2+2+2] cycloaddition reaction, inarguably the combination of cationic rhodium catalysts and BINAP-type intermediates is the rhodium-based catalytic system with more application especially when enantioselective reactions are to be performed (*vide infra*). In another work from our group, the mechanism of the rhodium-catalysed [2+2+2] cycloaddition reaction of diynes with monoynes was also examined by using ESI-MS and ESI-CID-MS analysis and DFT calculations (**Scheme 12**).^{9j} For this study, $[\text{Rh}(\text{cod})_2]\text{BF}_4$ was combined with BINAP ligand to generate the active catalytic species, which could be easily detected through ESI-MS for being cationic. For the first time, online-monitoring ESI-MS allowed the detection of all the intermediates in the catalytic system, and the data collected was further supported by DFT calculations, which were crucial in determining the structure of the intermediate formed upon insertion of the third alkyne moiety. This mass spectrometric study provided new insight into the reactivity of cationic rhodacyclopentadienes, which should facilitate the design of related rhodium-catalysed carbon-carbon couplings.



Scheme 12. ESI-MS monitoring of the [2+2+2] cycloaddition reaction of a diyne and a monoyne

1.2. Versatility of the [2+2+2] cycloaddition reaction

The transition metal-catalysed [2+2+2] cycloaddition reactions have been improved to involve not only alkynes but also other unsaturated substrates such as olefins, nitriles, aldehydes, ketones, allenes, carbon dioxide, carbon disulfide, carbodiimides, isocyanates, isothiocyanates and, as shown in recent publications, imines and phosphalkynes. As a result of the reaction of these unsaturations with two alkynes, the carbo- or heterocyclic compounds schematically represented in **Scheme 13** can be efficiently afforded. It is important to highlight that this is not an exhaustive list because different unsaturations can be combined in a single [2+2+2] cycloaddition reaction.



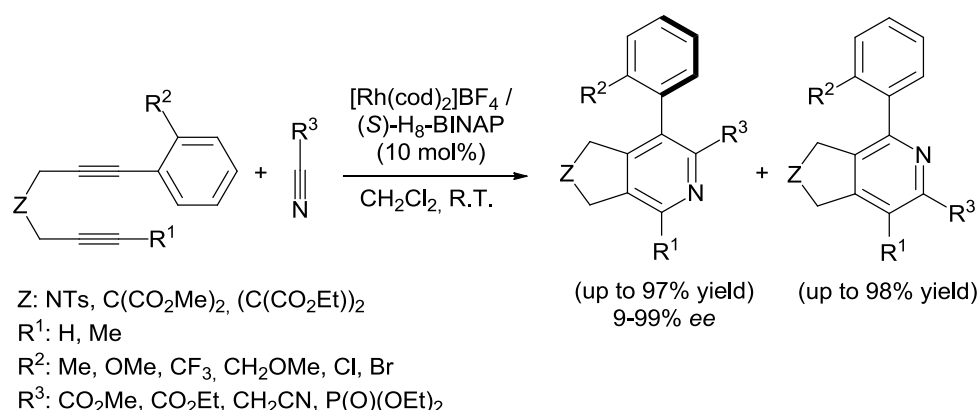
Scheme 13. Transition metal-catalysed [2+2+2] cycloaddition between two alkynes and other unsaturations

1.2.1. [2+2+2] cycloaddition involving nitriles

The introduction of a nitrile moiety in conjunction with two alkynes in [2+2+2] cycloadditions represents a good strategy to efficiently obtain substituted pyridine rings,^{2a,2l,18} which are common motifs in numerous natural products.

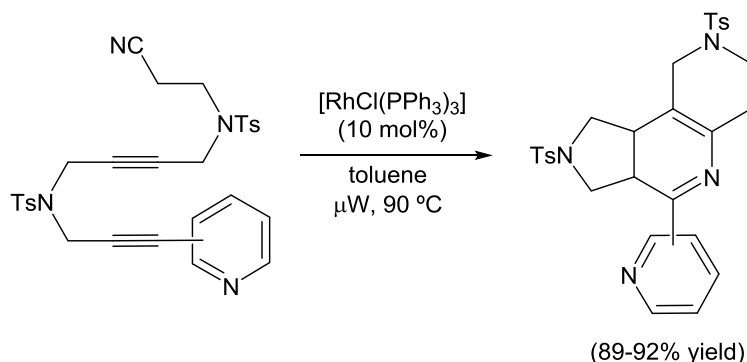
The preparation of pyridines throughout [2+2+2] cycloaddition reactions was pioneered by Wakatsuki,¹⁹ Vollhardt,²⁰ and Bönemann,²¹ who proposed that cobalt catalysts could promote this cyclization. In further studies, ruthenium was observed to behave as an excellent catalyst in this context, especially when activated nitriles bearing electron-withdrawing groups in the α -position are involved.²² Other transition metals such as nickel,²³ titanium,²⁴ and tantalum²⁵ have shown great efficiency in performing [2+2+2] cycloadditions with nitriles. Good results have been reported as well by using rhodium catalysts, though the process needs to be properly optimized so as to avoid the formation of arene by-products.²⁶

A remarkable example was reported in the research group of Tanaka,²⁷ who proved that cationic rhodium catalysts in combination with some chiral BINAP-type ligands could catalyse the [2+2+2] cycloaddition reaction. More specifically, when *ortho*-substituted phenyl diynes and nitriles are employed under these conditions, axially chiral 3-(*ortho*-substituted-phenyl)pyridines can be obtained in high yields and in variable enantioselectivities.^{27a} The authors observed that regio- and enantioselectivity are strongly related to the *ortho* substituents of the phenyl group of the diyne, since those bearing an electron-donating groups generally lead to axially chiral 3-arylpyridines, whereas alkyl groups give achiral 6-arylpyridines in high yields (**Scheme 14**).



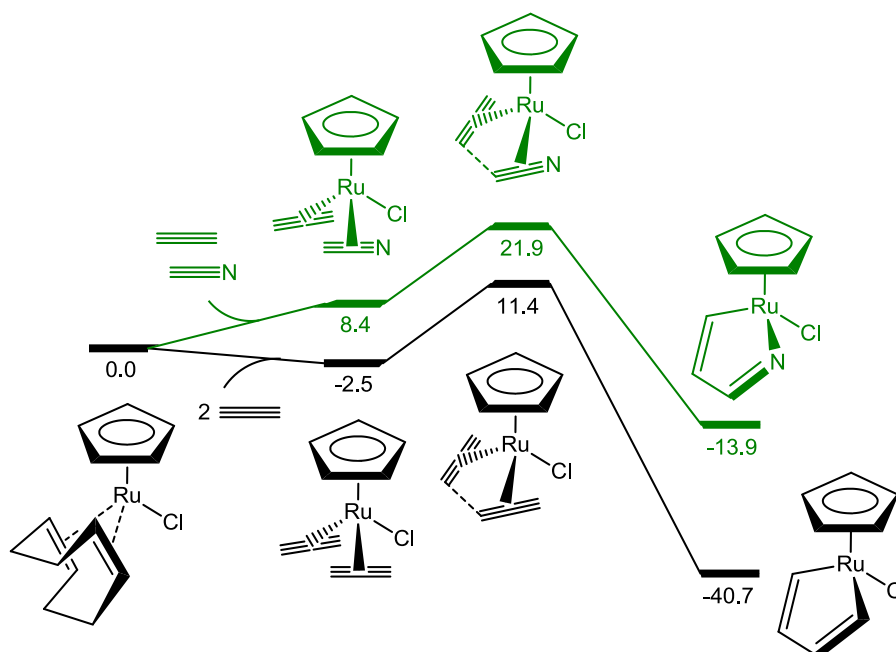
Scheme 14. Preparation of 3- and 6-arylpyridines through a [2+2+2] cycloaddition reaction

In our group, we have also introduced nitriles in the starting materials of our processes, thus generating pyridine-derived compounds.²⁸ Wilkinson's catalyst was found to promote the [2+2+2] cycloaddition reaction of cyanodiyne to furnish highly functionalised fused-tricyclic pyridines by submitting the system to microwave heating. The scope of the process was extended to obtain bipyridine scaffolds from pyridine-2-yl and pyridine-3-yl compounds (**Scheme 15**).



Scheme 15. $[\text{RhCl}(\text{PPh}_3)_3]$ -catalysed [2+2+2] cycloaddition of pyridine-yl compounds

From the theoretical perspective, Kirchner and co-workers^{22b,29} proposed a mechanism for the $[\text{CpRuCl}]$ -catalysed [2+2+2] cycloaddition reaction involving two acetylenes and HCN leading to the formation of pyridine rings. The authors determined that the oxidative addition between two acetylenes is kinetically and thermodynamically more favourable than between an acetylene unit and HCN, since the energy barrier decreases by about $8 \text{ kcal}\cdot\text{mol}^{-1}$ (**Scheme 16**). The later evaluation of the insertion step on the ruthenacyclopentadiene intermediate revealed that the insertion of HCN into a $\text{Rh-C}(sp^2)$ bond is preferred in front of the insertion of another acetylene unit. This fact explains the generation of the desired pyridine motif instead of benzene that would result from the acetylene insertion.



Scheme 16. Gibbs energy profile (kcal·mol⁻¹) for the oxidative addition step of the ruthenium-catalysed [2+2+2] cycloaddition reaction

The same transformation was computationally analysed in our group by considering the [RhCl(PPh₃)₃] complex to assist the process.⁹ⁱ The mechanistic profile found pointed out the same conclusions extracted by Kirchner and co-workers with regards to the thermodynamics of the process and the preference for the insertion of hydrogen cyanide instead of another acetylene unit into the Rh-C(sp²) bond of the rhodacyclopentadiene intermediate.

In addition to this, the fact that significant amounts of benzene resulting from the acetylene cyclotrimerisation are experimentally observed is in accordance with the theoretical results, as similar rate-determining energy barriers were found for the cyclotrimerisation of three acetylenes and the [2+2+2] cycloaddition of HCN with two acetylenes. Remarkably, the presence of electron withdrawing substituents like an acetyl group on the nitrile was observed to favour its insertion and thus improve the amount of pyridine afforded in front of benzene.

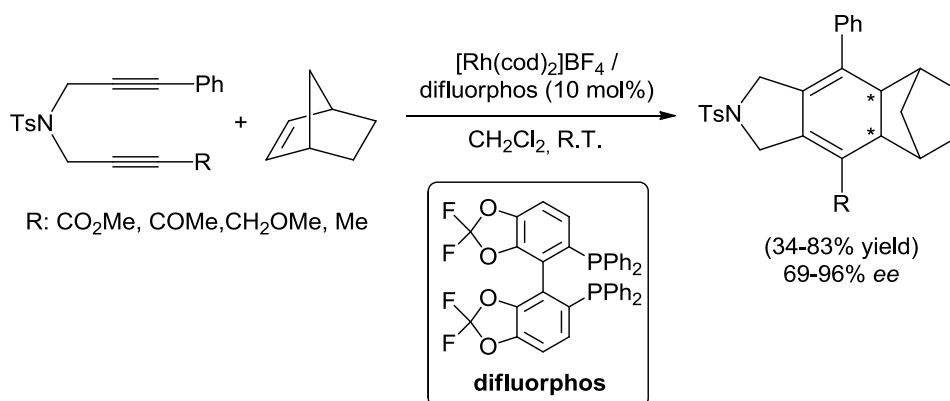
1.2.2. [2+2+2] cycloadditions involving alkenes

The involvement of alkenes as unsaturated partners with alkynes in [2+2+2] cycloaddition reactions was rather limited in the first years, likely due to their lower reactivity in front of alkynes. As a result of this, alkynes tended to cyclotrimerize instead of affording the desired cross-cyclotrimerization of alkynes with alkenes. Since the first studies, in which cobalt complexes were employed in stoichiometric amounts to

mediate the transformation,³⁰ great efforts have been undertaken to turn alkenes into suitable and efficient unsaturations to participate in the studied processes. This interest derives from the structural features that the resulting cyclohexadiene adducts present, as two stereocentres can be generated.³¹

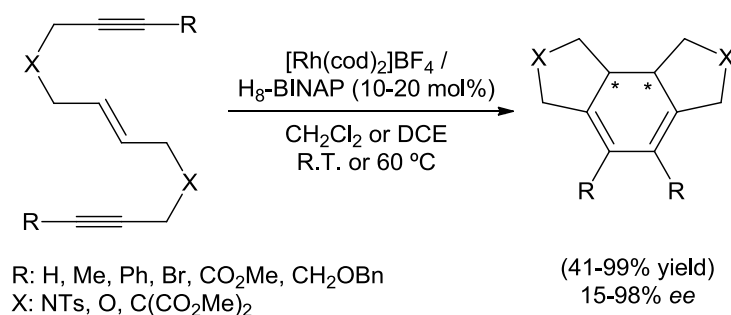
The possibility of controlling the regio- and stereoselectivity of the process has always been a remarkable challenge, which has often been successfully addressed by choosing the appropriate catalytic species. In this context, asymmetric induction is one of the most attractive points for the use of alkenes.

A representative example of the use of alkenes in [2+2+2] cycloaddition reactions is the case of the partially intermolecular cyclisation entailing a diyne and a cycloalkene that was reported by Shibata and co-workers.³² In their work, difluorophos – a chiral BINAP-type ligand – was employed in combination with $[\text{Rh}(\text{cod})_2]\text{BF}_4$ to afford the product with a high degree of enantioselectivity. The process proved efficient in the use of diynes with norbornene to afford chiral tetracyclic cyclohexa-1,3-dienes in good to excellent enantioselectivities (**Scheme 17**).



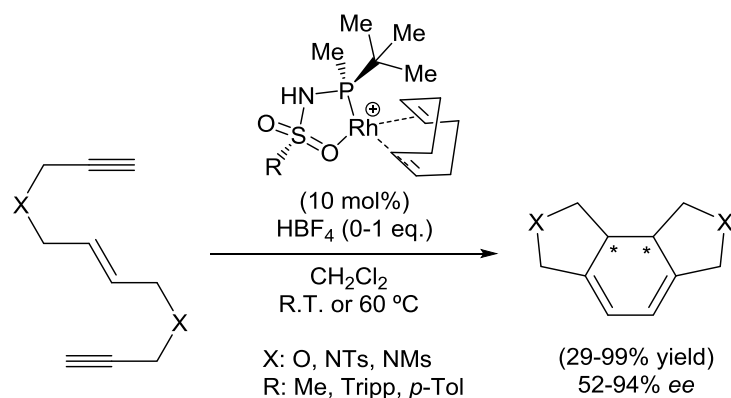
Scheme 17. [2+2+2] cycloaddition reaction of a diyne with norbornene

The same authors³³ reported the case of the totally intramolecular [2+2+2] cycloaddition of linear enediynes to afford cyclohexa-1,3-dienes bearing two stereocentres. The optimal catalytic species was generated from $[\text{Rh}(\text{cod})_2]\text{BF}_4$ and H₈-BINAP and led to different degrees of enantioselectivity (**Scheme 18**).



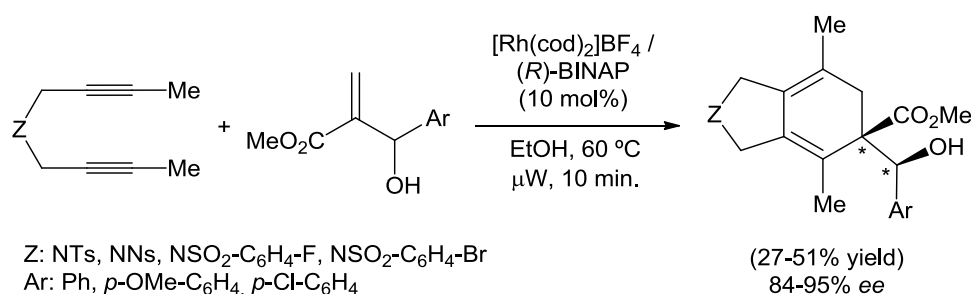
Scheme 18. Totally intramolecular [2+2+2] cycloaddition reaction of enediynes

A study carried out in our group in collaboration with Riera and co-workers³⁴ showed that the robustness of the previous process was improved when *P*-stereogenic *N*-sulfonyl secondary iminophosphorane ligands were employed (**Scheme 19**).^{34a} A remarkable feature of this sort of ligands is that they are especially stable and resistant to phosphorous oxidation due to the NH/PH tautomerism.



Scheme 19. [2+2+2] cycloaddition reaction in the presence of iminophosphorane ligands

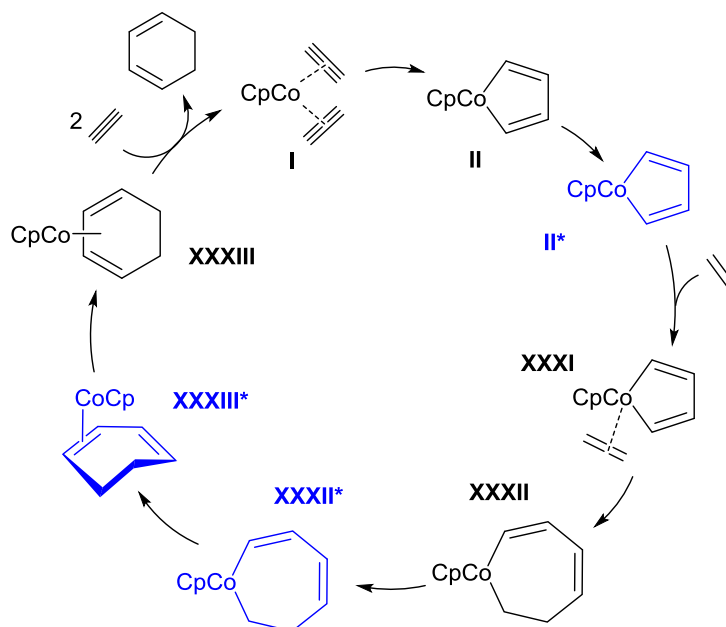
Our group developed a diastereo- and enantioselective [2+2+2] cycloaddition reaction between diynes and Morita-Baylis-Hillman adducts.³⁵ The process took place under the presence of a cationic rhodium catalyst and (*R*)-BINAP, achieving kinetic resolution of the Morita-Baylis-Hillman adduct. An optically pure 1,3-cyclohexadiene compound containing vicinal tertiary and quaternary carbon centres was afforded (**Scheme 20**).



Scheme 20. [2+2+2] cycloaddition reaction of a diyne and a Morita-Baylis-Hillman adduct

Considering the experimental results involving alkenes, several theoretical approaches have been carried in order to rationalise the chemoselectivity that alkenes display in front of alkynes when they participate in a [2+2+2] cycloaddition reaction. The first theoretical study aimed to such goal was published by Gandon, Vollhardt and co-workers,³⁶ who took the mechanistic proposal of Koga's group¹² as reference to propose the catalytic cycle.

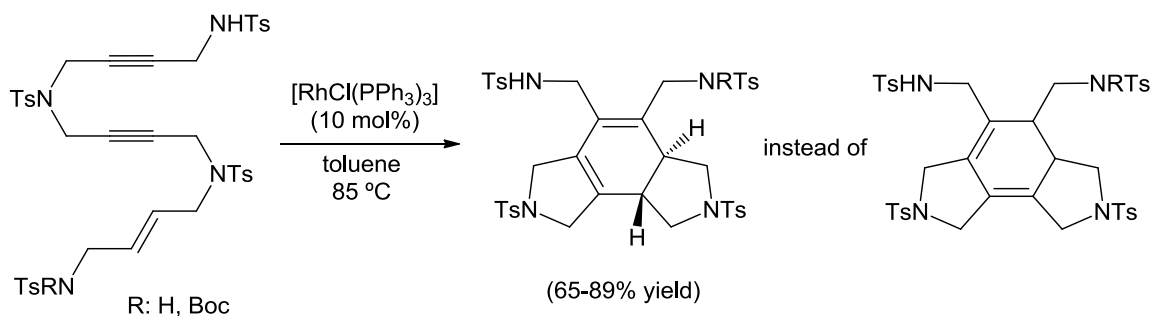
More concretely, they simulated the cyclisation of two acetylene and one ethylene units under the presence of a [CpCo]-based catalyst to afford cyclohexadienes (**Scheme 21**). They found that the most favourable oxidative addition step takes places between the two acetylenes in the singlet state of bisacetylene complex **I** to afford cobaltacyclopentadiene **II**, which spontaneously relaxes to the excited state **II***. After that, the incorporation of the alkene preferably takes places through the insertion into a Co-C(*sp*²) bond to generate cobaltacycloheptadiene **XXXII** in the singlet state. It should be highlighted that the insertion step proposed is more likely to take place than the [4+2] approach that the same authors find when three acetylenes are involved (**Scheme 6**). Finally, the reductive elimination was found to be more feasible at the triplet state to generate **XXXIII***, which bears a cyclohexadiene ring and can be released when two new acetylene units enter in the catalytic cycle.



Scheme 21. Catalytic cycle proposed for the [CpCo]-mediated [2+2+2] cycloaddition reaction involving two acetylenes and one ethylene. Singlet states are represented in black. Triplet states are represented in blue and marked with a *

A further approach was achieved in our group for the study of the totally intramolecular version of the [2+2+2] cycloaddition reaction involving alkenes. The work entailed the

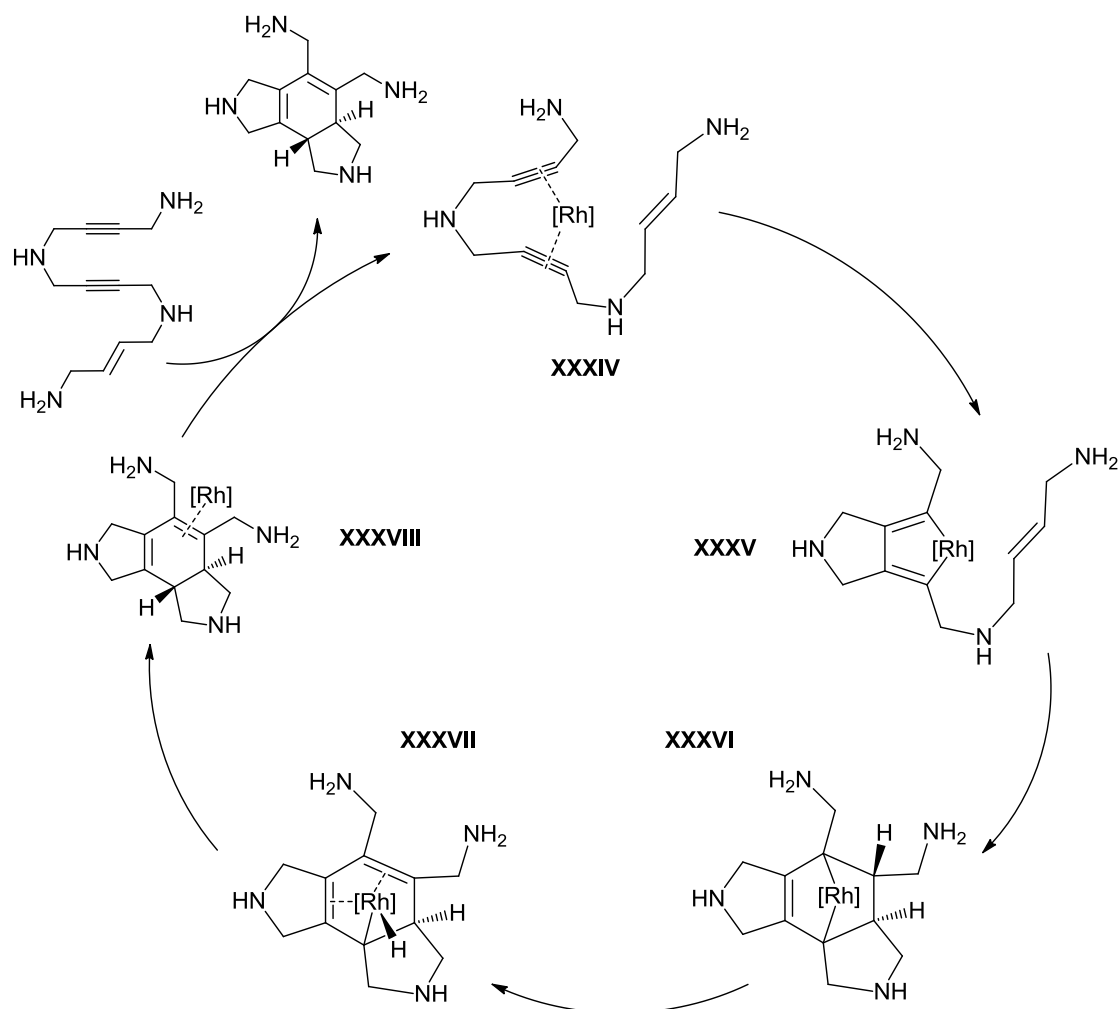
analysis of the cyclisation of alkyne-alkyne-alkene linear substrates under the presence of $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst. In the experimental work, the substrate was shown to be efficiently cyclized into a cyclohexadiene though the position of the double bonds was shifted from the positions where they would be expected upon a regular $[2+2+2]$ cycloaddition (**Scheme 22**).^{9k}



Scheme 22. $[2+2+2]$ cycloaddition reaction of alkyne-alkyne-alkene substrates

The study of the catalytic cycle was performed by considering several approximations in order to reduce the computational cost that bulky groups entail. Therefore, triphenylphosphine ligands were computed as PH_3 and tosyl groups as hydrogens.

The proposed mechanistic cycle (**Scheme 23**) starts with the oxidative addition between two alkynes to yield **XXXV**, which was found to be more favourable than between one alkyne and the alkene group and is in accordance with the higher reactivity displayed by alkynes. After that, the insertion of the alkene moiety into a $\text{Rh}-\text{C}(\text{sp}^2)$ bond leads to the bicyclic intermediate **XXXVI**, which is susceptible to undergo a β -hydride elimination process (**XXXVII**) thanks to the agostic interaction between rhodium and hydrogen. Last, a reductive elimination process can yield **XXXVIII**, which can finally release the cycloadduct that has been experimentally detected.

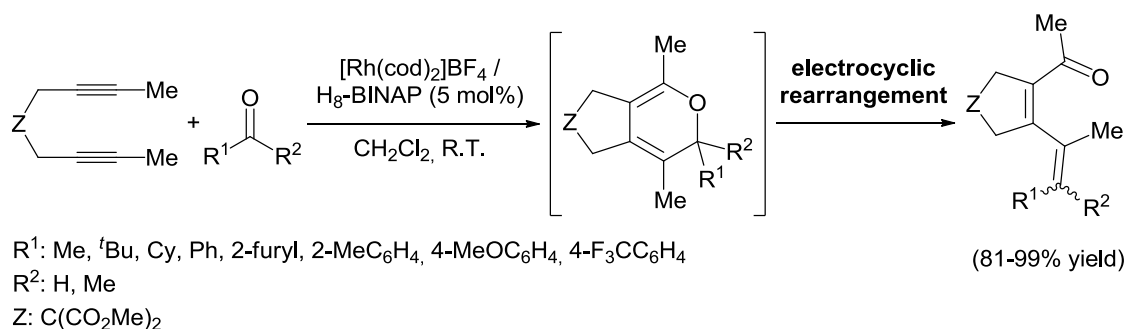


Scheme 23. Catalytic cycle proposed for the [RhCl(PPh₃)₃]-mediated [2+2+2] cycloaddition reaction of alkyne-alkyne-alkene substrates. [Rh] = RhCl(PH₃)₂

1.2.3. [2+2+2] cycloadditions involving carbonyl compounds

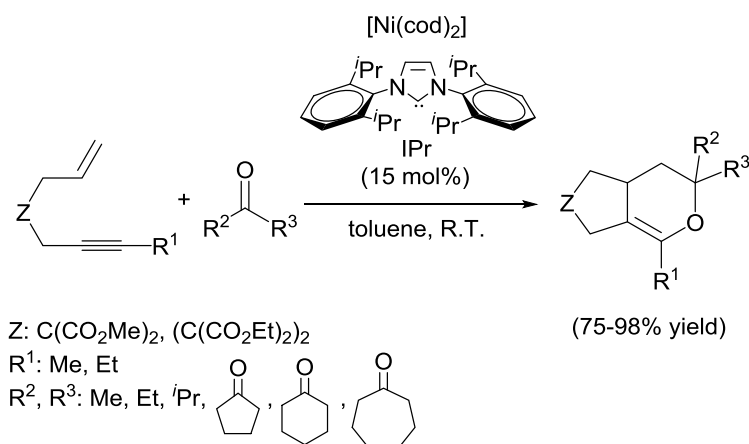
Turning our attention to unsaturations bearing one heteroatom, aldehydes and ketones have shown a more limited reactivity in the [2+2+2] cycloaddition with alkynes. The first case was reported in 1988 by Tsuda and Saegusa,³⁷ who managed to perform the reaction using 1,6- and 1,7-diynes with an aldehyde under nickel(0)/monophosphane catalysis. Later, the use of more complex catalytic species such as nickel(0)/imidazolidine allowed the [2+2+2] cycloaddition involving electron-rich aldehydes or ketones.³⁸ On the other hand, electron-deficient ketones were successfully reacted under the presence of [Cp*RuCl(cod)] catalyst.³⁹ However, in the previous cases, a thermal electrocyclic ring opening reaction was reported to take place on the cycloadduct, leading to the isolation of dienones instead of the expected pyrans.

Tanaka's research group⁴⁰ presented a cationic rhodium catalytic system to perform the [2+2+2] cycloaddition reaction of 1,6- and 1,7-diynes with both electron-deficient and electron-rich aldehydes and ketones. Nevertheless, they found that the end product corresponded as well to the dienone resulting from the electrocyclic rearrangement (**Scheme 24**).



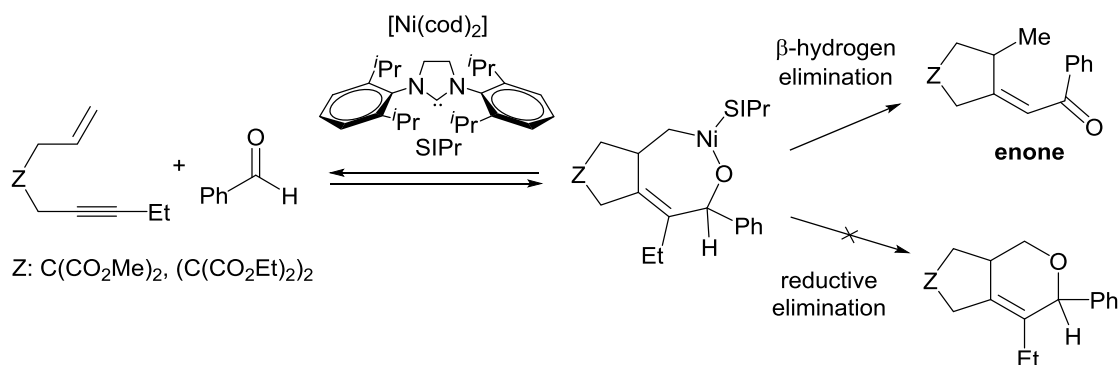
Scheme 24. Cyclisation of a diyne with a carbonyl compound followed by an electrocyclic ring opening process

Louie and co-workers^{38a} managed to successfully obtain dihydropyranes from enynes and ketones under Ni/carbene catalysis in a completely chemo- and regioselective [2+2+2] cycloaddition reaction (**Scheme 25**).



Scheme 25. [2+2+2] cycloaddition reaction of enynes and ketones

However, when they tried the same conditions with an aldehyde, an enone compound was observed instead. To explain such reactivity difference, they hypothesize that the insertion intermediate, which presents the opposite regioselectivity than the one displayed when a ketone is involved, can suffer a β -hydrogen elimination of the former aldehyde hydrogen (**Scheme 26**).

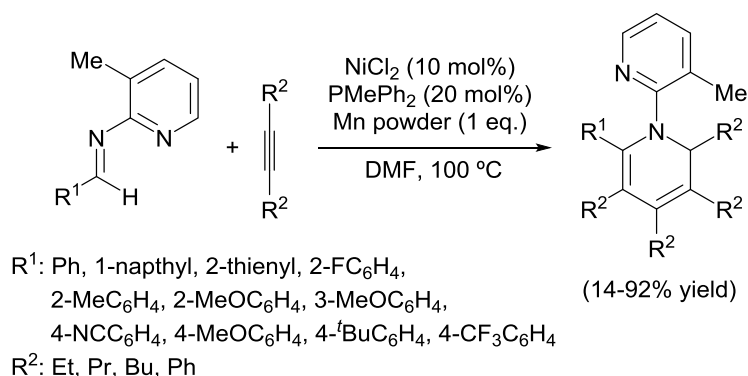


Scheme 26. Proposed mechanism for the obtaining of the observed enone

1.2.4. [2+2+2] cycloadditions involving imines

Imines have also been used in the context of [2+2+2] cycloaddition reactions to obtain 1,2-dihydropyridines. However, the number of publications involving imines in these processes is still relatively low and the scope of the imines employed is quite limited.⁴¹

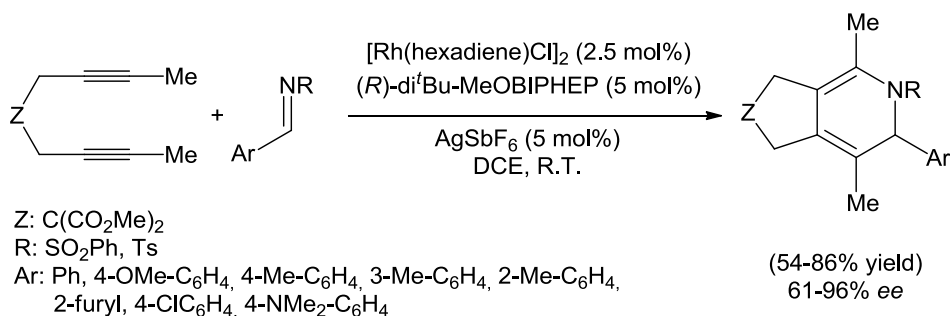
In 2011, Yoshikai and co-workers^{41e} reported that the totally intermolecular [2+2+2] cycloaddition reaction of an aldimine bearing an *N*-3-methyl-2-pyridyl group with two alkynes could be carried out under nickel catalysis (**Scheme 27**). However, the authors found that the main product corresponded to an isomerised form of the expected one. Remarkably, they observed that the presence of the pyridyl group is necessary for the reaction to proceed.



Scheme 27. [2+2+2] cycloaddition reaction of an aldimine and two alkynes

A few years later, Gandon and Aubert^{41d} proposed a partially intermolecular version involving a 1,6-diyne and a sulfonimine under rhodium catalysis in the presence of AgSbF₆. They found that the process afforded good yields of the expected 1,2-dihydropyridine when a silver salt was added, which allowed the *in situ* generation of a cationic rhodium species (**Scheme 28**). Furthermore, it should be highlighted that the authors only observed good results when sulfonimides were used, probably due to the

fact that the sulfonamide group allows the formation of a rhodapyrroline intermediate, which is key to the progress of the reaction.



Scheme 28. [2+2+2] cycloaddition reaction of a diyne with a sulfonimine

1.2.5. [2+2+2] cycloadditions involving allenes

Allenes are a class of organic compounds which have always fascinated chemists due to the intriguing features of the cumulated diene function. The *sp* hybridization of the central carbon atom causes the two CH_2 groups of the parent allene to be perpendicular to each other and consequently the two π orbitals are roughly orthogonal (**Figure 2**).

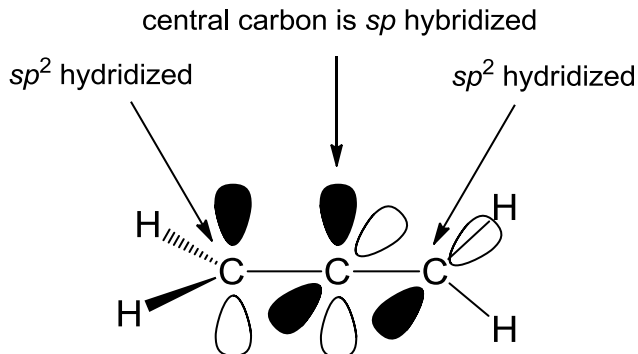


Figure 2. Hybridization and π bond in allene structure

The interest in this sort of compounds increases when their axial chirality is taken into account. According to the IUPAC, axial chirality is the stereoisomerism resulting from the non-planar arrangement of four groups in pairs about a chiral axis. In the case of allenes, axial chirality arises when the terminal ends of the cumulative π -system contain different substituents (**Figure 3**). This property has great potential from the synthetic point of view.

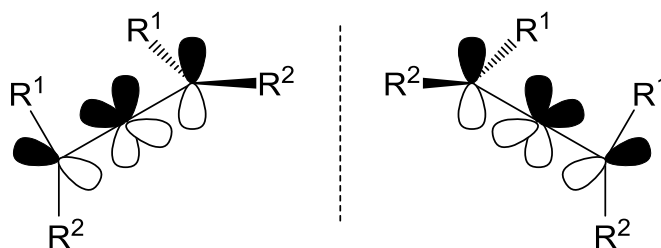


Figure 3. Representation of the axial chirality in the allenic geometry

Allenes were long considered to be chemical curiosities and unstable unsaturated moieties, a fact that greatly retarded the development both of methods for their preparation and synthetic applications. However, over the last 30 years, the allene chemistry has advanced greatly.⁴² It is also noteworthy that at the same time, isolation and characterisation of allenic natural compounds have been pursued and more than 150 natural products containing an allenic or a cumulenenic structure are now known.⁴³

Alkenes and alkynes have a prominent position among the organic substrates for transition metal-catalysed reactions and especially for cycloaddition reactions. From a general reactivity point of view, allenes can often be considered as hybrids of alkenes and alkynes with characteristic features that make them appealing substrates for cycloaddition and cyclization reactions.⁴⁴ The two orthogonal double bonds in the allene retain the linear geometry of alkynes, but only possess a single sp hybridized atom.

Considering the case in which two of the three allene carbons react, a new sp^3 centre is formed. Therefore, replacing alkynes with allenes should allow the development of cycloadditions that produce a greater number of sp^3 -hybridized stereocentres relative to the isomeric alkyne substrates. Furthermore, in this context, one of the allene double bonds remains in the product and is useful for further functionalisation reactions. It is also important to note that the allene isomer of a given alkyne is generally between 3 and 5 kcal·mol⁻¹ less stable due to strain energy.⁴³ Finally, the fact that allenes possess axial chirality is another clear advantage both compared to alkenes and alkynes.

On the other hand, the control of the selectivity in cycloaddition reactions involving allenes is more complex than with the alkene and alkyne counterparts. Aside from controlling the chemoselectivity, regioselectivity (leading to constitutional isomers) and stereoselectivity (leading to stereoisomers), in the cycloadditions that involve allenes the positional selectivity (which of the two double bonds reacts, thus again leading to constitutional isomers) needs also to be mastered (**Figure 4**).

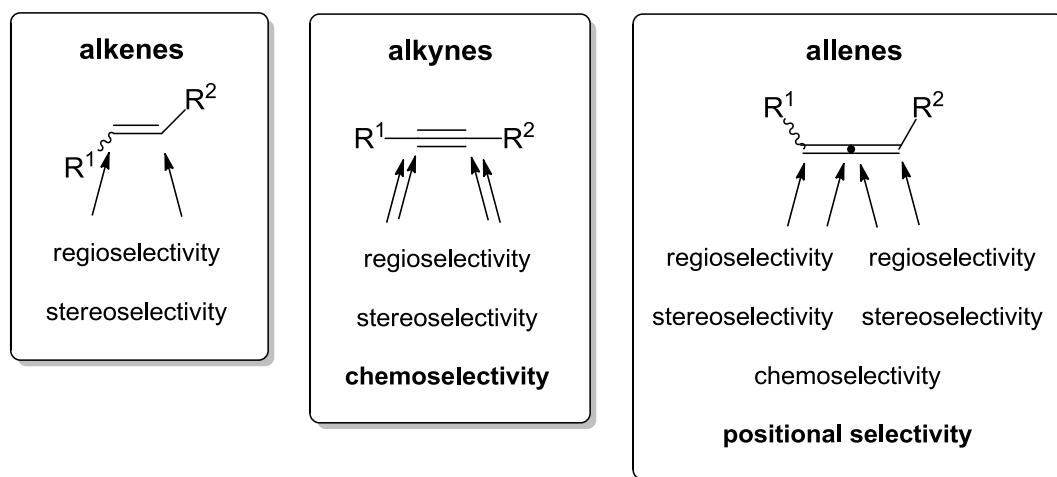
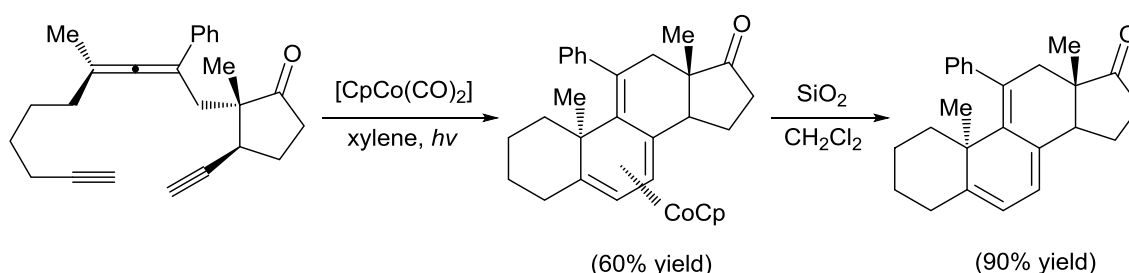


Figure 4. Selectivity aspects in different types of unsaturated substrates

[2+2+2] cycloaddition reactions of substrates including an allene as a coupling partner are still limited to several precedents.⁴⁵ Some completely intramolecular and partially or totally intermolecular cases will be commented below.

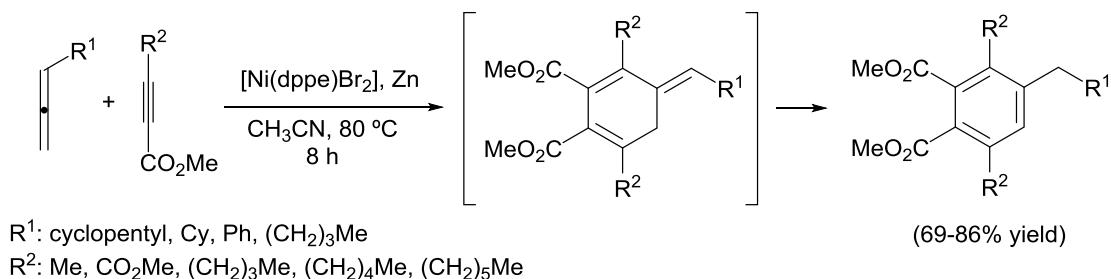
Pioneer work on the involvement of allenes in a completely intramolecular [2+2+2] cycloaddition reaction was undertaken by Malacria and co-workers.⁴⁶ The first work investigating this reaction demonstrated that it is possible to react regio- and diastereoselectively various allenediynes. Their approach is based on the use of cobalt catalysts in stoichiometric amounts to afford good yields. This represents a convenient route to the family of 11 β -steroid cores (**Scheme 29**).⁴⁷



Scheme 29. A convenient method leads to the synthesis of 11 β -steroid scaffolds

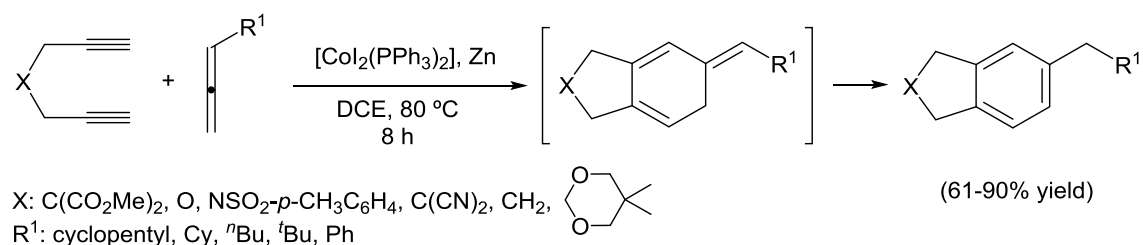
Cheng and co-workers⁴⁸ reported the first totally-intermolecular alkyne-allene cocyclotrimerization. The synthesis of polysubstituted benzenes in a highly regio- and chemoselective reaction was achieved using a nickel catalytic system. The cyclohexadiene formed, which bears an exocyclic double bond, isomerizes to the corresponding benzene derivative. Therefore, it was proved that allenes are synthetically equivalent to monosubstituted alkynes but are superior in terms of chemoselectivity (**Scheme 30**), which can be stated by the fact that stoichiometric

amounts of the starting materials are enough to obtain the desired cycloadduct without a significant generation of the cyclotrimerised product. Thanks to that, the reaction can proceed without the need of using excess of the substrates or slow addition of either reaction component.



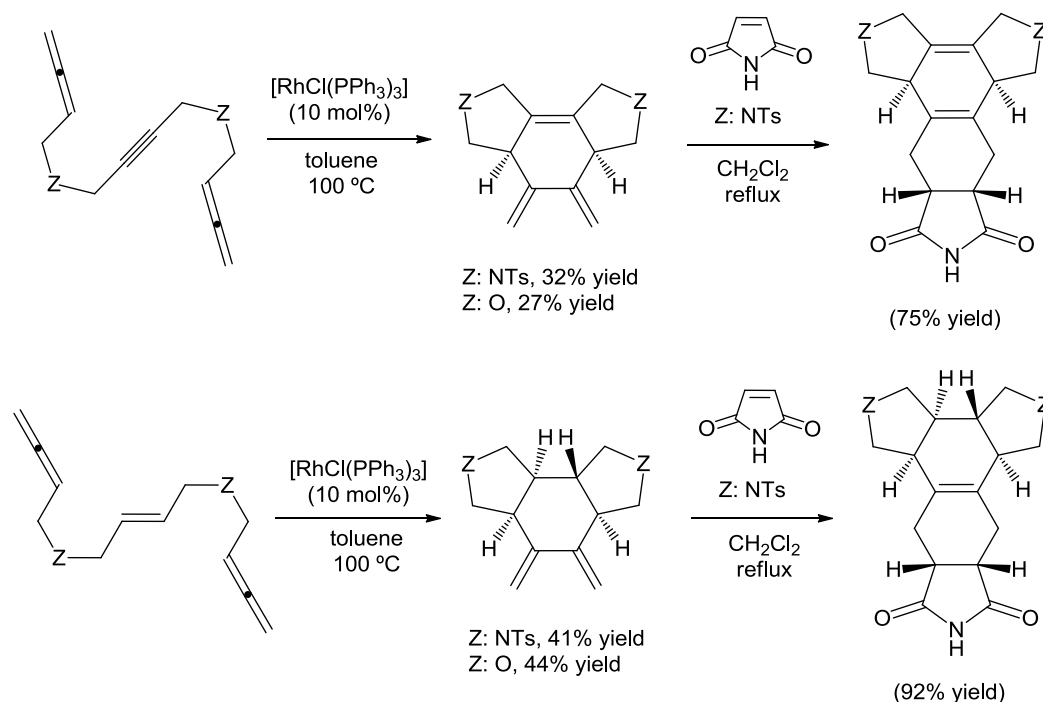
Scheme 30. Nickel-catalysed cocyclotrimerization of propiolates with allenes

The same authors also studied the partially intermolecular cobalt-catalysed [2+2+2] cycloaddition involving electron-deficient diynes⁴⁹ or electronically neutral diynes⁵⁰ with allenes (**Scheme 31**). Similarly to the previous cases, an isomerization process occurs on the cycloadduct formed to finally afford a benzene derivative. The reactions, which tolerate a variety of functional groups in the diynes, proceed in a highly regio- and chemoselective way. Additionally, it has been shown that the [CoI₂(PPh₃)₂]/Zn system, which is used for the electron-neutral diynes, is much more active and selective than the [NiBr₂(dppe)]/Zn system, which works for the electron-deficient diynes.



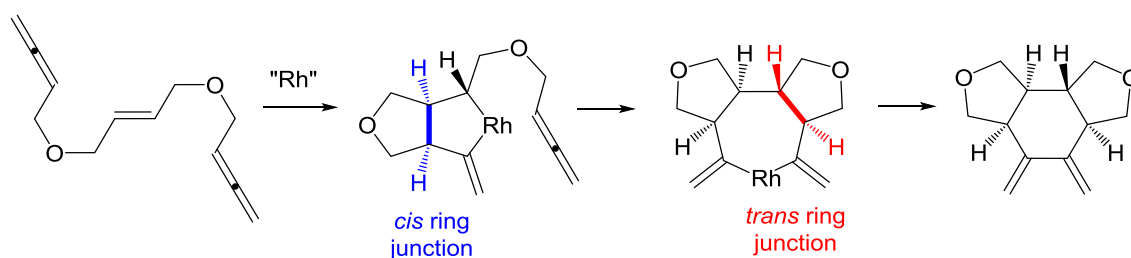
Scheme 31. Cobalt-catalysed cocyclotrimerization of electronically-neutral diynes with allenes

Our group has explored new versions of the rhodium-catalysed [2+2+2] cycloaddition reactions in which allenes are involved. We would like to highlight the synthesis of tricyclic 1,3-diene products from linear allene-yne/ene-allene substrates with complete chemo- and diastereoselectivity (**Scheme 32**).⁵¹ The products obtained could also undergo Diels-Alder reactions with maleimide, affording complex pentacyclic products in excellent yields and with total stereoselectivity.



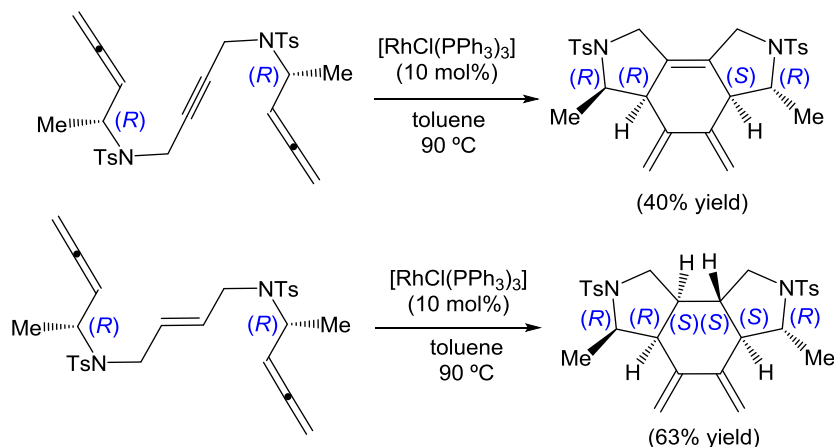
Scheme 32. Rhodium(I)-catalysed [2+2+2] cycloaddition of allene-ene-allene substrates

Additionally, detailed DFT calculations were carried out to rationalise the observed diastereoselectivity and to propose a mechanistic cycle for the allene-alkene-allene substrate bearing two oxygen tethers. After a detailed analysis of the many possibilities for the key reaction intermediates, oxidative addition was postulated as taking place between the central alkene and the internal double bond of one of the allenes to give a *cis*-fused ring junction. The remaining allene is then inserted into the Rh-C(sp^3) bond of the rhodacyclopentane to give a *trans*-fused ring junction (**Scheme 33**), so determining the diastereoselectivity of the process. Interestingly, the rate-determining step of the process was assigned to the insertion step, displaying an energy barrier of 24.0 kcal·mol⁻¹.



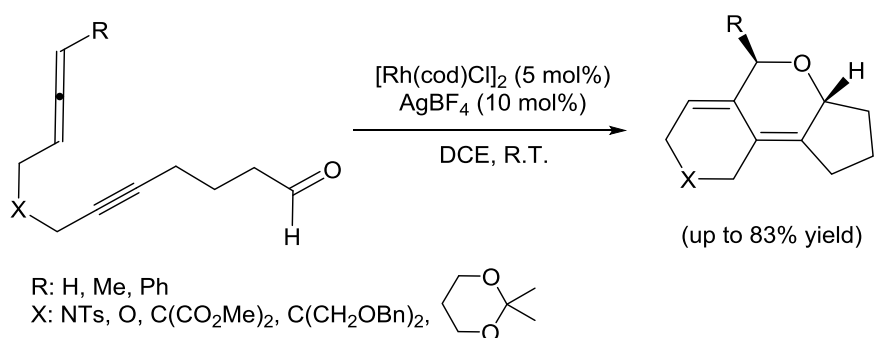
Scheme 33. Key intermediates proposed by DFT calculations in the rhodium(I)-catalysed [2+2+2] cycloaddition of allene-ene-allene substrates

Our group also envisaged that Wilkinson's catalyst could undergo the [2+2+2] cycloaddition reaction of allene-yne-allene and allene-ene-allene substrates bearing chiral centres in the α position of the allene functionality.⁵² The built-in chirality present in the starting materials was preserved and used to generate two or four more chiral centres with complete diastereoselectivity, thus demonstrating the chirality induction of the process (**Scheme 34**).



Scheme 34. [2+2+2] cycloaddition reaction of allene-yne/ene-allenes bearing chiral centres

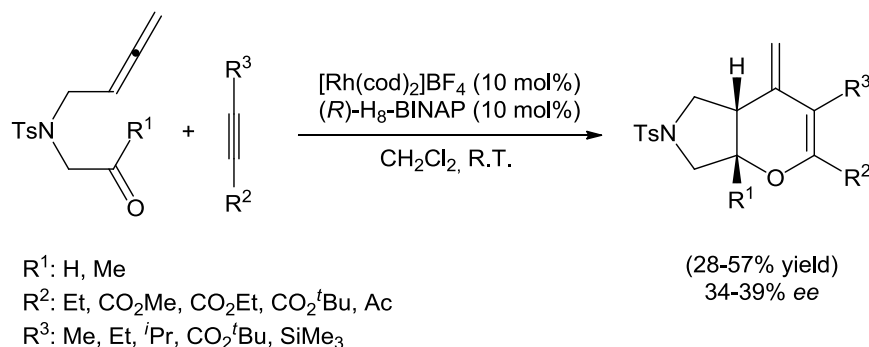
Other unsaturations such as aldehydes have also been combined with allenes in the context of [2+2+2] cycloaddition reactions. Sato's group⁵³ reported a novel rhodium-catalysed cycloaddition between an alkyne, an allene and an aldehyde, giving a tricyclic compound containing a pyran ring (**Scheme 35**).



Scheme 35. Rhodium-catalysed cyclization of allenynes with tethered aldehydes

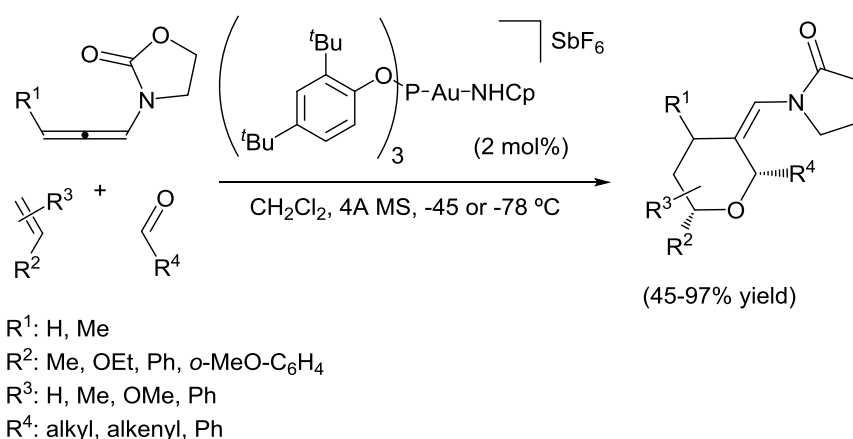
Oxygen heterocycles were also synthesized by Tanaka and co-workers⁵⁴ using a partially intramolecular strategy (**Scheme 36**). The enantioselective [2+2+2] cycloaddition reaction of tosylamide-linked 5-allenal and 5-allenone with internal alkynes using cationic rhodium(I)-BINAP complex was reported leading to bicyclic

heterocycles. Nevertheless, the yield and the enantioselectivity attained in such reactions were only moderate.



Scheme 36. Rhodium(I)-catalysed cycloaddition of tosylamide-linked 5-allenone and 5-allenone with internal alkynes leading to oxygen heterocycles

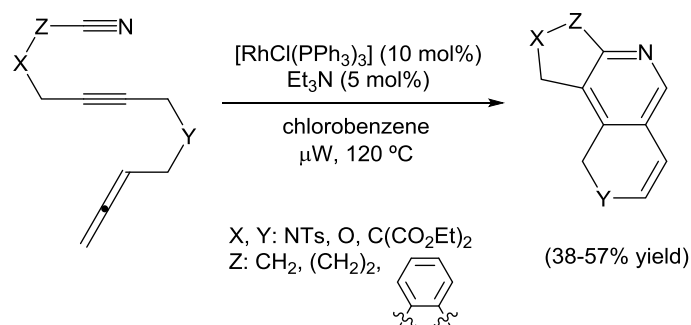
The totally intermolecular gold(I)-catalysed [2+2+2] cycloaddition of allenamides, alkenes and aldehydes for the synthesis of tetrahydropyrans was reported by Mascareñas and López.⁵⁵ The use of a phosphite gold complex in catalytic amounts proved crucial for this efficient transformation of three different π -unsaturated components at very low temperatures in a regio- and diastereoselective fashion (**Scheme 37**). It is worth mentioning that the mechanism postulated for this transformation is radically different from the ones described before.



Scheme 37. Au-catalysed [2+2+2] intermolecular cycloaddition for the synthesis of tetrahydropyrans

In our group, we have also introduced nitriles in the starting materials of our processes, thus generating dihydronaphthyridine and pyranopyridine scaffolds.⁵⁶ The use of the Wilkinson's catalyst and catalytic amounts of triethylamine, allowed the chemoselective reaction of allenes through their external double bond to give unsaturated pyridine-containing scaffolds after a dehydrogenative step (**Scheme 38**). Further treatment of

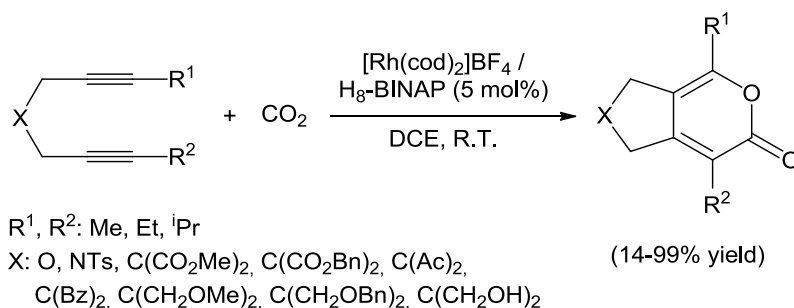
these products could lead to 2,6-naphththyridine scaffolds that have showed promising medicinal properties in HIV⁵⁷ and cancer research.⁵⁸



Scheme 38. [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition of allene-yne-cyano derivatives

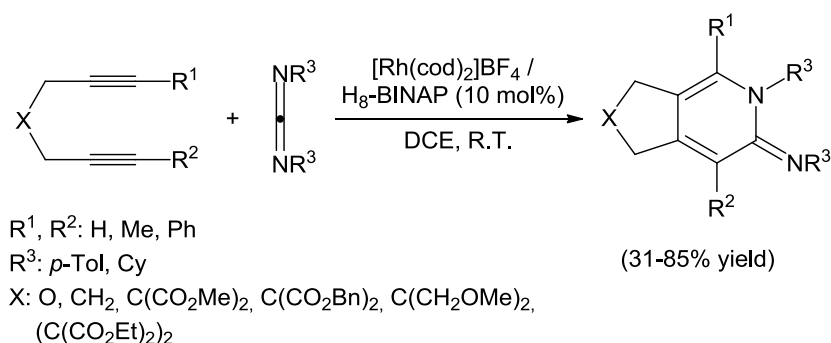
1.2.6. [2+2+2] cycloadditions involving CO₂, carbodiimies and CS₂

The use of rhodium catalysts to perform the [2+2+2] cycloaddition reaction of a diyne with carbon dioxide (CO₂) was first introduced by Tsuda and Saegusa in 1988.⁵⁹ Later, Tanaka and co-workers⁶⁰ found that a 1 atm pressure of CO₂ gas was enough to yield the corresponding 2-pyrones at room temperature (**Scheme 39**). They eventually found that the efficiency of the process was strongly influenced by the electronic nature of the tether, since malonic tethers yielded the product in a 70-99% yield and O or NTs tethers only gave a 14-27% yield. Furthermore, they reported that the regioselectivity of the process relies on the steric effects of the diyne.



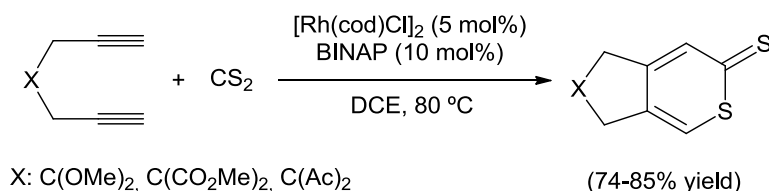
Scheme 39. [2+2+2] cycloaddition reaction involving carbon dioxide

The same reaction conditions, though with the double catalytic loading, performed well to involve carbodiimides. In this case, the nature of the tethers used was observed to have less influence on the success of the process (**Scheme 40**).⁶⁰



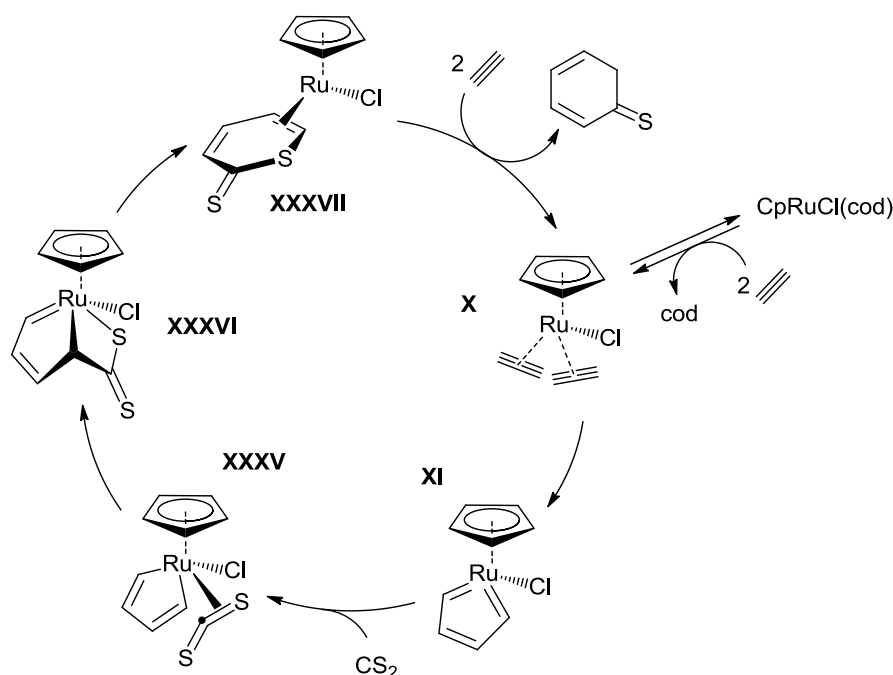
Scheme 40. [2+2+2] cycloaddition reaction involving carbodiimides

Tanaka's group⁶¹ also found that carbon disulfide (CS_2) could be used as an unsaturation unit for the studied cycloadditions. Dithiopyrones were obtained in excellent yields from 1,6-diynes and carbon disulfide, provided that the latter was present in the system in at least 5-fold excess (**Scheme 41**).



Scheme 41. [2+2+2] cycloaddition reaction involving carbon disulfide

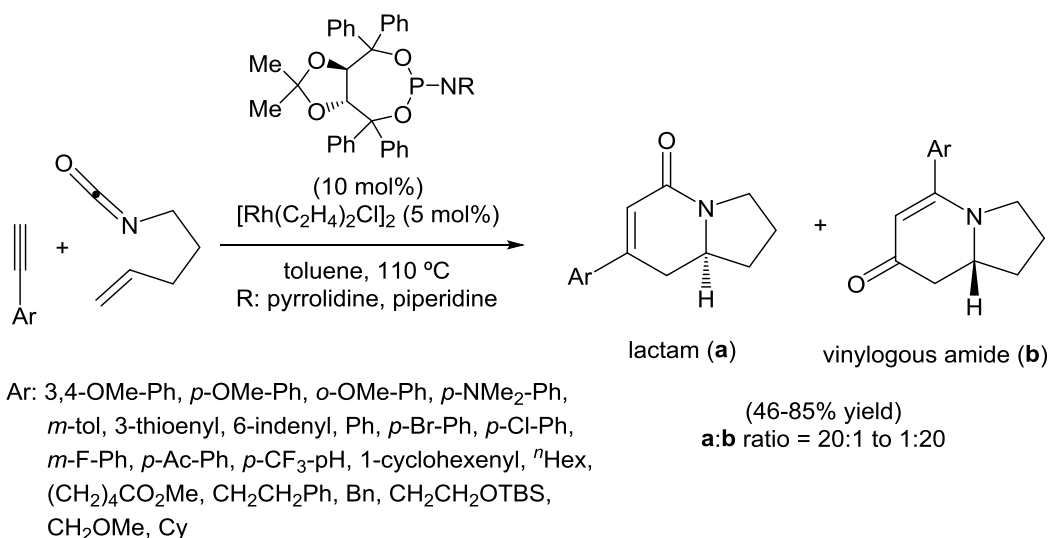
With regards to the mechanism of the transformation, Kirchner and co-workers,¹⁵ who pioneered the theoretical study of the [2+2+2] cycloaddition reactions involving several unsaturations under ruthenium-based catalysts, proposed a mechanistic pathway for the cyclisation of two acetylenes and a CS_2 unit under the presence of a $[\text{CpRuCl}]$ -based catalyst (**Scheme 42**). The cycle proceeds through the analogous intermediates proposed by the same author when three acetylenes cyclotrimerise (**Scheme 7**). The oxidative addition step was observed to be more favourable between two acetylenes, which is in accordance with the higher reactivity of alkynes in front of CS_2 . As a result of that, biscarbenic ruthenacyclopentatriene **XI** is afforded and can continue the cycle by coordinating to the CS_2 unit (**XXXV**). At this point, the most favourable route found generates ruthenabicyclo[3.2.0]heptadiene **XXXVI** that can finally yield the desired cycloadduct.



Scheme 42. Mechanism for the [2+2+2] cycloaddition reaction of two alkynes and CS_2 catalysed by $[\text{CpRuCl}]$ species

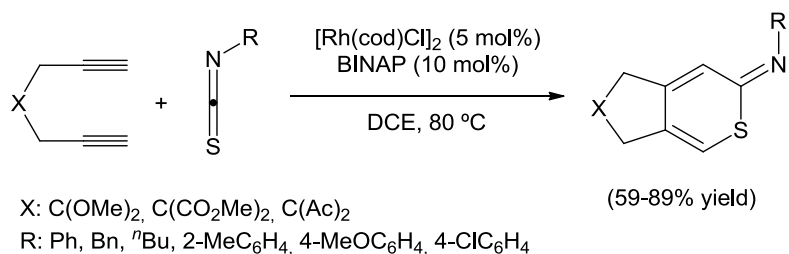
1.2.7. [2+2+2] cycloadditions involving isocyanates and isothiocyanates

The challenge of involving heterocumulenic unsaturations was tackled by Rovis and co-workers⁶² who reported the particular case of the [2+2+2] cycloaddition reaction of alkynes and alkenyl isocyanates to afford bicyclic lactams using chiral phosphoramidites as ligands. Furthermore, they found that a vinylogous amide was also obtained as a result of a carbonyl rearrangement (**Scheme 43**).^{62l}



Scheme 43. Partially intermolecular [2+2+2] cycloaddition between alkynes and alkene isocyanates

Tanaka and co-workers⁶¹ managed to incorporate isothiocyanates by reacting them with 1,6-diynes. Once the system was submitted to a $[\text{Rh}(\text{cod})\text{Cl}]_2$ catalyst in the presence of a BINAP ligand, thiopyranimines were afforded in high yields (**Scheme 44**).



Scheme 44. [2+2+2] cycloaddition of diynes and isothiocyanates

Chapter 2. General objectives

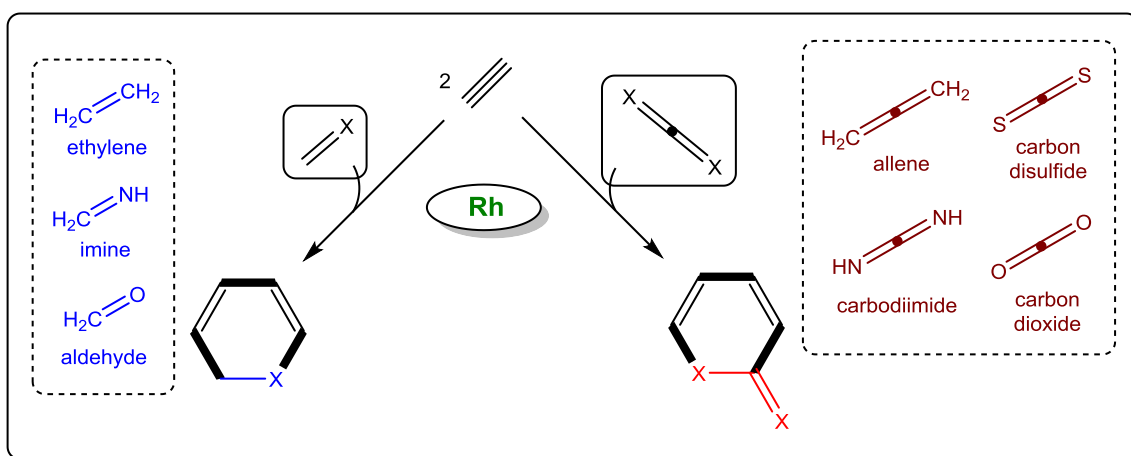
Considering the precedents exposed, we set the objectives of the present thesis, aiming to give a further insight into the versatility of the transition-metal catalysed [2+2+2] cycloaddition reactions when C(sp²) unsaturations are involved.

In the first part, the feasibility of the rhodium-catalysed [2+2+2] cycloaddition reaction involving two alkyne units and a C(sp²) unsaturation will be analysed from the theoretical point of view by performing DFT calculations (Chapter 3). This evaluation will consider several common rhodium catalysts ([RhCl(PPh₃)₃], [Rh(cod)₂]BF₄/BIPHEP and [RhCl(ethylene)₂]₂) that have displayed good experimental results to perform [2+2+2] cycloaddition reactions. The study is aimed to disclose, among the different that can arise, the most favourable mechanistic pathway for each C(sp²) unsaturations that leads to the experimentally-detected cycloadducts and to compare the efficiency of the three catalytic species considered.

Following our interest in C(sp²) unsaturations and with the goal of demonstrating the versatility of the [2+2+2] cycloaddition reactions, three different carbonated unsaturations will be combined in a linear substrate to cyclise it. More concretely, substrates combining an allene, an alkene and an alkyne units will be experimentally reacted under rhodium catalysis to afford tricyclic structures with three stereogenic centres (Chapter 4). This sort of substrates is interesting from the mechanistic point of view because the oxidative addition between the alkyne and the allene is not geometrically favoured. Furthermore, a theoretical and empirical mechanistic study will be performed to unravel the order of reactivity of the three unsaturated groups in this type of reactions under the presence of the most efficient catalysts.

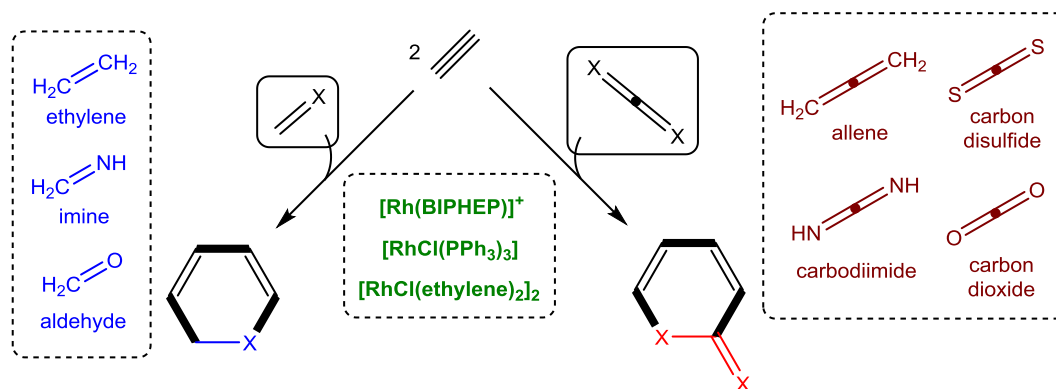
Finally, the involvement of new carbon allotropes in [2+2+2] cycloaddition reactions will be intended. More concretely, the theoretical feasibility of the [2+2+2] cycloaddition reaction of single-walled carbon nanotubes with alkynes will be analysed by means of DFT calculations (Chapter 5). Our aim will be to locate the most likely mechanistic pathway by taking into account the order of reactivity of the unsaturated counterparts and the regioselectivity of the process. The study will also include the evaluation of the efficiency of several catalytically-active species, bearing cobalt, rhodium or iridium metallic centres, and the trial of a different nanotube morphology (either zigzag or armchair) and size ((9,0) and (12,0)).

Chapter 3. Rhodium-catalysed [2+2+2] cycloaddition involving C(sp²) unsaturations



Taking as a reference the previous works in the group,^{9i-o} we were interested in unravelling the mechanism of the rhodium(I)-catalysed [2+2+2] cycloaddition of two acetylenes with several C(sp²) unsaturations. The objective of this study was to establish a reactivity order of the different systems and justify it on the basis of the electronic and steric nature of the unsaturations. More concretely, the studied C(sp²) unsaturations include ethylene, imine, aldehyde, allene, carbon disulfide, carbodiimide and carbon dioxide (**Scheme 45**).

To attain such goal, [Rh(BIPHEP)]⁺, [RhCl(PPh₃)₃] and [RhCl(ethylene)₂]₂ catalysts were selected to assist the process, as they are commercially available and have been widely experimentally employed. Each catalyst will be separately analysed in the subsections that follow.

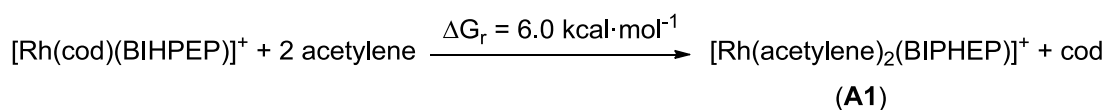


Scheme 45. Model system that will be studied in the present chapter

All calculations were performed with the Gaussian 09⁶³ program package. Geometry optimisations were performed without symmetry constraints using the hybrid DFT B3LYP⁶⁴ method with the all-electron cc-pVDZ basis set for P, Cl, O, C, and H⁶⁵ and the cc-pVDZ-PP basis set containing an effective core relativistic pseudopotential for Rh.⁶⁶ The D3 Grimme energy corrections for dispersion with its original damping function⁶⁷ were added in all B3LYP/cc-pVDZ-PP calculations. Single-point energy calculations were carried out with the B3LYP-D3/cc-pVTZ method. Calculations were simulated at 298.15K temperature to obtain the reported B3LYP-D3/cc-pVTZ // B3LYP-D3/cc-pVDZ relative Gibbs energies. Solvent effects were taken into account with a polarized continuum model (PCM),⁶⁸ considering dichloromethane solution for [Rh(BIPHEP)]⁺ and toluene solution for [RhCl(PPh₃)₃] and [RhCl(ethylene)₂]₂ catalytic systems. The change from 1 atm pressure to 1 M on the reference system was corrected by adding 1.89 kcal·mol⁻¹ on the entropic contribution to calculate the Gibbs energy values.

3.1. [Rh(BIPHEP)]⁺-catalysed [2+2+2] cycloaddition reaction

Starting with the simplest unsaturation, the mechanistic pathway for the [2+2+2] cycloaddition of two acetylenes and one ethylene was studied under the presence of cationic rhodium [Rh(BIPHEP)]⁺ catalyst. Even though chiral ligands such as BINAP, tol-BINAP or H₈-BINAP are often experimentally employed, calculations were performed with BIPHEP ligand in order to reduce the computational cost. The first catalytic species (**A1**, **Scheme 47**) can be afforded in a precatalytic endothermic process of 6.0 kcal·mol⁻¹, in which two acetylenes replace the 1,5-cyclooctadiene (cod) ligand of a cationic rhodium precursor that bears the BIPHEP ligand (**Scheme 46**).



Scheme 46. Precatalytic process to afford **A1**

The analysis entailed the evaluation of which oxidative addition combination, either acetylene/acetylene or acetylene/ethylene, displayed a lower energy barrier. After that, the possibility of occurring an insertion step of ethylene into a Rh-C(*sp*²) bond of the rhodacyclopentadiene intermediate or a [4+2] process on a C(*sp*²)-C(*sp*²) bond was evaluated (**Figure 5**), though we were unable to locate any transition state corresponding to a [4+2] process. Finally, the reductive elimination step to produce the ring closure was computed. **Scheme 47** displays the most favourable mechanism found for the system involving two acetylenes and one ethylene unit.

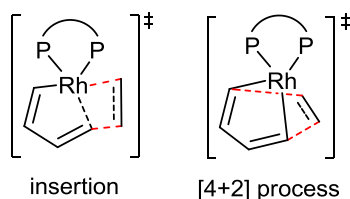
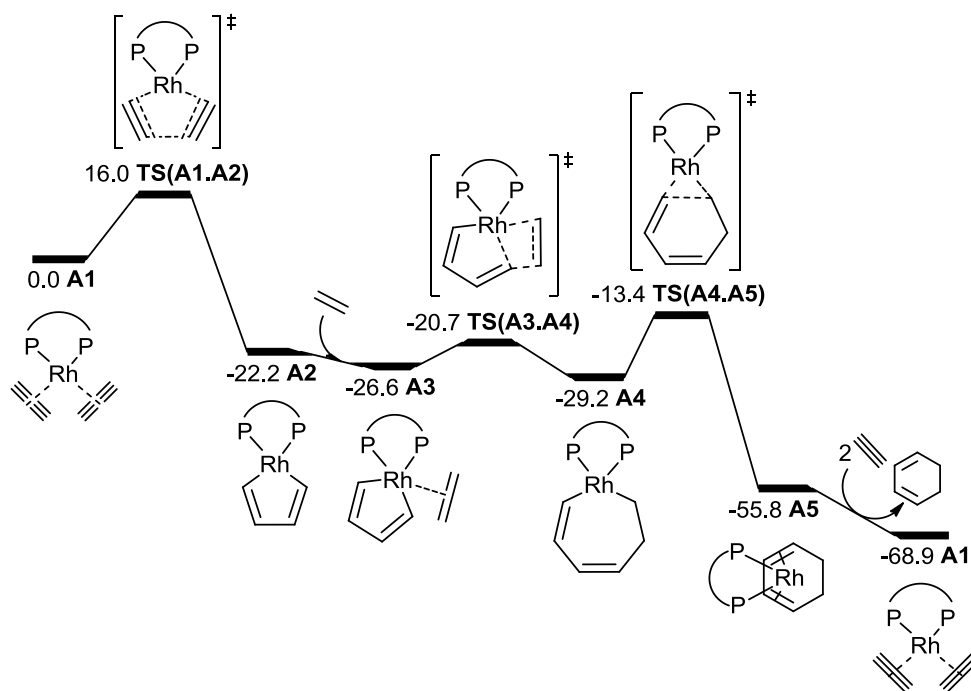


Figure 5. Possible approaches of ethylene towards rhodacyclopentadiene

Overall it can be observed that the oxidative addition, insertion and reductive elimination steps display 16.0 kcal·mol⁻¹, 5.9 kcal·mol⁻¹ and 15.8 kcal·mol⁻¹ Gibbs energy barriers, respectively. The oxidative addition was observed to preferably take place between two acetylene units, which is consistent with the higher reactivity of alkynes compared to alkenes. After that, an insertion step generates a Rh-C(*sp*³) bond when ethylene is inserted into a Rh-C(*sp*²) bond of rhodacyclopentadiene **A2**. The process is globally exothermic in 68.9 kcal·mol⁻¹ and the rate-determining step resides on the oxidative addition step.



Scheme 47. Gibbs energy profile (kcal·mol⁻¹) at 298.15K for the lowest-in-energy route for the [Rh(BIPHEP)]⁺-catalysed [2+2+2] cycloaddition of two acetylenes and one ethylene unit. BIPHEP ligand has been simplified for clarity

Compared to a previous work in the group in which the [2+2+2] cycloaddition of three acetylenes was analysed,^{9m} the exothermicity of the process becomes significantly lower. More concretely, $\Delta G_r = -134.5 \text{ kcal}\cdot\text{mol}^{-1}$ was appreciated for the cyclotrimerisation of acetylenes, whereas only $\Delta G_r = -68.9 \text{ kcal}\cdot\text{mol}^{-1}$ (**Scheme 47**) is found when ethylene participates in the cyclisation. Such a difference is in accordance with the fact that an aromatic ring is attained in the first case, which entails a higher degree of stabilisation than when a cyclohexadiene is afforded.

The same analysis was performed by using other C(sp²) unsaturations. More concretely, calculations involving an aldehyde, imine, allene, carbodiimide, carbon dioxide and carbon disulfide units were undertaken. It should be highlighted that, as exposed in the Introduction section of this thesis, all the previous C(sp²) unsaturations have already been experimentally tested.

As a result of our study, three mechanistic pathways (**Scheme 48**) have been found as the most favourable mechanistic routes that are likely to take place depending on the nature of the C(sp²) unsaturation.

All the studied C(sp²) unsaturations preferably undergo the oxidative addition step between the two acetylenes and generate a rhodacyclopentadiene intermediate. Later, alkenes, aldehydes and imines seem to follow the same catalytic pathway through a

rhodacycloheptadiene intermediate resulting from the insertion step. The two possible approaches to perform the insertion step into a Rh-C(sp^2) bond of the rhodacyclopentadiene intermediate were analysed in all cases, which can result in the formation of a Rh-X or a Rh-C(sp^3) bond when non-cumulenic C(sp^2) unsaturations are involved, or also a Rh-C(sp^2) bond when a cumulenic one is entailed (**Figure 6**). In none of the cases studied, the transition state corresponding to a [4+2] approach could be located.

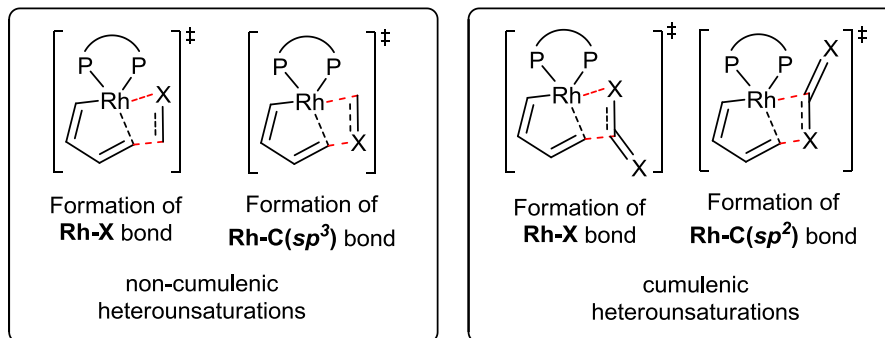
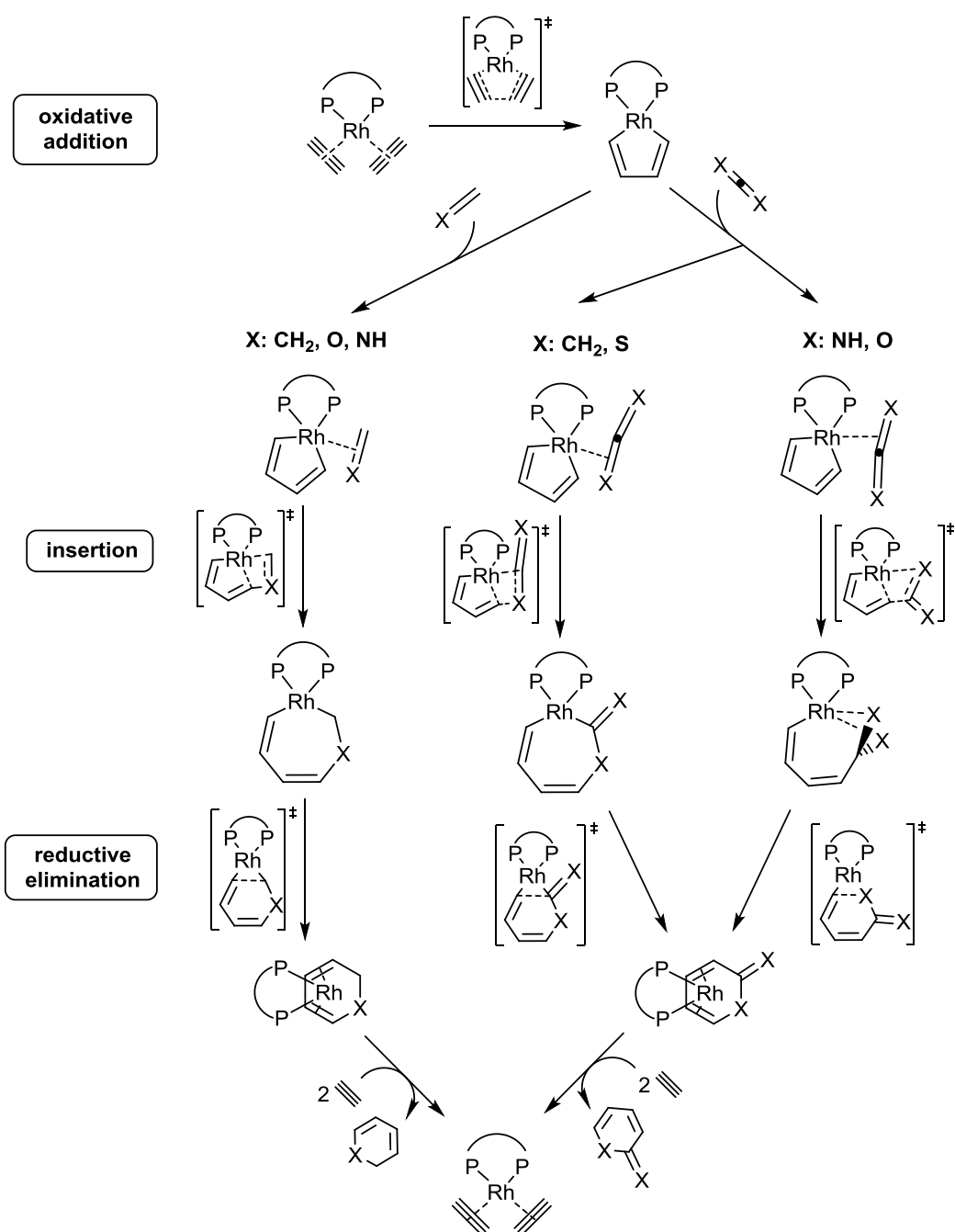


Figure 6. Possible approaches to perform the insertion step

While non-cumulenic unsaturations preferably generate a Rh-C(sp^3) bond, cumulenic unsaturations display a variable regioselectivity in the insertion step, since allenes and carbon disulfide are more likely to form a Rh-C(sp^2) bond at this point but, on the other hand, carbodiimides and carbon dioxide tend to acquire a bridge coordination in which both Rh-N (for carbodiimides) and Rh-O (for carbon dioxide) bonds display the same bond length (**Scheme 48**). In general terms, most approaches that determine the regioselectivity for the insertion step presented in **Scheme 48** are more favourable than the opposite ones by 5-10 kcal·mol⁻¹.



Scheme 48. Proposed mechanism for the [Rh(BIPHEP)]⁺-catalysed [2+2+2] cycloaddition of two acetylenes and the different C(sp²) unsaturations studied

From a quantitative point of view, the first energy barrier is observed to rely exclusively on the oxidative addition between two acetylenes and was, therefore, equal for all the cases (16.0 kcal·mol⁻¹). Nevertheless, once the C(sp²) unsaturation coordinates to the rhodium centre, a clear divergence of the energy barriers of each step is found, since they vary from 5 kcal·mol⁻¹ to about 35 kcal·mol⁻¹ for the insertion step and from 10 kcal·mol⁻¹ to approximately 39 kcal·mol⁻¹ for the reductive elimination (**Figure 7**).

All steps display relatively low energy barriers, with the exception of the insertion and reductive elimination of carbon dioxide, as well as the reductive elimination of carbodiimide, both evolving through the same mechanism depicted in **Scheme 48**.

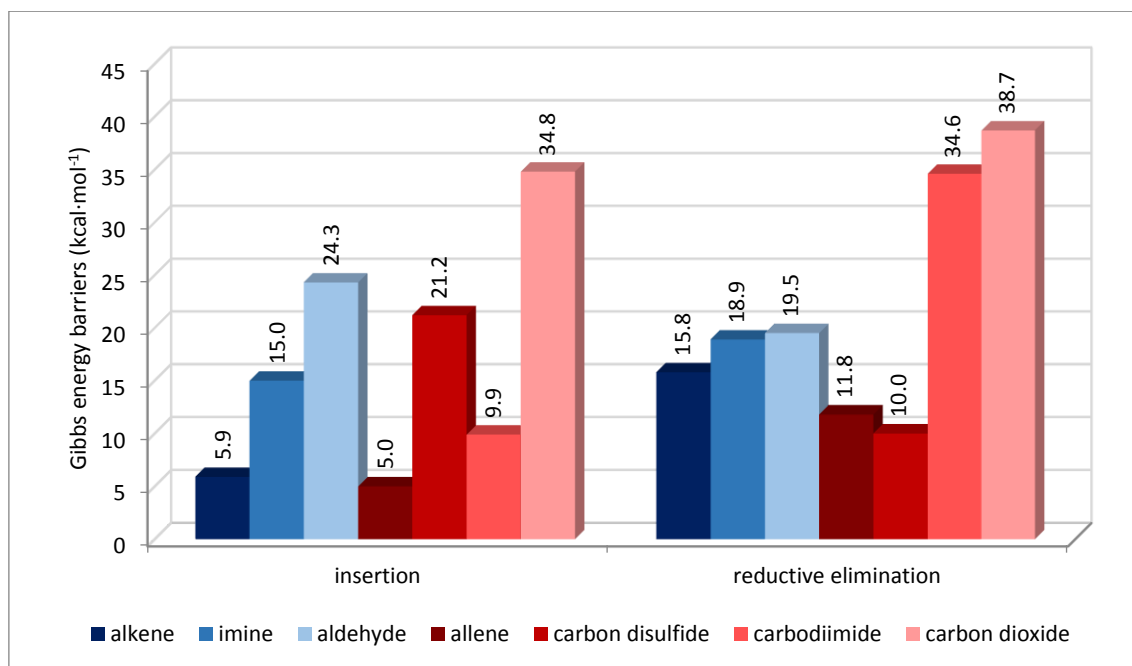


Figure 7. Gibbs energy barriers of the oxidative addition, insertion and reductive elimination steps of the $[\text{Rh}(\text{BIPHEP})]^+$ -catalysed $[2+2+2]$ cycloaddition involving the studied unsaturations

To explain the changes in reactivity in the insertion step, we make use of the activation strain model (ASM),⁶⁹ also known as distortion/interaction model (for more details, see the Methods section of this thesis), since it is a helpful tool to understand the origin of energy barriers. The barriers are analysed in terms of strain and interaction energies between the fragments participating in the formation or cleavage of chemical bonds.

The results of the ASM (**Table 1**) reveal that the interaction energies are generally responsible for the differences found in the insertion energy barriers, which tend to increase when less stabilisation interaction is generated. In a relatively lower extent, some contribution in the increase of the energy barriers is attributed to the strain energy required to distort the $\text{C}(\text{sp}^2)$ unsaturation when approaching the $\text{Rh}-\text{C}(\text{sp}^2)$ in which it is finally inserted, especially in the case of carbon dioxide that requires $40.0 \text{ kcal}\cdot\text{mol}^{-1}$ to distort the CO_2 molecule to reach the geometry that this fragment has in the TS of the insertion process. Therefore, it can be said that strain and interaction contributions are both important to explain the origin of the energy barriers.

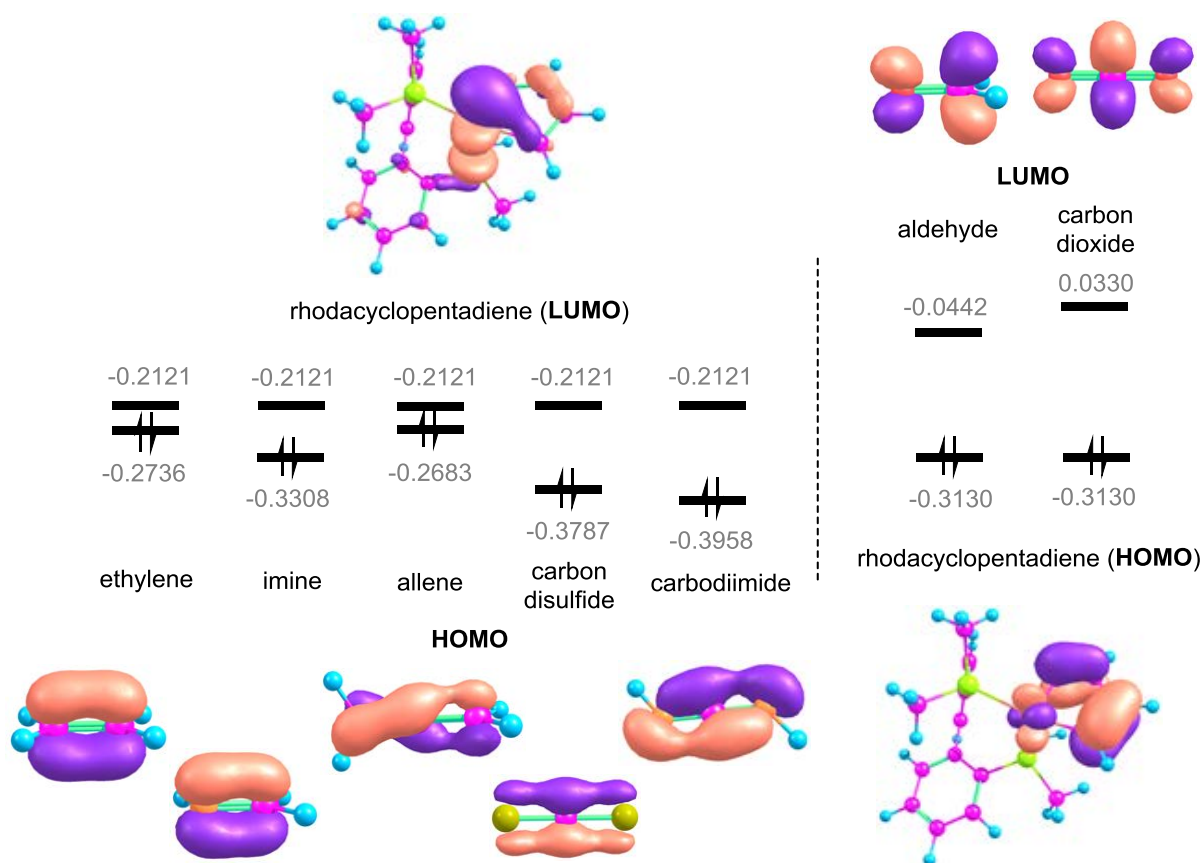
Table 1. Comparison of C(sp²) unsaturation strain ($\Delta E_{strain}^{\ddagger}$), rhodacyclopentadiene intermediate strain ($\Delta E_{strain}^{\ddagger}$), total strain ($\Delta E_{strain}^{\ddagger}$), interaction ($\Delta E_{int}^{\ddagger}$) and total ($\Delta E_{total}^{\ddagger}$) electronic energies (kcal·mol⁻¹) at the insertion step of the [2+2+2] cycloaddition catalysed by [Rh(BIPHEP)]⁺ species

C(sp ²) unsaturation	$\Delta E_{strain}^{\ddagger}$ <i>unsat.</i>	$\Delta E_{strain}^{\ddagger}$ <i>interm.</i>	$\Delta E_{strain}^{\ddagger}$	$\Delta E_{int}^{\ddagger}$	$\Delta E_{total}^{\ddagger}$
ethylene	12.6	6.0	18.6	-12.4	6.2
imine	7.0	4.8	11.8	4.2	16.0
aldehyde	8.7	5.9	14.6	8.6	23.2
allene	21.8	5.6	27.4	-24.0	3.4
carbon disulfide	18.3	11.1	29.4	-8.9	20.5
carbodiimide	26.0	5.7	31.7	-21.4	10.3
carbon dioxide	40.0	23.9	63.9	-33.0	30.9

The increasing order of the energy barriers may be related to the NPA charge of the C(sp²) unsaturation in the TS's of the insertion step (**Table 2**). In that sense, the interaction energies become lower when the charge of the C(sp²) unsaturation acquires a more positive charge, which reveals that a charge transfer from the C(sp²) unsaturation to the rhodacyclopentadiene preferably takes places. While ethylene and the allene fragments are more positively charged in the **TS(A3.A4)** geometries, which favours that the two lowest energy barriers are associated to them, the cases of the aldehyde and carbon dioxide are the most unfavourable ones and can be related to a charge transfer from the rhodacyclopentadiene to the C(sp²) unsaturation as the negative NPA charge values point out. These charge transfers can be discussed by analysing the HOMO and LUMO orbitals of the interacting system (**Scheme 49**).

Table 2. Relation between the interaction electronic energy ($\Delta E_{int}^\ddagger$, kcal·mol⁻¹) of the insertion step and the calculated NPA charges of the C(sp²) unsaturation fragment in the **TS(A3.A4)** geometries bearing [Rh(BIPHEP)]⁺ species

C(sp ²) unsaturation	$\Delta E_{int}^\ddagger$	NPA charge of the C(sp ²) unsaturation in TS(A3.A4) (e ⁻)
ethylene	-12.4	0.135
imine	4.2	0.081
aldehyde	8.6	-0.087
allene	-24.0	0.140
carbon disulfide	-8.9	0.119
carbodiimide	-21.4	0.086
carbon dioxide	-33.0	-0.293



Scheme 49. HOMO and LUMO orbitals most involved in the different charge transfer processes of the insertion step of the [2+2+2] cycloaddition catalysed by [Rh(BIPHEP)]⁺ species. Energy values expressed in a.u.

In the cases of ethylene and allene, which both present negative interaction energies, the gaps between the HOMO and LUMO orbitals are similar and relatively small, which explains that they are associated to the most positive NPA charges as the charge transfer from the HOMO orbital of the C(sp²) unsaturation to the LUMO of the rhodacyclopentadiene is more efficient. In the cases of the imine, carbon disulfide and carbodiimide, the HOMO orbitals are especially stable, which provokes that the charge transfer becomes less favourable than in the cases of ethylene and allene and, as a result of that, the C(sp²) unsaturation fragments are electronically slightly positive.

With regards to the cases of the aldehyde and carbon dioxide, they are featured by the negative charge that the C(sp²) unsaturation acquires, which reveals that the charge transfer from the HOMO of the rhodacyclopentadiene to the LUMO of the C(sp²) unsaturation is the most important interaction, as the oxygen heteroatoms stabilise the HOMO and LUMO orbitals of the C(sp²) unsaturation.

Finally, the fact that the most negative (or stabilising) interaction energy is associated to a highly-strained systems like carbon dioxide can be understood by considering that the deformation of the C(sp²) unsaturation at the TS structure provokes that HOMO orbitals tend to destabilise at the time that the LUMO orbitals tend to stabilise, thus facilitating a more effective charge transfer and allowing a better stabilisation by the interaction.

As a whole, the reactivity order of the different systems can be assessed by looking at the Gibbs energy barriers calculated (**Figure 8**). In that sense, the system involving an allene moiety is more reactive than when ethylene or carbon disulfide are involved, which are more reactive than when an imine or an aldehyde are entailed, at the time that are more reactive than a carbodiimide, which finally leaves carbon dioxide as the least reactive one.

Of special interest is the challenging case in which carbon dioxide is involved, which represents a great advancement in experimental terms because it entails the capture of gas particles to participate in the process. Such reaction was reported by Tanaka and co-workers⁶⁰ to be experimentally possible under [Rh(H₈-cod)₂]BF₄/BINAP catalysis. In their work, dramatic differences were observed in the outcome of the reaction when the ligand was changed, ranging from 78% yield for H₈-BINAP to only 9% when BIPHEP is employed. Such a reactivity variance can justify the fact that a high energy barrier has been computationally located in our case (38.7 kcal·mol⁻¹), as BIPHEP ligand was modelled for the present study. Nevertheless, the use of an alternative catalyst like

$[\text{RhCl}(\text{ethylene})_2]_2$ was observed to afford lower energy barriers that corroborate the experimental feasibility as will be explained in more detail in section 5.3.

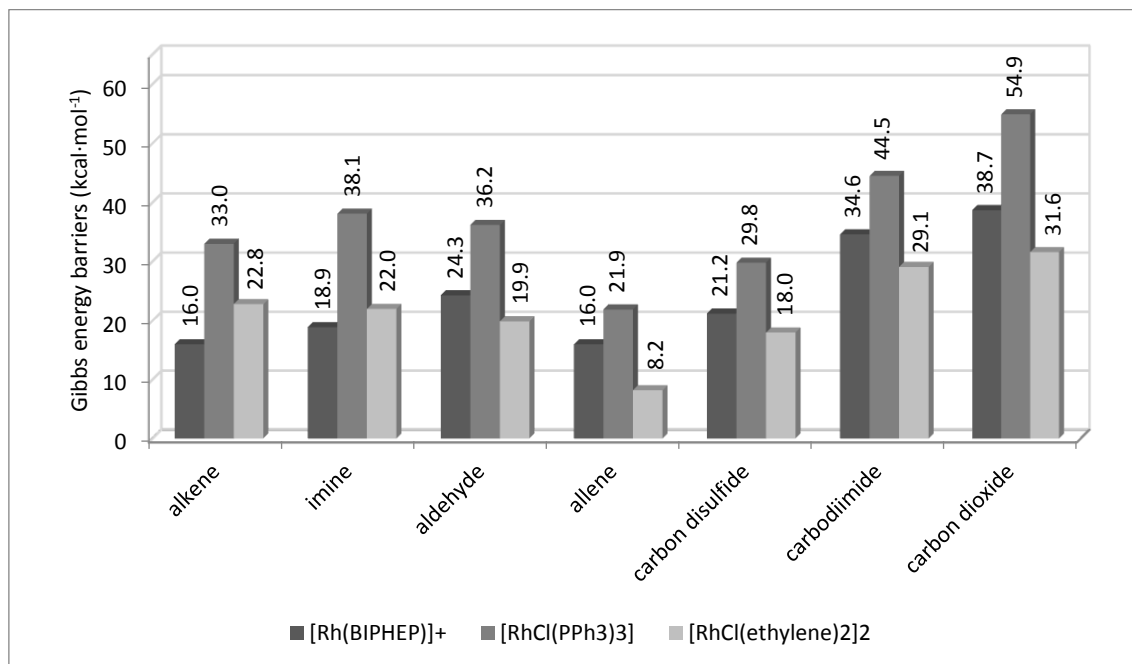


Figure 8. Gibbs energy barriers of the rate-determining steps of the three catalytic systems to perform the $[2+2+2]$ cycloaddition reaction

With regards to the Gibbs reaction energy, all processes were found to be exothermic (**Figure 9**). Though no general significant trend is appreciated, the case of carbon dioxide is observed to be the less favourable one, as it is the less exothermic and is associated to the highest rate-determining energy barrier. In none of the studied cases the exothermicity of the process is so dramatic as the one found for the $[2+2+2]$ cycloaddition of three acetylenes ($-134.5 \text{ kcal}\cdot\text{mol}^{-1}$),^{9m} which can be attributed to the fact that no aromaticity is attained when a $\text{C}(\text{sp}^2)$ unsaturation is employed to perform a $[2+2+2]$ cycloaddition reaction with two acetylenes.

Attending the Gibbs reaction energy values, the most exothermic processes are associated to the systems entailing an allene or a carbodiimide. Systems with ethylene or imine are less exothermic, at the time that the involvement of an aldehyde or carbon disulfide are less favourable and, at the last position, carbon dioxide remains as the least exothermic one.

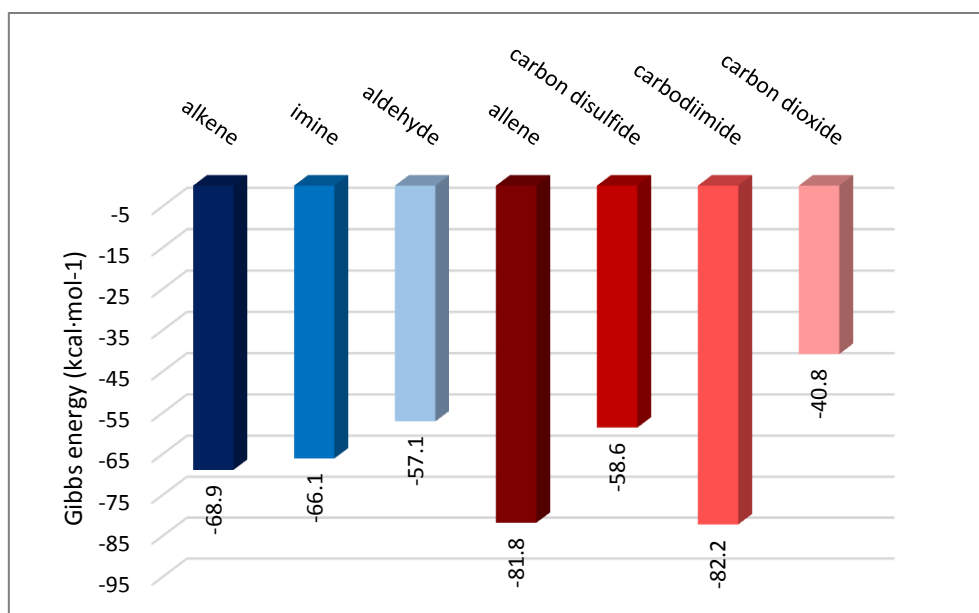
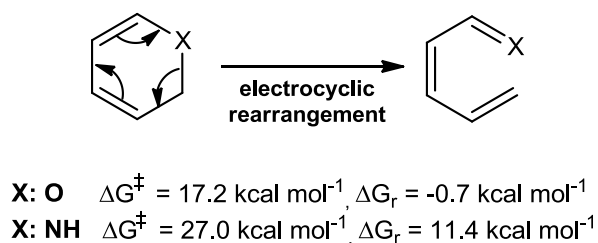


Figure 9. Gibbs reaction energies of the [2+2+2] cycloaddition involving the studied unsaturations

At this point, the stability of the resulting cycloadducts was evaluated. Interestingly, pyran and dihydropyridine rings resulting from the [2+2+2] cycloaddition reaction involving an aldehyde and an imine group, respectively, were found to be likely to undergo a thermally-allowed electrocyclic disrotatory rearrangement.

The process proved to be more kinetically possible for the pyran ring than for the dihydropyridine as can be stated by the respective Gibbs energy barriers of 17.2 kcal·mol⁻¹ and 27.0 kcal·mol⁻¹, respectively (**Scheme 50**). From the thermodynamic perspective, the electrocyclic rearrangement on pyrans will remain as an equilibrium, because the associated Gibbs energy of the reaction is nearly null ($\Delta G_r = -0.7$ kcal·mol⁻¹). Contrary, the fact that the ring-opening reaction for dihydropyridines is endothermic in 11.4 kcal·mol⁻¹ indicates that such process is not thermodynamically favoured and the product will not be generated (**Scheme 24**, page 29).



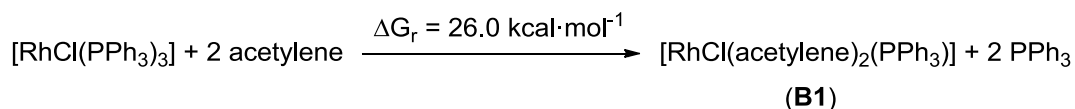
Scheme 50. Pyran and dihydropyridine electrocyclic rearrangement

Remarkably, the instability found for pyrans is corroborated by Tanaka and co-workers' work,⁴⁰ who described the ring-opening process of pyran rings, to the point that the open-chain structures are the unique compound detected.

3.2. [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition reaction

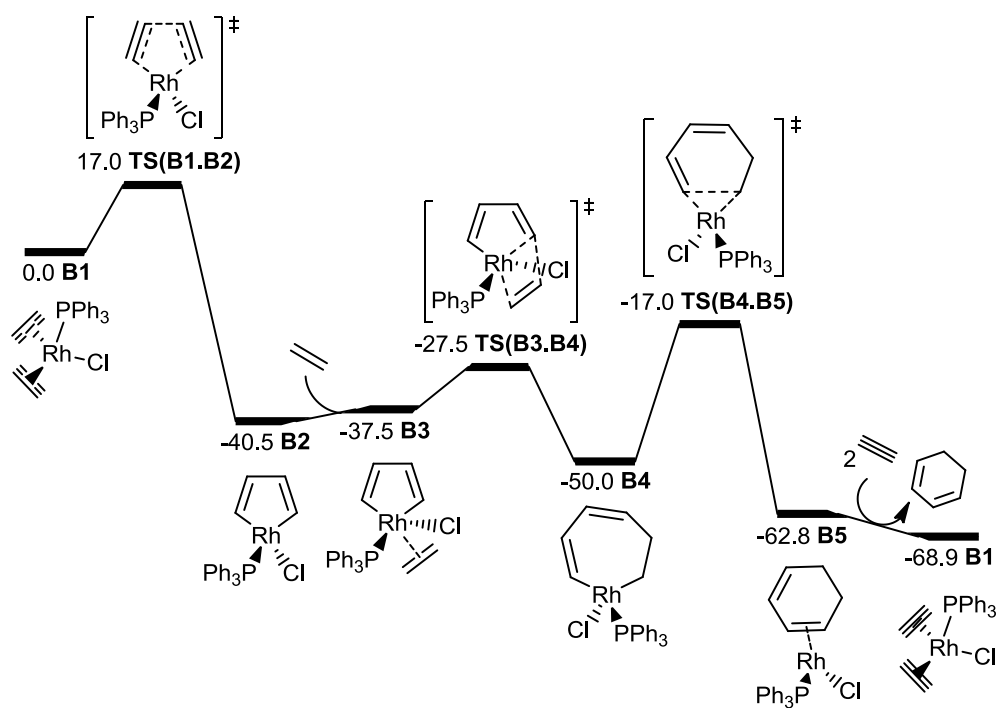
The lowest-in-energy pathway corresponding to the use of [RhCl(PPh₃)₃] catalyst was determined by performing the same analysis than in the previous subsection. In this case, the coordination of two, one or no triphenylphosphine was taken into account to locate the most favourable route.

Our calculations indicated that the mechanistic pathway depicted in **Scheme 52** is the most likely one taking place and the most probable intermediates, depending on the nature of the C(sp²) unsaturation introduced, are the ones represented in **Scheme 53** that only present one triphenylphosphine ligand coordinated to the rhodium centre. The cycle is proposed to start from bisacetylene complex **B1**, which can be afforded in a precatalytic endothermic process of 26.0 kcal·mol⁻¹ involving the substitution of two triphenylphosphine ligands of the [RhCl(PPh₃)₃] complex by two acetylenes (**Scheme 51**).

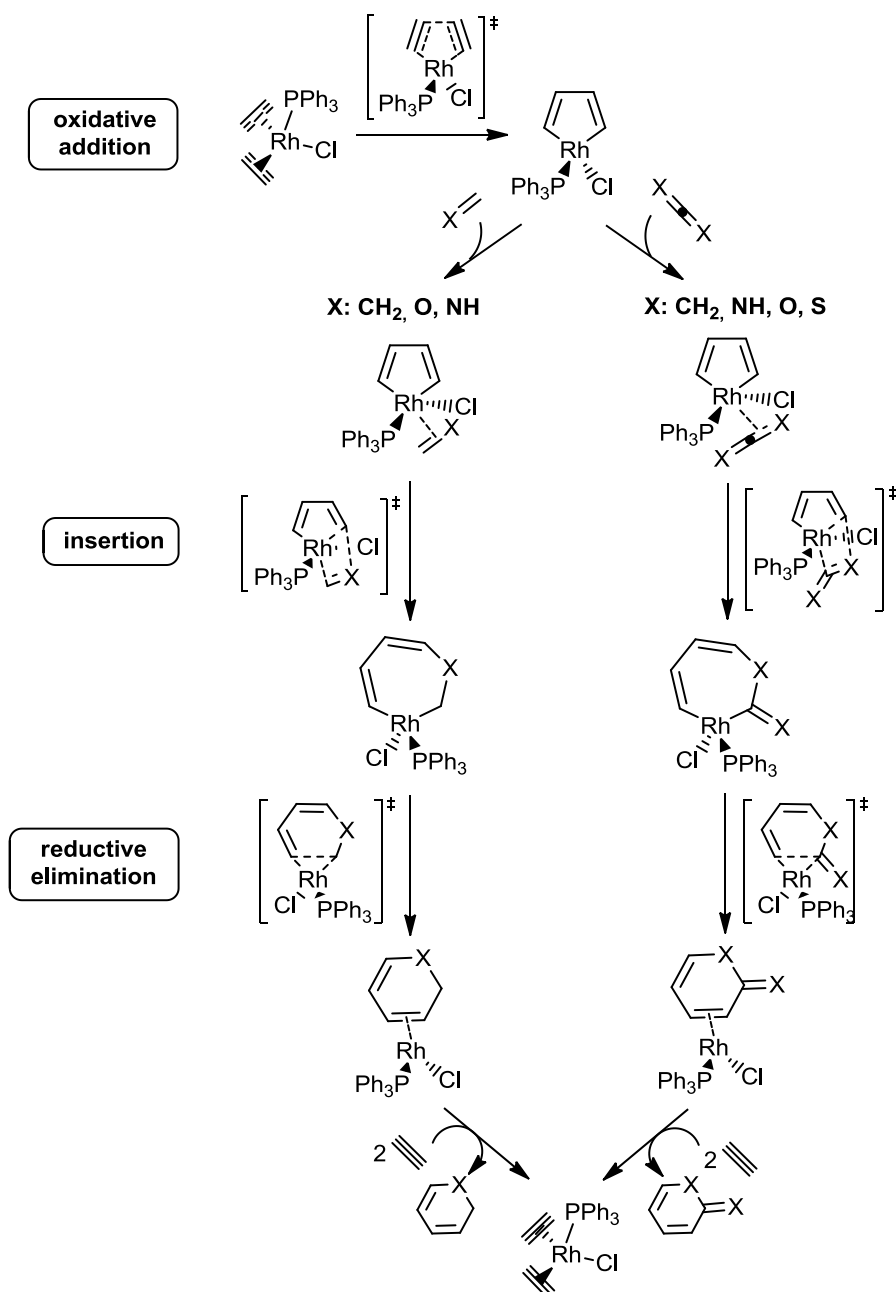


Scheme 51. Precatalytic process to afford **B1**

Contrary to the mechanistic proposal for the [Rh(BIPHEP)]⁺-catalysed mechanisms, our calculations indicate that all cumulenic unsaturations (allenes, carbodiimies, carbon dioxide and carbon disulfide) intermediates evolve through the same regioselectivity pattern in the insertion step by affording a Rh-C(sp²) bond. In all the cases, the insertion results in the formation of a new Rh-C bond and a C-X bond, and the breaking of the π C=X bond. In none of the cases, the transition state corresponding to a [4+2] approach could be found.



Scheme 52. Gibbs energy profile (kcal·mol⁻¹) at 298.15K for the lowest-in-energy route for the [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition of two acetylenes and one ethylene unit



Scheme 53. Proposed mechanism for the [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition of two acetylenes and different C(sp²) unsaturations

The oxidative addition step involves in all cases two acetylene units and, therefore, the energy barrier remains the same in all the studied cases (17.0 kcal·mol⁻¹). Looking at the insertion step (**Figure 10**), the energetic demand seems to be linked to the electronegativity of the heteroatom involved, since the use of alkenes and allenes is much more favourable than any of the other cases. The approaches represented in **Scheme 53** that determine the regioselectivity of the process were more favourable than the opposite ones by 6-14 kcal·mol⁻¹.

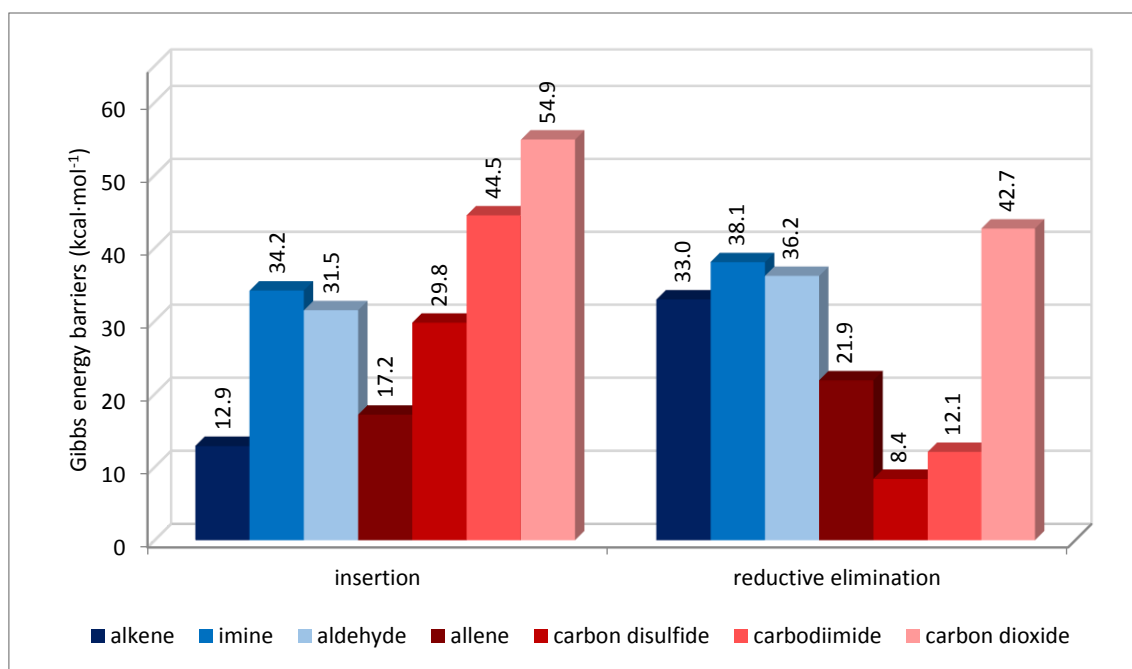


Figure 10. Gibbs energy barriers of the oxidative addition, insertion and reductive elimination steps of the $[\text{RhCl}(\text{PPh}_3)_3]$ -catalysed $[2+2+2]$ cycloaddition involving the studied unsaturations

According to the ASM analysis (**Table 3**), the energetic differences observed for the insertion step can be generally attributed to a combination between the interaction and the strain energies to distort the π bonds to be inserted in the rhodacyclopentadiene intermediate. The case of carbon dioxide should be highlighted for having a significantly high strain energy contribution to elongate the $\text{C}=\text{X}$ bond to be inserted, which provokes that the total energy barrier dramatically increases.

Table 3. Comparison of $\text{C}(\text{sp}^2)$ unsaturation strain ($\Delta E_{\text{unsat.}}^{\ddagger}$), rhodacyclopentadiene intermediate strain ($\Delta E_{\text{interm.}}^{\ddagger}$), total strain ($\Delta E_{\text{strain}}^{\ddagger}$), interaction ($\Delta E_{\text{int}}^{\ddagger}$) and total ($\Delta E_{\text{total}}^{\ddagger}$) electronic energies ($\text{kcal}\cdot\text{mol}^{-1}$) at the insertion step of the $[2+2+2]$ cycloaddition catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$ species

$\text{C}(\text{sp}^2)$ unsaturation	$\Delta E_{\text{unsat.}}^{\ddagger}$	$\Delta E_{\text{interm.}}^{\ddagger}$	$\Delta E_{\text{strain}}^{\ddagger}$	$\Delta E_{\text{int}}^{\ddagger}$	$\Delta E_{\text{total}}^{\ddagger}$
ethylene	12.5	10.6	23.1	-13.5	9.6
imine	11.8	11.1	22.9	11.9	34.8
aldehyde	11.4	10.9	22.3	4.9	27.2
allene	21.2	11.5	32.7	-23.8	8.9
carbon disulfide	20.1	15.7	35.8	-12.1	23.7
carbodiimide	26.0	1.5	27.5	5.6	33.1
carbon dioxide	35.1	23.2	58.3	-10.4	47.9

Focusing on the C(sp²) unsaturations, the calculation of the NPA charges of these fragments (**Table 4**) indicates that a charge transfer from the rhodacyclopentadiene structure to the C(sp²) unsaturation takes place, as the negative NPA charge indicates, for the cases where an imine, aldehyde, carbodiimide and carbon dioxide are involved. Contrary, a charge transfer from the C(sp²) unsaturation to rhodacyclopentadiene occurs when the system entails ethylene, an allene or carbon disulfide, as the positive NPA charges point out.

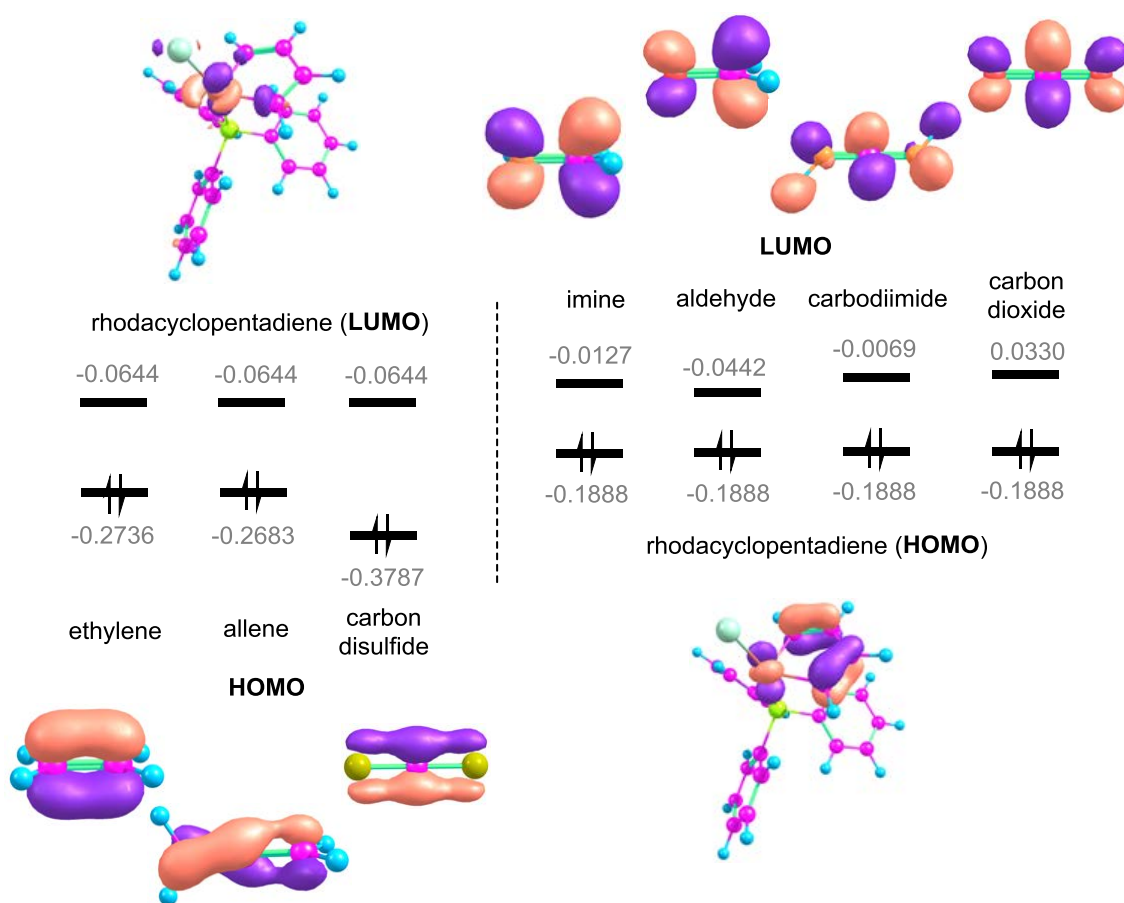
Table 4. Relation between the interaction electronic energy ($\Delta E_{int}^{\ddagger}$, kcal·mol⁻¹) of the insertion step and the calculated NPA charges of the C(sp²) unsaturation fragment in the **TS(B3.B4)** geometries of the [2+2+2] cycloaddition catalysed by [RhCl(PPh₃)] species

C(sp ²) unsaturation	$\Delta E_{int}^{\ddagger}$	NPA charge of the C(sp ²) unsaturation in TS(B3.B4) (e ⁻)
ethylene	-13.5	0.129
imine	11.9	-0.007
aldehyde	4.9	-0.127
allene	-23.8	0.129
carbon disulfide	-12.1	0.045
carbodiimide	5.6	-0.064
carbon dioxide	-10.4	-0.168

As it can be observed, the lowest interaction energies (ethylene, allene and carbon disulfide) are associated to the most positively charged C(sp²) unsaturations, which is related to an efficient HOMO (C(sp²) unsaturation) – LUMO (rhodacyclopentadiene) interaction (**Scheme 54**).

Compared to the orbitals of the rhodacyclopentadiene in the [Rh(BIPHEP)]⁺ catalytic system, it can be observed that the HOMO and LUMO orbitals of the rhodacyclopentadiene bearing [RhCl(PPh₃)] catalytic species are higher in energy. This fact can be attributed to the change of the global electronic charge of the system, since [Rh(BIPHEP)]⁺ system is cationic, which facilitates that the associated LUMO orbitals are more likely to accept an electron than [RhCl(PPh₃)] system, which is neutral and thus less prompted to do so. On the other hand, the HOMO orbitals associated to [Rh(BIPHEP)]⁺ system display a higher difficulty in releasing an electron than [RhCl(PPh₃)] system. Therefore, the higher-in-energy (and less stable) LUMO orbitals associated to the [RhCl(PPh₃)] system explain that the energy barriers for this system are bigger than those associated to [Rh(BIPHEP)]⁺ catalytic system and justify that,

contrary to the cationic system, the $C(sp^2)$ unsaturation fragments of the imine and carbodiimide cases tend to acquire a negative NPA charge.



Scheme 54. HOMO and LUMO orbitals involved in the different charge transfer processes entailing $[RhCl(PPh_3)]$ species. Energy values expressed in a.u.

With regards to the reductive elimination step, carbon disulfide and carbodiimide (structure **A**, **Figure 11**) are associated to significantly low energy barriers. Such a decrease may be due the *trans* effect, since the chloride ligand is preferably placed in *trans* orientation with respect to the heterocycle formed for the cases of carbon disulfide and carbodiimide, whereas in *cis* orientation for the carbon dioxide and allenes (structure **B**, **Figure 11**) cases. The *trans* effect provokes that the Rh-C bonds become weaker and, as a result of that, the reductive elimination takes place more easily. These conclusions were extracted after evaluating the possible orientations that the chloride and triphenylphosphine ligands can adopt in the structures involved in this step.

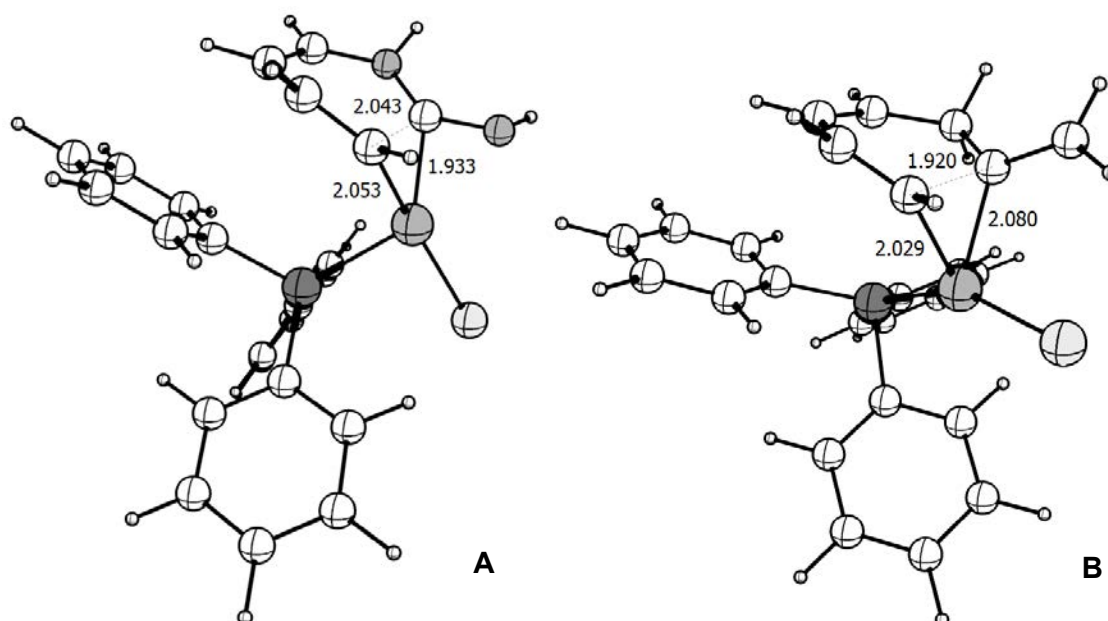


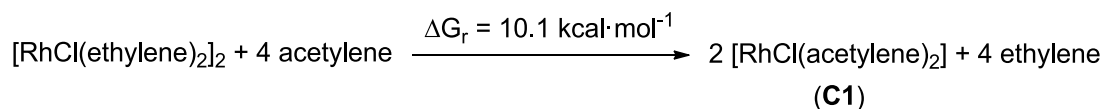
Figure 11. Optimized structures (B3LYP-D3/cc-pVDZ-PP) for **TS(B4.B5)** involving carbodiimide (**A**) and allene (**B**). Most relevant distances are given in Å

Taking as a reference the previous work in our group in which the [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition of three acetylene units was analysed,^{9m} it can be observed that, while the rate-determining energy barrier for the cyclisation of three acetylenes corresponds to the oxidative addition step and it is of 20.2 kcal·mol⁻¹, all the C(sp²) unsaturations have led to higher energetic values (**Figure 8**). From **Figure 8**, it can be extracted that the reactivity of alkynes is comparable to that of allenes under the presence of [RhCl(PPh₃)₃] catalyst, and both are superior than the reactivity of any other C(sp²) unsaturation analysed in the present work. The use of alkenes and carbon disulfide led to reasonable energy barriers near 30 kcal·mol⁻¹. However, imines, aldehydes, carbodiimides and carbon dioxide were all associated to excessively high energy barriers that make these systems unreactive when [RhCl(PPh₃)₃] catalyst is employed.

Overall, the rate-determining energy barriers reveal that the process is much less likely to take place than when the [Rh(BINAP)]⁺ catalyst is employed, as significantly higher values are associated to the use of [RhCl(PPh₃)₃] catalyst.

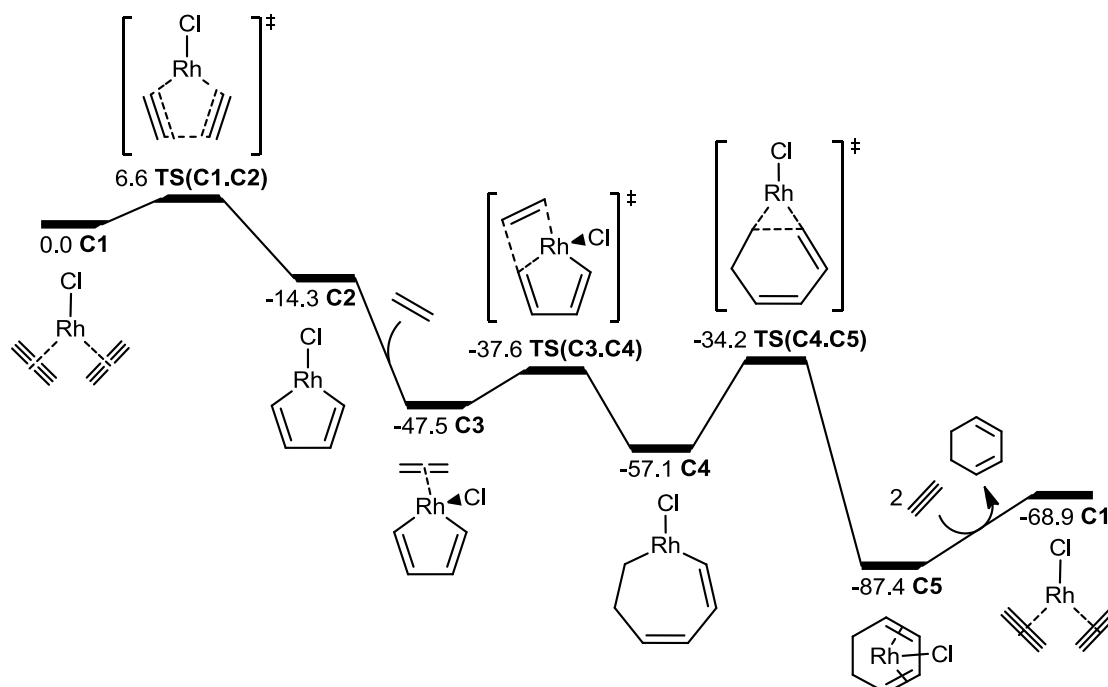
3.3. [RhCl(ethylene)₂]₂-catalysed [2+2+2] cycloaddition reaction

Last, the use of a phosphine-free catalytic species like [RhCl(ethylene)₂]₂ was analysed (**Scheme 56**). The catalytic intermediates for this catalytic cycle bear [RhCl] as the catalytic species, which can be obtained in a precatalytic endothermic process of 10.1 kcal·mol⁻¹, which entails the dissociation of the dimeric catalyst and the loss of ethylene ligands due to their lability to generate bisacetylene complex **C1** (**Scheme 55**).

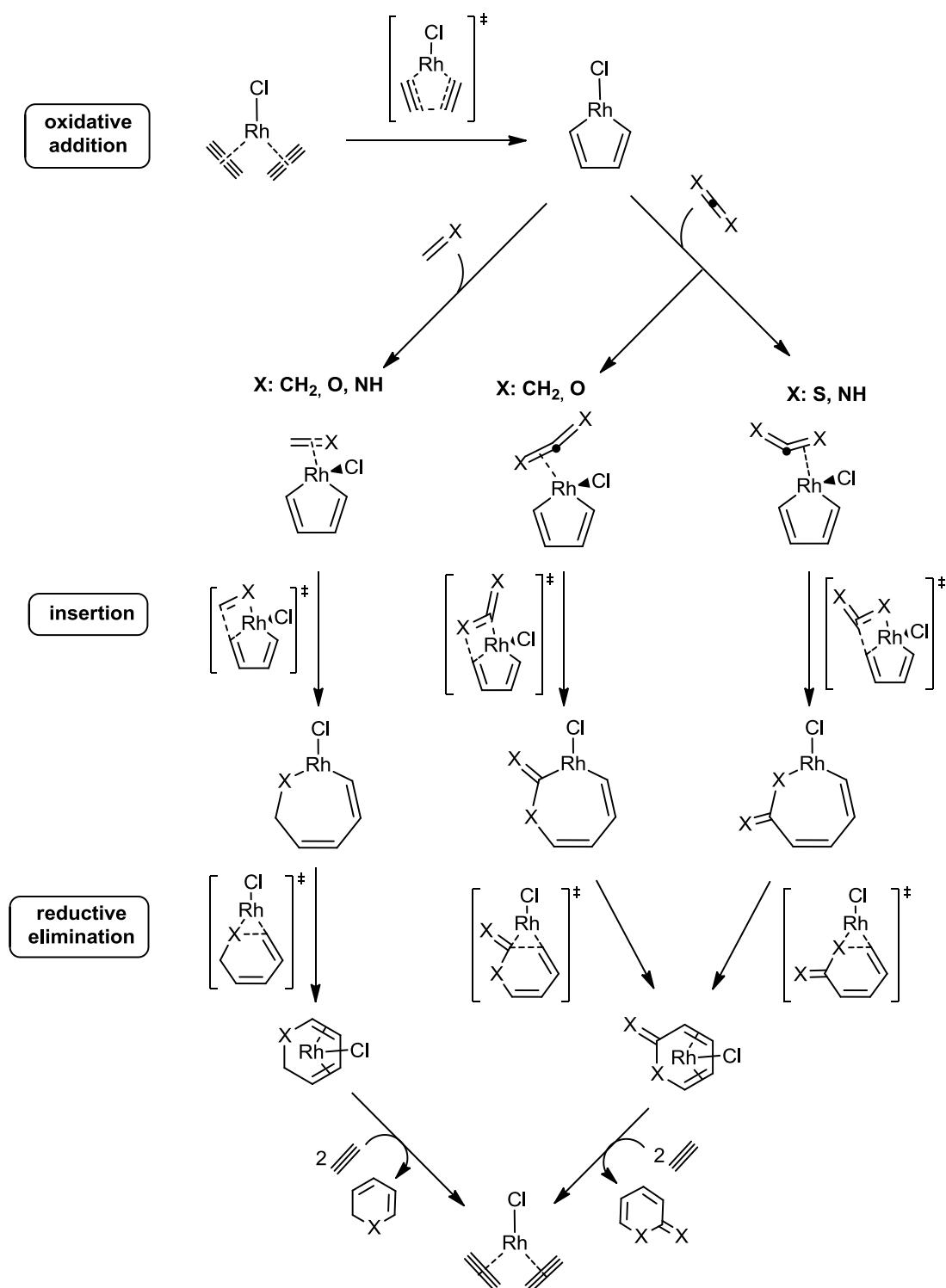


Scheme 55. Precatalytic process to afford **C1**

The intermediates proposed herein are the same when alkenes, aldehydes or imines are used and, contrary to the regioselectivity observed for this unsaturations when [Rh(BINAP)]⁺ catalyst is employed, a Rh-X bond is generated. On the other hand, the regioselectivity observed for the allene and carbon dioxide is different from that involving of carbon disulfide and carbodiimide, as a Rh-C(sp²) is formed in the first one and a Rh-X in the second one (**Scheme 57**). Similarly to the other catalysts, the transition state corresponding to the [4+2] approach could not be found.



Scheme 56. Gibbs energy profile (kcal·mol⁻¹) at 298.15K for the lowest-in-energy route for the [RhCl(ethylene)₂]₂-catalysed [2+2+2] cycloaddition of two acetylenes and one ethylene unit



Scheme 57. Proposed mechanism for the [RhCl(ethylene)₂]₂-catalysed [2+2+2] cycloaddition of two acetylenes and different C(sp²) unsaturations

Similarly to the mechanisms presented for the other catalysts, the oxidative addition preferably takes place between two acetylenes through an energy barrier of 6.6 kcal·mol⁻¹ which is, therefore, the same independently of the C(sp²) unsaturation that later enters in the catalytic cycle (**Scheme 57**).

Regarding the energy barriers corresponding to the insertion step (**Figure 12**), a clear favourability is stated when electronegativity of the heteroatom increases for non-cumulenic unsaturations (ethylene, imine and aldehyde). However, the opposite behaviour is observed for cumulenic unsaturations (allenes, carbon disulfide, carbodiimides and carbon dioxide), as the processes become less favourable when the electronegativity of the heteroatoms involved increase. The regioselective preferences for the insertion step depicted in **Scheme 57** are more favourable by 3-7 kcal·mol⁻¹ than the opposite ones.

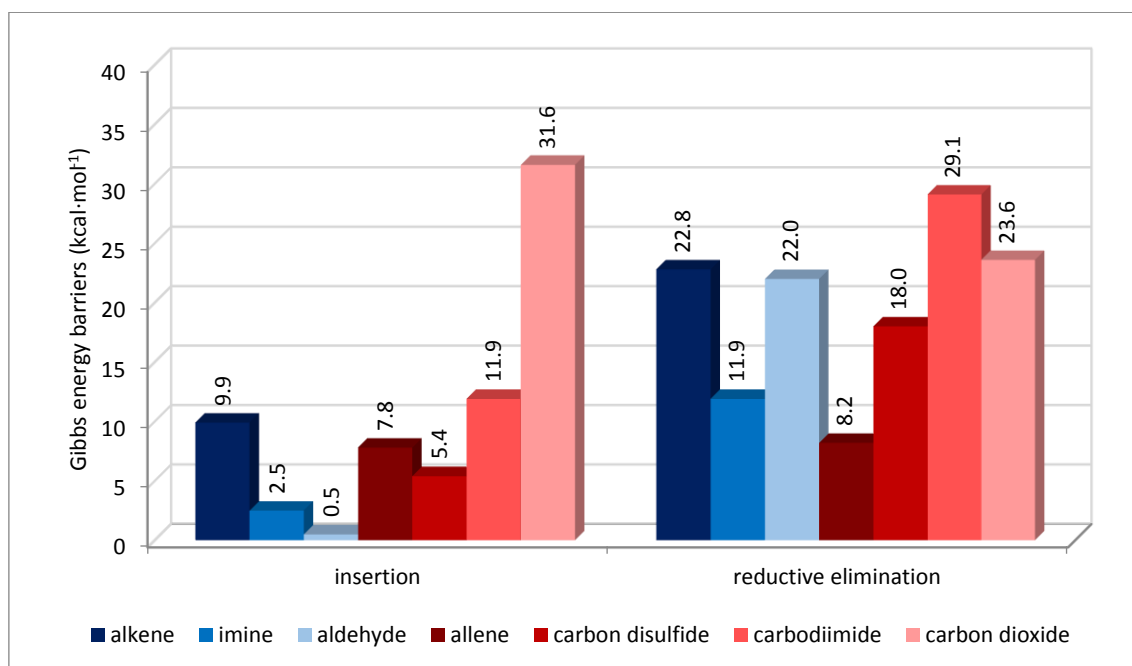


Figure 12. Gibbs energy barriers of the insertion and reductive elimination steps of the [RhCl(ethylene)₂]₂-catalysed [2+2+2] cycloaddition involving the studied unsaturations

The ASM analysis (**Table 5**) reveals that, even though high energies are required to provoke the distortion of the C(sp²) unsaturated fragments in the insertion step, the process is also accompanied by a remarkable stabilisation thanks to the attractive interaction between the two fragments. As a result of such combination, the total energy barriers are low in all cases except for carbon dioxide, though the process is still theoretically feasible.

Table 5. Comparison of C(sp²) unsaturation strain ($\Delta E_{strain}^{\ddagger}$), rhodacyclopentadiene intermediate strain ($\Delta E_{strain}^{\ddagger}$), total strain ($\Delta E_{strain}^{\ddagger}$), interaction ($\Delta E_{int}^{\ddagger}$) and total ($\Delta E_{total}^{\ddagger}$) electronic energies (kcal·mol⁻¹) at the insertion step of the [2+2+2] cycloaddition catalysed by [RhCl] species

C(sp ²) unsaturation	$\Delta E_{strain}^{\ddagger}$ unsat.	$\Delta E_{strain}^{\ddagger}$ interm.	$\Delta E_{strain}^{\ddagger}$	$\Delta E_{int}^{\ddagger}$	$\Delta E_{total}^{\ddagger}$
ethylene	14.3	21.3	35.6	-25.4	10.2
imine	4.7	8.4	13.1	-11.0	2.1
aldehyde	0.8	3.0	3.8	-3.7	0.1
allene	17.0	20.4	37.4	-30.3	7.1
carbon disulfide	9.7	2.0	11.7	-7.0	4.7
carbodiimide	22.3	5.1	27.4	-15.8	11.6
carbon dioxide	28.5	10.3	38.8	-6.3	32.5

The calculation of the NPA charges (**Table 6**) reveals the preference of the systems involving ethylene, imine, allene, carbon disulfide and carbodiimide to undergo a charge transfer from the C(sp²) unsaturation to rhodacyclopentadiene in **TS(C3.C4)** and, for aldehyde and carbon dioxide, the inverse charge transfer.

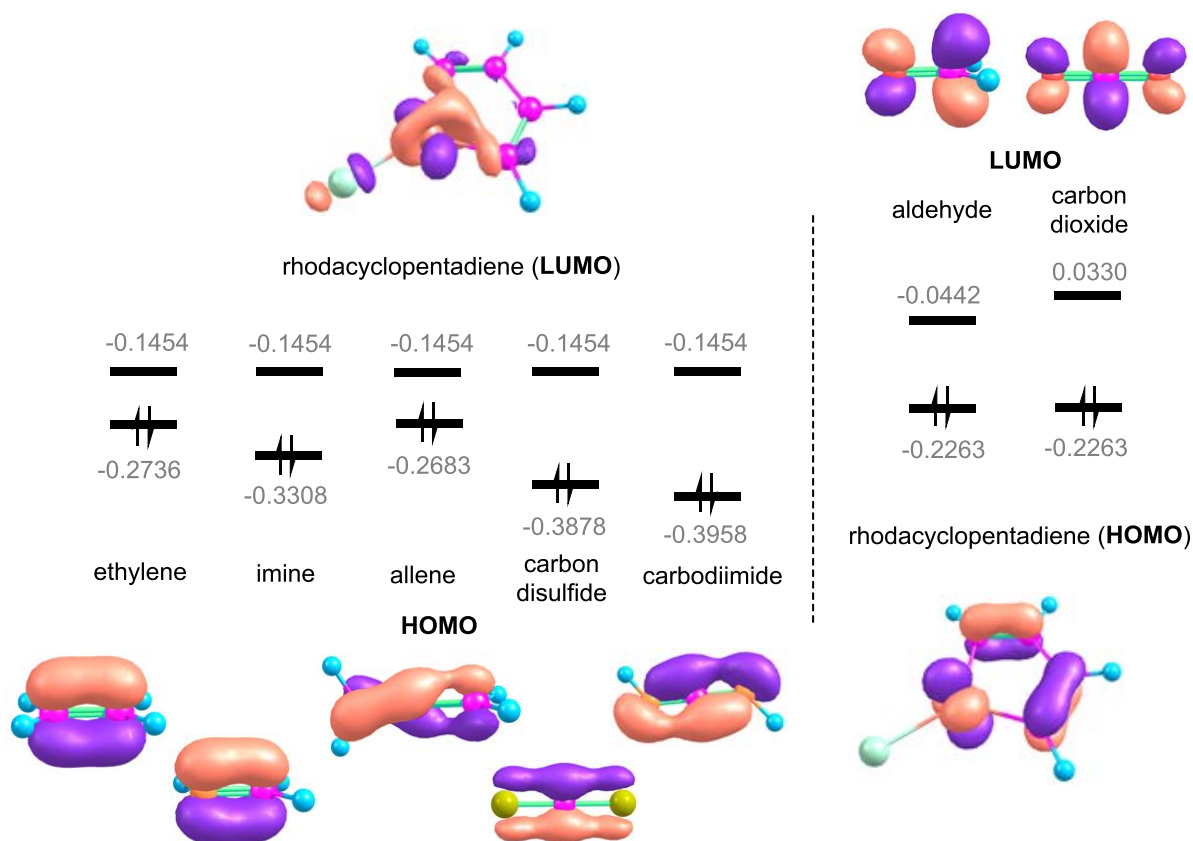
Table 6. Relation between the interaction electronic energy ($\Delta E_{int}^{\ddagger}$, kcal·mol⁻¹) of the insertion step and the calculated NPA charges of the C(sp²) unsaturation fragment in the **TS(C3.C4)** geometries of the [2+2+2] cycloaddition catalysed by [RhCl] species

C(sp ²) unsaturation	$\Delta E_{int}^{\ddagger}$	NPA charge of the C(sp ²) unsaturation in TS(C3.C4) (e ⁻)
ethylene	-25.4	0.169
imine	-11.0	0.025
aldehyde	-3.7	-0.033
allene	-30.3	0.155
carbon disulfide	-7.0	0.147
carbodiimide	-15.8	0.007
carbon dioxide	-6.3	-0.193

The most negative and stabilising interaction energies were found to be associated to the most positively-charged C(sp²) unsaturations, more concretely, the ethylene and allene cases. The analysis of the HOMO and LUMO orbitals for these systems (**Scheme 58**) reveals that they behave quite similarly to the cases presented for the

[Rh(BIPHEP)]⁺ catalyst. The most stabilising interaction energies are associated to the ethylene and allene cases, which can be attributed to a relatively low gap between the HOMO and LUMO orbitals.

On the other hand, it can be appreciated that both HOMO and LUMO orbitals of the [RhCl] catalytic system are higher in energy than those of [RhCl(PPh₃)] system. This fact can be directly related to concept that the phosphine is a σ -donor and π -acceptor ligand that tends to give electronic density to the rhodium center and thus decrease the charge of the metal from 0.209 to -0.134 in [RhCl] and [RhCl(PPh₃)] systems, respectively. As a result of that, the HOMO orbitals associated to [RhCl] system are less prompted to release electrons, as they are more stable, and the LUMO orbitals more likely to accept electrons, because they are more stable, than those associated to the [RhCl(PPh₃)] system.



Scheme 58. HOMO and LUMO orbitals involved in the different charge transfer processes entailing [RhCl] species. Energy values expressed in a.u.

Attending the relatively-low rate-determining energy barriers when a [RhCl]-based catalyst is used (**Figure 8**, page 58), all the [2+2+2] cycloaddition processes involving two acetylenes and one of the C(sp²) unsaturations studied are likely to take place. While alkenes, imines and aldehydes are approximately equally favourable, the feasibility of cumulenenic unsaturations seems to be linked to the electronegativity of the heteroatom as observed for the other catalytic species. The allene system is more reactive than the carbon disulfide one, which is more reactive than when carbodiimide is involved and, finally, the system entailing carbon dioxide remains as the least reactive one. From another perspective, it can be said as well that the systems bearing an alkene, imine or aldehyde are as reactive as carbon disulfide.

To sum up, in this work the reactivity of the rhodium(I)-catalysed [2+2+2] cycloaddition reaction involving two acetylenes and a C(sp²) unsaturation (ethylene, aldehyde, imine, allene, carbodiimide, carbon disulfide or carbon dioxide) was computationally analysed by means of DFT calculations for [Rh(BIPHEP)]⁺, [RhCl(PPh₃)₃] and [RhCl(ethylene)₂]₂ catalytic systems (**Table 7**).

The most favourable catalytic species found to undergo the studied cycloadditions is [RhCl] (derived from [RhCl(ethylene)₂]₂ catalyst), as low energy rate-determining energy barriers were associated to its use in all the cases evaluated. [Rh(BIPHEP)]⁺, which has been extensively reported to experimentally afford the desired cycloadducts, was observed to display reasonable rate-determining barriers, be favourable as well and represents a good alternative for the cases in which [RhCl] may not be efficient enough. In contrast to that, [RhCl(PPh₃)₃] catalyst showed a lower capacity to efficiently undergo the [2+2+2] cycloaddition in all the cases compared to the other two catalysts.

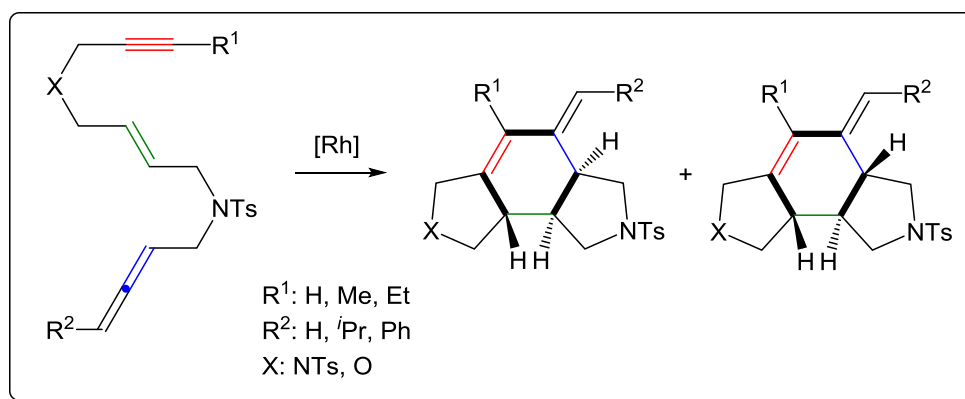
Table 7. Recommended catalytic species for each C(sp²) unsaturation in the rhodium-catalysed [2+2+2] cycloaddition reaction with two acetylenes

C(sp ²) unsaturation	Catalytic species		
	[RhCl]	[Rh(BIPHEP)] ⁺	[RhCl(PPh ₃) ₃]
alkene	✓	✓	✗
imine	✓	✓	✗
aldehyde	✓	✓	✗
allene	✓	✓	✓
carbon disulfide	✓	✓	✗
carbodiimide	✓	✗	✗
carbon dioxide	✓	✗	✗

Chapter 4. Rhodium-catalysed [2+2+2] cycloaddition of linear allene-ene-yne substrates

This chapter has been published on:

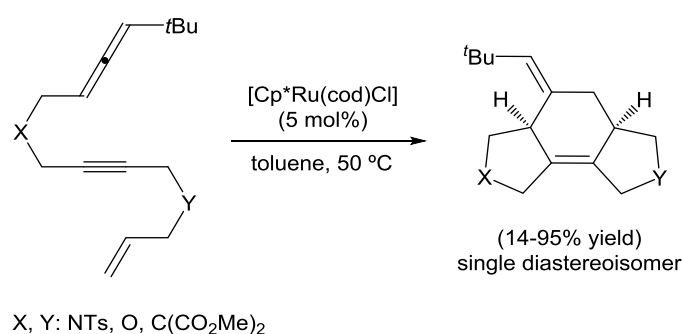
Cassú, D.; Parella, T.; Solà, M.; Pla-Quintana, A.; Roglans, A. *Chem. Eur. J.* **2017**, 23, 14889.



4.1. Precedents

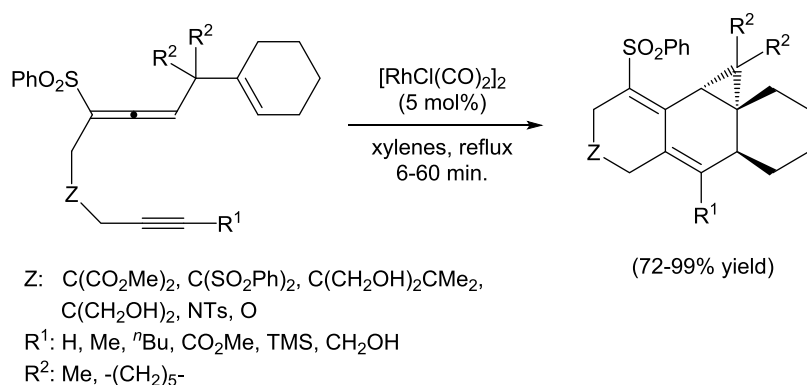
As mentioned in the introduction, the chemoselectivity of the [2+2+2] cycloaddition reaction is especially compromised when three different unsaturated groups are combined in a reaction. Therefore, we were interested in studying [2+2+2] cycloaddition reactions using three different carbon-based functionalities: an allene, an alkene, and an alkyne. To the best of our knowledge, only two previous cases have been reported evaluating this type of processes, both in a completely intramolecular manner.

Sato and co-workers⁷⁰ described a completely intramolecular cyclization of a linear allene-alkyne-alkene substrate under ruthenium catalysis to afford fused tricyclic skeletons (**Scheme 59**). The best results were obtained when a *tert*-butyl group was placed at the terminus of the allene group bearing different tethers.



Scheme 59. Ruthenium-catalysed cyclization of allene-yne-ene

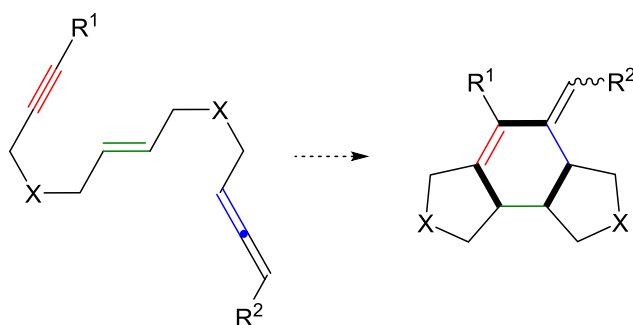
The second study that has evaluated the totally intramolecular cycloaddition reaction involving an alkyne, an allene and an alkene was provided by Mukai and co-workers.⁷¹ Contrary to the study of Sato's group, in this case the allene group was located between the alkyne and the alkene groups instead of at the terminus of the organic chain. Herein, bicyclo[4.1.0]heptene skeletons were obtained from alkyne-allene-alkene substrates under [RhCl(CO)₂]₂ catalysis. A great structural variability was obtained, thus allowing the formation of complex tri- and tetracyclic scaffolds in a totally diastereoselective fashion (**Scheme 60**)



Scheme 60. Polycyclic scaffolds synthesized by a rhodium(I)-catalysed [2+2+2] cycloaddition of yne-allene-ene substrates

In both studies, a plausible mechanism is proposed involving oxidative addition between the allene and the alkyne, which are in contiguous positions in the linear substrate thus favouring entropically the progress of the reaction. Based on the goal of synthesizing polycyclic structures, we designed the present project aimed at reacting allene-ene-yne substrates in which the oxidative addition of the alkyne and the allene is not geometrically favoured. Apart from the synthetic interest in the tricyclic scaffolds with stereogenic centres, we also wanted to study the process mechanistically, paying special attention to the order of reactivity of the three unsaturated groups in the [2+2+2] cycloaddition reaction.

Considering the precedents found in the literature related to the use of allenes in the context of [2+2+2] cycloaddition reactions as well as the previous work of the group in this field, we defined as our main objective for this chapter. It consisted of the study of the rhodium(I)-catalysed [2+2+2] cycloaddition of linear substrates combining an allene, an alkene and an alkyne unsaturated units to obtain fused tricyclic systems bearing an exocyclic double bond (**Scheme 61**). The process was designed as a totally-intramolecular cycloaddition, hence avoiding regio- and chemoselectivity problems and making it easier to focus on stereoselectivity and on the positional selectivity of the double bond of the allene group.



Scheme 61. Model linear allene-ene-yne substrate

The study entailed the synthesis of the linear substrates, the evaluation of the process and the proposal of a mechanistic pathway.

4.2. Synthesis of the model substrate

We designed substrate **1a** (**Figure 13**) for the study of the feasibility of the [2+2+2] cycloaddition reaction, which entails $R^1 = R^2 = H$ and $X = NTs$.

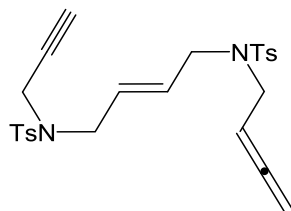
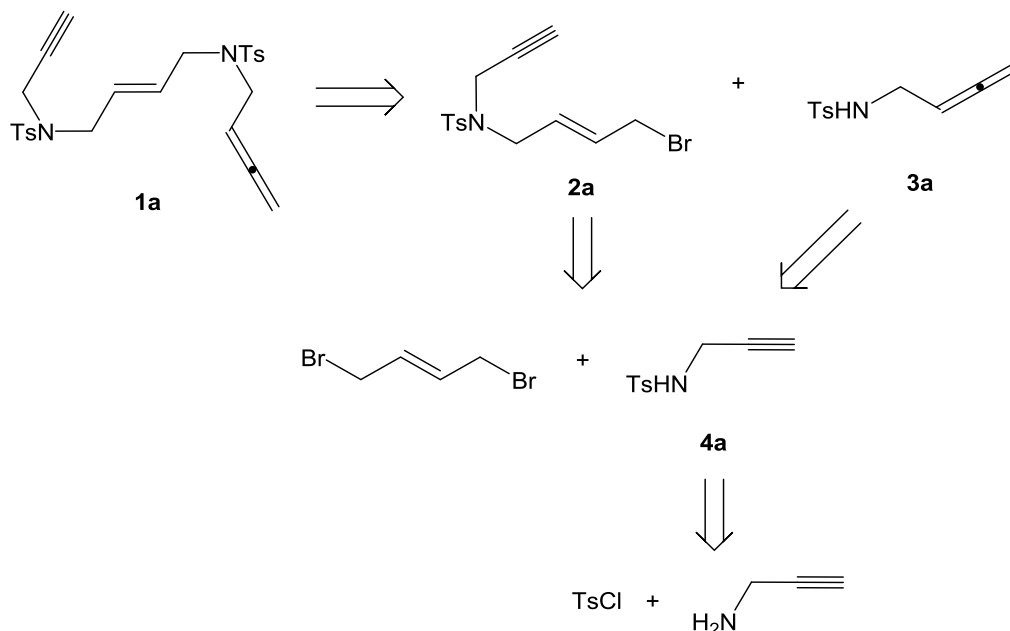


Figure 13. Model substrate **1a**

4.2.1. Retrosynthetic analysis of substrate **1a**

The retrosynthetic analysis proposed for the model substrate **1a** is based on the separate preparation of the allene motif and its later attachment (**Scheme 62**).

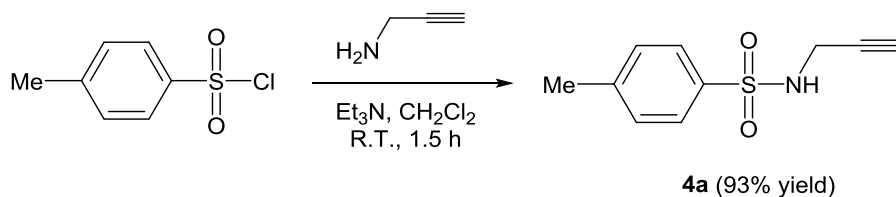


Scheme 62. Retrosynthetic analysis of model substrate **1a**

The preparation of the allene-ene-yne substrate **1a** was devised by performing a nucleophilic substitution to link the allene motif (**3a**) to the alkyne-alkene intermediate **2a**. **2a** could be readily prepared by a nucleophilic substitution of 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**4a**) to *trans*-1,4-dibromo-2-butene. On the other hand, the allene moiety could be prepared from **4a** as well through a homologation reaction for the synthesis of allenes. Finally, **4a** at the time could be obtained by the tosylation reaction of propargylamine. Due to the high reactivity of allenes, **3a** was introduced in the last steps of the synthetic process to avoid side reactions.

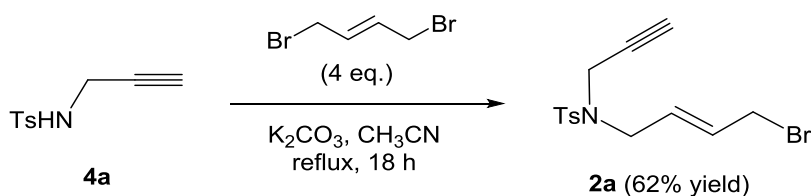
4.2.2. Synthesis of substrate **1a**

Following the disconnection scheme proposed for **1a**, its synthesis was started with the tosylation reaction of propargylamine, which is commercially available, using tosyl chloride and triethylamine as a base (**Scheme 63**) to obtain **4a** as a colourless solid in 93% yield.



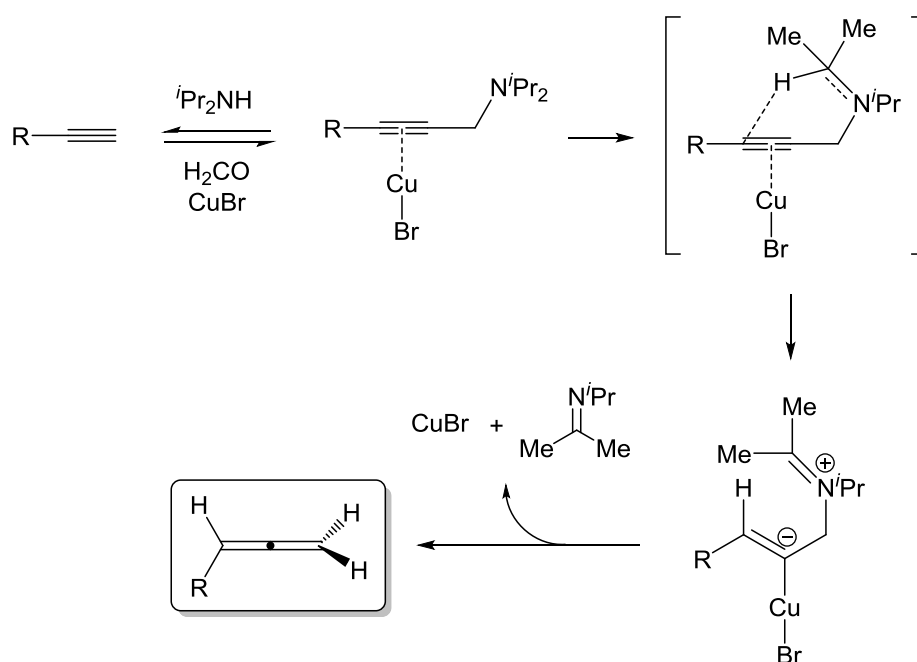
Scheme 63. Preparation of 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **4a**

The next step was the linkage of **4a** intermediate to *trans*-1,4-dibromo-2-butene by means of a base-promoted alkylation (**Scheme 64**). Since we intended to obtain the mono-alkylated product **2a**, we introduced 4 equivalents of *trans*-1,4-dibromo-2-butene and **4a** was slowly added to the reaction mixture in order to avoid the formation of the di-alkylated product. **2a** was afforded as a colourless solid in 62% yield.



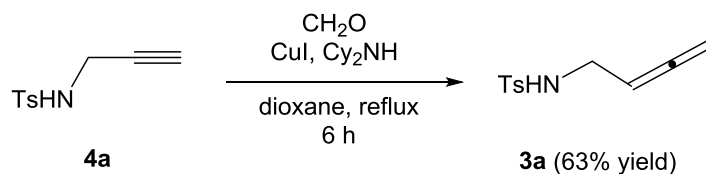
Scheme 64. Preparation of **2a**

On the other hand, **4a** intermediate also served to obtain the allene compound **3a**. Such a transformation could be accomplished using the so-called Crabbé homologation, which consists in the homologation of a terminal alkyne unit using formaldehyde, copper as a catalyst and diisopropylamine as a base.⁷² Cid and co-workers later proposed a mechanism for this transformation,⁷³ consisting in the initial formation of a Mannich base. Thanks to the alkyne activation provided by the Cu(I) catalyst, a hydride attack can be produced and the transition state for the formation of a vinyl carbanion can be stabilized (**Scheme 65**).



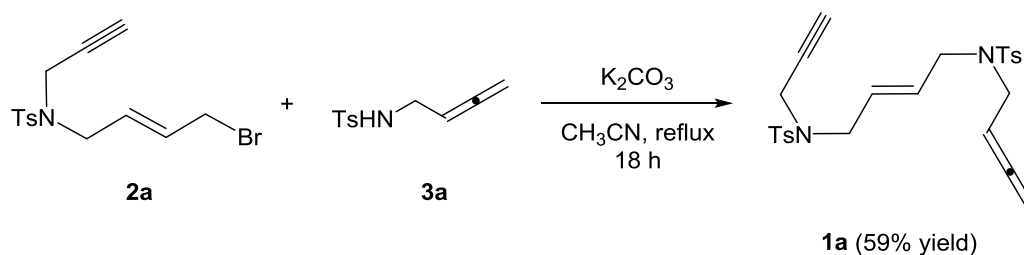
Scheme 65. Mechanism of allene formation in Crabbé homologation

Taking Crabbé's method to prepare allenes, Ma and co-workers managed to improve the outcome of the process by using dicyclohexylamine instead of diisopropylamine and CuI instead of CuBr.⁷⁴ With this procedure in hand, we successfully prepared allene **3a** in 63% yield (**Scheme 66**).



Scheme 66. Preparation of allene **3a**

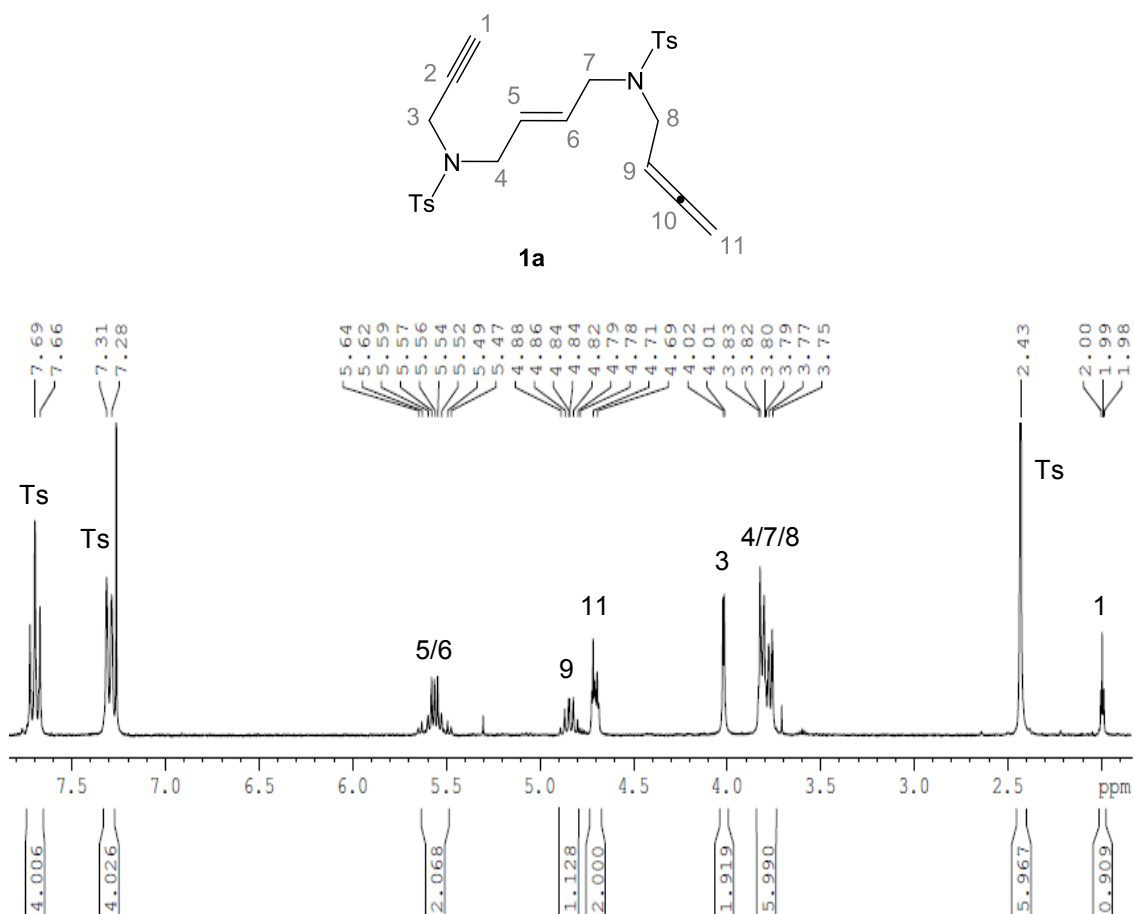
Finally, **2a** and **3a** intermediates were reacted under the presence of a base to perform a nucleophilic substitution reaction (**Scheme 67**). The product of this reaction corresponded to the target substrate **1a** and was afforded in 59% yield after its purification using flash column chromatography.



Scheme 67. Preparation of substrate **1a**

Among the different analytical techniques that we used to characterize **1a**, we would like to highlight ^1H and ^{13}C NMR spectroscopies for showing extremely revealing signals for the alkyne, the alkene and, especially, the allene groups. The complete assignation of all the signals was confirmed by means of 2D ^1H - ^1H COSY, ^1H - ^{13}C HSQC, ^1H - ^{13}C HMBC and NOESY experiments.

The ^1H NMR spectrum (**Figure 14**) showed a characteristic multiplicity for the olefinic protons (H_5 and H_6), which appear as a unique multiplet at 5.47-5.65 ppm, and the allenic protons, which are displayed as a quintuplet (H_9) at 4.84 ppm and a double triplet (H_{11}) at 4.69-4.72 ppm.



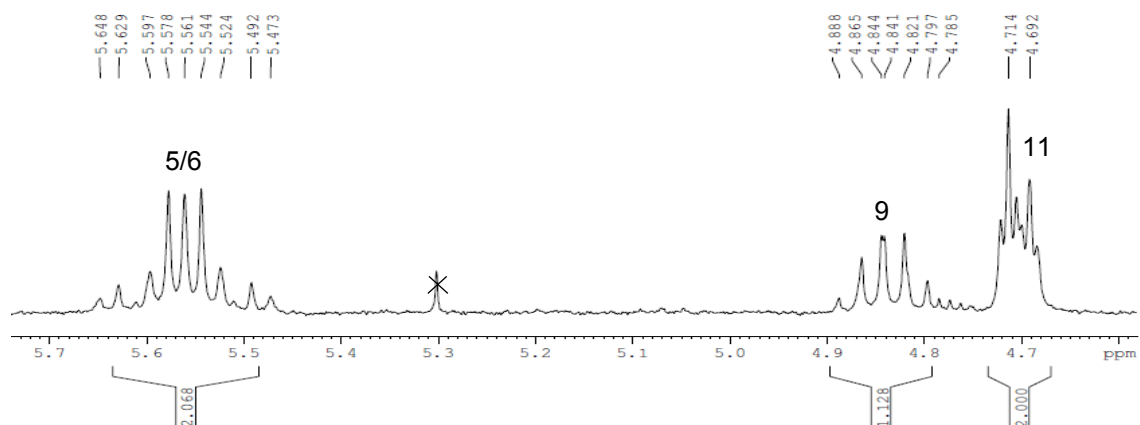


Figure 14. ^1H NMR (CDCl_3 , 300 MHz) of **1a** and zoomed range for H_5/H_6 and H_9/H_{11}

On the other hand, looking at the ^{13}C NMR spectrum (**Figure 15**), noticeable peaks can be appreciated at 85.1 ppm and at 209.2 ppm, corresponding to allenic C_9 and quaternary C_{10} , respectively.

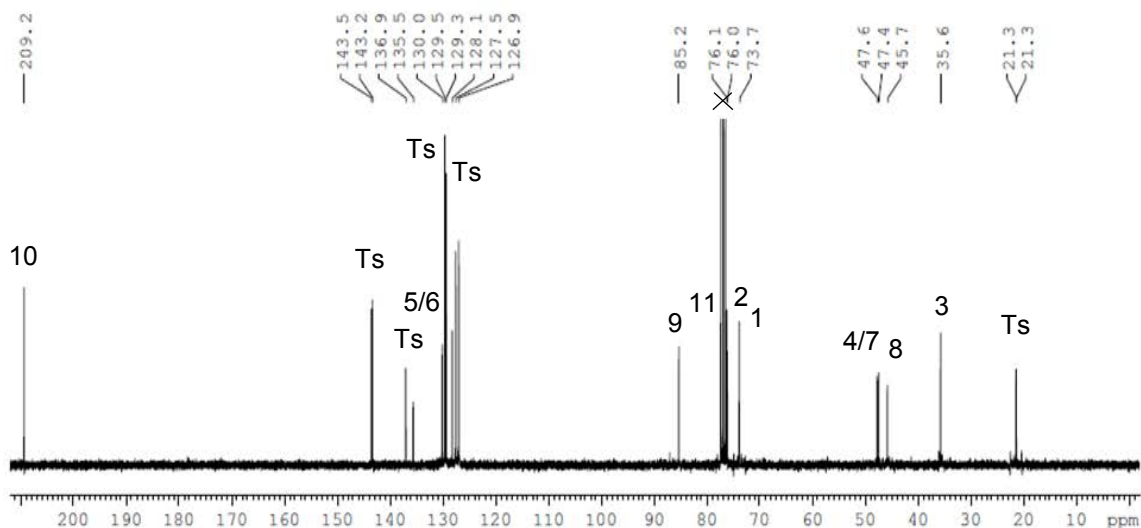
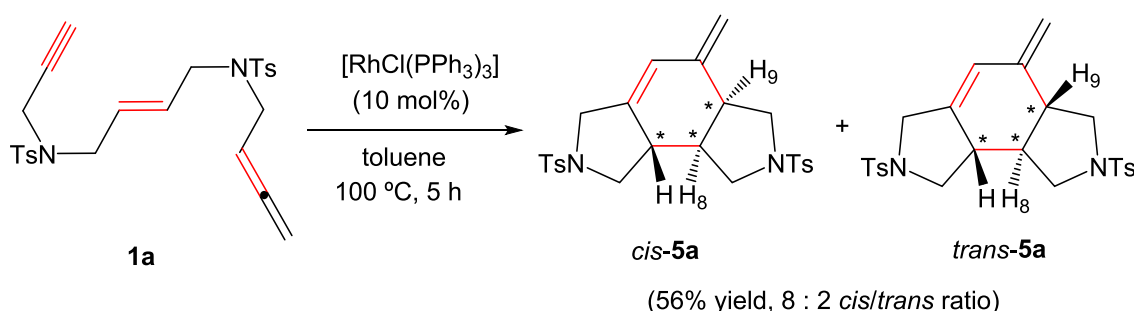


Figure 15. ^{13}C NMR (CDCl_3 , 75 MHz) of **1a**

4.3. Reactivity studies

After preparing the allene-ene-yne model substrate, we proceeded to evaluate the feasibility of the desired [2+2+2] cycloaddition reaction of **1a** with a Rh(I) catalyst.

Taking into account the previous work in the group with similar [2+2+2] cycloaddition reactions,⁵¹ we treated **1a** with the Wilkinson's catalyst (10 mol%) in toluene at 100 °C (**Scheme 68**). After 5 h, a mixture of two inseparable diastereoisomers in 8:2 ratio was isolated through silica column chromatography with an overall yield of 56%. Remarkably, the reaction is completely chemoselective with a cyclisation taking place only on the internal double bond of the allene. The two diastereoisomers obtained differ in the 6:5 ring fusions that can be either *cis* or *trans* (relative orientation of H₈ and H₉ in **Scheme 68**), thus giving rise to *cis*-**5a** and *trans*-**5a** cycloadducts.



Scheme 68. [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition of substrate **1a**

The fact that the cycloaddition process had taken place could be inferred by checking that the signals in the ¹H NMR spectrum had significantly changed whereas the mass had remained unchanged with respect to **1a**, peaking thereby at [M+Na⁺] = 507.14. Full ¹H and ¹³C NMR assignment was achieved by recording 2D NMR spectra, including ¹H-¹H COSY, ¹H-¹³C HSQC, ¹H-¹³C HMBC and ¹H-¹H NOESY. The key feature to differ the two geometries was the ³J_{H8-H9} coupling constant, which was higher for the *trans* than the *cis* diastereoisomers (**Figure 16**).

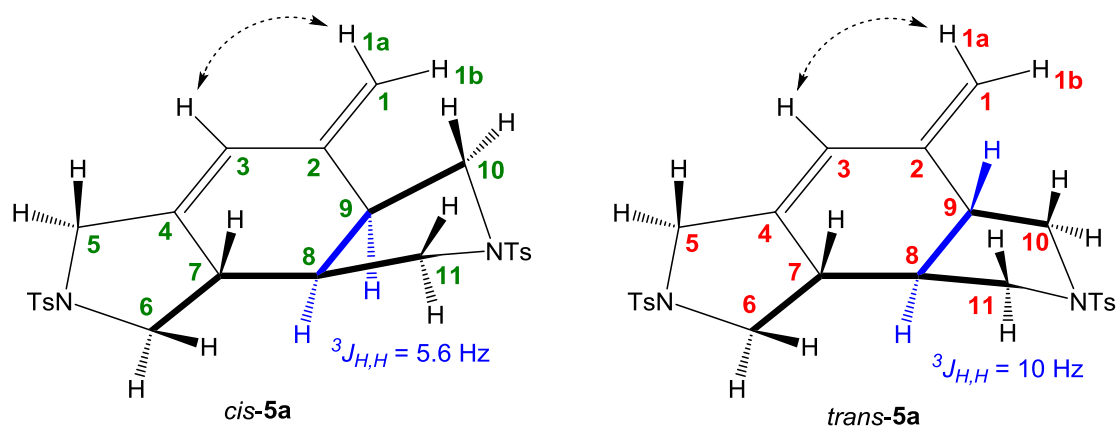
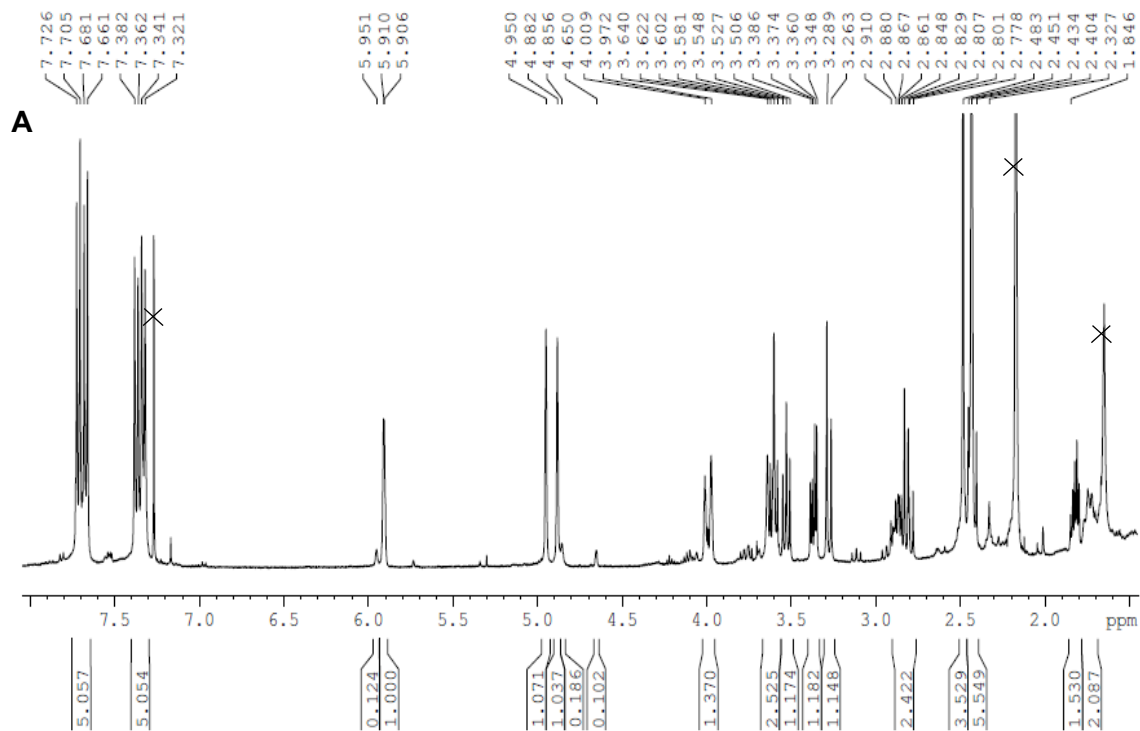


Figure 16. Representation of *cis*-5a and *trans*-5a cycloadducts showing the major NOESY ($\dashrightarrow$) correlation and ^1H - ^1H COSY (—) couplings that helped to confirm the proposed geometry



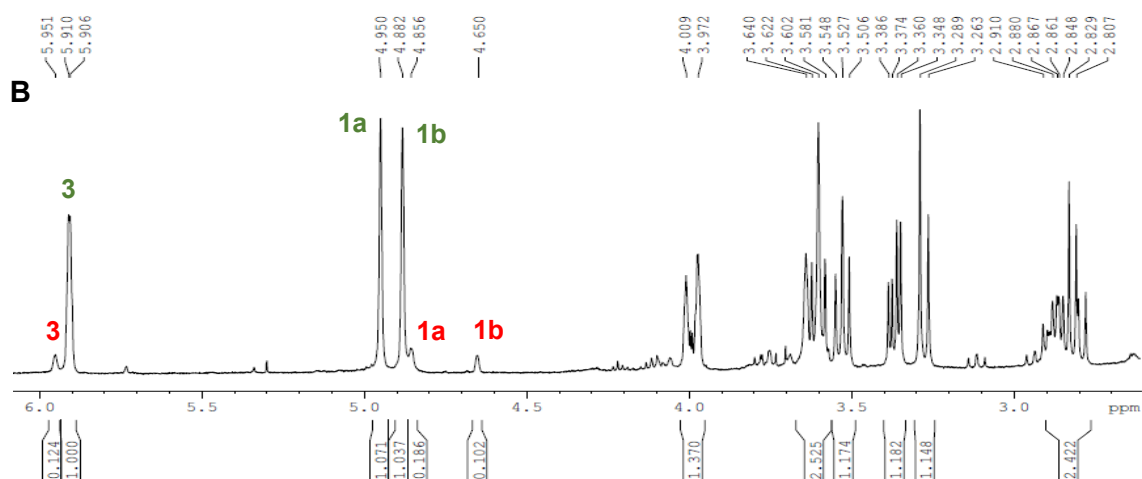


Figure 17. ^1H NMR of *cis*-**5a** and *trans*-**5a** (Spectrum A) and zoomed area (Spectrum B)

Table 8 shows the proton assignment of all ^1H NMR signals for both diastereoisomers.

Table 8. ^1H NMR chemical shift comparison of *cis*-**5a** and *trans*-**5a**

^1H label	<i>cis</i> - 5a	<i>trans</i> - 5a
1a	4.97 (s)	4.88 (s)
1b	4.91 (s)	4.68 (s)
3	5.93 (s)	5.98 (s)
5	3.55 (m) / 4.01 (d)	3.76 (m) / 3.84 (d)
6	2.37 (d) / 3.56 (m)	2.43 (m) / 3.79 (m)
7	1.74 (m)	2.43 (m)
8	1.84 (m)	1.48 (m)
9	2.83 (dd)	2.34 (m)
10	2.83 (dd) / 3.55 (m)	3.14 (m) / 3.76 (m)
11	3.30 (d) / 3.39 (dd)	2.90 (m) / 3.76 (m)

First of all, we must remark the clear signals displayed by protons 1a, 1b and 3. Proton 3 appears as a broad singlet at 5.93 ppm for *cis*-**5a** and 5.98 ppm for *trans*-**5a**. Such signals, which are located far from the rest, provide a useful clue to determine whether the cycloadduct is formed or not. With regards to protons 1a and 1b, we can see that both appear as singlets at 4.97 and 4.91 ppm for compound *cis*-**5a** and at 4.68 and 4.88 ppm for compound *trans*-**5a**. The identity of the two protons can be easily revealed through the NOESY spectrum, since only proton 1a is observed to be coupled in space through NOE effect with proton 3. The chemical shift difference reported between protons 1a and 1b signals for compound *cis*-**5a** is smaller and at lower magnetic fields than for compound *trans*-**5a**.

Thanks to the protons of the three stereocentres (7, 8 and 9), it was possible to differentiate between diastereoisomers *cis*-**5a** and *trans*-**5a**. Since [2+2+2] cycloaddition reactions of double bonds are known to be stereospecific, we deduced that the orientation of protons 7 and 8 had to be *trans*, as they come from the *trans*-alkene group of **1a**.

Having completed the assignation of the protons, we were able to state that the major product was *cis*-**5a**. A deeper analysis of the multiplets made it possible to calculate a $^3J_{H8-H9} = 5.6$ Hz coupling constant for product *cis*-**5a**, and a $^3J_{H8-H9} = 10$ Hz constant for product *trans*-**5a**, that as commented above, was key for the easy differentiation of the two diastereoisomers. Since the coupling constant displayed by *cis*-**5a** is smaller than that of *trans*-**5a**, we concluded that a *cis*-**5a**/*trans*-**5a** ratio of 8:2 had been achieved.

After having checked that the desired reaction is feasible, we proceeded to the optimisation process, which initially consisted in attempting the use of several Rh(I) sources in order to later analyse the effect of other variables like catalyst loading, solvent or temperature.

For the first tests (**Table 9**), we used reaction conditions similar to the ones previously described in our group for other [2+2+2] cycloaddition reactions.⁵¹

Table 9. Rhodium(I)-catalysed [2+2+2] cycloaddition reaction of **1a**

Entry	Rh complex	Biphosphine	Reaction time (h)	Conversion (%)	Yield (%) of 5 (<i>cis/trans</i> ratio)
1 ^[a]	[RhCl(PPh ₃) ₃]	-	5	92	56 (8 : 2)
2 ^[b]	[Rh(cod) ₂]BF ₄	-	6	100	-
3 ^[b]	[Rh(cod) ₂]BF ₄	(<i>R</i>)-BINAP	22	100	-
4 ^[b]	[Rh(cod) ₂]BF ₄	(<i>R</i>)-H ₈ -BINAP	4	0	-
5 ^[b]	[Rh(cod) ₂]BF ₄	(<i>R</i>)-tol-BINAP	21	100	traces
6 ^[b]	[Rh(cod) ₂]BF ₄	(<i>R</i>)-SegPhos	5	100	-
7 ^[b]	[Rh(cod) ₂]BF ₄	(<i>R</i>)-DTBM-SegPhos	5	75	22 (1 : 1)
8 ^[a]	[RhCl(CO) ₂] ₂	-	0.3	100	53 (1 : 9)
9 ^[a]	[Rh(OH)(cod)] ₂	-	0.3	100	24 (3 : 7)
10 ^[a]	[RhCl(cod)] ₂	-	3	100	-

[a] Reaction conditions: A solution of the catalytic system (10 mol%) in toluene was added to **1a** (0.03 M) in the same solvent under inert atmosphere and the reaction was heated to 100 °C.

[b] Reaction conditions: A solution of the catalytic system (10 mol%) in 1,2-dichloroethane was added to **1a** (0.03 M) in the same solvent under inert atmosphere and the reaction was heated to 80 °C.

Taking as a reference the [RhCl(PPh₃)₃]-catalysed conditions (Entry 1) that have already been discussed, we tried cationic rhodium(I)-based catalysts with chiral ligands (entries 2-6). The use of this sort of catalysts is especially relevant for designing potentially enantioselective processes.

The preparation of the cationic rhodium complexes can be done *in situ* by directly mixing bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate ([Rh(cod)₂]BF₄) with a BINAP-based chiral diphosphine (**Figure 18**) and bubbling H₂ to the system.

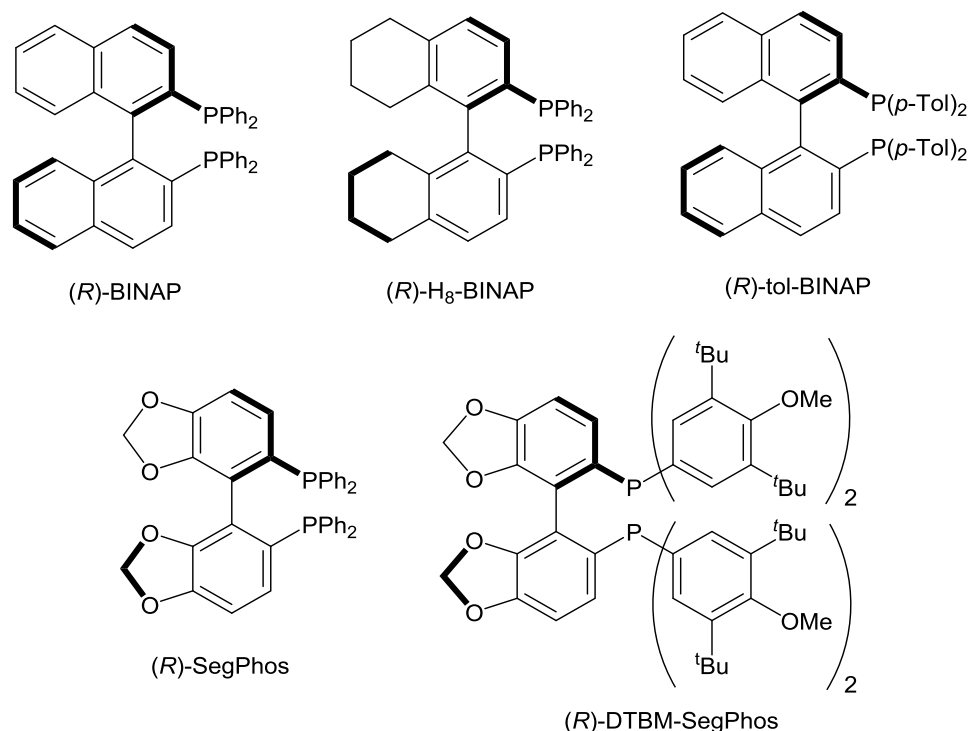


Figure 18. Selected BINAP-type chiral diphosphines

After checking with a blank test that $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (Entry 2) did not lead to the product but to decomposition of the starting material after heating the system to reflux for 6 h, we proceeded to evaluate the effect of introducing several chiral ligands. Although (R)-BINAP (Entry 3), (R)-H₈-BINAP (Entry 4), (R)-tol-BINAP (Entry 5) and (R)-SegPhos (Entry 6) did not produce any positive result, when (R)-DTBM-SegPhos was employed (Entry 7) a 22% yield of a 1:1 mixture of *cis/trans* products was attained after 5 h of heating the system to 80 °C.

We also intended to run the studied reaction by submitting the system to phosphine-free catalytic species. A carbonyl-containing catalyst like $[\text{RhCl}(\text{CO})_2]_2$ (Entry 8) actually improved the previous result giving 53% yield in only 20 minutes of a 1:9 *cis/trans* products mixture. A similar result was obtained when $[\text{Rh}(\text{OH})(\text{cod})]_2$ (Entry 9) was employed, though in a lower yield of 24%. Contrary, a similar species like $[\text{RhCl}(\text{cod})]_2$ (Entry 10) was unable to afford the desired products and only led to decomposition of the starting materials.

From this catalyst screening, we envisaged that three species are capable of giving good results in terms of reaction time and yield. The conditions for the use of $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{Rh}(\text{cod})_2]\text{BF}_4$ / (R)-DTBM-SegPhos and $[\text{RhCl}(\text{CO})_2]_2$ were optimised in Table 10, Table 11 and Table 12, respectively.

Table 10. Optimisation of the [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition of **1a**^[a]

Entry	Catalyst loading (mol%)	Solvent	Temperature (°C)	Reaction time (h)	Conversion (%)	Yield (%) of 5 (<i>cis/trans</i> ratio)
1	10	toluene	100	5	92	56 (8 : 2)
2	10	<i>p</i> -xylene	130	2.5	64	36 (10 : 0)
3	10	ethanol	70	22	100	-
4	10	toluene	100	21	93	54 (8 : 2)
5	10	toluene	μW / 90	0.16	10	8 (10 : 0)
6 ^[b]	10	toluene	100	2.5	100	traces
7	5 + 5	toluene	100	5	69	25 (8 : 2)
8	10 + 5	toluene	100	5	100	64 (9 : 1)
9 ^[c]	10 + 5	toluene	100	4	81	33 (9 : 1)

[a] Reaction conditions: A solution of [RhCl(PPh₃)₃] in the specified solvent was added to **1a** (0.03 M) in the same solvent under inert atmosphere and the reaction was heated to the specified temperature.

[b] Concentration of starting materials and [RhCl(PPh₃)₃] was increased to 0.1 M.

[c] 1.8 eq. of Et₃N were added.

Bearing in mind that a 10 mol% catalyst loading in toluene at 100 °C affords a 56% yield of *cis/trans* products in 8 : 2 ratio (Entry 1), we tried changing the solvent to another aromatic one like *p*-xylene (Entry 2), which caused the decrease of the yield to 36%, and to a polar solvent like ethanol (Entry 3), which provoked decomposition of **1a**. From these results and the previous work in the group, we took toluene as the optimal solvent.

In order to achieve full conversion of **1a**, we left the system overnight to react at 100 °C (Entry 4), but nearly the same results were attained. On the other hand, we intended to run the reaction under microwave irradiation (Entry 5) at 90 °C for only 10 minutes. However, this test only gave 8% of *cis*-**5a** and most **1a** was recovered. Trying to increase the rate of the reaction, concentration was raised to 0.1 M (Entry 6), thus concluding that concentration has a dramatic effect on the course of the reaction, as only traces were detected and **1a** was vastly decomposed.

We tried adding [RhCl(PPh₃)₃] in two turns: one at the beginning and another after 2 h. When 5 mol% was added in both turns (Entry 7), less conversion was attained, but when 10 mol% was introduced at the beginning and 5 mol% after 2 h (Entry 8), full conversion was achieved and 64% yield was afforded of *cis*-**5a** and *trans*-**5a** in 9:1 ratio. Looking at the precedents in the group,⁵⁶ we considered the addition of small amounts of triethylamine, since it could act as a labile ligand for intermediate rhodium

catalysts. When we introduced triethylamine to our system (Entry 9), we found that it has a negative influence on the catalytic system as only 33% yield was reported. Taking into account that no significant improvement was found between Entry 1 and Entry 8, we concluded that the best reaction conditions when $[\text{RhCl}(\text{PPh}_3)_3]$ was employed were the ones corresponding to Entry 1: addition of catalyst in 10 mol%, toluene as the solvent and 100 °C.

Table 11. Optimisation of the $[\text{Rh}(\text{cod})_2]\text{BF}_4$ / (*R*)-DTBM-SegPhos-catalysed [2+2+2] cycloaddition of **1a**^[a]

Entry	Temperature (°C)	Reaction time (h)	Conversion (%)	Yield (%) of 5 (<i>cis/trans</i> ratio)
1	80	4	92	22 (5 : 5)
2	R.T.	22	0	-
3	60	5	87	31 (7 : 3)

[a] Reaction conditions: A solution of **1a** in 1,2-dichloroethane was added to the catalytic mixture (10 mol%, 0.003 M) in the same solvent under inert atmosphere at the specified temperature.

With regards to the cationic rhodium-catalysed cycloaddition, we optimised the temperature for the reaction in which (*R*)-DTBM-SegPhos chiral ligand is employed. Taking as a reference the 22% yield previously reported (Entry 1), we tried running the process at room temperature (Entry 2), though we stated that no reaction took place. However, when we then submitted the system to 60 °C (Entry 3), 31% yield was obtained of a 7 : 3 *cis/trans* mixture. Therefore, we took 60 °C as the optimal temperature for such catalytic species.

At this point, we found it appropriate to check whether enantioselectivity was attained when a chiral ligand was employed. To do so, we first set up the HPLC conditions to separate the four peaks (2 pairs of enantiomers) in the racemic mixture of *cis*-**5a** and of *trans*-**5a** (obtained through $[\text{RhCl}(\text{PPh}_3)_3]$ catalysis). Unfortunately, when the product mixture obtained in Entry 2 was injected, the same four peaks on the chromatogram were observed, displaying in all cases similar peak areas. Therefore, we ended the analysis by reporting that no enantiomeric excess had been attained.

Table 12. Optimisation of the $[\text{RhCl}(\text{CO})_2]_2$ -catalysed [2+2+2] cycloaddition of **1a**^[a]

Entry	Temperature (°C)	Reaction time (h)	Conversion (%)	Yield (%) of 5 (<i>cis/trans</i> ratio)
1	100	0.3	100	53 (2 : 8)
2	0 – 5	1	100	38 (0 : 10)
3	60	0.3	100	49 (1 : 9)

[a] Reaction conditions: A solution of $[\text{RhCl}(\text{CO})_2]_2$ (10 mol%) in toluene was added to **1a** (0.03 M) in the same solvent under inert atmosphere and the reaction was submitted to the specified temperature.

Finally, considering that $[\text{RhCl}(\text{CO})_2]_2$ catalyst afforded 53% at 100 °C (Entry 1, **Table 12**), we tried lowering the reaction temperature. When we submitted the system between 0 and 5 °C (Entry 2), full consumption of **1a** was achieved, though only 38% of *trans* diastereoisomer was reported. When we heated the reaction mixture to 60 °C (Entry 3), 49% yield was obtained and *trans*-**5a** was obtained as the major diastereoisomer in a 1:9 *cis/trans* ratio. We concluded that the yield improvement at 100 °C (Entry 1) was not significant enough and, therefore, we fixed 60 °C (Entry 3) as the optimal temperature.

4.4. Scope study

With three optimised catalytic conditions in hand, we were encouraged to examine how broad was the scope of the [2+2+2] cycloaddition reaction of allene-ene-yne substrates. More concretely, the study consisted in introducing several substituents at the terminus of the alkyne and the allene, both aliphatic and aromatic substituents, and in changing the tether (**Figure 19**).

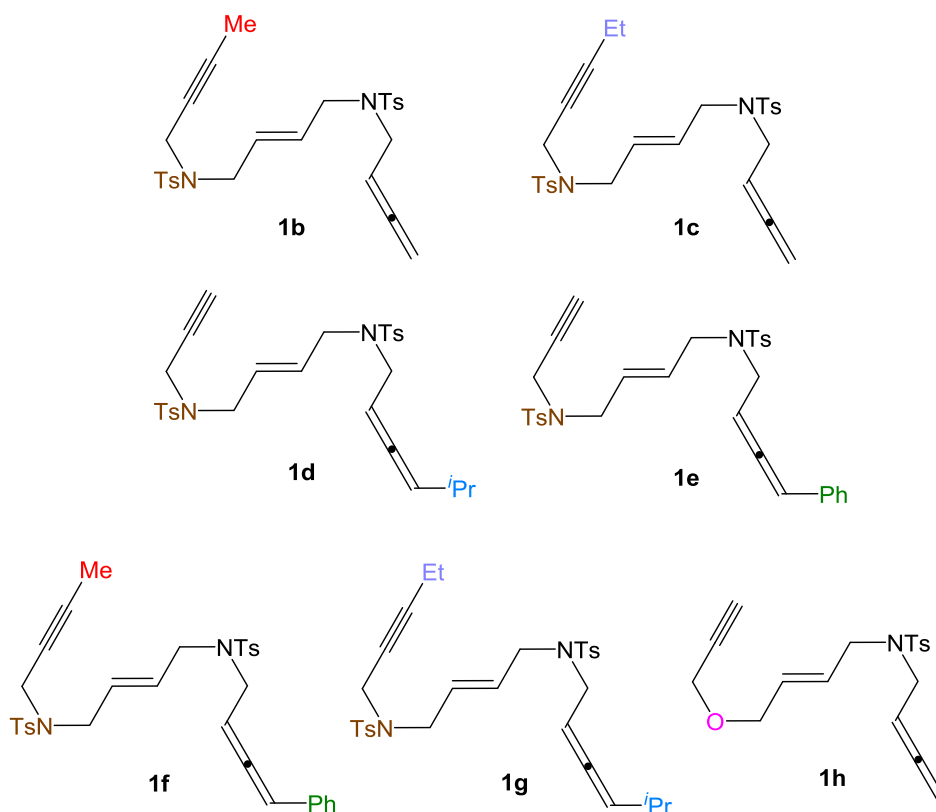
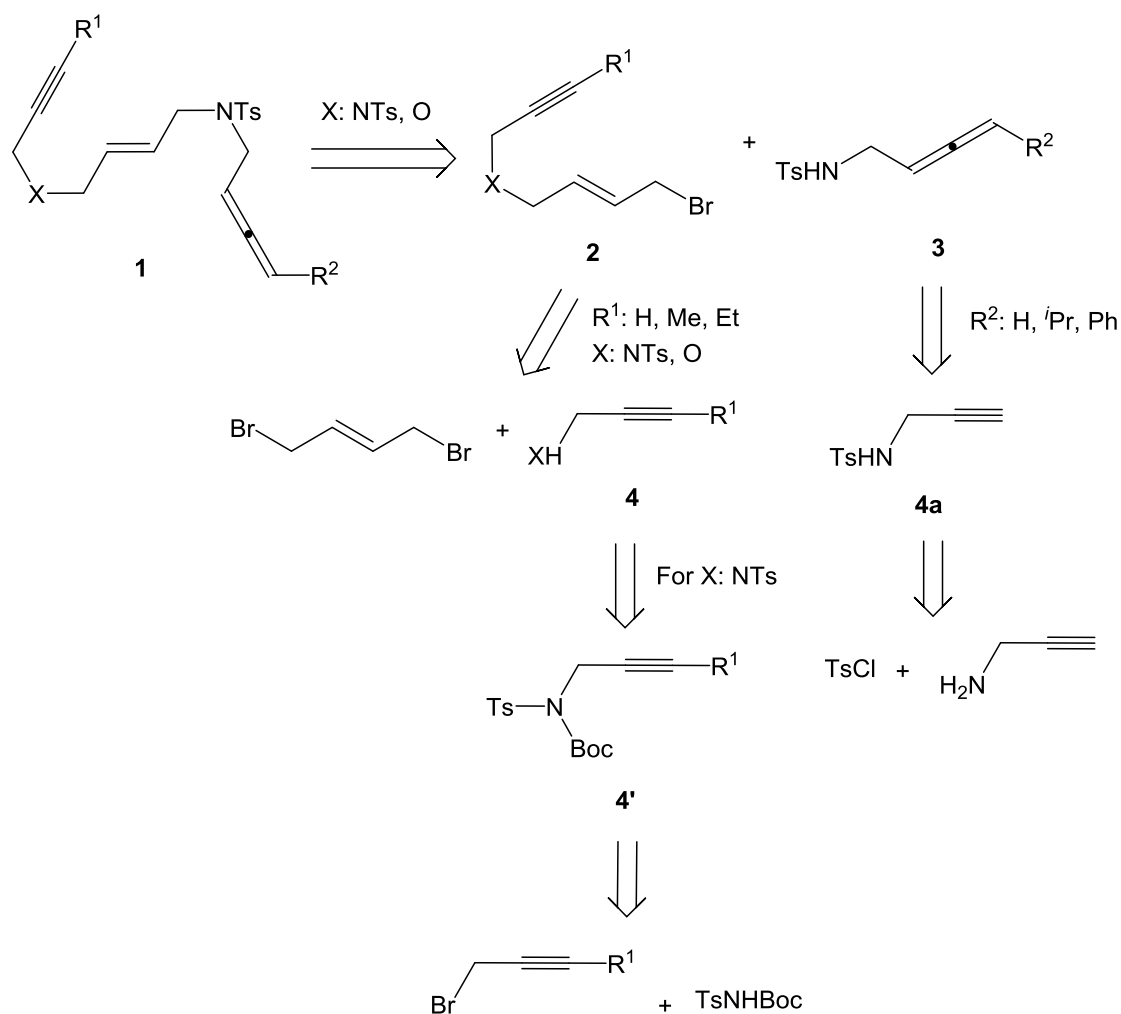


Figure 19. Allene-ene-yne substrates **1b** – **1h** designed and tested in this study

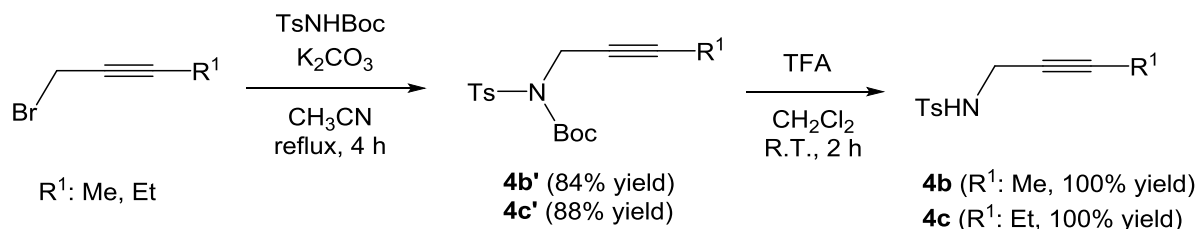
4.4.1. Synthesis of substrates **1b** – **1h**

The preparation of substrates **1b** – **1h** was carried out following synthetic routes analogous to the one used for **1a**, with only slight modifications in the synthesis of compounds **4**, since the corresponding propargyl amines are not commercially available.



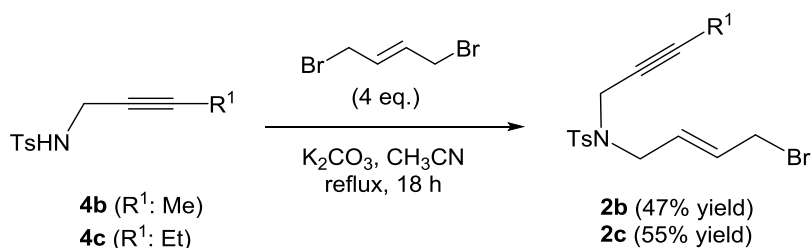
Scheme 69. General retrosynthetic analysis of substrates **1b** – **1h**

Intermediates **4** could be prepared by alkylation of 1-bromo-2-butyne (for **4b**) or 1-bromo-2-pentyne (for **4c**) with Boc-protected-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide to afford **4b'** and **4c'**, respectively. The Boc group could be removed from the resulting intermediates by stirring the solution of **4b'** or **4c'** in CH_2Cl_2 with an excess of TFA for 2 h. These syntheses could be readily accomplished in excellent yields in both cases (**Scheme 70**).



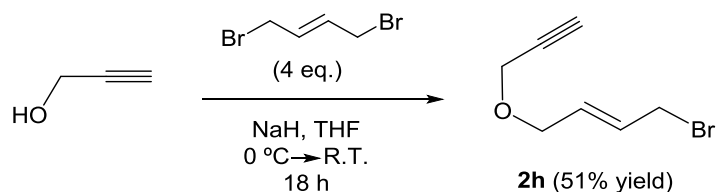
Scheme 70. Preparation of **4b** and **4c**

With the previous intermediates in hand, we could readily attach them to an alkene motif using *trans*-1,4-dibromo-2-butene as electrophile. Base-promoted alkylations were possible for both intermediates, leading to **2b** and **2c** in 47% and 55% yields, respectively (**Scheme 71**). We slowly introduced intermediates **4** onto the refluxing solution of 4 eq. of *trans*-1,4-dibromo-2-butene in order to avoid the generation of double-alkylated by-products.



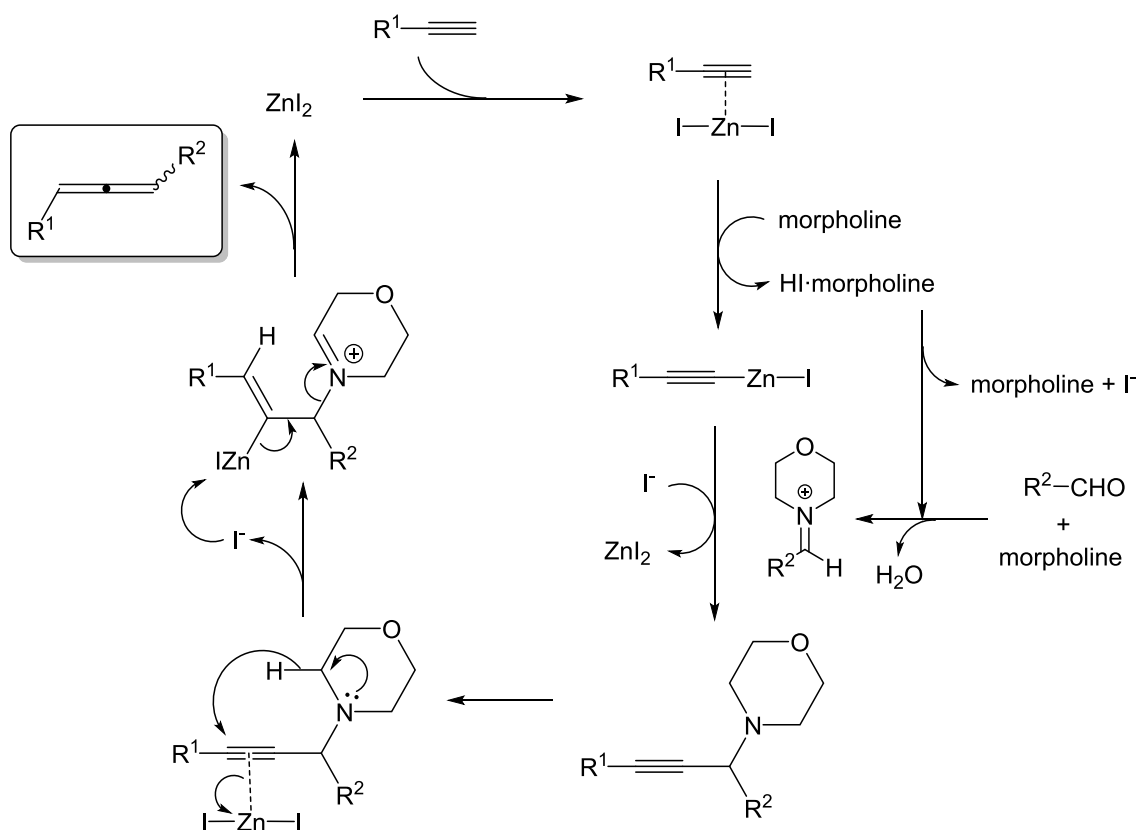
Scheme 71. Preparation of **2b** and **2c**

In the case of the *O*-tethered substrate **1h**, the alkylation was possible under the presence of sodium hydride (**Scheme 72**), affording **2h** as a colourless liquid in 51% yield after reacting overnight. The presence of a stronger base was necessary here since an alkoxide group had to be generated to act as the nucleophile.



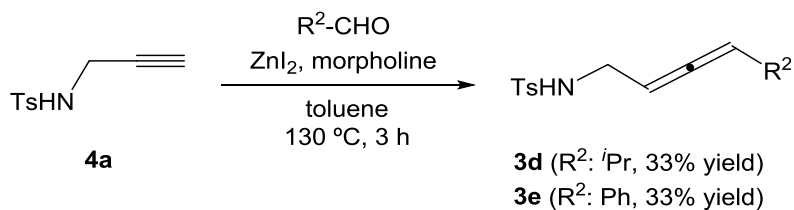
Scheme 72. Preparation of **2h**

On the other hand, internal allenes were prepared following an alternative experimental procedure reported by Ma and co-workers,⁷⁵ consisting in the use of an aldehyde, ZnI_2 and morpholine in toluene instead of the Crabbé homologation conditions (see for instance **Scheme 66**). These postulate that the current reaction proceeds through a catalytic cycle (**Scheme 73**) mediated by ZnI_2 . The cycle starts with the Zn-activation of the alkyne motif and the formation of a Mannich base from the aldehyde and morpholine. The reaction of these two intermediates regenerates ZnI_2 and the resulting compound is able to suffer a 1,5-hydride transfer and β -elimination to finally afford the desired allene product.



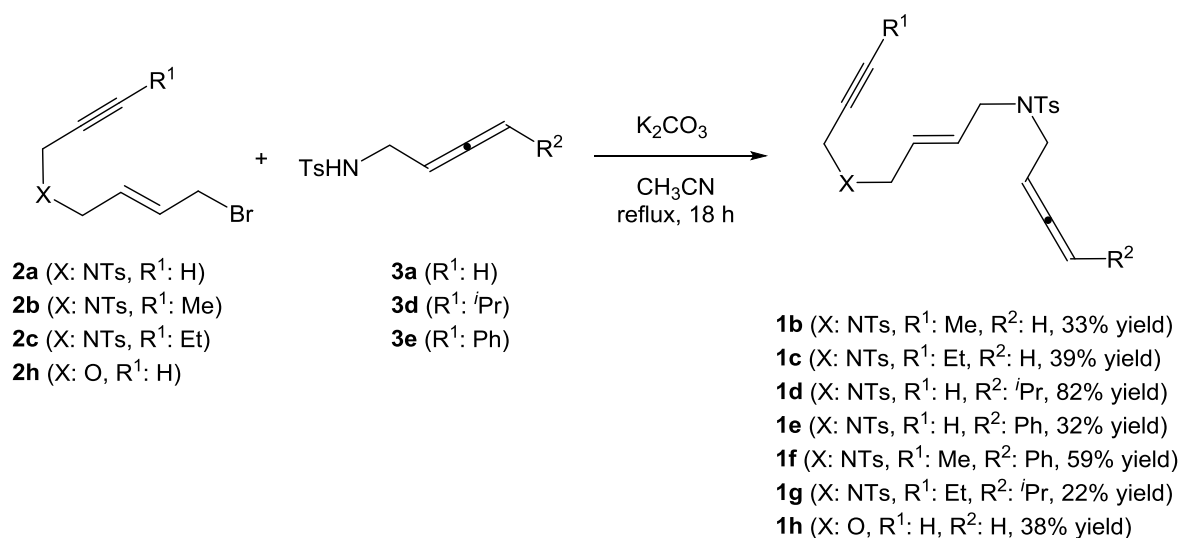
Scheme 73. Postulated mechanism of internal allene formation according to Ma and co-workers

When we applied these conditions on **4a** in the presence of isopropyl aldehyde or benzaldehyde, we managed to obtain both **3d** and **3e** in 33% yield after 3 h heating at 130 °C (**Scheme 74**).



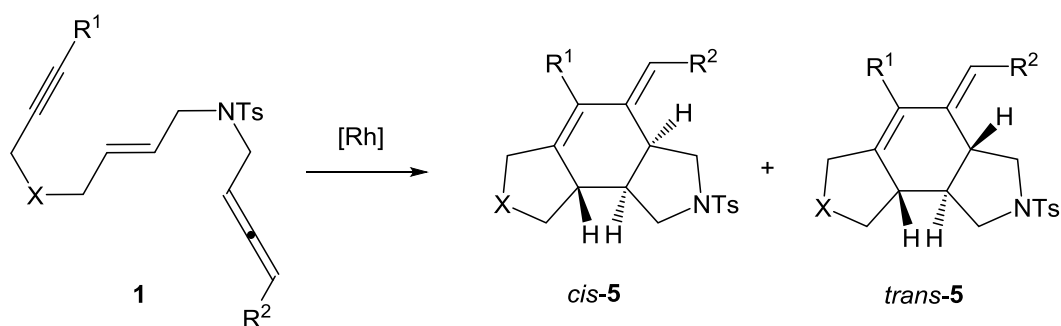
Scheme 74. Preparation of **3d** and **3e**

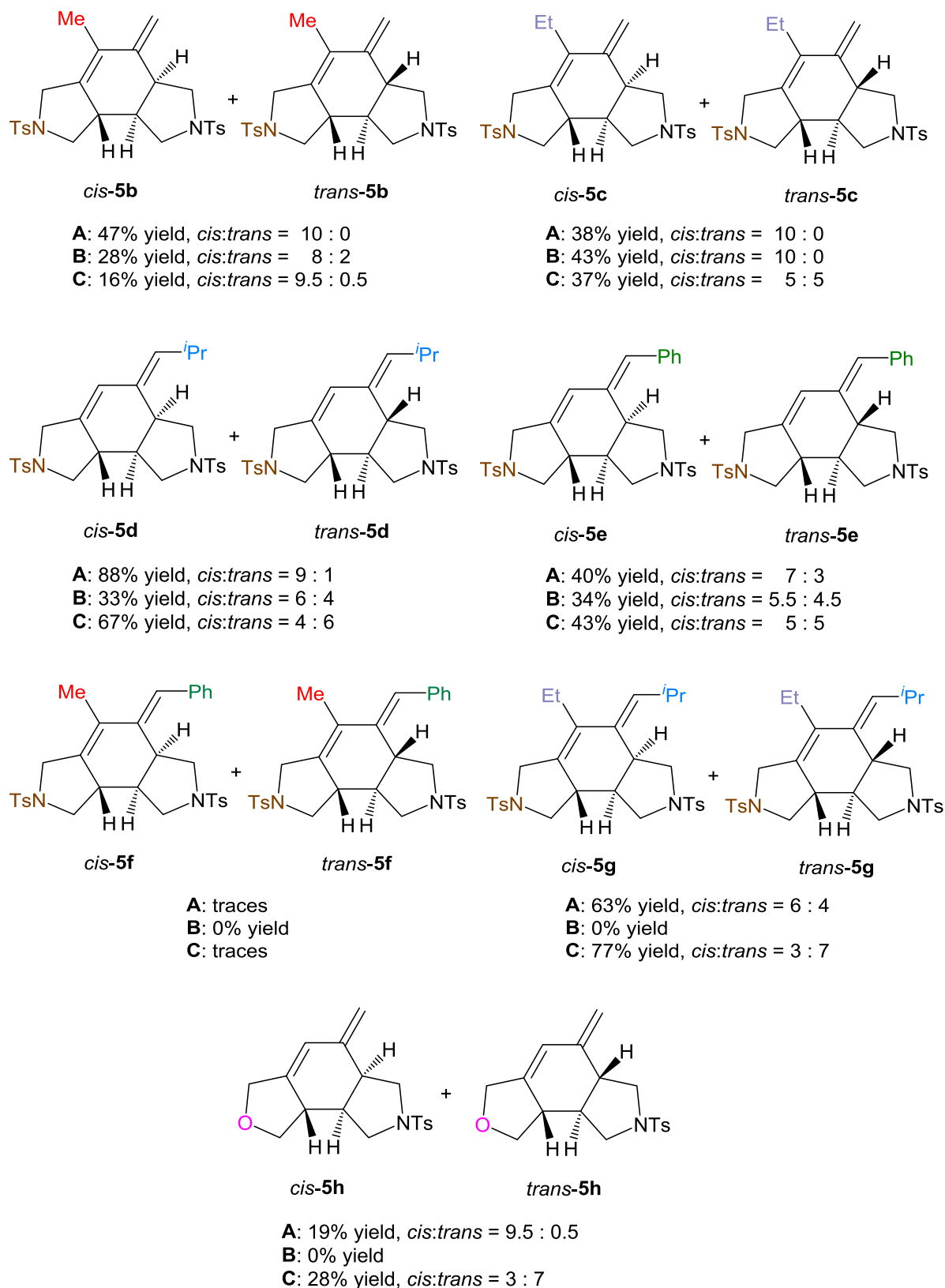
Finally, the linkage of the synthesized allene compounds (**3a**, **3d** or **3e**) to the alkyne-alkene intermediates (**2a**, **2b**, **2c** or **2h**) was achieved through a base-promoted alkylation by using K_2CO_3 (**Scheme 75**).

Scheme 75. Preparation of substrates **1b** – **1h**

4.4.2. Scope evaluation

After preparing all the planned substrates, we proceeded to submit substrates **1b** – **1h** to the three catalytic conditions optimised in Section 3.2: **A**) [RhCl(PPh₃)₃] (10 mol%), toluene, 100 °C, **B**) [Rh(cod)₂]BF₄ / (*R*)-DTBM-SegPhos (10 mol%), 1,2-dichloroethane, 60 °C and **C**) [RhCl(CO)₂]₂ (10 mol%), toluene, 60 °C. In all cases, the *cis/trans* diastereoisomeric ratio was checked and the obtained cycloadducts were characterized (**Scheme 76**).





Scheme 76. Scope of the [2+2+2] cycloaddition reactions of allene-ene-yne substrates (the results reported are an average of two runs)

All compounds were observed to react and successfully produce the expected cycloadducts at least under the activity of one of the catalysts employed. **5f** remains as an exception, since only traces were obtained. The fact that **1f** does not provide any positive result is not in accordance with the general trend of the process because **5g**, which is doubly-substituted as well, was efficiently afforded.

In general terms, we can say that the best yields are associated to those substrates that entailed an *i*-propyl substituent at the terminus of the allene (**1d** and **1g**). More concretely, it can be observed that neutral catalytic systems $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{RhCl}(\text{CO})_2]_2$ react more efficiently than the cationic system $[\text{Rh}(\text{cod})_2]\text{BF}_4$ / (*R*)-DTBM-SegPhos. The latter gives moderate yields of the alkyne-substituted cycloadducts (**5b** and **5c**) and the allene-substituted ones (**5d** and **5e**), whereas it failed to afford doubly-substituted cycloadducts (**5f** and **5g**) and O-tethered cycloadduct (**5h**). We attributed the worse catalytic results of the cationic rhodium system to the steric hindrance present in the corresponding intermediates.

From a global point of view, $[\text{RhCl}(\text{PPh}_3)_3]$ is featured in this system for displaying a higher selectivity for the *cis* cycloadduct. Actually, **5b** and **5c** cycloadducts were purely afforded in moderate yields. However, the system seems to be affected as well by the steric hindrance provided by the substrate because the diastereoselectivity of **5e** and **5g** was significantly worse. It is important to highlight that, even though a two-time catalytic loading of 10 and 5 mol% was necessary to obtain **5a** cycloadducts with full conversion of **1a**, only 10 mol% was necessary in the other cases to achieve full consumption of substrates **1b** – **1h**.

On the other hand, $[\text{RhCl}(\text{CO})_2]_2$ proved to be, in general, moderately selective in favour of the *trans* cycloadduct, though with some exceptions. While it becomes highly diastereoselective to give *trans*-**5a** for the model substrate, the introduction of methyl or ethyl as substituents at the terminus of the alkyne provokes the single generation of *cis*-**5b** and *cis*-**5c**.

4.5. Mechanistic study

After exploring the reactivity of the allene-ene-yne substrates from the experimental point of view, we focused on unravelling the most likely mechanism that takes place in the current [2+2+2] cycloaddition reaction. To do so, several empirical tests and computational calculations were undertaken. Herein we intended to establish which is the relative reactivity order of participating unsaturations and, furthermore, justify the fact that opposite *cis*-**5a**/*trans*-**5a** ratios are experimentally reported when $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{RhCl}(\text{CO})_2]_2$ are used.

4.5.1. $[\text{RhCl}(\text{PPh}_3)_3]$ -catalysed mechanism

In order to propose the most suitable mechanistic pathway for $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst, several catalytic species were considered to mediate the process: $[\text{RhCl}(\text{PPh}_3)_2]$, $[\text{RhCl}(\text{PPh}_3)]$ or $[\text{RhCl}]$, that is to say, with the release of one, two or three of triphenylphosphine units.

4.5.1.1. Characterization of catalytic precursors

Taking advantage of the presence of phosphorous atoms in the catalytic system, we tried to characterize the reaction precursors by means of ^{31}P NMR techniques.

The test consisted in mixing **1a** and Wilkinson's catalyst in toluene- D_8 in a screw-cap NMR tube. With the aim of avoiding the oxidation of triphenylphosphine, the deuterated solvent was previously degassed by N_2 bubbling and freeze-thaw cycles and, in addition to that, all manipulation procedures were carried out in a glovebox under inert atmosphere. Since the optimised conditions for this catalyst (10 mol% $[\text{RhCl}(\text{PPh}_3)_3]$ loading, toluene, 100 °C) were not ideal for the preparation of NMR samples, we opted to increase the catalytic loading to 50 mol% and lowering temperature to 80 °C.

The recorded ^1H NMR spectrum at 400 MHz of the prepared sample (Spectrum B, **Figure 20**) revealed the presence of two new species and substrate **1a**. In order to simplify the signal identification and to avoid their overlapping, we decided to rise the catalyst loading to 100 mol% (1 eq.) with respect to **1a**. The newly-recorded ^1H NMR spectrum (Spectrum C, **Figure 20**) showed the full banishing of **1a** and the two new species (from this point, **D0a** and **D0b**) were the only compounds observed.

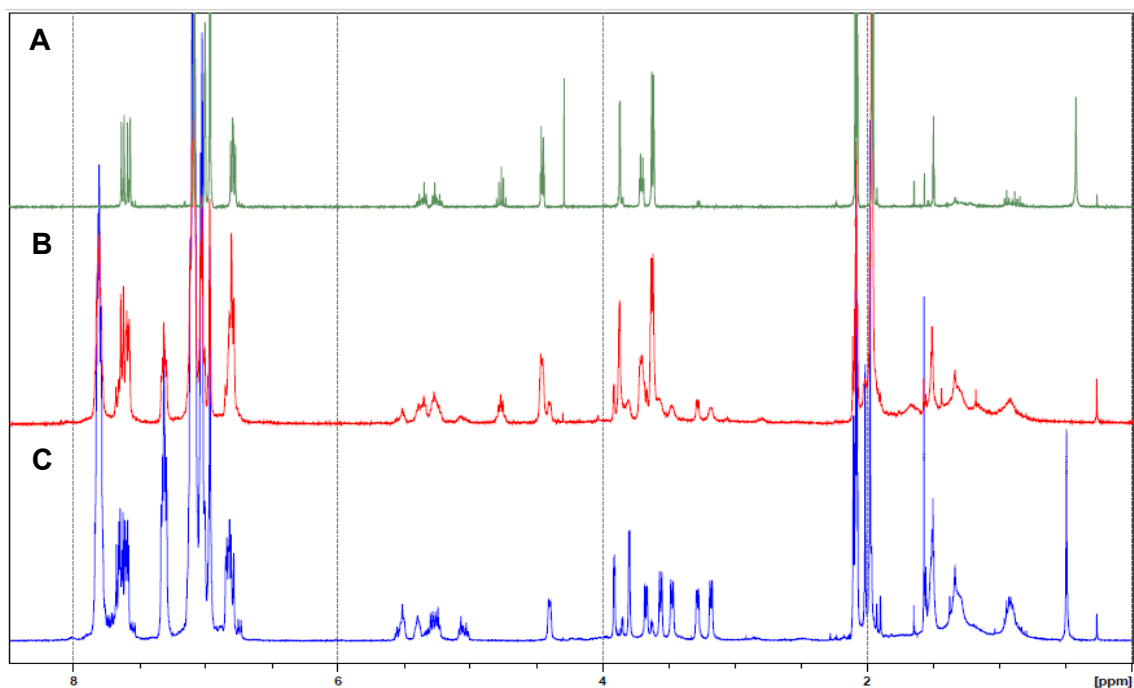


Figure 20. ^1H NMR (400 MHz, $\text{toluene-}D_8$, 298K) of free **1a** (Spectrum A), 50 mol% catalyst loading (Spectrum B) and 100 mol% catalyst loading (Spectrum C)

Taking into account that heat must be applied so that the cycloaddition proceeds and considering that the signals of **D0a** and **D0b** display similar multiplicities as the ones of free **1a**, we hypothesized that they corresponded to two coordination compounds between **1a** and the rhodium centre. This idea was reinforced by performing a DOSY experiment, which proved that **D0a** and **D0b** were heavier and bulkier than **1a**. After carrying out 2D ^1H - ^1H COSY, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC experiments we were able to properly assign all signals (**Figure 21**). Spectrum A corresponds to the ^1H NMR of **1a**, whereas Spectrum B to the mixture of **D0a** and **D0b**.

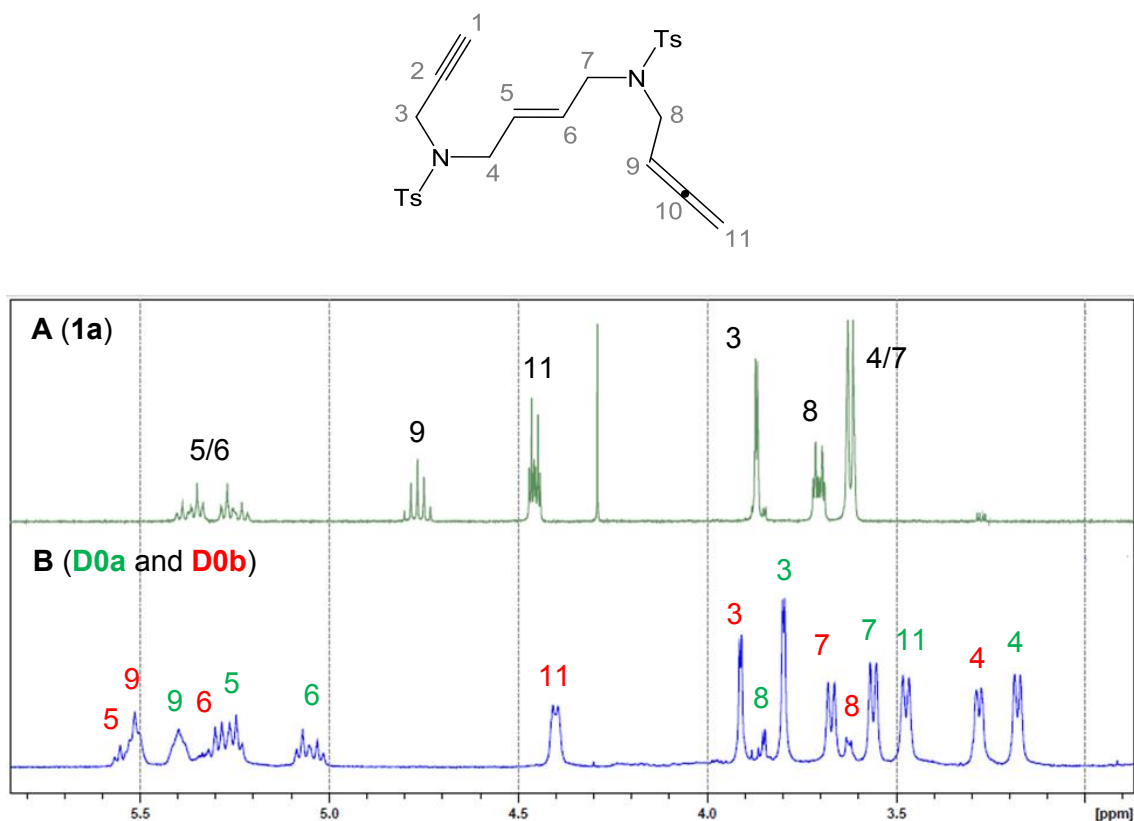


Figure 21. ^1H NMR (400 MHz, toluene- D_8 , 298K) signal assignment of free **1a** (Spectrum A) and of the mixture of **D0a** and **D0b** (Spectrum B)

When a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded (Spectrum B, **Figure 22**), **D0a** and **D0b** displayed two doublets in 1 : 0.8 intensity ratio at 31.93 (**D0a**, $^1J_{\text{P-Rh}} = 126.6$ Hz) and at 33.40 ppm (**D0b**, $^1J_{\text{P-Rh}} = 127.0$ Hz). Due to simple multiplicity of the signals and the lack of symmetry present in **D0a** or **D0b**, we postulated that they correspond to coordination species containing only one triphenylphosphine ligand. We also recorded the spectrum for Wilkinson's catalyst to compare the output (Spectrum A, **Figure 22**).

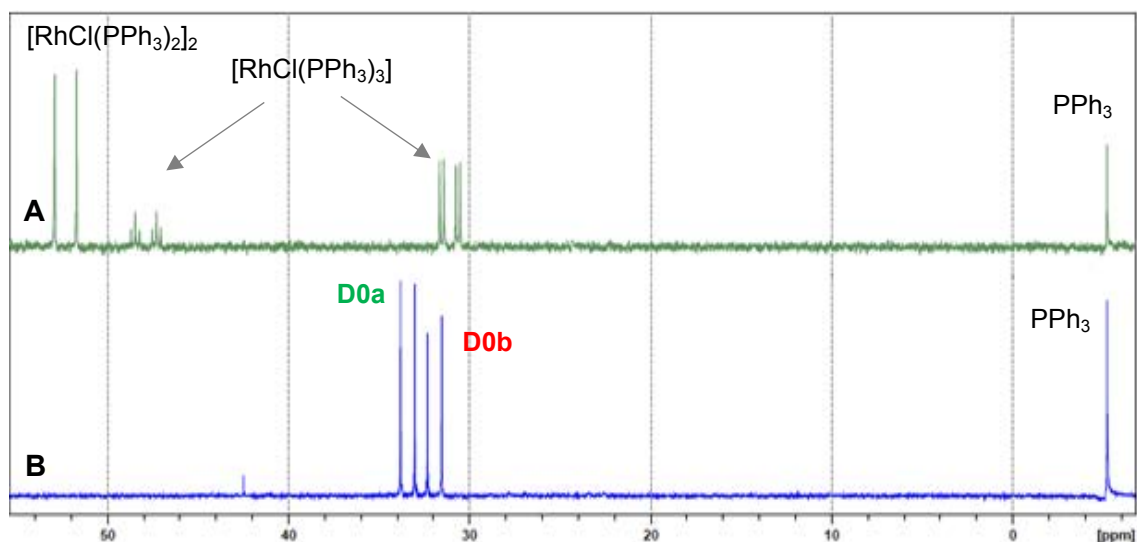


Figure 22. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.92 MHz, toluene- D_8 , 298K) of Wilkinson's catalyst (Spectrum A) and of **D0a** and **D0b** (Spectrum B)

In addition to that, thanks to the performance of ^1H - ^{31}P -HMBC (**Figure 23**), we could observe cross-peaks between ^{31}P and both the terminal alkyne proton (H_1) and the allenic protons (H_9 and H_{11}).

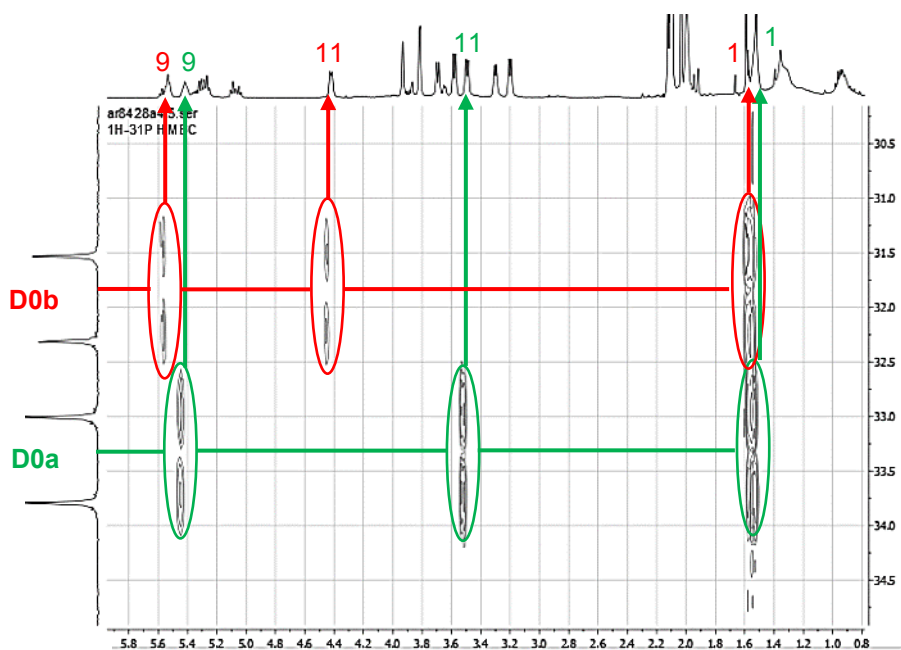
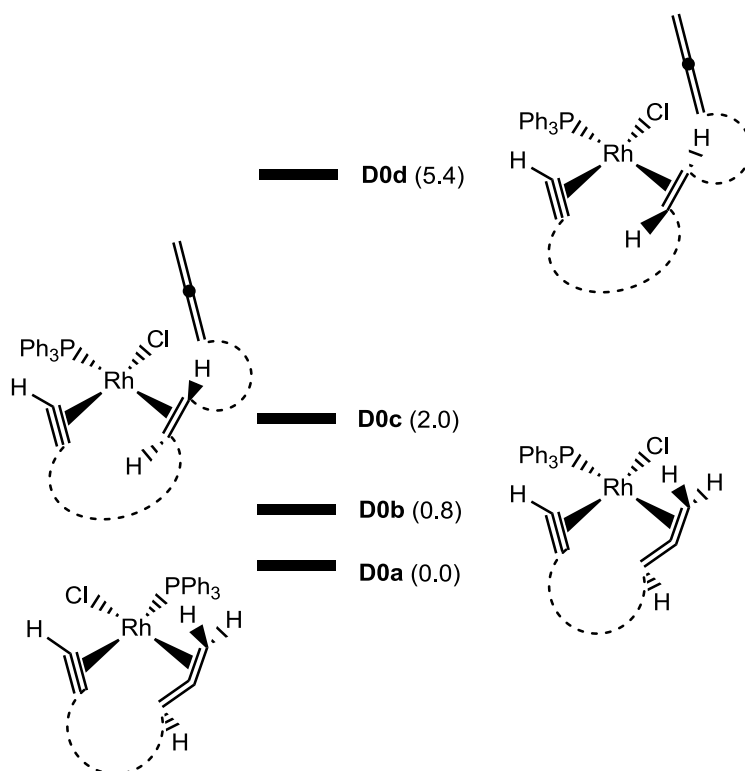


Figure 23. ^1H - ^{31}P HMBC (298K) of **D0a** and **D0b**

We thereby concluded that **D0a** and **D0b** corresponded to rhodium complexes with one PPh_3 . These complexes are characterized by the coordination of the alkyne and allene moieties of the substrate to the metal centre that acted as catalytic precursors.

To shed more light on this study, we undertook several computational calculations at B3LYP-D3/cc-pVDZ-PP level of theory to find the most stable coordination species

including one triphenylphosphine unit. As a result of that, we were able to establish the relative stability order of the coordinated species (**Scheme 77**). The two lowest-in-energy species consisted in the coordination of the rhodium atom to the alkyne and the distal double bond of the allene (A0a and A0b). In **D0a**, PPh₃ ligand is placed in *trans* orientation with respect to the alkyne motif, whereas in **D0b** it is located in *cis* (**Figure 24**). Higher-in-energy geometries consisted in alkyne-alkene coordination to the metal centre (**D0c** and **D0d**).



Scheme 77. Most stable coordination precursors computed by DFT calculations.

Energies in kcal·mol⁻¹

Last, we run a NOESY experiment. The results showed exchange cross peaks between the identified signals of **D0a** and **D0b**, thus indicating the presence of a dynamic equilibrium between them.

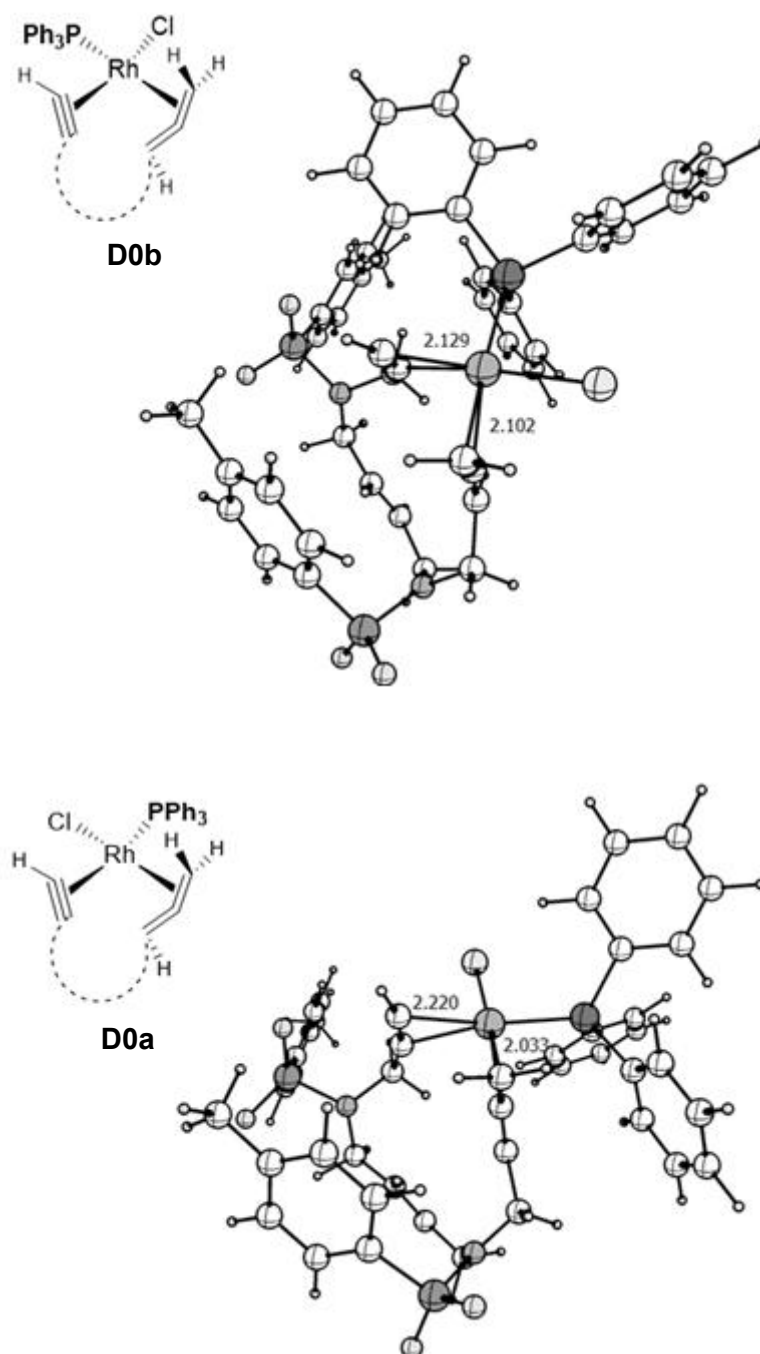
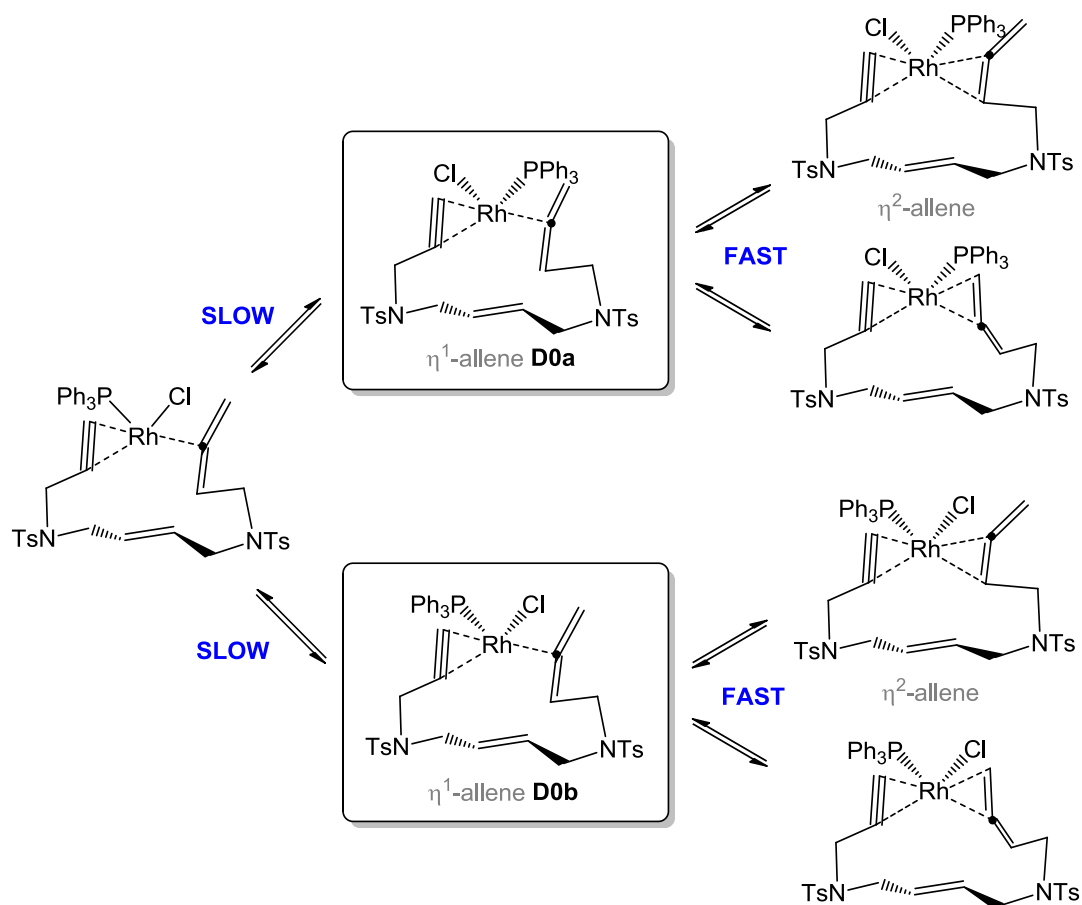


Figure 24. Optimised geometries (B3LYP-D3/cc-pVDZ-PP) of **D0a** and **D0b** with most relevant bond distances in Å.

To sum up, the conclusion that we reached in this study was that, probably, a series of equilibria between the two species **D0a** and **D0b** is achieved (**Scheme 78**). Such equilibria include the exchange between the two species (η^1 -allene coordination) by decoordination of the allene motif and also the coordination exchange between the internal and the external double bonds of the allene in a η^2 -allene coordination. Since no signal intensity differences were appreciated in ^1H - ^{31}P HMBC for H_9 and H_{11} , we

inferred that the internal-external double bond exchange would be a fast dynamic process. However, the observation of the two species indicates that the equilibrium between **D0a** and **D0b** is rather slow.

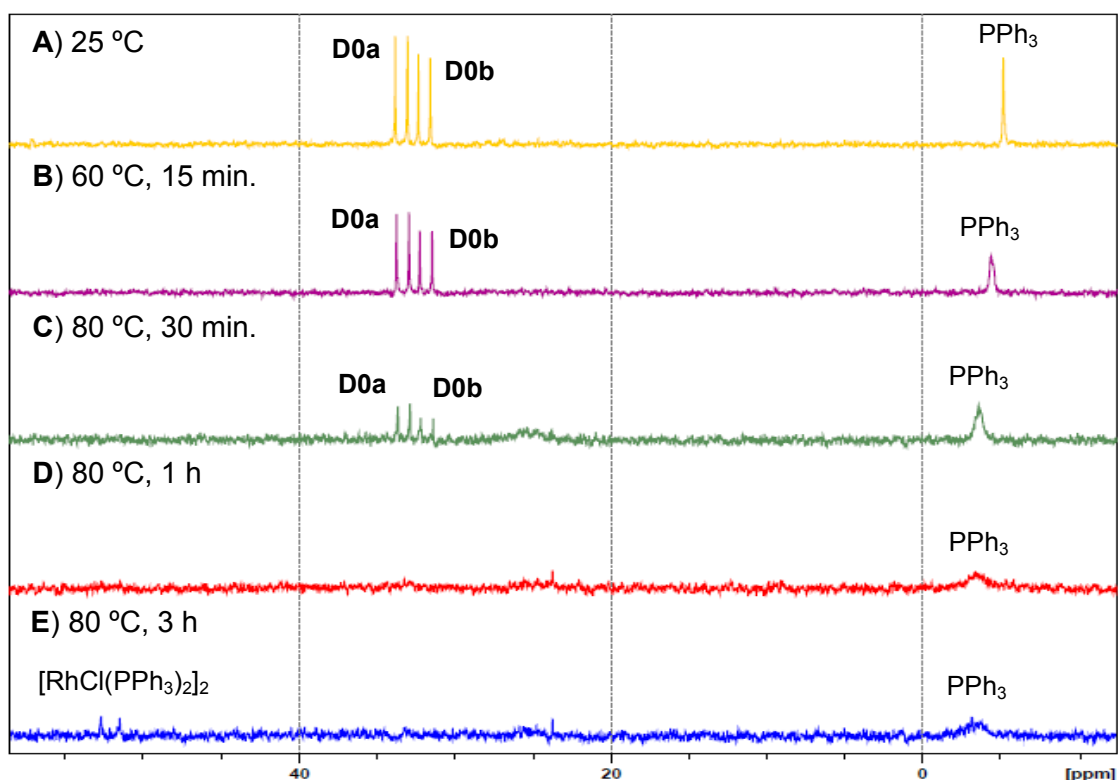


Scheme 78. Postulated equilibria for the catalytic precursors **D0a** and **D0b**

4.5.1.2. NMR monitoring

Having identified the reaction precursors, we proceeded to gradually heat the NMR sample inside the NMR apparatus in order to analyse which was the evolution of the system once the substrate enters in the catalytic cycle.

Since the catalyst loading had been raised to 100 mol% with respect to **1a**, we opted for lowering the target reaction temperature to 80 °C instead of the optimised 100 °C. Control experiments were carried out which indicated that the reaction works as well. By maintaining the system at 80 °C, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR experiments were periodically recorded until no further evolution was observed (**Scheme 79**).



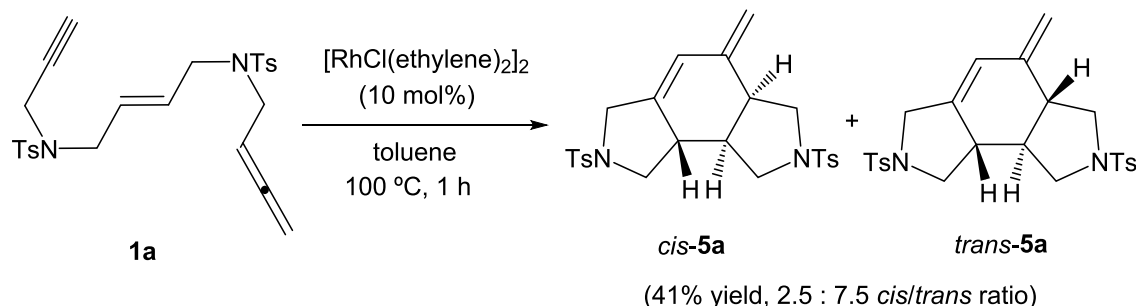
Scheme 79. $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of the ongoing [2+2+2] cycloaddition of **1a**

The only significant change observed when the system was heated to 60 °C (Spectrum B), was that the signal of free triphenylphosphine became broader, probably due to the fact that the fast triphenylphosphine coordination-decoordination dynamic processes start taking place when the system receives enough energy. **D0a** ($\delta = 31.93$ ppm) and **D0b** ($\delta = 33.40$ ppm) signals started to gradually vanish when the temperature was risen to 80 °C (Spectrum C).

When maintained at 80 °C for 1 h, **D0a** and **D0b** signals completely disappeared and only PPh_3 could be appreciated as a broad signal at $\delta \approx -4$ ppm (Spectrum D). Finally, after 3 h at the same temperature, $[\text{RhCl}(\text{PPh}_3)_2]_2$, which is a dimeric form of the Wilkinson's catalyst, was recovered (Spectrum E). The system achieved at this point a stationary state in which no further change was appreciated at larger reaction times. ^1H NMR spectra performed at the beginning and after 3 h let us check that the [2+2+2] cycloaddition had successfully taken place and **5a** diastereoisomers were present in the final reaction crude mixture.

From these NMR results, we concluded that **D0a** and **D0b** acted as stable catalytic precursors that led to the generation of further catalytic intermediates. Moreover, the lack of signals while the reaction was taking place pointed to the idea that these were probably phosphine-free catalytic intermediates.

In order to support the hypothesis of the existence of phosphine-free intermediates, we ran the reaction by using $[\text{RhCl}(\text{ethylene})_2]_2$ as catalyst. As a result of that, we found that the *cis*-**5a** and *trans*-**5a** cycloadducts were obtained in a 2.5 : 7.5 diastereoisomeric ratio after 1 h at 100 °C (**Scheme 80**).



Scheme 80. Phosphine-free-catalysed [2+2+2] cycloaddition reaction of **1a**

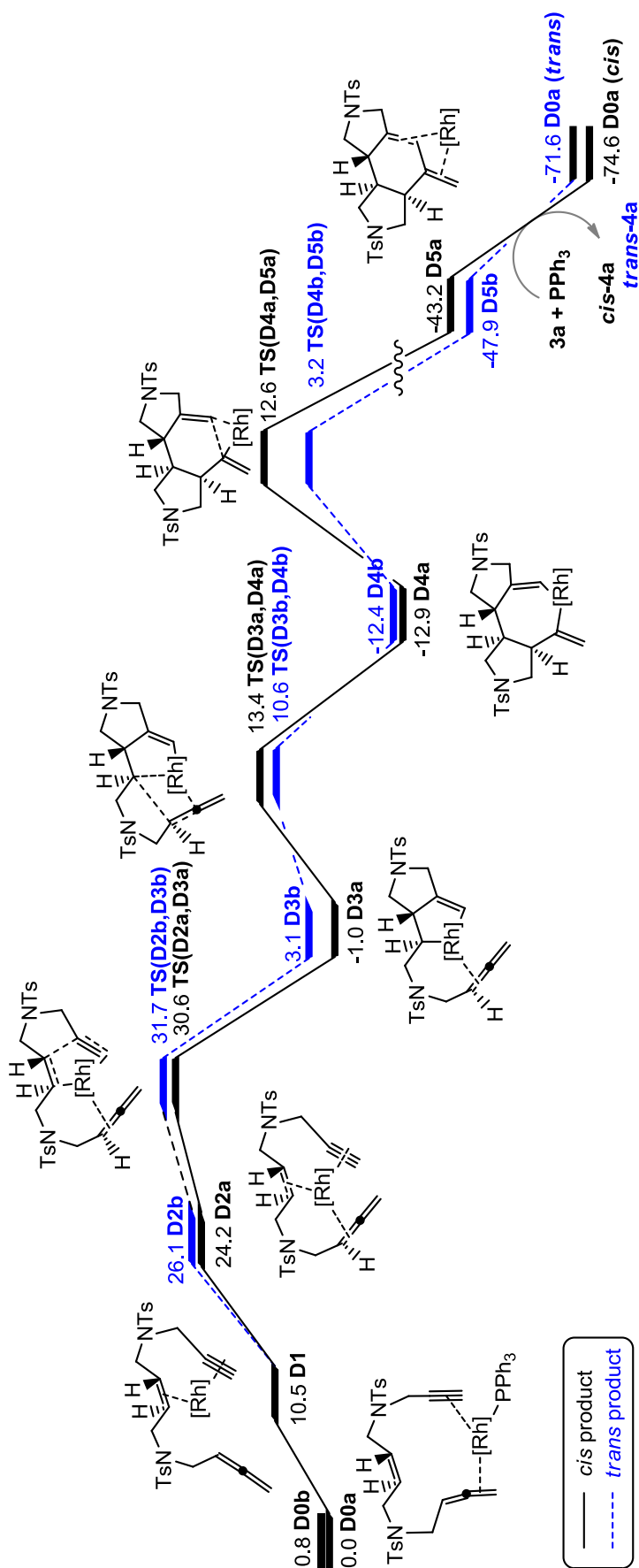
This result unambiguously indicated that the reaction can take place in the absence of PPh_3 ligands and probably through the same catalytic intermediates, since the ethylene ligand can be easily released due to its lability when the substrate enters the coordination sphere of the rhodium centre.

4.5.1.3. DFT calculations

Based on the precedents in our research group^{9i-o,51} and the results of the NMR study, we decided to propose a suitable mechanistic pathway by means of computational calculations. This theoretical study consisted in evaluating all the possible combinations that could lead to the experimentally-detected products *cis*-**5a** or *trans*-**5a**. In that sense, we considered catalytic species with one or no triphenylphosphine ligands and the different introduction order of the participating unsaturations with all the possible orientations were taken into account. We were delighted to find two mechanistic pathways that explain the formation of both observed **5a** diastereoisomers through reasonable energy barriers (**Scheme 81**).

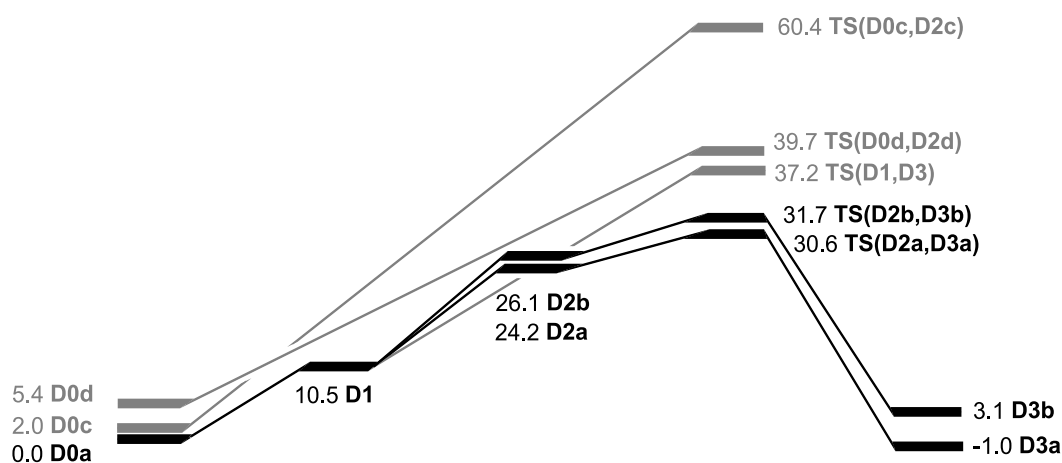
All the computational calculations were performed with the Gaussian 09⁶³ program package. Geometry optimisations were performed without symmetry constraints using the hybrid DFT B3LYP⁶⁴ method with the all-electron cc-pVDZ basis set for P, Cl, O, C, and H⁶⁵ and the cc-pVDZ-PP basis set containing an effective core relativistic pseudopotential for Rh.⁶⁶ The D3 Grimme energy corrections for dispersion with its original damping function⁶⁷ were added in all B3LYP/cc-pVDZ-PP calculations. Single-point energy calculations were carried out with the B3LYP-D3/cc-pVTZ method. Calculations were simulated at 298.15K temperature to obtain the reported relative Gibbs energies. Solvent effects were taken into account with a polarized continuum

model (PCM),⁶⁸ considering toluene solution. The change from 1 atm pressure to 1 M on the reference system was corrected by adding $1.89 \text{ kcal}\cdot\text{mol}^{-1}$ on the entropic contribution to calculate the Gibbs energy values.



Scheme 81. Gibbs energy profile ($\text{kcal}\cdot\text{mol}^{-1}$) for the most favourable route of the $[\text{RhCl}(\text{PPh}_3)_3]$ -catalysed [2+2+2] cycloaddition of allene-ene-yne **1a** leading to *cis*-**5a** and *trans*-**5a**. Energies are relative to complex **D0a**. Only the schematic drawings of the structures for the *cis* path are depicted. $[\text{Rh}] = \text{RhCl}$

Since the oxidative addition of the catalytic precursors that were detected by NMR would afford regiosomeric cycloadducts with respect to **5a** product, direct oxidative addition was not considered from these experimentally-detected species. Among the different accounted possibilities for the oxidative addition step that could finally lead to **5a**, only one gave reasonable energy barriers that could be surpassed at 100 °C. More concretely, the coordination of the three allene, alkene and alkyne unsaturations to the rhodium centre in the absence of triphenylphosphine ligands was observed to be the most feasible combination. Interestingly, direct oxidative addition between the alkene and an alkyne units with one triphenylphosphine ligand display significantly high energy barriers of 60.4 and 39.7 kcal·mol⁻¹ for **D0c** and **D0d** (Scheme 82).



Scheme 82. Summary of the oxidative addition barriers for the most stable coordination precursors

The loss of the phosphine through an endergonic process from **D0a** was considered to generate **D1**, from which a lower TS was located at $\Delta G^\ddagger = 37.2$ kcal·mol⁻¹. Though being lower, the energy barrier was still quite high to justify the experimental outcome. However, the coordination of the still uncoordinated allene motif to the rhodium centre (**D2a** and **D2b**) provokes a decrease in the energy barrier, which depends on the orientation that the allene adopts (**Figure 25**). In other words, when the allene moiety is perpendicular to Rh–Cl bond (**D2a**), the TS is placed at $\Delta G^\ddagger = 30.6$ kcal·mol⁻¹, whereas when it is parallel (**D2b**), the TS resides at $\Delta G^\ddagger = 31.7$ kcal·mol⁻¹. As expected from the molecular orbitals of a d^8 ML₄ fragment,⁷⁶ these two orientations lead to complexes with a small energy difference. The oxidative addition step to give **D3a** is exergonic by 1.0 kcal·mol⁻¹, while that for **D3b** is endergonic in 3.1 kcal·mol⁻¹.

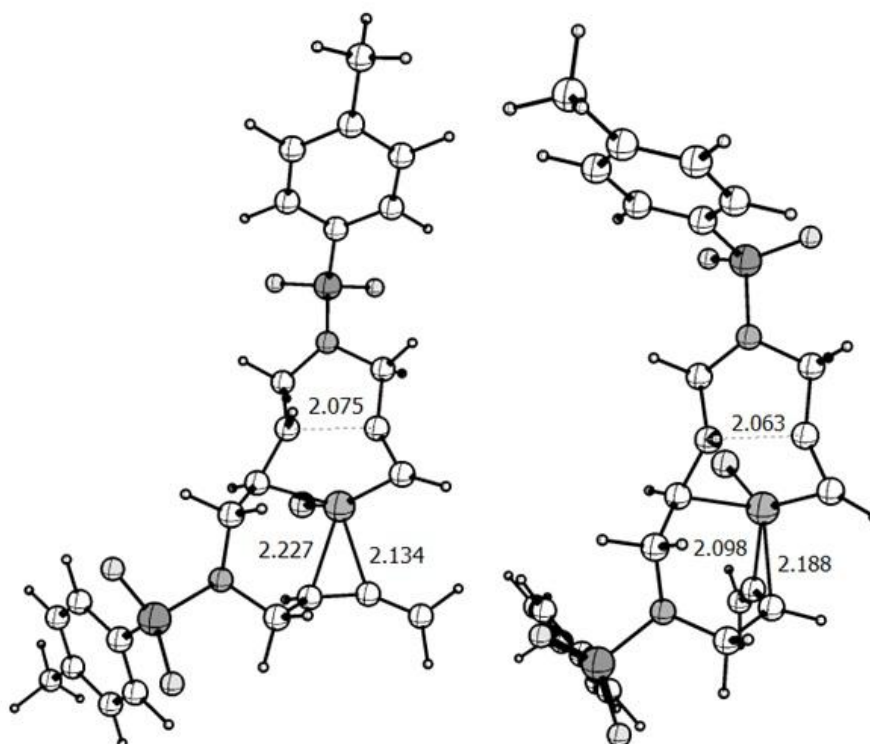
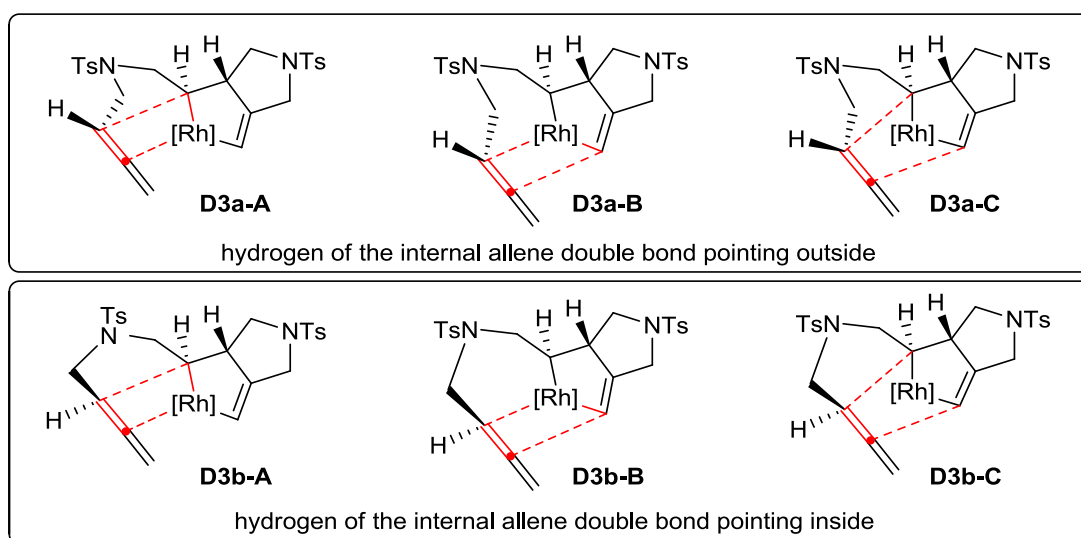


Figure 25. Optimised structures (B3LYP-D3/cc-pVDZ-PP) for **TS(D2a,D3a)** (left) and **TS(D2b,D3b)** (right)

The next step to be studied in the mechanism was the insertion process. Starting from **D3a** and **D3b** intermediates, several approaches of the internal bond of the allene moiety can take place (**Scheme 83**).



Scheme 83. Possible approaches to perform the insertion step onto **D3a** and **D3b**

A rhodacycloheptene can be generated by the attack of the allene into a Rh-C(sp^3) (**D3a-A** and **D3b-A**) or Rh-C(sp^2) (**D3a-B** and **D3b-B**) bonds. On the other hand, a rhodanorbornane intermediate can also be produced through a Diels-Alder-like TS

(**D3a-C** and **D3b-C**). However, after many attempts, we were unable to find any TS that corresponded to a [4+2] approach that led to a rhodanorbornane intermediate. After comparing the energy barriers found for the remaining cases, it became evident that the insertion in the Rh-C(sp^3) bond is preferable in front of the Rh-C(sp^2) one. **TS(D3a,D4a)** and **TS(D3b,D4b)** (**Figure 26**) displayed two low energy barriers of $\Delta G^\ddagger = 14.4 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta G^\ddagger = 7.5 \text{ kcal}\cdot\text{mol}^{-1}$, respectively.

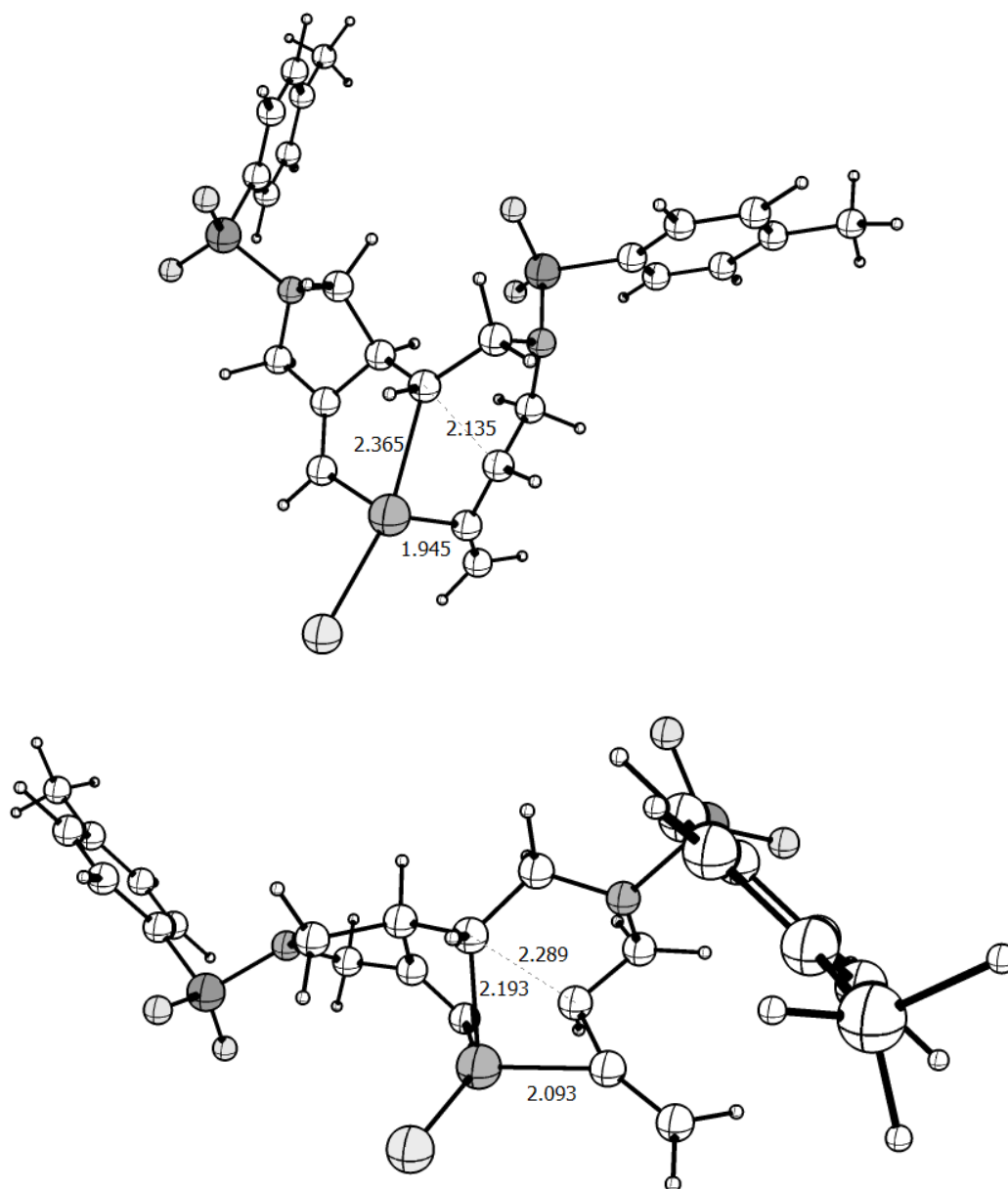


Figure 26. Optimised structures (B3LYP-D3/cc-pVDZ-PP) for **TS(D3a,D4a)** (top) and **TS(D3b,D4b)** (bottom)

Last, the reductive elimination step was evaluated. This process involves the formation of the last C-C bond that affords the final cyclohexene ring that still η^4 -coordinates to RhCl. **TS(D4a,D5a)** and **TS(D4b,D5b)** were located at $\Delta G^\ddagger = 25.5 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta G^\ddagger = 15.6 \text{ kcal}\cdot\text{mol}^{-1}$, respectively.

In general terms, both mechanistic pathways display highest energy barrier at oxidative addition step and so the rate-determining step resides at the beginning of the process. The overall reaction is exergonic by $71.6\text{-}74.6 \text{ kcal}\cdot\text{mol}^{-1}$, being the energy span between the turnover frequency (TOF) determining intermediate (TDI) and TOF determining TS (TDTS)⁷⁷ of $30.6 \text{ kcal}\cdot\text{mol}^{-1}$ and $31.7 \text{ kcal}\cdot\text{mol}^{-1}$ for pathways leading to *cis*-**5a** and *trans*-**5a**, respectively. Furthermore, the similarity between the energy barriers of the rate determining steps, which differ in only $1.1 \text{ kcal}\cdot\text{mol}^{-1}$, justify that a mixture of diastereoisomers is finally attained from the experimental perspective.

4.5.2. [RhCl(CO)₂]₂-catalysed mechanism

Having found a reasonable mechanistic proposal for the [RhCl(PPh₃)₃] catalyst, we turned our attention to [RhCl(CO)₂]₂, which was observed to experimentally afford the same diastereoisomers but in the opposite diastereoisomeric ratio, that is to say, favouring *trans*-**5a** in front of *cis*-**5a**. We were encouraged to find a mechanism to justify such an interesting behaviour.

4.5.2.1. Mass spectrometry experiments

The study entailed considering a different number of carbonyl ligands on the rhodium coordination sphere of the monomeric form of [RhCl(CO)₂]₂, either [RhCl(CO)₂], [RhCl(CO)] or [RhCl]. To shed more light on this aspect, we decided to use electrospray ionization spectrometry (ESI-MS) to detect possible catalytic intermediates in order to know how many carbonyl ligands are coordinated.⁷⁸

This empirical test consisted in running the reaction using [RhCl(CO)₂]₂ under the optimised conditions and periodically taking aliquots of the reaction crude. Unfortunately, no species could be detected by directly injecting the samples into the ESI-MS apparatus. However, based on the work of Metzger's group,⁷⁹ we managed to increase the sensibility and make it possible to detect some catalytic intermediates. It essentially consisted in mixing the aliquot with a solution of LiCl (0.01 M) in methanol prior to injection to the ESI-MS apparatus. Such change may be explained thanks to the capacity of Cl⁻ anions to negatively charge the catalytic species and thus allow their observation through the negative ESI ion mode.

When running the test for **1a**, we were able to detect two species corresponding to the substrate organic chain with the rhodium centre, with one CO ligand (Entry 1, **Table 13**) and with none (Entry 2, **Table 13**). Repeating the same experiment with **1d** instead, we observed the corresponding *m/z* values for the analogous species (entries 3 and 4, **Table 13**).

Table 13. Detected peaks through ESI-MS

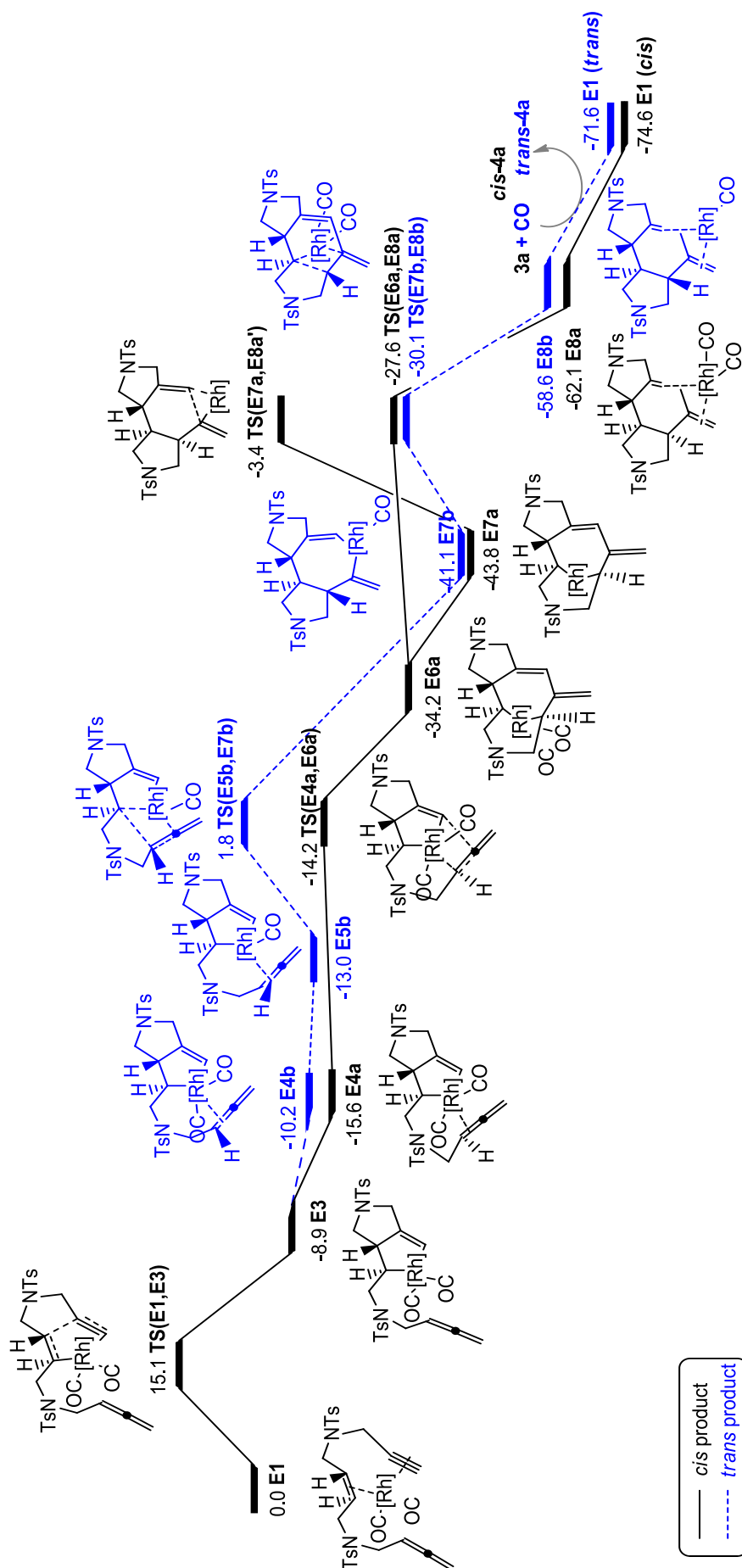
Entry	Substrate	<i>m/z</i> detected	Identified species
1	1a	684.8	[RhCl(1a)(CO) + Cl ⁻]
2	1a	656.9	[RhCl(1a) + Cl ⁻]
3	1d	726.9	[RhCl(1d)(CO) + Cl ⁻]
4	1d	698.8	[RhCl(1d) + Cl ⁻]

The identity of $[\text{RhCl}(\mathbf{1})(\text{CO}) + \text{Cl}]$ signals was corroborated by performing CID fragmentation (ESI-MS/MS), since it provoked the rising of peaks at $[\text{M}-28]^+$ corresponding to the loss of the CO ligand to give $[\text{RhCl}(\mathbf{1}) + \text{Cl}]$.

From these results, we inferred that the mechanism for $[\text{RhCl}(\text{CO})_2]$ catalytic species entails intermediates with a variable number of carbonyl ligands onto their coordination sphere.

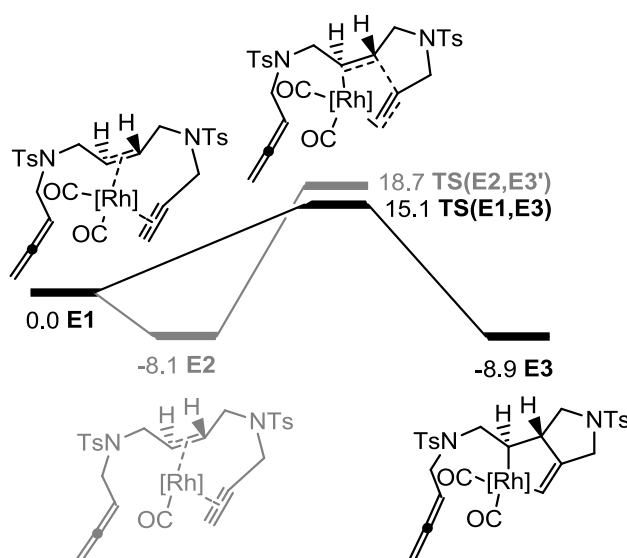
4.5.2.2. DFT calculations

From the theoretical point of view, we were devoted to perform a similar computational analysis of the different possible pathways that could lead to the observed compounds. Taking into account the precedents found in the literature⁸⁰ and the ESI-MS results, we considered the monomeric form of the catalyst $[\text{RhCl}(\text{CO})_2]$. The analysis started by analysing the different possibilities regarding the coordination of the allene, alkene and alkyne motifs to the rhodium centre. Furthermore, we also computed the different intermediates and TSs that can intervene with a variable number of carbonyl ligands, either two, one or none. The most reasonable mechanistic pathways are presented in **Scheme 84**.



Scheme 84. Gibbs energy profile ($\text{kcal} \cdot \text{mol}^{-1}$) for the most favourable route of the $[\text{RhCl}(\text{CO})_2]_2$ -catalysed $[2+2+2]$ cycloaddition of allene-ene-yne **1a** leading to *cis*-**5a** and *trans*-**5a**. Schematic drawings of the structures for the *cis* path in black and for the *trans* in blue. $[\text{Rh}] = \text{RhCl}$

The first calculations suggest that the catalytic cycle starts with the coordination of the alkyne and alkene unsaturations to the rhodium centre with two carbonyl ligands and the chloride (**E1**). Oxidative addition can take place from this intermediate to afford rhodacyclopentene **E3** by surpassing an energy barrier of $\Delta G^\ddagger = 15.1 \text{ kcal}\cdot\text{mol}^{-1}$. Similarly to the $[\text{RhCl}(\text{PPh}_3)_3]$ -catalysed mechanism, the alkene and alkyne unsaturations are the involved ones in the oxidative addition. Despite the fact that **E2** could be obtained from **E1** after the decooordination of a CO unit in an endergonic process of $8.1 \text{ kcal}\cdot\text{mol}^{-1}$, we observed that the corresponding **TS(E2,E3')** is located at $26.8 \text{ kcal}\cdot\text{mol}^{-1}$. Therefore, we could rule this alternative out as for requiring much more energy than for **TS(E1,E3)** (**Scheme 85**). Such thing is not unexpected because the CO ligand shows a higher σ -donation character than π -backdonation.⁸¹ Therefore, the presence of CO ligands favours the oxidation of Rh(I) to Rh(III), provoking the decrease of the energy barrier of the oxidative addition step when $[\text{RhCl}(\text{CO})_2]$ is involved instead of $[\text{RhCl}(\text{CO})]$.



Scheme 85. Oxidative addition barriers for the most stable coordination precursors

Rhodacyclopentene **E3** intermediate can later evolve to **E4a** or **E4b** depending on the orientation that the allene motif adopts once it coordinates to the rhodium centre. The orientation of the allenic protons gives rise to the generation of the *cis* and *trans* diastereoisomers.

For the synthesis of the *trans* cycloadduct, loss of a CO ligand in **E4b** occurs with the release of $2.8 \text{ kcal}\cdot\text{mol}^{-1}$ to yield **E5b**. From this last intermediate, the insertion of the internal double bond of the allene into the $\text{Rh-C}(sp^3)$ bond generates rhodacycloheptene intermediate **E7b** with a *trans* C-C fusion by surpassing an energy barrier of $14.8 \text{ kcal}\cdot\text{mol}^{-1}$ (**Figure 27**). On the other hand, **E4a** evolves to the

cycloadduct with the *cis* C-C fusion through a pathway that differs from the previous one in two aspects. Firstly, there is no CO dissociation and, secondly, the insertion of the allenic moiety takes place on the Rh-C(sp²) bond of **E4a**. In this last case, the energy barrier for the formation of **E6a** falls to only 1.4 kcal·mol⁻¹.

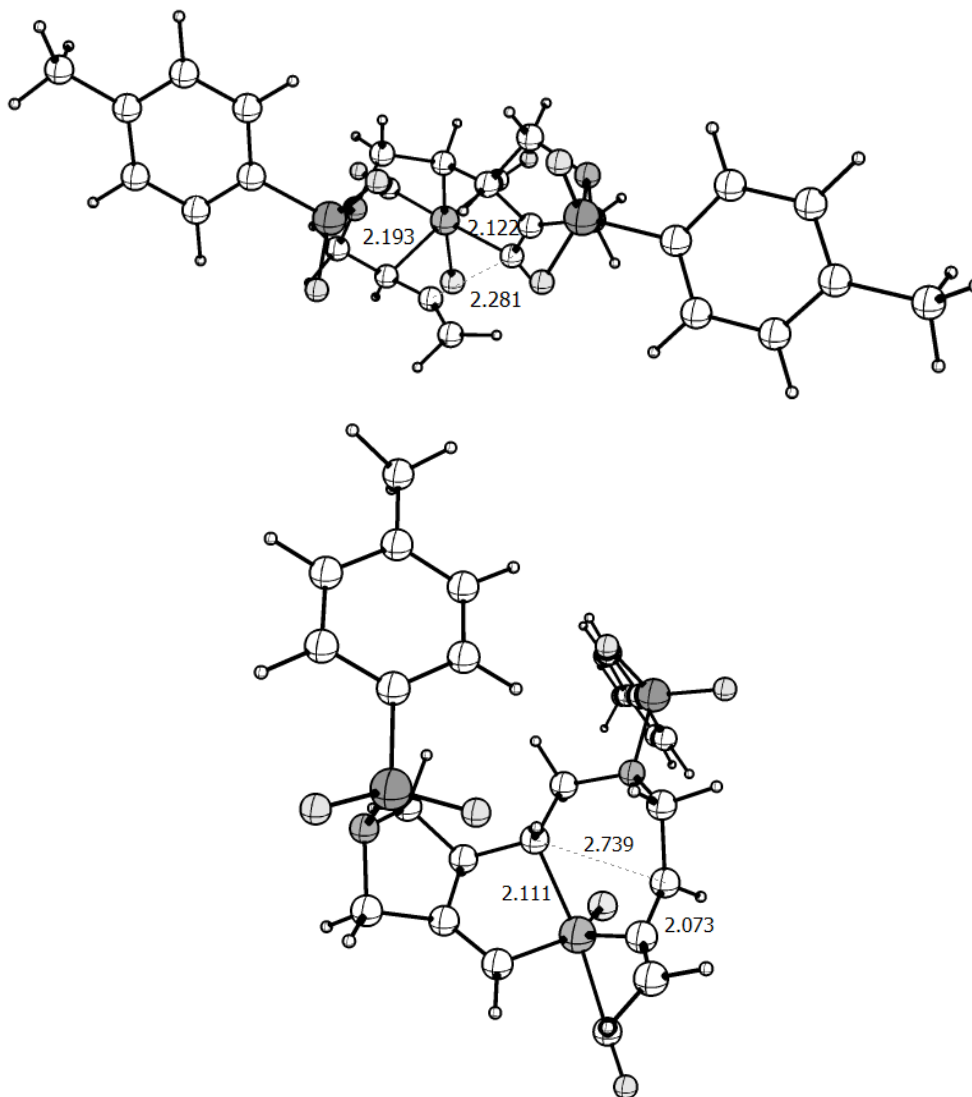


Figure 27. Optimised structures (B3LYP-D3/cc-pVDZ-PP) for **TS(E4a,E6a)** (top) and **TS(E5b,E7b)** (bottom)

The ring closure in **E7b** towards the *trans* diastereoisomer was computed to occur through an energy barrier of 11.0 kcal·mol⁻¹ to afford **E8b**. In the pathway leading to the *cis* diastereoisomer we observed that **E6a** was significantly stabilised by 9.6 kcal·mol⁻¹ when the two carbonyl ligands were lost to yield **E7a**. However, looking at the final step, the ring closure process was observed to be more favourable if the carbonyl ligands were recovered, since **TS(E6a,E8a)** was located at $\Delta G^\ddagger = 16.2$ kcal·mol⁻¹ with

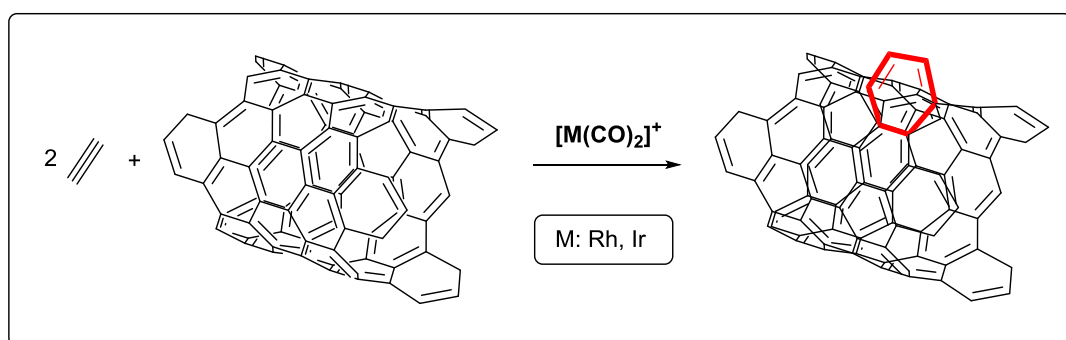
respect to the most stable intermediate **E7b**, which is a much more plausible value than the corresponding reductive elimination via **TS(E7a,E8a')**, $\Delta G^\ddagger = 40.4 \text{ kcal}\cdot\text{mol}^{-1}$.

As a whole, the catalytic cycle was found to be exergonic by $71.6\text{--}74.6 \text{ kcal}\cdot\text{mol}^{-1}$ and the energetic difference between TDI and TDTS was $15.1 \text{ kcal}\cdot\text{mol}^{-1}$ (oxidative addition) for the *trans* pathway, and $16.2 \text{ kcal}\cdot\text{mol}^{-1}$ (ring closure) for the *cis* pathway. The generation of the two diastereoisomers that have been experimentally detected could be justified by looking at the low energy span differences ($1.1 \text{ kcal}\cdot\text{mol}^{-1}$) of the rate-determining steps between the pathways leading to *cis*-**5a** and *trans*-**5a**, in favour of the *trans* diastereoisomer, which matches the empirical results. The results of the empirical tests carried out using ESI-MS to detect reaction intermediates support the type of intermediates proposed for this catalytic cycle. We were able to observe peaks corresponding to $[\text{RhCl}(\mathbf{1})(\text{CO})]$ species, which corroborate the coordination sphere of the intermediates depicted in **Scheme 84**.

Having completed the mechanistic study for both catalysts, several points could be extracted from the comparison of the two proposed catalytic cycle. From the computational point of view, the experimental detection of two diastereoisomers is reasonable, since very low energetic differences were found between similar potential energy surfaces leading to the *cis* and the *trans* diastereoisomers. In addition to that, the difference in selectivity of the two catalytic systems can be attributed to the variation in the coordination sphere of the catalytically-active species: the $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst cycle runs on a catalytic species with only a chloride ligand, while the outcome for the $[\text{RhCl}(\text{CO})_2]_2$ catalyst relies on the number of carbonyl units coordinated to the metallic centre. On the other hand, the need to heat the system to 100°C when $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst is employed and to only 60°C when $[\text{RhCl}(\text{CO})_2]_2$ is used is in accordance with the energy barriers found, since the first requires about $30 \text{ kcal}\cdot\text{mol}^{-1}$ to complete the cycle and only half the energy, about $15 \text{ kcal}\cdot\text{mol}^{-1}$, for the second.

To sum up, we have described a new stereoselective [2+2+2] cycloaddition reaction of linear allene-alkene-alkyne substrates mediated by Rh(I) catalysts. The study has been supported by NMR and ESI techniques and DFT calculations to propose a suitable catalytic mechanism explaining the generation of the experimentally cycloadducts and the observed stereoselectivity.

Chapter 5. Transition metal-catalysed [2+2+2] cycloaddition involving SWCNTs



5.1. Precedents

For many centuries, the only three known forms of carbon were diamond, graphite and amorphous carbon like soot and charcoal. However, in 1985, Kroto and co-workers⁸² described another carbon allotrope made of 60 carbon atoms (C_{60}) disposed in a ball-shaped geometry, which was later named as *Buckminsterfullerene*. Their work represented the finding of the first nanostructured carbon allotrope, which promoted the study of more fullerene-like structures,⁸³ which can be employed for several uses in biology, medicine and photovoltaics, among others.⁸⁴

Later, Iijima⁸⁵ in 1991 and Bethune⁸⁶ in 1993 independently discovered the *carbon nanotubes* (CNTs), which are carbon nanostructured allotropes consisting of carbon atoms disposed in a series of condensed benzene rings (graphene sheet) rolled into a cylinder. CNTs can be closed at the ends and, furthermore, they can contain or be contained in a second CNT. Therefore, depending on the number of comprised layers, single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) can be defined (**Figure 28**).

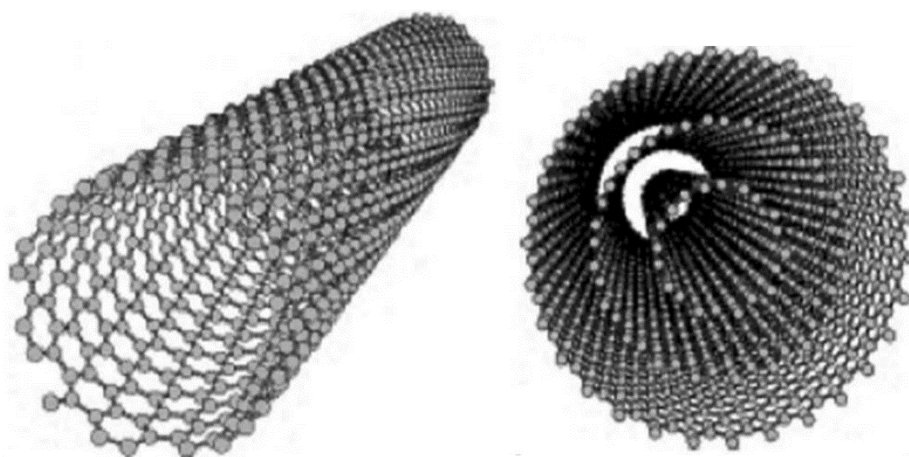


Figure 28. General structure of the SWCNT (left) and MWCNT (right)⁸⁷

CNTs drew our attention for their remarkable structural, physical and chemical properties. Since their discovery, numerous studies have been undertaken to deeply characterise them and several applications have been conceived in science of materials, biology or medicine.⁸⁸ For instance, research is currently being carried out in medicine to use them as drug delivery vehicles into cells because they protect the transported compound.⁸⁹ Furthermore, CNTs also serve as excellent enantiomeric separators of chiral drugs and chemicals, especially in the pharmaceutical field.⁹⁰

From the structural point of view, several morphological tests have shown that SWCNTs usually have diameters comprised between 4 and 20 Å and can be several millimetres long. The chemical reactivity has been observed to be different at the ends and at the sidewalls of the SWCNT. Furthermore, the reactivity is strongly influenced as well by the way the rolling up of graphene is produced to generate the tube.

Of special interest are their properties, like the large values of modulus of elasticity,⁹¹ their stability even at 750 °C in air and 2.800 °C under vacuum and their behaviour as better thermal conductors than traditionally good conductors like copper.⁹² Remarkably, electronic and optical properties, which can be as good as those of some metals or semiconductors, might vary depending on the sidewall curvature, the chirality and the local environment.⁹³

5.1.1. Classification of SWCNTs

From a geometrical point of view, the unit cell of a SWCNT can be considered as a cylinder defined by the length of the cell (**T**) and by the circumference of the base (**C**) (**Figure 29**).

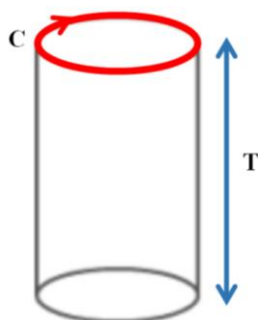


Figure 29. Geometrical definition of **C** and **T** in a unit cell of the SWCNT

Since a SWCNT is a rolled graphene sheet, **C** can be described by a roll-up vector (n,m) that characterizes the orientation of the benzene rings in the nanotube. Considering a model graphene sheet in which all carbon-carbon bonds display the same length and all angles are 120°, the vector **C** can be defined as $\mathbf{C} = na + mb$, where a and b are unitary vectors that form a basis. The modulus of vector **C** ($|\mathbf{C}|$) corresponds to the circumference of the tube (**Figure 30**).

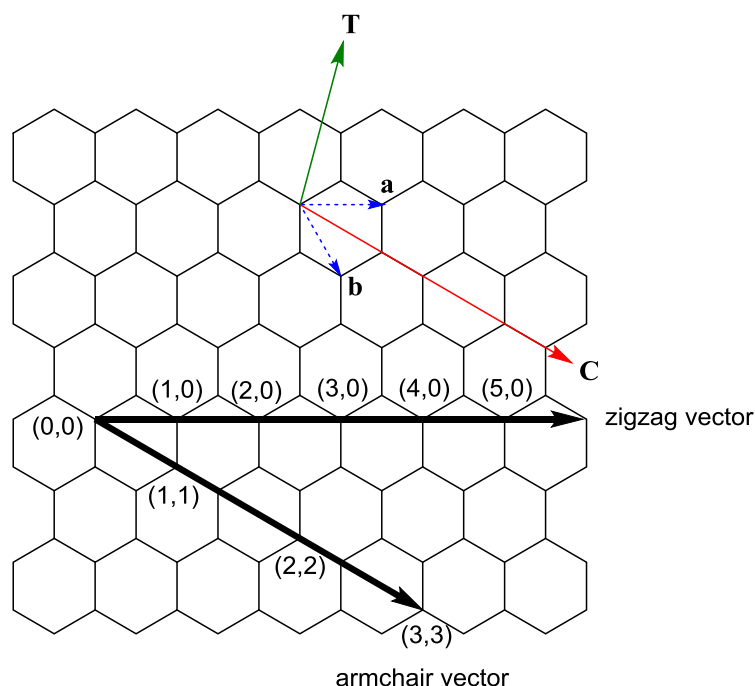


Figure 30. Model to construct a SWCNT from a graphene sheet via **C** and **T** vectors. Zigzag and armchair SWCNTs are represented.

In addition to that, the unit cell length is defined by the modulus of the translation vector **T**, which is perpendicular to **C**.⁹⁴

In this context, a SWCNT with an associated $(n,0)$ roll-up vector is known as a *zigzag* SWCNT, whereas a (n,n) vector corresponds to an *armchair* SWCNT. Any other combination of n and m refers to the so-called *chiral* SWCNTs (**Figure 31**)

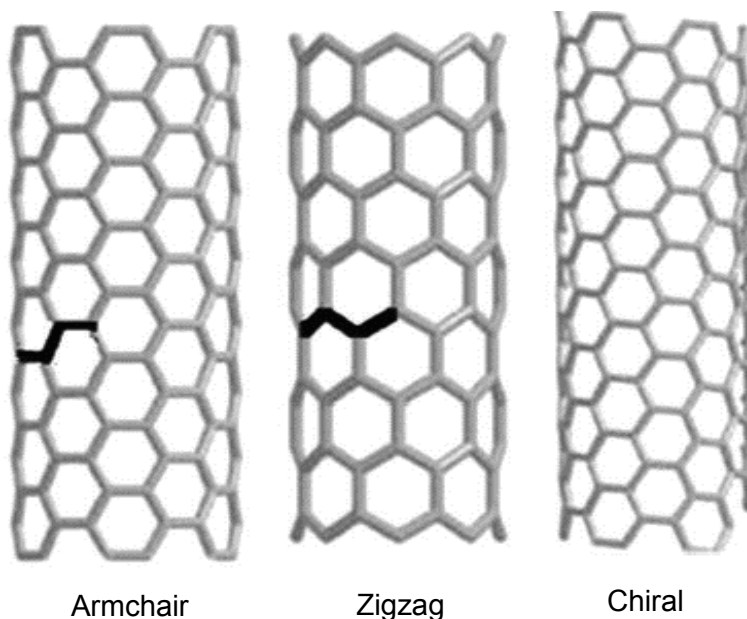


Figure 31. The three different types of SWCNTs⁹⁵

Focusing on the two symmetrical SWCNT morphologies (armchair and zigzag), two types of C-C bond orientations can be distinguished (**Figure 32**). Taking as the reference the length orientation of the nanotube, armchair SWCNTs have perpendicular and slanted (or oblique) bonds, whereas zigzag SWCNTs display parallel and slanted bonds.

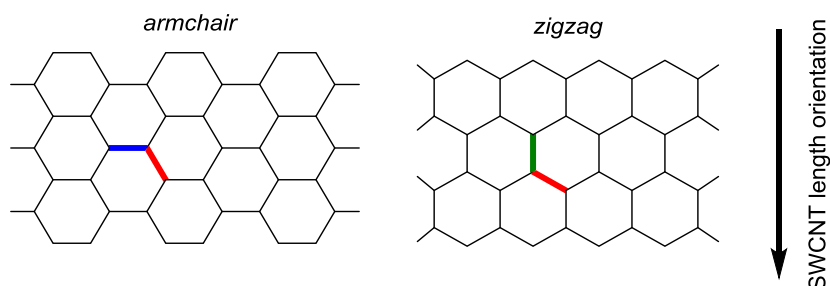


Figure 32. Representation of parallel (green), slanted (red) and perpendicular (blue) C-C bonds for armchair and zigzag SWCNTs

5.1.2. Clar structures

The so-called Clar's π -sextet rule⁹⁶ establishes that Kekulé resonance structures⁹⁷ (**Figure 33**) with the largest number of disjoint aromatic π -sextets are the polycyclic aromatic hydrocarbons that are more likely to be observed.⁹⁸

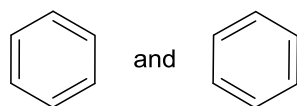
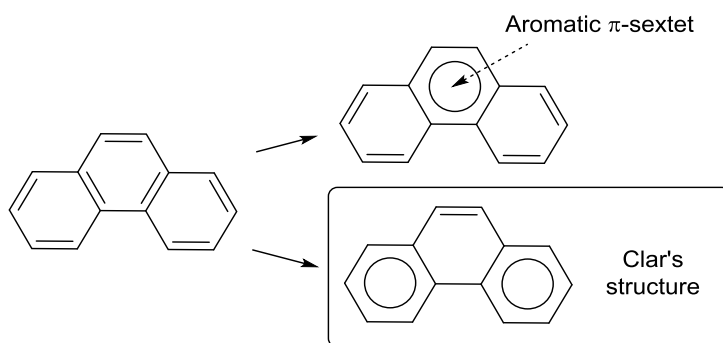


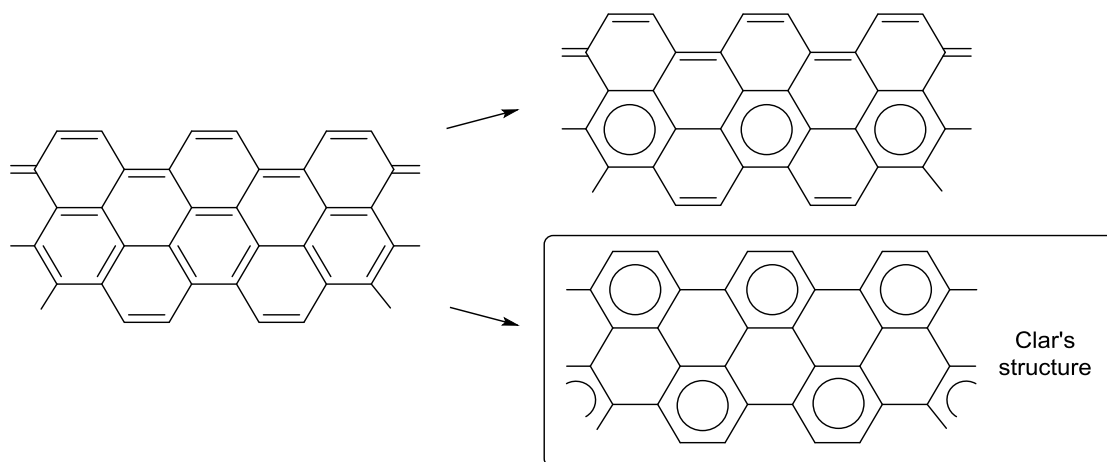
Figure 33. Representation of Kekulé structures for benzene

An aromatic π -sextet essentially consists of six π -electron that are localised on a single benzene-like ring which is separated from the contiguous rings by single C-C bonds. So, Clar's rule states that the most stable structure is the one with the largest number of aromatic π -sextets (**Scheme 86**).



Scheme 86. Graphical representation of the Clar's rule for phenanthrene

In the context of SWCNTs, Clar's theory also serves as a construction pattern to obtain nanotubes (**Scheme 87**). As a result of that, Finite-Length Clar Cells (FLCC) are afforded.⁹⁹ The resulting structures tend to be much more stable than the corresponding Kekulé structures due to the stability provided by aromaticity to conjugated systems.^{99b,100} Additionally, it should be noted that the aromatic character of a molecular system bearing π -electrons has been shown to be extremely affected by the geometry of the ring structure. In this sense, any distortion affecting the geometrical arrangement influences the aromaticity in the system.¹⁰¹



Scheme 87. Graphical representation of the Clar's rule for an armchair SWCNT

From a practical perspective, it should be noted that an appropriate segmentation of the geometry of the SWCNT needs to be done to perform the desired computational calculations. Armchair SWCNTs do not require any special consideration in this sense, as all fragments are closed-shell FLCCs and remain on a singlet ground state. This means that faster convergence is attained in the SWCNT electronic properties with respect to the number of cells of the nanotube. Contrary to that, zigzag SWCNTs need a convenient modelling, as multi-radicals can be generated at triplet, quintuplet or other

electronic state, which strongly and negatively affects to the convergence of the results with respect to the length of the nanotube.

5.1.3. Properties and uses of SWCNTs

One of the most interesting features of nanotubes is their elasticity and, at the same time, that they are still extremely resistant. For instance, these materials are six times more elastic than steel and more than ten times more resistant than Kevlar fibres, which are polyamides often used to build light equipment capable of supporting high temperatures and corrosion.¹⁰²

Another noteworthy property is electrical conductivity, as nanotubes can display an approximate value of 10^9 A/cm^2 . It has been hypothesized that the reason for such conductivity is due to the so-called *ballistic* conduction, which consists in that an electron placed inside the nanotube finds no impediment and is uniformly accelerated by the electric field.¹⁰³ Depending on the electronic conductivity efficiency of a particular nanotube, it will be classified as a *conductor* or a *semi-conductor* material. Actually an application of semiconductor SWCNTs is found in the development of molecular transistors.¹⁰⁴

Finally, it should be noted that they tend to agglomerate due of the strong van der Waals forces present between different nanotubes.¹⁰⁵ This fact constitutes an important drawback when trying to study their properties and, more importantly, it makes it difficult to dissolve nanotubes in conventional solvents. To date, the best methods to overcome such a problem are by adding surfactants or by functionalising the nanotube.¹⁰⁶

5.1.4. Preparation of SWCNTs

The most widely used method to efficiently obtain nanotubes is pyrolysis. The process essentially consists in reacting a suitable organic compound, like acetylene or carbon monoxide, under transition metal-catalysis and heating the system above 700 °C. The most common catalysts consist of metal alloys nanoparticles, usually Fe/Co, Co/Ni or Fe/Mo.¹⁰⁷ Depending on the size and composition of the catalyst nanoparticles, the nature of the organic precursor and the temperature, different yields and diameters of SWCNTs will be attained.

A synthetic alternative to obtain SWCNTs consists in the use of carbon monoxide as the precursor. In this case $\text{Fe}(\text{CO})_5$ catalyst is used under high pressure of CO, which

reacts to form highly pure SWCNTs.^{107a} Actually, commercial samples of nanotubes are often prepared by employing this technique.

Other synthetic methods to afford SWCNTs are vaporization of graphite by laser pulses¹⁰⁸ or arc discharge in graphite electrode.¹⁰⁹

5.1.5. Purification of SWCNTs

Since the synthetic methods mentioned above yield nanotubes with some metallic impurities, the raw material needs to be purified before its further use. Taking advantage of their chemical resistance in front of strong conditions, a good method to purify nanotubes is the addition of strong acids in aqueous solution, like nitric acid (3 M) or HNO₃/H₂SO₄ mixtures. This treatment facilitates that metals (and other carbonaceous residues) are dissolved and thus can be easily removed.

However, this simple technique may eventually provoke some partial oxidation of the SWCNT and, as a result of that, the nanotube might be shortened. This oxidative degradation leads to the functionalisation of the edges of the nanostructure with oxygenated groups, being carboxyl groups the most frequent ones.

5.1.6. Functionalisation of SWCNTs

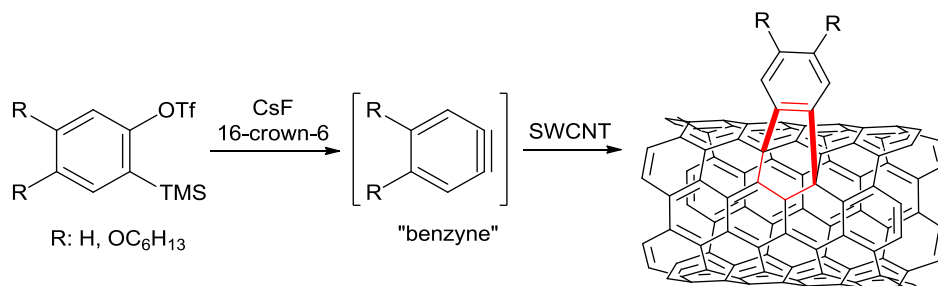
One step further is the preparation of functionalised carbon nanotubes, since their properties can be tuned by modifying the side chains linked to the nanotube. Thanks to these linkages, stiffness, strength and thermal and electrical conductivities can be greatly adjusted according to the application needs.

In addition to that, functionalisation also represents an excellent way to circumvent the main disadvantages of the use of CNTs: their insolubility in conventional solvents and their π -stacking tendency to form agglomerates.¹¹⁰

However, the experimental conditions employed to functionalise the nanotube need to be optimised, as an excessive degree of functionalisation might lead to the worsening of some SWCNT properties due to the interruption caused in the overlapping of the π -orbitals.

To date, the most frequent functionalisation reactions for CNTs, which are similar to the ones applied on fullerenes, are those performed through: i) the Diels-Alder [4+2] cycloaddition, ii) the 1,3-dipolar cycloaddition (also referred as Prato reaction), iii) the photochemical silylation, carbene and nitrene additions (also referred as Bingel-Hirsch

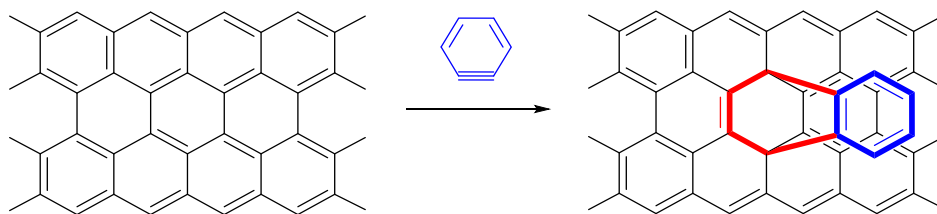
reaction) and iv) [2+2] cycloaddition.¹¹¹ Ten years ago, the formation of C-C bonds between a SWCNT and a functional group was confirmed by the addition of arynes to form paddle-wheel-like nanostructures.¹¹² Langa and co-workers^{110c,113} found that this process is possible by submitting the system to microwave conditions (**Scheme 88**). The success of the functionalisation was stated by looking at the average mass, since it increased in 5-19%.



Scheme 88. [4+2] cycloaddition reaction of a SWCNT and benzyne

Later, Nagase and co-workers¹¹⁴ described the [4+2] and [2+2] cycloaddition reactions of benzyne to armchair SWCNTs by means of DFT calculations. They concluded that the [4+2] cycloaddition is most likely to take place in a slanted (or oblique) position when the SWCNT diameter is relatively large. However, in SWCNTs with diameters minor to 10 Å, the [2+2] cycloaddition is thermodynamically preferred onto the slanted bond, but the perpendicular bond turn to be kinetically more favourable.

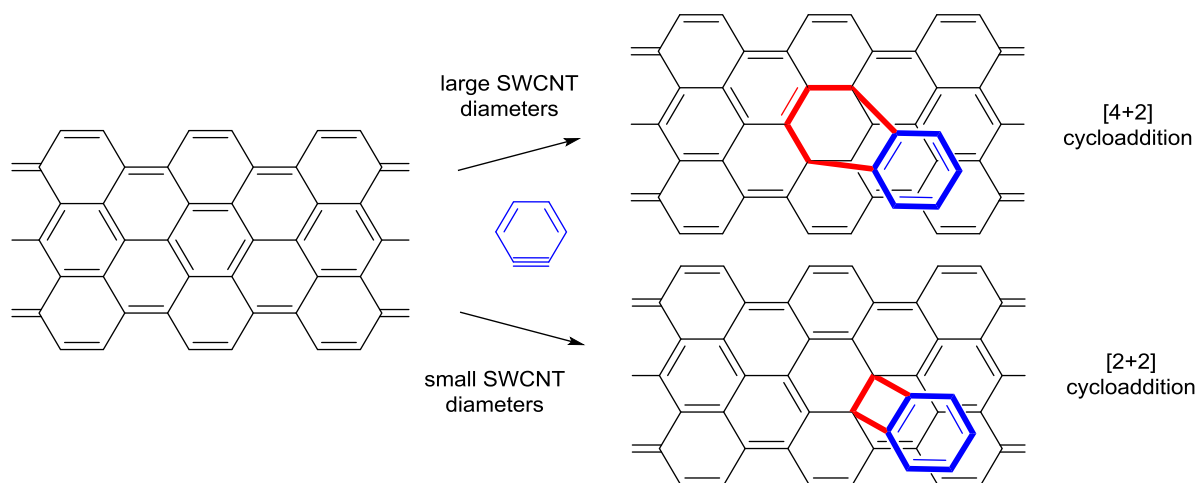
Our research group has contributed to the field with a theoretical study of the [2+2] and [4+2] cycloadditions of SWCNTs and fullerenes with an aryne unit.¹¹⁵ Focusing on the case of nanotubes, the conclusions of the work were that zigzag SWCNTs were more likely to undergo a [4+2] cycloaddition reaction of benzyne on the parallel direction of the SWCNT, instead of the [2+2] process, as it was kinetically favourable and thermodynamically preferred. Furthermore, when the diameter of the zigzag nanotube increases, the process becomes less favourable (**Scheme 89**).



Scheme 89. [4+2] cycloaddition of zigzag SWCNT with benzyne

On the other hand, when an armchair SWCNT is considered, the [4+2] cycloaddition of benzyne is favourable on a slanted orientation. Contrary to zigzag nanotubes, this

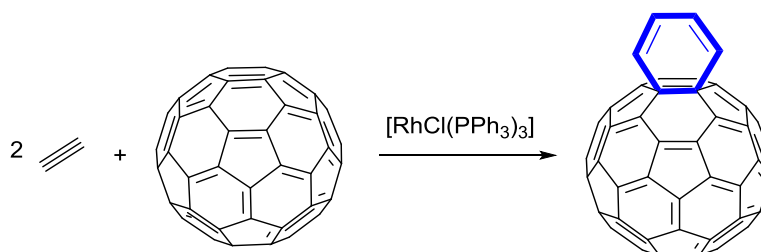
cycloaddition is only likely to happen when the armchair SWCNT diameter is sufficiently large, otherwise the [2+2] addition is thermodynamically preferable on a slanted orientation (**Scheme 90**).



Scheme 90. [4+2] and [2+2] cycloaddition reactions for large-diameter and small-diameter armchair SWCNTs with benzyne, respectively

When the same study was performed using fullerene, the [2+2] cycloaddition reaction was observed to be more likely than the [4+2] process. Furthermore, the analysis revealed that the cycloaddition behaved in a regioselective fashion, as the [6,6] bonds of the fullerene were kinetically and thermodynamically preferred in front of the [5,6], though the last remained in kinetical competence.

Focusing on the functionalisation of carbon allotropes, our group carried out a theoretical study to understand the feasibility of the [2+2+2] cycloaddition reaction of two alkyne units and a fullerene (C_{60}).¹¹⁶ By performing DFT calculations, the study concluded that the most likely product that could be formed was a cyclohexadiene ring fused to a [6,6] bond of C_{60} using the Wilkinson's catalyst to promote the reaction (**Scheme 91**).



Scheme 91. DFT study of the [2+2+2] cycloaddition reaction of two acetylene units and C_{60}

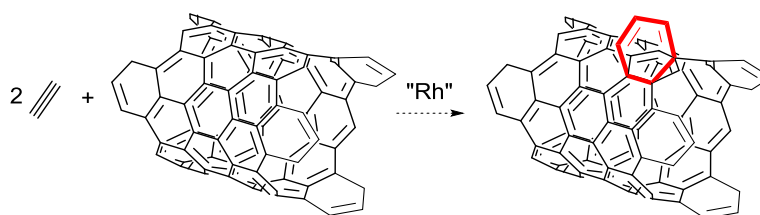
To sum up, it can be stated that a deep theoretical understanding of the [2+2] and [4+2] cycloaddition reactions has been attained when fullerene and SWCNTs are involved, but [2+2+2] cycloaddition reactions still remain quite unexplored, as only fullerenes have been entailed in this context (**Scheme 92**).

fullerene	[2+2]	}	J. P. Martínez, F. Langa, F. M. Bickelhaupt, S. Osuna, M. Solà
	[4+2]		
	[2+2+2]	→	A. Artigas, A. Lledó, A. Pla-Quintana, A. Roglans, M. Solà
<i>armchair</i> SWCNT	[2+2]	}	T. Yang, X. Zhao, S. Nagase J. P. Martínez, F. Langa, F. M. Bickelhaupt, S. Osuna, M. Solà
	[4+2]		
	[2+2+2]	→	<i>unexplored</i>
<i>zigzag</i> SWCNT	[2+2]	}	J. P. Martínez, F. Langa, F. M. Bickelhaupt, S. Osuna, M. Solà
	[4+2]		
	[2+2+2]	→	<i>unexplored</i>

Scheme 92. Summary of previous theoretical works cycloaddition reactions involving fullerenes and SWCNTs

Considering the relevance of the functionalisation of SWCNTs, we were encouraged to perform a computational study to analyse the feasibility of the transition metal-catalysed [2+2+2] cycloaddition of two acetylene units and a SWCNT.

Taking into account the precedents in the literature^{114,115,116} as well as the results presented in Chapter 3 of this thesis, we were encouraged to study the feasibility of the [2+2+2] cycloaddition reaction involving two acetylenes and a single-walled carbon nanotube (SWCNT). To attain so, our model system consisted of two acetylene molecules being added on a zigzag (9,0) SWCNT (**Scheme 93**). Moreover, considering the theoretical work in the field of [2+2+2] cycloaddition reactions presented in the first chapter of this thesis, [Rh-Cl] catalytic species was chosen for the first computational approach to promote the process.



Scheme 93. Model system for the rhodium-catalysed [2+2+2] cycloaddition reaction of two acetylenes with a zigzag (9,0) SWCNT

The study is also intended to provide an insight on the influence of the SWCNT nature on the feasibility of the reaction. That is to say, to determine which are the effects of the SWCNT morphology (zigzag or armchair) and size ((9,0) and (12,0)) on the reaction.

All calculations were performed with the Gaussian 09⁶³ program package. Geometry optimisations were performed without symmetry constraints using the hybrid DFT B3LYP⁶⁴ method with the all-electron 6-31G(d,p) basis set in conjunction with LANL2DZ pseudopotentials for Rh. The D3 Grimme energy corrections for dispersion with its original damping function⁶⁷ were added in all B3LYP/6-31G(d,p)-LANL2DZ calculations. Calculations were simulated at 298.15K temperature and under 1 atm to obtain the reported relative Gibbs energies. Considering that non-covalent solvents like toluene have a small effect on the calculated energetic values,¹¹⁶ no solvation model was applied for this system.

5.2. Feasibility study

In order to conveniently evaluate the target reaction, Clar theory (see Section 5.1.2.) needs to be taken into account to model the most appropriate SWCNT segment. Since the study will be based on a zigzag SWCNT model, the segmentation displayed in **Figure 34** needs to be ensured in order to avoid the generation of multi-radicals.

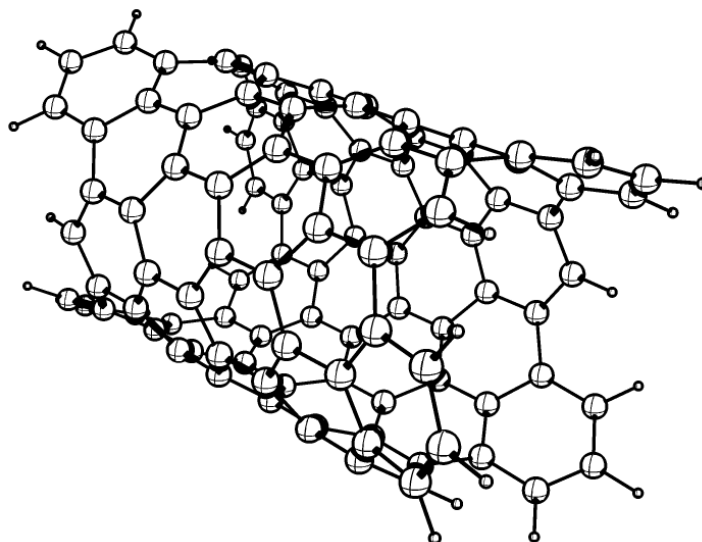


Figure 34. Segmentation of a zigzag (9,0) SWCNT

Furthermore, it should be highlighted that the desired [2+2+2] cycloaddition reaction can be produced either on a parallel (**Figure 35**, green line) or slanted (**Figure 35**, red line) C-C bond, with respect to the axis of the zigzag SWCNT. Despite the fact that computational studies in the literature conclude that the parallel C-C bond is more reactive than the slanted one,^{114,115} the reactivity of both was analysed in this work.

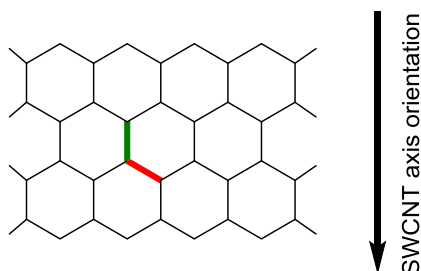
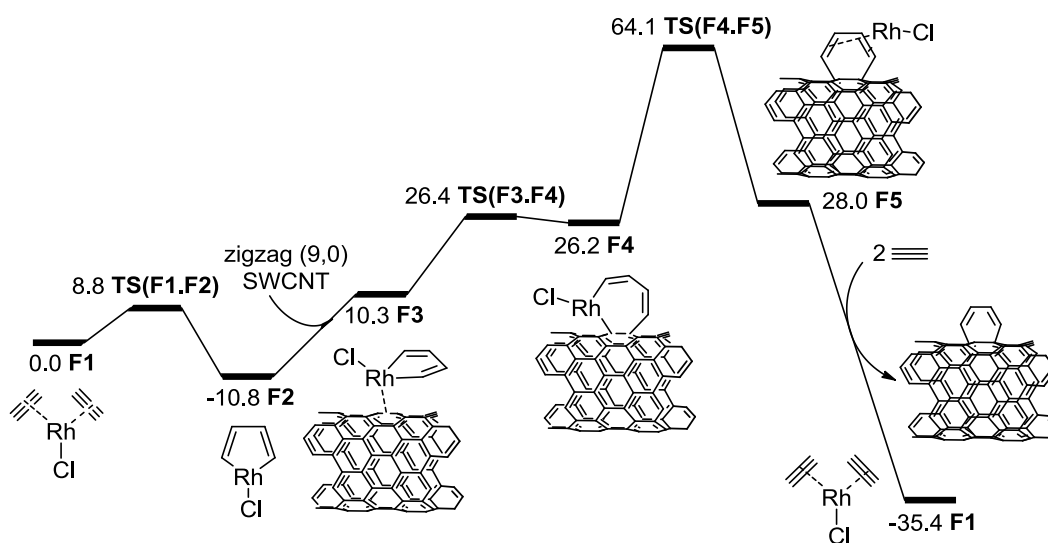


Figure 35. Representation of parallel (green) and slanted (red) C-C bonds for a zigzag SWCNT

Full analysis of all the possible pathways let us conclude that the lowest-in-energy route involving [RhCl] catalytic species follows the intermediates depicted in **Scheme 94**. The mechanistic proposal begins with bisacetylene complex **F1**, which bears two coordinated acetylenes on the Rh(I) metal centre and can be formed from [RhCl(ethylene)₂]₂ catalyst through the precatalyst scenario described in Chapter 3 of this thesis (**Scheme 55**, page 68).

Complex **F1** is able to evolve through an oxidative addition step to **F2** by surpassing an initial energy barrier of 8.8 kcal·mol⁻¹ through **TS(F1.F2)** transition state in an exothermic process of 10.8 kcal·mol⁻¹. At this point, the zigzag SWCNT can coordinate

to the rhodium centre (**F3**) and later overpass **TS(F3.F4)** to perform an insertion step on a C-C nanotube bond into a Rh-C(sp^2) bond to afford **F4**. The most favourable insertion was observed to take place on a C-C bond parallel to the SWCNT axis and required 37.2 kcal·mol⁻¹. Finally, **F4** could suffer a ring-closure through a reductive elimination process by overpassing **TS(F4.F5)**, which is located at 74.9 kcal·mol⁻¹ with respect to **F2**. After that, **F5** can release the desired cycloadduct of the SWCNT by coordinating two new acetylene units and, thus, start the catalytic cycle again. As a whole, the studied process is exothermic in 35.4 kcal·mol⁻¹ with a rate-determining step located on the reductive elimination step with an associated energy barrier of 74.9 kcal·mol⁻¹.



Scheme 94. Gibbs energy profile (kcal·mol⁻¹) at 298.15K for the lowest-in-energy route of the rhodium(I)-catalysed [2+2+2] cycloaddition reaction of two acetylenes with a zigzag (9,0) SWCNT considering [Rh-Cl] as the catalytic species.

However, the depicted energy barriers are clearly excessive to let us think that the reaction will experimentally occur. Therefore, we repeated the same analysis for other catalytic species in order to find more plausible rate-determining energy barriers. These tests are summarized in **Table 14** and entailed the change of the number and nature of the ligands coordinated to the metal centre.

Table 14. Rate-determining energy barriers for the theoretical optimization of the [2+2+2] cycloaddition of two acetylenes with a zigzag (9,0) SWCNT

Entry	Catalytic species	Temperature (K)	Rate-determining energy barrier (kcal·mol ⁻¹)
1	[RhCl]	298.15	74.9
2	[RhCl]	373.15	79.2
3	[RhCl(PPh ₃)]	298.15	> 200
4	[RhCl(PPh ₃) ₂]	298.15	> 200
5	[Rh(BIPHEP)] ⁺	298.15	51.2
6	[RhCl(CO)]	298.15	61.1
7	[RhCl(CO) ₂]	298.15	74.4
8	[Rh(CO)] ⁺	298.15	38.3
9	[Rh(CO) ₂] ⁺	298.15	32.0
10	[Rh(CO) ₂] ⁺	373.15	35.6
11	[Rh(CO) ₃] ⁺	298.15	48.3

Taking as a reference the energetic values of the mechanism depicted in **Scheme 94** (Entry 1), we computed the same intermediates at 373.15K (Entry 2), revealing that the rate-determining energy barrier increases in about 4 kcal·mol⁻¹ to 79.2 kcal·mol⁻¹.

Since the use of chloride as a single ligand did not afford sufficiently low energy barriers, we tried introducing one (Entry 3) and two (Entry 4) triphenylphosphine ligands, as these ligands have displayed good behaviour in [2+2+2] cycloaddition reactions from the experimental point of view in our group.⁵¹ It could be appreciated that the resulting geometries were sterically hindered and exhibited extremely high energy barriers.

Alternatively, we considered the use of a cationic rhodium metallic centre in combination with BINAP-type ligands. In order to reduce the computational cost, we calculated the pathway by using BIPHEP as a ligand (Entry 5). Even though the energy barriers were significantly lower, the process was still very unlikely to take place, since the rate-determining energy barrier required 51.2 kcal·mol⁻¹.

Taking into account that phosphine-based ligands did not improve the mechanistic profiles, we turned our attention to carbonyl ligands, as they showed good reactivity in when allene-alkene-alkyne substrates were employed (Chapter 4 of this thesis). Despite no significant improvement was reported when the chloride ligand was accompanied with one (Entry 6) or two (Entry 7) carbonyl ligands, the coordination of the metal centre to only one (Entry 8), two (entries 9 and 10) or three (Entry 11) carbonyl groups gave more acceptable energetic values. We were pleased to find that

the optimal pathway exhibited a rate determining barrier of 32.0 kcal·mol⁻¹ at 298.15K (Entry 9) and of 35.6 kcal·mol⁻¹ at 373.15K (Entry 10) when [Rh(CO)₂]⁺ catalytic species was employed.

Focusing on the pathway calculated at 298.15K (**Scheme 95**, blue line), the mechanism found begins with the generation of intermediate **G1**, which combines the coordination of two acetylene units and two carbonyl ligands on a rhodium(I) centre that displays a square-planar (D_{4h}) metal geometry. The catalytic species proposed ([Rh(CO)₂]⁺) could be experimentally generated from [RhCl(CO)₂]₂ catalyst, which is commercially available, in the presence of a chloride abstractor like AgBF₄.⁵³

From bisacetylene complex **G1**, the oxidative addition energy barrier through **TS(G1.G2)** (**Figure 36**) was computed to be 25.2 kcal·mol⁻¹. After exploring alternative oxidative addition combinations, we found that the most favourable one takes place between two acetylene units instead of between an acetylene unit and the SWCNT.

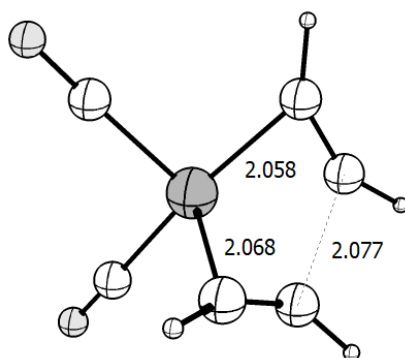


Figure 36. Optimized structure (B3LYP-D3/6-31G**-LANL2DZ) for **TS(G1.G2)** bearing [Rh(CO)₂]⁺ catalytic species. Most relevant distances are given in Å

G2 intermediate is able to coordinate to the π orbitals of the SWCNT and thus lead to intermediate **G3** through an endothermic process (ΔG = 10.4 kcal·mol⁻¹). Once the zigzag (9,0) SWCNT is introduced, the insertion step can take place through **TS(G3.G4)** (**Figure 37**) with 32.0 kcal·mol⁻¹ energy barrier. The lowest energy barrier was associated to the insertion process in which the C-C bonds of SWCNT that participates is oriented parallel to the axis of the nanotube, instead of a slanted orientation, since the energy barrier for such alternative insertion is 41.3 kcal·mol⁻¹. The regioselectivity observed is in accordance with the previous works in the group,^{114,115} in which higher reactivity was appreciated on the parallel orientations of the C-C bonds of SWCNT due to the lower structural distortion required for the process. Finally, the

reductive elimination step to afford the desired cycloadduct (**TS(G4.G5)**, **Figure 38**) was found to display a 27.2 kcal·mol⁻¹ barrier.

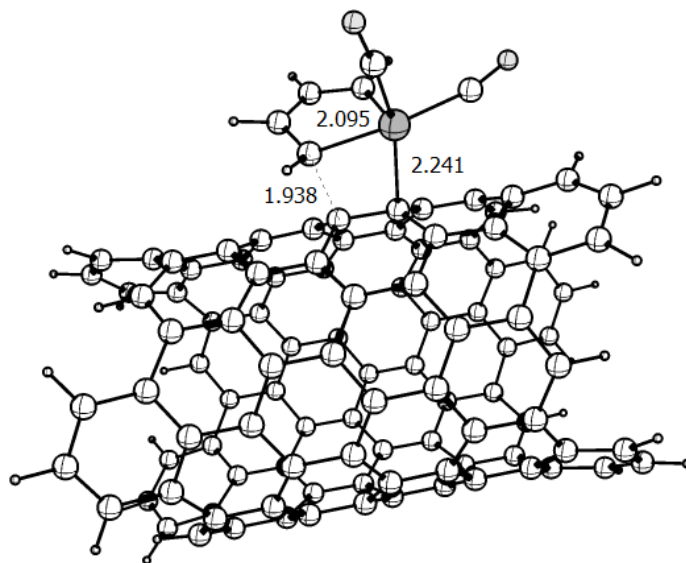


Figure 37. Optimized structure (B3LYP-D3/6-31G**-LANL2DZ) for **TS(G3.G4)** bearing [Rh(CO)₂]⁺ catalytic species. Most relevant distances are given in Å

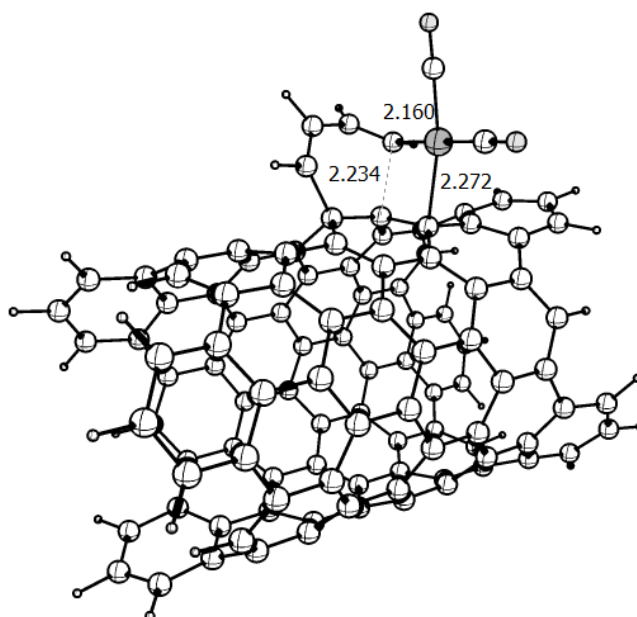


Figure 38. Optimized structure (B3LYP-D3/6-31G**-LANL2DZ) for **TS(G4.G5)** bearing [Rh(CO)₂]⁺ catalytic species. Most relevant distances are given in Å

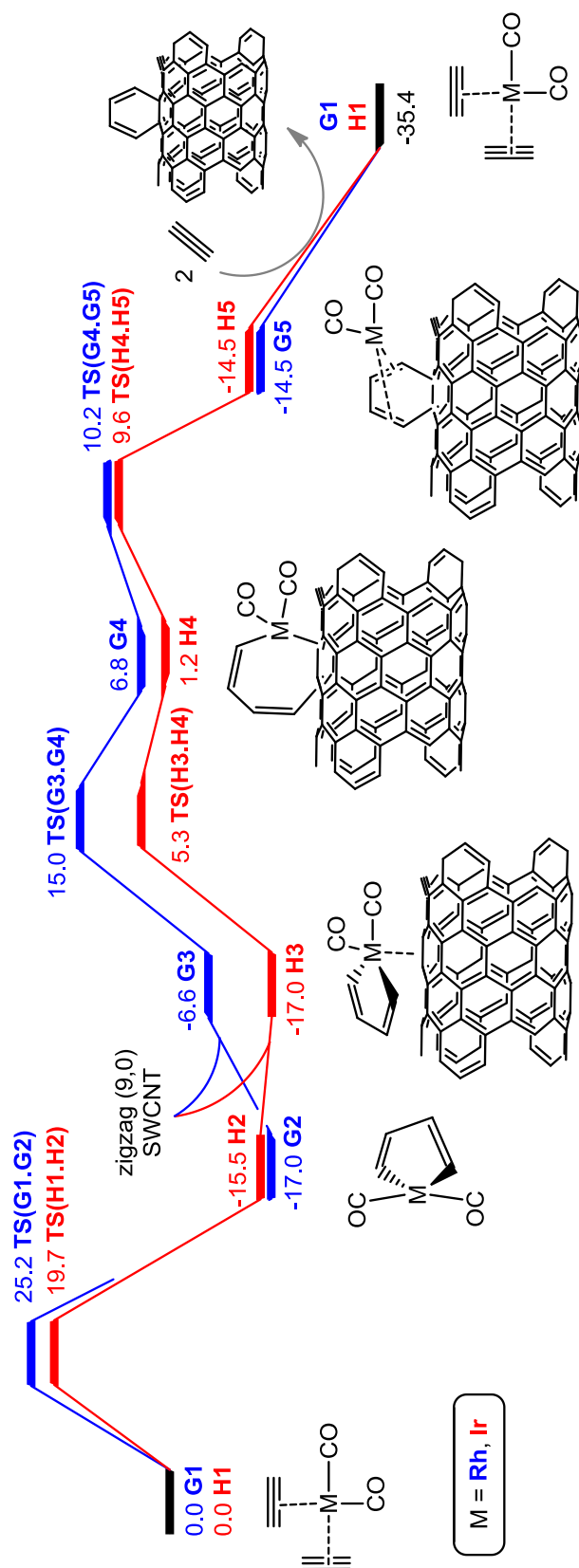
As a whole, the process was considered to be likely to take place, as it exhibits a rate-determining energy barrier of 32.0 kcal·mol⁻¹, which is given by the insertion step. Moreover, the analysis carried out reveals that the process is exothermic in 35.4 kcal·mol⁻¹.

In front of the successful results obtained, we decided to evaluate the feasibility of the catalytic process when different transition metal catalysts are used. Iridium and cobalt were chosen for the study for being isoelectronic to rhodium and probably involve similar catalytic intermediates.

Starting with the case of iridium, the analysis entailed the study of $[\text{Ir}(\text{CO})]^+$, $[\text{Ir}(\text{CO})_2]^+$ and $[\text{Ir}(\text{CO})_3]^+$ species, revealing that, similarly to the rhodium-catalysed mechanism, the most probable species participating is $[\text{Ir}(\text{CO})_2]^+$. Taking as a reference the work done by Wu, Jiao and co-workers on $[\text{IrCp}]$ -catalysed [2+2+2] cycloaddition reactions of three acetylenes,¹¹⁷ singlet and triplet electronic states were considered, though singlet intermediates were observed to be the most stable ones.

The proposed mechanistic pathway for $[\text{Ir}(\text{CO})_2]^+$ (**Scheme 95**, red line) essentially consists in the same geometries located for $[\text{Rh}(\text{CO})_2]^+$, though several significant energetic changes can be appreciated. The energy barriers for the oxidative addition, insertion and reductive elimination steps were computed to be 19.7 kcal·mol⁻¹, 22.3 kcal·mol⁻¹ and 26.6 kcal·mol⁻¹, respectively.

Globally, the whole process is exothermic in 35.4 kcal·mol⁻¹ and requires 26.6 kcal·mol⁻¹ to overpass the rate-determining energy barrier, which is associated to the reductive elimination step. Remarkably, it can be extracted that the use of iridium instead of rhodium as the metallic centre makes the process relatively more efficient, as the barrier of the rate-determining step is reduced in 5.4 kcal·mol⁻¹.



Scheme 95. Gibbs energy profiles (kcal·mol⁻¹) at 298.15K for the most favourable routes of the rhodium(I)- (blue) and iridium(I)- (red) catalysed [2+2+2] cycloaddition reaction of two acetylenes with a zigzag (9,0) SWCNT

Aside from rhodium and iridium metallic centres, the use of cobalt catalytic species was also analysed. Similarly to the other metals, $[\text{Co}(\text{CO})]^+$, $[\text{Co}(\text{CO})_2]^+$ and $[\text{Co}(\text{CO})_3]^+$ catalytic species were considered to evaluate all the possible mechanistic routes. In addition to that, singlet and triplet electronic states were evaluated, as several works on this topic have suggested the rapid exchange between intermediates of both states.^{12,13}

As a result of this study, we found that the most stable intermediates that could undergo the [2+2+2] cycloaddition are those bearing a triplet electronic state (green profile in **Scheme 96**. Triplet ground states indicated with an asterisk (*)). The process will preferably start from bisacetylene complex **I1***, which bears a triplet state and is $16.6 \text{ kcal}\cdot\text{mol}^{-1}$ more stable than **I1** (in a singlet state). The performance of the oxidative addition step can take place by surpassing an energy barrier of $26.0 \text{ kcal}\cdot\text{mol}^{-1}$ in the triplet state (**Figure 39**) to afford cobaltacyclopentadiene **I2*** which, similarly to the previous works found in the literature,^{12,13} is more stable in the triplet state than in its singlet state by $17.9 \text{ kcal}\cdot\text{mol}^{-1}$.

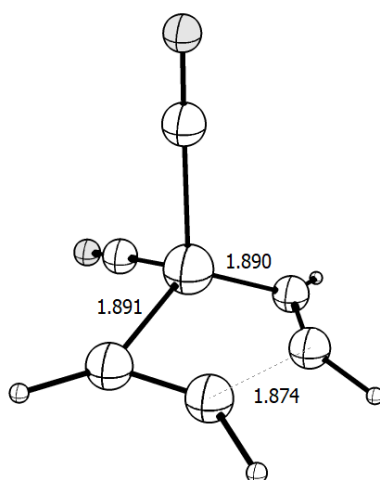


Figure 39. Optimized structure (B3LYP-D3/6-31G**-LANL2DZ) for **TS(I1*.I2*)** bearing $[\text{Co}(\text{CO})_2]^+$ catalytic species. Most relevant distances are given in Å

The cobaltacyclopentadiene intermediate **I2*** is able to coordinate to the SWCNT through an endergonic process of $7.2 \text{ kcal}\cdot\text{mol}^{-1}$ to later undergo the insertion process on a parallel C-C bond of the nanotube, which requires $27.5 \text{ kcal}\cdot\text{mol}^{-1}$. Remarkably, the intermediate **I4** reached at this point displays a singlet electronic state and can undergo the reductive elimination step by surpassing **TS(I4.I5*)** that requires $29.4 \text{ kcal}\cdot\text{mol}^{-1}$ and returns the system to the triplet state (**I5***).

Contrary to the other catalytic species, $[\text{Co}(\text{CO})_2]^+$ was observed to provoke the insertion of a carbonyl ligand to the cobaltacyclopentadiene cycle through **TS(I3*.J4*)** by only requiring $10.8 \text{ kcal}\cdot\text{mol}^{-1}$. Such a process is more favourable to drive the system to an alternative pathway that resembles the Pauson-Khand mechanism and yields a cobaltacyclohexadienone intermediate (**J4***, **Figure 40**). After that, the system can suffer a ring closure ($\Delta G^\ddagger = 11.5 \text{ kcal}\cdot\text{mol}^{-1}$) to afford **J5** at the singlet state, which bears cyclopenta-2,4-dienone and the SWCNT coordinated to the cobalt centre.

We concluded thereby that $[\text{Co}(\text{CO})_2]^+$ will yield the Pauson-Khand product instead of the [2+2+2] cycloadduct as the energy barriers for the insertion and reductive elimination steps are significantly lower for the first pathway.

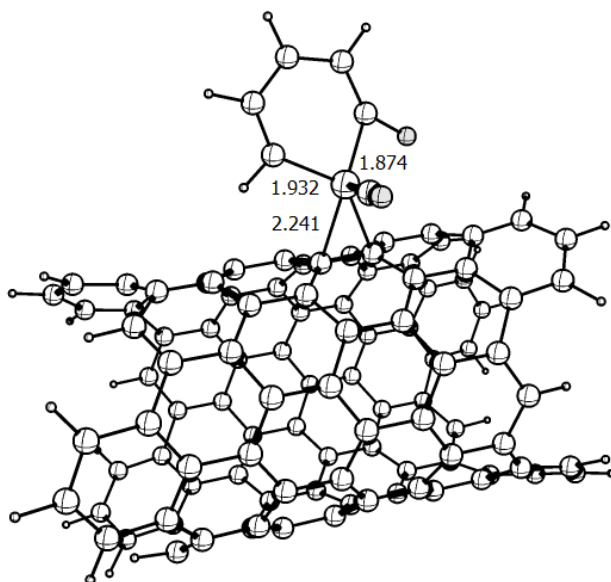
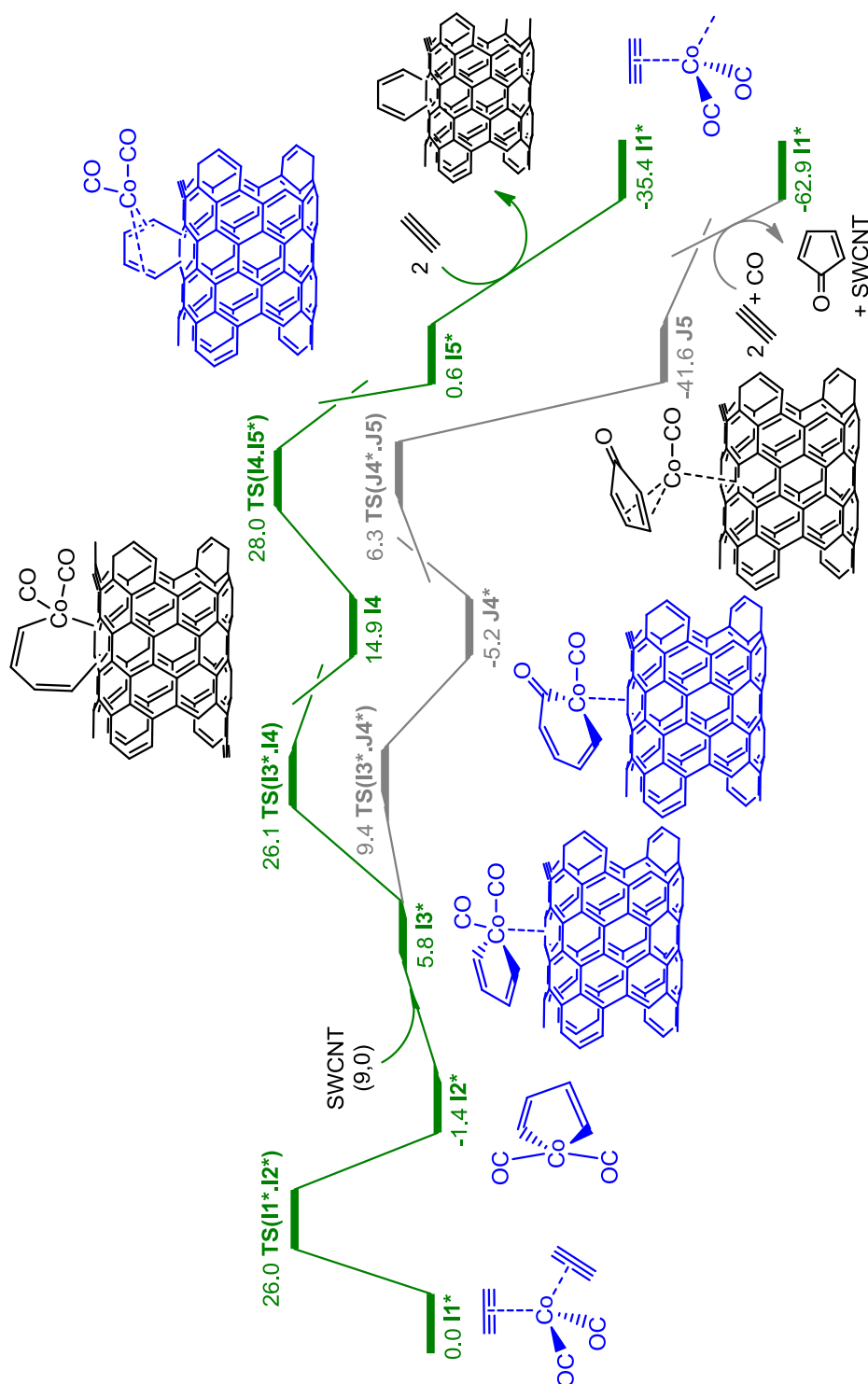


Figure 40. Optimized structure (B3LYP-D3/6-31G**-LANL2DZ) for **J4*** bearing $[\text{Co}(\text{CO})_2]^+$ catalytic species. Most relevant distances are given in Å

To sum up, our calculations indicate that the desired [2+2+2] cycloaddition reaction is possible under rhodium or iridium catalysis, since the two mechanistic pathways found exhibit reasonable rate-determining energy barriers, but tends to be shifted by a secondary process when cobalt is involved. Moreover, the higher reactivity of parallel C-C bonds in front of the slanted ones is in accordance with the regioselectivity found in other computational studies.^{114,115}



Scheme 96. Gibbs energy profiles (kcal·mol⁻¹) at 298.15K for the most favourable routes involving [Co(CO)₂]⁺ catalytic species. Green line corresponds to the profile for the studied [2+2+2] cycloaddition reaction of two acetylenes with a zigzag (9,0) SWCNT. Grey line corresponds to a Pauson-Khand-like by-process. Singlet electronic states are coloured in black. Triplet states are coloured in blue and marked with a * sign in the labels

5.3. Scope study

At this point, our aim was to determine which is the influence of the SWCNT nature on the efficiency of the reaction. To attain such goal, we located the same catalytic intermediates depicted in **Scheme 95** by simulating an armchair (6,6) SWCNT (diameter ≈ 8.6 Å) and a zigzag (12,0) SWCNT (diameter ≈ 9.8 Å) in order to compare the energy profiles with those obtained for zigzag (9,0) SWCNT (diameter ≈ 7.6 Å).

Contrary to zigzag SWCNTs, armchair nanotube models do not need to be segmented by following any remarkable pattern, since Clar's theory is fulfilled for all the possible structures.

With regards to the analysis to be performed, it should be noted that, while the reaction can be produced on parallel or slanted C-C bonds on zigzag SWCNTs, the reactivity can be different as well when armchair SWCNTs are employed, because slanted and perpendicular C-C bonds to the axis of the nanotube are present (**Figure 41**). Even though previous works indicate that the most reactive C-C bond is the slanted one,^{114,115} both pathways will be taken into account in our work.

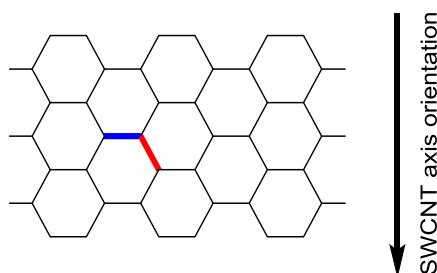


Figure 41. Representation of slanted (red) and perpendicular (blue) C-C bonds for an armchair SWCNT

After evaluating all the possible routes, we were able to compare the energy barriers for the insertion and reductive elimination steps by computing a different nanotube morphology and size when $[\text{Rh}(\text{CO})_2]^+$ (**Figure 42**) and $[\text{Ir}(\text{CO})_2]^+$ (**Figure 43**) catalytic species are employed. Noteworthy, the oxidative addition barrier remains equal in all cases ($25.2 \text{ kcal}\cdot\text{mol}^{-1}$ and $19.7 \text{ kcal}\cdot\text{mol}^{-1}$ for $[\text{Rh}(\text{CO})_2]^+$ and $[\text{Ir}(\text{CO})_2]^+$, respectively) because the SWCNT does not participate in such step.

With regards to the insertion and reductive elimination steps, a significant increase is observed when an armchair morphology is used and, more dramatically, when the radius of the nanotube becomes higher.

In the case of armchair (6,6) SWCNT, we observed that the cycloaddition preferably took place on the slanted position instead of the perpendicular one, which is in accordance with the previous works in the group.¹¹⁵

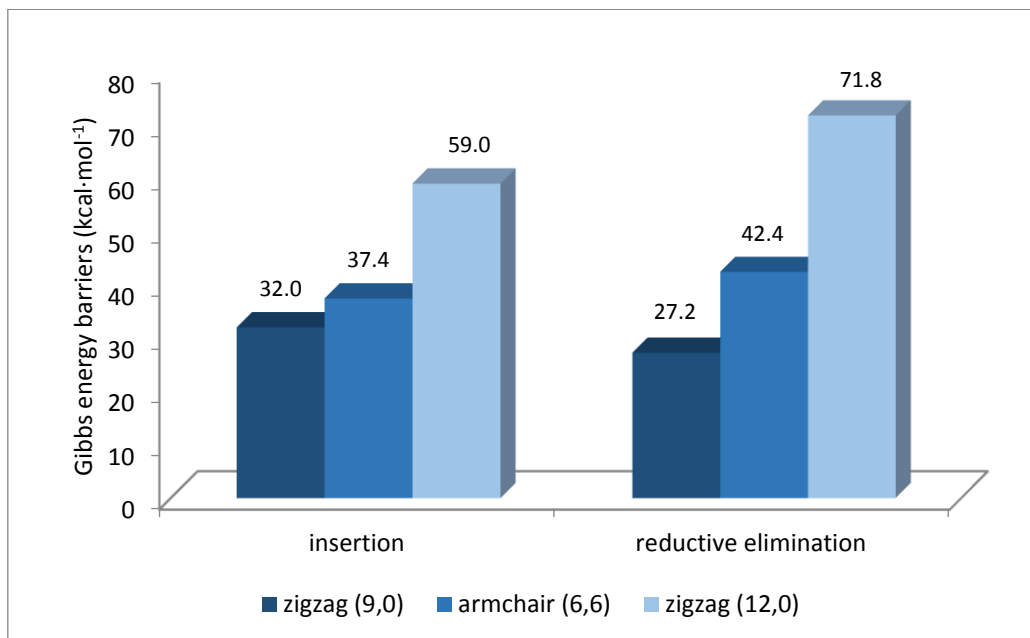


Figure 42. Gibbs energy barriers of the insertion and reductive elimination steps of the [Rh(CO)₂]⁺-catalysed [2+2+2] cycloaddition reaction at different SWCNT size and morphology

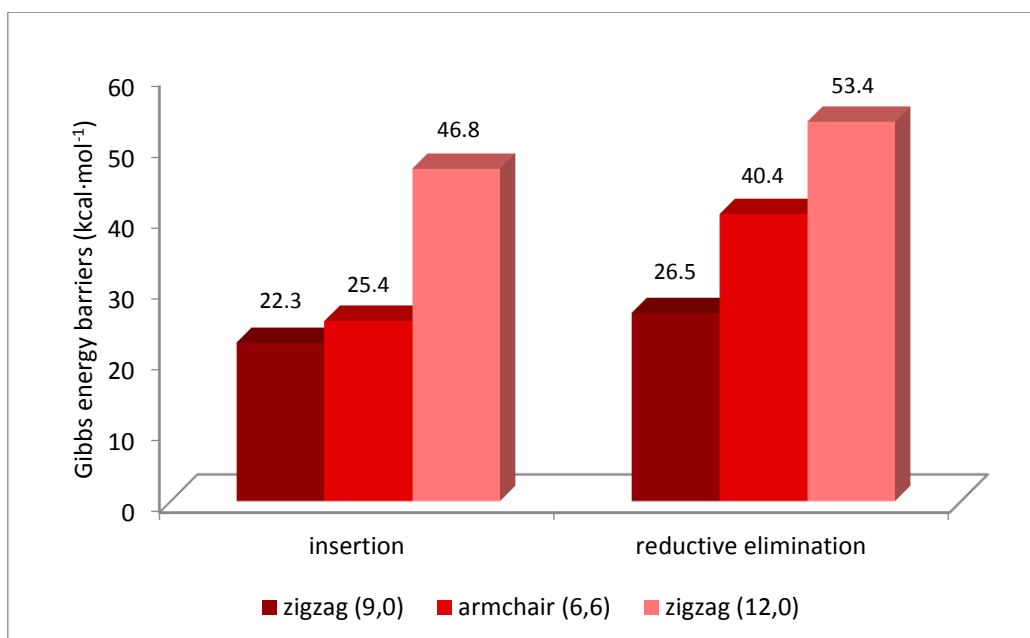


Figure 43. Gibbs energy barriers of the insertion and reductive elimination steps of the [Ir(CO)₂]⁺-catalysed [2+2+2] cycloaddition reaction at different SWCNT size and morphology

In order to justify the energetic changes observed in the insertion step, we make use of the activation strain model (ASM) (**Table 15**).⁶⁹ The energy barriers are analysed in terms of strain and interaction energies between the fragments that participate in the formation or cleavage of chemical bonds.

Table 15. Comparison of SWCNT strain ($\Delta E_{SWCNT}^{\ddagger strain}$), rhodacyclopentadiene intermediate strain ($\Delta E_{interm.}^{\ddagger strain}$), total strain ($\Delta E_{strain}^{\ddagger}$), interaction ($\Delta E_{int}^{\ddagger}$) and total ($\Delta E_{total}^{\ddagger}$) electronic energies (kcal·mol⁻¹) at the insertion step bearing [Rh(CO)₂]⁺ species

SWCNT	$\Delta E_{SWCNT}^{\ddagger strain}$	$\Delta E_{interm.}^{\ddagger strain}$	$\Delta E_{strain}^{\ddagger}$	$\Delta E_{int}^{\ddagger}$	$\Delta E_{total}^{\ddagger}$
zigzag (9,0)	16.7	17.4	34.1	-13.2	20.9
armchair (6,6)	11.5	16.9	28.4	-7.7	20.7
zigzag (12,0)	12.0	22.2	34.2	-3.8	30.4

The analysis indicates that the abrupt increase of the total electronic energy (from 20.9 or 20.7 kcal·mol⁻¹ for zigzag (9,0) and armchair (6,6), respectively, to 30.4 kcal·mol⁻¹ for zigzag (12,0)) is mainly due to the decrease of interaction energy, which passes from -13.2 kcal·mol⁻¹ for zigzag (9,0) to -3.8 kcal·mol⁻¹ for zigzag (12,0).

On the basis of the previous works done in the group,¹¹⁵ the higher rate-determining energy barrier observed in the scope are due to the fact that the increase of the diameter of the SWCNT provokes a smaller curvature which forces, from a geometrical perspective, that the change of hybridization of two SWCNT carbon atoms from ca. sp^2 to sp^3 becomes less favourable. The higher strain generated leads to a higher energy barrier (**Figure 44**). Therefore, the change from zigzag (9,0) to armchair (6,6) and to zigzag (12,0) SWCNTs should progressively entail an increase of the strain in the SWCNT. However, the strain values indicated in **Table 15** ($\Delta E_{SWCNT}^{\ddagger strain}$) do not follow the expected order.

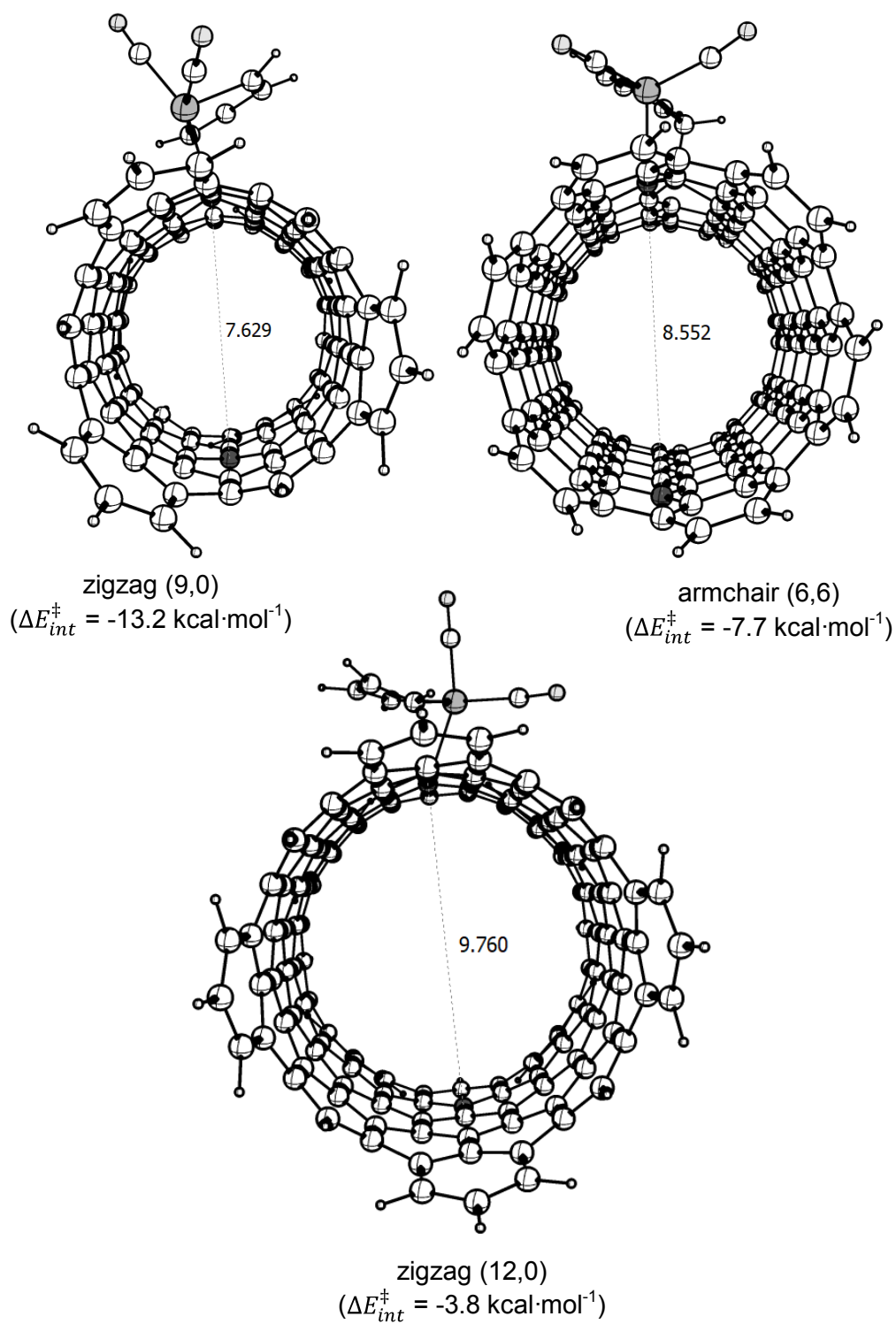


Figure 44. Comparison of the different SWCNT curvature for the corresponding **TS(G3.G4)** geometries bearing $[\text{Rh}(\text{CO})_2]^+$ catalytic species

Looking at the bond distances between the $C(sp^2)$ - $C(sp^2)$ (D1) and Rh - $C(sp^2)$ (D2) being formed in the insertion step (**Table 16**), it can be stated that the **TS(G3.G4)** geometries for the three SWCNTs involved have not equally progressed along the reaction coordinate.

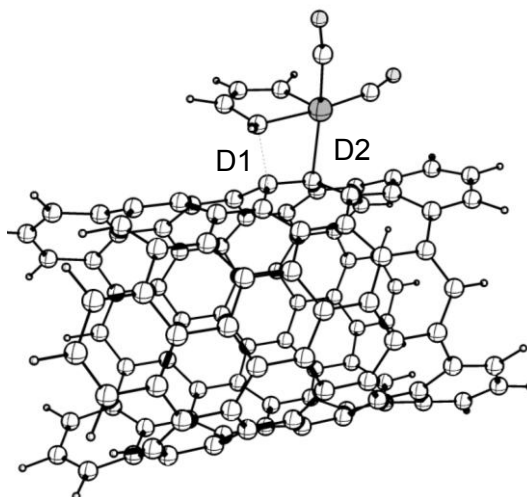
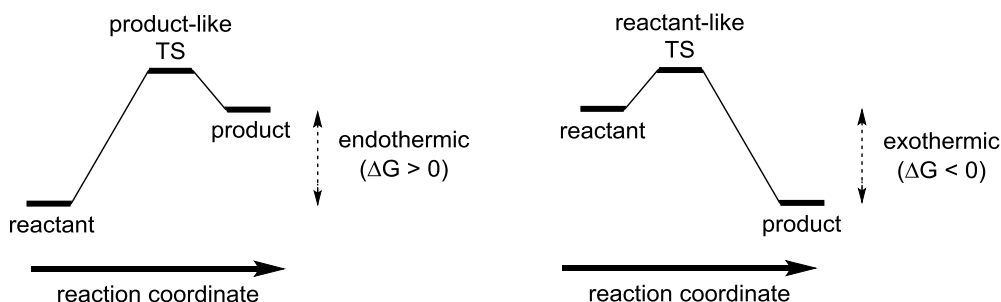


Table 16. Relation between the Gibbs energy (ΔG , in $\text{kcal}\cdot\text{mol}^{-1}$) of the insertion step and D1 and D2 bond distances (in Å) in **TS(G3.G4)** geometries

SWCNT	ΔG_r	D1	D2
zigzag (9,0)	13.3	1.939	2.241
armchair (6,6)	13.1	1.946	2.362
zigzag (12,0)	9.7	1.960	2.542

By applying Hammond's postulate (**Scheme 97**),¹¹⁸ it can be said that **TS(G3.G4)** involving a zigzag (12,0) SWCNT is the most reactant-like geometry, as it is the least endothermic insertion process ($9.7 \text{ kcal}\cdot\text{mol}^{-1}$) and the bond distances presented in **Table 16** are relatively high and similar to those displayed in **G3** geometry. Contrary, in the case of zigzag (9,0) the geometry is more product-like because it is the most endothermic one ($13.3 \text{ kcal}\cdot\text{mol}^{-1}$) and the distances are more similar to the ones present in the corresponding **G4** geometry.



Scheme 97. Representation of Hammond's postulate

The similarity between the total electronic energy barriers of the zigzag (9,0) and armchair (6,6) cases (20.9 and 20.7 kcal·mol⁻¹, respectively) results from the increase of interaction energy of the armchair (6,6) case, which destabilises the system, and the decrease of the strain energy of the SWCNT with respect to the zigzag (9,0) system. The strain energy of the SWCNT expected for the system bearing armchair (6,6) SWCNT should be higher than that of zigzag (9,0) but, as pointed out above, this strain energy value is justified by considering that the corresponding **TS(G3.G4)** geometry has not progressed as much as the zigzag (9,0) one along the reaction coordinate.

A similar approach can be applied to analyse the case in which zigzag (12,0) SWCNT is involved. Even though the total electronic energy barrier (30.4 kcal·mol⁻¹) is significantly higher than the one displayed by zigzag (9,0) case (20.9 kcal·mol⁻¹), the strain energy of the zigzag (12,0) should be much higher if the two **TS(G3.G4)** geometries were compared at a more similar reaction coordinate point. This is not the case because the geometry of the zigzag (12,0) case is more reactant-like than the one with zigzag (9,0), which is more product-like.

From a global point of view, the two catalytic species demonstrated a poorer behaviour to perform the desired [2+2+2] cycloaddition reaction, since energy barriers associated to both armchair (6,6) SWCNTs and zigzag (12,0) are significantly higher than the ones depicted in **Scheme 95** when a zigzag (9,0) SWCNT is computed (**Figure 45**). Furthermore, the [2+2+2] cycloaddition reactions on a zigzag (9,0) or an armchair (6,6) SWCNTs were observed to be exothermic in 35.4 kcal·mol⁻¹ and 34.7 kcal·mol⁻¹, respectively. Contrary to that, when zigzag (12,0) SWCNT is employed, the reaction becomes endothermic in 8.4 kcal·mol⁻¹.

Aside from that, it should be noted that the rate-determining energy barrier when [Rh(CO)₂]⁺ is used turns to be the reductive elimination (instead of the insertion) when armchair (6,6) and zigzag (12,0) SWCNTs are employed.

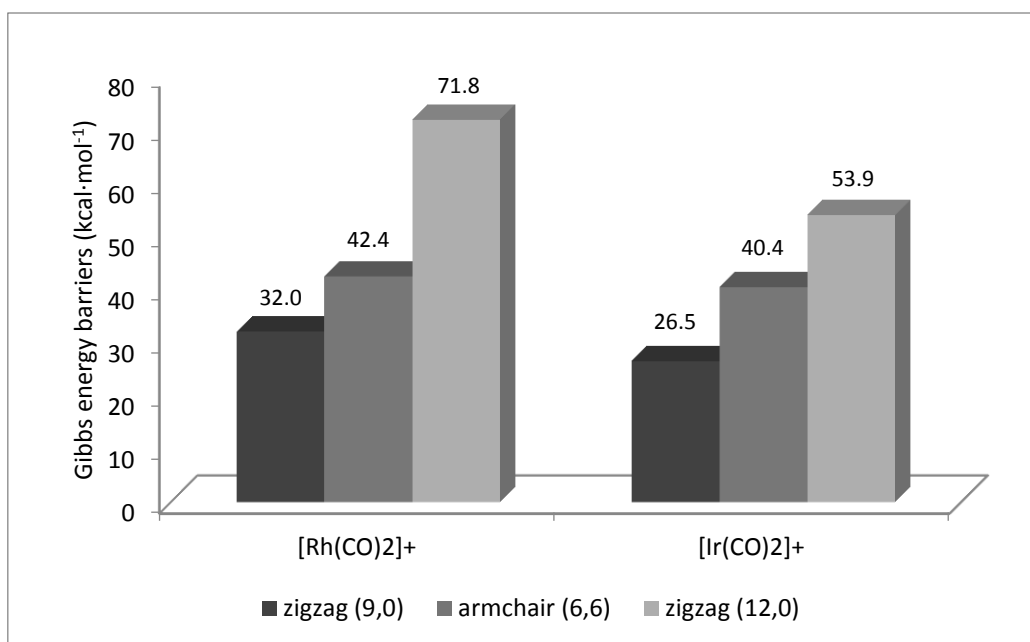


Figure 45. Comparison of the rate-determining energy barriers of the [Rh(CO)₂]⁺- and [Ir(CO)₂]⁺-catalysed [2+2+2] cycloaddition reaction at different SWCNT size and morphology

In conclusion, the feasibility of the sidewall [2+2+2] cycloaddition reaction of two acetylene units to SWCNTs has been confirmed. The results obtained show that the process is likely to occur in a regioselectively fashion on a C-C bond of a zigzag (9,0) SWCNT parallel to the axis of the tube. The cycloaddition was observed to be possible in the presence of [Rh(CO)₂]⁺ and [Ir(CO)₂]⁺ catalytic species, provided that relatively small-diameter (< 8 Å) zigzag SWCNTs are employed.

Chapter 6. General conclusions

In this thesis, the versatility of the rhodium-catalysed [2+2+2] cycloaddition reactions involving C(sp²) unsaturations has been analysed from both the theoretical and the experimental points of view. From this study, the following conclusions can be extracted:

1. The mechanism of the rhodium(I)-catalysed [2+2+2] cycloaddition reaction involving two alkynes and a C(sp²) unsaturation was computationally analysed by considering all the possible interactions among the three unsaturations. After comparing the mechanisms for each C(sp²) unsaturation involved (alkene, aldehyde, imine, allene, carbodiimide, carbon dioxide and carbon disulfide), a clear influence of heteroatoms was appreciated on the regioselectivity displayed on the insertion step. From a global perspective, the most efficient catalytic species to undergo the cyclisation proved to be [RhCl], which derives from [RhCl(ethylene)₂]₂ complex. [Rh(BIPHEP)]⁺ catalyst, which has been extensively reported to experimentally afford the desired products, was observed to behave in a similar efficiency and can represent a good alternative to [RhCl]-based catalysts. Contrary, [RhCl(PPh₃)₃] catalyst demonstrated a more limited capacity to undergo the [2+2+2] cycloaddition compared to the other two catalytic species.
2. The reactivity of linear allene-alkene-alkyne substrates bearing an *N*-tosyl tether was evaluated in the rhodium-catalysed [2+2+2] cycloaddition reaction both experimentally and theoretically. Three catalytic systems were employed: neutral [RhCl(PPh₃)₃] complex, cationic [Rh(cod)₂]BF₄ combined with a biphosphine ligand, and dimeric [RhCl(CO)₂]₂ complex. For all catalytic systems, the cycloaddition was promoted regioselectively involving the internal double bonds of the allene, allowing for the preparation of scaffolds featuring exocyclic dienes. Nevertheless, the diastereoselectivity of the process seems to be strongly related to the catalyst. With regards to the mechanism, a remarkable feature is that the oxidative addition always takes place between the alkyne and the alkene and that the diastereoselectivity is defined later during the allene insertion step. The allene inserts with the inner double bond preferentially as the Rh-C(sp²) bond. The variable and low diastereoselectivity of the process can be ascribed to the small differences in the rate-determining energy barriers.
3. The transition-metal catalysed [2+2+2] cycloaddition reaction of two alkynes and a single-walled carbon nanotube (SWCNT) was computationally evaluated

and found to be theoretically possible under the presence of $[\text{Rh}(\text{CO})_2]^+$ and $[\text{Ir}(\text{CO})_2]^+$ catalytically-active species. Zigzag SWCNTs are more likely to undergo the process than armchair SWCNTs and, in addition to that, smaller nanotube diameters ($< 8 \text{ \AA}$) are preferred in front of larger, essentially due to the lower strain energy required to perform the reductive elimination steps. Furthermore, the process is theoretically regioselective on carbon-carbon bonds of the SWCNT that are oriented parallel to the axis of the zigzag SWCNTs or slanted to the axis in case armchair SWCNTs are employed. Last, the use of $[\text{Co}(\text{CO})_2]^+$ catalytically-active species was found to preferably promote a Pauson-Khand-like process instead of the desired $[2+2+2]$ cycloaddition reaction.

Chapter 7. Methods

7.1. General materials and instrumentation

7.1.1. General conditions

MATERIALS

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. All reactions requiring anhydrous conditions were conducted in oven dried glassware under a dry nitrogen atmosphere. Dichloromethane and tetrahydrofuran were degassed and anhydried under nitrogen by passing through solvent purification columns (MBraun, SPS-800). Toluene was degassed by performing several freezing-melting cycles under vacuum/N₂ atmosphere. Solvents were removed under reduced pressure with a rotary evaporator. When necessary, reaction mixtures were chromatographed on silica gel (230-400 mesh) using a gradient solvent system as the eluent.

SPECTROSCOPY

- **NMR spectroscopy:** ¹H, ¹³C and ³¹P{¹H} NMR spectra were recorded using Bruker Ultrashield Avance III 400 [¹H (400 MHz), Bruker Avance III HD Nanobay 400 [¹H (400 MHz) and ¹³C (100 MHz)] and ¹³C (100 MHz)] or Bruker Ultrashield DPX300 [¹H (300 MHz) and ¹³C (75 MHz)] NMR spectrometers of the *Serveis Tècnics de Recerca* of the Universitat de Girona. Chemical shifts (δ) for ¹H and ¹³C NMR were referenced to internal solvent resonances and reported relative to SiMe₄.
- **Infrared spectroscopy:** IR spectra were recorded on a Bruker Alpha FT-IR spectrometer with a DTGS detector and an ATR adapter or a FT-IR spectrophotometer Mattson-Galaxy Satellite, using a MKII Golden Gate Single Reflection ATR System of the Chemistry Department of the Universitat de Girona.

SPECTROMETRY

- **Electrospray Mass Spectrometry:** ESI-MS analyses were recorded on an Esquire 6000 Ion Trap Mass Spectrometer (Bruker Daltonics) equipped with an electrospray ion source of the *Serveis Tècnics de Recerca* of the Universitat de Girona.

- **High Resolution Mass Spectrometry:** HRMS analyses were registered in a Bruker Micro Q-TOF spectrometer with a Quadrupole-Time-Of-Flight hybrid analyser of the *Serveis Tècnics de Recerca* of the Universitat de Girona.

CHROMATOGRAPHY

- **Thin Layer Chromatography:** TLCs were performed with pre-coated (0.20 mm width) chromatography plates Alugram Sil G/UV254.
- **Columns Chromatography:** flash columns were performed using silica gel SDS with a 35-70 μm mesh particle size.
- **High-Performance Liquid Chromatography:** HPLC analyses have been performed using a Chiralpak AD-H column (4.6 x 250 mm, 5 μm) on a Spectra System Thermo chromatograph (Shimadzu) equipped with a SN400 connector, a SCM1000 degasser, a P2000 pump and a UV6000LP detector with a 20 μL loop.

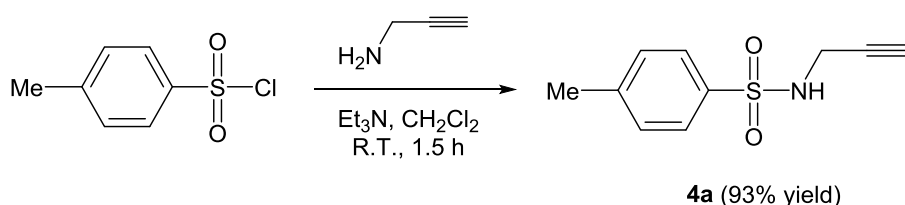
Elemental analyses were recorded on a Perkin Elmer EA2400 series II in the *Serveis Tècnics de Recerca* of the Universitat de Girona.

Microwave heating: a CEM Discover S-Class microwave synthesizer was used (250 W/250psi). Microwave heated reactions were performed in sealed vials in an Ethos SEL Lab station Milestone INC.), a multimode microwave with a dual magnetron (1600 W). During the experiments, time, temperature, and the power were measured with an “EasyControl” software package. Temperature was monitored and controlled throughout the reaction by an ATC-400FO Automatic Fibre Optic Temperature Control System. The wattage was automatically adjusted to maintain the desired temperature for the desired period of time.

7.2. Experimental procedures for the compounds synthesized in Chapter 3

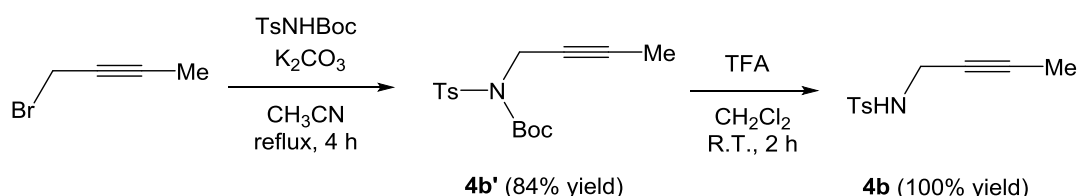
7.2.1. Preparation of substrates 1a – 1h

7.2.1.1. Synthesis of 4a



In a 50 mL two-necked round-bottom flask, *p*-toluenesulfonyl chloride (10.09 g, 52.90 mmol) and triethylamine (8 mL, 57.40 mmol) were dissolved in anhydrous dichloromethane (200 mL) at room temperature. Propargylamine (3.5 mL, 54.65 mmol) was then slowly added to the reaction mixture. The mixture was vigorously stirred for 1.5 h until completion (TLC monitoring). The reaction mixture was washed with HCl 1 M (3 x 10 mL), saturated aqueous solution of NaHCO₃ (3 x 10 mL) and distilled water (3 x 10 mL). The organic phase was dried with anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure to afford 4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide¹¹⁹ **4a** as a colourless solid (10.25 g, 93% yield). **MW**: 209.26 g/mol; **m.p.**: 76-78 °C; **¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm)**: 2.11 (t, ⁴J_{H,H} = 2.6 Hz, 1H), 2.43 (s, 3H), 3.83 (dd, ³J_{H,H} = 5.8 Hz, ⁴J_{H,H} = 2.6 Hz, 2H), 4.62 (t, ³J_{H,H} = 5.8 Hz, 1H), 7.32 (d, ³J_{H,H} = 8.4 Hz, 2H), 7.77 (d, ³J_{H,H} = 8.4 Hz, 2H); **ESI-MS (m/z)**: 210 [M+H]⁺, 232 [M+Na]⁺.

7.2.1.2. Synthesis of 4b

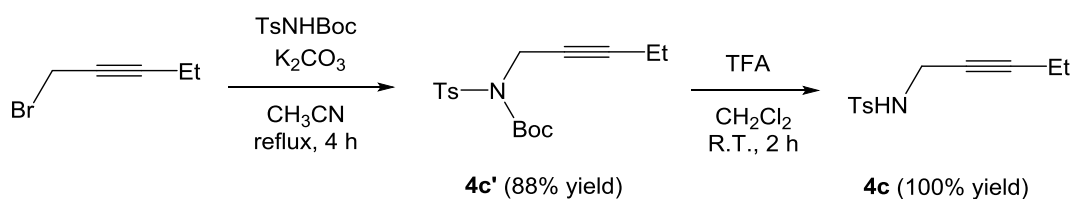


In a 250 mL two-necked round-bottom flask, a mixture of *N*-*tert*-butoxycarbonyl-(4-methylphenyl)sulfonamide (3.06 g, 11.28 mmol) and potassium carbonate (3.11 g, 22.50 mmol) in acetonitrile (100 mL) was heated to reflux. 1-bromo-2-butyne (0.80 mL, 9.14 mmol) was slowly added to the reaction mixture. The mixture was stirred for 18 h until completion (TLC monitoring). The salts were filtered off and the solvent was

removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (10:1) as the eluent to afford *N*-*tert*-butoxycarbonyl-*N*-(but-2-yn-1-yl)-(4-methylphenyl)sulfonamide **4b'** (2.47 g, 84% yield) as a colourless solid. **MW**: 323.41 g/mol; **m.p.**: 125-127°C; **IR (ATR) ν (cm⁻¹)**: 2981, 1720, 1352, 1144; **¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm)**: 1.35 (s, 9H), 1.84 (t, ⁵*J*_{H,H} = 2.4 Hz, 3H), 2.45 (s, 3H), 4.58 (q, ⁵*J*_{H,H} = 2.4 Hz, 2H), 7.31 (d, ³*J*_{H,H} = 8.4 Hz, 2H), 7.91 (d, ³*J*_{H,H} = 8.4 Hz, 2H); **¹³C NMR (75 MHz, CDCl₃, TMS) δ (ppm)**: 3.6, 21.7, 27.9, 36.3, 74.3, 80.0, 84.7, 128.2, 129.1, 136.9, 144.2, 150.4; **ESI-MS (*m/z*)**: 346.1 [M+Na]⁺, 362.1 [M+K]⁺; **E.A.** calcd (%) for C₁₆H₂₁NO₄S: C, 59.42%, H, 6.54%; N, 4.33%. Found: C, 59.48%; H, 6.40%; N, 4.47%.

In a 50 mL round-bottom flask, trifluoroacetic acid (4.5 mL, 58.77 mmol) was slowly added to a solution of derivative **4b'** (2.18 g, 6.74 mmol) in dichloromethane (70 mL). The mixture was stirred at room temperature for 2 h until completion (TLC monitoring). The reaction crude was extracted with EtOAc (60 mL), washed with saturated aqueous solution of NaHCO₃ (3 x 15 mL) and with water (3 x 15 mL). The organic phase was dried with anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure to afford *N*-(but-2-yn-1-yl)-(4-methylphenyl)sulfonamide **4b**¹²⁰ (1.50 g, 100% yield) as a brown solid. **MW**: 223.29 g/mol; **m.p.**: 73-75 °C; **¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm)**: 1.61 (t, ⁵*J*_{H,H} = 2.4 Hz, 3H), 2.43 (s, 3H), 3.76 (dq, ³*J*_{H,H} = 5.6 Hz, ⁵*J*_{H,H} = 2.4 Hz, 2H), 4.48 (t, ³*J*_{H,H} = 5.6 Hz, 1H), 7.32 (d, ³*J*_{H,H} = 8.4 Hz, 2H), 7.77 (d, ³*J*_{H,H} = 8.4 Hz, 2H); **ESI-MS (*m/z*)**: 246.0 [M+Na]⁺, 262.0 [M+K]⁺.

7.2.1.3. Synthesis of **4c**

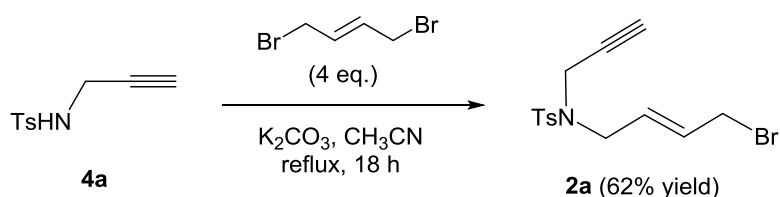


In a 100 mL two-necked round-bottom flask, a mixture of *N*-*tert*-butoxycarbonyl-(4-methylphenyl)sulfonamide (1.30 g, 9.85 mmol) and potassium carbonate (3.22 g, 23.30 mmol) in acetonitrile (60 mL) was heated to reflux. 1-bromopent-2-yne (1.0 mL, 9.78 mmol) was slowly added to the reaction mixture. The mixture was stirred for 5 h until completion (TLC monitoring). The salts were filtered off and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (10:1) as the eluent to afford *N*-*tert*-butoxycarbonyl-*N*-(pent-2-yn-1-yl)-(4-methylphenyl)sulfonamide **4c'** (2.90 g, 88% yield)

as a colourless solid. **MW**: 337.43 g/mol; m.p.: 122-124 °C; **IR (ATR) ν (cm^{-1})**: 2979, 1721, 1350, 1145; **^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm)**: 1.14 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 3H), 1.35 (s, 9H), 2.22 (qt, $^3J_{\text{H,H}} = 7.6$ Hz, $^5J_{\text{H,H}} = 2.4$ Hz, 2H), 2.44 (s, 3H), 4.60 (t, $^5J_{\text{H,H}} = 2.4$ Hz, 2H), 7.30 (d, $^3J_{\text{H,H}} = 8.6$ Hz, 2H), 7.94 (d, $^5J_{\text{H,H}} = 8.6$ Hz, 2H); **^{13}C NMR (75 MHz, CDCl_3 , TMS) δ (ppm)**: 12.4, 13.7, 21.6, 27.8, 36.3, 74.5, 84.6, 85.7, 128.3, 129.1, 136.9, 144.2, 150.3; **ESI-MS (m/z)**: 360.4 $[\text{M}+\text{Na}]^+$; **E.A.** calcd (%) for $\text{C}_{17}\text{H}_{23}\text{NO}_4\text{S}$: C, 60.51%, H, 6.78%; N, 4.15%. Found: C, 60.56%; H, 6.95%; N, 4.14%.

In a 250 mL round-bottom flask, trifluoroacetic acid (8.7 mL, 113.61 mmol) was slowly added to a solution of derivative **4c'** (2.50 g, 7.41 mmol) in dichloromethane (80 mL). The mixture was stirred at room temperature for 1.5 h until completion (TLC monitoring). The reaction crude was extracted with EtOAc (70 mL), washed with saturated aqueous solution of NaHCO_3 (3 x 20 mL) and with water (3 x 20 mL). The organic phase was dried with anhydrous Na_2SO_4 , filtered and the solvent was removed under reduced pressure to afford 4-methyl-*N*-(pent-2-yn-1-yl)benzenesulfonamide **4c** (1.75 g, 100% yield) as a colourless solid. **MW**: 237.32 g/mol; m.p.: 72-74 °C; **IR (ATR) ν (cm^{-1})**: 3273 (NH), 2918, 1322, 1154; **^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm)**: 0.95 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 3H), 1.97 (qt, $^3J_{\text{H,H}} = 7.6$ Hz, $^5J_{\text{H,H}} = 2.4$ Hz, 2H), 2.43 (s, 3H), 3.79 (dt, $^3J_{\text{H,H}} = 6.0$ Hz, $^5J_{\text{H,H}} = 2.4$ Hz, 2H), 4.52 (t, $^3J_{\text{H,H}} = 6.0$ Hz, 1H), 7.31 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.77 (d, $^5J_{\text{H,H}} = 8.4$ Hz, 2H); **^{13}C NMR (75 MHz, CDCl_3 , TMS) δ (ppm)**: 12.1, 13.4, 21.5, 31.0, 73.4, 86.8, 127.5, 129.7, 136.8, 143.6; **HRMS** calcd for $[\text{C}_{12}\text{H}_{15}\text{NO}_2\text{S} + \text{Na}]^+$: 260.0716. Found: 260.0715.

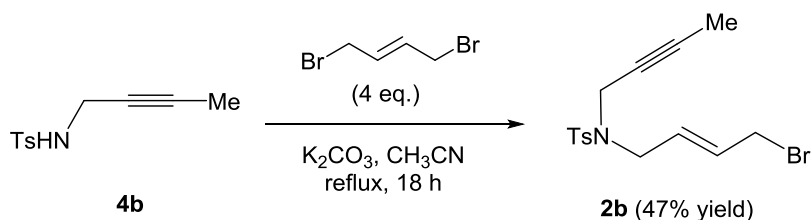
7.2.1.4. Synthesis of **2a**



In a 250 mL two-necked round-bottom flask, a mixture of *trans*-1,4-dibromo-2-butene (6.01 g, 28.11 mmol) and potassium carbonate (2.60 g, 18.80 mmol) in acetonitrile (100 mL) was heated to reflux. Benzenesulfonamide **4a** (1.50 g, 7.16 mmol) was slowly added to the reaction mixture. The mixture was stirred for 18 h until completion (TLC monitoring). The salts were filtered off and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (9:1) as the eluent to afford (*E*)-*N*-(4-bromobut-2-en-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **2a** (1.52 g, 62% yield) as a colourless

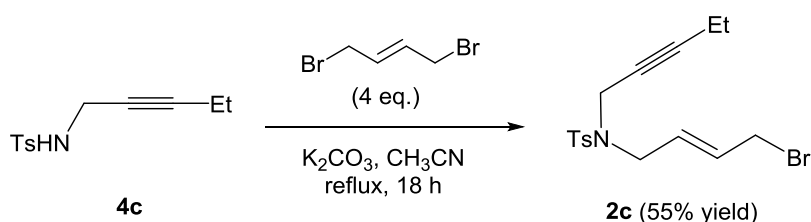
solid. **MW**: 342.25 g/mol; **m.p.**: 78–80 °C (lit.¹¹⁹: opaque oil); **¹H NMR (300 MHz, CDCl₃, TMS) δ(ppm)**: 2.04 (t, ⁴J_{H,H} = 2.4 Hz, 1H), 2.43 (s, 3H), 3.84 (d, ³J_{H,H} = 6.6 Hz, 2H), 3.92 (dd, ³J_{H,H} = 7.5 Hz, ⁴J_{H,H} = 0.9 Hz, 2H), 4.08 (d, ⁴J_{H,H} = 2.4 Hz, 2H), 5.70 (m, 1H), 5.94 (m, 1H), 7.30 (d, ³J_{H,H} = 8.4 Hz, 2H), 7.72 (d, ³J_{H,H} = 8.4 Hz, 2H); **ESI-MS (m/z)**: 364–366 [M+Na]⁺.

7.2.1.5. Synthesis of 2b



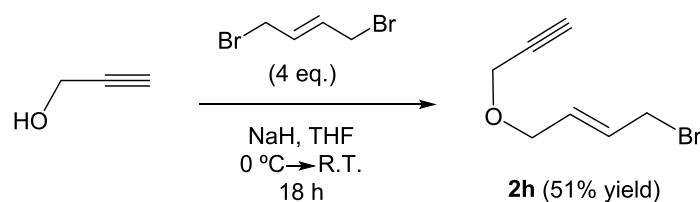
In a 100 mL two-necked round-bottom flask, a mixture of *trans*-1,4-dibromo-2-butene (5.90 g, 27.58 mmol) and potassium carbonate (2.40 g, 17.36 mmol) in acetonitrile (50 mL) was heated to reflux. Compound **4b** (1.53 g, 6.85 mmol) was then slowly added to the reaction mixture. The mixture was stirred for 18 h until completion (TLC monitoring). The salts were filtered off and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (10:1) as the eluent to afford (*E*)-*N*-(4-bromobut-2-en-1-yl)-*N*-(but-2-yn-1-yl)-(4-methylphenyl)sulfonamide **2b** (1.15 g, 47% yield) as a colourless solid. **MW**: 356.28 g/mol; **m.p.**: 57–59 °C; **IR (ATR) ν (cm⁻¹)**: 2928, 1343, 1155; **¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm)**: 1.56 (t, ⁵J_{H,H} = 2.4 Hz, 3H), 2.43 (s, 3H), 3.81 (d, ³J_{H,H} = 6.4 Hz, 2H), 3.93 (dd, ³J_{H,H} = 7.6 Hz, ⁴J_{H,H} = 0.8 Hz, 2H), 4.01 (q, ⁵J_{H,H} = 2.4 Hz, 2H), 5.70 (m, 1H), 5.92 (m, 1H), 7.30 (d, ³J_{H,H} = 8.4 Hz, 2H), 7.73 (d, ³J_{H,H} = 8.4 Hz, 2H); **¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm)**: 3.3, 21.5, 31.3, 36.7, 47.4, 71.5, 81.8, 127.9, 129.2, 129.3, 131.0, 136.0, 143.4; **ESI-MS (m/z)**: 356.0–358.0 [M+H]⁺, 378.0–380.0 [M+Na]⁺; **E.A.** calcd (%) for C₁₅H₁₈BrNO₂S: C, 50.57%, H, 5.09%; N, 3.93%. Found: C, 50.90%; H, 4.92%; N, 4.05%.

7.2.1.6. Synthesis of 2c

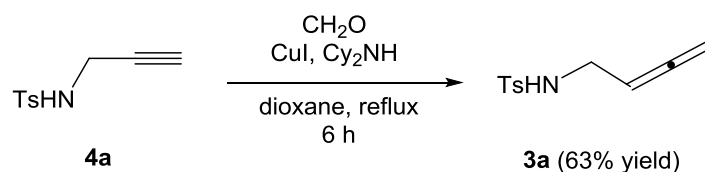


In a 250 mL two-necked round-bottom flask, a mixture of *trans*-1,4-dibromo-2-butene (5.64 g, 26.37 mmol) and potassium carbonate (2.14 g, 15.48 mmol) in acetonitrile (100 mL) was heated to reflux. Compound **4c** (1.51 g, 6.36 mmol) was then slowly added to the reaction mixture. The mixture was stirred for 17 h until completion (TLC monitoring). The salts were filtered off and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (10:1) as the eluent to afford (*E*)-*N*-(4-bromobut-2-en-1-yl)-4-methyl-*N*-(pent-2-yn-1-yl)benzenesulfonamide **2c** (1.29 g, 55% yield) as a yellow solid. **MW**: 370.30 g/mol; **m.p.**: 43–45 °C; **IR (ATR) ν (cm⁻¹)**: 2922, 2358, 1343, 1157; **¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm)**: 0.91 (t, ³*J*_{H,H} = 7.6 Hz, 3H), 1.93 (qt, ³*J*_{H,H} = 7.6 Hz, ⁵*J*_{H,H} = 2.4 Hz, 2H), 2.43 (s, 3H), 3.82 (d, ³*J*_{H,H} = 6.4 Hz, 2H), 3.93 (dd, ³*J*_{H,H} = 7.6 Hz, ⁴*J*_{H,H} = 0.8 Hz, 2H), 4.04 (t, ⁵*J*_{H,H} = 2.4 Hz, 2H), 5.71 (m, 1H), 5.93 (m, 1H), 7.30 (d, ³*J*_{H,H} = 8.4 Hz, 2H), 7.73 (d, ³*J*_{H,H} = 8.4 Hz, 2H); **¹³C NMR (75 MHz, CDCl₃, TMS) δ (ppm)**: 12.1, 13.5, 21.5, 31.3, 36.6, 47.3, 71.6, 87.8, 127.8, 129.2, 129.4, 131.0, 136.0, 143.4; **HRMS** calcd for [C₁₆H₂₀BrNO₂S + Na]⁺: 394.0290. Found: 394.0260.

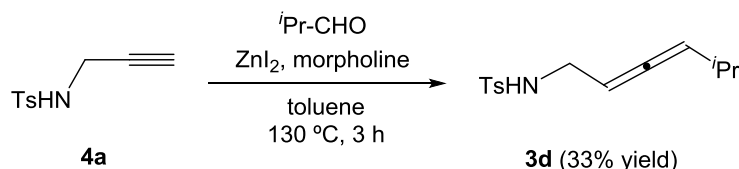
7.2.1.7. Synthesis of 2h



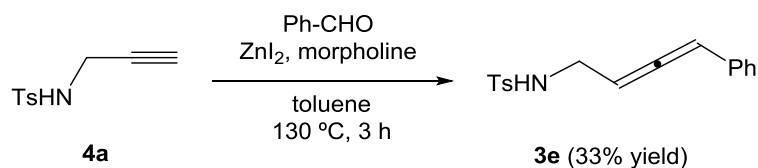
In a 250 mL two-necked round-bottom flask, a mixture of *trans*-1,4-dibromo-2-butene (15.05 g, 70.36 mmol) in anhydrous THF (40 mL) was added to a solution of sodium hydride (60% mineral oil, 1.80 g, 75.00 mmol) in 50 mL of anhydrous THF at 0 °C and stirred for 1 h. A solution of propargylic alcohol (1.00 g, 17.84 mmol) in anhydrous THF (10 mL) was slowly added at 0 °C. The resulting mixture was stirred for 18 h at room temperature until completion (TLC monitoring). Diethyl ether (20 mL) was added to the reaction mixture and it was washed with saturated aqueous solution of NaCl (3 x 20 mL). The organic phase was dried with anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (20:1) as the eluent to afford (*E*)-1-bromo-4-(prop-2-yn-1-yloxy)but-2-ene **4h** (1.72 g, 51% yield) as a colourless oil¹²¹; **MW**: 223.29 g/mol; **¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm)**: 2.47 (t, ³*J*_{H,H} = 2.4 Hz, 1H), 3.95–3.97 (m, 2H), 4.07–4.10 (m, 2H), 4.15 (d, ³*J*_{H,H} = 2.4 Hz, 2H), 5.84 (m, 1H), 5.98 (m, 1H).

7.2.1.8. Synthesis of **3a**

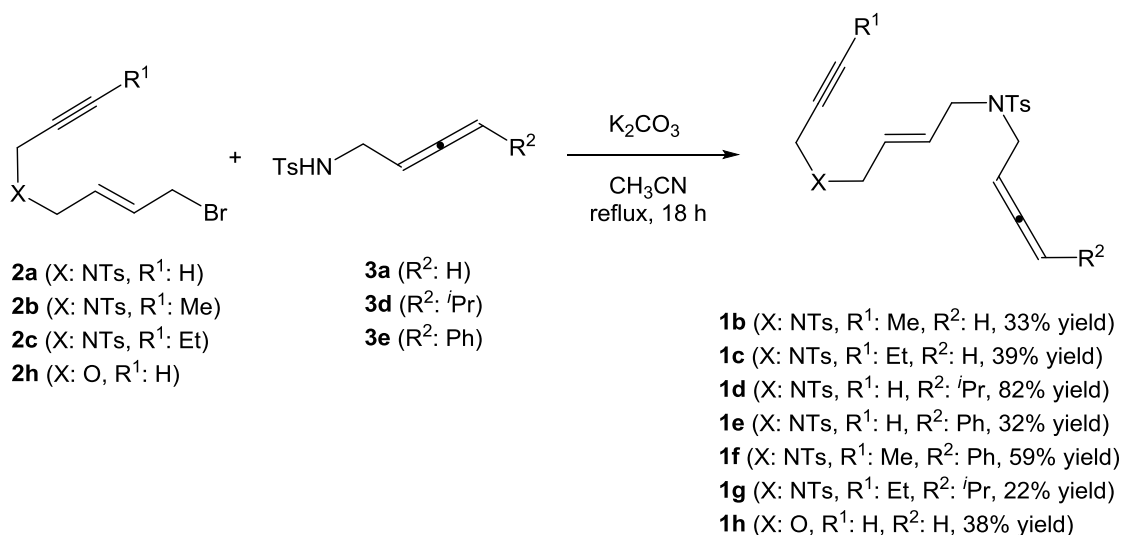
In a 50 mL two-necked round-bottom flask, a mixture of *N*-(prop-2-yn-1-yl)-(4-methylphenyl)sulfonamide **4a** (4.92 g, 23.51 mmol), paraformaldehyde (1.75 g, 58.27 mmol), and copper(I) iodide (2.37 g, 12.44 mmol) in dioxane (100 mL) was heated to reflux. Dicyclohexylamine (8.6 mL, 43.26 mmol) was then slowly added to the reaction mixture and was stirred for 6 h until completion (TLC monitoring). The salts were filtered off and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (8:2) as the eluent to afford *N*-(but-2,3-dienyl)-(4-methylphenyl)sulfonamide **3a** (3.29 g, 63% yield) as a brown oil. **MW**: 223.29 g/mol; oil (lit.¹²² m.p.: 41-42°C); **¹H NMR (300 MHz, CDCl₃, TMS) δ(ppm)**: 2.43 (s, 3H), 3.59 (hept., $J_{\text{H,H}} = 3.2$ Hz, 2H), 4.72 (ba, 1H), 4.73-4.78 (m, 2H), 5.06 (quint., $J_{\text{H,H}} = 6.3$ Hz, 1H), 7.33 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.76 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H); **ESI-MS (*m/z*)**: 246.0 [$\text{M}+\text{Na}$]⁺.

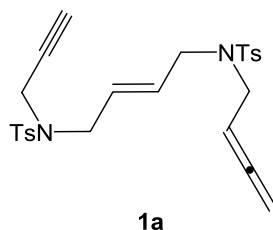
7.2.1.9. Synthesis of **3d**

In a 100 mL two-necked round-bottom flask, a mixture of *N*-(prop-2-yn-1-yl)-(4-methylphenyl)sulfonamide **4a** (1.47 g, 7.02 mmol), isobutyraldehyde (1.2 mL, 13.15 mmol), morpholine (0.9 mL, 10.44 mmol) and zinc(II) iodide (1.83 g, 5.73 mmol) in toluene (70 mL) was heated at 130 °C. The reaction mixture was stirred for 3 h until completion (TLC monitoring). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (11:1) as the eluent to afford **3d** (0.61 g, 33% yield) as an orange oil. **MW**: 265.37 g/mol; oil (lit.¹²³ yellow liquid). **¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm)**: 0.96 (dd, $^3J_{\text{H,H}} = 6.8$ Hz, $^4J_{\text{H,H}} = 1.2$ Hz, 6H), 2.27 (m, 1H), 2.42 (s, 3H), 3.55 (td, $^3J_{\text{H,H}} = 5.8$ Hz, $^5J_{\text{H,H}} = 2.8$ Hz, 2H), 4.67 (t, NH, $^3J_{\text{H,H}} = 5.8$ Hz, 1H), 5.09 (m, 1H), 5.22 (m, 1H), 7.30 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.76 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H); **ESI(-)-MS (*m/z*)**: 263.9 [$\text{M}-\text{H}$]⁻.

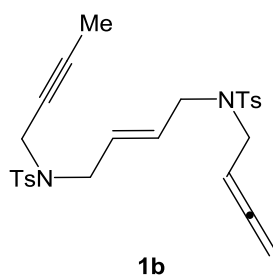
7.2.1.10. Synthesis of **3e**

In a 100 mL two-necked round-bottom flask, a mixture of *N*-(prop-2-yn-1-yl)-(4-methylphenyl)sulfonamide **4a** (1.49 g, 7.12 mmol), distilled benzaldehyde (1.35 mL, 13.28 mmol), morpholine (0.87 mL, 10.05 mmol) and zinc(II) iodide (1.83 g, 5.73 mmol) in toluene (70 mL) was heated at 130 °C. The reaction mixture was stirred for 3 h until completion (TLC monitoring). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (10:1) as the eluent to afford **3e** (0.70 g, 33% yield) as a yellow solid. **MW**: 299.39 g/mol; **m.p.**: 76-79 °C (lit.¹²⁴ yellow oil). **¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm)**: 2.42 (s, 3H), 3.71 (td, ³*J*_{H,H} = 6.0 Hz, ⁵*J*_{H,H} = 3.2 Hz, 2H), 4.55 (t, NH, ³*J*_{H,H} = 6.0 Hz, 1H), 5.54 (q, *J*_{H,H} = 6.0 Hz, 1H), 6.21 (dt, ⁴*J*_{H,H} = 6.0 Hz, ⁵*J*_{H,H} = 3.2 Hz, 1H), 7.19-7.31 (m, 7H), 7.74 (d, ³*J*_{H,H} = 8.0 Hz, 2H); **ESI-MS (*m/z*)**: 300.1 [M+H]⁺, 322.1 [M+Na]⁺, 338.1 [M+K]⁺.

7.2.1.11. Synthesis of substrates **1a – 1h**

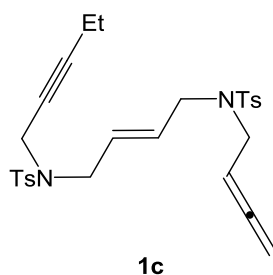


General procedure for substrate 1a. A stirred mixture of bromo derivative **2a** (0.71 g, 2.07 mmol), potassium carbonate (0.72 g, 5.21 mmol) and acetonitrile (60 mL) was heated at reflux for 10 min. A solution of N-(but-2,3-dienyl)-(4-methylphenyl)sulfonamide **3a** (0.55 g, 2.46 mmol) in acetonitrile (3 mL) was then added slowly to the reaction mixture. The reaction was heated for 18 h until completion (TLC monitoring). The salts were filtered off and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (9:1) as the eluent to afford **1a** (0.59 g, 59% yield) as a colourless solid. **MW**: 484.63 g/mol; **m.p.**: 115-118°C; **IR (ATR) ν (cm⁻¹)**: 3260, 1957, 1332, 1158; **¹H NMR (300 MHz, CDCl₃, TMS) δ (ppm)**: 1.99 (t, ⁴*J*_{H,H} = 2.4 Hz, 1H), 2.43 (s, 6H), 3.76-3.83 (m, 6H), 4.02 (d, ⁴*J*_{H,H} = 2.4 Hz, 2H), 4.69-4.72 (m, 2H), 4.84 (m, 1H), 5.47-5.65 (m, 2H), 7.30 (d, ³*J*_{H,H} = 8.1 Hz, 4H), 7.68 (d, ³*J*_{H,H} = 8.1 Hz, 2H), 7.71 (d, ³*J*_{H,H} = 8.1 Hz, 2H); **¹³C NMR (75 MHz, CDCl₃, TMS) δ (ppm)**: 21.3, 21.4, 35.7, 45.7, 47.4, 47.6, 73.8, 76.1, 76.2, 85.2, 126.9, 127.5, 128.2, 129.3, 129.6, 130.1, 135.6, 137.0, 143.3, 143.5, 209.3; **HRMS** calcd for [C₂₅H₂₈N₂O₄S₂ + Na]⁺: 507.1388. Found: 507.1394.

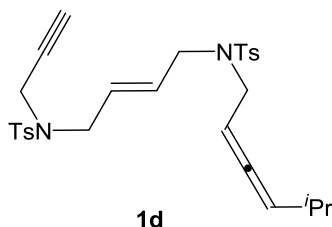


Substrate 1b. The residue was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (10:1) as the eluent to afford **1b** (33% yield) as a colourless solid. **MW**: 498.66 g/mol; **m.p.**: 98-100°C; **IR (ATR) ν (cm⁻¹)**: 2918, 1339, 1154; **¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm)**: 1.54 (t, ⁵*J*_{H,H} = 2.4 Hz, 3H), 2.43 (s, 6H), 3.74 (d, ³*J*_{H,H} = 5.6 Hz, 2H), 3.80-3.82 (m, 4H), 3.94 (q, ⁵*J*_{H,H} = 2.4 Hz, 2H), 4.69-4.71 (m, 2H), 4.84 (m, 1H), 5.48-5.62 (m, 2H), 7.30 (d, ³*J*_{H,H} = 8.0 Hz, 4H), 7.68 (d, ³*J*_{H,H} = 8.0 Hz, 2H), 7.69 (d, ³*J*_{H,H} = 8.0 Hz, 2H); **¹³C NMR (100 MHz, CDCl₃, TMS) δ (ppm)**: 3.3, 21.6, 36.5, 45.9, 47.9, 71.4, 76.4, 81.8, 85.4, 128.9, 129.3, 129.8, 136.0, 137.3,

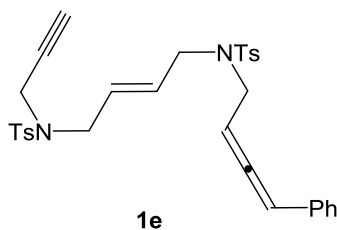
143.5, 209.5; **ESI-MS** (m/z): 499.1 $[M+H]^+$; **HRMS** calcd for $[C_{26}H_{30}N_2O_4S_2 + Na]^+$: 521.1539. Found: 521.1543.



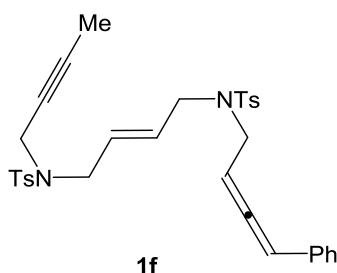
Substrate 1c. The residue was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (10:1) as the eluent to afford **1c** (39% yield) as a colourless solid. **MW**: 512.68 g/mol; **m.p.**: 84-86 °C; **IR (ATR) ν (cm^{-1})**: 2919, 1342, 1157; **^1H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm)**: 0.89 (t, $^3J_{H,H} = 7.6$ Hz, 3H), 1.90 (qt, $^3J_{H,H} = 7.6$ Hz, $^5J_{H,H} = 2.4$ Hz, 2H), 2.42 (s, 3H), 2.43 (s, 3H), 3.76 (d, $^3J_{H,H} = 5.6$ Hz, 2H), 3.78-3.83 (m, 4H) 3.97 (t, $^5J_{H,H} = 2.4$ Hz, 2H), 4.69-4.72 (m, 2H), 4.83 (m, 1H), 5.49-5.62 (m, 2H), 7.29 (d, $^3J_{H,H} = 8.4$ Hz, 2H), 7.31 (d, $^3J_{H,H} = 8.4$ Hz, 2H), 7.68 (d, $^3J_{H,H} = 8.4$ Hz, 2H), 7.71 (d, $^3J_{H,H} = 8.4$ Hz, 2H); **^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ (ppm)**: 12.1, 13.5, 21.5, 36.4, 45.8, 47.5, 47.9, 71.4, 76.4, 85.4, 87.8, 127.0, 127.2, 127.7, 127.9, 128.8, 129.3, 129.8, 129.9, 136.0, 137.2, 143.4, 143.5, 209.5; **HRMS** calcd for $[C_{27}H_{32}N_2O_4S_2 + Na]^+$: 535.1696. Found: 535.1689.



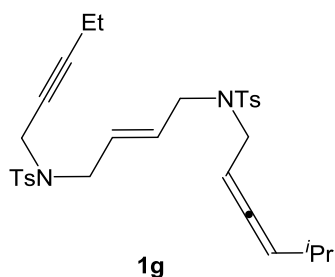
Substrate 1d. The residue was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (9:1) as the eluent to afford **1d** (82% yield) as a yellow oil. **MW**: 526.71 g/mol; **IR (ATR) ν (cm^{-1})**: 2961, 1345, 1157; **^1H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm)**: 0.97 (d, $^3J_{H,H} = 6.8$ Hz, 6H), 2.04 (t, $^3J_{H,H} = 2.4$ Hz, 1H), 2.24 (m, 1H), 2.40 (s, 6H), 3.69-3.88 (m, 6H), 4.00 (ba, 2H), 4.89 (qd, $^3J_{H,H} = 6.8$ Hz, $^4J_{H,H} = 3.0$ Hz, 1H), 5.14 (m, 1H), 5.47-5.61 (m, 2H), 7.29 (d, $^3J_{H,H} = 8.0$ Hz, 4H), 7.67 (d, $^3J_{H,H} = 8.0$ Hz, 2H), 7.70 (d, $^3J_{H,H} = 8.0$ Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm)**: 21.7, 22.7, 28.0, 36.1, 47.0, 47.9, 74.4, 76.6, 87.8, 100.4, 127.3, 127.9, 128.2, 129.8, 130.0, 130.5, 136.0, 137.6, 143.6, 144.0, 203.9; **HRMS** calcd for $[C_{28}H_{34}N_2O_4S_2 + Na]^+$: 549.1858. Found: 549.1850.



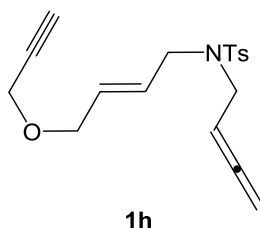
Substrate 1e. The residue was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (9:1) as the eluent to afford **1e** (32% yield) as a colourless oil. Due to the unstability of this derivative, we were unable to fully purify it. **MW:** 560.73 g/mol; **IR (ATR) ν (cm^{-1}):** 2921, 1334, 1156; **^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm):** 1.95 (t, $^4J_{\text{H,H}} = 2.4$ Hz, 1H), 2.41 (s, 3H), 2.42 (s, 3H), 3.71 (d, $^3J_{\text{H,H}} = 6.0$ Hz, 2H), 3.80-3.88 (m, 2H), 3.84 (d, $^3J_{\text{H,H}} = 6.0$ Hz, 2H), 3.94 (d, $^4J_{\text{H,H}} = 2.4$ Hz, 2H), 5.32 (q, $^4J_{\text{H,H}} = 6.4$ Hz, 1H), 5.47 (m, 1H), 5.56 (m, 1H), 6.13 (dt, $^3J_{\text{H,H}} = 6.4$ Hz, $^4J_{\text{H,H}} = 2.4$ Hz, 1H), 7.18-7.30 (m, 9H), 7.68 (d, $^3J_{\text{H,H}} = 9.6$ Hz, 2H), 7.70 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H); **^{13}C NMR (75 MHz, CDCl_3 , TMS) δ (ppm):** 21.6, 35.8, 46.0, 47.6, 48.0, 74.0, 76.3, 90.3, 96.2, 126.9, 127.1, 127.2, 127.4, 127.6, 127.8, 128.4, 128.8, 129.5, 129.8, 130.1, 133.3, 135.7, 137.1, 143.6, 143.7, 206.2; **HRMS** calcd for $[\text{C}_{31}\text{H}_{32}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 583.1696. Found: 583.1703.



Substrate 1f. The residue was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (9:1) as the eluent to afford **1f** (59% yield) as a colourless solid. Due to the unstability of this derivative, we were unable to fully purify it. **MW:** 574.75 g/mol; **m.p.:** 109-110 °C; **IR (ATR) ν (cm^{-1}):** 2919, 1346, 1158; **^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm):** 1.51 (t, $^5J_{\text{H,H}} = 2.4$ Hz, 3H), 2.42 (s, 3H), 2.43 (s, 3H), 3.68 (d, $^3J_{\text{H,H}} = 6.4$ Hz, 2H), 3.82-3.90 (m, 6H), 5.32 (q, $J_{\text{H,H}} = 6.4$ Hz, 1H), 5.44-5.60 (m, 2H), 6.13 (dt, $^4J_{\text{H,H}} = 6.4$ Hz, $^5J_{\text{H,H}} = 2.4$ Hz, 1H), 7.19-7.30 (m, 9H), 7.68-7.69 (m, 4H); **^{13}C NMR (75 MHz, CDCl_3 , TMS) δ (ppm):** 3.1, 21.4, 36.3, 45.8, 47.4, 48.0, 71.3, 77.1, 81.6, 126.8, 127.0, 127.3, 127.7, 128.6, 129.2, 129.7, 133.2, 135.8, 137.0, 143.2, 143.4, 206.1; **HRMS** calcd for $[\text{C}_{32}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 597.1852. Found: 597.1851.



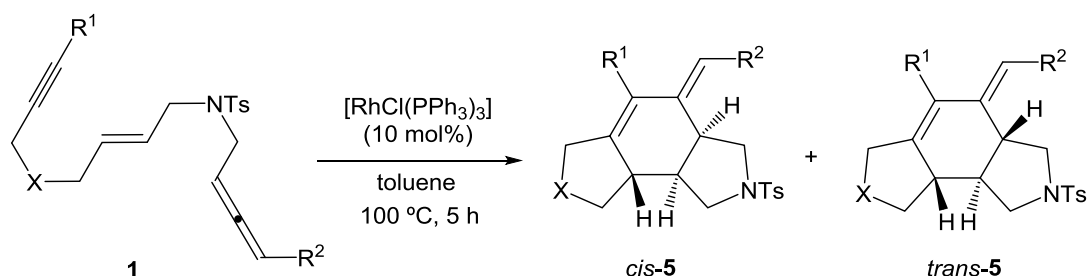
Substrate 1g. The residue was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (9:1) as the eluent to afford **1g** (22% yield) as a yellow oil. **MW:** 554.76 g/mol; **IR (ATR) ν (cm^{-1}):** 2962, 1334, 1157; **^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm):** 0.89 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3H), 0.97 (d, $^3J_{\text{H,H}} = 6.8$ Hz, 6H), 1.90 (qt, $^3J_{\text{H,H}} = 7.4$ Hz, $^5J_{\text{H,H}} = 2.2$ Hz, 2H), 2.26 (m, 1H), 2.42 (s, 3H), 2.43 (s, 3H), 3.69-3.88 (m, 6H), 3.95-3.97 (m, 2H), 4.87 (m, 1H), 5.14 (m, 1H), 5.48-5.62 (m, 2H), 7.29 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 4H), 7.68 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.71 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H); **^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm):** 12.1, 13.5, 21.5, 22.4, 27.8, 36.4, 46.7, 47.5, 47.7, 71.5, 87.4, 87.8, 100.2, 127.1, 127.8, 128.4, 129.4, 129.7, 130.0, 136.0, 137.4, 143.4, 203.7; **HRMS** calcd for $[\text{C}_{30}\text{H}_{38}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 577.2171. Found: 577.2176.



Substrate 1h. The residue was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (10:1) as the eluent to afford **1h** (38% yield) as a yellow oil. Due to the unstability of this derivative, we were unable to fully purify it. **MW:** 331.43 g/mol; **IR (ATR) ν (cm^{-1}):** 2924, 1335, 1156; **^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm):** 2.42 (s, 3H), 2.45 (t, $^4J_{\text{H,H}} = 2.4$ Hz, 1H), 3.18-3.22 (m, 2H), 3.81 (dd, $^3J_{\text{H,H}} = 6.4$ Hz, $^4J_{\text{H,H}} = 0.8$ Hz, 2H), 4.00 (dd, $^3J_{\text{H,H}} = 5.2$ Hz, $^4J_{\text{H,H}} = 0.8$ Hz, 2H), 4.08 (d, $^4J_{\text{H,H}} = 2.4$ Hz, 2H), 4.67 (td, $^4J_{\text{H,H}} = 6.4$ Hz, $^5J_{\text{H,H}} = 3.2$ Hz, 2H), 5.02 (quint., $J_{\text{H,H}} = 6.7$ Hz, 1H), 5.56-5.72 (m, 2H), 7.30 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 2H), 7.69 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 2H); **^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm):** 21.5, 46.9, 49.5, 57.1, 69.1, 74.6, 75.4, 79.5, 86.5, 127.1, 128.6, 129.7, 130.1, 137.0, 143.3, 208.8; **HRMS** calcd for $[\text{C}_{18}\text{H}_{21}\text{NO}_3\text{S} + \text{Na}]^+$: 354.1140. Found: 354.1137.

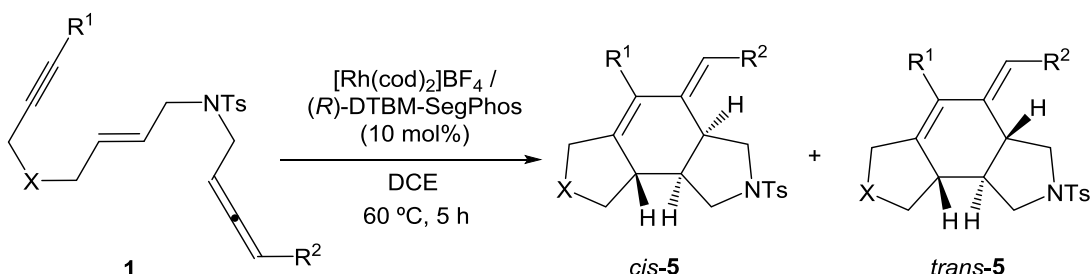
7.2.1. [2+2+2] cycloaddition reactions of substrates **1a** – **1h**

7.2.1.1. [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition reaction of **1a** – **1h**



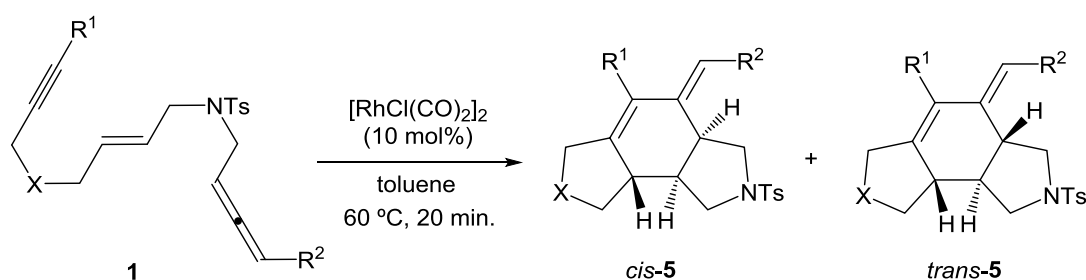
In a 10 mL two-necked round-bottom flask, a mixture of **1a** (24.6 mg, 0.050 mmol) and tris(triphenylphosphine)rhodium(I) chloride (5.6 mg, 0.006 mmol, 10 mol%) was dissolved in anhydrous toluene (3 mL) and heated to 100 °C. The mixture was stirred for 5 h until completion (TLC monitoring). The solvent was removed under reduced pressure and the reaction crude was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (8:2) as the eluent to afford **5a** (13.8 mg, 56% yield, 8:2 *cis/trans* d.r.) as a colourless solid.

7.2.1.2. [Rh(cod)₂]BF₄ / (*R*)-DTBM-SegPhos-catalysed [2+2+2] cycloaddition reaction of **1a** – **1h**



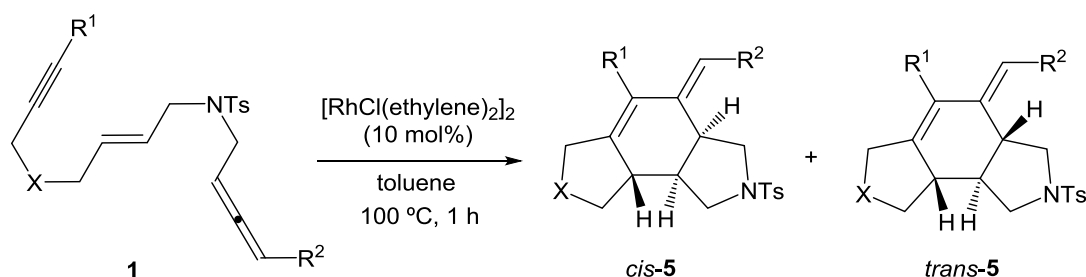
In a 10 mL two-necked round-bottom flask, a mixture of bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (2.1 mg, 0.0052 mmol, 10 mol%) and (*R*)-DTBM-SegPhos (6.6 mg, 0.0056 mmol) was dissolved in anhydrous dichloromethane (3 mL) and hydrogenated for 30 min. The solvent was then removed under vacuum, anhydrous dichloroethane (3 mL) was introduced, and the reaction mixture was heated to 60 °C. Allene-ene-yne **1a** (25.4 mg, 0.052 mmol) was slowly added to the previous mixture. The mixture was stirred for 5 h until completion (TLC monitoring). The solvent was removed under reduced pressure and the reaction crude was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (8:2) as the eluent to afford **5a** (7.8 mg, 31% yield, 7:3 *cis/trans* d.r.) as a colourless solid.

7.2.1.3. $[\text{RhCl}(\text{CO})_2]_2$ -catalysed [2+2+2] cycloaddition reaction of **1a** – **1h**

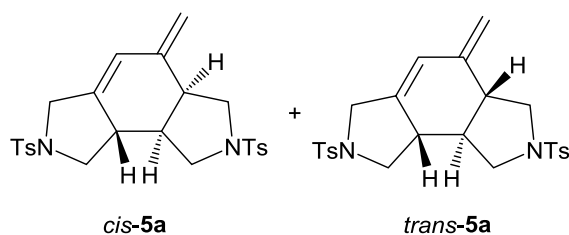


In a 10 mL two-necked round-bottom flask, **1a** (24.2 mg, 0.050 mmol) was dissolved in anhydrous toluene (3 mL) and heated to 60 °C. Di- μ -chloro-tetracarbonyldirhodium(I) (2.37 mg, 0.006 mmol, 10 mol%) was slowly added to the previous solution. The mixture was stirred for 20 min. until completion (TLC monitoring). The solvent was removed under reduced pressure and the reaction crude was purified by column chromatography on silica gel using a mixture of hexane/EtOAc (8:2) as the eluent to afford **5a** (11.8 mg, 49% yield, 1:9 *cis/trans* d.r.) as a colourless solid.

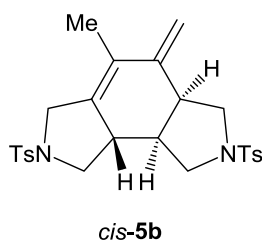
7.2.1.4. $[\text{RhCl}(\text{ethylene})_2]_2$ -catalysed [2+2+2] cycloaddition reaction of **1a**



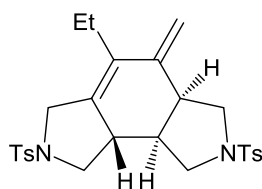
In a 10 mL two-necked round-bottom flask, a mixture of **1a** (21.3 mg, 0.044 mmol) and bis(ethylene)rhodium(I) chloride dimer (1.94 mg, 0.005 mmol, 11 mol%) was dissolved in anhydrous toluene (3 mL) and heated to 100 °C. The mixture was stirred for 1 h until completion (TLC monitoring). The solvent was removed under reduced pressure and the reaction crude was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (8:2) as the eluent to afford **2a** (8.8 mg, 41% yield, 2.5:7.5 *cis/trans* d.r.) as a colourless solid.



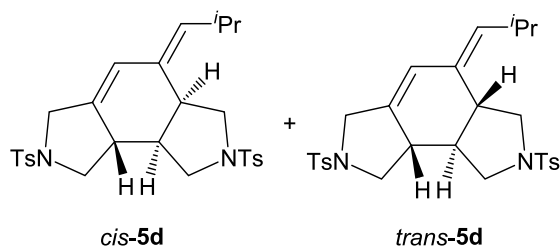
Cycloadduct 5a was obtained as an inseparable mixture of the two diastereoisomers *cis* and *trans*. **MW**: 484.63 g/mol; $^1\text{H NMR}$ (500 MHz, CDCl_3 , TMS) $\delta(\text{ppm})$: 1.48 (m, 1H_{trans}), 1.74 (m, 1H_{cis}), 1.84 (m, 1H_{cis}), 2.34 (m, 1H_{trans}), 2.43 (m, 1H_{cis}), 2.46 (s, 3H_{cis} + 3H_{trans}), 2.46-2.52 (m, 2H_{trans}), 2.51 (s, 3H_{cis} + 3H_{trans}), 2.83 (dd, $^2J_{\text{H,H}} = 11.5 \text{ Hz}$, $^3J_{\text{H,H}} = 8.8 \text{ Hz}$, 1H_{cis}), 2.90 (m, 1H_{cis}), 2.97 (m, 1H_{trans}), 3.14 (dd, $^2J_{\text{H,H}} = ^3J_{\text{H,H}} = 10.5 \text{ Hz}$, 1H_{trans}), 3.30 (d, $^2J_{\text{H,H}} = 10.5 \text{ Hz}$, 1H_{cis}), 3.39 (dd, $^2J_{\text{H,H}} = 10.5 \text{ Hz}$, $^3J_{\text{H,H}} = 4.5 \text{ Hz}$, 1H_{cis}), 3.55 (m, 1H_{cis}), 3.60-3.66 (m, 2H_{cis} + 1H_{trans}), 3.69 (d, $^2J_{\text{H,H}} = 15.0 \text{ Hz}$, 1H_{trans}), 3.76-3.84 (m, 2H_{trans}), 4.01 (d, $^2J_{\text{H,H}} = 15.0 \text{ Hz}$, 1H_{cis}), 4.10 (d, $^2J_{\text{H,H}} = 15.0 \text{ Hz}$, 1H_{cis}), 4.68 (s, 1H_{trans}), 4.88 (s, 1H_{trans}), 4.91 (s, 1H_{cis}), 4.97 (s, 1H_{cis}), 5.93 (s, 1H_{cis}), 5.98 (s, 1H_{trans}), 7.35 (d, $^3J_{\text{H,H}} = 8.0 \text{ Hz}$, 2H_{cis} + 2H_{trans}), 7.40 (d, $^3J_{\text{H,H}} = 8.0 \text{ Hz}$, 2H_{cis} + 2H_{trans}), 7.69 (d, $^3J_{\text{H,H}} = 8.0 \text{ Hz}$, 2H_{cis} + 2H_{trans}), 7.74 (d, $^3J_{\text{H,H}} = 8.0 \text{ Hz}$, 2H_{cis} + 2H_{trans}); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , TMS, *cis*) $\delta(\text{ppm})$: 21.6, 29.7, 38.3, 39.9, 42.2, 50.8, 51.0, 52.5, 52.9, 115.2, 120.6, 127.1, 127.6, 129.9, 138.0, 138.7, 143.9, 144.3; **HRMS** calcd. For $[\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 507.1388. Found: 507.1388.



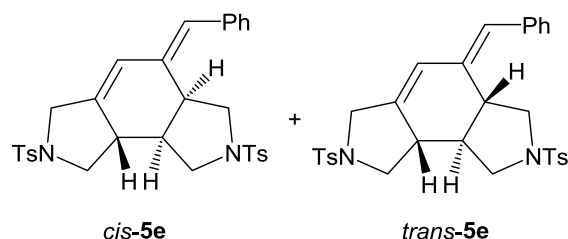
Cycloadduct 5b: was obtained as pure *cis* diastereoisomer. **MW**: 498.66 g/mol; **IR(ATR)** $\nu(\text{cm}^{-1})$: 2922, 1334, 1153; $^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) $\delta(\text{ppm})$: 1.63 (br, 3H), 1.73 (m, 1H), 1.81 (m, 1H), 2.35 (dd, $^2J_{\text{H,H}} = 10.4 \text{ Hz}$, $^3J_{\text{H,H}} = 8.6 \text{ Hz}$, 1H), 2.44 (s, 3H), 2.49 (s, 3H), 2.81 (dd, $^2J_{\text{H,H}} = 11.6 \text{ Hz}$, $^3J_{\text{H,H}} = 9.6 \text{ Hz}$, 1H), 2.94 (s, 1H), 3.23 (d, $^2J_{\text{H,H}} = 10.4 \text{ Hz}$, 1H), 3.38 (dd, $^2J_{\text{H,H}} = 10.4 \text{ Hz}$, $^3J_{\text{H,H}} = 4.8 \text{ Hz}$, 1H), 3.52-3.62 (m, 3H), 3.98 (d, $^2J_{\text{H,H}} = 15.2 \text{ Hz}$, 1H), 4.85 (s, 1H), 5.06 (s, 1H), 7.33 (d, $^3J_{\text{H,H}} = 8.4 \text{ Hz}$, 2H), 7.38 (d, $^3J_{\text{H,H}} = 8.4 \text{ Hz}$, 2H), 7.68 (d, $^3J_{\text{H,H}} = 8.4 \text{ Hz}$, 2H), 7.72 (d, $^3J_{\text{H,H}} = 8.4 \text{ Hz}$, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , TMS) $\delta(\text{ppm})$: 21.6, 30.9, 38.3, 40.0, 42.2, 50.8, 51.0, 52.5, 53.0, 115.2, 120.6, 127.1, 127.6, 129.8, 129.9, 138.1, 138.8, 144.2; **HRMS** calcd. For $[\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 521.1539. Found: 521.1548.

*cis-5c*

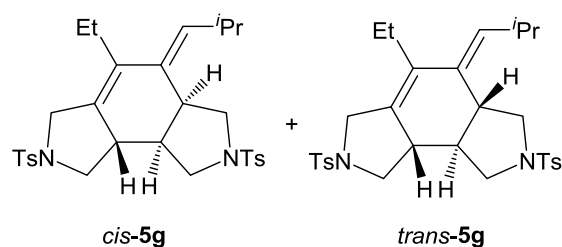
Cycloadduct 5c: was obtained as pure *cis* diastereoisomer. **MW:** 512.68 g/mol; **IR(ATR) ν (cm^{-1}):** 2925, 1339, 1155; **^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm):** 0.91 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 3H), 1.79-1.82 (m, 2H), 2.06 (q, $^3J_{\text{H,H}} = 7.6$ Hz, 2H), 2.36 (m, 1H), 2.44 (s, 3H), 2.49 (s, 3H), 2.82 (dd, $^2J_{\text{H,H}} = 11.6$ Hz, $^3J_{\text{H,H}} = 9.6$ Hz, 3H), 2.92 (m, 1H), 3.23 (d, $^2J_{\text{H,H}} = 10.4$ Hz, 1H), 3.36 (dd, $^2J_{\text{H,H}} = 10.4$ Hz, $^3J_{\text{H,H}} = 4.4$ Hz, 1H), 3.52-3.63 (m, 3H), 3.98 (m, 1H), 4.87 (s, 1H), 5.10 (s, 1H), 7.34 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.38 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.68 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.72 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H); **^{13}C NMR (100 MHz, CDCl_3 , TMS) δ (ppm):** 13.0, 21.6, 21.8, 29.7, 38.9, 39.8, 43.5, 51.4, 52.5, 53.2, 111.8, 127.1, 127.7, 130.8, 132.6, 133.6, 133.8, 138.3, 143.9, 144.2; **HRMS** calcd. For $[\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 535.1696. Found: 535.1675.



Cycloadduct 5d: was obtained as an inseparable mixture of the two diastereoisomers *cis* and *trans*. **MW:** 526.71 g/mol; **^1H NMR (400 MHz, CDCl_3 , TMS, *cis*) δ (ppm):** 0.90 (d, $^3J_{\text{H,H}} = 6.8$ Hz, 3H), 0.95 (d, $^3J_{\text{H,H}} = 6.8$ Hz, 3H), 1.63 (m, 1H), 1.75 (m, 1H), 2.35-2.45 (m, 1H + 1H), 2.42 (s, 3H), 2.48 (s, 3H), 2.71 (dd, $^2J_{\text{H,H}} = 11.6$ Hz, $^3J_{\text{H,H}} = 9.6$ Hz, 1H), 2.98 (m, 1H), 3.26 (d, $^2J_{\text{H,H}} = 10.4$ Hz, 1H), 3.38 (dd, $^2J_{\text{H,H}} = 10.4$ Hz, $^3J_{\text{H,H}} = 4.8$ Hz, 1H), 3.54-3.60 (m, 1H + 1H + 1H), 3.95 (m, 1H), 5.19 (d, $^3J_{\text{H,H}} = 10.4$ Hz, 1H), 5.76 (d, $^3J_{\text{H,H}} = 2.4$ Hz, 1H), 7.32 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.38 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.66 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H), 7.72 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2H); **^{13}C NMR (100 MHz, CDCl_3 , TMS, *cis*) δ (ppm):** 21.6, 23.0, 23.3, 27.6, 38.1, 38.5, 39.9, 50.0, 50.8, 52.3, 53.2, 122.2, 127.1, 127.6, 128.2, 129.8, 129.9, 132.7, 133.7, 134.5, 140.0, 143.8, 144.3; **HRMS** calcd. For $[\text{C}_{28}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 549.1858. Found: 549.1855.

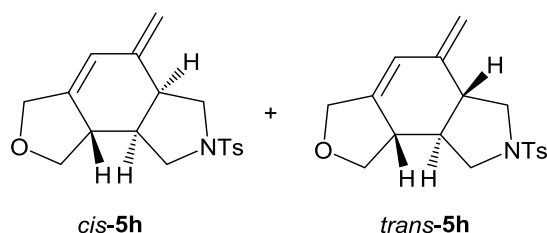


Cycloadduct 5e: was obtained as an inseparable mixture of the two diastereoisomers *cis* and *trans*. **MW:** 560.73 g/mol; **¹H NMR (300 MHz, CDCl₃, TMS) δ(ppm):** 1.28 (m, 1H_{*trans*}), 1.82-1.88 (m, 2H_{*cis*}), 2.38 (m, 1H_{*trans*}), 2.42-2.48 (m, 1H_{*cis*} + 2H_{*trans*}), 2.44 (s, 3H_{*cis*} + 3H_{*trans*}), 2.50 (s, 3H_{*cis*} + 3H_{*trans*}), 2.77-2.94 (m, 2H_{*cis*} + 1H_{*trans*}), 3.01 (m, 1H_{*trans*}), 3.14 (m, 1H_{*trans*}), 3.27-3.38 (m, 2H_{*cis*}), 3.59-3.78 (m, 3H_{*cis*} + 4H_{*trans*}), 4.04 (d, ²J_{H,H} = 15.0 Hz, 1H_{*cis*}), 4.13 (d, ²J_{H,H} = 15.3 Hz, 1H_{*trans*}), 5.97 (s, 1H_{*cis*}), 6.03 (s, 1H_{*trans*}), 6.38 (s, 1H_{*cis*}), 6.41 (s, 1H_{*trans*}), 7.13-7.38 (m, 9H_{*cis*} + 9H_{*trans*}), 7.54-7.75 (m, 4H_{*cis*} + 4H_{*trans*}); **¹³C NMR (75 MHz, CDCl₃, TMS) δ(ppm):** 21.6, 38.4, 38.7, 40.3, 42.5, 50.7, 51.0, 52.4, 122.8, 125.1, 127.2, 127.5, 127.7, 128.2, 128.6, 128.8, 129.8, 131.3, 132.6, 132.8, 133.4, 134.9, 136.8, 136.9, 143.9, 144.3; **HRMS** calcd. For [C₃₁H₃₂N₂O₄S₂ + Na]⁺: 583.1701. Found: 583.1697.



Cycloadduct 5g: was obtained as an inseparable mixture of the two diastereoisomers *cis* and *trans*. **MW:** 554.76 g/mol; **¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm):** 0.86-0.97 (m, 6H_{*cis*} + 3H_{*cis*} + 6H_{*trans*} + 3H_{*trans*}), 1.47 (m, 1H_{*trans*}), 1.67-1.74 (m, 2H_{*cis*}), 1.90 (m, 1H_{*cis*}), 1.98-2.05 (m, 2H_{*cis*}), 2.07-2.11 (m, 2H_{*trans*}), 2.30 (m, 1H_{*trans*}), 2.35-2.43 (m, 1H_{*cis*} + 2H_{*trans*}), 2.43 (s, 6H_{*cis*} + 6H_{*trans*}), 2.70 (dd, ²J_{H,H} = 11.6 Hz, ³J_{H,H} = 10.0 Hz, 1H_{*trans*}), 2.82 (dd, ²J_{H,H} = 10.8 Hz, ³J_{H,H} = 9.6 Hz, 1H_{*cis*}), 3.01 (m, 1H_{*trans*}), 3.01 (m, 1H_{*trans*}), 3.15 (dd, ²J_{H,H} = 10.8 Hz, ³J_{H,H} = 9.2 Hz, 1H_{*cis*}), 3.21 (d, ³J_{H,H} = 10.8 Hz, 1H_{*trans*}), 3.70 (dd, ²J_{H,H} = 10.4 Hz, ⁴J_{H,H} = 4.4 Hz, 1H_{*cis*}), 3.46 (dd, ²J_{H,H} = 9.2 Hz, ³J_{H,H} = 7.2 Hz, 1H_{*cis*}), 3.51-3.74 (m, 6H_{*cis*} + 6H_{*trans*}), 3.94-4.12 (m, 1H_{*cis*} + 1H_{*trans*}), 5.30 (dd, ²J_{H,H} = 10.4 Hz, ³J_{H,H} = 2.4 Hz, 1H_{*cis*}), 5.34 (d, ²J_{H,H} = 10.0 Hz, 1H_{*trans*}), 7.32-7.39 (m, 4H_{*cis*} + 4H_{*trans*}), 7.68-7.72 (m, 4H_{*cis*} + 4H_{*trans*}); **¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm):** 13.3, 21.6, 21.9, 23.1, 23.2, 23.5, 23.9, 27.8, 28.1, 38.4, 38.9, 40.0, 43.2, 43.8, 45.5, 50.3, 50.4, 52.3, 53.5, 126.8, 127.2, 127.4, 127.8, 129.8, 129.9, 130.0, 130.9, 131.3, 132.6, 133.9,

134.6, 143.7, 143.9, 144.0 144.3; **HRMS** calcd. For $[C_{30}H_{38}N_2O_4S_2 + Na]^+$: 577.2171. Found: 577.2171.



Cycloadduct 5h: was obtained as an inseparable mixture of the two diastereoisomers *cis* and *trans*. **MW:** 331.43 g/mol; **^1H NMR (400 MHz, toluene- D_8 , TMS) δ (ppm):** 1.53 (m, 1H_{*cis*}), 1.81 (m, 1H_{*trans*}), 1.95-1.99 (m, 2H_{*cis*} + 2H_{*trans*}), 1.95 (s, 3H_{*cis*} + 3H_{*trans*}), 2.39 (m, 1H_{*cis*}), 2.63 (dd, $^2J_{H,H} = 10.4$ Hz, $^3J_{H,H} = 9.2$ Hz, 1H_{*trans*}), 2.72 (dd, $^2J_{H,H} = 10.4$ Hz, $^3J_{H,H} = 8.0$ Hz, 1H_{*trans*}), 2.78-2.82 (m, 1H_{*cis*} + 1H_{*trans*}), 3.04 (m, 1H_{*cis*}), 3.35 (dd, $^2J_{H,H} = 9.2$ Hz, $^3J_{H,H} = 7.2$ Hz, 1H_{*trans*}), 3.50 (t, $^2J_{H,H} = 9.5$ Hz, 1H_{*trans*}), 3.67-3.78 (m, 1H_{*cis*} + 3H_{*trans*}), 3.89-3.96 (m, 2H_{*cis*}), 4.08 (d, $^3J_{H,H} = 14.8$ Hz, 1H_{*trans*}), 4.18 (d, $^3J_{H,H} = 14.0$ Hz, 1H_{*cis*}), 4.42 (s, 1H_{*cis*}), 4.62 (s, 1H_{*trans*}), 4.74 (s, 1H_{*cis*}), 5.49 (s, 1H_{*trans*}), 6.80 (d, $^3J_{H,H} = 8.0$ Hz, 2H_{*cis*}), 6.84 (d, $^3J_{H,H} = 8.0$ Hz, 2H_{*trans*}), 7.64 (d, $^3J_{H,H} = 8.0$ Hz, 2H_{*cis*}), 7.72 (d, $^3J_{H,H} = 8.0$ Hz, 2H_{*trans*}); **^{13}C NMR (100 MHz, toluene- D_8 , TMS) δ (ppm):** 13.7, 41.4, 42.1, 45.9, 48.9, 50.4, 51.6, 51.9, 60.9, 107.5, 113.1, 115.7, 129.4, 129.5, 130.2, 134.3, 136.0, 142.5, 143.5, 144.5, 144.5; **HRMS** calcd. For $[C_{18}H_{21}NO_3S + Na]^+$: 354.1140. Found: 354.1134.

7.3. Computational chemistry

Aiming to a deeper understanding of the intrinsic nature of chemical systems, computational chemistry represents one of the greatest advancements in the field of theoretical chemistry, as it allows a fast way to solve complex quantum mechanical equations. In the recent years, a vast number of chemists have become interested in using computers to solve quantum mechanics equations and thus analyse the properties of a specific molecular system or study the feasibility of a particular reaction.

The main advantage of computational calculations is that they represent a good way to know whether a specific reaction is likely to take place or not. This contrasts with the classical experimental point of view, which requires laboratory work to reach the same conclusion, demanding in some cases a high number of tests. Furthermore, computational chemistry is advantageous from the economical point of view, as no reagents or expensive materials need to be purchased.

However, several drawbacks arise when the results of computational calculations are obtained. For instance, it should be noted that quantum chemistry does not generally provide us with exact results, and so neither does computational chemistry. Another disadvantage is that there is not a unique way to perform computational calculations as several theoretical frameworks can be used. Therefore, the accuracy of the results obtained for a particular type of chemical system must be assessed prior to the actual research study.

Despite these facts, the results obtained by computational chemistry can efficiently predict real chemical systems and should be considered as a good starting point for the experimental counterpart to better design the tests. Contrary to that, the opposite approach is also possible, as computational calculations represent a good tool to explain why some empirical observations have taken place.

7.3.1. Computational numerical techniques

Depending on the accuracy required in the application of physics, *ab initio*, *empirical* (or *semi-empirical*) or *molecular mechanics* approaches can be employed.

- *Ab initio* (Latin translation for “from the beginning”) techniques consist of a group of methods which are strictly based on the Schrödinger equation, using the atomic numbers and the atoms of the studied system and the values of the fundamental constants. Despite the excellent accuracy attained by these

methods, they are usually limited to relatively small systems, as their computational demand is often quite high.

- *Empirical* or *semi-empirical* techniques are essentially based on the same equations than *ab initio* techniques, but several input parameters that would be theoretically calculated by *ab initio* methods are replaced by experimental values. As a result of this modification, computational costs are significantly reduced and bigger systems can be studied. However, results are usually less exact than those coming from the *ab initio* methodologies application.
- *Molecular mechanics* techniques employs classical (instead of quantum) physics combined with empirical or semi-empirical force fields. This sort of methods is especially useful for large systems like proteins.

Since the molecular systems studied in this thesis are relatively small, all the computational calculations were performed with *ab initio* methods. For this reason, the so-called Hartree-Fock (HF) method will be discussed in the next sub-sections, as it represents one of the simplest bases of *ab initio* calculations. Later on, DFT methods will be described as for being the most suitable ones in terms of results accuracy and computational costs.

7.3.2. The Hartree-Fock approximation

Among the different ways to calculate the electron wavefunctions of atoms and molecules, the *Hartree-Fock* (HF) approach is the most common one. This *ab initio* approach represents the starting point for later developing more advanced, accurate and sophisticated calculations methods.

The HF approximation theoretically consists in placing electrons into spin orbitals. The central algorithm is aimed to solve the Schrödinger equation for a multi-electronic atom or molecule. More concretely, it represents an extension of the molecular orbital theory, in which the Coulombic electron-electron repulsion is not specifically taken into account, but the average effect is included in the calculation. The momentum of each electron is described by orbitals, which are simple function that are independent from the motion of other electrons.

The *Born-Oppenheimer* (BO) *approximation* consists in separating the wavefunction of a molecule into its electronic and nuclear (vibrational, rotational and translational) components (Eq. 1).

$$\Psi_{\text{total}} = \Psi_{\text{electronic}} \cdot \Psi_{\text{nuclear}} \quad (\text{Eq. 1})$$

Therefore, the wavefunction of the multi-electron molecule relies on the electronic and nuclear coordinates: $\Psi(R, r)$, where R states for the nuclear coordinates and r for the electron coordinates. Taken this into account, the motion of electrons and nuclei are coupled. Nevertheless, since nuclei are much heavier than electrons, nuclei move much slower than electrons ($m_{proton} \geq 2000m_{electron}$). Such a contrast enforces the concept that nuclei appear to be fixed from the electronic point of view. For this reason, the resolution of the full Schrödinger equation (Eq. 2) can be simplified by splitting it into Eq. 3 and Eq. 4.

$$H\Psi_{total}(R, r) = E_{total}\Psi_{total}(R, r) \quad (\text{Eq. 2})$$

$$H_{el}\Psi_{el}^n(R, r) = U_n(R)\Psi_{el}^n(R, r) \quad (\text{Eq. 3})$$

$$T + U_n(R)\Psi_{nucl}^n(R) = E_{total}\Psi_{nucl}^n(R) \quad (\text{Eq. 4})$$

Eq. 3 represents the electronic Schrödinger equation that describes the electronic motion of electrons considering that nuclei remain fixed. On the other hand, Eq. 4 is the so-called nuclear Schrödinger equation, which contains the motion of nuclei when the U_n potential is applied by the electrons.

In a deeper inside into the electronic Hamiltonian term (H_{el}), Eq. 5 describes the exact contributions to take into account for an N -electrons system in the presence of M nuclei with Z_A charge.

$$H_{el} = \sum_i^N h_i + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (\text{Eq. 5})$$

where

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} \quad (\text{Eq. 6})$$

Unfortunately, the process to solve the previous Hamiltonian is extremely complex, since the $1/r_{ij}$ term correlates the motion of all the electrons among them. However, apart from the Born-Oppenheimer approximation, the HF method applies two simplifications to efficiently solve the Schrödinger equation:

- Use of Slater determinant as a wavefunction for a closed-shell situation (Eq. 7)

$$\Phi_0 = \frac{1}{N!} \begin{vmatrix} \varphi_{1\alpha} 1 & \varphi_{1\alpha} 2 & \cdots & \varphi_{1\alpha} N \\ \varphi_{1\beta} 1 & \varphi_{1\beta} 2 & \cdots & \varphi_{1\beta} N \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{N/2,\beta} 1 & \varphi_{N/2,\beta} 2 & \cdots & \varphi_{N/2,\beta} N \end{vmatrix} \quad (\text{Eq. 7})$$

Considering that N delimitates the number of electrons in the system, α and β state for spin functions (spin-up and spin-down, respectively) and φ_i are spatial functions (molecular orbitals). The $\varphi_i\alpha$ and $\varphi_i\beta$ junctions correspond to the so-called *spin orbitals*. Furthermore, the Slater determinant is in mathematical accordance with the Pauli (or anti-symmetry) principle with respect to the exchange of any two electrons.¹²⁵

- The molecular orbitals to constitute Slater determinants are obtained from the Linear Combination of Atomic Orbitals (LCAO-MO). The finite basis set is assumed to be approximately complete (Eq. 8).

$$\varphi_i = \sum_k^M c_{ki} \chi_k \quad (\text{Eq. 8})$$

Where c_{ki} represent the molecular orbital coefficients and χ_k are the basis functions, which are atom-centred functions that mimic the solutions of the hydrogen atom. So, when the expansion is bigger, the calculation becomes more accurate, though at the same time it is more expensive.

The one-electron functions $\varphi_i\alpha$ are called spin orbitals and are chosen to be orthonormal (Eq. 9).

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} \quad (\text{Eq. 9})$$

The way to choose the most appropriate basis set of spin orbitals is based on the *variational principle*, which claims that it is the one that minimizes the electronic energy. The application of the principle consists in taking a trial parameter-dependent wavefunction and finding the values of the parameter for which the value of the energy is the minimum one. The wavefunction that results from fixing the parameters found represents an approximation of the ground state wavefunction, and the expectation value of the energy in that state is the upper bound to the ground state energy (Eq. 10).

$$E_{HF} = \langle \Phi_0 | H | \Phi_0 \rangle = \sum_i^N \langle i | h | i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \langle ii | jj \rangle - \langle ij | ji \rangle \quad (\text{Eq. 10})$$

The best spin orbitals, which minimize the energy, may be determined by means of the HF equation (Eq. 11).

$$f_i \varphi_i = \varepsilon_i \varphi_i \quad (\text{Eq. 10})$$

being f_i the Fock operator that can be defined as:

$$f_k = h_k + \sum_b J_b k - K_b k \quad (\text{Eq. 11})$$

In Eq. 11, the $h\ k$ term includes the kinetic energy and the attractive electron-nucleus potential, $J_b\ k$ represents the Coulomb operator that defines the electron-electron repulsion energy, and $K_b\ k$ corresponds to the exchange operator that defines the electron exchange energy.

The Hartree-Fock method is also named as Self-Consistent Field (SCF) method, in which a set of spin orbitals is required to start the progression of solving the Fock equations. This process sequentially obtains a new set of orbitals until the coefficients represented in Eq. 8 have the minimum associated energy. The main limitation that this method has is the lack of accuracy for most chemical systems, which is due to the fact that the average potential cannot describe the correlation of electronic motion. As this correlation needs to be included to obtain successful results, the so-called *post-HF methods* were proposed.

This modification resulted in that the true wavefunction of a multi-electron system is never a unique Slater determinant. The correlation energy (E_{corr}) is defined as the difference between the exact non-relativistic Born-Oppenheimer energy for a particular basis set and the HF expression (Eq. 12).

$$E_{corr} = E_{exact} - E_{HF} \quad (\text{Eq. 12})$$

Aside from that, the accuracy of the results is strongly linked to the basis function employed for the calculation, as the real form of the molecular orbital is unknown. Therefore, the HF solution will be closer to the exact numerical single-electron value when more complete basis functions are employed. The most common approaches consist in combining the Slater-type orbitals (STO, e^{-r}) or Gaussian-type orbitals (GTO, e^{-r^2}) relying on r , which is the distance of the electron to the atomic nucleus.

Mathematically speaking, GTOs allow the addition of the quadratic dependence of r in the exponential part (**Figure 46**). Such a modification implies that GTOs cannot correctly describe electrons near from the nucleus (while STOs can) and, as a result of that, the wavefunction is not properly described at long distances from the nucleus. However, the positive aspect of GTOs is that their integrals can be easily and efficiently computed because the analytical expressions for all the entailed integrals are known.

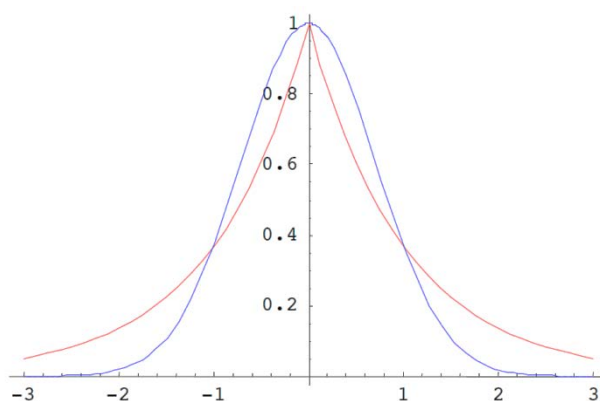


Figure 46. Graphical representation of a STO (red) and a GTO (blue)

7.3.3. The Density Functional Theory

Density Functional Theory (DFT) methods represent an alternative to the HF approach. Though being another *ab initio* methodology, DFT is based on expressing the total energy in terms of total electron density instead of wavefunctions. This theory provides us with very accurate results and, at the same time, it requires a moderate computational cost and can, therefore, be applied to large systems to predict their properties.

Contrary to the post-HF methodologies, DFT is not based on multi-electron wavefunctions, which can become extremely complicated, but on electron density. While the HF and post-HF multi-electron wavefunctions rely on $3N$ variables, electron density is only a function of three variables, allowing a much simpler mathematical treatment that makes it more practical. For DFT, the Schrödinger equation is not solved, but *Hohenberg-Kohn* (HK) theorem is applied. More concretely, two HK theorems have been postulated:

1. The first HK theorem establishes, in the first instance, that electronic density is the only determinant of the energy of a non-degenerate electronic ground state.¹²⁶ Actually, the Hamiltonian can be derived from the electron density and the energy and other observable properties of the system can be predicted from the electron density.
2. The second HK theorem represents the variational principle for DFT. Herein, it is stated that the energy of the system ($E[\rho]$) is a minimum (E_0) when the exact electronic density of the system (ρ_0) is taken into account (Eq. 13).

$$E_0[\rho_0] \leq E[\rho] \quad (\text{Eq. 13})$$

From here the variational equation can be deduced (Eq. 14).

$$\frac{\delta E}{\delta \rho} - \mu = 0 \quad (\text{Eq. 14})$$

In this context, μ is the electronic chemical potential given as the derivative of the energy E in front of the electronic density (ρ). From the mathematical point of view, μ is a Lagrange multiplier to normalize the electronic density (Eq. 15).

$$\int dr \rho(r) = N \quad (\text{Eq. 15})$$

The implementation of DFT can be carried out by means of the Kohn-Sham (KS) method.¹²⁷ KS is based on a self-consistent methodology similar to SCF for the HF theory. Similarly to the latter, the KS orbitals can be expanded in a set of basis functions (Eq. 16).

$$\varphi_i = \sum_k^M c_{ki} \chi_k \quad i = 1, 2, \dots, M \quad (\text{Eq. 16})$$

Turning our attention to the calculation of kinetic energy, a reference state formed by a system of N non-interacting electrons has to be considered. Thereby, most of the kinetic energy value can be computed with good accuracy. The remaining energy is merged with the non-classical contributions to the electron-electron repulsion, which are not known. Thanks to this method, most of the energy is exactly computed, leaving only a small part to be determined by an approximate functional.

To sum up, the key point in KS theory is the calculated kinetic energy considering that electrons are not interacting among them. Although electrons are actually interacting and thus the concept does not allow the obtaining of the total kinetic energy, the error committed at this point is small.

A partial way to correct the electron kinetic energy value is by separating it in two contributions: the exchange-correlation term and a general DFT energy expression (Eq. 17).

$$H_\lambda = T + V_{ext} + \lambda V_{ee} \quad (\text{Eq. 17})$$

In the previous expression, T is the kinetic energy, V_{ee} is the Coulomb repulsion and λ is a coupling parameter ranging from 0 to 1, meaning that it is a non-interacting system or an interacting system, respectively. The external potential (V_{ext}) corresponds to the electron-nuclear attraction ($V_{ext}(\lambda)$) for the interaction of one electron ($\lambda = 1$). Since the Born-Oppenheimer approximation is taken into account, the repulsion potential between nuclei is calculated aside and can be simply added to the final expression of

the energy. Last, the electronic correlation can be divided into the Coulomb and exchange parts (Eq. 18).

$$E[\rho] = T_s[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \quad (\text{Eq. 18})$$

Where $T_s[\rho]$ is the kinetic energy functional for non-interacting electron systems, $E_{ne}[\rho]$ includes the electron-nucleus interaction and $J[\rho]$ is the classical Coulomb repulsion of the electron cloud. $E_{xc}[\rho]$ represents the exchange-interaction energy functional that entails non-classical effects of the electronic correlation. This last term involves contributions to the potential energy of the system, though it also contains a part that corresponds to the kinetic energy difference $T[\rho] - T_s[\rho]$.

Therefore, the energy functional can adopt the developed form of Eq. 19.

$$E[\rho] = T_s[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] \quad (\text{Eq. 19})$$

When the variational principle is introduced to the previous equation, the effective Kohn-Sham potential ($v_{eff}(\mathbf{r})$) can be obtained (Eq. 20 and Eq. 21).

$$v_{eff}(\mathbf{r}) + \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = \mu \quad (\text{Eq. 20})$$

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (\text{Eq. 21})$$

The Hamiltonian for non-interacting system can be obtained with the kinetic energy operator and the effective KS potential (Eq. 22).

$$H_s = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 + v_{eff}(\mathbf{r}) \right) \varphi_i \quad (\text{Eq. 22})$$

So, the equation to be solved becomes:

$$-\frac{1}{2} \nabla_i^2 \varphi_i + v_{eff}(\mathbf{r}) \varphi_i = \epsilon_i \varphi_i \quad (\text{Eq. 23})$$

Having found the different contributions to this equation, the effective KS potential can be introduced into the one-particle equations, which define the orbitals and the ground state density and energy. The solution of H_s forms the set of the orbitals φ_i , the electronic density of which is exact.

Analogously to SCF, KS procedure introduces an initial guess for the orbitals φ_i and starts solving Eq. 23 iteratively. At the end, the DFT energy is obtained. It is important to notice that the exact total energy cannot be known because the exchange-correlation $E_{xc}[\rho]$ functional is undetermined.

As a whole, the DFT methodology affords very successful and reliable results by requiring a significantly lower computational cost than HF.

The *Local Density Approximation* (LDA) states that, from a local point of view, density can be understood as a uniform electron gas and, thus, density is a slowly varying function. Slater proposed the first LDA method, named as X_α method,¹²⁸ in which the correlation contribution is neglected and the exchange term is given by Eq. 24.

$$\epsilon_x^{LDA} \rho r = -\frac{9}{4}\alpha \frac{3}{4\pi} \rho r^{\frac{1}{3}} \quad (\text{Eq. 24})$$

The previous expression adopts a slightly modified form for spin polarized systems, as α and β electrons are considered to be independent one from the other. Therefore, the *Local Spin Density* (LSD) is depicted as Eq. 25.

$$\epsilon_x^{LDA} \rho r = -\frac{9}{4}\alpha \frac{3}{4\pi} \rho_\alpha r^{\frac{1}{3}} + \rho_\beta r^{\frac{1}{3}} \quad (\text{Eq. 25})$$

With regards to the correlation part, Vosko, Wilk and Nusair (VWN)¹²⁹ later proposed Eq. 26.

$$\epsilon_{xc}^{LDA} \rho r = \rho r \epsilon_x^{LSD} \rho r + \epsilon_c^{LSD} \rho r \quad (\text{Eq. 26})$$

LDA approximation assumes that the exchange-correlation effects are local and rely exclusively on the value of electron density at each point. LDA approach usually works well for all types of systems, though the simplicity of its base model. The main drawback of LDA is that results are rather poor for systems bearing weak bonds like hydrogen bonds. So, these methodologies tend to overestimate the bond energy by 30%.¹³⁰ In order to circumvent this weakness, LDA approach can be improved by considering a non-uniform electron gas. To do so, the exchange and correlation energies are made dependent on electron density and derivatives of density. The resulting method is named as *Gradient-Corrected* or *Generalized Gradient Approximation* (GGA) methods.

Perdew and Wang¹³¹ took into account local density and their local gradients. The resulting approach (Eq. 27) is known as PW86.

$$E_{xc}^{GGA} \rho = \int dr f^{GGA} \rho_\sigma, \nabla \rho_\sigma \quad \sigma = \alpha, \beta \quad (\text{Eq. 27})$$

f^{GGA} can be obtained in different ways, among them:

- Through a exchange density functional (B or B88) proposed by Becke,¹³² which introduced a parameter chosen using a least-squares fit to the exact HF exchange energy of noble gases. Such an exchange functional is often employed with the correlation functional proposed by Lee, Yang and Parr,^{64b} thus obtaining the *BLYP* functional.
- Through the gradient correction proposed by Perdew,¹³³ known as *BP86* used in conjunction with Becke exchange functional.¹³²

The use of GGA provides us with successful results for most molecular systems and ground state energies. However, more advanced functionals have been developed, like hybrids and meta-GGA functionals, which include the gradient of the density, the Laplacian (second derivative) of the density and the KS orbital kinetic energy density for electrons of spin σ (τ_σ) (Eq. 28).

$$E_{xc}^{mGGA} \rho = \int dr f^{mGGA} \rho_\sigma, \nabla \rho_\sigma, \nabla^2 \rho_\sigma, \tau_\sigma \quad \sigma = \alpha, \beta \quad (\text{Eq. 28})$$

Focusing on the work presented in this thesis, a hybrid exchange-correlation functional has been employed. It is a linear combination of the HF exchange (E_x^{HF}) and any other one, or combination of exchange and correlation functionals. The parameters that define the proportion of each functional can be randomly assigned and are usually fitted to reproduce well some set of observables like bond distances, ionization potentials, electron affinities or band gaps, among others. Herein, B3LYP⁶⁴ (Becke, three parameter, Lee-Yang-Parr) exchange-correlation functional is the following:

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0 E_x^{HF} - E_x^{LDA} + a_x E_x^{GGA} - E_x^{LDA} + a_c E_c^{GGA} - E_c^{LDA} \quad (\text{Eq. 29})$$

In Eq. 29, a_0 , a_x and a_c are the three empirical parameters and their values are 0.20, 0.72 and 0.81, respectively. E_c^{GGA} refers to the generalized gradient approximation introduced by Becke 88 exchange functional¹³² and the correlation functional of Lee, Yang and Parr.^{64b} Finally, E_c^{LDA} corresponds to the VWN correlation functional.

7.3.4. Basis functions

The most widespread basis sets were developed by Dunning and co-workers¹³⁴ and were designed to systematically converge to the complete basis set limit by means of extrapolation techniques. The basis sets for first- and second-row atoms are *cc-pVNZ*. In this notation, “cc-p” stands for “correlation consistent polarized”, “V” refers to the fact that only the valence has splitted basis functions, and “N” can be D (double), T (triple),

Q (quadruple), etc. Following this series, shells of polarization (correlating) functions (d, f, g, etc.) are successively included. The most common basis sets are cc-pVDZ (double-zeta), cc-pVTZ (triple-zeta), cc-pVQZ (quadruple-zeta), cc-pV5Z (quintuple-zeta) or aug-cc-pVNZ (augmented version of the previous basis sets with added diffuse functions).

With regards to third-row atoms, the previous functions are not descriptive enough and further functions are required. These new functions are known as cc-pV(N+d)Z basis sets. When the studied system deals with large atoms, *pseudopotentials* (PP) are needed, thus generating the cc-pVNZ-PP basis sets.

The use of pseudopotentials for third-row (or higher) atoms is due to the large number of core electrons. These electrons often exert a regardless effect on the global system, but they have to be taken into account because, otherwise, the valence orbitals would not be correctly described due to the lack of some electron-electron repulsions. The use of a large number of basis functions to expand the corresponding orbitals makes it possible to consider the mentioned internal electrons. At this point, pseudopotentials, initially introduced by Hellmann¹³⁵ and also known as Effective Core Potentials (ECP), allow the practical introduction of these corrections.

To sum up, it can be said that pseudopotentials represent a way to replace the complex effects of internal electrons of an atom and its nucleus by an effective potential, thus simplifying the Schrödinger equation.

Looking at the outcome of the use of pseudopotentials, better results can be obtained when the orbitals in the next lower shell in the valence space are explicitly treated and are not included in the pseudopotential. The improvement is more significant for systems bearing heavy atoms, especially those where relativistic effects are important.

Another sort of commonly-used basis set is the *split-valence* type. These can include two (double-zeta), three (triple-zeta) or more functionals to describe the valence orbitals. The most common ones are 6-31G (double-zeta) and 6-311G (triple-zeta) basis sets.

In addition to that, further polarization functions can be included in the previous basis sets. This means that some angular momentum functions, which are higher than the valence level, can be added. The main basis sets of this type are 6-31G(d) (or 6-31G*, involving the addition of *d* functions to all atoms but hydrogen) and 6-31G(d,p) (or 6-31G**, involving the addition of *d* functions to all atoms and a *p* function to hydrogen).

7.3.5. Geometry optimisation

With the aid of all the theoretical fundamentals explained in the previous subsections, the most stable geometry of a specific molecule can be computed. The process to do so essentially consists in a series of iterations that gradually modify the geometry of the molecule until the energy of the system cannot become lower, that is to say, it has been minimized. These minimum-in-energy points, known as *stationary points*, can be classified into actual minima or saddle-points, which describe the so-called *Potential Energy Surfaces* (PES) of a studied reaction (**Figure 47**).

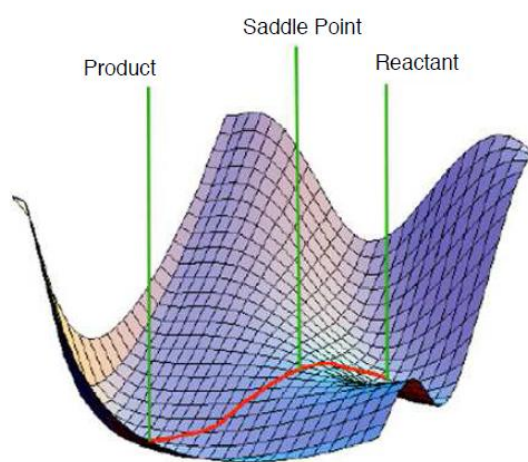


Figure 47. Graphical representation of a three-dimensional Potential Energy Surface

The location of a minimum or saddle-point requires the first derivatives of the energy with respect to the coordinates system, which is known as the *gradient*. A structure is considered to be optimised when the gradient is null, which implies that a stationary point has been found.

The minimization of the energy can be carried out throughout several numerical methods. One of the first algorithms to do so is the *steepest-descent* method, which mainly consists in repeatedly calculating the gradient of the function ($\nabla f \ x_n$) and taking a fixed step (x_{n+1}) in the opposite direction of it (Eq. 30).

$$x_{n+1} = x_n - k_n \nabla f \ x_n \quad (\text{Eq. 30})$$

This approach represents a safe strategy to reach the minimum, as convergence is ensured (**Figure 48**). It is relatively cheap in terms of computational cost, and can be easily implemented. However, its main drawback is that it becomes very slow when it is close to the minimum. Furthermore, it cannot be applied to noisy functions because it always converges to the nearest local minimum.

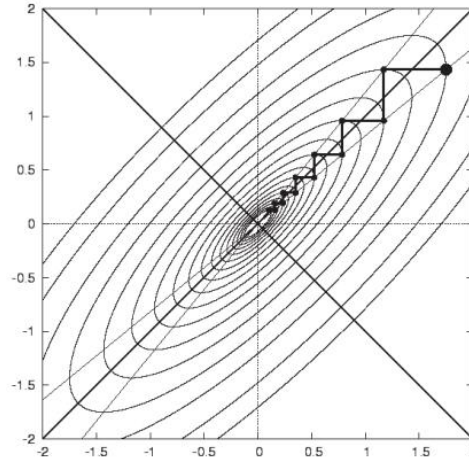


Figure 48. Graphical evolution of the steepest-descent method

An intrinsic factor that makes the steepest-descent approach a relatively inefficient methodology is the zigzag movement that it performs to reach the minimum. In an attempt to avoid so, the *conjugate gradients* method takes into account the gradient values in previous points ($\nabla f x_{n-1}$) to assess which direction is the most suitable for the following step (Eq. 31).

$$x_{n+1} = x_n - k_n h_n = x_n - k_n \nabla f x_n + \gamma_n h_{n-1} \quad (\text{Eq. 31})$$

Herein, the *Fletcher-Reeves* method (Eq. 32) supplies the required information regarding the gradient history.

$$\gamma_n = \frac{\nabla f x_n^2}{\nabla f x_{n-1}^2} \quad (\text{Eq. 32})$$

The conjugate gradients method does not evolve by drawing the zigzag patterns of the steepest-descent method, but moves in a more straightforward way to the minimum (**Figure 49**). Nevertheless, the approach becomes rather slow when non-linear functions are treated.

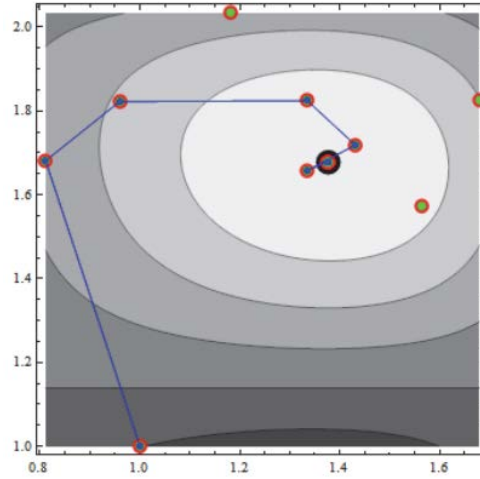


Figure 49. Graphical evolution of the conjugate gradients method

The *Newton-Raphson* method is a more sophisticated numerical approach to perform the minimization of energy. It approximates the function by a quadratic surface at each step, and moves to the minimum of that surface (Eq. 33).

$$f(x + \Delta x) \approx f(x) + \nabla f(x)^T \Delta x + \frac{1}{2} \Delta x^T \mathbf{H} \Delta x \quad (\text{Eq. 33})$$

From here, it can be extracted that:

$$\nabla f(x + \Delta x) = \nabla f(x) + \mathbf{H} \Delta x \quad (\text{Eq. 34})$$

Considering the case in which $\nabla f(x + \Delta x)$ is established to be zero to locate a minimum or saddle-point, Δx is related to the Hessian matrix ($\mathbf{H}$) through:

$$\Delta x = -\mathbf{H}^{-1} \nabla f(x) \quad (\text{Eq. 35})$$

The application of the Newton-Raphson methodology results in a very fast convergence (**Figure 50**), especially if Hessians are cheap. However, the Newton-Raphson approach is computationally expensive and, in addition to that, it cannot be used with noisy functions because it tends to converge to the nearest local minimum.

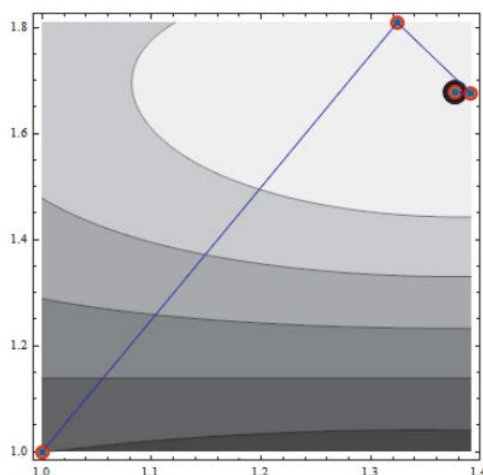


Figure 50. Graphical evolution of the Newton-Raphson method

Since the main drawback of the Newton-Raphson method is the expensive calculation of the Hessian, the latter can be approximated from the gradient history by means of the so-called *Broyden-Fletcher-Goldfarb-Shanno* (BFGS) update (Eq. 36).

$$\mathbf{H}_{k+1} = \mathbf{H}_k + \frac{g_k g_k^T}{g_k^T s_k} - \frac{\mathbf{H}_k s_k \mathbf{H}_k s_k^T}{s_k^T \mathbf{H}_k s_k} \quad (\text{Eq. 36})$$

where

$$g_k = \nabla f(x_{k+1}) - \nabla f(x_k) \quad (\text{Eq. 37})$$

$$s_k = x_{k+1} - x_k \quad (\text{Eq. 38})$$

The resulting method is named as a *quasi-Newton* method and gives a very rapid linear convergence at the expensiveness of the steepest-descent method. The initial Hessian is often computed through inexpensive methods based on molecular mechanics or semi-empirical approaches.

Furthermore, the calculation of the Hessian derivative (the second derivative of energy with respect to the coordinates system) allows the differentiation between a *minimum* (reactant, product and intermediates) and a *saddle-point* (transition state or TS) when the Hessian becomes positive or negative, respectively. Therefore, a TS geometry is observed as a maximum along the reaction coordinate and a minimum in the other orthogonal directions (**Figure 51**).

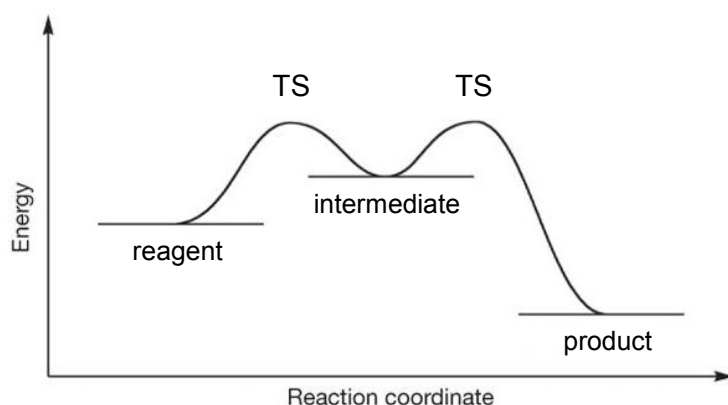


Figure 51. Graphical representation of three minima and two transition states along the reaction coordinate

When optimising a transition state geometry, Eq. 35 is employed as well, with the difference that a negative eigenvalue needs to be located.

Once the optimisation of the geometry is attained, several geometrical properties can be analysed, like the bond distances, bond angles and dihedral angles. Due to the existence of populated vibrational and rotational states for each electronic state, the previous properties do not remain equal (**Figure 52**). The optimised geometry displays the average values of distances and angles resulting from the equilibrium of bond distances. Therefore, the minimum located is a representation of several molecular geometries that remain in equilibrium among them.

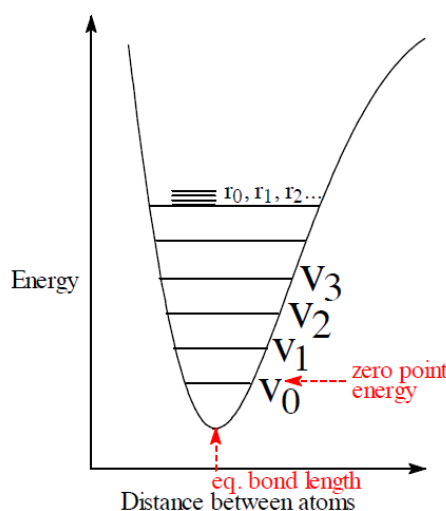


Figure 52. Representation of the equilibrium of a bond distance. V (vibrational state) and r (rotational state) are populated for each electronic state

7.3.6. Thermodynamic properties

Having reached the optimal structures, either being an actual minimum or a transition state, the key thermodynamic data can be calculated.

The thermodynamic functions of enthalpy (ΔH), entropy (ΔS) and Gibbs energy (ΔG) can be predicted within the ideal approximation. If temperature is assumed to be 298K and the pressure remaining at 1 atm, the Gibbs energy can be obtained through Eq. 39.

$$\Delta G_{298} = \Delta H_{298} - T\Delta S_{298} \quad (\text{Eq. 39})$$

The obtaining of the Gibbs energy values for the different geometries along a reaction pathway makes it possible to obtain remarkable reaction data that inform about the feasibility of the process. Eq. 40 represents the reaction energy, which indicates whether a process will spontaneously take place ($\Delta G^0 < 0$), will remain in equilibrium ($\Delta G^0 \approx 0$) or will not spontaneously occur ($\Delta G^0 > 0$).

$$\Delta G^0 = G_{products}^0 - G_{reactant}^0 \quad (\text{Eq. 40})$$

On the other hand, the *activation energy* or *energy barrier* ($\Delta G^\ddagger$, Eq. 41) can be defined as the necessary amount of Gibbs energy so that a particular reaction takes place by surpassing the transition state that separates two minima.

$$\Delta G^\ddagger = G_{transition\ state}^\ddagger - G_{reactant}^0 \quad (\text{Eq. 41})$$

7.3.7. Analysis of the binding energy

According to the activation strain model (ASM)⁶⁹ or distortion/interaction model,¹³⁶ the amount of energy required to establish a bond, known as *bonding energy* (ΔE_{total}), can be separated into two contributions (Eq. 42): the *strain energy* (ΔE_{strain}), which is associated to the deformation exerted on the individual reactants, and the *interaction energy* (ΔE_{int}) between the deformed reactants.

$$\Delta E_{total} = \Delta E_{strain} + \Delta E_{int} \quad (\text{Eq. 42})$$

More concretely, the strain energy depends on the rigidity of the reactants and on the extent of which groups need to be rearranged in the studied reaction mechanism. On the other hand, the interaction energy arises from the electronic nature of the orbitals and how they approach each other in the course of the reaction.

Since the magnitudes of ΔE_{strain} and ΔE_{int} determine the increase (or decrease) of a particular energy barrier, the activation energy of a reaction ($\Delta E_{total}^{\ddagger}$) can be split as well into the strain activation energy ($\Delta E_{strain}^{\ddagger}$) and the TS interaction energy ($\Delta E_{int}^{\ddagger}$) (Eq. 43).

$$\Delta E_{total}^{\ddagger} = \Delta E_{strain}^{\ddagger} + \Delta E_{int}^{\ddagger} \quad (\text{Eq. 43})$$

Focusing on the interaction energy between the strained reactants, a deeper understanding can be gained by analysing the conceptual framework provided by the Kohn-Sham molecular orbital (KS-MO) model,¹³⁷ since ΔE_{int} can be decomposed into three contributions (Eq. 44).

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} \quad (\text{Eq. 44})$$

where:

- ΔE_{elstat} states for the classical electrostatic interaction between the unperturbed charge distributions of the deformed reactants.
- ΔE_{Pauli} corresponds to the destabilizing interactions between occupied orbitals and is responsible of any steric repulsion.^{137a} It usually acquires a positive value.
- ΔE_{oi} refers to the orbital interaction and accounts for charge transfer (interaction between occupied orbitals on one moiety with unoccupied orbitals of the other, including HOMO-LUMO interactions), polarization (empty-occupied orbital mixing on one fragment caused by the presence of another fragment), and bond pairs formation (interaction with two singly-occupied molecular orbitals in each fragment).

As a whole, considering that DFT methodologies provides us with relatively accurate energetic values, the analysis carried out by finding the different energetic contributions represent a practical way to understand the energetic demand of the chemical reactions.

7.3.8. Solvent effects

Since chemical systems are generally located in a solvation framework, solvent effects might be taken into account from the theoretical point of view. In the previous subsections, all calculations were performed at the gas phase and, therefore, the

results might not be representative and accurate enough to predict the behaviour of a particular system.

A straightforward strategy to compute the effect of the solvent is by directly including the discrete solvent molecules in the system. However, this approach is rather tedious, since the size of the system is not voluminous enough to fully include the solvation model and, on the other hand, the associated computational costs would be too high.

Considering the previous drawbacks, several alternative methodologies have been devised. One of the most widely used is the use of *continuum solvation models*, which provoke the decrease of the number of degrees of freedom associated to the molecules of a solvent.¹³⁸ An example of that is the *polarizable continuum model* (PCM)¹³⁹, which essentially consists in placing a cavity around the solute molecule, which interacts with the solvent through a dielectric (**Figure 53**). From the physical point of view, the charge distribution of the solute provokes the polarization of the dielectric medium. As a result of that, the model generates point charges, which can be computed relying on the simpler boundary condition for the conductor that depends on the dielectric constant (ϵ_s) of the solvent being employed. This implies that the polarizability of the continuum material is strongly linked to the dielectric constant.

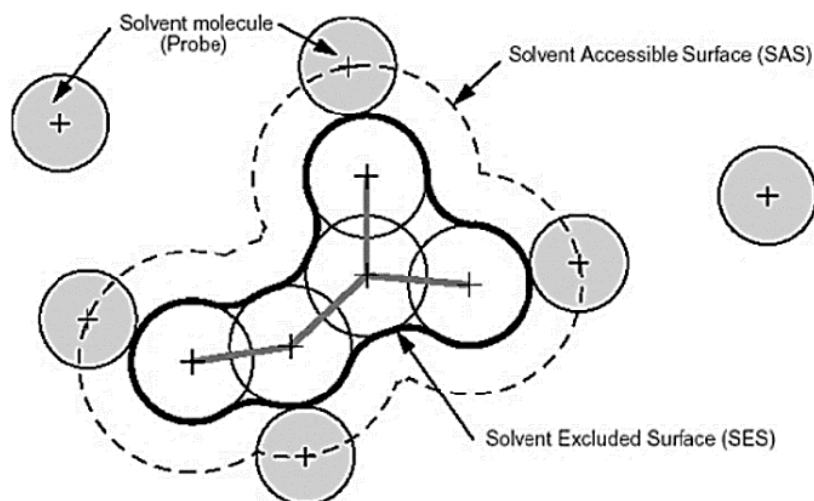


Figure 53. Representation of the solvation model¹⁴⁰

7.3.9. Practical computational details

All geometry optimisations in the present thesis were performed without symmetry constraints using the hybrid DFT B3LYP⁶⁴ method with the all-electron cc-pVDZ basis set for P, Cl, O, C, and H⁶⁵ and the cc-pVDZ-PP basis set containing an effective core relativistic pseudopotential for Rh.⁶⁶ 6-31G(d,p) basis set was also employed for some optimisations in conjunction with LANL2DZ pseudopotentials. The D3 Grimme energy corrections for dispersion with its original damping function⁶⁷ were added in all B3LYP/cc-pVDZ-PP and B3LYP/6-31G(d,p) calculations. When found appropriate, single-point energy calculations were carried out with the B3LYP-D3/cc-pVTZ method. Analytical Hessians were computed at the B3LYP-D3/cc-pVDZ and B3LYP-D3/6-31G(d,p) levels of theory to determine the nature of stationary points (one or zero imaginary frequencies for transition states and minima, respectively) and to calculate unscaled zero-point energies (ZPEs) as well as thermal corrections and entropy effects by using the standard statistical-mechanics relationships for an ideal gas.¹⁴¹ Different temperatures were computed for the several studied systems, always under 1 atm to obtain the reported relative Gibbs energies. Furthermore, the connectivity between stationary points was established by intrinsic reaction path calculations.¹⁴²

All calculations were performed with the Gaussian 09⁶³ program package. When considered appropriate, solvent effects were taken into account with a polarized continuum model (PCM).⁶⁸ In the case of including solvent effects, the change from 1 atm pressure to 1 M on the reference system has been corrected by adding 1.89 kcal·mol⁻¹ on the entropic contribution to calculate the Gibbs energy values.

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Annex 1

XYZ coordinates of the catalytic intermediates for the rhodium-catalysed [2+2+2] cycloaddition involving C(sp²) unsaturations

PPh₃

G = -1036.37210

15	0.000797000	0.001524000	-1.274155000
6	1.578547000	0.526451000	-0.439168000
6	2.781904000	0.063941000	-1.001253000
6	1.636309000	1.349119000	0.697783000
6	4.012048000	0.398345000	-0.430428000
1	2.753404000	-0.567061000	-1.893949000
6	2.869175000	1.693798000	1.261367000
1	0.714084000	1.722313000	1.146776000
6	4.058764000	1.217312000	0.702737000
1	4.937177000	0.025386000	-0.876509000
1	2.898247000	2.336165000	2.145035000
1	5.020306000	1.486963000	1.145802000
6	-1.243590000	1.104328000	-0.438900000
6	-1.992940000	0.737365000	0.690926000
6	-1.439143000	2.381519000	-0.994562000
6	-2.910549000	1.630584000	1.253653000
1	-1.859534000	-0.250715000	1.135082000
6	-2.346479000	3.277339000	-0.424465000
1	-0.872125000	2.677121000	-1.881693000
6	-3.087215000	2.902582000	0.701545000
1	-3.487687000	1.330052000	2.131677000
1	-2.481879000	4.267747000	-0.865752000
1	-3.803683000	3.598758000	1.143802000
6	-0.333030000	-1.628203000	-0.440373000
6	-1.345379000	-2.432365000	-0.994271000
6	0.360828000	-2.097305000	0.687134000
6	-1.670121000	-3.665668000	-0.424808000
1	-1.886178000	-2.086245000	-1.879502000
6	0.043416000	-3.338212000	1.249232000
1	1.152878000	-1.491171000	1.130495000
6	-0.973623000	-4.123458000	0.698760000
1	-2.463438000	-4.274938000	-0.864596000
1	0.593431000	-3.690468000	2.125443000
1	-1.220495000	-5.091592000	1.140755000

acetylene

G = -77.35714

6	0.000000000	0.000000000	0.605026000
6	0.000000000	0.000000000	-0.605026000
1	0.000000000	0.000000000	1.677682000
1	0.000000000	0.000000000	-1.677682000

ethylene

G = -78.59475

6	0.000000000	0.000000000	0.666800000

6	0.000000000	0.000000000	-0.666800000
1	0.000000000	0.931579000	1.241507000
1	0.000000000	-0.931579000	1.241507000
1	0.000000000	0.931579000	-1.241507000
1	0.000000000	-0.931579000	-1.241507000

imine

$G = -94.65446$

6	0.586145000	0.028778000	-0.000001000
1	1.247974000	-0.852984000	0.000171000
1	1.097623000	1.010997000	-0.000107000
7	-0.671652000	-0.154840000	-0.000047000
1	-1.160905000	0.753197000	0.000270000

formaldehyde

$G = -114.54748$

6	-0.526813000	0.000000000	0.000034000
8	0.677420000	0.000002000	-0.000009000
1	-1.129255000	0.945260000	-0.000068000
1	-1.129227000	-0.945273000	-0.000068000

allene

$G = -116.67771$

6	-1.310263000	-0.000081000	0.000051000
1	-1.877442000	0.743172000	0.569163000
1	-1.877465000	-0.743140000	-0.569329000
6	-0.000006000	0.000145000	-0.000090000
6	1.310290000	0.000054000	0.000055000
1	1.877065000	-0.569813000	0.742934000
1	1.877720000	0.569073000	-0.742863000

carbon disulfide

$G = -834.58862$

6	0.000000000	0.000000000	0.000000000
16	0.000000000	0.000000000	1.569801000
16	0.000000000	0.000000000	-1.569801000

carbodiimide

$G = -148.83077$

6	0.000000000	0.000000000	0.000000000
7	0.000000000	1.221485000	0.000000000
1	0.793442000	1.847043000	0.000000000
7	0.000000000	-1.221485000	0.000000000
1	-0.793442000	-1.847043000	0.000000000

carbon dioxide

$G = -188.67087$

6	0.000000000	0.000000000	0.000000000
8	0.000000000	0.000000000	1.167521000
8	0.000000000	0.000000000	-1.167521000

cycloadduct 2 acetylenes + ethylene

$G = -233.41884$

6	0.726328000	0.251401000	-1.192926000
6	-0.726328000	-0.251401000	-1.192926000
6	-1.425826000	0.063358000	0.109747000
6	-0.726328000	0.107835000	1.259395000
6	0.726328000	-0.107835000	1.259395000
6	1.425826000	-0.063358000	0.109747000
1	0.737113000	1.352706000	-1.333338000
1	-1.275728000	0.171650000	-2.049038000
1	-2.512563000	0.186483000	0.111640000
1	-1.231143000	0.282854000	2.213442000
1	1.231143000	-0.282854000	2.213442000
1	2.512563000	-0.186483000	0.111640000
1	1.275728000	-0.171650000	-2.049038000
1	-0.737113000	-1.352706000	-1.333338000

cycloadduct 2 acetylenes + imine

$G = -94.65446$

6	-0.930436000	-1.102088000	-0.058028000
6	-1.429091000	0.254172000	0.126602000
6	-0.539699000	1.273217000	0.000542000
6	1.377335000	-0.237373000	0.202888000
6	0.394464000	-1.351670000	-0.089501000
1	-0.845570000	2.322528000	-0.002272000
1	-2.491841000	0.457586000	0.249684000
1	-1.646531000	-1.913362000	-0.217592000
1	2.325821000	-0.394123000	-0.336702000
1	1.629773000	-0.218814000	1.292663000
1	0.785641000	-2.356323000	-0.264486000
7	0.799122000	1.035358000	-0.235314000
1	1.413424000	1.837451000	-0.169117000

cycloadduct 2 acetylenes + formaldehyde

$G = -269.35278$

6	0.187935000	1.423183000	-0.059915000
6	1.313794000	0.516726000	0.145852000
6	1.097600000	-0.806873000	-0.017050000
6	-1.236347000	-0.541960000	0.227513000
6	-1.059924000	0.920237000	-0.092217000
1	1.887679000	-1.560649000	-0.060603000
1	2.326514000	0.887254000	0.301807000
1	0.380542000	2.481918000	-0.251005000
1	-2.128892000	-0.972641000	-0.247270000
1	-1.320820000	-0.699497000	1.325916000

1	-1.937784000	1.530465000	-0.314955000
8	-0.128198000	-1.341841000	-0.247373000

cycloadduct 2 acetylenes + allene

G = -271.52226

6	-1.848062000	0.050095000	-0.104874000
6	-1.075561000	1.284541000	0.032998000
6	0.276897000	1.265525000	0.089707000
6	0.243795000	-1.281200000	0.159500000
6	-1.239964000	-1.149217000	-0.073304000
1	0.842415000	2.200266000	0.140762000
1	-1.611237000	2.236834000	0.056693000
1	-2.930538000	0.121366000	-0.237513000
1	0.668091000	-2.059017000	-0.497857000
1	0.384432000	-1.670322000	1.189306000
1	-1.818845000	-2.072132000	-0.169021000
6	2.373299000	0.015498000	-0.138380000
6	1.034466000	0.015996000	0.021947000
1	2.939675000	-0.915225000	-0.224440000
1	2.936790000	0.950793000	-0.183496000

cycloadduct 2 acetylenes + carbon disulfide

G = -989.39624

6	-2.287168000	0.393117000	0.000314000
6	-1.392613000	1.512153000	0.000247000
6	-0.025940000	1.418178000	0.000045000
6	-1.838674000	-0.891224000	0.000212000
1	0.574650000	2.330929000	0.000030000
1	-1.834208000	2.512116000	0.000366000
1	-3.363531000	0.576313000	0.000489000
1	-2.521492000	-1.745107000	0.000303000
6	0.743973000	0.199403000	-0.000186000
16	-0.159711000	-1.343790000	-0.000056000
16	2.406405000	0.127290000	-0.000256000

cycloadduct 2 acetylenes + carbodiimide

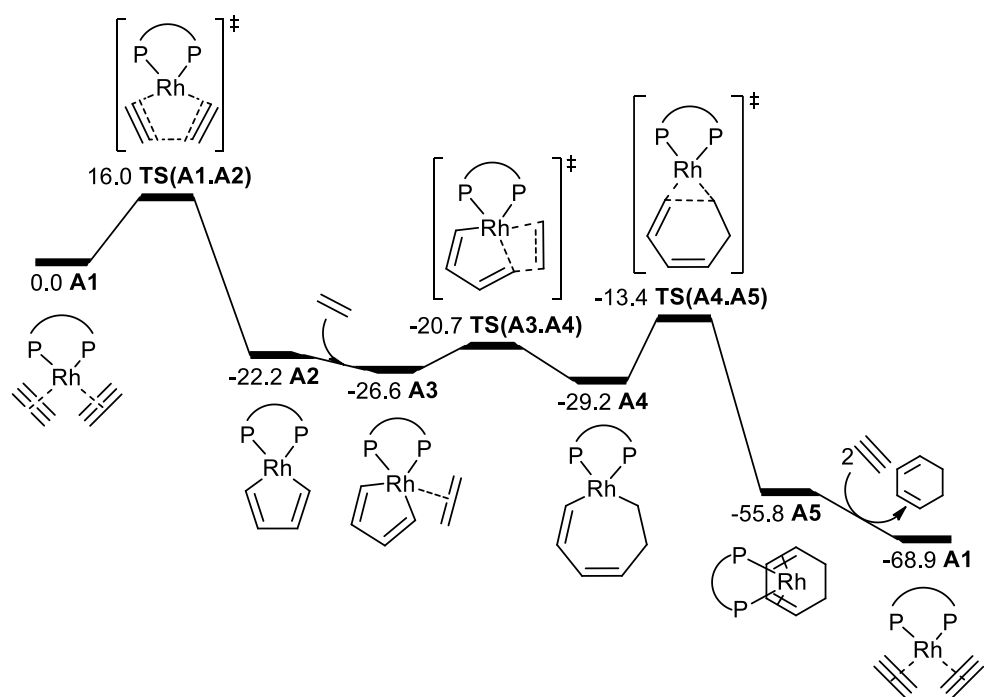
G = -303.67603

6	-1.829494000	-0.022499000	-0.000005000
6	-1.114449000	1.221437000	-0.000036000
6	0.249514000	1.254954000	0.000039000
6	-1.094370000	-1.173120000	-0.000045000
1	0.790031000	2.203599000	-0.000042000
1	-1.676747000	2.159077000	-0.000056000
1	-2.917270000	-0.058898000	-0.000100000
1	-1.543277000	-2.167777000	0.000263000
6	1.049918000	0.033814000	-0.000007000
7	0.267336000	-1.137814000	0.000175000
7	2.331036000	-0.122070000	-0.000018000
1	2.787741000	0.795184000	0.000045000
1	0.804202000	-1.999512000	-0.000886000

cycloadduct 2 acetylenes + carbon dioxide

$G = -343.45011$

6	-1.782052000	-0.055874000	0.000464000
6	-1.102967000	1.207802000	-0.000207000
6	0.257647000	1.257642000	-0.000419000
6	-1.023389000	-1.179493000	-0.000215000
1	0.813886000	2.195020000	-0.000505000
1	-1.684776000	2.133107000	0.000416000
1	-2.868588000	-0.127574000	0.001498000
1	-1.420330000	-2.196896000	0.000221000
6	1.063908000	0.047811000	0.000011000
8	0.320781000	-1.165590000	-0.000469000
8	2.264335000	-0.043283000	0.000540000



A1 (ethylene)

G = -1569.41773

6	1.988913000	1.098136000	0.001425000
6	2.976922000	1.859428000	0.647261000
6	2.776857000	3.206436000	0.953113000
6	1.570529000	3.822017000	0.612883000
6	0.584199000	3.090490000	-0.050395000
6	0.781687000	1.736760000	-0.378453000
1	3.910057000	1.368981000	0.931218000
1	3.559410000	3.770444000	1.464154000
1	1.396286000	4.871943000	0.854626000
1	-0.345424000	3.593826000	-0.315220000
6	2.277382000	-0.348972000	-0.245931000
6	3.356463000	-0.671239000	-1.084192000
6	1.528997000	-1.396217000	0.347714000
6	3.681468000	-1.998237000	-1.372291000
1	3.935268000	0.140440000	-1.529955000
6	1.868097000	-2.727436000	0.050179000
6	2.930013000	-3.029413000	-0.807195000
1	4.517984000	-2.223216000	-2.036355000
1	1.309184000	-3.551945000	0.493250000
1	3.172236000	-4.071983000	-1.021786000
15	0.044888000	-1.039581000	1.389021000
15	-0.582805000	0.846303000	-1.232969000
45	-1.872579000	-0.336834000	0.141422000
6	-2.994148000	-1.421594000	-1.301894000
6	-3.396206000	1.072603000	0.575928000
6	-1.961475000	-2.107300000	-1.026408000
6	-2.469698000	1.231178000	1.431248000
1	-3.931130000	-1.274308000	-1.825410000
1	-1.339378000	-2.980546000	-1.187863000
1	-4.360262000	1.329246000	0.153493000
1	-2.056894000	1.757999000	2.283983000

6	0.139988000	-0.120995000	-2.617696000
1	-0.689240000	-0.428183000	-3.270028000
1	0.844872000	0.517498000	-3.170873000
1	0.655373000	-1.013212000	-2.245794000
6	-1.571027000	2.128737000	-2.098011000
1	-2.090570000	2.767133000	-1.373557000
1	-0.919853000	2.731376000	-2.749005000
1	-2.322381000	1.600712000	-2.701680000
6	-0.329983000	-2.613755000	2.270601000
1	-0.704957000	-3.368701000	1.566503000
1	0.555537000	-2.995182000	2.801192000
1	-1.126605000	-2.399284000	2.998639000
6	0.625456000	0.045143000	2.764723000
1	-0.169090000	0.063336000	3.525990000
1	1.550468000	-0.351847000	3.208650000
1	0.797331000	1.067537000	2.405423000

TS(A1.A2) (ethylene)

G = -1569.39222

6	-2.274565000	-0.711873000	0.226233000
6	-3.342147000	-1.154545000	1.023120000
6	-3.391135000	-2.461510000	1.511379000
6	-2.362494000	-3.352490000	1.201813000
6	-1.304037000	-2.936958000	0.389792000
6	-1.248525000	-1.627085000	-0.116082000
1	-4.133968000	-0.447033000	1.277510000
1	-4.227588000	-2.778876000	2.136817000
1	-2.382396000	-4.375196000	1.582675000
1	-0.520795000	-3.656564000	0.152591000
6	-2.274366000	0.712321000	-0.226273000
6	-3.341765000	1.155267000	-1.023254000
6	-1.248122000	1.627269000	0.116116000
6	-3.390352000	2.462233000	-1.511550000
1	-4.133758000	0.447966000	-1.277693000
6	-1.303205000	2.937136000	-0.389824000
6	-2.361480000	3.352936000	-1.201944000
1	-4.226669000	2.779814000	-2.137060000
1	-0.519759000	3.656518000	-0.152605000
1	-2.381061000	4.375630000	-1.582855000
15	0.192483000	1.125120000	1.159035000
15	0.192277000	-1.125297000	-1.158920000
45	1.811241000	-0.000141000	-0.000022000
6	3.825408000	-0.198360000	-1.024891000
6	3.825441000	0.198103000	1.024896000
6	2.846494000	0.123266000	-1.789160000
6	2.846515000	-0.123615000	1.789108000
1	4.823884000	-0.620558000	-1.019696000
1	2.618968000	0.132833000	-2.851442000
1	4.823828000	0.620512000	1.019784000
1	2.618979000	-0.133522000	2.851383000
6	-0.517210000	-0.389797000	-2.695093000
1	0.275513000	-0.365232000	-3.456968000
1	-1.351380000	-1.009121000	-3.057072000

1	-0.866361000	0.632842000	-2.509661000
6	0.915516000	-2.703232000	-1.775019000
1	1.404857000	-3.246408000	-0.955408000
1	0.140839000	-3.331074000	-2.239967000
1	1.681151000	-2.446739000	-2.520965000
6	0.915962000	2.702882000	1.775319000
1	1.406332000	3.245547000	0.955984000
1	0.141188000	3.331263000	2.239371000
1	1.680775000	2.446234000	2.522057000
6	-0.517194000	0.389596000	2.695110000
1	0.275474000	0.364963000	3.457040000
1	-1.351353000	1.008953000	3.057056000
1	-0.866389000	-0.633016000	2.509623000

A2 (ethylene)

G = -1569.45313

6	2.170712000	0.751722000	-0.152923000
6	3.402211000	1.175395000	0.372725000
6	3.589320000	2.476651000	0.843109000
6	2.535104000	3.390168000	0.789902000
6	1.310891000	3.000095000	0.245057000
6	1.113955000	1.694013000	-0.243814000
1	4.220556000	0.454649000	0.426253000
1	4.556002000	2.772475000	1.255020000
1	2.663779000	4.408757000	1.160054000
1	0.508472000	3.736257000	0.195287000
6	2.072137000	-0.671700000	-0.610119000
6	2.835059000	-1.047894000	-1.727074000
6	1.291356000	-1.652112000	0.053052000
6	2.805099000	-2.353249000	-2.222031000
1	3.447881000	-0.291658000	-2.222267000
6	1.272790000	-2.962646000	-0.455031000
6	2.015056000	-3.311892000	-1.586808000
1	3.397482000	-2.617403000	-3.099949000
1	0.680427000	-3.735954000	0.033963000
1	1.980998000	-4.336939000	-1.960540000
15	0.213845000	-1.202814000	1.488045000
15	-0.547080000	1.265965000	-0.917499000
45	-1.649181000	0.142205000	0.665625000
6	-3.528403000	-1.138934000	-0.976165000
6	-4.177414000	0.136788000	-0.617389000
6	-2.251180000	-1.296823000	-0.582549000
6	-3.394820000	1.017300000	0.041581000
1	-4.053792000	-1.914041000	-1.546229000
1	-1.579984000	-2.118595000	-0.855810000
1	-5.219445000	0.328643000	-0.895185000
1	-3.742562000	2.019513000	0.329801000
6	-0.350172000	0.368969000	-2.506363000
1	-1.350514000	0.289147000	-2.954347000
1	0.320335000	0.946422000	-3.160304000
1	0.054308000	-0.635814000	-2.346001000
6	-1.312271000	2.853752000	-1.435848000
1	-1.592627000	3.460316000	-0.564854000

1	-0.615568000	3.411613000	-2.079053000
1	-2.226819000	2.603420000	-1.989570000
6	-0.328911000	-2.809398000	2.214059000
1	-1.037010000	-3.313987000	1.541821000
1	0.526616000	-3.468456000	2.425590000
1	-0.851382000	-2.584952000	3.156246000
6	1.339730000	-0.541982000	2.796358000
1	0.759469000	-0.450817000	3.727451000
1	2.185369000	-1.227022000	2.958638000
1	1.718163000	0.448589000	2.514318000

A3 (ethylene)

G = -1648.05484

6	2.130295000	1.011179000	-0.282683000
6	3.196189000	1.775789000	0.221867000
6	3.081286000	3.152939000	0.417033000
6	1.883962000	3.798309000	0.100541000
6	0.823087000	3.063030000	-0.429659000
6	0.930431000	1.675072000	-0.641537000
1	4.125262000	1.264685000	0.482181000
1	3.923832000	3.718119000	0.819880000
1	1.776365000	4.873777000	0.252364000
1	-0.094103000	3.592033000	-0.688821000
6	2.349952000	-0.463246000	-0.426574000
6	3.304252000	-0.890700000	-1.363607000
6	1.679472000	-1.430271000	0.363408000
6	3.574457000	-2.246534000	-1.558393000
1	3.827247000	-0.139958000	-1.959770000
6	1.966240000	-2.790981000	0.161205000
6	2.898437000	-3.200038000	-0.796347000
1	4.310784000	-2.554214000	-2.303097000
1	1.465026000	-3.555016000	0.755420000
1	3.098525000	-4.263916000	-0.936319000
15	0.392771000	-0.916649000	1.589255000
15	-0.538219000	0.787341000	-1.318389000
45	-1.601427000	-0.118028000	0.425400000
6	-2.706864000	-2.224098000	-1.185742000
6	-3.686576000	-1.135040000	-1.303139000
6	-1.569738000	-1.930864000	-0.526126000
6	-3.342288000	0.032595000	-0.725244000
1	-2.897570000	-3.211032000	-1.621963000
1	-0.748545000	-2.650768000	-0.434272000
1	-4.635547000	-1.283517000	-1.830751000
1	-3.991883000	0.913759000	-0.781173000
6	0.016007000	-0.331277000	-2.661045000
1	-0.889763000	-0.700331000	-3.161460000
1	0.641579000	0.240101000	-3.363232000
1	0.574652000	-1.182831000	-2.260705000
6	-1.492845000	2.053346000	-2.249671000
1	-1.969158000	2.778563000	-1.578667000
1	-0.823515000	2.574660000	-2.950012000
1	-2.280218000	1.521423000	-2.798806000
6	0.003754000	-2.429736000	2.569203000

1	-0.535964000	-3.161636000	1.953251000
1	0.915159000	-2.882939000	2.986950000
1	-0.655021000	-2.122767000	3.395758000
6	1.321493000	0.096384000	2.824621000
1	0.670387000	0.278354000	3.691989000
1	2.220454000	-0.446748000	3.151553000
1	1.616281000	1.059744000	2.390004000
6	-2.636215000	1.781823000	1.372212000
6	-1.541902000	1.556008000	2.159390000
1	-3.623536000	1.407870000	1.656026000
1	-2.624533000	2.534939000	0.582115000
1	-1.638177000	1.002871000	3.097899000
1	-0.609420000	2.103519000	2.009416000

TS(A3.A4) (ethylene)

G = -1648.04554

6	-2.432807000	0.815330000	-0.140829000
6	-3.518270000	1.278028000	-0.901751000
6	-3.552072000	2.579250000	-1.406843000
6	-2.491304000	3.447906000	-1.145428000
6	-1.415961000	3.014619000	-0.366358000
6	-1.371613000	1.707816000	0.153912000
1	-4.340476000	0.590398000	-1.110497000
1	-4.403870000	2.910569000	-2.003715000
1	-2.501384000	4.467513000	-1.535013000
1	-0.610762000	3.719261000	-0.157560000
6	-2.475124000	-0.596060000	0.354519000
6	-3.469071000	-0.925681000	1.289763000
6	-1.571943000	-1.600876000	-0.073095000
6	-3.554525000	-2.205054000	1.841297000
1	-4.170200000	-0.149181000	1.602543000
6	-1.666329000	-2.883942000	0.495333000
6	-2.640573000	-3.184449000	1.450981000
1	-4.328841000	-2.432005000	2.576427000
1	-0.980125000	-3.675279000	0.193793000
1	-2.688348000	-4.188152000	1.877400000
15	-0.218913000	-1.243176000	-1.281857000
15	0.120430000	1.183396000	1.111533000
45	1.558631000	0.066679000	-0.371485000
6	3.039930000	-0.872873000	1.877869000
6	3.649252000	0.409821000	1.638798000
6	2.011374000	-1.214344000	1.053848000
6	3.259410000	1.052330000	0.493058000
1	3.372555000	-1.540771000	2.679467000
1	1.418881000	-2.131333000	1.160200000
1	4.350555000	0.847610000	2.356998000
1	3.589763000	2.076545000	0.286934000
6	-0.444132000	0.331790000	2.644568000
1	0.430628000	0.264165000	3.307213000
1	-1.238988000	0.917201000	3.129214000
1	-0.801472000	-0.680687000	2.427340000
6	0.822164000	2.741179000	1.797505000
1	1.254599000	3.361424000	1.001277000

1	0.052014000	3.305518000	2.343563000
1	1.633699000	2.453588000	2.479818000
6	0.308353000	-2.902655000	-1.887922000
1	0.903566000	-3.423646000	-1.124987000
1	-0.558799000	-3.516428000	-2.172402000
1	0.942173000	-2.746606000	-2.772298000
6	-1.034343000	-0.537548000	-2.783040000
1	-0.286776000	-0.518688000	-3.590997000
1	-1.885056000	-1.165478000	-3.087163000
1	-1.383239000	0.485374000	-2.593363000
6	3.894396000	0.048708000	-1.198522000
6	2.868218000	-0.521666000	-1.995961000
1	4.546161000	-0.631487000	-0.648401000
1	4.363797000	0.979351000	-1.525791000
1	2.855715000	-1.608732000	-2.105670000
1	2.512890000	0.036320000	-2.872867000

A4 (ethylene)

G = -1648.05897

6	-2.234464000	1.172540000	0.312205000
6	-3.333674000	1.939168000	-0.109141000
6	-3.183769000	3.257677000	-0.542110000
6	-1.914970000	3.840485000	-0.557721000
6	-0.813833000	3.107792000	-0.113243000
6	-0.954359000	1.781709000	0.341097000
1	-4.321153000	1.473442000	-0.113139000
1	-4.055978000	3.824638000	-0.872920000
1	-1.779835000	4.866992000	-0.902932000
1	0.164030000	3.590167000	-0.114586000
6	-2.493547000	-0.242764000	0.722596000
6	-3.278810000	-0.460779000	1.864960000
6	-2.009385000	-1.357930000	-0.006868000
6	-3.555981000	-1.751624000	2.319488000
1	-3.660518000	0.403682000	2.412491000
6	-2.297179000	-2.651133000	0.461971000
6	-3.056648000	-2.849821000	1.618607000
1	-4.158061000	-1.895995000	3.218429000
1	-1.934293000	-3.527713000	-0.074434000
1	-3.263521000	-3.865312000	1.961531000
15	-0.917213000	-1.121896000	-1.480390000
15	0.577423000	0.899929000	0.876753000
45	1.313969000	-0.168675000	-0.947703000
6	2.925986000	-1.948966000	0.905658000
6	3.822817000	-1.012668000	1.590662000
6	1.928914000	-1.772268000	0.019567000
6	4.342979000	0.177363000	1.226550000
1	3.065174000	-2.991547000	1.229007000
1	1.362308000	-2.657841000	-0.303293000
1	4.168412000	-1.393576000	2.558808000
1	5.014244000	0.638527000	1.961780000
6	0.218628000	-0.170040000	2.326212000
1	1.191256000	-0.419274000	2.772974000
1	-0.399787000	0.391601000	3.041359000

1	-0.287320000	-1.093493000	2.029062000
6	1.615024000	2.212869000	1.637616000
1	1.983385000	2.925664000	0.890665000
1	1.011827000	2.739990000	2.391862000
1	2.470049000	1.721032000	2.118890000
6	-0.835173000	-2.782752000	-2.282717000
1	-0.259090000	-3.489776000	-1.669308000
1	-1.840208000	-3.190616000	-2.468173000
1	-0.313359000	-2.659353000	-3.243681000
6	-1.932161000	-0.173100000	-2.703610000
1	-1.403093000	-0.188825000	-3.669030000
1	-2.923679000	-0.634761000	-2.823715000
1	-2.050138000	0.868761000	-2.379571000
6	4.216072000	0.991443000	-0.031685000
6	3.206850000	0.569618000	-1.092290000
1	5.223956000	1.034603000	-0.491826000
1	4.029027000	2.037131000	0.272179000
1	3.609845000	-0.273108000	-1.695710000
1	3.024871000	1.423931000	-1.782341000

TS(A4.A5) (ethylene)

G = -1648.03388

6	-2.311974000	1.314401000	0.032621000
6	-3.281188000	2.132188000	-0.571748000
6	-2.953426000	3.380289000	-1.103023000
6	-1.634371000	3.832256000	-1.035827000
6	-0.663078000	3.044937000	-0.414010000
6	-0.982652000	1.792090000	0.139952000
1	-4.305911000	1.761921000	-0.642951000
1	-3.724483000	3.991816000	-1.575287000
1	-1.358226000	4.800704000	-1.456891000
1	0.356625000	3.426625000	-0.362203000
6	-2.743937000	-0.034447000	0.509950000
6	-3.734442000	-0.109600000	1.500810000
6	-2.212530000	-1.234744000	-0.022642000
6	-4.179421000	-1.339521000	1.990048000
1	-4.145837000	0.818709000	1.902488000
6	-2.666617000	-2.466160000	0.478639000
6	-3.639282000	-2.521174000	1.480876000
1	-4.944070000	-1.372217000	2.768358000
1	-2.269222000	-3.403954000	0.090539000
1	-3.975997000	-3.489792000	1.854841000
15	-0.862318000	-1.201488000	-1.282713000
15	0.381648000	0.811497000	0.921343000
45	1.286891000	-0.741893000	-0.447054000
6	3.703206000	-0.669838000	1.690527000
6	4.497376000	0.504043000	1.320606000
6	2.691841000	-1.233773000	0.989324000
6	4.639945000	1.012757000	0.082016000
1	3.989217000	-1.153251000	2.633556000
1	2.326477000	-2.219890000	1.317286000
1	5.048898000	0.984311000	2.134905000
1	5.252892000	1.910564000	-0.045887000

6	-0.258482000	0.150448000	2.519149000
1	0.618222000	-0.206679000	3.079008000
1	-0.767221000	0.948703000	3.080282000
1	-0.946055000	-0.686613000	2.355343000
6	1.559398000	2.099311000	1.506067000
1	2.155282000	2.505852000	0.679790000
1	0.997234000	2.902558000	2.004788000
1	2.245080000	1.623016000	2.216084000
6	-0.814456000	-2.904352000	-1.993600000
1	-0.433707000	-3.623823000	-1.255609000
1	-1.812152000	-3.214793000	-2.339900000
1	-0.123751000	-2.885470000	-2.849783000
6	-1.481093000	-0.203673000	-2.709441000
1	-0.810287000	-0.391595000	-3.561230000
1	-2.504967000	-0.511037000	-2.970461000
1	-1.464750000	0.866513000	-2.471063000
6	4.019114000	0.477031000	-1.185243000
6	3.295237000	-0.846078000	-1.000829000
1	4.815515000	0.349052000	-1.943598000
1	3.338823000	1.244513000	-1.596606000
1	3.990460000	-1.674306000	-0.826473000
1	2.656857000	-1.124743000	-1.906688000

A5 (ethylene)

$G = -1648.10136$

6	-2.507949000	1.129761000	0.091123000
6	-3.630999000	1.802339000	-0.418450000
6	-3.530266000	3.081757000	-0.966507000
6	-2.287461000	3.714207000	-1.011712000
6	-1.163463000	3.070905000	-0.488690000
6	-1.251478000	1.786387000	0.077638000
1	-4.596551000	1.292916000	-0.401219000
1	-4.418560000	3.576677000	-1.363403000
1	-2.187466000	4.710801000	-1.445523000
1	-0.208993000	3.594304000	-0.527744000
6	-2.715463000	-0.261036000	0.598821000
6	-3.617720000	-0.457296000	1.656453000
6	-2.077400000	-1.387814000	0.024831000
6	-3.875933000	-1.731926000	2.164405000
1	-4.111963000	0.413447000	2.092143000
6	-2.345151000	-2.665634000	0.544491000
6	-3.235155000	-2.839560000	1.607319000
1	-4.575258000	-1.857093000	2.993125000
1	-1.862887000	-3.547536000	0.122727000
1	-3.427957000	-3.842440000	1.992766000
15	-0.801489000	-1.194261000	-1.297076000
15	0.294296000	0.997524000	0.727516000
45	1.254009000	-0.621827000	-0.476574000
6	3.170598000	-1.122480000	0.882572000
6	3.850126000	-0.184946000	1.784208000
6	3.387476000	-1.039457000	-0.485564000
6	4.564488000	0.850399000	1.296970000
1	2.703877000	-2.006395000	1.323540000

1	3.115844000	-1.917265000	-1.109645000
1	3.792097000	-0.369490000	2.859448000
1	5.083199000	1.527742000	1.981081000
6	-0.104086000	0.426856000	2.436954000
1	0.848480000	0.186559000	2.931514000
1	-0.619487000	1.229531000	2.986386000
1	-0.734021000	-0.470004000	2.409403000
6	1.414690000	2.418378000	1.055300000
1	1.748027000	2.881973000	0.118647000
1	0.898703000	3.161558000	1.681584000
1	2.288403000	2.024119000	1.589653000
6	-0.616139000	-2.869224000	-2.055302000
1	-0.143982000	-3.569313000	-1.352288000
1	-1.595374000	-3.261390000	-2.370364000
1	0.031333000	-2.766461000	-2.939181000
6	-1.574747000	-0.246238000	-2.681261000
1	-0.918486000	-0.352370000	-3.558115000
1	-2.568327000	-0.659718000	-2.911071000
1	-1.665505000	0.817193000	-2.431565000
6	4.606064000	1.150566000	-0.179699000
6	4.437309000	-0.108057000	-1.045448000
1	5.536938000	1.673640000	-0.445491000
1	3.785884000	1.860337000	-0.409068000
1	5.388372000	-0.675558000	-1.074115000
1	4.207110000	0.170204000	-2.084730000

A3 (imine)

G = -1664.11031

6	2.092745000	1.009426000	-0.320345000
6	3.160709000	1.774561000	0.178678000
6	3.041797000	3.150146000	0.384251000
6	1.837450000	3.792047000	0.087676000
6	0.773285000	3.057330000	-0.436662000
6	0.887493000	1.672150000	-0.664432000
1	4.094557000	1.265639000	0.426071000
1	3.886447000	3.716128000	0.781704000
1	1.725589000	4.865178000	0.252617000
1	-0.155672000	3.577350000	-0.667629000
6	2.316664000	-0.464049000	-0.472020000
6	3.246867000	-0.884847000	-1.435769000
6	1.678195000	-1.436401000	0.338256000
6	3.522296000	-2.238644000	-1.637903000
1	3.747031000	-0.130146000	-2.046343000
6	1.968736000	-2.795033000	0.127243000
6	2.875876000	-3.197218000	-0.856879000
1	4.239601000	-2.540668000	-2.403215000
1	1.490829000	-3.562832000	0.735591000
1	3.080026000	-4.259559000	-1.002540000
15	0.424909000	-0.935140000	1.603543000
15	-0.584947000	0.789310000	-1.333730000
45	-1.581140000	-0.129981000	0.441032000
6	-2.764190000	-2.259336000	-1.070524000
6	-3.740074000	-1.163012000	-1.167600000

6	-1.610678000	-1.965884000	-0.439609000
6	-3.349836000	0.009062000	-0.629790000
1	-2.968766000	-3.247200000	-1.497762000
1	-0.784936000	-2.683566000	-0.371693000
1	-4.715101000	-1.310857000	-1.645295000
1	-3.970889000	0.912826000	-0.663253000
6	-0.062201000	-0.344529000	-2.673414000
1	-0.979547000	-0.717965000	-3.149388000
1	0.548317000	0.215290000	-3.397770000
1	0.503308000	-1.191966000	-2.273130000
6	-1.585895000	2.056743000	-2.200239000
1	-2.060963000	2.713909000	-1.461911000
1	-0.947095000	2.630452000	-2.887697000
1	-2.367448000	1.526968000	-2.759786000
6	0.056119000	-2.457458000	2.577493000
1	-0.507237000	-3.179262000	1.971065000
1	0.976920000	-2.920852000	2.962160000
1	-0.574073000	-2.156222000	3.427993000
6	1.387557000	0.057190000	2.832493000
1	0.738001000	0.274628000	3.694042000
1	2.263550000	-0.515162000	3.172233000
1	1.725801000	1.001995000	2.388067000
6	-1.445661000	1.739557000	2.137338000
1	-1.774882000	1.411268000	3.137557000
1	-0.393508000	2.023065000	2.025671000
7	-2.251462000	1.977986000	1.143793000
1	-3.231288000	1.801451000	1.403014000

TS(A3.A4) (imine)

G = -1664.08648

6	-2.382225000	0.888766000	-0.162362000
6	-3.426717000	1.406574000	-0.944820000
6	-3.393583000	2.714834000	-1.432067000
6	-2.305907000	3.536643000	-1.131815000
6	-1.268846000	3.048751000	-0.333851000
6	-1.293137000	1.734313000	0.168159000
1	-4.272127000	0.757541000	-1.182399000
1	-4.215842000	3.088738000	-2.044992000
1	-2.265299000	4.561091000	-1.506243000
1	-0.439860000	3.715102000	-0.094388000
6	-2.502689000	-0.521954000	0.324098000
6	-3.530575000	-0.803708000	1.237960000
6	-1.642843000	-1.570706000	-0.088453000
6	-3.691985000	-2.078820000	1.782734000
1	-4.198293000	0.005894000	1.539876000
6	-1.813174000	-2.848572000	0.473227000
6	-2.821011000	-3.102172000	1.407664000
1	-4.491657000	-2.267993000	2.501215000
1	-1.160501000	-3.671916000	0.183333000
1	-2.928066000	-4.103244000	1.829462000
15	-0.252374000	-1.272145000	-1.269589000
15	0.150815000	1.139014000	1.152847000
45	1.533192000	0.033833000	-0.338752000

6	3.096252000	-0.930995000	1.822265000
6	3.749252000	0.316152000	1.535251000
6	1.988465000	-1.239277000	1.085435000
6	3.279344000	0.992390000	0.432627000
1	3.463800000	-1.614268000	2.596244000
1	1.362288000	-2.123708000	1.252321000
1	4.543325000	0.706797000	2.179295000
1	3.642296000	1.983974000	0.151104000
6	-0.470784000	0.261568000	2.647439000
1	0.382512000	0.172534000	3.334800000
1	-1.274612000	0.847227000	3.116853000
1	-0.832606000	-0.741315000	2.397399000
6	0.916857000	2.639304000	1.888758000
1	1.366322000	3.271566000	1.112054000
1	0.174138000	3.210319000	2.465117000
1	1.724113000	2.291906000	2.548763000
6	0.262861000	-2.953984000	-1.823653000
1	0.816011000	-3.471493000	-1.027465000
1	-0.602726000	-3.557219000	-2.135115000
1	0.935574000	-2.826547000	-2.684044000
6	-1.026996000	-0.588739000	-2.802727000
1	-0.263111000	-0.584771000	-3.595699000
1	-1.875436000	-1.214990000	-3.116609000
1	-1.372538000	0.439317000	-2.634387000
6	2.879430000	-0.388315000	-2.034614000
1	2.816411000	-1.452091000	-2.299218000
1	2.479561000	0.327908000	-2.770581000
7	3.867148000	0.054930000	-1.237314000
1	4.334110000	-0.732718000	-0.768046000

A4 (imine)

G = -1664.12259

6	-2.191126000	1.238474000	0.263249000
6	-3.238074000	2.050179000	-0.205577000
6	-3.012680000	3.356104000	-0.644028000
6	-1.719560000	3.882715000	-0.615731000
6	-0.669718000	3.105049000	-0.126499000
6	-0.886838000	1.790183000	0.330519000
1	-4.245505000	1.630734000	-0.240464000
1	-3.845824000	3.957984000	-1.011790000
1	-1.526745000	4.899733000	-0.961726000
1	0.329924000	3.540265000	-0.093075000
6	-2.534109000	-0.155603000	0.688162000
6	-3.373890000	-0.309124000	1.802052000
6	-2.080841000	-1.310762000	0.001832000
6	-3.737608000	-1.573833000	2.268955000
1	-3.730336000	0.585180000	2.317714000
6	-2.456031000	-2.576980000	0.482090000
6	-3.271295000	-2.711388000	1.609449000
1	-4.381243000	-1.667164000	3.145577000
1	-2.117940000	-3.482125000	-0.022104000
1	-3.546270000	-3.707145000	1.962192000
15	-0.923555000	-1.164169000	-1.430953000

15	0.591390000	0.845821000	0.901553000
45	1.309973000	-0.222799000	-0.928983000
6	2.970805000	-1.945348000	0.936315000
6	3.952628000	-1.024105000	1.489923000
6	1.939000000	-1.807513000	0.076671000
6	4.390473000	0.204757000	1.090727000
1	3.080973000	-2.969527000	1.325083000
1	1.303978000	-2.679391000	-0.130360000
1	4.478419000	-1.411332000	2.365503000
1	5.161219000	0.674061000	1.709484000
6	0.158488000	-0.237545000	2.320641000
1	1.112179000	-0.532529000	2.780236000
1	-0.455048000	0.332919000	3.033157000
1	-0.374479000	-1.135546000	1.995403000
6	1.665239000	2.097317000	1.710293000
1	2.132594000	2.768300000	0.981534000
1	1.048716000	2.667420000	2.421243000
1	2.456246000	1.555916000	2.244594000
6	-0.852599000	-2.852783000	-2.171833000
1	-0.328433000	-3.551762000	-1.504896000
1	-1.858122000	-3.238833000	-2.396836000
1	-0.277907000	-2.777450000	-3.107282000
6	-1.865593000	-0.226597000	-2.719893000
1	-1.298811000	-0.273276000	-3.662669000
1	-2.860114000	-0.672744000	-2.870139000
1	-1.977574000	0.824211000	-2.422396000
6	3.195939000	0.577739000	-1.066434000
1	3.698849000	-0.208113000	-1.674714000
1	3.029158000	1.462337000	-1.713544000
7	4.015357000	0.998768000	0.040131000
1	4.622647000	1.792094000	-0.130724000

TS(A4.A5) (imine)

G = -1664.09251

6	2.567409000	-0.621688000	0.459679000
6	3.906409000	-0.972312000	0.219347000
6	4.262498000	-2.252906000	-0.205062000
6	3.269054000	-3.214264000	-0.396220000
6	1.935622000	-2.893407000	-0.135346000
6	1.562179000	-1.610197000	0.306875000
1	4.675626000	-0.208306000	0.348580000
1	5.310329000	-2.494058000	-0.393327000
1	3.526762000	-4.218168000	-0.738469000
1	1.184438000	-3.669219000	-0.278541000
6	2.292981000	0.796904000	0.844026000
6	2.854512000	1.285374000	2.034035000
6	1.534359000	1.674353000	0.031816000
6	2.653416000	2.604963000	2.443310000
1	3.446423000	0.606666000	2.651622000
6	1.337945000	2.999702000	0.454927000
6	1.888805000	3.463556000	1.652154000
1	3.092509000	2.958660000	3.377993000
1	0.749766000	3.691557000	-0.147723000

1	1.721945000	4.497578000	1.959353000
15	0.689791000	1.075597000	-1.497475000
15	-0.234161000	-1.275092000	0.605120000
45	-1.302180000	-0.034387000	-0.983759000
6	-3.571728000	1.559864000	0.492244000
6	-4.055683000	0.804385000	1.622756000
6	-2.838278000	1.027909000	-0.507517000
6	-4.147072000	-0.553364000	1.617284000
1	-3.862957000	2.613438000	0.401166000
1	-2.871132000	1.413285000	-1.562098000
1	-4.444225000	1.340605000	2.488416000
1	-4.572826000	-1.067787000	2.482528000
6	-0.385463000	-0.429307000	2.232449000
1	-1.458671000	-0.381437000	2.469649000
1	0.156887000	-0.997937000	3.003093000
1	0.008975000	0.591340000	2.169518000
6	-0.939305000	-2.940354000	0.949096000
1	-0.967947000	-3.554418000	0.039657000
1	-0.343620000	-3.442388000	1.725332000
1	-1.962559000	-2.776282000	1.304479000
6	0.258932000	2.593588000	-2.455018000
1	-0.516809000	3.170844000	-1.934480000
1	1.149877000	3.219158000	-2.617170000
1	-0.139050000	2.269558000	-3.428246000
6	1.969970000	0.298867000	-2.579094000
1	1.523734000	0.172660000	-3.577102000
1	2.851272000	0.954018000	-2.648981000
1	2.270210000	-0.683281000	-2.195068000
6	-3.287374000	-1.045453000	-0.706817000
1	-4.105176000	-0.749882000	-1.381138000
1	-2.797689000	-1.928366000	-1.162764000
7	-3.732361000	-1.415176000	0.624376000
1	-4.151065000	-2.339048000	0.678010000

A5 (imine)

G = -1664.16116

6	-2.398580000	1.268723000	0.039816000
6	-3.414919000	2.052712000	-0.532046000
6	-3.147189000	3.306138000	-1.083792000
6	-1.841412000	3.799150000	-1.071446000
6	-0.822806000	3.045375000	-0.485131000
6	-1.080762000	1.787479000	0.088420000
1	-4.429985000	1.651481000	-0.560706000
1	-3.954986000	3.889639000	-1.529411000
1	-1.612136000	4.772396000	-1.509320000
1	0.187118000	3.455548000	-0.478917000
6	-2.776084000	-0.085314000	0.548741000
6	-3.749792000	-0.170797000	1.556095000
6	-2.217073000	-1.280405000	0.031823000
6	-4.154339000	-1.402948000	2.073413000
1	-4.181173000	0.752653000	1.947899000
6	-2.631285000	-2.513922000	0.561743000
6	-3.589775000	-2.578409000	1.576625000

1	-4.906483000	-1.442068000	2.863538000
1	-2.211310000	-3.446966000	0.186124000
1	-3.895279000	-3.549219000	1.971276000
15	-0.870980000	-1.234171000	-1.233935000
15	0.346761000	0.853044000	0.810792000
45	1.238396000	-0.709078000	-0.499431000
6	3.307534000	-1.305937000	0.688316000
6	3.918159000	-0.488671000	1.711294000
6	3.391424000	-0.929405000	-0.652321000
6	4.486422000	0.695188000	1.338875000
1	2.923979000	-2.290764000	0.965076000
1	3.218586000	-1.699881000	-1.428168000
1	3.914659000	-0.798320000	2.754579000
1	4.927256000	1.377140000	2.069992000
6	-0.205197000	0.202444000	2.448607000
1	0.699953000	-0.124128000	2.981857000
1	-0.705443000	1.001487000	3.017188000
1	-0.881720000	-0.651344000	2.332502000
6	1.513374000	2.177798000	1.336528000
1	2.063928000	2.586520000	0.481413000
1	0.955859000	2.967717000	1.861202000
1	2.234079000	1.715739000	2.022331000
6	-0.792878000	-2.947031000	-1.924194000
1	-0.404389000	-3.653548000	-1.177927000
1	-1.784980000	-3.275736000	-2.270097000
1	-0.103021000	-2.928103000	-2.781580000
6	-1.537588000	-0.286671000	-2.674703000
1	-0.862004000	-0.459131000	-3.525941000
1	-2.547865000	-0.642899000	-2.926609000
1	-1.567419000	0.787502000	-2.456823000
6	4.337135000	0.183188000	-1.058710000
1	5.330795000	-0.250573000	-1.309731000
1	3.972859000	0.711483000	-1.951315000
7	4.450489000	1.148989000	0.045607000
1	5.034951000	1.953761000	-0.153886000

A3 (formaldehyde)

G = -1683.99645

6	2.086807000	0.987990000	-0.320703000
6	3.170604000	1.725760000	0.185254000
6	3.079423000	3.100828000	0.408540000
6	1.887698000	3.770344000	0.122554000
6	0.807623000	3.063091000	-0.407200000
6	0.893866000	1.678766000	-0.652271000
1	4.095597000	1.195980000	0.421938000
1	3.936271000	3.644967000	0.810322000
1	1.797943000	4.843525000	0.300073000
1	-0.110428000	3.605631000	-0.630229000
6	2.286088000	-0.486655000	-0.498340000
6	3.194093000	-0.903909000	-1.484652000
6	1.651903000	-1.463791000	0.309476000
6	3.452326000	-2.257532000	-1.709770000
1	3.691308000	-0.146045000	-2.093720000

6	1.925633000	-2.822413000	0.075822000
6	2.811326000	-3.220162000	-0.929302000
1	4.152457000	-2.556109000	-2.492135000
1	1.450822000	-3.593745000	0.682123000
1	3.002612000	-4.282370000	-1.092226000
15	0.423887000	-0.971495000	1.601995000
15	-0.599067000	0.829603000	-1.318339000
45	-1.579365000	-0.115739000	0.457550000
6	-2.782009000	-2.198819000	-1.096517000
6	-3.760039000	-1.100514000	-1.139331000
6	-1.623064000	-1.930613000	-0.464443000
6	-3.354083000	0.050846000	-0.573930000
1	-2.990938000	-3.172141000	-1.553899000
1	-0.796344000	-2.648268000	-0.424483000
1	-4.752980000	-1.236042000	-1.581937000
1	-3.958270000	0.961597000	-0.500221000
6	-0.116058000	-0.270363000	-2.698882000
1	-1.045696000	-0.634380000	-3.157735000
1	0.472782000	0.309208000	-3.425741000
1	0.463145000	-1.124856000	-2.334351000
6	-1.614472000	2.131474000	-2.113864000
1	-2.077671000	2.757422000	-1.340865000
1	-0.991959000	2.735643000	-2.790002000
1	-2.407624000	1.624083000	-2.677897000
6	0.027428000	-2.506976000	2.542195000
1	-0.550556000	-3.203413000	1.920166000
1	0.939978000	-2.995802000	2.914951000
1	-0.595746000	-2.212323000	3.400153000
6	1.413413000	-0.024942000	2.844656000
1	0.771059000	0.197872000	3.710483000
1	2.272147000	-0.627617000	3.176140000
1	1.778328000	0.915717000	2.412723000
6	-1.352260000	1.703274000	2.093146000
1	-1.683211000	1.282310000	3.066606000
1	-0.308654000	2.068007000	2.025988000
8	-2.171588000	1.934213000	1.181820000

TS(A3.A4) (formaldehyde)

G = -1683.96181

6	-2.289522000	1.014147000	-0.202670000
6	-3.247816000	1.603604000	-1.042724000
6	-3.103305000	2.911103000	-1.512239000
6	-1.989365000	3.662990000	-1.135020000
6	-1.034426000	3.104510000	-0.283346000
6	-1.171244000	1.789196000	0.199438000
1	-4.117564000	1.012535000	-1.336982000
1	-3.861624000	3.339741000	-2.170130000
1	-1.864335000	4.686608000	-1.492479000
1	-0.180943000	3.714944000	0.013326000
6	-2.544651000	-0.383589000	0.275662000
6	-3.625019000	-0.570268000	1.152593000
6	-1.772693000	-1.508369000	-0.112257000
6	-3.925426000	-1.826465000	1.682718000

1	-4.224515000	0.297355000	1.436109000
6	-2.085958000	-2.767044000	0.430401000
6	-3.145790000	-2.927375000	1.327340000
1	-4.763464000	-1.940929000	2.372686000
1	-1.506842000	-3.648185000	0.154589000
1	-3.364238000	-3.915932000	1.735426000
15	-0.318493000	-1.330131000	-1.238379000
15	0.187334000	1.090074000	1.228943000
45	1.498322000	-0.059168000	-0.289655000
6	3.188934000	-1.076363000	1.729092000
6	3.848825000	0.139531000	1.418347000
6	2.003893000	-1.332440000	1.068723000
6	3.284305000	0.860620000	0.375941000
1	3.600735000	-1.799678000	2.441676000
1	1.378842000	-2.211240000	1.271170000
1	4.726031000	0.479311000	1.977139000
1	3.667010000	1.840815000	0.078425000
6	-0.528901000	0.188492000	2.665242000
1	0.295809000	0.025983000	3.374369000
1	-1.316449000	0.795934000	3.134737000
1	-0.936662000	-0.780972000	2.359577000
6	1.039209000	2.503090000	2.031787000
1	1.538301000	3.134502000	1.285687000
1	0.329738000	3.098390000	2.625319000
1	1.813841000	2.077220000	2.685959000
6	0.162629000	-3.048644000	-1.695181000
1	0.614043000	-3.564084000	-0.835971000
1	-0.695403000	-3.623891000	-2.073466000
1	0.923179000	-2.975556000	-2.486270000
6	-0.998724000	-0.676286000	-2.827081000
1	-0.195916000	-0.699865000	-3.580084000
1	-1.839713000	-1.297723000	-3.169311000
1	-1.337404000	0.359847000	-2.697067000
6	2.854155000	-0.251471000	-1.986215000
1	2.728675000	-1.291708000	-2.343515000
1	2.392841000	0.547695000	-2.617477000
8	3.903028000	0.018561000	-1.291343000

A4 (formaldehyde)

G = -1683.99918

6	-2.147251000	1.294873000	0.199538000
6	-3.144966000	2.131464000	-0.328967000
6	-2.853932000	3.413596000	-0.798687000
6	-1.543080000	3.891997000	-0.742723000
6	-0.540509000	3.090084000	-0.197298000
6	-0.824935000	1.798893000	0.290993000
1	-4.167101000	1.751567000	-0.383439000
1	-3.650724000	4.035025000	-1.211737000
1	-1.299820000	4.889987000	-1.111411000
1	0.474681000	3.485647000	-0.144351000
6	-2.563924000	-0.066654000	0.664684000
6	-3.437093000	-0.137863000	1.761185000
6	-2.152263000	-1.267688000	0.032661000

6	-3.876297000	-1.365049000	2.262481000
1	-3.760952000	0.791138000	2.235311000
6	-2.603886000	-2.495161000	0.546502000
6	-3.453255000	-2.547660000	1.655416000
1	-4.545251000	-1.393934000	3.124512000
1	-2.300974000	-3.433805000	0.082744000
1	-3.788277000	-3.514909000	2.034587000
15	-0.957631000	-1.229110000	-1.375604000
15	0.602861000	0.821295000	0.922837000
45	1.296307000	-0.295279000	-0.887699000
6	3.111658000	-1.938039000	0.894534000
6	4.101087000	-0.968646000	1.354666000
6	2.006466000	-1.829241000	0.126811000
6	4.402195000	0.303938000	0.999558000
1	3.287562000	-2.949240000	1.289710000
1	1.364977000	-2.713891000	0.008209000
1	4.736715000	-1.337510000	2.164214000
1	5.160123000	0.849734000	1.567798000
6	0.109943000	-0.242269000	2.336654000
1	1.044895000	-0.585269000	2.801648000
1	-0.476388000	0.355311000	3.050011000
1	-0.468966000	-1.110566000	2.008880000
6	1.702851000	2.042379000	1.739691000
1	2.214968000	2.684061000	1.014956000
1	1.091395000	2.640009000	2.432134000
1	2.461825000	1.479757000	2.298986000
6	-0.904100000	-2.956888000	-2.020387000
1	-0.427514000	-3.629580000	-1.293202000
1	-1.909296000	-3.330082000	-2.267610000
1	-0.288933000	-2.948595000	-2.932811000
6	-1.851308000	-0.340102000	-2.732048000
1	-1.262467000	-0.435892000	-3.657423000
1	-2.848582000	-0.778525000	-2.886828000
1	-1.954702000	0.724575000	-2.483484000
6	3.167252000	0.517645000	-1.035251000
1	3.782850000	-0.266849000	-1.521256000
1	3.004376000	1.350963000	-1.748199000
8	3.910676000	1.102251000	0.025739000

TS(A4.A5) (formaldehyde)

G = -1683.96955

6	2.571546000	-0.582727000	0.462236000
6	3.919436000	-0.899079000	0.225187000
6	4.305707000	-2.160592000	-0.229328000
6	3.334068000	-3.136018000	-0.456483000
6	1.992035000	-2.850346000	-0.197857000
6	1.588547000	-1.587861000	0.276638000
1	4.671275000	-0.122761000	0.380526000
1	5.359947000	-2.375304000	-0.413767000
1	3.615022000	-4.124494000	-0.824280000
1	1.259129000	-3.637779000	-0.368230000
6	2.263730000	0.822051000	0.870022000
6	2.800705000	1.303044000	2.074108000

6	1.498588000	1.696362000	0.060832000
6	2.568097000	2.612318000	2.499883000
1	3.398737000	0.627093000	2.688835000
6	1.271087000	3.011559000	0.499869000
6	1.797391000	3.467712000	1.711102000
1	2.988149000	2.960739000	3.445217000
1	0.678472000	3.701576000	-0.100580000
1	1.606861000	4.493717000	2.031079000
15	0.685142000	1.102134000	-1.487055000
15	-0.215359000	-1.307279000	0.587236000
45	-1.302614000	-0.035042000	-0.976805000
6	-3.728633000	1.485629000	0.352531000
6	-4.209999000	0.721300000	1.489559000
6	-2.873542000	0.972404000	-0.548325000
6	-4.083064000	-0.616064000	1.622273000
1	-4.105749000	2.502928000	0.201987000
1	-2.779946000	1.351992000	-1.611985000
1	-4.733039000	1.248801000	2.288543000
1	-4.429111000	-1.149911000	2.509269000
6	-0.382118000	-0.518687000	2.240094000
1	-1.455389000	-0.490024000	2.476645000
1	0.160955000	-1.111429000	2.991755000
1	0.005908000	0.505991000	2.214781000
6	-0.880727000	-3.002997000	0.858634000
1	-0.899529000	-3.572271000	-0.080055000
1	-0.255430000	-3.523067000	1.599104000
1	-1.906106000	-2.898056000	1.230047000
6	0.232571000	2.624178000	-2.427742000
1	-0.560291000	3.178692000	-1.908044000
1	1.112188000	3.270304000	-2.569680000
1	-0.147019000	2.306556000	-3.410323000
6	1.986105000	0.360999000	-2.567996000
1	1.552742000	0.248367000	-3.573267000
1	2.859062000	1.029172000	-2.615166000
1	2.295157000	-0.624198000	-2.199132000
6	-3.247867000	-1.115397000	-0.596835000
1	-4.173522000	-0.854101000	-1.126704000
1	-2.816642000	-2.008587000	-1.076304000
8	-3.509118000	-1.490824000	0.745354000

A5 (formaldehyde)

G = -1684.03452

6	-2.296421000	1.349321000	0.004980000
6	-3.234370000	2.192339000	-0.615239000
6	-2.859621000	3.413329000	-1.177151000
6	-1.523210000	3.814367000	-1.126413000
6	-0.581509000	3.002642000	-0.491786000
6	-0.948641000	1.776598000	0.092630000
1	-4.273821000	1.863202000	-0.673299000
1	-3.608412000	4.043704000	-1.660350000
1	-1.210815000	4.760758000	-1.571543000
1	0.454422000	3.340521000	-0.454184000
6	-2.785307000	0.034144000	0.520888000

6	-3.790947000	0.032817000	1.499461000
6	-2.297241000	-1.205536000	0.037631000
6	-4.295111000	-1.160228000	2.021629000
1	-4.168281000	0.990080000	1.864989000
6	-2.811878000	-2.399111000	0.570721000
6	-3.800899000	-2.380011000	1.558125000
1	-5.070340000	-1.134313000	2.789657000
1	-2.449059000	-3.365285000	0.220253000
1	-4.185203000	-3.320601000	1.956948000
15	-0.921309000	-1.267384000	-1.191555000
15	0.395880000	0.769026000	0.871175000
45	1.238520000	-0.772085000	-0.504297000
6	3.307379000	-1.410508000	0.366550000
6	3.903141000	-0.786039000	1.542427000
6	3.382397000	-0.739197000	-0.853382000
6	4.377263000	0.475014000	1.440734000
1	3.050165000	-2.472265000	0.419413000
1	3.281256000	-1.297807000	-1.799587000
1	3.975886000	-1.323959000	2.486494000
1	4.804752000	1.037678000	2.273901000
6	-0.253370000	0.064376000	2.449453000
1	0.619410000	-0.296561000	3.013488000
1	-0.767164000	0.851344000	3.022546000
1	-0.936889000	-0.771999000	2.270800000
6	1.557144000	2.043281000	1.518696000
1	2.191470000	2.458358000	0.728134000
1	0.970670000	2.833801000	2.009706000
1	2.204246000	1.554805000	2.257550000
6	-0.900723000	-3.003685000	-1.821576000
1	-0.569083000	-3.699903000	-1.039077000
1	-1.894728000	-3.299999000	-2.190519000
1	-0.183750000	-3.045907000	-2.655705000
6	-1.502646000	-0.329051000	-2.673638000
1	-0.812484000	-0.548432000	-3.501988000
1	-2.519876000	-0.649131000	-2.945219000
1	-1.493515000	0.749987000	-2.477824000
6	4.236902000	0.501972000	-0.938939000
1	5.271976000	0.221271000	-1.222929000
1	3.859752000	1.222378000	-1.676432000
8	4.289185000	1.224557000	0.312381000

A3 (allene)

G = -1686.12990

6	2.160122000	0.876851000	-0.370665000
6	3.269689000	1.619534000	0.071439000
6	3.269681000	3.014911000	0.072218000
6	2.145631000	3.702566000	-0.387500000
6	1.037641000	2.986470000	-0.842496000
6	1.021960000	1.577699000	-0.845167000
1	4.147611000	1.076557000	0.427049000
1	4.146292000	3.560014000	0.427360000
1	2.127118000	4.793836000	-0.398772000
1	0.173935000	3.549252000	-1.192949000

6	2.317305000	-0.615722000	-0.352382000
6	3.250971000	-1.165046000	-1.247173000
6	1.662455000	-1.470446000	0.567889000
6	3.527077000	-2.533475000	-1.263117000
1	3.761893000	-0.498936000	-1.945712000
6	1.963184000	-2.843194000	0.551791000
6	2.882687000	-3.374932000	-0.356131000
1	4.248025000	-2.936011000	-1.977046000
1	1.476072000	-3.521922000	1.251827000
1	3.093209000	-4.445983000	-0.348546000
15	0.335535000	-0.809903000	1.674007000
15	-0.500589000	0.720232000	-1.443661000
45	-1.588860000	-0.200704000	0.288759000
6	-2.482781000	-2.403128000	-1.274492000
6	-3.511022000	-1.373981000	-1.498245000
6	-1.388832000	-2.026179000	-0.583168000
6	-3.254079000	-0.169365000	-0.951101000
1	-2.606732000	-3.422812000	-1.657125000
1	-0.535760000	-2.690580000	-0.409474000
1	-4.416624000	-1.599131000	-2.072320000
1	-3.938737000	0.680574000	-1.072092000
6	0.016132000	-0.380454000	-2.815748000
1	-0.893370000	-0.818378000	-3.248390000
1	0.553560000	0.221511000	-3.564176000
1	0.660998000	-1.183707000	-2.442292000
6	-1.489412000	2.012169000	-2.297925000
1	-1.929781000	2.703522000	-1.566768000
1	-0.862485000	2.560683000	-3.015729000
1	-2.298616000	1.495765000	-2.829121000
6	-0.149568000	-2.219963000	2.762613000
1	-0.668750000	-2.992290000	2.178066000
1	0.719785000	-2.655403000	3.277718000
1	-0.847773000	-1.826718000	3.517274000
6	1.227573000	0.285143000	2.864646000
1	0.506860000	0.669537000	3.600181000
1	2.014211000	-0.291900000	3.373346000
1	1.684626000	1.132544000	2.338838000
6	-2.919347000	1.210028000	1.625803000
1	-3.737935000	1.569260000	0.998146000
1	-3.158879000	0.410507000	2.341656000
6	-0.848790000	2.785527000	2.022350000
6	-1.796877000	1.922051000	1.755810000
1	0.135774000	2.749789000	1.559240000
1	-1.048420000	3.584768000	2.744976000

TS(A3.A4) (allene)

G = -1686.12279

6	2.528253000	0.708550000	0.271099000
6	3.588246000	1.070594000	1.117307000
6	3.651305000	2.336303000	1.703203000
6	2.646640000	3.268815000	1.439718000
6	1.600959000	2.936922000	0.575168000
6	1.530225000	1.667842000	-0.028959000

1	4.363151000	0.331216000	1.330020000
1	4.480660000	2.589884000	2.366098000
1	2.678300000	4.260545000	1.894594000
1	0.841041000	3.690656000	0.368927000
6	2.519280000	-0.672932000	-0.299404000
6	3.552126000	-1.018741000	-1.185214000
6	1.523030000	-1.632294000	0.008773000
6	3.591578000	-2.269151000	-1.803886000
1	4.321764000	-0.276200000	-1.405828000
6	1.573012000	-2.885940000	-0.626984000
6	2.589433000	-3.201241000	-1.532717000
1	4.398625000	-2.509863000	-2.498294000
1	0.819261000	-3.644165000	-0.417174000
1	2.600110000	-4.181485000	-2.012813000
15	0.131254000	-1.260060000	1.174520000
15	0.082044000	1.279416000	-1.112476000
45	-1.546913000	0.157057000	0.202864000
6	-2.707296000	-0.747335000	-2.256131000
6	-3.296762000	0.564648000	-2.116592000
6	-1.843545000	-1.131093000	-1.283200000
6	-3.025336000	1.203249000	-0.945430000
1	-2.934457000	-1.405559000	-3.101472000
1	-1.290726000	-2.076660000	-1.285432000
1	-3.898599000	1.012197000	-2.913503000
1	-3.376100000	2.219779000	-0.736047000
6	0.695750000	0.491453000	-2.659623000
1	1.007779000	-0.543582000	-2.483468000
1	-0.146954000	0.490818000	-3.365795000
1	1.532234000	1.075671000	-3.070115000
6	-0.475238000	2.921039000	-1.737198000
1	-0.952193000	3.506073000	-0.939618000
1	0.376445000	3.477025000	-2.155975000
1	-1.223918000	2.733344000	-2.517874000
6	-0.520347000	-2.922769000	1.628702000
1	-1.050936000	-3.370230000	0.777294000
1	0.291036000	-3.587395000	1.959095000
1	-1.246919000	-2.788357000	2.439344000
6	0.939689000	-0.704548000	2.740948000
1	0.191970000	-0.727657000	3.546479000
1	1.769014000	-1.381038000	2.994857000
1	1.318135000	0.319692000	2.638460000
6	-3.855427000	0.100469000	0.729007000
1	-4.404877000	1.031136000	0.896241000
1	-4.349771000	-0.638773000	0.091781000
6	-2.866833000	-0.648248000	2.981716000
6	-2.938321000	-0.335346000	1.689424000
1	-3.775858000	-0.694195000	3.591741000
1	-1.929122000	-0.872252000	3.490567000

A4 (allene)

G = -1686.16398

6	2.209458000	1.260380000	-0.321188000
6	3.182090000	2.163505000	0.138666000

6	2.868702000	3.493681000	0.425099000
6	1.560984000	3.950947000	0.249308000
6	0.585063000	3.079306000	-0.234309000
6	0.892734000	1.738629000	-0.541211000
1	4.200434000	1.799429000	0.288830000
1	3.644822000	4.168582000	0.790935000
1	1.299431000	4.985667000	0.477562000
1	-0.426714000	3.458554000	-0.379483000
6	2.639361000	-0.149672000	-0.583020000
6	3.537138000	-0.368899000	-1.639216000
6	2.205543000	-1.252367000	0.195788000
6	3.977491000	-1.653724000	-1.963368000
1	3.877746000	0.487934000	-2.224506000
6	2.659825000	-2.539204000	-0.140412000
6	3.531200000	-2.742828000	-1.214333000
1	4.665054000	-1.800446000	-2.798332000
1	2.341131000	-3.406917000	0.436983000
1	3.865798000	-3.753740000	-1.454585000
15	0.971513000	-1.024223000	1.554805000
15	-0.495673000	0.669096000	-1.112719000
45	-1.250403000	-0.191805000	0.807854000
6	-2.681108000	-2.215746000	-0.981203000
6	-3.565357000	-1.333942000	-1.745245000
6	-1.802869000	-1.911736000	-0.003102000
6	-4.293102000	-0.324798000	-1.226948000
1	-2.733545000	-3.279407000	-1.258679000
1	-1.240350000	-2.738201000	0.456128000
1	-3.703047000	-1.585284000	-2.803123000
1	-4.942996000	0.248467000	-1.895463000
6	0.072840000	-0.517421000	-2.392262000
1	-0.833500000	-0.907968000	-2.875177000
1	0.693644000	0.018756000	-3.124831000
1	0.634616000	-1.348048000	-1.953942000
6	-1.602931000	1.776563000	-2.071338000
1	-2.085168000	2.512871000	-1.419008000
1	-1.013744000	2.273987000	-2.856257000
1	-2.384567000	1.148492000	-2.517528000
6	0.930693000	-2.640424000	2.443493000
1	0.477849000	-3.421629000	1.816765000
1	1.938679000	-2.954424000	2.753329000
1	0.302185000	-2.509863000	3.337244000
6	1.805660000	0.067341000	2.794093000
1	1.183595000	0.089198000	3.702224000
1	2.804303000	-0.321756000	3.042858000
1	1.897443000	1.088419000	2.401603000
6	-4.314938000	0.037411000	0.238635000
1	-4.439380000	-0.894621000	0.821080000
1	-5.179140000	0.685868000	0.458266000
6	-2.988830000	1.896230000	1.312407000
6	-3.039598000	0.701677000	0.692702000
1	-3.894336000	2.448343000	1.596943000
1	-2.039992000	2.376380000	1.597241000

TS(A4.A5) (allene)

G = -1686.14512

6	-1.903032000	1.564316000	-0.368021000
6	-2.431685000	2.443244000	-1.330028000
6	-1.678971000	3.494926000	-1.853352000
6	-0.367501000	3.689283000	-1.414355000
6	0.168513000	2.841740000	-0.444142000
6	-0.585165000	1.784715000	0.100901000
1	-3.452477000	2.278217000	-1.680699000
1	-2.114863000	4.156262000	-2.604470000
1	0.237277000	4.503562000	-1.817781000
1	1.192361000	3.013418000	-0.109667000
6	-2.790940000	0.456411000	0.108749000
6	-3.967209000	0.811787000	0.787072000
6	-2.522380000	-0.916473000	-0.123970000
6	-4.856896000	-0.154803000	1.260418000
1	-4.173897000	1.870606000	0.956539000
6	-3.428242000	-1.879002000	0.354204000
6	-4.584205000	-1.505802000	1.045415000
1	-5.758640000	0.149453000	1.795021000
1	-3.245215000	-2.940992000	0.190822000
1	-5.269946000	-2.274115000	1.407265000
15	-0.954242000	-1.459382000	-0.934104000
15	0.272992000	0.687143000	1.315051000
45	1.140991000	-1.079490000	0.181287000
6	3.942802000	-0.191747000	1.425222000
6	4.213007000	1.064669000	0.720191000
6	2.904310000	-1.041967000	1.242923000
6	3.860407000	1.386120000	-0.539006000
1	4.685895000	-0.452185000	2.190698000
1	2.949955000	-2.003053000	1.784443000
1	4.811490000	1.796957000	1.272744000
1	4.146641000	2.366767000	-0.930930000
6	-0.919444000	0.195384000	2.639119000
1	-0.315218000	-0.187811000	3.475171000
1	-1.489251000	1.076665000	2.969633000
1	-1.612628000	-0.584971000	2.307503000
6	1.366790000	1.819110000	2.262853000
1	2.173331000	2.210660000	1.634332000
1	0.759294000	2.643791000	2.664487000
1	1.816503000	1.241530000	3.081455000
6	-1.188636000	-3.245039000	-1.329021000
1	-1.207621000	-3.846500000	-0.409390000
1	-2.110633000	-3.411303000	-1.906301000
1	-0.321709000	-3.558800000	-1.929213000
6	-0.948492000	-0.680449000	-2.609040000
1	-0.111352000	-1.116352000	-3.174669000
1	-1.897570000	-0.883089000	-3.127544000
1	-0.797873000	0.402818000	-2.522181000
6	2.701466000	-0.806020000	-0.959024000
6	3.125353000	0.508639000	-1.524407000
6	2.894205000	-2.060096000	-1.424967000
1	2.811542000	-2.951887000	-0.796464000
1	3.154496000	-2.219465000	-2.477738000
1	2.228410000	1.057190000	-1.865995000

1	3.761548000	0.349586000	-2.415629000

A5 (allene)

G = -1686.20551

6	-2.446123000	1.314558000	0.261568000
6	-3.545295000	2.097296000	-0.129122000
6	-3.376219000	3.334526000	-0.751907000
6	-2.087332000	3.811036000	-0.996159000
6	-0.982727000	3.060142000	-0.588962000
6	-1.137757000	1.818916000	0.055483000
1	-4.550407000	1.705670000	0.039824000
1	-4.248488000	3.917065000	-1.054203000
1	-1.935622000	4.769971000	-1.494981000
1	0.011252000	3.463198000	-0.780543000
6	-2.732742000	-0.030340000	0.846514000
6	-3.484432000	-0.101862000	2.029232000
6	-2.308426000	-1.231294000	0.226820000
6	-3.794356000	-1.329410000	2.618290000
1	-3.815340000	0.827501000	2.497416000
6	-2.626562000	-2.460059000	0.828975000
6	-3.359883000	-2.511819000	2.017676000
1	-4.372667000	-1.359709000	3.543574000
1	-2.307801000	-3.398682000	0.375539000
1	-3.594754000	-3.478823000	2.466327000
15	-1.242175000	-1.196344000	-1.282600000
15	0.391315000	0.889983000	0.541471000
45	0.999174000	-0.733855000	-0.854571000
6	2.854081000	-1.637616000	-0.019140000
6	3.282013000	-1.392274000	1.359090000
6	3.219245000	-0.768004000	-1.047520000
6	4.113184000	-0.365019000	1.654530000
1	2.511683000	-2.655751000	-0.248952000
1	3.203785000	-1.136675000	-2.083463000
1	2.947396000	-2.080780000	2.137427000
1	4.450920000	-0.217597000	2.684265000
6	0.144057000	0.304329000	2.271161000
1	1.129558000	-0.017656000	2.637749000
1	-0.239185000	1.128821000	2.891510000
1	-0.550685000	-0.542619000	2.303557000
6	1.645599000	2.218674000	0.764638000
1	1.965396000	2.627367000	-0.202211000
1	1.218630000	3.019250000	1.387272000
1	2.519713000	1.789401000	1.266354000
6	-1.319930000	-2.908883000	-1.973838000
1	-0.802981000	-3.621876000	-1.316688000
1	-2.364558000	-3.225553000	-2.116588000
1	-0.812097000	-2.898891000	-2.950238000
6	-2.158391000	-0.234848000	-2.568120000
1	-1.668352000	-0.423138000	-3.535332000
1	-3.205770000	-0.568882000	-2.614599000
1	-2.122228000	0.840017000	-2.353856000
6	4.168469000	0.389154000	-0.802213000
1	5.075623000	0.192786000	-1.401926000

1	3.754400000	1.325383000	-1.211395000
6	4.588787000	0.588155000	0.653808000
6	5.375173000	1.622353000	1.016654000
1	5.681265000	1.763687000	2.055760000
1	5.738793000	2.349175000	0.286271000

A3 (carbon disulfide)

G = -2404.04511

6	1.048729000	1.991218000	-0.703018000
6	1.041506000	3.385055000	-0.524918000
6	-0.030070000	4.173772000	-0.947628000
6	-1.127075000	3.572633000	-1.566047000
6	-1.134254000	2.191836000	-1.768725000
6	-0.054542000	1.387043000	-1.359272000
1	1.897741000	3.849736000	-0.031902000
1	-0.006175000	5.253913000	-0.791074000
1	-1.975352000	4.173241000	-1.899240000
1	-1.998898000	1.746980000	-2.260318000
6	2.259293000	1.251177000	-0.218965000
6	3.472514000	1.504423000	-0.879900000
6	2.250683000	0.367719000	0.889420000
6	4.657407000	0.875796000	-0.492427000
1	3.474597000	2.197444000	-1.723883000
6	3.452324000	-0.253019000	1.271739000
6	4.645029000	-0.010432000	0.584968000
1	5.584548000	1.079949000	-1.031104000
1	3.474265000	-0.936861000	2.120207000
1	5.562665000	-0.509612000	0.901696000
15	0.668643000	-0.047945000	1.752599000
15	-0.161981000	-0.430489000	-1.662091000
45	-0.683375000	-1.425421000	0.266293000
6	0.522728000	-3.911234000	-0.386251000
6	-0.851378000	-4.035289000	-0.903987000
6	0.874444000	-2.708131000	0.105494000
6	-1.602956000	-2.918079000	-0.833548000
1	1.219624000	-4.757073000	-0.409158000
1	1.882487000	-2.457694000	0.455345000
1	-1.212398000	-4.986057000	-1.311606000
1	-2.635404000	-2.885736000	-1.208680000
6	1.385930000	-0.972797000	-2.481129000
1	1.241646000	-2.019476000	-2.782477000
1	1.562954000	-0.336460000	-3.361284000
1	2.235176000	-0.911476000	-1.792640000
6	-1.422799000	-0.644863000	-2.980553000
1	-2.429144000	-0.445555000	-2.589487000
1	-1.201123000	0.020116000	-3.828198000
1	-1.376989000	-1.694588000	-3.298400000
6	1.161538000	-1.005084000	3.250858000
1	1.550901000	-1.991322000	2.962834000
1	1.907167000	-0.463342000	3.852186000
1	0.254697000	-1.156697000	3.855891000
6	0.096365000	1.542729000	2.494192000
1	-0.772094000	1.334968000	3.136859000

1	0.901637000	1.988529000	3.097010000
1	-0.202513000	2.244479000	1.706551000
6	-3.124633000	1.020325000	1.004793000
16	-3.078705000	-0.535474000	0.679989000
16	-3.228344000	2.545116000	1.292478000

TS(A3.A4) (carbon disulfide)

G = -2404.01128

6	-2.696501000	-0.768351000	0.035657000
6	-3.724612000	-1.429424000	0.726686000
6	-3.787124000	-2.822842000	0.785641000
6	-2.812611000	-3.586255000	0.141153000
6	-1.798639000	-2.950072000	-0.577826000
6	-1.732013000	-1.546579000	-0.653162000
1	-4.474455000	-0.828325000	1.244798000
1	-4.592365000	-3.308832000	1.339689000
1	-2.843174000	-4.676364000	0.184707000
1	-1.061723000	-3.568404000	-1.090260000
6	-2.698005000	0.729512000	0.068860000
6	-3.764028000	1.394302000	-0.558802000
6	-1.714318000	1.492874000	0.747175000
6	-3.853257000	2.787614000	-0.560655000
1	-4.526542000	0.798811000	-1.065324000
6	-1.820093000	2.895134000	0.740676000
6	-2.873449000	3.540653000	0.087388000
1	-4.686897000	3.280227000	-1.064518000
1	-1.081121000	3.505987000	1.259708000
1	-2.930207000	4.630705000	0.098616000
15	-0.256806000	0.687003000	1.551213000
15	-0.358478000	-0.771368000	-1.606384000
45	1.321018000	-0.048216000	-0.138362000
6	2.069340000	1.865242000	-2.120138000
6	2.893094000	0.773145000	-2.483558000
6	1.252774000	1.681358000	-1.026401000
6	2.875087000	-0.299486000	-1.592270000
1	2.084697000	2.818928000	-2.658075000
1	0.577407000	2.455589000	-0.644594000
1	3.495099000	0.775346000	-3.397390000
1	3.406102000	-1.231430000	-1.813758000
6	-1.115320000	0.406151000	-2.798186000
1	-0.320949000	0.741872000	-3.479155000
1	-1.908279000	-0.107731000	-3.362042000
1	-1.528617000	1.273650000	-2.271502000
6	0.306556000	-2.081590000	-2.711592000
1	0.830911000	-2.853658000	-2.132353000
1	-0.499906000	-2.533655000	-3.307709000
1	1.034163000	-1.594104000	-3.375964000
6	0.469604000	1.968380000	2.654941000
1	0.936149000	2.765928000	2.060512000
1	-0.285784000	2.391893000	3.333224000
1	1.256665000	1.473289000	3.242014000
6	-0.947576000	-0.535920000	2.747553000
1	-0.147176000	-0.803116000	3.450153000

1	-1.792256000	-0.088202000	3.291312000
1	-1.278401000	-1.442366000	2.226600000
6	2.881682000	-0.478331000	1.252277000
16	4.020213000	0.171791000	0.252109000
16	2.583320000	-1.337661000	2.594932000

A4 (carbon disulfide)

G = -2404.06089

6	2.580963000	1.196067000	-0.191650000
6	3.578811000	2.009799000	0.368759000
6	3.331799000	3.342872000	0.702366000
6	2.067657000	3.889443000	0.474753000
6	1.070460000	3.106167000	-0.109166000
6	1.311491000	1.765451000	-0.464685000
1	4.560204000	1.572181000	0.562555000
1	4.123875000	3.948963000	1.146099000
1	1.855791000	4.926533000	0.740825000
1	0.096397000	3.559741000	-0.292522000
6	2.926662000	-0.231501000	-0.478241000
6	3.899740000	-0.491085000	-1.455220000
6	2.331930000	-1.318634000	0.210322000
6	4.260306000	-1.797885000	-1.790620000
1	4.363777000	0.352545000	-1.970602000
6	2.704257000	-2.628330000	-0.137167000
6	3.653598000	-2.869677000	-1.134732000
1	5.011130000	-1.975553000	-2.562791000
1	2.261044000	-3.483450000	0.373236000
1	3.923559000	-3.896834000	-1.387209000
15	1.010864000	-1.028411000	1.468867000
15	-0.084263000	0.797360000	-1.193341000
45	-1.094872000	-0.212923000	0.590298000
6	-2.383119000	-1.892008000	-1.627263000
6	-3.246534000	-0.927592000	-2.305285000
6	-1.513223000	-1.745372000	-0.606509000
6	-4.030994000	0.070666000	-1.845072000
1	-2.399562000	-2.886599000	-2.095749000
1	-0.928078000	-2.630014000	-0.315199000
1	-3.316369000	-1.078105000	-3.390997000
1	-4.645980000	0.645760000	-2.542491000
6	0.564245000	-0.183126000	-2.607728000
1	-0.300016000	-0.507113000	-3.203405000
1	1.227250000	0.448539000	-3.216582000
1	1.107467000	-1.067528000	-2.256089000
6	-1.138822000	2.054667000	-2.027821000
1	-1.702148000	2.639408000	-1.288731000
1	-0.518562000	2.720179000	-2.646411000
1	-1.855463000	1.514117000	-2.658069000
6	0.768411000	-2.648679000	2.312294000
1	0.301954000	-3.376556000	1.633606000
1	1.718475000	-3.051040000	2.694695000
1	0.079103000	-2.473817000	3.151322000
6	1.782313000	-0.004035000	2.797345000
1	1.086218000	0.014238000	3.649483000

1	2.742981000	-0.439273000	3.110754000
1	1.938818000	1.023081000	2.443908000
6	-2.986045000	0.284302000	0.694045000
16	-2.730054000	0.165372000	2.350113000
16	-4.430263000	0.500807000	-0.165631000

TS(A4.A5) (carbon disulfide)

G = -2404.4501

6	-2.132262000	1.514214000	-0.585891000
6	-2.623476000	2.245737000	-1.681549000
6	-1.864563000	3.243547000	-2.293328000
6	-0.584751000	3.528267000	-1.812064000
6	-0.089421000	2.829152000	-0.711206000
6	-0.852828000	1.834082000	-0.072814000
1	-3.616051000	2.003284000	-2.066532000
1	-2.268584000	3.789488000	-3.147836000
1	0.027228000	4.297202000	-2.287135000
1	0.912519000	3.065794000	-0.350872000
6	-3.009121000	0.438016000	-0.027569000
6	-4.235550000	0.821353000	0.536737000
6	-2.673847000	-0.938831000	-0.073874000
6	-5.113140000	-0.118331000	1.080817000
1	-4.491275000	1.882797000	0.559025000
6	-3.568091000	-1.874566000	0.476140000
6	-4.774886000	-1.471446000	1.054020000
1	-6.055996000	0.207849000	1.523716000
1	-3.336474000	-2.939265000	0.459520000
1	-5.449353000	-2.219749000	1.474293000
15	-1.050620000	-1.520093000	-0.741413000
15	-0.046454000	0.923803000	1.318652000
45	0.992134000	-0.945546000	0.433508000
6	3.605134000	0.240789000	1.858017000
6	3.836646000	1.479904000	1.143984000
6	2.725534000	-0.741902000	1.544305000
6	3.781754000	1.664447000	-0.194823000
1	4.240477000	0.094896000	2.741932000
1	2.829500000	-1.700822000	2.078368000
1	4.190938000	2.333842000	1.731583000
1	4.063049000	2.616238000	-0.652010000
6	-1.313791000	0.512159000	2.603543000
1	-0.759838000	0.317454000	3.534520000
1	-1.988328000	1.368016000	2.751557000
1	-1.902059000	-0.374332000	2.343532000
6	0.884261000	2.221951000	2.233697000
1	1.645767000	2.697082000	1.608353000
1	0.169904000	2.978614000	2.590938000
1	1.382534000	1.741322000	3.086602000
6	-1.240517000	-3.341037000	-0.952717000
1	-1.267870000	-3.845784000	0.022942000
1	-2.147961000	-3.580581000	-1.526670000
1	-0.356709000	-3.695974000	-1.500735000
6	-0.947220000	-0.921494000	-2.482394000
1	-0.066112000	-1.399579000	-2.935673000

1	-1.855622000	-1.200867000	-3.036332000
1	-0.815021000	0.167205000	-2.502246000
6	2.581758000	-0.786330000	-0.651933000
16	2.353569000	-2.373510000	-1.122891000
16	3.544911000	0.411741000	-1.415476000

A5 (carbon disulfide)

G = -2404.07007

6	-2.451005000	1.648548000	-0.034840000
6	-3.244356000	2.610607000	-0.682431000
6	-2.675182000	3.690073000	-1.359480000
6	-1.286174000	3.824681000	-1.399516000
6	-0.481450000	2.893172000	-0.741293000
6	-1.043279000	1.809662000	-0.040915000
1	-4.329203000	2.488101000	-0.668938000
1	-3.315892000	4.417441000	-1.861432000
1	-0.824514000	4.656186000	-1.934964000
1	0.600012000	3.024253000	-0.778934000
6	-3.151602000	0.495906000	0.609382000
6	-4.077638000	0.762576000	1.629183000
6	-2.941435000	-0.847315000	0.209468000
6	-4.768679000	-0.267463000	2.270997000
1	-4.241677000	1.799109000	1.930740000
6	-3.641383000	-1.875524000	0.862978000
6	-4.546378000	-1.591050000	1.889342000
1	-5.476454000	-0.034139000	3.068538000
1	-3.492791000	-2.917039000	0.578107000
1	-5.078517000	-2.406466000	2.382562000
15	-1.681416000	-1.267822000	-1.070234000
15	0.122466000	0.620295000	0.761935000
45	0.563489000	-1.179015000	-0.494407000
6	2.557531000	-2.092991000	-0.035337000
6	3.207490000	-1.812688000	1.227248000
6	2.701489000	-1.257731000	-1.151198000
6	4.042438000	-0.757345000	1.447609000
1	2.210884000	-3.123715000	-0.187559000
1	2.513778000	-1.634145000	-2.165177000
1	3.040057000	-2.522142000	2.041196000
1	4.512954000	-0.641585000	2.427202000
6	-0.557756000	0.161678000	2.415824000
1	0.270292000	-0.286995000	2.984135000
1	-0.912464000	1.067354000	2.930896000
1	-1.374440000	-0.563328000	2.335162000
6	1.546310000	1.675069000	1.252953000
1	2.139661000	1.998983000	0.391091000
1	1.151039000	2.551615000	1.788168000
1	2.192317000	1.097333000	1.924980000
6	-2.026518000	-3.015310000	-1.556422000
1	-1.792128000	-3.704985000	-0.733898000
1	-3.078846000	-3.134960000	-1.856741000
1	-1.381379000	-3.258201000	-2.414491000
6	-2.133578000	-0.333983000	-2.597071000
1	-1.549645000	-0.750900000	-3.430986000

1	-3.208655000	-0.451344000	-2.800946000
1	-1.890373000	0.729445000	-2.485835000
6	4.385995000	0.280960000	0.495992000
16	3.733796000	0.174432000	-1.165583000
16	5.319591000	1.598037000	0.861525000

A3 (carbodiimide)

G = -1718.30548

6	2.109041000	0.729137000	-0.501987000
6	3.192655000	1.535017000	-0.112520000
6	3.155220000	2.925447000	-0.235874000
6	2.021006000	3.540004000	-0.772513000
6	0.934907000	2.756560000	-1.172390000
6	0.959024000	1.354788000	-1.047757000
1	4.080514000	1.049210000	0.297091000
1	4.014186000	3.523423000	0.074842000
1	1.984973000	4.624319000	-0.900028000
1	0.064681000	3.256632000	-1.597867000
6	2.279582000	-0.757462000	-0.391251000
6	3.207959000	-1.352058000	-1.261234000
6	1.584418000	-1.572112000	0.537528000
6	3.426851000	-2.731020000	-1.258253000
1	3.749371000	-0.716668000	-1.965391000
6	1.816777000	-2.957773000	0.529811000
6	2.721815000	-3.537061000	-0.364060000
1	4.143791000	-3.170866000	-1.953935000
1	1.292243000	-3.607711000	1.230058000
1	2.878904000	-4.617237000	-0.350802000
15	0.327071000	-0.834266000	1.674128000
15	-0.559084000	0.406165000	-1.513452000
45	-1.606711000	-0.082750000	0.386137000
6	-3.124055000	-2.192351000	-0.762375000
6	-3.976194000	-0.996680000	-0.912354000
6	-1.886369000	-1.982277000	-0.269415000
6	-3.406138000	0.175789000	-0.564132000
1	-3.489351000	-3.186211000	-1.045045000
1	-1.142810000	-2.783761000	-0.172285000
1	-5.004024000	-1.084621000	-1.282883000
1	-3.932943000	1.136822000	-0.663429000
6	-0.070284000	-0.983155000	-2.607182000
1	-0.996096000	-1.396198000	-3.030474000
1	0.582980000	-0.600369000	-3.405564000
1	0.442202000	-1.767932000	-2.041735000
6	-1.494652000	1.501917000	-2.652505000
1	-1.924398000	2.350822000	-2.105271000
1	-0.841358000	1.857511000	-3.463079000
1	-2.321999000	0.906237000	-3.060042000
6	-0.165186000	-2.194985000	2.818936000
1	-0.744271000	-2.958051000	2.281199000
1	0.708312000	-2.652582000	3.307033000
1	-0.813520000	-1.752367000	3.590506000
6	1.318166000	0.250660000	2.796500000
1	0.652334000	0.670532000	3.564911000

1	2.114720000	-0.337223000	3.276879000
1	1.762578000	1.079352000	2.232402000
6	-0.861160000	2.706805000	1.655367000
7	-1.794466000	1.983622000	1.251618000
1	-2.712069000	2.433447000	1.192436000
7	0.083971000	3.270178000	2.162752000
1	0.746403000	3.797043000	1.589527000

TS(A3.A4) (carbodiimide)

G = -1718.28964

6	-2.607000000	0.793692000	-0.172289000
6	-3.692690000	1.254743000	-0.934691000
6	-3.753807000	2.570633000	-1.396986000
6	-2.719706000	3.456852000	-1.092543000
6	-1.644471000	3.024980000	-0.312807000
6	-1.573748000	1.703961000	0.165616000
1	-4.492950000	0.553534000	-1.180079000
1	-4.605399000	2.899076000	-1.995736000
1	-2.749587000	4.487687000	-1.450165000
1	-0.858862000	3.741690000	-0.073231000
6	-2.627768000	-0.639937000	0.261842000
6	-3.634944000	-1.032988000	1.157615000
6	-1.708510000	-1.612117000	-0.207463000
6	-3.722697000	-2.345415000	1.625530000
1	-4.348395000	-0.282184000	1.503531000
6	-1.808669000	-2.930418000	0.272047000
6	-2.800014000	-3.295707000	1.186867000
1	-4.508651000	-2.621729000	2.330815000
1	-1.114550000	-3.698052000	-0.070721000
1	-2.853827000	-4.325880000	1.543829000
15	-0.317364000	-1.155409000	-1.333431000
15	-0.087072000	1.190816000	1.136132000
45	1.412323000	0.078938000	-0.233762000
6	2.799813000	-1.109030000	1.940375000
6	3.545526000	0.102629000	1.718747000
6	1.690126000	-1.269022000	1.167265000
6	3.130241000	0.907887000	0.673126000
1	3.093598000	-1.846005000	2.694384000
1	0.983470000	-2.099718000	1.291621000
1	4.367042000	0.372542000	2.394344000
1	3.529792000	1.927148000	0.588096000
6	-0.686876000	0.346172000	2.659199000
1	0.174428000	0.249441000	3.335987000
1	-1.474549000	0.947316000	3.136121000
1	-1.070617000	-0.654127000	2.427991000
6	0.613437000	2.748574000	1.822260000
1	1.071391000	3.353202000	1.027766000
1	-0.159248000	3.331241000	2.345098000
1	1.404343000	2.458177000	2.527974000
6	0.307448000	-2.753601000	-2.006097000
1	0.850299000	-3.312790000	-1.231208000
1	-0.508560000	-3.369378000	-2.412617000
1	1.010850000	-2.514655000	-2.817891000

6	-1.068283000	-0.372424000	-2.828042000
1	-0.276040000	-0.278891000	-3.586626000
1	-1.884154000	-0.996843000	-3.221730000
1	-1.452224000	0.627185000	-2.588951000
6	4.026294000	0.090312000	-0.982992000
7	5.215810000	0.362822000	-1.175455000
1	5.816839000	0.627133000	-0.399569000
7	2.940848000	-0.404501000	-1.512031000
1	3.088775000	-1.205359000	-2.127314000

A4 (carbodiimide)

G = -1718.33530

6	-2.695256000	-0.507060000	0.076949000
6	-3.847533000	-0.856894000	0.799678000
6	-4.116495000	-2.181847000	1.148715000
6	-3.230503000	-3.189779000	0.766317000
6	-2.091457000	-2.866285000	0.025499000
6	-1.811203000	-1.536448000	-0.336459000
1	-4.533370000	-0.064046000	1.105247000
1	-5.014461000	-2.422629000	1.720764000
1	-3.424180000	-4.229728000	1.035143000
1	-1.420108000	-3.672141000	-0.271461000
6	-2.498947000	0.942533000	-0.246980000
6	-3.445306000	1.546949000	-1.090802000
6	-1.439363000	1.733999000	0.265444000
6	-3.341578000	2.888557000	-1.463208000
1	-4.267122000	0.938506000	-1.473729000
6	-1.344145000	3.083096000	-0.121121000
6	-2.280908000	3.657772000	-0.983616000
1	-4.086850000	3.328031000	-2.128818000
1	-0.534955000	3.708797000	0.255282000
1	-2.183149000	4.706868000	-1.268474000
15	-0.128408000	1.021625000	1.346424000
15	-0.237162000	-1.170651000	-1.228397000
45	1.338984000	-0.407198000	0.289792000
6	3.083700000	1.490809000	-1.271486000
6	4.407369000	0.930291000	-0.954114000
6	1.836352000	1.117226000	-0.911259000
6	4.681951000	-0.109284000	-0.141245000
1	3.123145000	2.362846000	-1.937343000
1	0.999731000	1.712654000	-1.296132000
1	5.248927000	1.420919000	-1.450895000
1	5.704523000	-0.462170000	0.009651000
6	-0.647181000	-0.147536000	-2.702138000
1	0.272477000	-0.041825000	-3.296599000
1	-1.423116000	-0.650208000	-3.297976000
1	-0.999385000	0.848012000	-2.408847000
6	0.303763000	-2.758112000	-1.983645000
1	0.668337000	-3.445454000	-1.208677000
1	-0.509675000	-3.221813000	-2.560869000
1	1.141660000	-2.521999000	-2.656251000
6	0.740320000	2.449301000	2.111149000
1	1.357804000	2.958531000	1.358442000

1	0.033074000	3.154230000	2.571920000
1	1.403022000	2.036122000	2.885123000
6	-0.952401000	0.211180000	2.779677000
1	-0.162929000	-0.082687000	3.487977000
1	-1.644674000	0.916804000	3.263075000
1	-1.500188000	-0.683637000	2.459092000
6	3.567571000	-0.814142000	0.549592000
7	2.966040000	-0.315251000	1.650460000
1	3.405401000	0.565967000	1.931567000
7	2.893874000	-1.834382000	-0.021628000
1	3.283432000	-2.059196000	-0.941779000

TS(A4.A5) (carbodiimide)

G = -1718.28009

6	-2.831634000	-0.382115000	-0.153925000
6	-4.117430000	-0.617984000	0.360687000
6	-4.550111000	-1.904446000	0.686124000
6	-3.694457000	-2.988943000	0.489660000
6	-2.419530000	-2.777854000	-0.040303000
6	-1.971619000	-1.487566000	-0.374844000
1	-4.779596000	0.234945000	0.522942000
1	-5.550831000	-2.055794000	1.095018000
1	-4.015309000	-4.001378000	0.741591000
1	-1.773106000	-3.642505000	-0.190646000
6	-2.466279000	1.038980000	-0.455703000
6	-3.229901000	1.711050000	-1.424521000
6	-1.429290000	1.745881000	0.204235000
6	-2.971247000	3.038959000	-1.768313000
1	-4.033284000	1.166787000	-1.925050000
6	-1.180677000	3.083912000	-0.150190000
6	-1.938833000	3.727836000	-1.130587000
1	-3.575779000	3.531477000	-2.532197000
1	-0.391349000	3.648785000	0.346446000
1	-1.725417000	4.767499000	-1.385503000
15	-0.298587000	0.929734000	1.411529000
15	-0.235953000	-1.274354000	-0.967611000
45	1.298144000	-0.416624000	0.504160000
6	3.373754000	1.350474000	-1.273140000
6	4.570615000	0.558922000	-1.399432000
6	2.401778000	1.204204000	-0.312162000
6	4.876209000	-0.447793000	-0.528835000
1	3.269364000	2.227569000	-1.920366000
1	1.854889000	2.103980000	-0.012670000
1	5.269618000	0.805174000	-2.202412000
1	5.762305000	-1.076081000	-0.620167000
6	-0.310668000	-0.274652000	-2.515030000
1	0.688656000	-0.315057000	-2.973602000
1	-1.061091000	-0.687019000	-3.205868000
1	-0.547821000	0.770255000	-2.283074000
6	0.277621000	-2.928416000	-1.596818000
1	0.431265000	-3.629618000	-0.765617000
1	-0.460602000	-3.333051000	-2.305141000
1	1.238464000	-2.786194000	-2.113196000

6	0.423138000	2.293896000	2.421029000
1	1.123284000	2.908649000	1.839593000
1	-0.369668000	2.935162000	2.833590000
1	0.982399000	1.820655000	3.241303000
6	-1.336742000	0.061762000	2.665769000
1	-0.679606000	-0.196623000	3.509547000
1	-2.140471000	0.728815000	3.011874000
1	-1.770987000	-0.856424000	2.254540000
6	3.777541000	-0.768427000	0.389241000
7	3.190991000	0.217834000	1.185871000
1	3.798651000	0.986794000	1.467496000
7	2.986118000	-1.804006000	0.260259000
1	3.304448000	-2.462286000	-0.454978000

A5 (carbodiimide)

G = -1718.34873

6	-2.495493000	1.274068000	0.209649000
6	-3.603349000	2.024425000	-0.218859000
6	-3.448756000	3.254104000	-0.859855000
6	-2.165925000	3.756113000	-1.084561000
6	-1.053845000	3.037283000	-0.641660000
6	-1.194845000	1.804235000	0.020924000
1	-4.602985000	1.613402000	-0.064149000
1	-4.327174000	3.810998000	-1.191190000
1	-2.025488000	4.709786000	-1.596642000
1	-0.064559000	3.457728000	-0.821232000
6	-2.763495000	-0.064490000	0.817849000
6	-3.552281000	-0.127678000	1.976902000
6	-2.281346000	-1.268648000	0.248147000
6	-3.844168000	-1.347513000	2.590451000
1	-3.926287000	0.803098000	2.408361000
6	-2.580386000	-2.489388000	0.875799000
6	-3.352579000	-2.531880000	2.039838000
1	-4.451888000	-1.370057000	3.496921000
1	-2.214962000	-3.429375000	0.462220000
1	-3.571543000	-3.492841000	2.508991000
15	-1.162671000	-1.244922000	-1.222774000
15	0.343358000	0.907702000	0.535828000
45	1.015379000	-0.743112000	-0.795161000
6	3.116270000	-1.435593000	-0.545411000
6	3.455229000	-1.598452000	0.861254000
6	3.528698000	-0.271768000	-1.184943000
6	4.092812000	-0.610664000	1.535598000
1	2.883437000	-2.318941000	-1.157794000
1	3.493149000	-0.143884000	-2.267341000
1	3.188271000	-2.530621000	1.361878000
1	4.354534000	-0.699949000	2.590098000
6	0.089643000	0.336043000	2.271543000
1	1.074946000	0.026197000	2.650366000
1	-0.303961000	1.162741000	2.882685000
1	-0.597196000	-0.516933000	2.309902000
6	1.567382000	2.267955000	0.777647000
1	1.952670000	2.629941000	-0.184179000

1	1.077982000	3.092837000	1.316870000
1	2.404817000	1.898187000	1.382048000
6	-1.176016000	-2.974518000	-1.876069000
1	-0.672124000	-3.662656000	-1.183478000
1	-2.208362000	-3.314388000	-2.051741000
1	-0.632122000	-2.974768000	-2.832850000
6	-2.057635000	-0.336974000	-2.560556000
1	-1.537263000	-0.545773000	-3.507186000
1	-3.097416000	-0.692201000	-2.623152000
1	-2.046409000	0.744068000	-2.378365000
6	4.474053000	0.650733000	0.898578000
7	5.004864000	1.601927000	1.578865000
1	5.222559000	2.423438000	1.001167000
7	4.173316000	0.709972000	-0.487127000
1	4.453947000	1.550676000	-0.981540000

A3 (carbon dioxide)

G = -1758.11798

6	2.093387000	0.691030000	-0.570678000
6	3.170384000	1.524902000	-0.224794000
6	3.098532000	2.912031000	-0.364875000
6	1.937197000	3.495782000	-0.874104000
6	0.864577000	2.685189000	-1.248750000
6	0.923494000	1.284487000	-1.109662000
1	4.076351000	1.064750000	0.174820000
1	3.947914000	3.533627000	-0.075689000
1	1.864880000	4.578684000	-0.988453000
1	-0.024907000	3.160780000	-1.662749000
6	2.282767000	-0.786475000	-0.399441000
6	3.204830000	-1.415480000	-1.251058000
6	1.613052000	-1.559685000	0.582584000
6	3.440909000	-2.789822000	-1.178965000
1	3.728713000	-0.810998000	-1.994528000
6	1.861093000	-2.941779000	0.643868000
6	2.759823000	-3.556205000	-0.232799000
1	4.153234000	-3.257265000	-1.861256000
1	1.356908000	-3.561125000	1.385653000
1	2.931588000	-4.632040000	-0.164720000
15	0.348745000	-0.790606000	1.689752000
15	-0.581484000	0.308654000	-1.543197000
45	-1.608484000	-0.130498000	0.385752000
6	-3.222040000	-2.221394000	-0.597006000
6	-4.040667000	-1.007889000	-0.790019000
6	-1.965181000	-2.027974000	-0.151836000
6	-3.415461000	0.159224000	-0.533051000
1	-3.618655000	-3.220337000	-0.811134000
1	-1.215877000	-2.820680000	-0.038263000
1	-5.083245000	-1.082685000	-1.118516000
1	-3.897762000	1.139253000	-0.653396000
6	-0.102098000	-1.143738000	-2.555090000
1	-1.031788000	-1.579763000	-2.946246000
1	0.545185000	-0.811180000	-3.380168000
1	0.415309000	-1.892010000	-1.945995000

6	-1.530238000	1.344973000	-2.724291000
1	-1.972498000	2.208439000	-2.210947000
1	-0.876796000	1.677613000	-3.544425000
1	-2.348255000	0.723877000	-3.112447000
6	-0.052432000	-2.075562000	2.949900000
1	-0.617245000	-2.897089000	2.487761000
1	0.852765000	-2.464856000	3.439682000
1	-0.695736000	-1.602853000	3.707589000
6	1.275115000	0.455880000	2.696407000
1	0.601378000	0.839852000	3.478318000
1	2.151660000	-0.008302000	3.172643000
1	1.609429000	1.290990000	2.067354000
6	-0.728916000	2.973679000	1.575332000
8	-1.518723000	2.201173000	1.174343000
8	0.045166000	3.738574000	1.974144000

TS(A3.A4) (carbon dioxide)

G = -1758.06850

6	-2.000454000	1.438896000	0.078960000
6	-2.710563000	2.470062000	-0.556054000
6	-2.139751000	3.728978000	-0.757441000
6	-0.836271000	3.980907000	-0.324675000
6	-0.116580000	2.978773000	0.326697000
6	-0.693037000	1.715584000	0.553225000
1	-3.721878000	2.267262000	-0.914091000
1	-2.712004000	4.508250000	-1.264357000
1	-0.373500000	4.954367000	-0.494402000
1	0.908419000	3.183876000	0.635463000
6	-2.678671000	0.113911000	0.238770000
6	-3.857233000	0.073642000	1.000247000
6	-2.202281000	-1.091920000	-0.339524000
6	-4.542087000	-1.122897000	1.223567000
1	-4.227488000	1.001964000	1.439930000
6	-2.898037000	-2.290442000	-0.105316000
6	-4.057195000	-2.310394000	0.674774000
1	-5.449883000	-1.124977000	1.829710000
1	-2.547056000	-3.228613000	-0.534553000
1	-4.580119000	-3.253423000	0.843322000
15	-0.662420000	-1.124843000	-1.344490000
15	0.352209000	0.431976000	1.336510000
45	1.359132000	-0.621290000	-0.372437000
6	2.877998000	-2.166408000	1.358191000
6	3.874059000	-1.335470000	0.673050000
6	1.577767000	-2.075290000	0.988595000
6	3.627522000	-0.268176000	-0.140039000
1	3.227883000	-2.921659000	2.071505000
1	0.810543000	-2.735942000	1.409459000
1	4.901293000	-1.724062000	0.677954000
1	4.467112000	-0.022745000	-0.805756000
6	-0.644261000	-0.553831000	2.525226000
1	0.058151000	-1.009632000	3.235864000
1	-1.318686000	0.135188000	3.054569000
1	-1.231234000	-1.336827000	2.035293000

6	1.566454000	1.248669000	2.437312000
1	2.258122000	1.887426000	1.877822000
1	1.015675000	1.831151000	3.191274000
1	2.138464000	0.443874000	2.920484000
6	-0.554937000	-2.791772000	-2.111478000
1	-0.387870000	-3.557770000	-1.342005000
1	-1.464828000	-3.018468000	-2.687391000
1	0.309488000	-2.785728000	-2.792279000
6	-0.925902000	0.024185000	-2.754633000
1	-0.092114000	-0.105083000	-3.459779000
1	-1.883552000	-0.200265000	-3.247296000
1	-0.918298000	1.060093000	-2.392123000
6	2.776898000	1.259528000	-0.683407000
8	2.007707000	1.008134000	-1.653237000
8	3.197912000	2.234814000	-0.127457000

A4 (carbon dioxide)

$G = -1758.11965$

6	-2.719360000	-0.474853000	0.063255000
6	-3.887569000	-0.814943000	0.764305000
6	-4.185821000	-2.140566000	1.087826000
6	-3.314834000	-3.159880000	0.701435000
6	-2.157359000	-2.846544000	-0.014968000
6	-1.847461000	-1.516068000	-0.348692000
1	-4.564032000	-0.015098000	1.072356000
1	-5.096720000	-2.372963000	1.642626000
1	-3.534083000	-4.200120000	0.948314000
1	-1.497790000	-3.659756000	-0.318348000
6	-2.495509000	0.975670000	-0.240164000
6	-3.431555000	1.612053000	-1.071666000
6	-1.421406000	1.740917000	0.282210000
6	-3.306026000	2.959705000	-1.415978000
1	-4.264034000	1.025907000	-1.466005000
6	-1.304095000	3.096359000	-0.073696000
6	-2.234147000	3.703321000	-0.921143000
1	-4.044836000	3.424476000	-2.071495000
1	-0.484064000	3.699604000	0.315676000
1	-2.121767000	4.756842000	-1.183089000
15	-0.124218000	0.988453000	1.344414000
15	-0.259926000	-1.164529000	-1.212895000
45	1.301146000	-0.440006000	0.292612000
6	3.106754000	1.444887000	-1.254389000
6	4.447731000	0.931238000	-0.920817000
6	1.853176000	1.074079000	-0.917963000
6	4.737766000	-0.098065000	-0.104692000
1	3.132076000	2.314141000	-1.926424000
1	1.019135000	1.659864000	-1.319552000
1	5.276188000	1.456202000	-1.402964000
1	5.758874000	-0.431071000	0.083963000
6	-0.625474000	-0.145394000	-2.696687000
1	0.310215000	-0.037310000	-3.264259000
1	-1.380616000	-0.659417000	-3.309521000
1	-0.996737000	0.846859000	-2.415237000

6	0.347980000	-2.745694000	-1.919156000
1	0.645294000	-3.436595000	-1.118826000
1	-0.413117000	-3.206971000	-2.565643000
1	1.247547000	-2.504437000	-2.503842000
6	0.846351000	2.353390000	2.088372000
1	1.422106000	2.866145000	1.306290000
1	0.196419000	3.059550000	2.625244000
1	1.561247000	1.888628000	2.782818000
6	-0.942724000	0.180210000	2.780187000
1	-0.150984000	-0.146793000	3.471301000
1	-1.599384000	0.904679000	3.285294000
1	-1.529828000	-0.689233000	2.458986000
6	3.580877000	-0.796471000	0.519302000
8	3.022576000	-0.288263000	1.560014000
8	2.981887000	-1.724468000	-0.133676000

TS(A4.A5) (carbon dioxide)

G = -1758.06225

6	-2.814683000	-0.388160000	-0.203879000
6	-4.117872000	-0.637946000	0.256393000
6	-4.557916000	-1.932918000	0.537141000
6	-3.693187000	-3.011733000	0.349945000
6	-2.398869000	-2.787202000	-0.125110000
6	-1.944542000	-1.488291000	-0.413036000
1	-4.789026000	0.209079000	0.412141000
1	-5.572899000	-2.095154000	0.904553000
1	-4.021188000	-4.029850000	0.566949000
1	-1.744280000	-3.646353000	-0.270682000
6	-2.440451000	1.038902000	-0.463670000
6	-3.180272000	1.735796000	-1.433443000
6	-1.418952000	1.730155000	0.236353000
6	-2.914695000	3.072613000	-1.735687000
1	-3.971143000	1.205353000	-1.967551000
6	-1.162662000	3.077170000	-0.075694000
6	-1.899253000	3.746143000	-1.055636000
1	-3.501618000	3.584367000	-2.500633000
1	-0.385930000	3.628717000	0.454637000
1	-1.682232000	4.792521000	-1.277581000
15	-0.317614000	0.887736000	1.448981000
15	-0.196215000	-1.252445000	-0.941802000
45	1.297811000	-0.397705000	0.535703000
6	3.259518000	1.404249000	-1.319615000
6	4.373362000	0.529030000	-1.564585000
6	2.384090000	1.284714000	-0.276698000
6	4.696056000	-0.480716000	-0.706689000
1	3.139453000	2.300087000	-1.937496000
1	1.941130000	2.176889000	0.170893000
1	4.980602000	0.694305000	-2.457486000
1	5.475927000	-1.214357000	-0.906760000
6	-0.220728000	-0.274939000	-2.500743000
1	0.798907000	-0.291479000	-2.913022000
1	-0.927836000	-0.720036000	-3.216633000
1	-0.501624000	0.764003000	-2.291227000

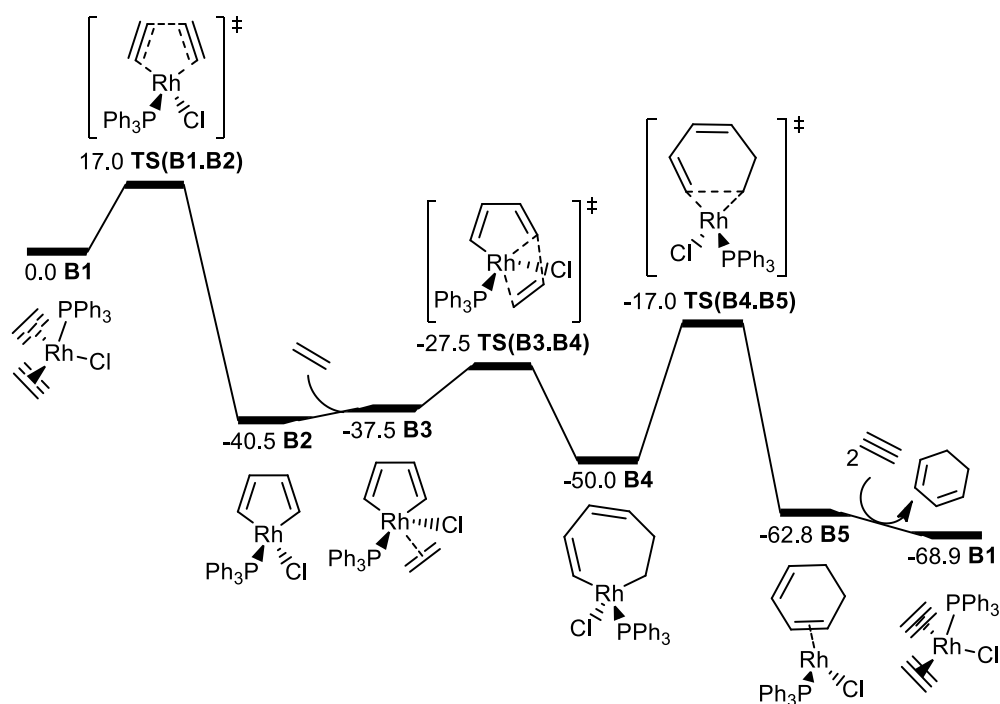
6	0.419788000	-2.901232000	-1.477447000
1	0.510060000	-3.577163000	-0.616449000
1	-0.238515000	-3.338783000	-2.242795000
1	1.426574000	-2.747506000	-1.892607000
6	0.390448000	2.211413000	2.516979000
1	1.084519000	2.863135000	1.970430000
1	-0.415962000	2.819560000	2.953310000
1	0.954434000	1.710338000	3.317212000
6	-1.368401000	-0.033170000	2.651999000
1	-0.723713000	-0.318886000	3.496435000
1	-2.177347000	0.622369000	3.008352000
1	-1.796146000	-0.935866000	2.201772000
6	3.714010000	-0.736390000	0.341795000
8	3.255092000	0.310820000	1.072584000
8	3.096793000	-1.814925000	0.438400000

A5 (carbon dioxide)

G = -1758.12644

6	-2.250116000	1.514502000	-0.060897000
6	-3.069994000	2.436991000	-0.733009000
6	-2.541748000	3.578155000	-1.338157000
6	-1.167503000	3.816929000	-1.279913000
6	-0.338705000	2.924437000	-0.598192000
6	-0.861045000	1.778632000	0.030022000
1	-4.141138000	2.235045000	-0.795627000
1	-3.202065000	4.272966000	-1.860408000
1	-0.736494000	4.698819000	-1.757086000
1	0.729969000	3.135645000	-0.559811000
6	-2.904212000	0.297493000	0.510236000
6	-3.917743000	0.473988000	1.464735000
6	-2.566131000	-1.018851000	0.106992000
6	-4.575093000	-0.616352000	2.038469000
1	-4.178817000	1.489171000	1.770542000
6	-3.233859000	-2.108025000	0.691893000
6	-4.229472000	-1.911927000	1.652987000
1	-5.353378000	-0.451380000	2.785829000
1	-2.988989000	-3.130114000	0.403331000
1	-4.734384000	-2.774047000	2.092450000
15	-1.189726000	-1.321294000	-1.083983000
15	0.339451000	0.649032000	0.865248000
45	1.008684000	-1.045926000	-0.426663000
6	3.152904000	-1.611925000	-0.340758000
6	3.878929000	-1.550456000	0.912703000
6	3.112137000	-0.465716000	-1.136266000
6	4.490992000	-0.399993000	1.284724000
1	2.963168000	-2.591307000	-0.800803000
1	2.905557000	-0.465857000	-2.209740000
1	3.945297000	-2.446188000	1.534067000
1	5.070298000	-0.309198000	2.203659000
6	-0.400531000	0.076829000	2.457267000
1	0.423436000	-0.327401000	3.063689000
1	-0.854384000	0.934455000	2.976697000
1	-1.152597000	-0.704035000	2.304497000

6	1.647557000	1.780743000	1.491077000
1	2.231508000	2.240883000	0.687229000
1	1.158353000	2.562301000	2.092045000
1	2.323225000	1.201817000	2.134375000
6	-1.356087000	-3.087039000	-1.599067000
1	-1.122525000	-3.763810000	-0.765620000
1	-2.372079000	-3.289024000	-1.971576000
1	-0.636905000	-3.268228000	-2.412349000
6	-1.625396000	-0.412239000	-2.630111000
1	-0.951184000	-0.758291000	-3.427500000
1	-2.669102000	-0.625329000	-2.906793000
1	-1.491257000	0.667093000	-2.490579000
6	4.410163000	0.811563000	0.473697000
8	3.679129000	0.702177000	-0.741158000
8	4.854316000	1.894098000	0.741128000



B1 (ethylene)

G = -1761.67860

45	0.813630000	-1.818021000	-0.000922000
15	-0.155561000	0.170063000	-0.000026000
17	3.172795000	-1.101294000	0.000794000
6	0.225769000	1.258851000	1.442550000
6	-0.668410000	2.277717000	1.816305000
6	1.458861000	1.138047000	2.100801000
6	-0.339817000	3.150890000	2.855101000
1	-1.625660000	2.390872000	1.304905000
6	1.780852000	2.020836000	3.135912000
1	2.172024000	0.374362000	1.783678000
6	0.884505000	3.022092000	3.519130000
1	-1.043531000	3.934583000	3.144698000
1	2.743703000	1.922511000	3.642076000
1	1.139839000	3.706092000	4.331818000
6	0.226635000	1.260369000	-1.441218000
6	-0.667644000	2.278986000	-1.815366000
6	1.460878000	1.141018000	-2.097608000
6	-0.338025000	3.153327000	-2.852876000
1	-1.625721000	2.391015000	-1.305290000
6	1.783858000	2.024967000	-3.131418000
1	2.174036000	0.377446000	-1.780139000
6	0.887397000	3.025949000	-3.515116000
1	-1.041795000	3.936823000	-3.142871000
1	2.747564000	1.927785000	-3.636170000
1	1.143518000	3.710871000	-4.326781000
6	-1.988376000	-0.042999000	-0.000472000
6	-2.679580000	-0.204123000	1.211847000
6	-2.679171000	-0.202874000	-1.213205000
6	-4.046078000	-0.494289000	1.208694000
1	-2.147491000	-0.109561000	2.159528000
6	-4.045676000	-0.493009000	-1.210819000

1	-2.146808000	-0.107309000	-2.160628000
6	-4.732749000	-0.636976000	-0.001248000
1	-4.574724000	-0.611920000	2.157267000
1	-4.574001000	-0.609612000	-2.159699000
1	-5.801133000	-0.864149000	-0.001543000
6	0.746101000	-2.133816000	-2.095795000
6	-0.335770000	-2.575521000	-1.601879000
1	1.419589000	-1.933488000	-2.919204000
1	-1.322888000	-3.015394000	-1.668921000
6	-0.336658000	-2.578468000	1.597697000
6	0.745074000	-2.137858000	2.093026000
1	1.417896000	-1.939006000	2.917345000
1	-1.323730000	-3.018591000	1.664080000

TS(B1.B2) (ethylene)

G = -1761.65145

45	2.054508000	-0.166657000	-0.008594000
6	2.427649000	1.904625000	-0.471726000
6	2.140093000	1.158936000	-1.491012000
6	3.672628000	1.029681000	0.766957000
6	4.050880000	-0.146809000	0.385715000
17	1.934962000	-2.523259000	-0.208960000
1	3.840185000	1.850827000	1.460109000
1	4.854353000	-0.874270000	0.432043000
1	2.046569000	1.068229000	-2.569618000
1	2.320328000	2.919358000	-0.097990000
15	-0.368538000	0.007867000	0.025873000
6	-1.154445000	-0.579456000	1.595662000
6	-2.239132000	0.083883000	2.195122000
6	-0.653499000	-1.754051000	2.184232000
6	-2.812639000	-0.420490000	3.365898000
1	-2.636558000	0.998836000	1.752598000
6	-1.234204000	-2.253139000	3.352996000
1	0.183485000	-2.280013000	1.720236000
6	-2.311566000	-1.589018000	3.947386000
1	-3.655111000	0.103526000	3.823597000
1	-0.837866000	-3.167050000	3.801280000
1	-2.760357000	-1.980674000	4.863272000
6	-1.308518000	-0.879056000	-1.291476000
6	-2.703597000	-1.032638000	-1.219526000
6	-0.613899000	-1.390010000	-2.398013000
6	-3.394419000	-1.673170000	-2.249569000
1	-3.251583000	-0.655690000	-0.353482000
6	-1.310054000	-2.029766000	-3.428476000
1	0.473163000	-1.312610000	-2.437506000
6	-2.698354000	-2.169811000	-3.357844000
1	-4.478813000	-1.789291000	-2.185165000
1	-0.760428000	-2.430589000	-4.283019000
1	-3.239578000	-2.674664000	-4.161521000
6	-0.927038000	1.762337000	-0.121098000
6	-1.604032000	2.251881000	-1.246668000
6	-0.549423000	2.661252000	0.893290000
6	-1.907548000	3.614633000	-1.350769000

1	-1.897706000	1.570914000	-2.046995000
6	-0.862781000	4.017052000	0.792475000
1	-0.008524000	2.291919000	1.768082000
6	-1.542430000	4.498566000	-0.333428000
1	-2.435518000	3.983016000	-2.233443000
1	-0.573244000	4.701909000	1.593053000
1	-1.784003000	5.560700000	-0.415324000

B2 (ethylene)

G = -1761.74311

45	1.877787000	-0.405608000	0.032190000
15	-0.379943000	-0.082638000	0.005517000
17	3.934704000	-1.423060000	0.071255000
6	-1.147788000	-1.233895000	-1.223397000
6	-2.408568000	-1.818621000	-1.024936000
6	-0.436049000	-1.519283000	-2.401696000
6	-2.947674000	-2.670144000	-1.992466000
1	-2.970085000	-1.617837000	-0.111263000
6	-0.980231000	-2.368616000	-3.368711000
1	0.547420000	-1.073573000	-2.566953000
6	-2.236995000	-2.945670000	-3.165166000
1	-3.927719000	-3.123217000	-1.826707000
1	-0.416525000	-2.582846000	-4.279156000
1	-2.660731000	-3.614347000	-3.917730000
6	-1.177336000	-0.512853000	1.614416000
6	-2.424708000	0.007529000	1.999066000
6	-0.518861000	-1.414138000	2.467294000
6	-3.000105000	-0.370211000	3.215428000
1	-2.944326000	0.716573000	1.352278000
6	-1.096728000	-1.790027000	3.681998000
1	0.454098000	-1.825677000	2.186047000
6	-2.338293000	-1.268438000	4.058295000
1	-3.968873000	0.042577000	3.505828000
1	-0.572084000	-2.488844000	4.336898000
1	-2.788324000	-1.559113000	5.010153000
6	-1.070211000	1.570303000	-0.429485000
6	-1.569282000	1.832876000	-1.714028000
6	-1.014532000	2.609574000	0.514306000
6	-2.005047000	3.117470000	-2.050076000
1	-1.618520000	1.036909000	-2.458410000
6	-1.453407000	3.890444000	0.174285000
1	-0.617388000	2.417905000	1.510921000
6	-1.946980000	4.148567000	-1.108536000
1	-2.391824000	3.310508000	-3.053197000
1	-1.404749000	4.691512000	0.915292000
1	-2.287605000	5.152236000	-1.372900000
6	1.965183000	1.059011000	1.370803000
6	2.247814000	2.268104000	0.836591000
1	1.851565000	0.833287000	2.438236000
1	2.398489000	3.163438000	1.448738000
6	2.313439000	2.298955000	-0.619772000
6	2.085879000	1.115760000	-1.229230000
1	2.074711000	0.945140000	-2.312827000

1	2.514127000	3.219137000	-1.177762000

B3 (ethylene)

G = -1840.33307

45	1.799561000	0.068694000	0.130911000
15	-0.496077000	-0.044754000	0.013639000
17	4.058262000	0.073444000	0.774889000
6	-1.120761000	-1.347874000	-1.145523000
6	-1.863260000	-2.455449000	-0.707034000
6	-0.776465000	-1.256265000	-2.507304000
6	-2.258074000	-3.445693000	-1.613130000
1	-2.133751000	-2.555244000	0.344710000
6	-1.182964000	-2.240312000	-3.410465000
1	-0.183206000	-0.410298000	-2.857487000
6	-1.923704000	-3.340382000	-2.965051000
1	-2.831610000	-4.303759000	-1.255312000
1	-0.912331000	-2.150286000	-4.464882000
1	-2.234827000	-4.114311000	-3.670088000
6	-1.177065000	-0.543816000	1.661711000
6	-2.540310000	-0.388700000	1.968582000
6	-0.319515000	-1.100757000	2.623484000
6	-3.033201000	-0.790903000	3.211403000
1	-3.215968000	0.054617000	1.234591000
6	-0.814323000	-1.500007000	3.868761000
1	0.744630000	-1.224387000	2.407175000
6	-2.171477000	-1.347481000	4.163543000
1	-4.094159000	-0.665395000	3.439104000
1	-0.134142000	-1.926497000	4.608993000
1	-2.558341000	-1.657284000	5.136947000
6	-1.494397000	1.460240000	-0.386299000
6	-2.197947000	1.617697000	-1.588348000
6	-1.529991000	2.494204000	0.566048000
6	-2.914224000	2.792889000	-1.838919000
1	-2.204000000	0.825843000	-2.336329000
6	-2.251969000	3.661540000	0.316511000
1	-0.992654000	2.384049000	1.507775000
6	-2.941492000	3.817302000	-0.890389000
1	-3.456358000	2.901189000	-2.780974000
1	-2.270061000	4.454800000	1.067055000
1	-3.502864000	4.733461000	-1.087465000
6	1.666328000	1.978192000	0.762861000
6	1.653184000	2.905734000	-0.219146000
1	1.678045000	2.220486000	1.833606000
1	1.623426000	3.984468000	-0.034408000
6	1.705049000	2.357145000	-1.568187000
6	1.751810000	1.009918000	-1.643161000
1	1.886353000	0.434110000	-2.565714000
1	1.733173000	2.989919000	-2.462447000
6	2.386206000	-1.994391000	-1.183645000
6	1.973293000	-2.435334000	0.029625000
1	3.428994000	-1.724298000	-1.359807000
1	1.707943000	-2.000423000	-2.039085000
1	2.681839000	-2.539445000	0.855341000

1	0.961913000	-2.824767000	0.174446000

TS(B3.B4) (ethylene)

G = -1840.31724

45	-1.711217000	-0.567377000	-0.302959000
15	0.523215000	0.015946000	0.066148000
17	-1.059816000	-2.740802000	-1.149803000
6	1.163110000	-1.104896000	1.386667000
6	2.435426000	-1.691437000	1.337343000
6	0.313557000	-1.398789000	2.468589000
6	2.854337000	-2.545920000	2.361453000
1	3.098962000	-1.494245000	0.494747000
6	0.738022000	-2.246601000	3.493188000
1	-0.687777000	-0.961294000	2.510821000
6	2.011379000	-2.822376000	3.441098000
1	3.845585000	-3.001982000	2.309974000
1	0.068547000	-2.465619000	4.327906000
1	2.342144000	-3.492849000	4.237428000
6	1.749747000	-0.069106000	-1.309456000
6	2.986303000	0.594685000	-1.204472000
6	1.456466000	-0.803473000	-2.468707000
6	3.913229000	0.525615000	-2.246562000
1	3.222585000	1.174974000	-0.310669000
6	2.389169000	-0.866746000	-3.508561000
1	0.513144000	-1.345628000	-2.541787000
6	3.614924000	-0.204259000	-3.402256000
1	4.869435000	1.046075000	-2.155597000
1	2.152274000	-1.442444000	-4.406076000
1	4.339412000	-0.255677000	-4.218500000
6	0.768627000	1.723210000	0.731841000
6	0.847574000	1.984740000	2.107809000
6	0.764537000	2.802227000	-0.168873000
6	0.925235000	3.300951000	2.573398000
1	0.858207000	1.163093000	2.824883000
6	0.845560000	4.114662000	0.299156000
1	0.693482000	2.613762000	-1.240595000
6	0.922987000	4.368885000	1.672251000
1	0.992453000	3.489243000	3.647420000
1	0.844015000	4.942575000	-0.413608000
1	0.984525000	5.396421000	2.037958000
6	-1.728306000	0.688388000	-1.787238000
6	-2.130674000	1.974215000	-1.544704000
1	-1.406232000	0.307332000	-2.764335000
1	-2.188353000	2.729967000	-2.335299000
6	-2.453927000	2.246560000	-0.177171000
6	-2.491000000	1.133794000	0.636918000
1	-2.585303000	1.251602000	1.723733000
1	-2.606896000	3.265975000	0.192273000
6	-4.112563000	-0.026941000	0.184761000
6	-3.714222000	-1.340377000	-0.167260000
1	-4.524154000	0.610525000	-0.600059000
1	-4.508898000	0.157675000	1.186562000
1	-3.898519000	-1.708673000	-1.179207000

1	-3.662186000	-2.116461000	0.604348000

B4 (ethylene)

G = -1840.35297

6	3.969415000	1.267471000	-0.435644000
6	4.119991000	0.841223000	0.832410000
6	3.060840000	0.454755000	1.762691000
6	2.652219000	1.499483000	-1.124996000
6	1.910112000	-0.198390000	1.502787000
6	1.946605000	0.232947000	-1.619286000
45	1.347536000	-1.075097000	-0.160556000
1	2.620284000	-0.385884000	-2.232791000
1	1.975674000	2.053421000	-0.455318000
1	4.875581000	1.474923000	-1.014331000
1	5.137091000	0.786750000	1.236976000
1	3.260119000	0.671178000	2.822913000
1	1.226837000	-0.422711000	2.338463000
17	3.030521000	-2.628900000	-0.475891000
1	1.058646000	0.506008000	-2.216215000
1	2.814084000	2.148322000	-2.006386000
15	-0.673159000	-0.014870000	0.013584000
6	-1.861725000	-0.520033000	-1.313215000
6	-3.228895000	-0.208657000	-1.216037000
6	-1.396501000	-1.219532000	-2.437381000
6	-4.110808000	-0.585007000	-2.229752000
1	-3.606669000	0.325328000	-0.341949000
6	-2.282833000	-1.597002000	-3.451737000
1	-0.338645000	-1.474857000	-2.528802000
6	-3.639091000	-1.279307000	-3.350274000
1	-5.171598000	-0.338865000	-2.143854000
1	-1.908440000	-2.142700000	-4.320387000
1	-4.331564000	-1.575313000	-4.141477000
6	-0.685514000	1.827052000	-0.055491000
6	-0.156533000	2.551614000	1.028910000
6	-1.073024000	2.514930000	-1.215289000
6	-0.037457000	3.939908000	0.956747000
1	0.180230000	2.026719000	1.923637000
6	-0.940748000	3.905693000	-1.286758000
1	-1.478266000	1.968275000	-2.068186000
6	-0.426846000	4.620584000	-0.202378000
1	0.373105000	4.490909000	1.805647000
1	-1.242783000	4.429904000	-2.196218000
1	-0.325466000	5.706607000	-0.259945000
6	-1.580075000	-0.440513000	1.568326000
6	-2.432396000	0.454997000	2.233755000
6	-1.420399000	-1.741219000	2.076844000
6	-3.111131000	0.054038000	3.388478000
1	-2.562681000	1.470629000	1.856726000
6	-2.101610000	-2.139180000	3.228902000
1	-0.760888000	-2.450219000	1.569058000
6	-2.947362000	-1.241181000	3.887961000
1	-3.769589000	0.759774000	3.900025000
1	-1.966801000	-3.152081000	3.614186000

1	-3.476244000	-1.550430000	4.792214000

TS(B4.B5) (ethylene)

G = -1840.30045

6	0.861419000	-2.850683000	-1.914260000
6	0.694371000	-3.375358000	-0.682811000
6	-0.545063000	-3.277202000	0.071237000
6	-0.165726000	-2.042365000	-2.667277000
6	-1.520950000	-2.350845000	-0.134638000
6	-1.530138000	-1.844182000	-1.999090000
45	-1.513788000	-0.335184000	-0.377095000
1	-2.208770000	-2.697183000	-2.130527000
1	0.273228000	-1.051978000	-2.885210000
1	1.808160000	-3.022972000	-2.438158000
1	1.501222000	-3.977556000	-0.252552000
1	-0.749611000	-4.077950000	0.791708000
1	-2.517417000	-2.555401000	0.276898000
17	-3.879932000	-0.207697000	-0.348396000
1	-2.064724000	-0.994493000	-2.461163000
1	-0.325046000	-2.511047000	-3.659260000
15	0.598247000	0.265987000	0.101304000
6	1.853311000	1.043748000	-0.998574000
6	2.028929000	2.435071000	-1.072255000
6	2.654591000	0.205021000	-1.792379000
6	2.984929000	2.976781000	-1.937268000
1	1.423135000	3.097002000	-0.451423000
6	3.613145000	0.750524000	-2.648368000
1	2.531425000	-0.878018000	-1.728683000
6	3.776946000	2.137948000	-2.726521000
1	3.113576000	4.060389000	-1.988882000
1	4.232424000	0.089486000	-3.258956000
1	4.523191000	2.564427000	-3.400563000
6	1.568053000	-0.363335000	1.531613000
6	0.942359000	-1.253549000	2.421441000
6	2.895346000	0.031871000	1.765789000
6	1.634914000	-1.730986000	3.536485000
1	-0.081314000	-1.574547000	2.225040000
6	3.584757000	-0.455097000	2.879328000
1	3.393527000	0.718436000	1.079285000
6	2.956628000	-1.335094000	3.766216000
1	1.141196000	-2.421796000	4.223615000
1	4.617188000	-0.143953000	3.054269000
1	3.498837000	-1.714863000	4.635282000
6	-0.530420000	1.581898000	0.712113000
6	-0.876986000	1.732226000	2.079227000
6	-1.299793000	2.262593000	-0.271040000
6	-1.952656000	2.531171000	2.440915000
1	-0.297454000	1.209530000	2.841618000
6	-2.393951000	3.054294000	0.116338000
1	-1.006574000	2.231187000	-1.322494000
6	-2.720498000	3.184387000	1.460227000
1	-2.212781000	2.639863000	3.496101000
1	-2.990670000	3.551745000	-0.649563000

1	-3.578271000	3.791001000	1.757400000

B5 (ethylene)

G = -1840.37350

6	2.729860000	2.129808000	0.836153000
6	2.414709000	1.033741000	1.550237000
6	2.664886000	-0.312676000	1.007291000
6	3.321322000	2.043341000	-0.550495000
6	2.897139000	-0.462314000	-0.397903000
6	2.897302000	0.764602000	-1.302326000
45	1.127631000	-1.469870000	0.155700000
1	3.573033000	0.589645000	-2.154216000
1	3.030708000	2.927068000	-1.141558000
1	2.606253000	3.122959000	1.280395000
1	2.020860000	1.123798000	2.565590000
1	3.122466000	-1.029628000	1.698758000
1	3.540877000	-1.288819000	-0.713034000
17	2.186319000	-3.527367000	0.358073000
1	1.901216000	0.925082000	-1.736545000
1	4.424853000	2.088678000	-0.459347000
15	-0.519797000	0.098565000	-0.027774000
6	-0.514350000	1.523675000	-1.212665000
6	-0.838831000	1.326480000	-2.565579000
6	-0.057553000	2.788871000	-0.801805000
6	-0.704141000	2.368838000	-3.485913000
1	-1.200286000	0.355703000	-2.907794000
6	0.074234000	3.829090000	-1.724975000
1	0.201414000	2.960020000	0.242764000
6	-0.244582000	3.622207000	-3.070227000
1	-0.963208000	2.199434000	-4.533511000
1	0.430019000	4.805760000	-1.388517000
1	-0.139127000	4.435623000	-3.791530000
6	-1.160695000	0.836396000	1.544415000
6	-0.748866000	0.256412000	2.754983000
6	-2.077164000	1.902098000	1.574094000
6	-1.241127000	0.732856000	3.972937000
1	-0.033979000	-0.570198000	2.736153000
6	-2.565433000	2.379382000	2.793408000
1	-2.410088000	2.364257000	0.642787000
6	-2.148275000	1.796372000	3.994546000
1	-0.911363000	0.272671000	4.906974000
1	-3.274955000	3.210043000	2.804259000
1	-2.530051000	2.172043000	4.946651000
6	-1.925502000	-0.967151000	-0.618044000
6	-3.231646000	-0.891315000	-0.108063000
6	-1.629496000	-1.941590000	-1.592309000
6	-4.220688000	-1.761672000	-0.573334000
1	-3.479711000	-0.158472000	0.660472000
6	-2.621726000	-2.810173000	-2.054959000
1	-0.614216000	-2.020372000	-1.995018000
6	-3.920250000	-2.720390000	-1.546569000
1	-5.232871000	-1.692713000	-0.168042000
1	-2.374024000	-3.561462000	-2.807742000

1	-4.696431000	-3.401524000	-1.902508000

B3 (imine)

G = -1856.40689

45	-1.721702000	-0.336871000	0.198482000
15	0.517814000	0.088783000	0.032674000
17	-3.915898000	-0.746342000	0.958115000
6	0.857106000	1.739122000	-0.746723000
6	1.513538000	2.782631000	-0.076031000
6	0.352041000	1.974428000	-2.040725000
6	1.672417000	4.029907000	-0.690979000
1	1.901120000	2.628816000	0.931701000
6	0.521244000	3.217067000	-2.655074000
1	-0.181585000	1.177688000	-2.561836000
6	1.181879000	4.250099000	-1.980209000
1	2.183916000	4.832565000	-0.154754000
1	0.130086000	3.379961000	-3.661991000
1	1.309234000	5.224187000	-2.457725000
6	1.280077000	0.221376000	1.713194000
6	2.674229000	0.205625000	1.892986000
6	0.446544000	0.357408000	2.834153000
6	3.220880000	0.333030000	3.171548000
1	3.332477000	0.086687000	1.030116000
6	0.995857000	0.482228000	4.113752000
1	-0.640224000	0.356652000	2.714100000
6	2.382791000	0.472279000	4.283798000
1	4.305552000	0.318622000	3.300541000
1	0.335616000	0.581069000	4.977952000
1	2.812249000	0.566718000	5.283783000
6	1.666119000	-1.071770000	-0.838057000
6	2.268302000	-0.772301000	-2.068466000
6	1.929451000	-2.313277000	-0.233136000
6	3.108628000	-1.702094000	-2.689103000
1	2.096311000	0.188960000	-2.551712000
6	2.772585000	-3.236519000	-0.853088000
1	1.471072000	-2.559048000	0.723969000
6	3.360360000	-2.936459000	-2.085873000
1	3.569405000	-1.454332000	-3.648041000
1	2.965823000	-4.197336000	-0.370882000
1	4.017180000	-3.661505000	-2.572013000
6	-1.274627000	-2.285714000	0.520444000
6	-1.225567000	-3.030696000	-0.608922000
1	-1.153270000	-2.723588000	1.521057000
1	-1.046349000	-4.111465000	-0.621312000
6	-1.448245000	-2.284915000	-1.843834000
6	-1.666666000	-0.960835000	-1.694230000
1	-1.928081000	-0.261380000	-2.497630000
1	-1.458000000	-2.767252000	-2.828046000
6	-3.526393000	2.151479000	-0.516091000
1	-4.361463000	1.455109000	-0.373180000
1	-3.728612000	3.187127000	-0.827358000
7	-2.342715000	1.726780000	-0.295663000
1	-1.629091000	2.446975000	-0.452857000

TS(B3.B4) (imine) $G = -1856.35238$

45	-1.634799000	-0.600893000	-0.415406000
15	0.539298000	0.031925000	0.079295000
17	-1.062347000	-2.802273000	-1.228478000
6	1.066386000	-1.006836000	1.511145000
6	2.331535000	-1.606105000	1.587095000
6	0.136107000	-1.230582000	2.542629000
6	2.663676000	-2.405708000	2.684549000
1	3.056405000	-1.459992000	0.785601000
6	0.474059000	-2.024474000	3.640009000
1	-0.858734000	-0.780037000	2.487065000
6	1.740170000	-2.614223000	3.712443000
1	3.650049000	-2.872524000	2.731498000
1	-0.256497000	-2.190701000	4.434684000
1	2.002973000	-3.242751000	4.566177000
6	1.864238000	-0.133566000	-1.190585000
6	3.083822000	0.554040000	-1.046198000
6	1.660010000	-0.958153000	-2.307383000
6	4.084245000	0.417342000	-2.010676000
1	3.249360000	1.203445000	-0.184479000
6	2.667040000	-1.088319000	-3.268756000
1	0.726085000	-1.513342000	-2.407161000
6	3.876381000	-0.403156000	-3.124901000
1	5.027102000	0.956268000	-1.892415000
1	2.500553000	-1.733243000	-4.134364000
1	4.658944000	-0.506769000	-3.880285000
6	0.715612000	1.776990000	0.651868000
6	0.726476000	2.124234000	2.010837000
6	0.734067000	2.796252000	-0.315759000
6	0.761755000	3.468666000	2.394221000
1	0.717031000	1.348962000	2.777757000
6	0.774367000	4.136442000	0.070529000
1	0.711209000	2.538027000	-1.375388000
6	0.785208000	4.476918000	1.427313000
1	0.775758000	3.725978000	3.455811000
1	0.791324000	4.918046000	-0.692335000
1	0.813562000	5.526300000	1.729415000
6	-1.684079000	0.598932000	-1.913021000
6	-2.155034000	1.880276000	-1.714659000
1	-1.345105000	0.203816000	-2.879490000
1	-2.250772000	2.600195000	-2.534569000
6	-2.504167000	2.178918000	-0.376593000
6	-2.495257000	1.078490000	0.475234000
1	-2.597556000	1.234025000	1.556779000
1	-2.738799000	3.194847000	-0.043424000
6	-3.687069000	-1.238627000	-0.142455000
1	-3.860223000	-1.539239000	-1.183462000
1	-3.631031000	-2.065263000	0.583686000
7	-4.143433000	-0.002411000	0.211576000
1	-4.318514000	0.004245000	1.224531000

B4 (imine) $G = -1856.41614$

6	3.001521000	2.088097000	-0.596926000
6	3.286453000	1.906595000	0.719458000
6	2.801482000	0.943160000	1.699563000
6	1.985838000	-0.133202000	1.598718000
6	2.450911000	-0.188212000	-1.369147000
45	1.397284000	-1.216685000	0.086927000
1	3.460983000	-0.504217000	-1.076983000
1	3.285211000	3.035354000	-1.067541000
1	3.880154000	2.716314000	1.154124000
1	3.080724000	1.208385000	2.729112000
1	1.589516000	-0.564268000	2.533309000
17	2.848856000	-3.039055000	-0.023886000
1	2.138361000	-0.658264000	-2.314274000
15	-0.559083000	-0.032024000	0.020869000
6	-1.744034000	-0.830342000	-1.161755000
6	-3.136024000	-0.732855000	-1.000450000
6	-1.231151000	-1.535590000	-2.263074000
6	-3.995716000	-1.326418000	-1.927337000
1	-3.551288000	-0.197213000	-0.145110000
6	-2.093601000	-2.128281000	-3.190069000
1	-0.151155000	-1.627638000	-2.398616000
6	-3.477153000	-2.024103000	-3.023669000
1	-5.076544000	-1.246800000	-1.790138000
1	-1.680799000	-2.677199000	-4.039163000
1	-4.152136000	-2.490795000	-3.744617000
6	-0.581567000	1.741937000	-0.493987000
6	-0.004182000	2.696931000	0.360072000
6	-1.080028000	2.146928000	-1.742787000
6	0.060896000	4.036364000	-0.026164000
1	0.415028000	2.383152000	1.317245000
6	-0.998567000	3.488531000	-2.131371000
1	-1.534024000	1.417698000	-2.415899000
6	-0.431332000	4.435637000	-1.273321000
1	0.516488000	4.767802000	0.644701000
1	-1.387616000	3.793346000	-3.105676000
1	-0.371881000	5.483484000	-1.576378000
6	-1.484316000	-0.043723000	1.624360000
6	-2.330678000	0.998958000	2.033931000
6	-1.343616000	-1.173928000	2.447724000
6	-3.020109000	0.911554000	3.247305000
1	-2.449496000	1.885679000	1.409501000
6	-2.035856000	-1.259967000	3.657263000
1	-0.688877000	-1.995112000	2.143377000
6	-2.874288000	-0.215743000	4.060647000
1	-3.672984000	1.730738000	3.557384000
1	-1.914923000	-2.143477000	4.287719000
1	-3.411501000	-0.280035000	5.009538000
7	2.379669000	1.205140000	-1.467758000
1	1.747701000	1.608240000	-2.149915000

TS(B4.B5) (imine) $G = -1856.35547$

6	0.971526000	-2.124356000	-2.492291000
6	0.885021000	-2.920456000	-1.399985000
6	-0.385024000	-3.102505000	-0.723009000
6	-1.417985000	-2.220378000	-0.766855000
6	-1.383455000	-1.211828000	-2.403053000
45	-1.516773000	-0.196156000	-0.477445000
1	-2.120145000	-1.901400000	-2.846874000
1	1.901589000	-2.051841000	-3.063474000
1	1.759406000	-3.496414000	-1.094520000
1	-0.565149000	-4.067937000	-0.234047000
1	-2.426035000	-2.568301000	-0.515795000
17	-3.895317000	-0.194770000	-0.593048000
1	-1.772407000	-0.190224000	-2.629013000
15	0.573071000	0.273519000	0.186733000
6	1.638998000	1.523996000	-0.635904000
6	2.335980000	2.494236000	0.104897000
6	1.717216000	1.526791000	-2.036846000
6	3.114423000	3.449246000	-0.551824000
1	2.262540000	2.504860000	1.194917000
6	2.502078000	2.483494000	-2.688722000
1	1.152141000	0.781632000	-2.601386000
6	3.201132000	3.441848000	-1.949217000
1	3.651244000	4.204312000	0.027033000
1	2.561729000	2.484222000	-3.779551000
1	3.809842000	4.190758000	-2.461173000
6	1.692949000	-0.819879000	1.145142000
6	1.112671000	-1.840638000	1.920171000
6	3.090251000	-0.713546000	1.079054000
6	1.922203000	-2.723845000	2.635199000
1	0.027699000	-1.952927000	1.936556000
6	3.896447000	-1.607840000	1.790193000
1	3.554783000	0.059964000	0.466165000
6	3.315839000	-2.610777000	2.570977000
1	1.462421000	-3.512188000	3.235431000
1	4.983579000	-1.519385000	1.730021000
1	3.947913000	-3.308513000	3.125078000
6	-0.501593000	1.177322000	1.368866000
6	-0.626074000	0.906731000	2.751605000
6	-1.481951000	1.984346000	0.729752000
6	-1.697917000	1.427216000	3.464187000
1	0.120028000	0.287955000	3.251980000
6	-2.579658000	2.473105000	1.464559000
1	-1.338570000	2.318817000	-0.303193000
6	-2.686771000	2.195737000	2.819829000
1	-1.782002000	1.225234000	4.534687000
1	-3.342350000	3.062034000	0.953765000
1	-3.538041000	2.573072000	3.390046000
7	-0.035476000	-1.299383000	-2.966442000
1	-0.000624000	-1.120863000	-3.966064000

B5 (imine)

G = -1856.43346

6	0.710006000	-3.273978000	-0.178280000
6	-0.516074000	-3.232678000	0.396399000
6	-1.610306000	-2.545865000	-0.276773000
6	-1.422239000	-2.071248000	-1.612527000
6	-0.130007000	-2.419775000	-2.322482000
45	-1.602696000	-0.389688000	-0.412470000
1	-0.310306000	-3.344863000	-2.914358000
1	1.569098000	-3.733957000	0.314385000
1	-0.669769000	-3.683492000	1.376605000
1	-2.625761000	-2.738135000	0.076815000
1	-2.292030000	-2.044832000	-2.277460000
17	-3.943977000	-0.343353000	-0.637455000
1	0.158021000	-1.627187000	-3.030621000
15	0.496047000	0.298866000	0.047309000
6	1.636025000	1.139465000	-1.145368000
6	1.842715000	2.528442000	-1.112633000
6	2.303790000	0.374543000	-2.116213000
6	2.692863000	3.137790000	-2.040667000
1	1.338882000	3.138938000	-0.361696000
6	3.159158000	0.984447000	-3.036061000
1	2.156797000	-0.704601000	-2.127192000
6	3.351788000	2.369573000	-3.004491000
1	2.841900000	4.219525000	-2.006195000
1	3.673655000	0.376174000	-3.783726000
1	4.014553000	2.848449000	-3.728812000
6	1.611856000	-0.388061000	1.340215000
6	1.019202000	-1.114393000	2.388269000
6	3.006462000	-0.238777000	1.309407000
6	1.809650000	-1.666898000	3.397828000
1	-0.064597000	-1.241730000	2.402321000
6	3.796119000	-0.806842000	2.314110000
1	3.479851000	0.320522000	0.500861000
6	3.200597000	-1.518917000	3.359621000
1	1.338470000	-2.223316000	4.211309000
1	4.881528000	-0.686750000	2.281130000
1	3.819869000	-1.958886000	4.144796000
6	-0.439455000	1.671602000	0.856583000
6	-0.405729000	1.972969000	2.231547000
6	-1.443156000	2.259097000	0.048120000
6	-1.348884000	2.841035000	2.779192000
1	0.357668000	1.522466000	2.867822000
6	-2.403010000	3.108753000	0.615553000
1	-1.448523000	2.094615000	-1.035635000
6	-2.355515000	3.399700000	1.977259000
1	-1.308565000	3.078078000	3.845026000
1	-3.186762000	3.529577000	-0.016299000
1	-3.102535000	4.060841000	2.421733000
7	0.983752000	-2.628791000	-1.378626000
1	1.825368000	-2.969827000	-1.833795000

B3 (formaldehyde)

G = -1876.27474

45	-1.784375000	-0.229991000	-0.043651000
15	0.484239000	0.072467000	0.040687000
17	-4.005241000	-0.283306000	0.681444000
6	1.002715000	1.712887000	-0.640395000
6	1.729529000	2.649175000	0.113151000
6	0.612936000	2.042405000	-1.951658000
6	2.071061000	3.886721000	-0.440882000
1	2.029066000	2.419929000	1.136164000
6	0.966859000	3.274866000	-2.503756000
1	0.020794000	1.339395000	-2.536003000
6	1.694809000	4.200822000	-1.749565000
1	2.634684000	4.607035000	0.156396000
1	0.659394000	3.516262000	-3.523507000
1	1.963137000	5.168261000	-2.180002000
6	1.037598000	0.105050000	1.804818000
6	2.393315000	-0.033678000	2.150645000
6	0.087820000	0.295526000	2.820677000
6	2.787741000	0.024220000	3.489032000
1	3.140508000	-0.194114000	1.371158000
6	0.484958000	0.351290000	4.159657000
1	-0.972652000	0.389685000	2.571331000
6	1.834897000	0.217433000	4.495383000
1	3.843412000	-0.086114000	3.747080000
1	-0.265438000	0.493437000	4.940133000
1	2.145337000	0.257838000	5.541902000
6	1.631876000	-1.149161000	-0.739406000
6	2.284325000	-0.893836000	-1.954410000
6	1.815508000	-2.393415000	-0.112124000
6	3.097702000	-1.869894000	-2.537107000
1	2.170476000	0.068177000	-2.453547000
6	2.630672000	-3.364356000	-0.696392000
1	1.315539000	-2.605602000	0.832273000
6	3.269900000	-3.107985000	-1.913154000
1	3.599666000	-1.656594000	-3.483483000
1	2.762567000	-4.327355000	-0.198050000
1	3.905295000	-3.869723000	-2.370656000
6	-1.479308000	-2.110913000	0.561347000
6	-1.354956000	-2.988589000	-0.459103000
1	-1.479368000	-2.379205000	1.624322000
1	-1.234489000	-4.066142000	-0.305893000
6	-1.384385000	-2.401086000	-1.794909000
6	-1.512287000	-1.058482000	-1.836134000
1	-1.603526000	-0.431266000	-2.729151000
1	-1.315851000	-3.008864000	-2.703449000
6	-2.307065000	2.388078000	-0.228044000
1	-3.262375000	2.460950000	0.331438000
1	-1.412453000	2.895640000	0.203995000
8	-2.237334000	1.803083000	-1.303628000

TS(B3.B4) (formaldehyde)

G = -1876.24035

45	-1.619228000	-0.575501000	-0.398882000
15	0.556793000	0.058529000	0.071166000

17	-1.201858000	-2.787331000	-1.244138000
6	1.041184000	-0.974120000	1.517462000
6	2.235069000	-1.708593000	1.546494000
6	0.142744000	-1.068982000	2.596935000
6	2.530775000	-2.517437000	2.647503000
1	2.930288000	-1.657809000	0.707491000
6	0.445049000	-1.875795000	3.694952000
1	-0.796487000	-0.509640000	2.579749000
6	1.640512000	-2.601831000	3.721522000
1	3.461156000	-3.089371000	2.661026000
1	-0.258621000	-1.943302000	4.527358000
1	1.873836000	-3.239296000	4.577141000
6	1.871294000	-0.174444000	-1.195535000
6	3.064614000	0.567612000	-1.125608000
6	1.691143000	-1.114647000	-2.222008000
6	4.066613000	0.369155000	-2.077813000
1	3.209146000	1.304379000	-0.333440000
6	2.701373000	-1.306286000	-3.169203000
1	0.771870000	-1.702362000	-2.265404000
6	3.886048000	-0.567568000	-3.101222000
1	4.989710000	0.950443000	-2.020317000
1	2.556025000	-2.039393000	-3.965637000
1	4.670288000	-0.719323000	-3.846632000
6	0.767632000	1.806007000	0.603800000
6	1.070749000	2.171274000	1.923647000
6	0.564805000	2.807927000	-0.361311000
6	1.177700000	3.522279000	2.270010000
1	1.233293000	1.406052000	2.683648000
6	0.679478000	4.153639000	-0.012133000
1	0.314616000	2.528752000	-1.385959000
6	0.983861000	4.514210000	1.305214000
1	1.419168000	3.797183000	3.299213000
1	0.522447000	4.924020000	-0.770265000
1	1.068480000	5.568325000	1.578798000
6	-1.842796000	0.455460000	-1.983733000
6	-2.397228000	1.719095000	-1.847400000
1	-1.570571000	-0.014159000	-2.936707000
1	-2.654334000	2.332110000	-2.718695000
6	-2.628552000	2.138585000	-0.521826000
6	-2.395256000	1.151675000	0.441758000
1	-2.419636000	1.394447000	1.508623000
1	-2.953276000	3.153672000	-0.274418000
6	-3.600118000	-1.078835000	0.304601000
1	-4.003985000	-1.652412000	-0.550502000
1	-3.254051000	-1.690716000	1.171141000
8	-4.043072000	0.121548000	0.508710000

B4 (formaldehyde)

G = -1876.29326

6	-2.566028000	2.138091000	0.633760000
6	-2.818961000	2.105969000	-0.690668000
6	-2.612905000	1.099761000	-1.731903000
6	-2.017628000	-0.109820000	-1.689723000

6	-2.508732000	-0.184078000	1.185340000
45	-1.426725000	-1.196206000	-0.177806000
1	-3.546787000	-0.234505000	0.822173000
1	-2.665921000	3.072007000	1.190990000
1	-3.175643000	3.069031000	-1.067911000
1	-2.943484000	1.428592000	-2.726404000
1	-1.869174000	-0.664375000	-2.630261000
17	-2.933995000	-2.966877000	-0.237861000
1	-2.370258000	-0.758543000	2.115453000
15	0.532443000	0.002975000	0.023706000
6	1.308388000	-0.334756000	1.672251000
6	2.555422000	-0.970402000	1.787528000
6	0.596851000	-0.003321000	2.841918000
6	3.084469000	-1.261367000	3.048630000
1	3.118055000	-1.245437000	0.894856000
6	1.135788000	-0.289436000	4.097982000
1	-0.371366000	0.493069000	2.768832000
6	2.378855000	-0.921599000	4.205426000
1	4.054227000	-1.758588000	3.123531000
1	0.576295000	-0.021267000	4.996990000
1	2.794194000	-1.151751000	5.189113000
6	0.633152000	1.829711000	-0.217110000
6	0.430500000	2.331463000	-1.514507000
6	0.845634000	2.725864000	0.839835000
6	0.431194000	3.707031000	-1.745215000
1	0.258497000	1.644424000	-2.343331000
6	0.841179000	4.103954000	0.604386000
1	1.015246000	2.357564000	1.851372000
6	0.630399000	4.597843000	-0.685352000
1	0.268030000	4.084477000	-2.757133000
1	1.007193000	4.792649000	1.435894000
1	0.625483000	5.675144000	-0.866267000
6	1.767442000	-0.639490000	-1.196330000
6	2.913212000	0.092560000	-1.551327000
6	1.566173000	-1.910148000	-1.759276000
6	3.836721000	-0.439337000	-2.453961000
1	3.080082000	1.083006000	-1.124279000
6	2.490761000	-2.440368000	-2.663453000
1	0.684660000	-2.500134000	-1.490097000
6	3.627127000	-1.705194000	-3.012096000
1	4.723460000	0.138695000	-2.723950000
1	2.319144000	-3.428317000	-3.095800000
1	4.349339000	-2.117236000	-3.720492000
8	-2.141430000	1.140684000	1.476155000

TS(B4.B5) (formaldehyde)

G = -1876.23550

6	0.984678000	-1.736351000	-2.660529000
6	0.887024000	-2.723575000	-1.750352000
6	-0.368434000	-3.022434000	-1.082061000
6	-1.396183000	-2.137509000	-1.004052000
6	-1.330417000	-0.987927000	-2.499586000
45	-1.512385000	-0.157165000	-0.485643000

1	-1.949490000	-1.690237000	-3.078375000
1	1.906985000	-1.502718000	-3.195951000
1	1.768999000	-3.339861000	-1.567887000
1	-0.529328000	-4.043841000	-0.720396000
1	-2.400270000	-2.509322000	-0.769989000
17	-3.888876000	-0.141923000	-0.636902000
1	-1.783782000	0.011641000	-2.661642000
15	0.579335000	0.251966000	0.220568000
6	1.606732000	1.603822000	-0.480216000
6	2.340067000	2.469631000	0.350215000
6	1.609506000	1.800344000	-1.870035000
6	3.078849000	3.514250000	-0.208148000
1	2.325660000	2.329361000	1.433657000
6	2.355420000	2.846667000	-2.422930000
1	1.019480000	1.140680000	-2.509115000
6	3.089380000	3.701196000	-1.595770000
1	3.643666000	4.187782000	0.440420000
1	2.354981000	2.997371000	-3.504743000
1	3.666340000	4.520726000	-2.030451000
6	1.720000000	-0.931415000	1.033486000
6	1.156556000	-2.041246000	1.689028000
6	3.115682000	-0.803737000	0.966525000
6	1.981531000	-2.992388000	2.290660000
1	0.072940000	-2.165237000	1.701939000
6	3.936979000	-1.765744000	1.562416000
1	3.566806000	0.040662000	0.443887000
6	3.373227000	-2.857571000	2.228050000
1	1.535399000	-3.849364000	2.800199000
1	5.022544000	-1.659687000	1.503338000
1	4.017264000	-3.607438000	2.693036000
6	-0.499939000	0.995322000	1.503552000
6	-0.606670000	0.571077000	2.848526000
6	-1.505975000	1.840552000	0.960051000
6	-1.684943000	0.983968000	3.619116000
1	0.159050000	-0.079072000	3.273856000
6	-2.610285000	2.217885000	1.750454000
1	-1.374738000	2.297547000	-0.027126000
6	-2.698437000	1.792392000	3.067579000
1	-1.754825000	0.665671000	4.662003000
1	-3.391360000	2.839097000	1.310842000
1	-3.553677000	2.083693000	3.680631000
8	-0.006322000	-0.873133000	-3.035158000

B5 (formaldehyde)

G = -1876.31202

6	0.788218000	-3.207297000	-0.149025000
6	-0.450698000	-3.256283000	0.376921000
6	-1.559876000	-2.581547000	-0.296587000
6	-1.337567000	-2.080478000	-1.615367000
6	-0.002967000	-2.390573000	-2.247763000
45	-1.592594000	-0.431529000	-0.391705000
1	-0.080757000	-3.346322000	-2.806876000
1	1.680443000	-3.623117000	0.322653000

1	-0.609986000	-3.780670000	1.319400000
1	-2.575360000	-2.824218000	0.022903000
1	-2.172113000	-2.061312000	-2.325339000
17	-3.931672000	-0.451934000	-0.611597000
1	0.325094000	-1.605648000	-2.943078000
15	0.499133000	0.308875000	0.050832000
6	1.664018000	1.057116000	-1.174605000
6	1.754751000	2.448978000	-1.341005000
6	2.463013000	0.217302000	-1.972530000
6	2.620616000	2.990713000	-2.295941000
1	1.150465000	3.115791000	-0.724268000
6	3.332320000	0.765849000	-2.918290000
1	2.409100000	-0.863995000	-1.841351000
6	3.410318000	2.152327000	-3.087050000
1	2.679307000	4.074932000	-2.416510000
1	3.950431000	0.103602000	-3.529007000
1	4.086501000	2.577853000	-3.832011000
6	1.573183000	-0.299820000	1.415138000
6	0.955819000	-1.030578000	2.445654000
6	2.955562000	-0.066304000	1.467488000
6	1.709982000	-1.508126000	3.518799000
1	-0.117938000	-1.221380000	2.395198000
6	3.709418000	-0.557912000	2.537841000
1	3.447218000	0.497272000	0.673086000
6	3.089499000	-1.276773000	3.564096000
1	1.220691000	-2.070584000	4.317219000
1	4.785747000	-0.373957000	2.570011000
1	3.681181000	-1.658207000	4.399501000
6	-0.471080000	1.710505000	0.758553000
6	-0.448318000	2.100274000	2.111431000
6	-1.494600000	2.208970000	-0.084938000
6	-1.418193000	2.972967000	2.601575000
1	0.326059000	1.712427000	2.775197000
6	-2.480448000	3.064684000	0.426713000
1	-1.496221000	1.970276000	-1.155500000
6	-2.440831000	3.447051000	1.765666000
1	-1.387140000	3.279695000	3.649740000
1	-3.278045000	3.416106000	-0.229589000
1	-3.208119000	4.112481000	2.167023000
8	1.083598000	-2.531092000	-1.298457000

B3 (allene)

G = -1878.35545

45	-1.728601000	-0.427842000	0.025835000
15	0.516332000	0.095005000	-0.001621000
17	-3.943764000	-0.913506000	0.632307000
6	0.883740000	1.652113000	-0.934148000
6	1.391752000	2.809249000	-0.325020000
6	0.552636000	1.694912000	-2.301557000
6	1.580431000	3.976740000	-1.071021000
1	1.630543000	2.812380000	0.738459000
6	0.750423000	2.859747000	-3.045687000
1	0.132251000	0.811431000	-2.785291000

6	1.265473000	4.005800000	-2.431516000
1	1.972742000	4.870284000	-0.580140000
1	0.493373000	2.872658000	-4.107261000
1	1.413949000	4.919554000	-3.011038000
6	1.130663000	0.392398000	1.718933000
6	2.490619000	0.654744000	1.963395000
6	0.244863000	0.313336000	2.804148000
6	2.946446000	0.859739000	3.266376000
1	3.195183000	0.689523000	1.129756000
6	0.704026000	0.515009000	4.110316000
1	-0.808595000	0.074875000	2.638473000
6	2.052941000	0.793392000	4.342244000
1	4.004454000	1.065180000	3.444170000
1	0.003673000	0.446256000	4.945284000
1	2.412327000	0.949793000	5.361808000
6	1.765163000	-1.129065000	-0.617902000
6	2.415560000	-1.007513000	-1.853945000
6	2.050833000	-2.239323000	0.195784000
6	3.323751000	-1.984126000	-2.274527000
1	2.231913000	-0.148011000	-2.496743000
6	2.959582000	-3.210875000	-0.225703000
1	1.558965000	-2.345675000	1.162189000
6	3.594818000	-3.089712000	-1.465395000
1	3.822210000	-1.873850000	-3.240225000
1	3.168386000	-4.068068000	0.418206000
1	4.304131000	-3.851896000	-1.796000000
6	-1.223808000	-2.288983000	0.630321000
6	-1.015059000	-3.165260000	-0.376858000
1	-1.201364000	-2.566420000	1.692144000
1	-0.782831000	-4.223844000	-0.220641000
6	-1.132581000	-2.597493000	-1.714165000
6	-1.427182000	-1.281059000	-1.764375000
1	-1.617442000	-0.711403000	-2.681075000
1	-1.003892000	-3.197633000	-2.621768000
6	-2.715532000	1.478494000	-1.194859000
1	-2.110141000	1.616753000	-2.093368000
1	-3.709902000	1.037468000	-1.295038000
6	-1.995727000	2.695440000	1.024725000
6	-2.307019000	1.983140000	-0.032682000
1	-2.326442000	3.737230000	1.089588000
1	-1.418312000	2.295766000	1.859762000

TS(B3.B4) (allene)

G = -1878.39341

45	-1.740050000	-0.007873000	-0.231645000
15	0.621712000	-0.098932000	0.063721000
17	-1.567652000	-2.253305000	-1.117330000
6	0.924111000	-1.380982000	1.358063000
6	1.942488000	-2.339110000	1.262530000
6	0.053838000	-1.412680000	2.462857000
6	2.097140000	-3.301346000	2.264712000
1	2.608267000	-2.348652000	0.399305000
6	0.215872000	-2.370278000	3.465576000

1	-0.760136000	-0.686330000	2.538620000
6	1.240013000	-3.317472000	3.368185000
1	2.890386000	-4.047148000	2.176624000
1	-0.467004000	-2.383117000	4.317856000
1	1.362747000	-4.073256000	4.147172000
6	1.745880000	-0.502912000	-1.342804000
6	3.132436000	-0.297070000	-1.212471000
6	1.234546000	-1.002996000	-2.549362000
6	3.991973000	-0.592507000	-2.272179000
1	3.541005000	0.104768000	-0.283320000
6	2.100534000	-1.291768000	-3.608609000
1	0.166152000	-1.191607000	-2.647215000
6	3.476352000	-1.089222000	-3.474194000
1	5.066289000	-0.429796000	-2.159193000
1	1.691819000	-1.681795000	-4.543398000
1	4.148562000	-1.317116000	-4.304811000
6	1.374679000	1.450023000	0.735178000
6	1.536540000	1.669107000	2.111128000
6	1.691568000	2.483600000	-0.163033000
6	2.008519000	2.899072000	2.579470000
1	1.303820000	0.878743000	2.825636000
6	2.163678000	3.709650000	0.307958000
1	1.563897000	2.329322000	-1.235188000
6	2.320781000	3.922957000	1.681194000
1	2.136106000	3.053474000	3.653442000
1	2.407113000	4.502921000	-0.402632000
1	2.689716000	4.883036000	2.049292000
6	-1.447874000	1.211991000	-1.739012000
6	-1.380640000	2.547243000	-1.473503000
1	-1.336645000	0.753535000	-2.728069000
1	-1.224773000	3.290458000	-2.262869000
6	-1.522012000	2.899547000	-0.084947000
6	-1.863489000	1.856165000	0.733003000
1	-1.921704000	1.975772000	1.821437000
1	-1.319326000	3.908833000	0.285674000
6	-3.778195000	1.138392000	0.251801000
1	-4.056908000	1.398147000	1.277852000
1	-3.972109000	1.907456000	-0.501699000
6	-4.610055000	-1.242984000	-0.357816000
6	-3.813442000	-0.202266000	-0.145637000
1	-4.207432000	-2.204387000	-0.680481000
1	-5.694643000	-1.143727000	-0.229719000

B4 (allene)

G = -1878.44172

6	-2.006164000	2.854411000	0.101370000
6	-2.157256000	2.621795000	-1.217796000
6	-2.215549000	1.403796000	-2.024385000
6	-1.967411000	0.115442000	-1.726108000
6	-2.333432000	0.516930000	1.247885000
45	-1.619722000	-0.805182000	-0.042703000
1	-1.937319000	3.912694000	0.379125000
1	-2.224337000	3.529298000	-1.828390000

1	-2.466767000	1.590352000	-3.078175000
1	-2.054785000	-0.644845000	-2.517366000
17	-3.393711000	-2.311726000	-0.263017000
15	0.576598000	-0.102060000	0.030628000
6	1.393452000	-0.327566000	1.677217000
6	2.791966000	-0.442560000	1.770488000
6	0.619842000	-0.370274000	2.847561000
6	3.404113000	-0.590942000	3.015404000
1	3.405274000	-0.419717000	0.868003000
6	1.239120000	-0.519468000	4.093569000
1	-0.467183000	-0.289942000	2.793402000
6	2.628457000	-0.629111000	4.180310000
1	4.491069000	-0.680415000	3.076711000
1	0.626917000	-0.553101000	4.997425000
1	3.109615000	-0.748788000	5.153700000
6	1.128732000	1.570631000	-0.514335000
6	1.007358000	1.925271000	-1.869245000
6	1.593493000	2.523568000	0.405002000
6	1.344861000	3.211064000	-2.292476000
1	0.636526000	1.197696000	-2.590995000
6	1.920102000	3.813681000	-0.022052000
1	1.702373000	2.262602000	1.458844000
6	1.795699000	4.160537000	-1.369811000
1	1.244481000	3.474941000	-3.347555000
1	2.277462000	4.547672000	0.703647000
1	2.051917000	5.169054000	-1.702118000
6	1.511112000	-1.268918000	-1.068358000
6	2.664810000	-0.896233000	-1.777945000
6	1.049197000	-2.593816000	-1.164508000
6	3.338932000	-1.831153000	-2.568572000
1	3.037219000	0.127533000	-1.721827000
6	1.723197000	-3.524317000	-1.958644000
1	0.158249000	-2.910846000	-0.614006000
6	2.869515000	-3.144615000	-2.662907000
1	4.234656000	-1.528255000	-3.115641000
1	1.347786000	-4.547459000	-2.026402000
1	3.395772000	-3.871333000	-3.285756000
6	-1.877895000	1.954362000	1.303691000
6	-3.182141000	0.025085000	2.168320000
1	-0.817588000	1.983499000	1.626695000
1	-2.426642000	2.440346000	2.133235000
1	-3.559165000	0.681972000	2.963847000
1	-3.538576000	-1.005116000	2.165030000

TS(B4.B5) (allene)

G = -1878.40676

6	0.772805000	-2.590726000	-1.786735000
6	0.601268000	-3.192777000	-0.594783000
6	-0.659944000	-3.162700000	0.125370000
6	-1.622360000	-2.211621000	-0.013614000
6	-1.602528000	-1.531717000	-1.809442000
45	-1.556375000	-0.194213000	-0.216856000
1	1.741673000	-2.665575000	-2.291070000

1	1.426675000	-3.764618000	-0.159405000
1	-0.896105000	-4.027543000	0.756943000
1	-2.622440000	-2.417905000	0.382088000
17	-3.874604000	0.071335000	0.210362000
15	0.643291000	0.281288000	0.070048000
6	1.625937000	1.299644000	-1.117416000
6	2.824754000	1.933994000	-0.744327000
6	1.081228000	1.554910000	-2.385225000
6	3.481007000	2.779187000	-1.640508000
1	3.241386000	1.776537000	0.252539000
6	1.739193000	2.405812000	-3.279454000
1	0.126885000	1.103171000	-2.662722000
6	2.942694000	3.011774000	-2.911833000
1	4.412512000	3.265895000	-1.342573000
1	1.305483000	2.595953000	-4.263572000
1	3.458342000	3.674469000	-3.610452000
6	1.815381000	-0.752812000	1.032840000
6	1.317728000	-1.394913000	2.181269000
6	3.116630000	-1.043569000	0.594465000
6	2.124148000	-2.281353000	2.896895000
1	0.287022000	-1.223635000	2.495341000
6	3.918185000	-1.936050000	1.311344000
1	3.503123000	-0.594342000	-0.320590000
6	3.426883000	-2.552782000	2.465525000
1	1.726550000	-2.773283000	3.787275000
1	4.928338000	-2.156193000	0.958882000
1	4.054191000	-3.252219000	3.022675000
6	-0.054976000	1.548667000	1.216035000
6	0.221664000	1.690011000	2.588005000
6	-1.132910000	2.270678000	0.650273000
6	-0.563251000	2.535556000	3.369712000
1	1.048986000	1.139403000	3.037536000
6	-1.938084000	3.089849000	1.453654000
1	-1.311592000	2.247842000	-0.433684000
6	-1.651349000	3.223435000	2.809728000
1	-0.335399000	2.652893000	4.431801000
1	-2.787264000	3.610079000	1.008614000
1	-2.273220000	3.862968000	3.439565000
6	-0.303152000	-1.853008000	-2.540866000
6	-2.785530000	-1.663166000	-2.456665000
1	-3.736786000	-1.410948000	-1.990754000
1	-2.802249000	-2.053835000	-3.481228000
1	-0.543919000	-2.428711000	-3.457270000
1	0.131062000	-0.910795000	-2.913797000

B5 (allene)

G = -1878.47911

6	2.165459000	-2.322982000	-1.103048000
6	2.390210000	-1.188995000	-1.790174000
6	2.726198000	0.068620000	-1.116016000
6	2.945184000	0.073278000	0.304100000
6	2.860941000	-1.189243000	1.059867000
45	1.254045000	1.260074000	-0.151461000

1	1.906507000	-3.244990000	-1.630410000
1	2.335742000	-1.187742000	-2.881259000
1	3.246508000	0.818542000	-1.718599000
1	3.646556000	0.807945000	0.711154000
17	2.505620000	3.217664000	-0.281219000
15	-0.568817000	-0.080304000	0.011070000
6	-1.133185000	-0.728661000	1.649919000
6	-2.478968000	-1.073228000	1.872672000
6	-0.216258000	-0.811749000	2.707323000
6	-2.891534000	-1.518276000	3.129098000
1	-3.205575000	-0.983883000	1.061773000
6	-0.634266000	-1.257426000	3.966345000
1	0.823596000	-0.524004000	2.548186000
6	-1.967982000	-1.613522000	4.178036000
1	-3.938086000	-1.784664000	3.294181000
1	0.088321000	-1.319418000	4.783167000
1	-2.293937000	-1.957965000	5.162226000
6	-0.972020000	-1.402655000	-1.210965000
6	-0.737103000	-1.114269000	-2.567473000
6	-1.399914000	-2.688375000	-0.851686000
6	-0.958730000	-2.082022000	-3.546878000
1	-0.359280000	-0.128520000	-2.848850000
6	-1.601877000	-3.664410000	-1.834165000
1	-1.568331000	-2.939878000	0.196099000
6	-1.389052000	-3.363079000	-3.181449000
1	-0.778467000	-1.841625000	-4.597049000
1	-1.928555000	-4.664720000	-1.540820000
1	-1.550857000	-4.125935000	-3.946355000
6	-1.827448000	1.253653000	-0.293331000
6	-2.749093000	1.256149000	-1.351955000
6	-1.777858000	2.363678000	0.574679000
6	-3.599433000	2.349355000	-1.540392000
1	-2.811136000	0.403169000	-2.028365000
6	-2.622895000	3.457340000	0.375675000
1	-1.088182000	2.365791000	1.424075000
6	-3.534997000	3.452708000	-0.683842000
1	-4.316869000	2.337578000	-2.364241000
1	-2.567740000	4.312670000	1.052209000
1	-4.197160000	4.307076000	-0.840305000
6	2.150689000	-2.358924000	0.400259000
1	1.089636000	-2.358321000	0.726269000
1	2.558040000	-3.311958000	0.775379000
6	3.432125000	-1.308059000	2.273553000
1	3.424245000	-2.255704000	2.818280000
1	3.920548000	-0.455941000	2.752781000

B3 (carbon disulfide)

G = -2596.32427

45	0.134568000	1.789286000	0.168086000
15	-0.465115000	-0.434894000	0.056310000
17	0.869175000	3.932206000	0.735569000
6	0.494560000	-1.505451000	-1.113956000
6	0.842127000	-2.826898000	-0.790303000

6	0.872264000	-0.986549000	-2.362461000
6	1.559462000	-3.609929000	-1.697938000
1	0.566700000	-3.247399000	0.177452000
6	1.588580000	-1.772396000	-3.268763000
1	0.607147000	0.036762000	-2.624939000
6	1.937652000	-3.084505000	-2.937004000
1	1.829657000	-4.634104000	-1.430829000
1	1.879561000	-1.353068000	-4.234324000
1	2.505241000	-3.695985000	-3.641984000
6	-0.136846000	-1.207377000	1.706497000
6	-0.889013000	-2.277237000	2.219980000
6	0.942640000	-0.709766000	2.457143000
6	-0.567464000	-2.832689000	3.461646000
1	-1.730576000	-2.676111000	1.651673000
6	1.262596000	-1.267585000	3.696952000
1	1.545467000	0.116788000	2.071757000
6	0.506616000	-2.329406000	4.202268000
1	-1.161356000	-3.662391000	3.851753000
1	2.102360000	-0.867430000	4.268836000
1	0.752862000	-2.763242000	5.173976000
6	-2.217598000	-0.865775000	-0.333201000
6	-2.579094000	-1.355731000	-1.596263000
6	-3.220321000	-0.627887000	0.622260000
6	-3.920929000	-1.609067000	-1.896600000
1	-1.816759000	-1.541786000	-2.353386000
6	-4.557418000	-0.894310000	0.323801000
1	-2.954892000	-0.231995000	1.602749000
6	-4.911643000	-1.381609000	-0.938449000
1	-4.189246000	-1.987586000	-2.885416000
1	-5.325815000	-0.709874000	1.077822000
1	-5.959172000	-1.583112000	-1.173910000
6	-1.701942000	2.229712000	0.828943000
6	-2.584147000	2.527735000	-0.147555000
1	-1.901213000	2.282641000	1.906098000
1	-3.620615000	2.816671000	0.054965000
6	-2.053662000	2.445548000	-1.503056000
6	-0.756632000	2.080165000	-1.591362000
1	-0.171102000	2.053052000	-2.518747000
1	-2.655809000	2.690566000	-2.384410000
6	3.332858000	0.236661000	-0.422111000
16	3.923075000	-1.145993000	0.009849000
16	2.726104000	1.637350000	-0.823919000

TS(B3.B4) (carbon disulfide)

G = -2596.28418

45	-1.409816000	0.026175000	-0.513225000
15	0.839488000	-0.070642000	0.080171000
17	-1.365043000	-1.924861000	-1.948553000
6	0.984760000	-1.332834000	1.423334000
6	0.257614000	-2.529506000	1.288639000
6	1.840939000	-1.161057000	2.524938000
6	0.380152000	-3.530240000	2.255754000
1	-0.392981000	-2.685311000	0.424845000

6	1.957076000	-2.168641000	3.485668000
1	2.418070000	-0.242508000	2.639043000
6	1.224721000	-3.352725000	3.355187000
1	-0.192291000	-4.453430000	2.144253000
1	2.623758000	-2.025627000	4.339127000
1	1.314351000	-4.137057000	4.110243000
6	2.140909000	-0.571121000	-1.126573000
6	3.468234000	-0.694212000	-0.676392000
6	1.835164000	-0.830076000	-2.468352000
6	4.479361000	-1.053884000	-1.567196000
1	3.713679000	-0.506756000	0.370846000
6	2.854092000	-1.194302000	-3.355469000
1	0.801816000	-0.792247000	-2.807330000
6	4.173256000	-1.301964000	-2.910852000
1	5.508109000	-1.143913000	-1.211277000
1	2.606508000	-1.403136000	-4.398419000
1	4.965170000	-1.587331000	-3.607238000
6	1.450391000	1.512124000	0.783497000
6	2.255382000	2.369309000	0.018347000
6	0.978884000	1.948371000	2.034369000
6	2.604694000	3.630250000	0.508653000
1	2.608393000	2.054453000	-0.964587000
6	1.340037000	3.203948000	2.526510000
1	0.329042000	1.301697000	2.626518000
6	2.153372000	4.048349000	1.763973000
1	3.233709000	4.288130000	-0.095100000
1	0.976889000	3.526215000	3.504860000
1	2.431664000	5.032855000	2.146579000
6	-0.947778000	1.250353000	-1.918389000
6	-0.918651000	2.603026000	-1.620253000
1	-0.793591000	0.823900000	-2.914308000
1	-0.650202000	3.351292000	-2.373358000
6	-1.290157000	2.937998000	-0.308102000
6	-1.760859000	1.854694000	0.455869000
1	-1.943899000	1.977266000	1.528011000
1	-1.200737000	3.952311000	0.091869000
6	-3.399554000	-0.276696000	0.118482000
16	-3.814744000	-1.749305000	0.640932000
16	-3.852415000	1.318467000	-0.021338000

B4 (carbon disulfide)

G = -2596.32998

6	-3.421860000	1.499482000	0.641420000
6	-3.038657000	2.236273000	-0.426691000
6	-2.103493000	2.079758000	-1.526822000
6	-1.309743000	1.049405000	-1.884368000
6	-1.954496000	-1.036692000	0.511149000
45	-1.045586000	-0.742715000	-1.132455000
1	-4.183141000	1.938011000	1.295369000
1	-3.575015000	3.192030000	-0.466314000
1	-2.072544000	2.955870000	-2.188182000
1	-0.711610000	1.173231000	-2.801052000
17	-2.603059000	-1.652636000	-2.598075000

15	0.821532000	0.066791000	0.029548000
6	2.040671000	-1.225219000	0.536688000
6	3.133368000	-0.884677000	1.353200000
6	1.926149000	-2.533933000	0.047029000
6	4.089892000	-1.845136000	1.682663000
1	3.236191000	0.133660000	1.733638000
6	2.891064000	-3.492115000	0.374292000
1	1.078193000	-2.813023000	-0.579768000
6	3.970127000	-3.151227000	1.192698000
1	4.933289000	-1.573351000	2.321363000
1	2.791661000	-4.509393000	-0.010061000
1	4.720492000	-3.902059000	1.450460000
6	0.377861000	0.962146000	1.570930000
6	-0.136882000	2.266707000	1.486048000
6	0.379254000	0.296892000	2.807614000
6	-0.615675000	2.905779000	2.630582000
1	-0.182115000	2.772939000	0.520969000
6	-0.108530000	0.940235000	3.947532000
1	0.743348000	-0.728686000	2.877925000
6	-0.601734000	2.245399000	3.863055000
1	-1.015457000	3.919108000	2.553756000
1	-0.108980000	0.413722000	4.904291000
1	-0.983256000	2.745087000	4.756308000
6	1.893918000	1.207319000	-0.951325000
6	2.584788000	2.285407000	-0.377967000
6	2.083021000	0.915761000	-2.312527000
6	3.440917000	3.066254000	-1.160322000
1	2.453668000	2.522580000	0.678797000
6	2.942753000	1.693994000	-3.089499000
1	1.562131000	0.070977000	-2.770501000
6	3.620539000	2.774399000	-2.515264000
1	3.970518000	3.906503000	-0.705655000
1	3.080424000	1.456948000	-4.146588000
1	4.288923000	3.387251000	-3.124001000
16	-1.533354000	-2.570495000	0.975460000
16	-3.063261000	-0.059728000	1.398482000

TS(B4.B5) (carbon disulfide)

G = -2596.31838

6	-2.679614000	1.893064000	1.062250000
6	-2.185023000	2.441051000	-0.071818000
6	-2.241480000	1.829274000	-1.380013000
6	-2.099399000	0.508485000	-1.667160000
6	-2.859741000	-0.587168000	-0.127820000
45	-1.132076000	-1.096349000	-0.822846000
1	-2.687518000	2.439723000	2.007860000
1	-1.803104000	3.464191000	-0.008609000
1	-2.432536000	2.518317000	-2.212649000
1	-2.391198000	0.172885000	-2.673835000
17	0.085606000	-3.092717000	-0.889535000
15	0.747124000	0.049422000	-0.034503000
6	0.861305000	0.012433000	1.812923000
6	2.044969000	0.406669000	2.464948000

6	-0.224873000	-0.432327000	2.577777000
6	2.124680000	0.378373000	3.857909000
1	2.910034000	0.724853000	1.879734000
6	-0.140958000	-0.462959000	3.973638000
1	-1.132299000	-0.769922000	2.079874000
6	1.029804000	-0.054209000	4.615817000
1	3.048239000	0.686377000	4.353384000
1	-0.993873000	-0.817996000	4.556215000
1	1.096491000	-0.082559000	5.705873000
6	0.893620000	1.839018000	-0.491717000
6	0.784837000	2.176513000	-1.852265000
6	1.079785000	2.862486000	0.447939000
6	0.882150000	3.506019000	-2.265569000
1	0.599596000	1.392338000	-2.589449000
6	1.167241000	4.196213000	0.033820000
1	1.140263000	2.628675000	1.510717000
6	1.071297000	4.521769000	-1.321438000
1	0.798345000	3.750662000	-3.326837000
1	1.307812000	4.983079000	0.778554000
1	1.139411000	5.563559000	-1.642753000
6	2.418756000	-0.617362000	-0.505308000
6	3.249376000	0.004111000	-1.449532000
6	2.857905000	-1.802073000	0.113990000
6	4.493965000	-0.548514000	-1.769980000
1	2.946837000	0.931328000	-1.934569000
6	4.102273000	-2.345268000	-0.204451000
1	2.223673000	-2.302292000	0.844690000
6	4.923915000	-1.723005000	-1.149992000
1	5.129473000	-0.049224000	-2.504994000
1	4.426714000	-3.265919000	0.285378000
1	5.896808000	-2.152263000	-1.400257000
16	-3.471437000	-2.027586000	-0.738534000
16	-3.545479000	0.361287000	1.159514000

B5 (carbon disulfide)

G = -2596.34718

6	1.054695000	1.862506000	-2.373849000
6	-0.210399000	1.490638000	-2.663675000
6	-1.338121000	1.718276000	-1.778770000
6	-1.230162000	2.450990000	-0.551199000
6	0.014983000	2.995997000	-0.020100000
45	-1.548210000	0.396498000	-0.091487000
1	1.893258000	1.663580000	-3.045121000
1	-0.401957000	0.994660000	-3.617790000
1	-2.329408000	1.672068000	-2.235294000
1	-2.123342000	2.940614000	-0.155126000
17	-3.877794000	0.738101000	-0.105535000
15	0.451944000	-0.646363000	0.171555000
6	1.487284000	-0.556939000	1.687696000
6	2.077378000	-1.721099000	2.212863000
6	1.671816000	0.671844000	2.335801000
6	2.852750000	-1.649310000	3.370485000
1	1.925482000	-2.682777000	1.717010000

6	2.451904000	0.737379000	3.495158000
1	1.203602000	1.577489000	1.951291000
6	3.042415000	-0.418298000	4.011572000
1	3.307266000	-2.555710000	3.776859000
1	2.589794000	1.699086000	3.993714000
1	3.648224000	-0.364682000	4.919093000
6	1.588378000	-1.150066000	-1.178303000
6	1.039894000	-1.536502000	-2.414911000
6	2.981347000	-1.047678000	-1.045972000
6	1.873887000	-1.846488000	-3.489243000
1	-0.044277000	-1.575082000	-2.537595000
6	3.813226000	-1.343053000	-2.131047000
1	3.419642000	-0.729639000	-0.099046000
6	3.263651000	-1.747423000	-3.350459000
1	1.437733000	-2.153684000	-4.442394000
1	4.896264000	-1.256283000	-2.019298000
1	3.915948000	-1.980791000	-4.194941000
6	-0.737700000	-2.015999000	0.466932000
6	-0.846399000	-3.225859000	-0.246620000
6	-1.794240000	-1.619650000	1.327085000
6	-1.978326000	-4.020487000	-0.089017000
1	-0.043588000	-3.537107000	-0.916716000
6	-2.947736000	-2.414751000	1.445773000
1	-1.678428000	-0.744976000	1.985180000
6	-3.035725000	-3.610235000	0.742380000
1	-2.050919000	-4.967491000	-0.629082000
1	-3.765525000	-2.077754000	2.083568000
1	-3.928156000	-4.232811000	0.832572000
16	0.110231000	3.932702000	1.350050000
16	1.538044000	2.666916000	-0.887841000

B3 (carbodiimide)

G = -1910.55914

45	-1.587300000	-0.677982000	0.102724000
15	0.676949000	0.031108000	0.041561000
17	-3.886576000	-1.219767000	0.428258000
6	1.011646000	1.333597000	-1.241989000
6	1.302985000	2.654214000	-0.806560000
6	0.884115000	1.114529000	-2.627031000
6	1.457737000	3.691868000	-1.718700000
1	1.411065000	2.871899000	0.252973000
6	1.047173000	2.169474000	-3.540000000
1	0.660266000	0.118764000	-3.002116000
6	1.330170000	3.454854000	-3.090629000
1	1.686816000	4.698120000	-1.353693000
1	0.945933000	1.963115000	-4.606587000
1	1.453054000	4.279605000	-3.796666000
6	1.019521000	0.909578000	1.634077000
6	2.277444000	1.079100000	2.199230000
6	-0.117308000	1.439272000	2.271267000
6	2.405419000	1.771842000	3.404118000
1	3.161943000	0.644774000	1.708115000
6	0.016304000	2.146667000	3.473571000

1	-1.105044000	1.271491000	1.827060000
6	1.277368000	2.320328000	4.040392000
1	3.400346000	1.875529000	3.849221000
1	-0.872139000	2.554331000	3.964509000
1	1.384560000	2.859972000	4.982074000
6	2.128815000	-1.020977000	-0.140839000
6	2.996680000	-0.806747000	-1.199439000
6	2.400362000	-2.033242000	0.802365000
6	4.119060000	-1.619589000	-1.359558000
1	2.809854000	0.005114000	-1.917502000
6	3.516332000	-2.853863000	0.635089000
1	1.727410000	-2.200938000	1.641613000
6	4.372669000	-2.658358000	-0.456650000
1	4.785124000	-1.442234000	-2.208053000
1	3.704580000	-3.648729000	1.355438000
1	5.243138000	-3.302760000	-0.598014000
6	-1.066913000	-2.459676000	0.844214000
6	-0.757653000	-3.462294000	-0.004515000
1	-1.091487000	-2.649252000	1.930516000
1	-0.476469000	-4.480199000	0.297759000
6	-0.887211000	-3.070389000	-1.369048000
6	-1.247086000	-1.771588000	-1.529615000
1	-1.492926000	-1.329957000	-2.505424000
1	-0.730284000	-3.751555000	-2.215649000
6	-3.466538000	1.641502000	-0.682495000
7	-4.568620000	2.036290000	-0.167077000
1	-5.393754000	1.535866000	-0.303143000
7	-2.291422000	1.305911000	-0.878501000
1	-1.972178000	1.689647000	-1.733295000

TS(B3.B4) (carbodiimide)

G = -1910.50293

45	-1.642222000	-0.280911000	-0.320886000
15	0.630560000	-0.018990000	0.070270000
17	-1.532511000	-2.414571000	-1.420597000
6	1.110183000	-1.092030000	1.497689000
6	2.099562000	-0.709746000	2.420833000
6	0.505744000	-2.356680000	1.612801000
6	2.469986000	-1.576989000	3.450951000
1	2.581231000	0.265978000	2.341838000
6	0.882950000	-3.217104000	2.647918000
1	-0.242953000	-2.678384000	0.884540000
6	1.860469000	-2.830558000	3.568566000
1	3.239088000	-1.270753000	4.163808000
1	0.406242000	-4.196253000	2.728982000
1	2.150232000	-3.505616000	4.377118000
6	1.864062000	-0.448090000	-1.233012000
6	3.231428000	-0.230144000	-0.983599000
6	1.460416000	-1.005455000	-2.453176000
6	4.180605000	-0.549847000	-1.954370000
1	3.556677000	0.194418000	-0.031832000
6	2.418810000	-1.327177000	-3.420688000
1	0.408265000	-1.226812000	-2.628537000

6	3.774434000	-1.097003000	-3.177490000
1	5.240070000	-0.373629000	-1.754976000
1	2.096963000	-1.767489000	-4.366899000
1	4.518590000	-1.349357000	-3.936535000
6	1.052500000	1.701025000	0.559362000
6	0.690011000	2.173447000	1.832907000
6	1.565049000	2.603535000	-0.384306000
6	0.877397000	3.515730000	2.168587000
1	0.262282000	1.487135000	2.566014000
6	1.740738000	3.948605000	-0.049065000
1	1.822690000	2.257723000	-1.386345000
6	1.403241000	4.406841000	1.227881000
1	0.603221000	3.867406000	3.165708000
1	2.142945000	4.641232000	-0.791733000
1	1.545505000	5.458040000	1.488470000
6	-1.547107000	0.821166000	-1.882585000
6	-1.721002000	2.182563000	-1.725820000
1	-1.400151000	0.312031000	-2.840894000
1	-1.707458000	2.868262000	-2.579733000
6	-1.973420000	2.606336000	-0.402221000
6	-2.121996000	1.559811000	0.500953000
1	-2.291375000	1.755731000	1.566409000
1	-2.040380000	3.662232000	-0.122767000
6	-3.680872000	-0.542334000	0.416049000
7	-4.037063000	0.701166000	0.204548000
1	-4.366167000	1.172947000	1.052565000
7	-3.953873000	-1.702694000	0.818004000
1	-4.953816000	-1.806029000	1.053884000

B4 (carbodiimide)

G = -1910.59780

6	-3.749670000	0.870480000	1.062750000
6	-3.673097000	1.641335000	-0.047955000
6	-2.746757000	1.691064000	-1.166450000
6	-1.772416000	0.834882000	-1.526811000
6	-1.975802000	-0.966648000	1.047075000
45	-1.287192000	-0.902080000	-0.774813000
1	-4.568610000	1.087702000	1.752539000
1	-4.471609000	2.387178000	-0.095932000
1	-2.881397000	2.565651000	-1.817355000
1	-1.161893000	1.065668000	-2.413463000
17	-3.053668000	-2.058100000	-1.724077000
15	0.716708000	0.009964000	-0.010493000
6	2.036775000	-1.257948000	0.250689000
6	3.375457000	-1.013712000	-0.100245000
6	1.680724000	-2.490279000	0.827403000
6	4.346874000	-1.993633000	0.120727000
1	3.661987000	-0.061652000	-0.549598000
6	2.660154000	-3.463478000	1.043861000
1	0.641831000	-2.667249000	1.118913000
6	3.991058000	-3.220068000	0.690703000
1	5.385135000	-1.797110000	-0.156563000
1	2.377243000	-4.419962000	1.489313000

1	4.751851000	-3.986253000	0.857667000
6	0.637940000	0.954239000	1.570072000
6	-0.386478000	1.904198000	1.725425000
6	1.553593000	0.745142000	2.611541000
6	-0.483799000	2.639537000	2.908215000
1	-1.107811000	2.066605000	0.923620000
6	1.445995000	1.480067000	3.796295000
1	2.347193000	0.004428000	2.503311000
6	0.429887000	2.428135000	3.946674000
1	-1.284264000	3.374540000	3.018868000
1	2.160542000	1.308196000	4.604555000
1	0.348163000	3.000373000	4.873769000
6	1.479931000	1.174685000	-1.221955000
6	1.900975000	2.466585000	-0.879603000
6	1.617978000	0.733751000	-2.550353000
6	2.451541000	3.306084000	-1.854429000
1	1.796681000	2.822889000	0.146115000
6	2.171844000	1.571568000	-3.518635000
1	1.291853000	-0.272326000	-2.828628000
6	2.588275000	2.862343000	-3.171795000
1	2.774109000	4.312731000	-1.578939000
1	2.274380000	1.218275000	-4.546966000
1	3.016758000	3.521094000	-3.930416000
7	-2.961950000	-0.165974000	1.572152000
7	-1.422460000	-1.955311000	1.644574000
1	-1.852232000	-2.213487000	2.542943000
1	-3.209576000	-0.426442000	2.523285000

TS(B4.B5) (carbodiimide)

G = -1910.57847

6	-3.573146000	1.184664000	0.677615000
6	-2.963952000	1.948490000	-0.262074000
6	-2.552119000	1.423275000	-1.541285000
6	-2.136008000	0.148538000	-1.782776000
6	-3.045281000	-0.958964000	-0.326972000
45	-1.179693000	-1.306926000	-0.695408000
1	-4.012698000	1.611428000	1.580052000
1	-2.897909000	3.022806000	-0.081531000
1	-2.648552000	2.112322000	-2.390533000
1	-2.127329000	-0.197398000	-2.828478000
17	0.160330000	-3.184869000	-0.185831000
15	0.562479000	0.034821000	-0.016189000
6	1.148969000	-0.426498000	1.682840000
6	2.455744000	-0.166865000	2.120851000
6	0.228334000	-0.999160000	2.574506000
6	2.831824000	-0.467480000	3.432909000
1	3.191772000	0.258873000	1.438403000
6	0.603818000	-1.288306000	3.888472000
1	-0.779003000	-1.232623000	2.225733000
6	1.906534000	-1.023167000	4.321097000
1	3.855292000	-0.269111000	3.759663000
1	-0.121105000	-1.737149000	4.571429000
1	2.203434000	-1.258783000	5.345799000

6	0.248564000	1.853761000	0.170149000
6	0.236652000	2.678349000	-0.967945000
6	-0.043612000	2.418748000	1.419534000
6	-0.053041000	4.038725000	-0.856653000
1	0.458073000	2.251875000	-1.947757000
6	-0.336026000	3.782749000	1.530187000
1	-0.041721000	1.795450000	2.314785000
6	-0.342076000	4.596198000	0.394791000
1	-0.052722000	4.666684000	-1.750732000
1	-0.556608000	4.208648000	2.511837000
1	-0.566115000	5.661892000	0.482378000
6	2.092186000	0.018488000	-1.072536000
6	3.030485000	1.066924000	-1.030208000
6	2.327757000	-1.071637000	-1.926004000
6	4.180758000	1.022131000	-1.821525000
1	2.861340000	1.930291000	-0.384706000
6	3.480196000	-1.110806000	-2.716564000
1	1.619887000	-1.900273000	-1.955885000
6	4.408393000	-0.067586000	-2.667729000
1	4.899247000	1.844083000	-1.777182000
1	3.649789000	-1.966573000	-3.373883000
1	5.306719000	-0.101092000	-3.288754000
7	-3.765250000	-0.188359000	0.528153000
7	-3.205877000	-2.158983000	-0.793371000
1	-4.630803000	-0.585091000	0.890014000
1	-3.699429000	-2.856154000	-0.232893000

B5 (carbodiimide)

G = -1910.62228

6	-2.240237000	2.284185000	-0.831970000
6	-2.636635000	1.201992000	-1.543866000
6	-2.921010000	-0.034830000	-0.848690000
6	-2.836819000	-0.079435000	0.586782000
6	-2.498171000	1.148867000	1.339819000
45	-1.297776000	-1.288072000	-0.174740000
1	-1.971554000	3.234923000	-1.292748000
1	-2.728152000	1.265606000	-2.627057000
1	-3.548345000	-0.770626000	-1.356720000
1	-3.464603000	-0.772325000	1.151883000
17	-2.594684000	-3.210361000	-0.329186000
15	0.537534000	0.052396000	-0.031859000
6	1.223676000	0.437722000	1.642530000
6	2.543181000	0.903927000	1.795528000
6	0.450125000	0.170761000	2.781481000
6	3.068623000	1.124890000	3.068528000
1	3.163931000	1.083818000	0.914703000
6	0.983111000	0.392752000	4.057172000
1	-0.570839000	-0.197939000	2.681463000
6	2.286421000	0.871464000	4.203125000
1	4.093671000	1.486717000	3.177817000
1	0.369062000	0.185904000	4.936414000
1	2.700148000	1.041120000	5.200034000
6	0.785141000	1.584372000	-1.032404000

6	0.526053000	1.507199000	-2.412628000
6	1.098177000	2.830264000	-0.468881000
6	0.610335000	2.644767000	-3.216616000
1	0.240465000	0.549687000	-2.853742000
6	1.163020000	3.973817000	-1.272804000
1	1.285180000	2.915345000	0.602288000
6	0.925420000	3.883942000	-2.647405000
1	0.414467000	2.566469000	-4.288370000
1	1.406300000	4.938360000	-0.820784000
1	0.982501000	4.776954000	-3.273904000
6	1.826090000	-1.131372000	-0.663086000
6	2.736313000	-0.855173000	-1.694951000
6	1.841321000	-2.405783000	-0.061133000
6	3.636343000	-1.836965000	-2.120566000
1	2.752637000	0.127944000	-2.166605000
6	2.735944000	-3.385660000	-0.495641000
1	1.165050000	-2.630277000	0.769749000
6	3.635071000	-3.103412000	-1.528556000
1	4.343660000	-1.607900000	-2.921136000
1	2.730614000	-4.369716000	-0.022362000
1	4.336727000	-3.868267000	-1.868535000
7	-2.586570000	1.175521000	2.623827000
1	-2.327142000	2.099222000	2.995904000
7	-2.089368000	2.230561000	0.541588000
1	-1.844636000	3.086083000	1.026549000

B3 (carbon dioxide)

G = -1950.40447

45	-1.035301000	-1.380338000	0.167104000
15	0.555756000	0.232123000	-0.044541000
17	-3.121470000	-2.372731000	0.190595000
6	-0.274742000	1.597741000	-0.976682000
6	-0.253295000	2.932520000	-0.545953000
6	-1.022797000	1.253815000	-2.118713000
6	-0.970774000	3.906825000	-1.246729000
1	0.312454000	3.210928000	0.344256000
6	-1.738755000	2.230174000	-2.814483000
1	-1.051390000	0.216480000	-2.463152000
6	-1.715579000	3.558772000	-2.377571000
1	-0.951914000	4.942924000	-0.901156000
1	-2.325091000	1.948905000	-3.691440000
1	-2.283158000	4.321055000	-2.915693000
6	1.115415000	1.018504000	1.528627000
6	2.379874000	1.616913000	1.648280000
6	0.232834000	1.045869000	2.621705000
6	2.755666000	2.230713000	2.846795000
1	3.076049000	1.598670000	0.808151000
6	0.612253000	1.662285000	3.815888000
1	-0.756029000	0.592779000	2.539440000
6	1.874236000	2.254362000	3.931518000
1	3.743201000	2.689868000	2.931818000
1	-0.080733000	1.675936000	4.659891000
1	2.171283000	2.731722000	4.868052000

6	2.119056000	-0.094332000	-0.960493000
6	2.453144000	0.583514000	-2.141340000
6	2.991187000	-1.070377000	-0.447762000
6	3.649019000	0.286707000	-2.804371000
1	1.785359000	1.344788000	-2.547037000
6	4.184854000	-1.356532000	-1.110112000
1	2.725946000	-1.604567000	0.465872000
6	4.515713000	-0.680699000	-2.290645000
1	3.902590000	0.819088000	-3.723886000
1	4.857087000	-2.116932000	-0.706451000
1	5.449361000	-0.909961000	-2.809384000
6	0.105959000	-2.274247000	1.528719000
6	0.789909000	-3.338461000	1.052306000
1	0.089687000	-1.931304000	2.570219000
1	1.394120000	-3.987585000	1.695267000
6	0.684151000	-3.540626000	-0.389413000
6	-0.086437000	-2.640371000	-1.034702000
1	-0.252634000	-2.591995000	-2.117506000
1	1.214643000	-4.343863000	-0.911007000
6	-3.553922000	1.046881000	0.249229000
8	-4.337280000	1.138852000	-0.606023000
8	-2.760902000	0.984042000	1.109460000

TS(B3.B4) (carbon dioxide)

$G = -1950.32650$

45	-1.556438000	-0.377497000	-0.500322000
15	0.718929000	0.020271000	0.053327000
17	-1.347865000	-2.552362000	-1.425683000
6	1.080029000	-1.004087000	1.537314000
6	2.256213000	-1.758870000	1.658456000
6	0.111209000	-1.056837000	2.557477000
6	2.465135000	-2.545716000	2.794296000
1	3.005173000	-1.737264000	0.865433000
6	0.327084000	-1.844146000	3.689571000
1	-0.817018000	-0.485775000	2.468597000
6	1.505009000	-2.589004000	3.809606000
1	3.382301000	-3.132187000	2.882383000
1	-0.431802000	-1.882919000	4.473620000
1	1.670153000	-3.210755000	4.692183000
6	2.041224000	-0.347337000	-1.170616000
6	3.246308000	0.378918000	-1.159296000
6	1.858958000	-1.387667000	-2.096482000
6	4.258725000	0.063345000	-2.068045000
1	3.394772000	1.191261000	-0.445924000
6	2.880543000	-1.695964000	-2.999168000
1	0.922348000	-1.950249000	-2.106557000
6	4.077692000	-0.974199000	-2.988807000
1	5.191481000	0.631749000	-2.055992000
1	2.732522000	-2.505187000	-3.717535000
1	4.870575000	-1.217297000	-3.700023000
6	1.034585000	1.757882000	0.548378000
6	1.464595000	2.125398000	1.832258000
6	0.781130000	2.754935000	-0.411408000

6	1.653490000	3.475023000	2.145487000
1	1.657555000	1.360373000	2.586039000
6	0.980646000	4.099807000	-0.095409000
1	0.429046000	2.472355000	-1.405608000
6	1.415339000	4.461962000	1.183952000
1	1.992932000	3.754559000	3.145313000
1	0.786517000	4.867059000	-0.847965000
1	1.565324000	5.514875000	1.432776000
6	-2.189127000	0.550213000	-2.011656000
6	-2.611052000	1.885642000	-1.858933000
1	-2.100306000	0.041806000	-2.979273000
1	-3.039377000	2.455512000	-2.690952000
6	-2.466069000	2.396913000	-0.576178000
6	-2.050924000	1.413601000	0.365631000
1	-1.820204000	1.721085000	1.391010000
1	-2.682624000	3.433904000	-0.308509000
6	-3.530585000	-0.577507000	0.470289000
8	-4.033511000	-1.664085000	0.486278000
8	-3.726595000	0.571175000	0.930208000

B4 (carbon dioxide)

G = -1950.38570

6	3.747949000	1.217505000	-0.695899000
6	3.697844000	1.480738000	0.622965000
6	2.775401000	1.137420000	1.693551000
6	1.803362000	0.208559000	1.705143000
6	1.971302000	-0.393058000	-1.369304000
45	1.321398000	-1.081729000	0.320332000
1	4.575315000	1.606610000	-1.290786000
1	4.551692000	2.088413000	0.939506000
1	2.933242000	1.696686000	2.624900000
1	1.211244000	0.061258000	2.621335000
17	3.069123000	-2.540864000	0.705132000
15	-0.712598000	0.014666000	0.016111000
6	-1.962083000	-1.083751000	-0.785876000
6	-3.294054000	-1.138070000	-0.341828000
6	-1.560400000	-1.870140000	-1.880984000
6	-4.212380000	-1.972416000	-0.984774000
1	-3.616967000	-0.532023000	0.505951000
6	-2.486480000	-2.700043000	-2.517799000
1	-0.530589000	-1.823082000	-2.239022000
6	-3.810569000	-2.754995000	-2.071640000
1	-5.245807000	-2.010253000	-0.632804000
1	-2.166709000	-3.308309000	-3.366613000
1	-4.529936000	-3.408743000	-2.570117000
6	-0.712190000	1.556712000	-0.988215000
6	0.318878000	2.489460000	-0.783771000
6	-1.712854000	1.822509000	-1.935194000
6	0.340102000	3.677737000	-1.516095000
1	1.102938000	2.287338000	-0.053646000
6	-1.681599000	3.011716000	-2.668903000
1	-2.511451000	1.099536000	-2.108285000
6	-0.657760000	3.940380000	-2.460473000

1	1.147557000	4.394807000	-1.353498000
1	-2.459810000	3.209550000	-3.409372000
1	-0.633962000	4.866865000	-3.038660000
6	-1.494072000	0.482221000	1.619356000
6	-1.969593000	1.773629000	1.883426000
6	-1.585200000	-0.505869000	2.616242000
6	-2.529352000	2.071944000	3.130720000
1	-1.901353000	2.549397000	1.119428000
6	-2.147757000	-0.205351000	3.857104000
1	-1.219274000	-1.517665000	2.419994000
6	-2.619459000	1.086872000	4.117111000
1	-2.895756000	3.081589000	3.329329000
1	-2.214459000	-0.980038000	4.623985000
1	-3.055086000	1.324032000	5.090202000
8	1.501240000	-0.948915000	-2.338878000
8	2.898251000	0.569447000	-1.576732000

TS(B4.B5) (carbon dioxide)

G = -1950.34594

6	0.156355000	-2.876635000	1.207605000
6	0.355417000	-3.233367000	-0.085440000
6	1.537610000	-2.803229000	-0.769529000
6	2.255237000	-1.684374000	-0.433510000
6	2.113542000	-1.395725000	1.381974000
45	1.691638000	0.172759000	0.141036000
1	-0.672973000	-3.253032000	1.810956000
1	-0.328063000	-3.950561000	-0.540109000
1	1.951088000	-3.467195000	-1.538874000
1	3.272337000	-1.575418000	-0.824021000
17	3.752418000	1.189202000	-0.231320000
15	-0.575711000	0.152673000	-0.045858000
6	-1.760785000	0.251537000	1.368848000
6	-3.045218000	0.794361000	1.173454000
6	-1.360197000	-0.121694000	2.660023000
6	-3.922177000	0.932482000	2.249421000
1	-3.354540000	1.120287000	0.177730000
6	-2.242795000	0.023063000	3.736765000
1	-0.360796000	-0.521580000	2.825789000
6	-3.522618000	0.543293000	3.533974000
1	-4.917049000	1.353619000	2.087728000
1	-1.920562000	-0.268868000	4.738649000
1	-4.208384000	0.656388000	4.376725000
6	-1.393246000	-0.858493000	-1.351292000
6	-0.698190000	-1.029860000	-2.562237000
6	-2.610549000	-1.527961000	-1.159293000
6	-1.225713000	-1.838187000	-3.569886000
1	0.271109000	-0.547257000	-2.702697000
6	-3.131286000	-2.344677000	-2.168330000
1	-3.150091000	-1.430452000	-0.217002000
6	-2.444012000	-2.499287000	-3.374923000
1	-0.677416000	-1.961303000	-4.506463000
1	-4.077582000	-2.865451000	-2.005300000
1	-2.852358000	-3.138719000	-4.160709000

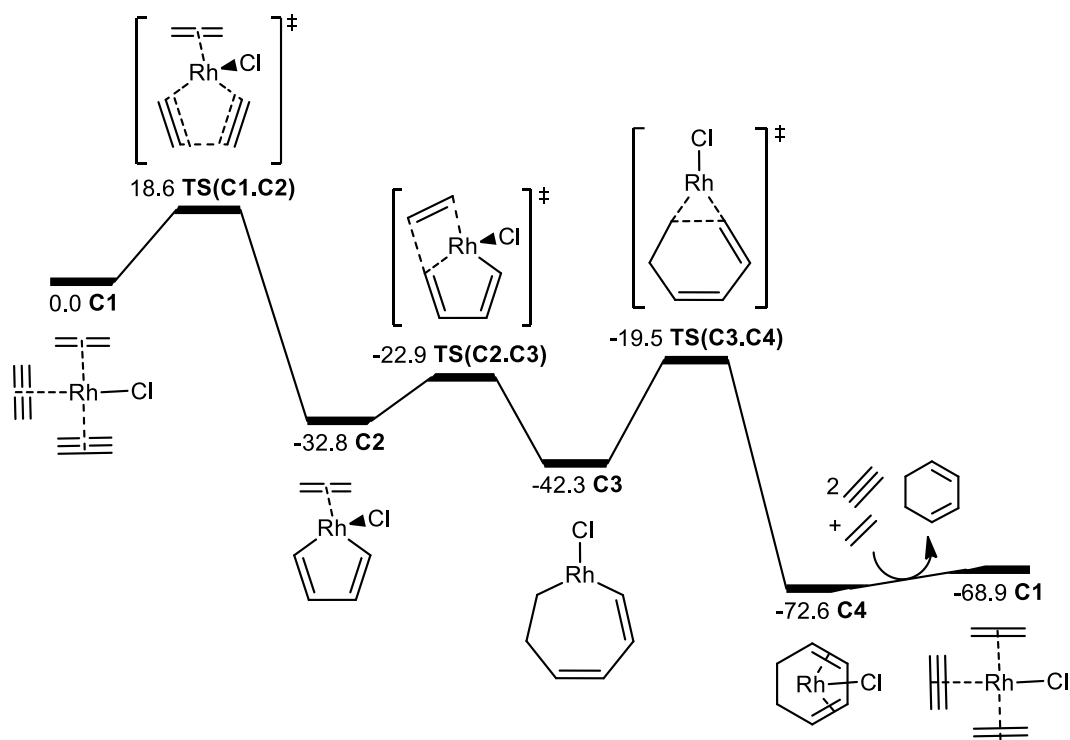
6	-0.584428000	1.899919000	-0.658355000
6	-0.907744000	2.281535000	-1.970866000
6	-0.106011000	2.872965000	0.244888000
6	-0.752243000	3.610911000	-2.370216000
1	-1.287003000	1.544797000	-2.679807000
6	0.057921000	4.197214000	-0.165378000
1	0.125429000	2.596339000	1.277595000
6	-0.263778000	4.567772000	-1.474061000
1	-1.011931000	3.900489000	-3.390958000
1	0.438590000	4.938235000	0.540195000
1	-0.135247000	5.603206000	-1.796514000
8	0.983142000	-2.107962000	1.935948000
8	3.090074000	-1.339982000	2.081424000

B5 (carbon dioxide)

G = -1950.40213

6	1.868940000	-2.581138000	-0.818771000
6	2.446397000	-1.554881000	-1.471318000
6	2.905652000	-0.403411000	-0.720963000
6	2.772249000	-0.425901000	0.708888000
6	2.181720000	-1.605644000	1.369150000
45	1.471504000	1.039435000	-0.032143000
1	1.474061000	-3.479885000	-1.292819000
1	2.562529000	-1.603436000	-2.553313000
1	3.673892000	0.229725000	-1.170380000
1	3.474081000	0.116422000	1.347438000
17	3.061377000	2.733830000	-0.061541000
15	-0.563876000	0.010343000	-0.037760000
6	-1.409130000	-0.317995000	1.569469000
6	-2.799924000	-0.529937000	1.613547000
6	-0.675587000	-0.281160000	2.763225000
6	-3.441537000	-0.719556000	2.836785000
1	-3.380617000	-0.540313000	0.688256000
6	-1.324945000	-0.471770000	3.988295000
1	0.400555000	-0.113600000	2.744140000
6	-2.702791000	-0.692264000	4.027079000
1	-4.521204000	-0.883654000	2.864181000
1	-0.743423000	-0.449974000	4.912121000
1	-3.206885000	-0.840481000	4.984890000
6	-1.006442000	-1.401827000	-1.131546000
6	-0.732881000	-1.291359000	-2.507540000
6	-1.470687000	-2.623296000	-0.621710000
6	-0.955591000	-2.371426000	-3.361530000
1	-0.326985000	-0.359121000	-2.906680000
6	-1.677284000	-3.709646000	-1.478675000
1	-1.653403000	-2.737599000	0.447045000
6	-1.427628000	-3.585560000	-2.847787000
1	-0.747628000	-2.270344000	-4.429081000
1	-2.033261000	-4.657706000	-1.069461000
1	-1.593584000	-4.434612000	-3.514660000
6	-1.519143000	1.468205000	-0.672243000
6	-2.401899000	1.450027000	-1.763253000
6	-1.265649000	2.690494000	-0.015591000

6	-3.008966000	2.633130000	-2.193631000
1	-2.623429000	0.513584000	-2.276287000
6	-1.864401000	3.871972000	-0.458526000
1	-0.618080000	2.720048000	0.867592000
6	-2.736572000	3.844907000	-1.550330000
1	-3.699656000	2.606886000	-3.039644000
1	-1.650651000	4.811354000	0.055148000
1	-3.208034000	4.766947000	-1.897192000
8	1.665970000	-2.605888000	0.531980000
8	2.095952000	-1.787968000	2.557966000



C1 (ethylene)

G = -803.88008

45	-0.120220000	0.051861000	-0.009443000
6	0.396913000	2.200045000	0.394983000
6	-0.476961000	2.223250000	-0.475584000
6	-2.206848000	-0.008000000	-0.479432000
6	-2.099862000	0.029047000	0.768975000
6	-0.049505000	-2.040601000	-0.733058000
6	-0.117738000	-2.067740000	0.650221000
1	-1.254564000	2.509879000	-1.160888000
1	1.216296000	2.385284000	1.067457000
1	-1.057248000	-2.297549000	1.158555000
1	0.910376000	-2.109733000	-1.247715000
17	2.246057000	-0.027814000	-0.025040000
1	-0.943942000	-2.228660000	-1.334068000
1	0.795622000	-2.142416000	1.244861000
1	-2.704949000	-0.047632000	-1.438447000
1	-2.410642000	0.053928000	1.804251000

TS(C1.C2) (ethylene)

G = -803.85043

45	0.065691000	-0.065590000	0.000870000
6	0.938903000	-1.886226000	-0.078848000
6	1.804292000	-1.151109000	-0.694548000
6	2.122719000	0.579862000	0.152173000
6	1.432858000	0.729559000	1.232977000
6	-0.592302000	1.891621000	-1.074629000
6	-0.998203000	2.068365000	0.219611000

1	2.555253000	-1.111372000	-1.479459000
1	0.609280000	-2.903929000	0.100141000
1	-0.414302000	2.681423000	0.910105000
1	-1.265873000	1.451751000	-1.815431000
17	-2.079711000	-0.981330000	0.161101000
1	0.317901000	2.363153000	-1.454259000
1	-1.992011000	1.759156000	0.546761000
1	2.949020000	1.005682000	-0.410997000
1	1.390116000	0.995855000	2.284872000

C2 (ethylene)

G = -803.93229

45	-0.110915000	-0.471588000	-0.038062000
6	0.668740000	2.186759000	-0.589667000
6	0.329318000	1.065062000	-1.249601000
6	0.745617000	2.054707000	0.861782000
6	0.435351000	0.836449000	1.347156000
17	-2.355239000	-0.125166000	0.002765000
1	1.038311000	2.886165000	1.511080000
1	0.426684000	0.529222000	2.399022000
1	0.246531000	0.918590000	-2.331637000
1	0.876630000	3.128716000	-1.107219000
6	1.990224000	-0.894590000	-0.599500000
6	1.609050000	-1.692967000	0.471695000
1	1.973190000	-1.279530000	-1.623994000
1	2.593308000	0.000233000	-0.432967000
1	1.926896000	-1.439701000	1.487937000
1	1.278897000	-2.726930000	0.312388000

TS(C2.C3) (ethylene)

G = -803.91655

45	0.314430000	0.166730000	-0.158268000
6	-2.198163000	-1.062144000	-0.582680000
6	-1.548036000	0.039085000	-1.060593000
6	-1.713027000	-1.581274000	0.681251000
6	-0.546102000	-1.049229000	1.122616000
17	2.465506000	-0.576977000	-0.134718000
1	-2.257736000	-2.346600000	1.244133000
1	-0.028552000	-1.294577000	2.055580000
1	-1.765356000	0.496672000	-2.030483000
1	-3.006613000	-1.543660000	-1.140412000
6	-1.425263000	1.575657000	0.197479000
6	-0.144120000	1.914509000	0.774941000
1	-1.803762000	2.241485000	-0.584464000
1	-2.187417000	1.202536000	0.887700000
1	-0.006766000	1.802770000	1.856852000
1	0.441522000	2.727512000	0.325283000

C3 (ethylene)

G = -803.94752

6	1.919645000	-0.802210000	-0.595582000
6	1.867014000	0.583037000	-0.631293000
6	1.700314000	1.510663000	0.573737000
6	1.594831000	-1.613653000	0.603614000
6	0.189627000	1.637747000	0.680492000
6	0.375074000	-1.261798000	1.046167000
45	-0.290853000	-0.062429000	-0.334390000
17	-2.530519000	-0.047375000	0.090411000
1	2.242386000	-2.416014000	0.975925000
1	-0.198826000	-1.607347000	1.910778000
1	2.234191000	-1.320930000	-1.510029000
1	2.092236000	1.058562000	-1.592445000
1	2.121942000	1.036063000	1.472760000
1	-0.242417000	1.603580000	1.689502000
1	-0.240401000	2.469655000	0.099327000
1	2.219074000	2.468393000	0.401942000

TS(C3.C4) (ethylene)

G = -803.91112

6	1.686702000	-1.056083000	-0.476130000
6	1.708114000	0.274517000	-0.952426000
6	1.905679000	1.428312000	0.030121000
6	1.432967000	-1.357245000	0.930708000
6	0.675154000	1.357288000	0.924423000
6	0.448246000	-0.536329000	1.409755000
45	-0.325723000	-0.125123000	-0.371295000
17	-2.568112000	0.117635000	0.125607000
1	1.851704000	-2.228744000	1.444131000
1	-0.048853000	-0.584342000	2.379778000
1	1.938527000	-1.875902000	-1.158803000
1	1.941846000	0.436056000	-2.009335000
1	2.844647000	1.312121000	0.597664000
1	0.860991000	1.503413000	1.993812000
1	-0.157556000	2.018615000	0.635485000
1	1.942959000	2.386772000	-0.508478000

C4 (ethylene)

G = -803.99581

6	1.370717000	-1.180130000	-0.708073000
6	1.091386000	0.104821000	-1.298578000
6	1.763454000	1.363192000	-0.773404000
6	1.369987000	-1.178913000	0.710807000
6	1.762750000	1.364612000	0.772078000
6	1.090069000	0.107076000	1.298893000
45	-0.462680000	-0.388208000	-0.000164000
1	2.788940000	1.422112000	-1.182530000
1	1.218398000	2.239934000	1.156715000
17	-2.493081000	0.626844000	-0.000237000
1	0.839182000	0.114532000	2.366035000
1	1.408292000	-2.108813000	1.283572000
1	2.787737000	1.424029000	1.182367000
1	1.219436000	2.237836000	-1.159999000

1	0.841263000	0.110470000	-2.365912000
1	1.409563000	-2.111024000	-1.279181000

C1 (imine)

G = -819.95773

45	0.203760000	-0.060232000	-0.009649000
6	1.940257000	1.080231000	-0.619476000
6	1.741671000	1.336679000	0.579611000
6	1.336799000	-1.679733000	0.723522000
6	1.414387000	-1.720052000	-0.531899000
6	-2.688301000	-1.129221000	-0.006484000
1	1.787435000	1.797823000	1.553036000
1	2.358372000	1.069335000	-1.612997000
1	-3.026233000	-0.087620000	0.042345000
17	-1.260377000	1.792043000	-0.011739000
1	-3.418279000	-1.950130000	-0.018691000
1	1.537607000	-1.995774000	1.739086000
1	1.748313000	-2.096433000	-1.490128000
7	-1.430918000	-1.352897000	-0.050875000
1	-1.182457000	-2.348630000	-0.094413000

TS(C1.C2) (imine)

G = -819.92601

45	0.188626000	-0.044802000	-0.037503000
6	1.649412000	-1.403793000	-0.207552000
6	2.175596000	-0.368141000	-0.782771000
6	1.829879000	1.302540000	0.136712000
6	1.172956000	1.116089000	1.240923000
6	-2.543609000	1.460016000	-0.446708000
1	2.839325000	-0.025588000	-1.573448000
1	1.761114000	-2.472236000	-0.052780000
1	-3.168497000	2.359715000	-0.535767000
17	-1.541040000	-1.611464000	0.262562000
1	-3.001899000	0.468428000	-0.539951000
1	2.431474000	2.038463000	-0.391798000
1	1.097532000	1.266105000	2.314341000
7	-1.288753000	1.522226000	-0.217380000
1	-0.933700000	2.480226000	-0.118467000

C2 (imine)

G = -819.98208

45	-0.033315000	-0.507849000	0.006698000
6	0.343270000	2.204813000	-0.659569000
6	0.181048000	1.021579000	-1.280295000
6	0.377413000	2.154054000	0.800892000
6	0.231594000	0.931130000	1.345457000
17	-2.292247000	-0.374453000	-0.052858000
1	0.514799000	3.051622000	1.412670000
1	0.195602000	0.665686000	2.407058000
1	0.115112000	0.836408000	-2.357597000

1	0.440716000	3.144179000	-1.213448000
6	2.205899000	-0.509539000	-0.352033000
1	2.496893000	-0.616668000	-1.407564000
1	2.515304000	0.408988000	0.156237000
7	1.776528000	-1.529225000	0.381792000
1	1.717904000	-2.378949000	-0.199436000

TS(C2.C3) (imine)

G = -819.97809

45	0.280996000	-0.460313000	-0.194303000
6	-1.187205000	1.730329000	0.797562000
6	-0.889778000	0.429871000	1.178897000
6	-0.909718000	2.038385000	-0.561642000
6	-0.253484000	1.039955000	-1.248333000
17	2.399623000	0.170085000	0.397606000
1	-1.214322000	2.977070000	-1.033519000
1	0.019822000	1.088672000	-2.311006000
1	-0.901609000	0.080026000	2.216607000
1	-1.646558000	2.448406000	1.485147000
6	-2.292842000	-0.828959000	0.270217000
1	-2.966669000	-1.186998000	1.062852000
1	-2.682740000	-0.036369000	-0.374345000
7	-1.373928000	-1.643647000	-0.278569000
1	-1.230669000	-2.500129000	0.268390000

C3 (imine)

G = -819.98173

6	-2.614790000	-0.825301000	0.306665000
6	-2.742808000	0.520654000	0.272361000
6	-1.736794000	1.566617000	0.441194000
6	-1.338837000	-1.607755000	0.499795000
6	-0.397979000	1.571111000	0.223765000
45	0.674597000	0.167206000	-0.563679000
1	-0.840516000	-1.342635000	1.446796000
1	-3.526275000	-1.413898000	0.159552000
1	-3.760282000	0.905828000	0.143497000
1	-2.158810000	2.533619000	0.751611000
1	0.184878000	2.465430000	0.497995000
17	2.215701000	-0.237759000	0.996181000
1	-1.566181000	-2.687740000	0.548484000
7	-0.361066000	-1.411530000	-0.582758000
1	-0.841904000	-1.414201000	-1.500818000

TS(C3.C4) (imine)

G = -819.96314

6	-1.764844000	0.559954000	-0.810881000
6	-1.831321000	-0.827218000	-0.615097000
6	-1.586179000	-1.418733000	0.710089000
6	-1.704965000	1.464990000	0.416396000
6	-0.467770000	-0.854278000	1.251421000

45	0.317090000	-0.067964000	-0.405866000
1	-1.686220000	2.528116000	0.135896000
1	-1.963715000	0.985238000	-1.797798000
1	-2.130094000	-1.467077000	-1.454864000
1	-2.145644000	-2.262258000	1.121014000
1	0.066385000	-1.059797000	2.178620000
17	2.541472000	0.030392000	0.154094000
1	-2.557342000	1.277791000	1.100756000
7	-0.453050000	1.035873000	1.048698000
1	0.244378000	1.740287000	1.308297000

C4 (imine)

G = -820.04935

6	1.140494000	0.202749000	1.280457000
6	1.357137000	-1.125817000	0.759711000
6	1.372848000	-1.194313000	-0.657295000
6	1.117140000	0.081603000	-1.276503000
6	1.816400000	1.322308000	-0.738099000
45	-0.465704000	-0.388208000	-0.002832000
1	2.861015000	1.348212000	-1.102768000
1	0.893840000	0.308955000	2.341079000
1	1.382253000	-2.012131000	1.396514000
1	1.428531000	-2.142086000	-1.196573000
1	0.922903000	0.093828000	-2.354602000
17	-2.506764000	0.619115000	-0.016983000
1	1.310160000	2.222640000	-1.120536000
7	1.787993000	1.316977000	0.732044000
1	1.432886000	2.186980000	1.119090000

C1 (formaldehyde)

G = -839.81957

45	-0.099660000	-0.075563000	-0.071357000
6	0.407177000	-2.134575000	-0.183897000
6	-0.276691000	-2.000333000	0.850716000
6	-2.224277000	-0.180955000	0.323303000
6	-2.058199000	-0.118050000	-0.912021000
6	-0.135335000	2.038100000	0.826296000
1	-0.838807000	-2.249501000	1.737045000
1	1.095454000	-2.540632000	-0.908790000
1	0.895175000	2.116122000	1.217044000
17	2.231858000	0.145483000	-0.106795000
1	-0.971047000	2.182466000	1.543824000
1	-2.737403000	-0.259643000	1.269861000
1	-2.262895000	-0.039066000	-1.969596000
8	-0.364177000	2.011531000	-0.411147000

TS(C1.C2) (formaldehyde)

G = -839.80441

45	-0.221282000	0.061866000	-0.059975000
6	-1.728852000	1.312517000	-0.265960000

6	-2.198461000	0.217661000	-0.785382000
6	-1.725782000	-1.388287000	0.239542000
6	-1.073315000	-1.077073000	1.316685000
6	2.585181000	-1.395316000	-0.427056000
1	-2.887067000	-0.202336000	-1.513965000
1	-1.903170000	2.369336000	-0.087391000
1	3.263287000	-2.269454000	-0.533111000
17	1.496323000	1.625597000	0.278823000
1	3.008030000	-0.371234000	-0.466210000
1	-2.280348000	-2.187471000	-0.244493000
1	-0.965737000	-1.149886000	2.395249000
8	1.391573000	-1.578136000	-0.257272000

C2 (formaldehyde)

G = -839.86790

45	-0.038844000	-0.526753000	0.016805000
6	0.354674000	2.199200000	-0.647354000
6	0.145489000	1.024509000	-1.265258000
6	0.449777000	2.133015000	0.809118000
6	0.287539000	0.908228000	1.342504000
17	-2.282286000	-0.322174000	-0.047812000
1	0.644951000	3.016957000	1.424543000
1	0.299703000	0.626301000	2.400682000
1	0.035074000	0.833788000	-2.337282000
1	0.444473000	3.139647000	-1.200371000
6	2.116590000	-0.624577000	-0.505218000
1	2.219068000	-0.951612000	-1.559050000
1	2.578284000	0.339602000	-0.227912000
8	1.775109000	-1.458260000	0.394152000

TS(C2.C3) (formaldehyde)

G = -839.86713

45	0.259154000	-0.489786000	-0.170802000
6	-1.136748000	1.769562000	0.782290000
6	-0.802554000	0.502198000	1.199190000
6	-0.819335000	2.063164000	-0.582904000
6	-0.150417000	1.061819000	-1.236044000
17	2.380483000	0.119013000	0.369135000
1	-1.106469000	2.999656000	-1.069666000
1	0.179487000	1.112249000	-2.282265000
1	-0.864457000	0.139677000	2.230948000
1	-1.631818000	2.490299000	1.441986000
6	-2.346517000	-0.829446000	0.198132000
1	-3.026848000	-1.171837000	0.999044000
1	-2.673417000	0.015196000	-0.428064000
8	-1.434150000	-1.621485000	-0.205646000

C3 (formaldehyde)

G = -839.87116

6	-2.736286000	-0.612499000	0.317773000

6	-2.748138000	0.720113000	0.110876000
6	-1.646179000	1.672229000	0.241691000
6	-1.527541000	-1.412044000	0.722202000
6	-0.314779000	1.517037000	0.078128000
45	0.656528000	-0.055563000	-0.538918000
1	-1.065558000	-1.003762000	1.641381000
1	-3.666211000	-1.166909000	0.161287000
1	-3.708917000	1.174559000	-0.154285000
1	-1.965798000	2.699800000	0.468863000
1	0.362749000	2.358800000	0.282215000
17	2.381357000	0.065921000	0.863429000
1	-1.793885000	-2.464383000	0.915062000
8	-0.543959000	-1.440930000	-0.320691000

TS(C3.C4) (formaldehyde)

G = -839.83605

6	1.751931000	-0.495759000	-0.852397000
6	1.749847000	0.901511000	-0.703879000
6	1.500316000	1.482164000	0.610451000
6	1.822002000	-1.309005000	0.429280000
6	0.502059000	0.777722000	1.240465000
45	-0.345355000	-0.017420000	-0.386639000
1	1.821090000	-2.392403000	0.243895000
1	1.972133000	-0.957297000	-1.817337000
1	1.997825000	1.544920000	-1.556401000
1	1.912950000	2.430901000	0.956644000
1	-0.006863000	0.933303000	2.191243000
17	-2.565114000	-0.002014000	0.171030000
1	2.683881000	-1.024291000	1.065252000
8	0.601248000	-0.982100000	1.133051000

C4 (formaldehyde)

G = -839.92714

6	-1.142697000	0.096920000	-1.249907000
6	-1.406683000	-1.176005000	-0.612914000
6	-1.366380000	-1.100663000	0.801406000
6	-1.072582000	0.232399000	1.266206000
6	-1.764815000	1.403562000	0.596821000
45	0.456856000	-0.381114000	0.000699000
1	-2.821557000	1.470273000	0.916225000
1	-0.959531000	0.131915000	-2.328051000
1	-1.472056000	-2.117778000	-1.161556000
1	-1.417031000	-1.983831000	1.441520000
1	-0.835908000	0.374515000	2.325909000
17	2.504299000	0.589897000	-0.013013000
1	-1.260017000	2.348636000	0.851628000
8	-1.730822000	1.270110000	-0.833198000

C1 (allene)

G = -725.27245

45	0.000135000	-0.353137000	-0.000078000
6	-1.856093000	-1.014675000	-0.508380000
6	-2.011251000	-0.218762000	0.466960000
6	1.856475000	-1.013699000	0.508664000
6	2.011479000	-0.217849000	-0.466792000
17	-0.000640000	1.949715000	0.000007000
1	2.172194000	-1.674130000	1.308475000
1	2.570685000	0.443238000	-1.116629000
1	-2.570361000	0.442196000	1.116998000
1	-2.171365000	-1.675355000	-1.308157000

TS(C1.C2) (allene)

G = -725.26186

45	-0.016373000	-0.000006000	-0.216957000
6	1.826148000	-0.987041000	-0.112045000
6	0.911044000	-1.483894000	0.669437000
6	1.826127000	0.987065000	-0.112043000
6	0.911010000	1.483910000	0.669427000
17	-2.288025000	-0.000002000	0.086591000
1	2.749725000	1.212980000	-0.637894000
1	0.643856000	2.203449000	1.439069000
1	0.643911000	-2.203426000	1.439092000
1	2.749741000	-1.212942000	-0.637908000

C2 (allene)

G = -725.26482

45	0.000000000	0.167183000	0.000000000
6	0.753060000	-2.238469000	0.000000000
6	1.472591000	-1.103899000	0.000000000
6	-0.747910000	-2.240096000	0.000000000
6	-1.469833000	-1.107051000	0.000000000
17	-0.003361000	2.408176000	0.000000000
1	-1.249027000	-3.214117000	0.000000000
1	-2.550487000	-0.952494000	0.000000000
1	2.552924000	-0.947098000	0.000000000
1	1.256283000	-3.211408000	0.000000000

C3 (allene)

G = -842.01507

45	0.053338000	-0.334606000	-0.208134000
6	-1.351357000	2.115737000	-0.150667000
6	-0.956330000	1.189185000	-1.040796000
6	-0.880975000	1.909546000	1.216258000
6	-0.142983000	0.800651000	1.410485000
17	-1.687907000	-1.762980000	0.118328000
1	-1.103347000	2.612923000	2.025008000
1	0.330397000	0.471475000	2.341081000
1	-1.144613000	1.162265000	-2.118766000
1	-1.978298000	2.966830000	-0.435526000
6	1.680869000	0.899978000	-1.005330000

1	1.755659000	0.697103000	-2.079577000
1	1.567086000	1.949036000	-0.715684000
6	2.108439000	-0.018861000	-0.080509000
6	2.925628000	-0.703487000	0.698235000
1	4.006713000	-0.535875000	0.645393000
1	2.560842000	-1.452329000	1.406476000

TS(C3.C4) (allene)

G = -842.00265

45	0.232953000	-0.106169000	-0.241594000
6	-2.527173000	-0.713440000	-0.283057000
6	-1.672078000	0.014371000	-1.050827000
6	-2.076624000	-1.003485000	1.069200000
6	-0.788659000	-0.690535000	1.341992000
17	2.077870000	-1.433608000	-0.085232000
1	-2.743629000	-1.437469000	1.821631000
1	-0.269795000	-0.803991000	2.298096000
1	-1.854248000	0.284948000	-2.094741000
1	-3.479976000	-1.083646000	-0.672574000
6	-1.005091000	1.752746000	-0.206924000
1	-1.278405000	2.286021000	-1.124248000
1	-1.758667000	1.779674000	0.588636000
6	0.361402000	1.804154000	0.193454000
6	1.372623000	2.561349000	0.596870000
1	2.358446000	2.134983000	0.791464000
1	1.233216000	3.637466000	0.748150000

C4 (allene)

G = -842.03159

6	2.654035000	0.400930000	0.649993000
6	2.740398000	-0.837208000	0.120421000
6	1.681198000	-1.810417000	-0.124109000
6	1.393585000	1.087548000	1.123001000
6	0.345263000	-1.667253000	-0.300212000
45	-0.750263000	-0.103126000	-0.565028000
1	0.889041000	0.478193000	1.891553000
1	3.581482000	0.973525000	0.745120000
1	3.744233000	-1.193126000	-0.134644000
1	2.043016000	-2.844206000	-0.225802000
1	-0.278070000	-2.572489000	-0.397279000
17	-2.131829000	-0.208083000	1.190821000
1	1.646017000	2.056780000	1.583488000
6	0.436199000	1.318797000	-0.022292000
6	0.365024000	2.420673000	-0.789097000
1	1.061056000	3.256240000	-0.641651000
1	-0.378068000	2.544744000	-1.584698000

TS(C4.C5) (allene)

G = -842.01855

6	-1.773450000	-0.361033000	-0.966331000

6	-1.747203000	-1.263498000	0.111171000
6	-1.511332000	-0.798771000	1.484318000
6	-0.477520000	0.088880000	1.481147000
6	-0.566646000	1.375098000	0.040652000
45	0.305554000	-0.443876000	-0.284819000
1	-2.018410000	-0.741804000	-1.961572000
1	-1.992231000	-2.317316000	-0.065166000
1	-2.009317000	-1.220344000	2.363010000
1	0.030758000	0.540231000	2.332981000
17	2.555204000	-0.100543000	0.027281000
6	-1.857523000	1.140152000	-0.693548000
6	0.065229000	2.531491000	0.306535000
1	-2.753317000	1.405609000	-0.101759000
1	-0.380292000	3.484524000	0.003172000
1	1.020103000	2.550703000	0.833137000
1	-1.875037000	1.708137000	-1.634383000

C5 (allene)

G = -842.09425

6	-1.197872000	0.037313000	-1.089375000
6	-0.961324000	-1.378423000	-0.962513000
6	-0.666102000	-1.825863000	0.351000000
6	-0.656961000	-0.778919000	1.341150000
6	-1.754391000	0.272851000	1.341637000
45	0.689759000	-0.300108000	-0.181144000
1	-2.689309000	-0.160923000	1.745016000
1	-1.205290000	0.452214000	-2.103022000
1	-0.862876000	-2.036321000	-1.828799000
1	-0.326588000	-2.846053000	0.544693000
1	-0.218205000	-1.019789000	2.315299000
17	2.404926000	1.136587000	0.191434000
1	-1.470601000	1.100637000	2.008832000
6	-2.676714000	1.880849000	-0.375176000
6	-1.951478000	0.793548000	-0.069457000
1	-3.202891000	2.448053000	0.396353000
1	-2.758084000	2.236934000	-1.404867000

C3 (carbon disulfide)

G = -1559.91332

45	0.832910000	-0.436239000	0.000082000
6	-0.278917000	2.030189000	0.732897000
6	0.203050000	0.913058000	1.311105000
6	-0.278778000	2.030352000	-0.732400000
6	0.203310000	0.913356000	-1.310764000
17	3.013393000	0.127943000	0.000359000
1	-0.653615000	2.878485000	-1.314827000
1	0.296489000	0.712657000	-2.384260000
1	0.296025000	0.712124000	2.384574000
1	-0.653865000	2.878193000	1.315439000
6	-2.322238000	-0.661489000	-0.000294000
16	-1.180202000	-1.780558000	-0.000291000
16	-3.391812000	0.463150000	-0.000582000

TS(C3.C4) (carbon disulfide) $G = -1559.90474$

45	-0.891969000	-0.439853000	0.091059000
6	0.511977000	1.977679000	-0.261272000
6	0.284482000	0.797458000	-0.921635000
6	-0.091217000	2.079200000	1.039981000
6	-0.834471000	0.996098000	1.401128000
17	-2.925765000	-0.051679000	-0.847522000
1	0.043925000	2.949792000	1.688167000
1	-1.397481000	0.900059000	2.338382000
1	0.575710000	0.581729000	-1.954951000
1	1.103418000	2.786739000	-0.701481000
6	2.222353000	-0.360048000	-0.083844000
16	3.623422000	0.106448000	-0.630922000
16	1.188597000	-1.324492000	0.749296000

C4 (carbon disulfide) $G = -1559.91775$

6	-1.850924000	1.279932000	0.793069000
6	-1.000239000	2.273002000	0.401526000
6	0.052221000	2.334366000	-0.584028000
6	0.910857000	1.377341000	-1.015902000
45	1.220420000	-0.425333000	-0.473224000
1	-2.616780000	1.561423000	1.522742000
1	-1.211904000	3.243874000	0.864233000
1	0.217593000	3.339904000	-0.995364000
1	1.687593000	1.651405000	-1.753027000
17	2.413169000	-0.211534000	1.393290000
6	-2.071536000	-0.054320000	0.267290000
16	-3.591790000	-0.698756000	0.081659000
16	-0.799556000	-1.196397000	-0.156733000

TS(C4.C5) (carbon disulfide) $G = -1559.88900$

6	-1.743592000	0.934276000	1.065821000
6	-0.919055000	2.027654000	1.188488000
6	0.126250000	2.420632000	0.299498000
6	0.737932000	1.575463000	-0.583123000
45	1.494376000	-0.242887000	-0.332193000
1	-2.543098000	0.819695000	1.802152000
1	-1.150381000	2.718601000	2.004759000
1	0.418887000	3.476094000	0.288659000
1	1.323553000	1.979181000	-1.433797000
17	0.939187000	-1.326542000	1.526065000
6	-1.836572000	-0.007932000	-0.018933000
16	-0.565003000	-0.085214000	-1.291561000
16	-3.150736000	-0.990598000	-0.293859000

C5 (carbon disulfide) $G = -1559.94995$

6	0.783037000	-0.004806000	-1.137093000
6	0.253305000	1.323911000	-1.373189000
6	-0.166204000	2.040655000	-0.231367000
6	-0.004466000	1.331589000	1.018943000
45	-1.113131000	0.144195000	-0.251079000
1	0.874430000	-0.659513000	-2.009626000
1	0.041848000	1.684309000	-2.382313000
1	-0.717877000	2.980235000	-0.314299000
1	-0.498595000	1.730477000	1.911342000
17	-2.377275000	-1.577501000	0.472036000
6	1.817135000	-0.284803000	-0.101625000
16	3.101362000	-1.274137000	-0.377370000
16	1.567883000	0.533759000	1.440796000

C3 (carbodiimide) $G = -874.17317$

45	0.483682000	-0.506936000	-0.004897000
6	-0.694178000	1.926141000	0.756220000
6	-0.149033000	0.827032000	1.317153000
6	-0.701676000	1.939945000	-0.710017000
6	-0.166150000	0.850331000	-1.294447000
17	2.678355000	0.051314000	-0.015939000
1	-1.104855000	2.780751000	-1.284251000
1	-0.055115000	0.677147000	-2.371709000
1	-0.019040000	0.645520000	2.391363000
1	-1.077928000	2.763969000	1.349082000
6	-2.493318000	-0.810605000	0.017453000
7	-1.419364000	-1.452797000	0.034537000
1	-1.512739000	-2.452382000	0.229933000
7	-3.493601000	-0.151721000	-0.170376000
1	-3.911178000	0.359328000	0.609595000

TS(C3.C4) (carbodiimide) $G = -874.15416$

45	0.501305000	-0.433819000	-0.210772000
6	-1.109479000	1.694507000	0.706952000
6	-0.762952000	0.406187000	1.084551000
6	-0.559739000	2.151239000	-0.530855000
6	0.313256000	1.264304000	-1.102351000
17	2.622323000	-0.135723000	0.598753000
1	-0.789189000	3.131412000	-0.957215000
1	0.904998000	1.485188000	-2.001472000
1	-0.894204000	0.022320000	2.103165000
1	-1.744741000	2.332027000	1.333251000
6	-2.228063000	-0.651414000	0.058388000
7	-3.378873000	-0.744785000	0.513235000
1	-3.737386000	0.022190000	1.077158000
7	-1.349705000	-1.114056000	-0.776084000
1	-1.695792000	-1.341045000	-1.709113000

C4 (carbodiimide)

G = -874.16771

6	-2.455788000	0.441371000	0.672899000
6	-1.962439000	1.698777000	0.545043000
6	-0.793607000	2.257276000	-0.111506000
6	0.333280000	1.652974000	-0.542830000
45	0.834620000	-0.200890000	-0.490913000
1	-3.376241000	0.337277000	1.252198000
1	-2.578301000	2.464717000	1.029174000
1	-0.825208000	3.348672000	-0.230728000
1	1.147271000	2.251564000	-0.984156000
17	2.311131000	-0.338755000	1.169734000
6	-2.061547000	-0.866562000	0.128648000
7	-0.846735000	-1.021342000	-0.567580000
1	-0.731933000	-2.017448000	-0.804795000
7	-2.910257000	-1.832325000	0.268638000
1	-2.543163000	-2.713240000	-0.117020000

TS(C4.C5) (carbodiimide)

G = -874.12675

6	-2.106390000	-0.359843000	0.782012000
6	-1.963442000	0.894299000	1.289727000
6	-1.215325000	1.941665000	0.642638000
6	-0.250852000	1.669807000	-0.273458000
45	1.136177000	0.266847000	-0.354648000
1	-2.731841000	-1.080358000	1.313864000
1	-2.504934000	1.147814000	2.205856000
1	-1.472373000	2.986547000	0.841428000
1	0.076956000	2.402918000	-1.035538000
17	1.243029000	-1.311329000	1.230133000
6	-1.634625000	-0.800251000	-0.538201000
7	-0.628585000	-0.032621000	-1.169598000
7	-2.108825000	-1.778991000	-1.232468000
1	-2.889222000	-2.221970000	-0.733262000
1	-0.552358000	-0.343229000	-2.147279000

C5 (carbodiimide)

G = -874.22653

6	1.271854000	0.147772000	-1.058420000
6	1.000058000	1.510563000	-0.696728000
6	0.619894000	1.676417000	0.660567000
6	0.648441000	0.443720000	1.418095000
45	-0.674382000	0.290205000	-0.209753000
1	1.391536000	-0.110990000	-2.113171000
1	0.940691000	2.321071000	-1.425118000
1	0.242790000	2.617449000	1.064575000
1	0.222976000	0.427735000	2.424201000
17	-2.472582000	-1.056085000	0.104628000
6	2.005138000	-0.758057000	-0.125799000

7	2.763033000	-1.680004000	-0.580716000
1	3.188107000	-2.224229000	0.182408000
7	1.714922000	-0.465343000	1.219376000
1	1.777000000	-1.241851000	1.870423000

C3 (carbon dioxide)

G = -913.98204

45	0.521192000	-0.514423000	0.000071000
6	-0.741973000	1.877324000	0.735671000
6	-0.121250000	0.828070000	1.309509000
6	-0.741656000	1.877540000	-0.735446000
6	-0.120603000	0.828482000	-1.309299000
17	2.685437000	0.053377000	-0.000070000
1	-1.188146000	2.691955000	-1.315738000
1	0.043591000	0.676036000	-2.382933000
1	0.042491000	0.675148000	2.383145000
1	-1.188763000	2.691533000	1.316036000
6	-2.562228000	-0.747058000	-0.000227000
8	-3.568974000	-0.177406000	-0.000224000
8	-1.567147000	-1.382491000	-0.000245000

TS(C3.C4) (carbon dioxide)

G = -913.93175

45	-0.387417000	-0.091108000	-0.374143000
6	1.846403000	-1.340742000	0.905839000
6	0.635865000	-0.631964000	1.181213000
6	2.142561000	-1.372182000	-0.441783000
6	1.105740000	-0.825166000	-1.260247000
17	-2.516012000	-0.430583000	0.431203000
1	3.081870000	-1.764016000	-0.844657000
1	1.108944000	-1.021899000	-2.345572000
1	0.236436000	-0.515797000	2.192555000
1	2.465245000	-1.781454000	1.690605000
6	0.717899000	1.671850000	0.191805000
8	0.463992000	2.596939000	-0.529507000
8	1.363842000	1.339582000	1.198515000

C4 (carbon dioxide)

G = -913.96202

6	-2.153540000	-0.776609000	-0.892224000
6	-1.840564000	-1.623177000	0.096992000
6	-1.160416000	-1.338634000	1.364698000
6	-0.113536000	-0.514572000	1.546457000
45	0.810543000	0.513478000	0.162282000
1	-2.682932000	-1.064889000	-1.798346000
1	-2.162585000	-2.656050000	-0.068240000
1	-1.525081000	-1.901067000	2.234542000
1	0.361857000	-0.402879000	2.532930000
17	1.685894000	-1.292797000	-0.827763000
6	-0.892239000	1.158414000	-0.344163000

8	-1.976205000	0.615921000	-0.868050000
8	-0.794311000	2.317002000	0.022781000

TS(C4.C5) (carbon dioxide)

G = -913.94450

6	-1.584286000	-0.348814000	-1.050702000
6	-1.675236000	-1.284973000	0.015160000
6	-1.572926000	-0.830825000	1.390804000
6	-0.621190000	0.143532000	1.452806000
6	-0.682180000	1.362364000	0.016680000
45	0.356713000	-0.433116000	-0.217529000
1	-1.857363000	-0.634766000	-2.069110000
1	-1.930895000	-2.319351000	-0.230360000
1	-2.103999000	-1.295690000	2.227839000
1	-0.211493000	0.673663000	2.312403000
17	2.558440000	0.044333000	0.058394000
8	-0.350527000	2.478901000	0.274408000
8	-1.727840000	1.029226000	-0.823548000

C5 (carbon dioxide)

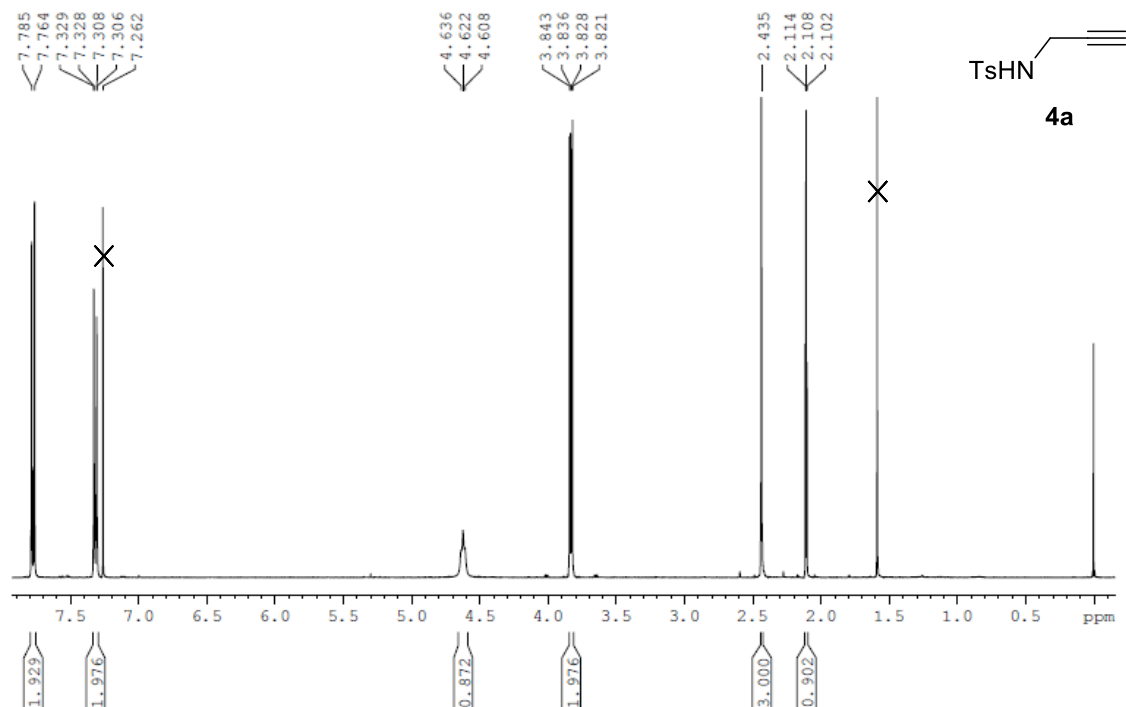
G = -914.00846

6	1.108414000	-0.131011000	-1.090917000
6	1.020338000	1.305849000	-0.946050000
6	0.830736000	1.712410000	0.394869000
6	0.778613000	0.583878000	1.301635000
45	-0.682671000	0.332089000	-0.127702000
1	1.100024000	-0.574762000	-2.089357000
1	0.973432000	1.995631000	-1.790617000
1	0.598476000	2.737726000	0.687582000
1	0.469279000	0.714045000	2.341356000
17	-2.456481000	-1.033196000	0.123530000
6	1.925837000	-0.886776000	-0.086702000
8	2.686978000	-1.781302000	-0.322920000
8	1.732464000	-0.438499000	1.205498000

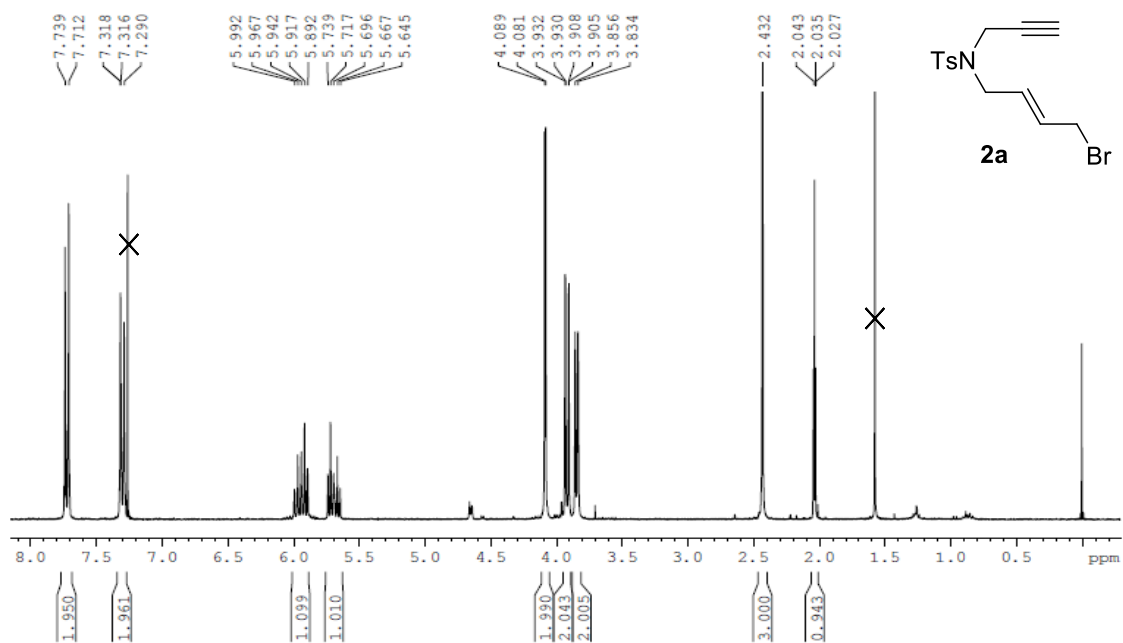
Annex 2

Spectra for the synthetic intermediates

Spectra for compound 4a



Spectra for compound 2a



Spectra for compound **4b'**

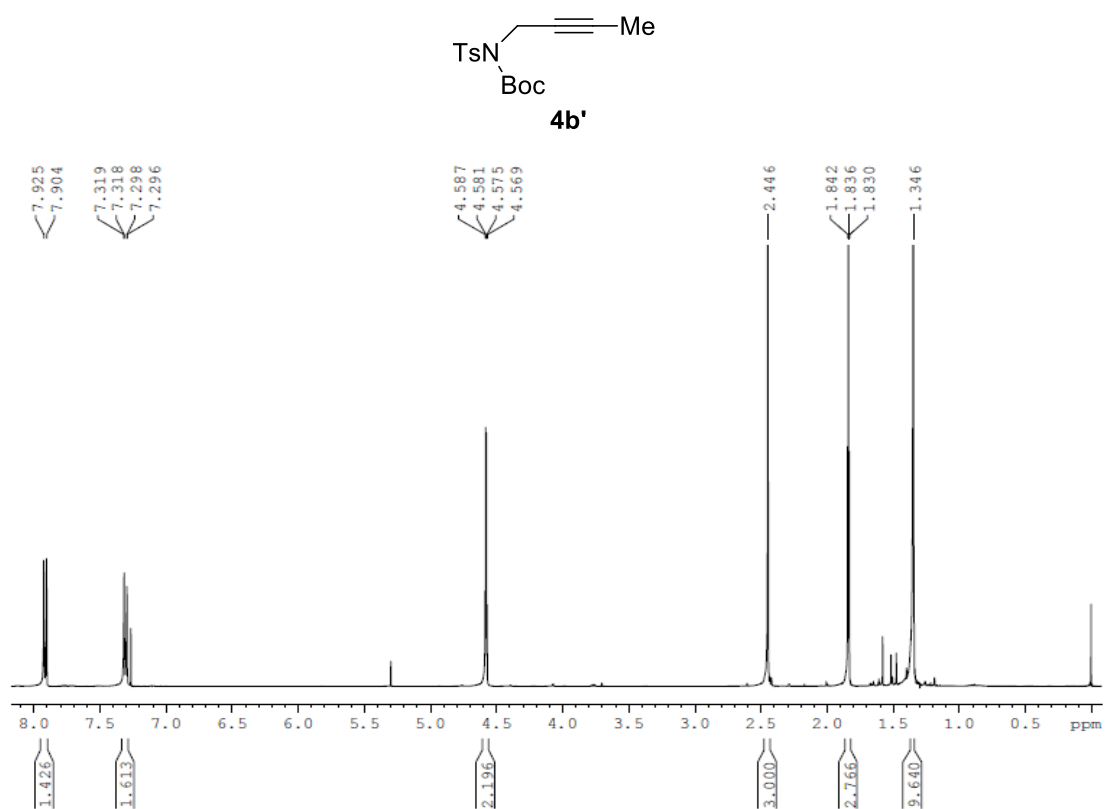


Figure 3. ¹H NMR spectrum (400 MHz) of **4b'** in CDCl₃.

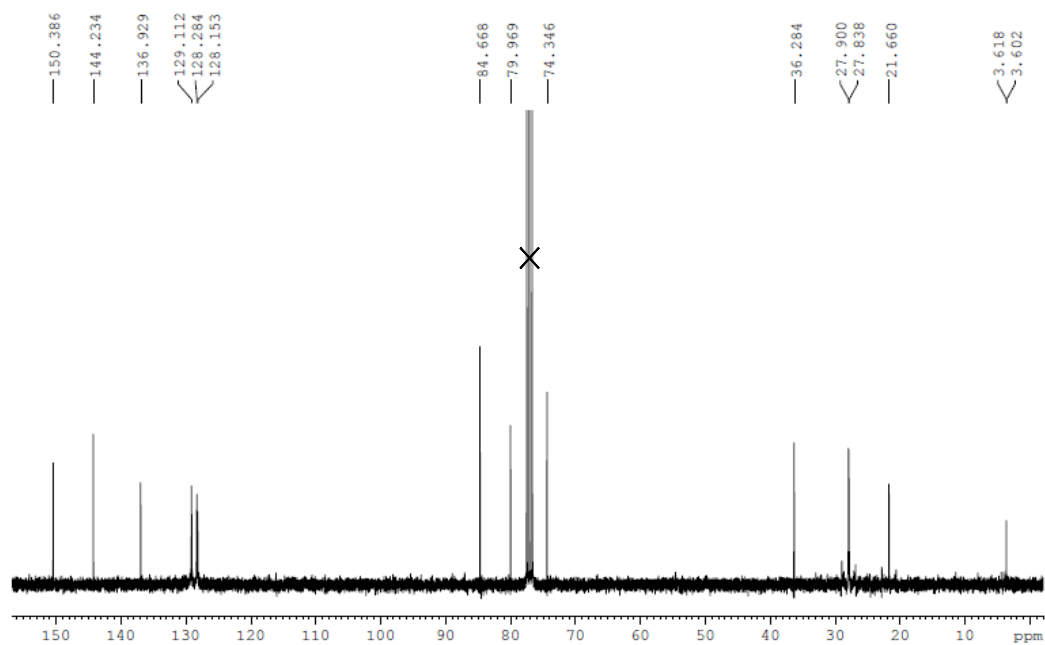


Figure 4. ¹H-decoupled ¹³C NMR spectrum (75 MHz) of **4b'** in CDCl₃.

Spectra for compound 4b

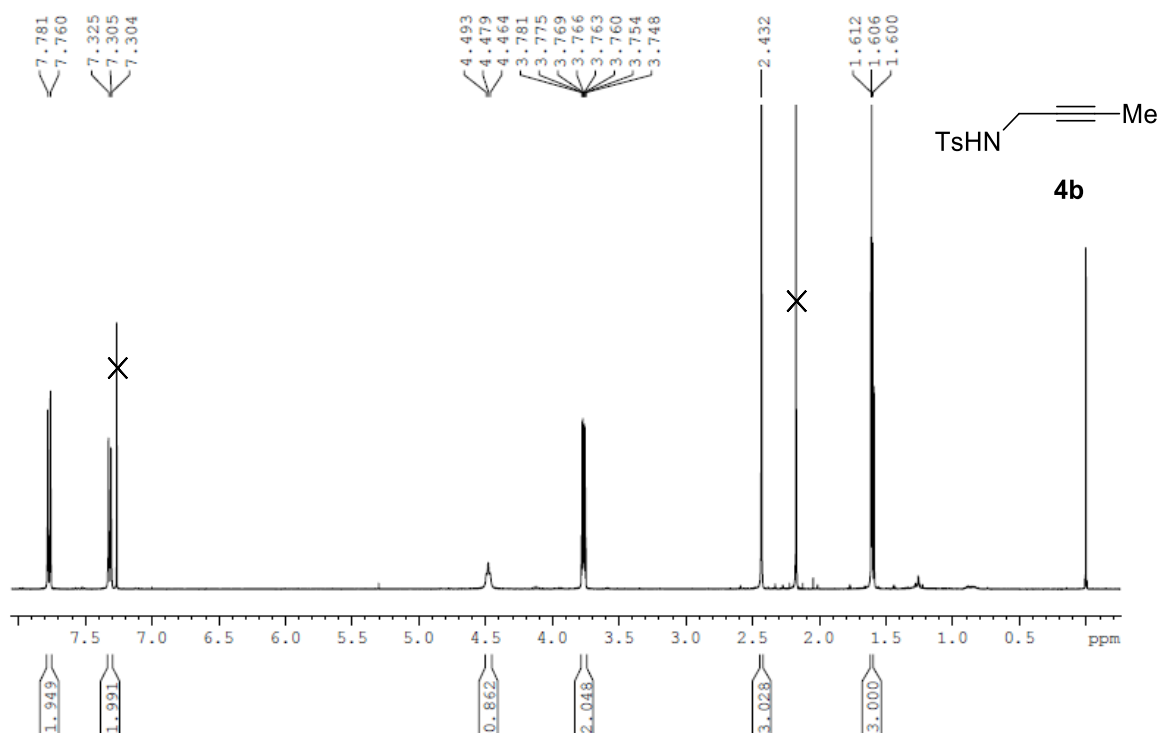


Figure 5. ¹H NMR spectrum (400 MHz) of **4b** in CDCl₃.

Spectra for compound 2b

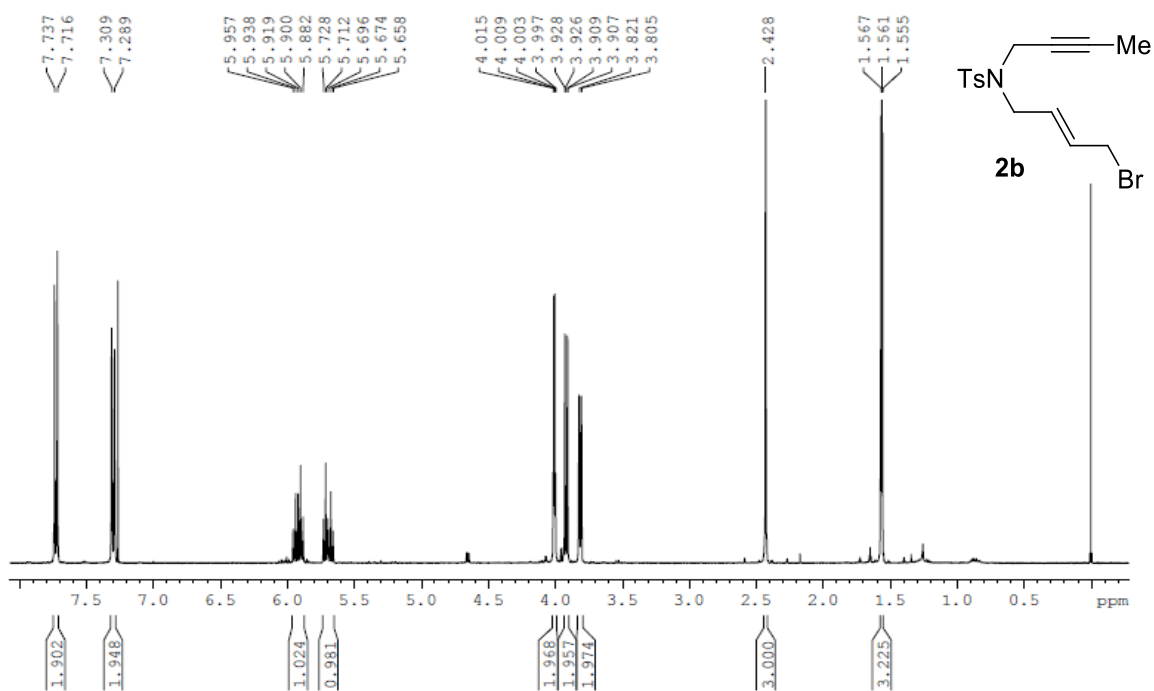


Figure 6. ¹H NMR spectrum (400 MHz) of **2b** in CDCl₃.

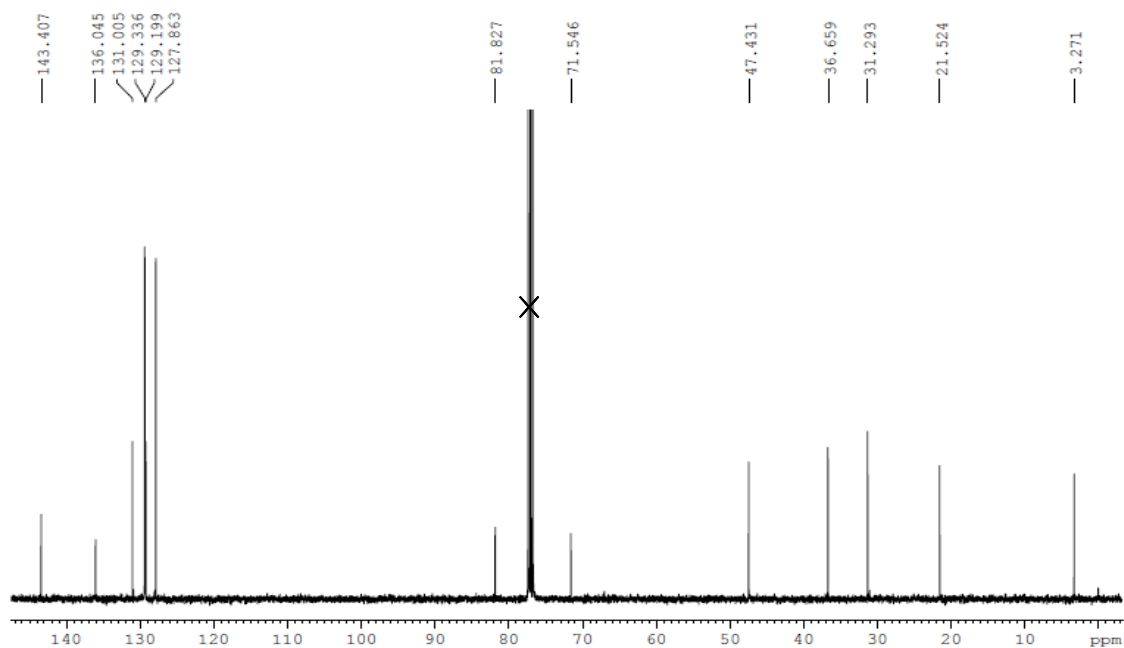


Figure 7. ^1H -decoupled ^{13}C NMR spectrum (100 MHz) of **2b** in CDCl_3 .

Spectra for compound **4c'**

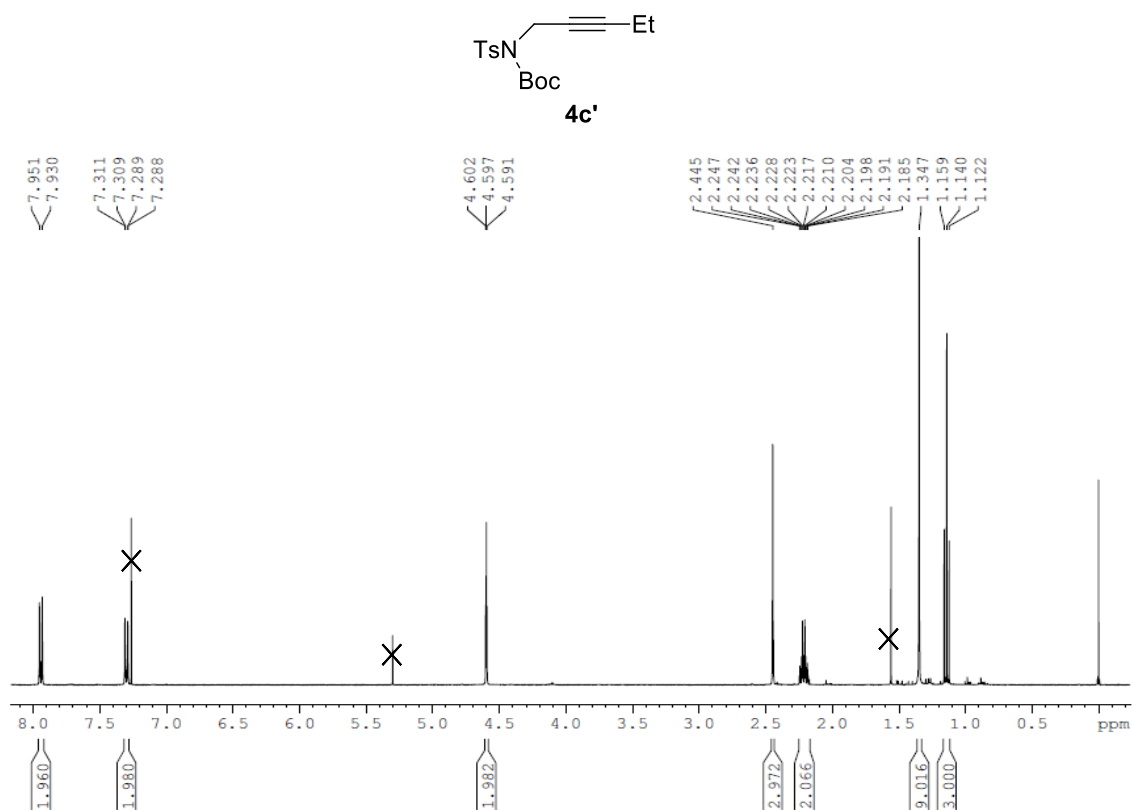


Figure 8. ^1H NMR spectrum (400 MHz) of **4c'** in CDCl_3 .

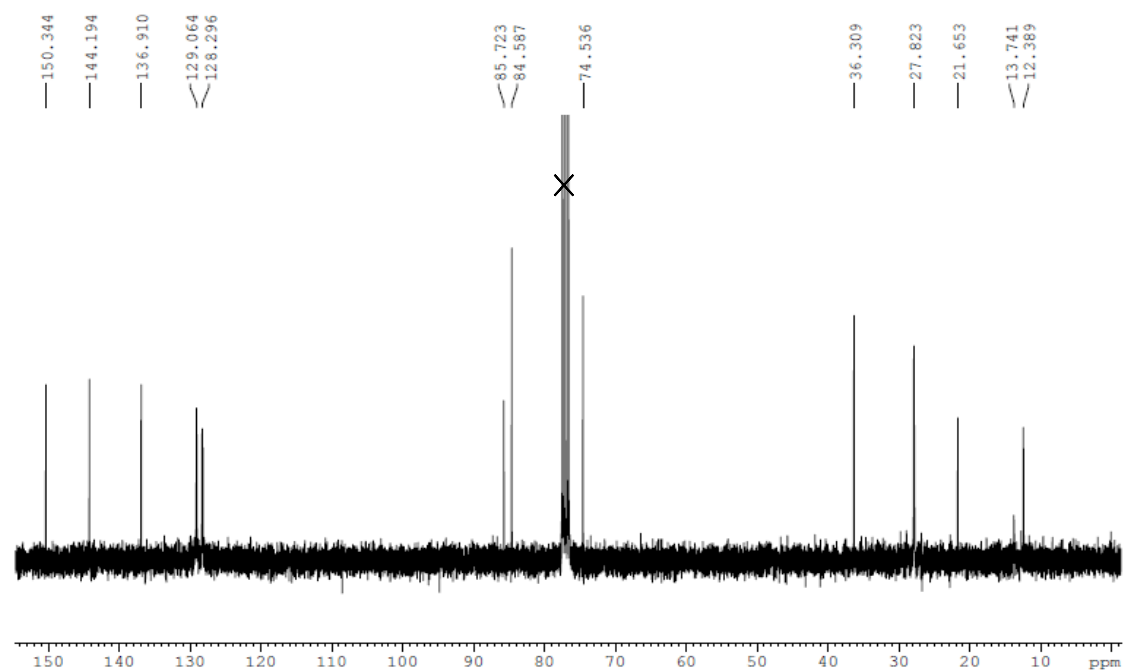


Figure 9. ^1H -decoupled ^{13}C NMR spectrum (75 MHz) of **4c'** in CDCl_3 .

Spectra for compound **4c**

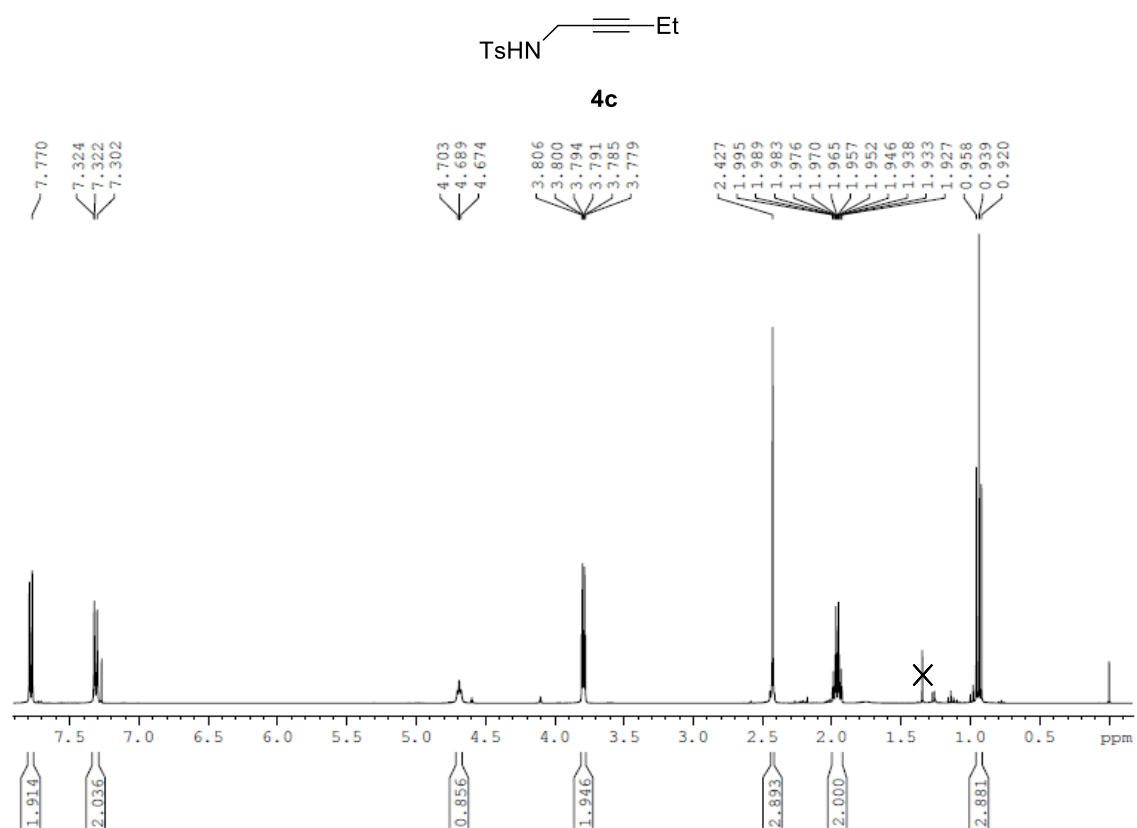


Figure 10. ^1H NMR spectrum (400 MHz) of **4c** in CDCl_3 .

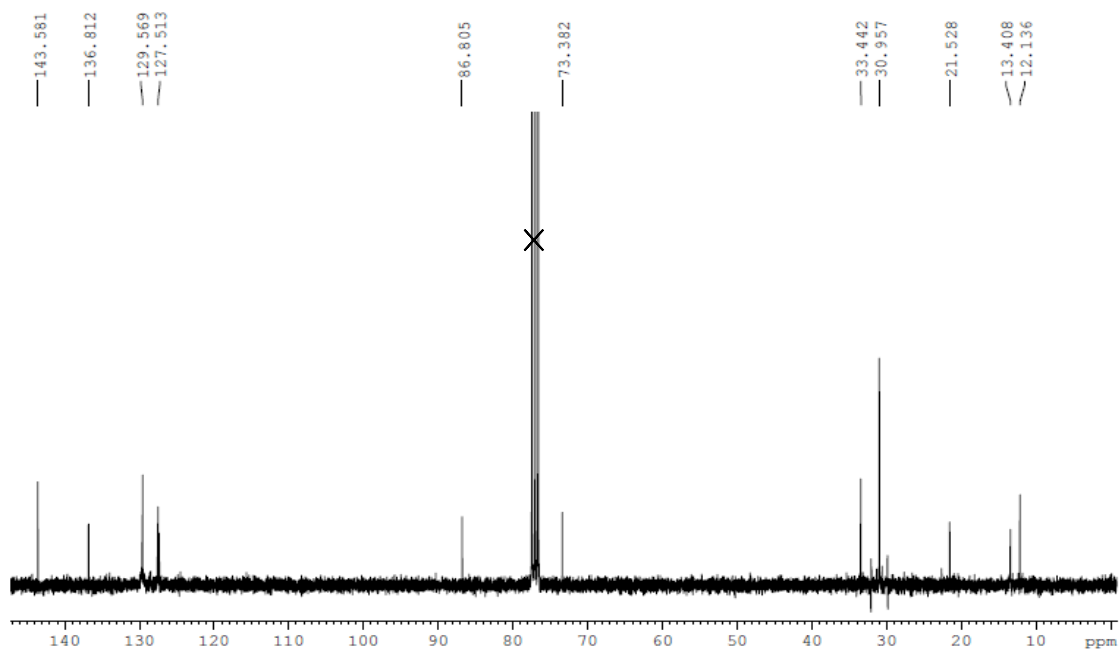


Figure 11. ^1H -decoupled ^{13}C NMR spectrum (75 MHz) of **4c** in CDCl_3 .

Spectra for compound **2c**

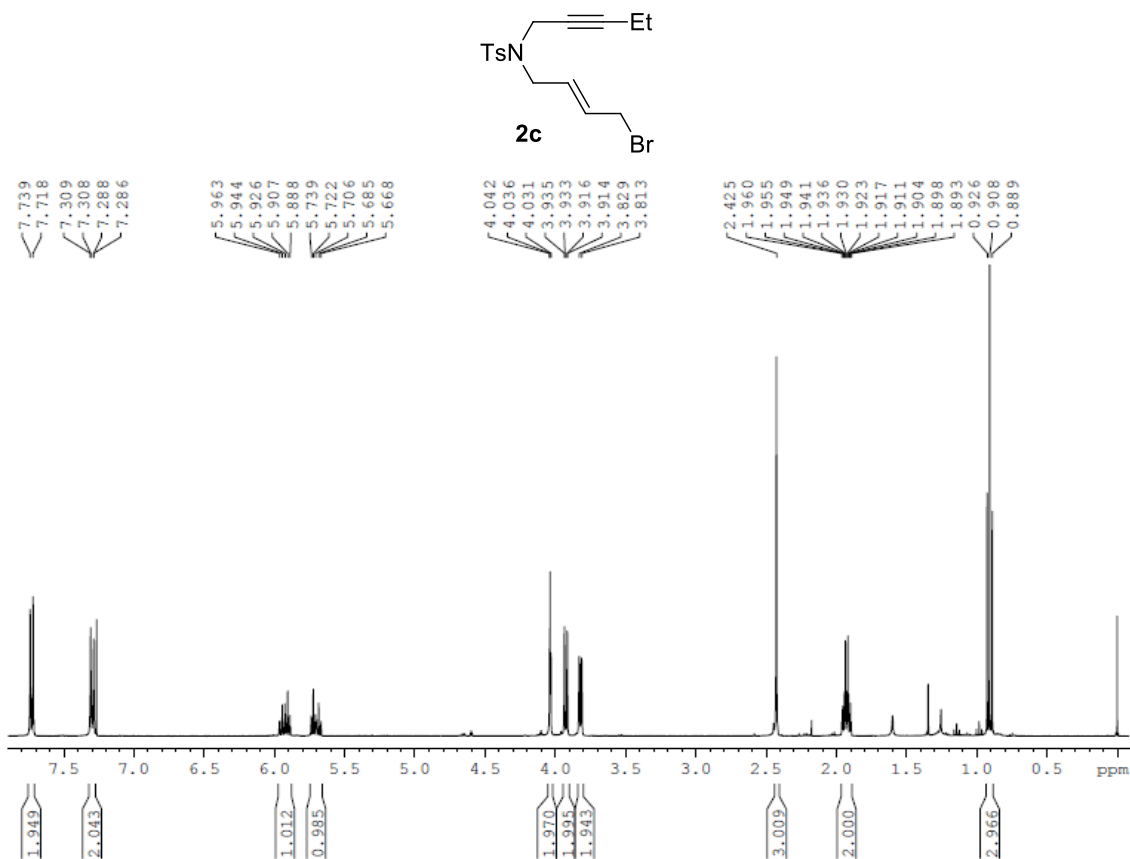


Figure 12. ^1H NMR spectrum (400 MHz) of **2c** in CDCl_3 .

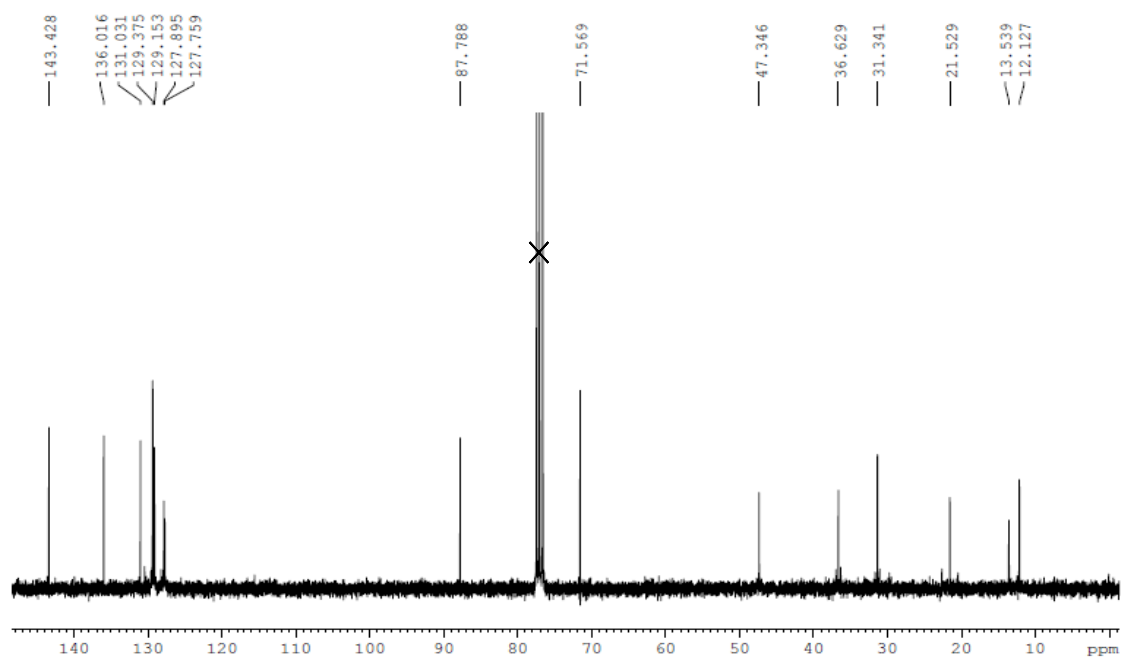


Figure 13. ^1H -decoupled ^{13}C NMR spectrum (75 MHz) of **2c** in CDCl_3 .

Spectra for compound 2h

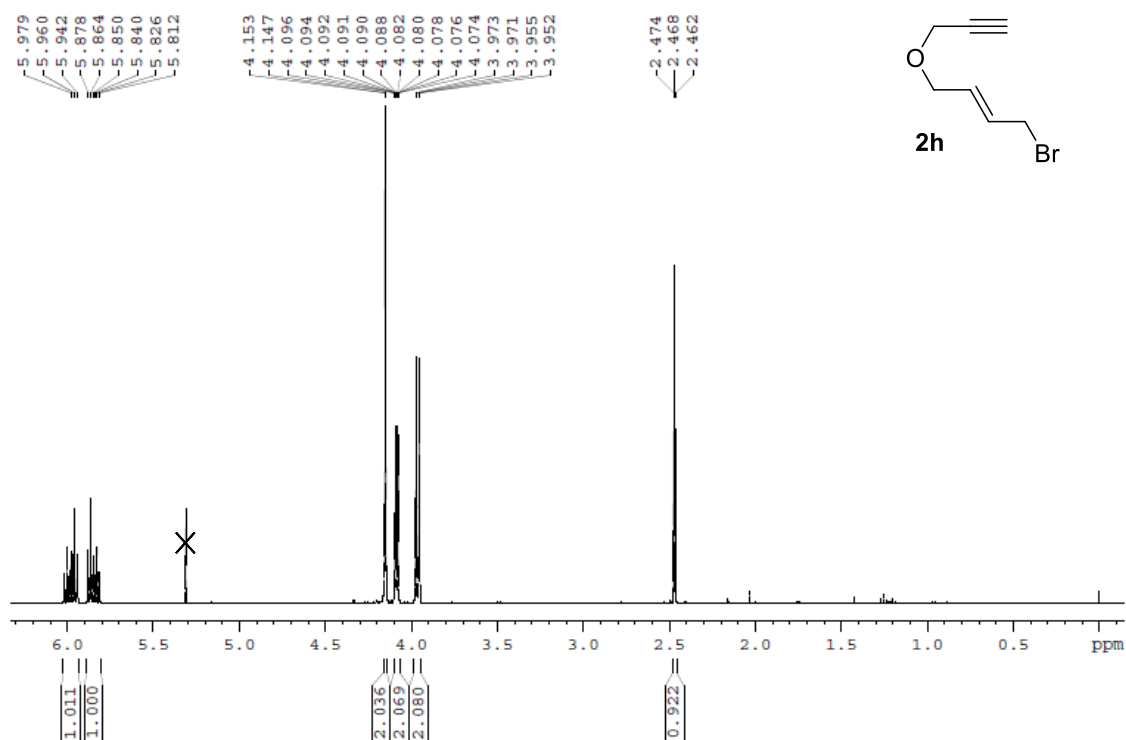


Figure 14. ^1H NMR spectrum (400 MHz) of **2h** in CDCl_3 .

Spectra for compound 3a

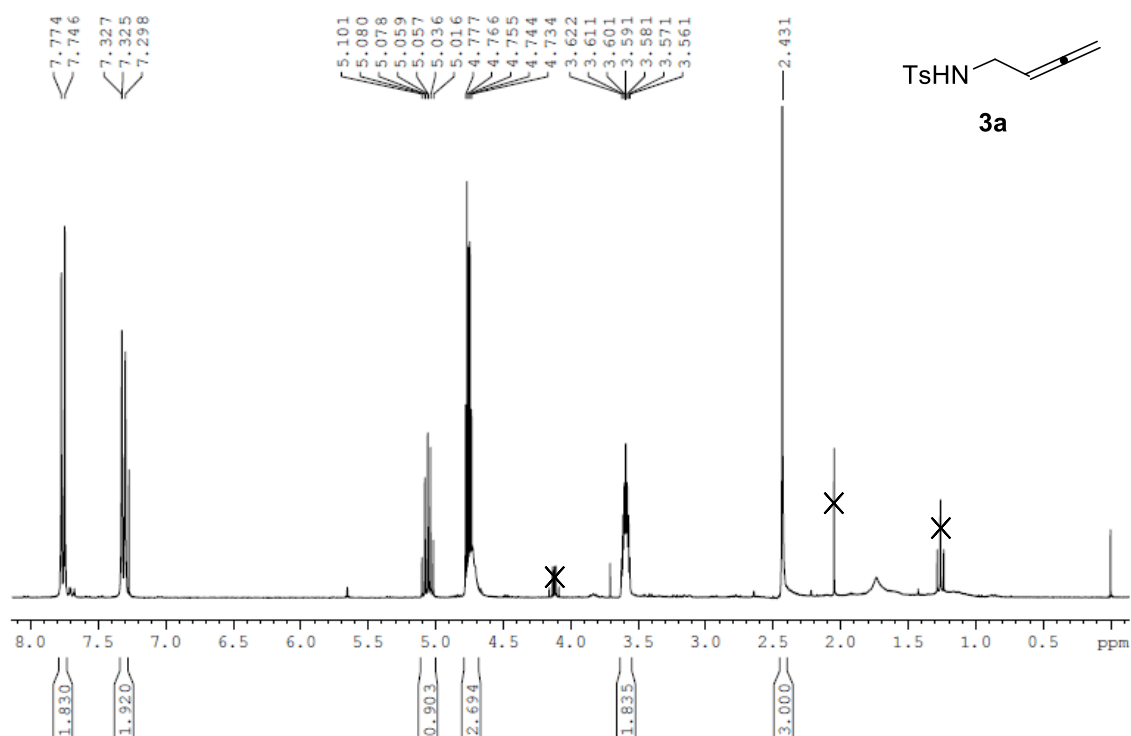


Figure 15. ¹H NMR spectrum (300 MHz) of **3a** in CDCl₃.

Spectra for compound 3d

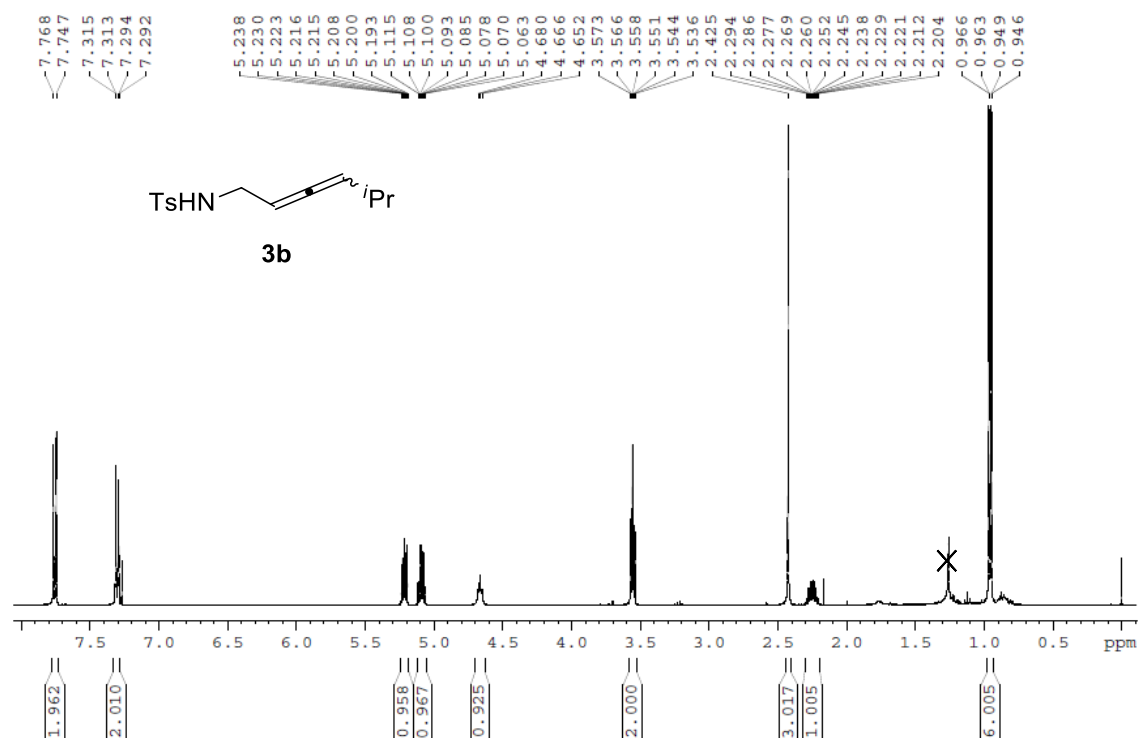


Figure 16. ¹H NMR spectrum (400 MHz) of **3d** in CDCl₃.

Spectra for compound **3e**

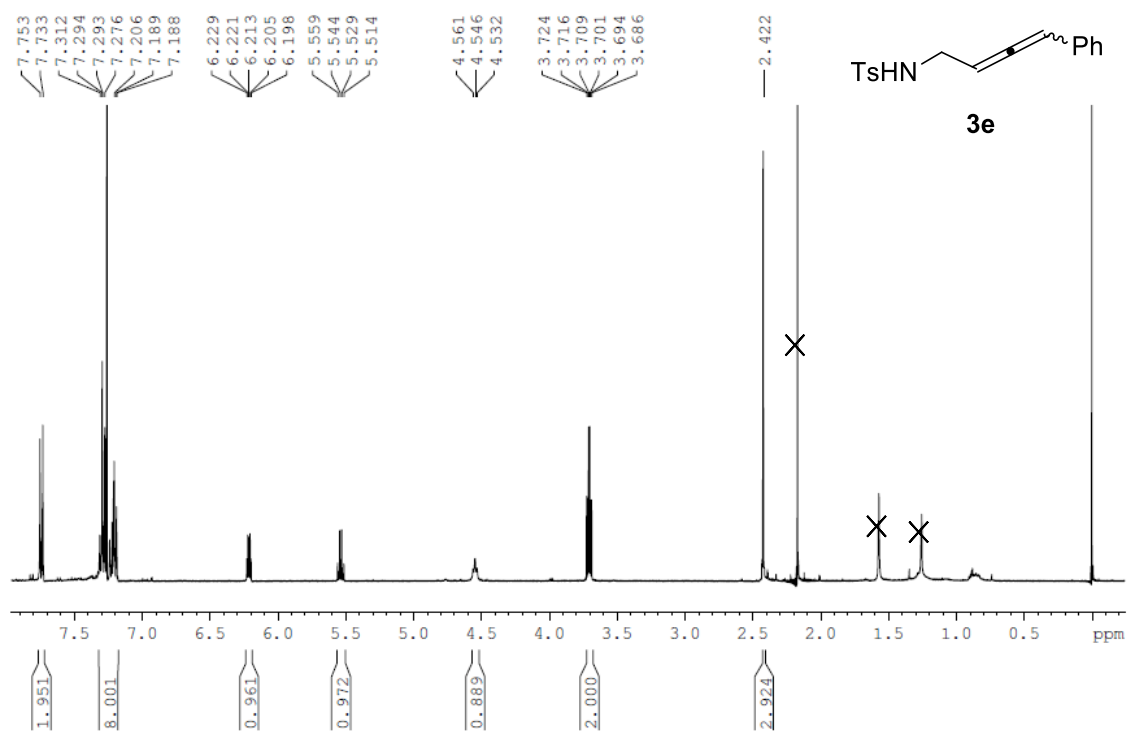


Figure 17. ¹H NMR spectrum (400 MHz) of **3e** in CDCl₃.

Spectra for the linear allene-ene-yne substrates

Spectra for compound 1a

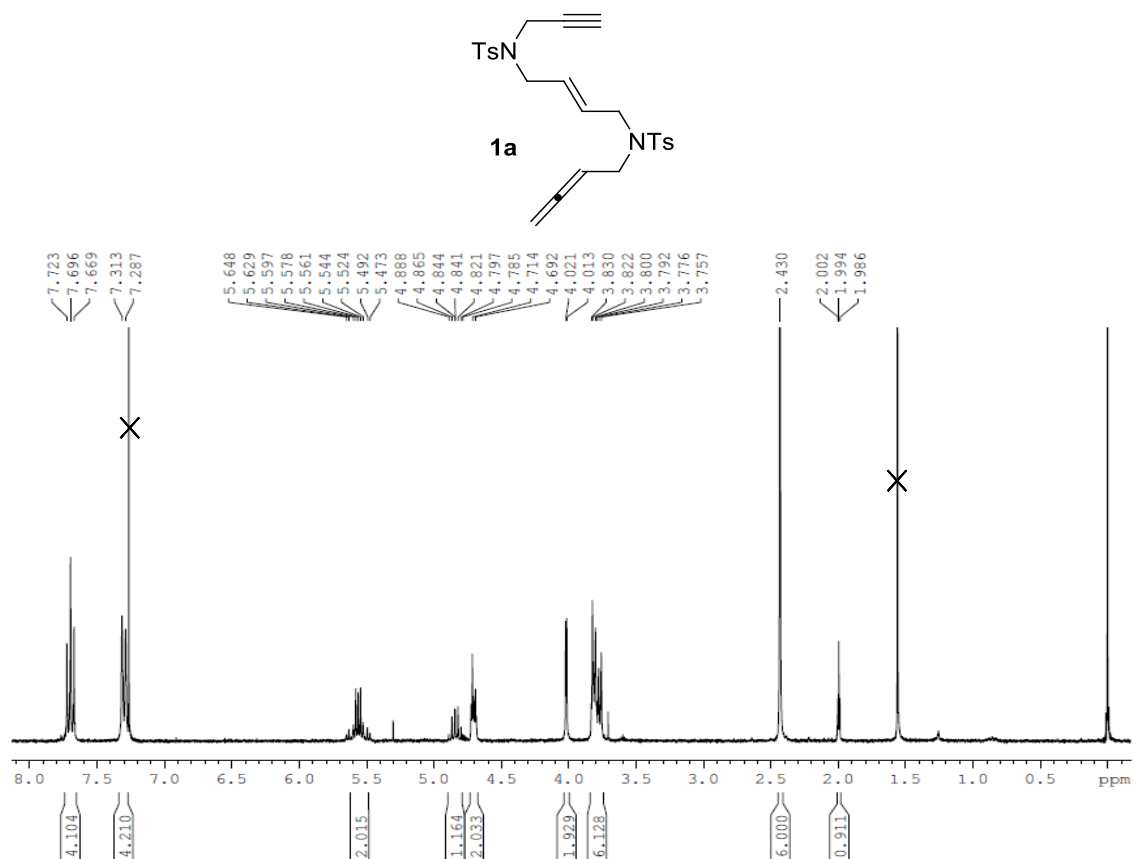


Figure 18. ^1H NMR spectrum (300 MHz) of **1a** in CDCl_3 .

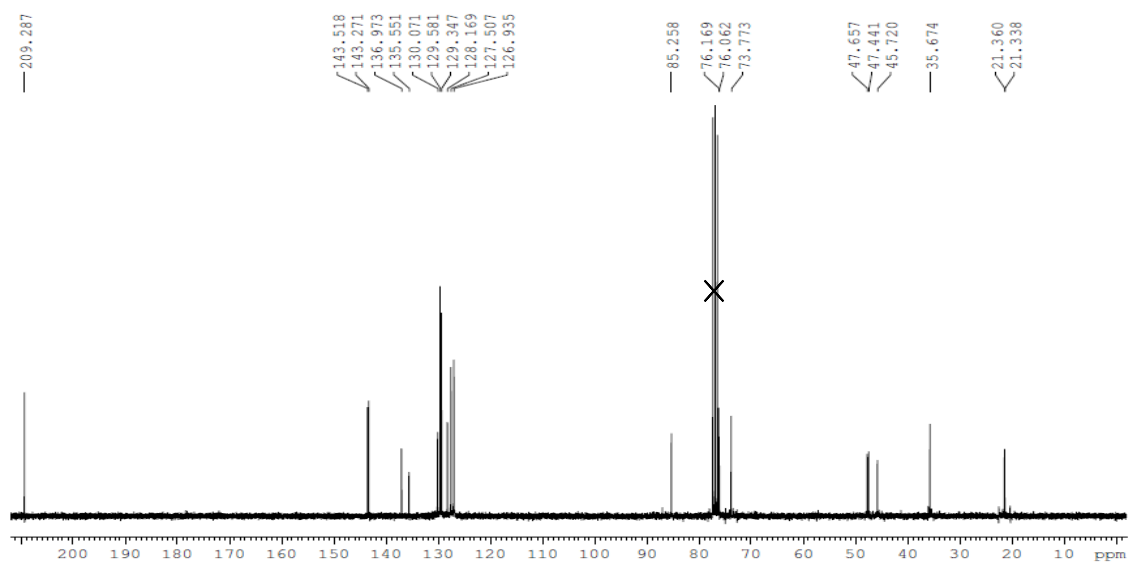


Figure 19. ^1H -decoupled ^{13}C NMR spectrum (75 MHz) of **1a** in CDCl_3 .

Spectra for compound **1b**

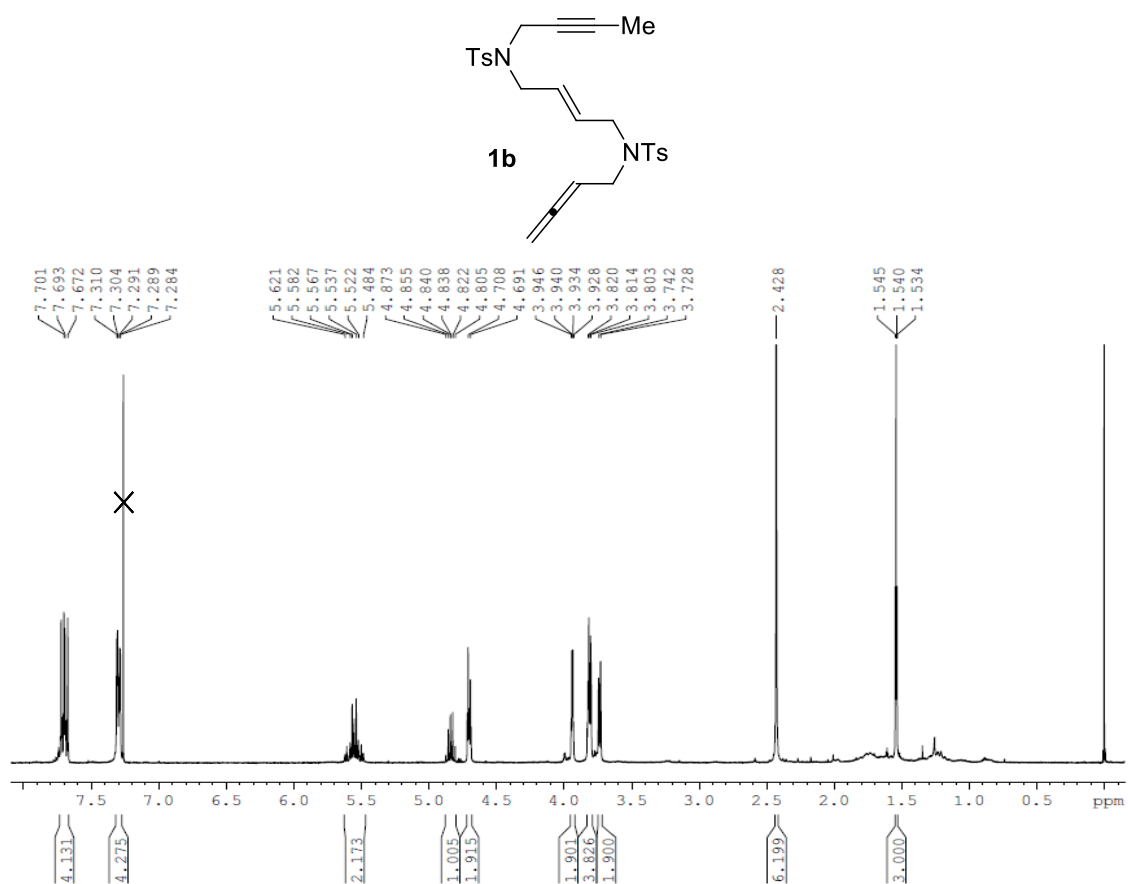


Figure 20. ¹H NMR spectrum (400 MHz) of **1b** in CDCl₃.

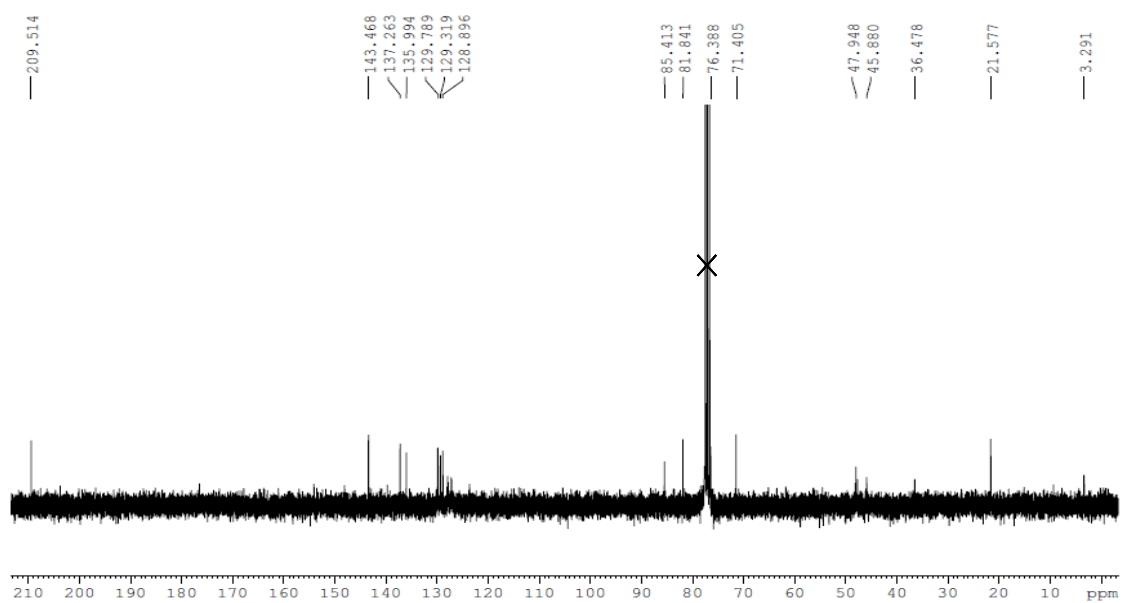


Figure 21. ¹H-decoupled ¹³C NMR spectrum (100 MHz) of **1b** in CDCl₃.

Spectra for compound 1c

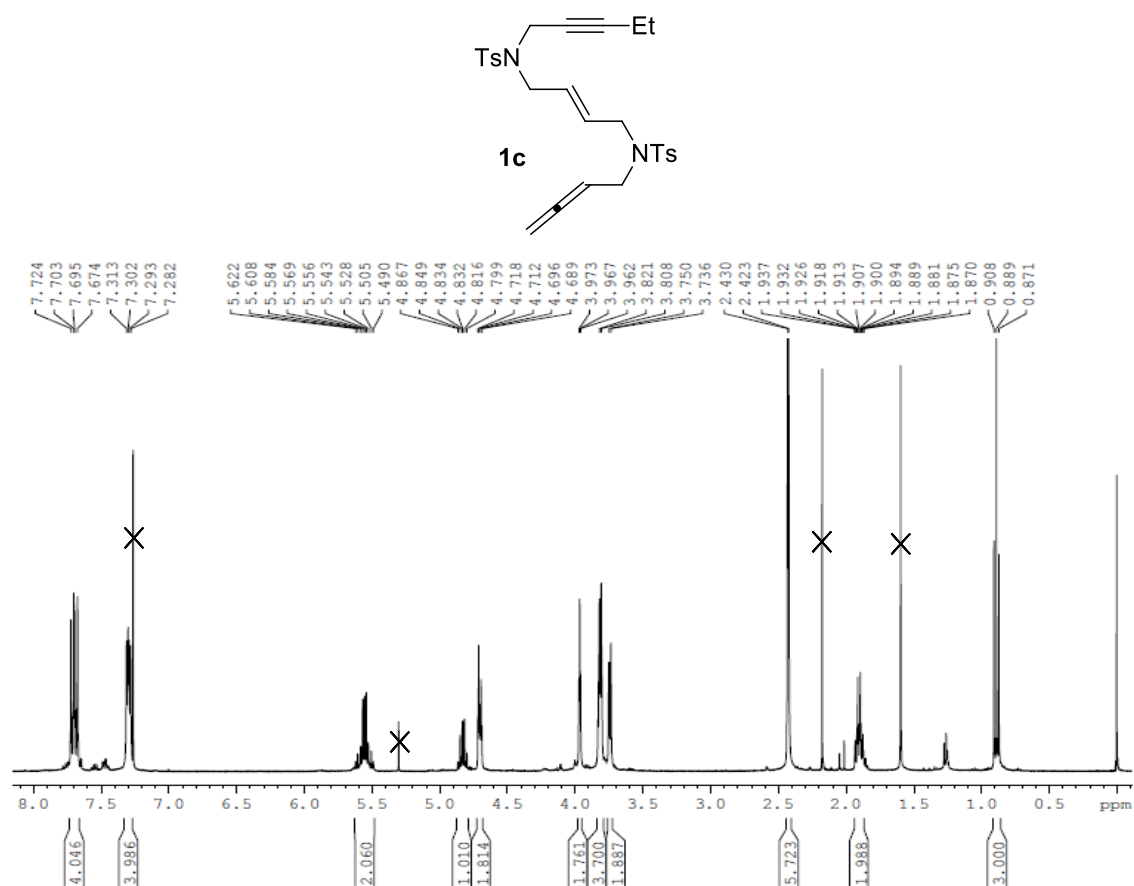


Figure 22. ^1H NMR spectrum (400 MHz) of **1c** in CDCl_3 .

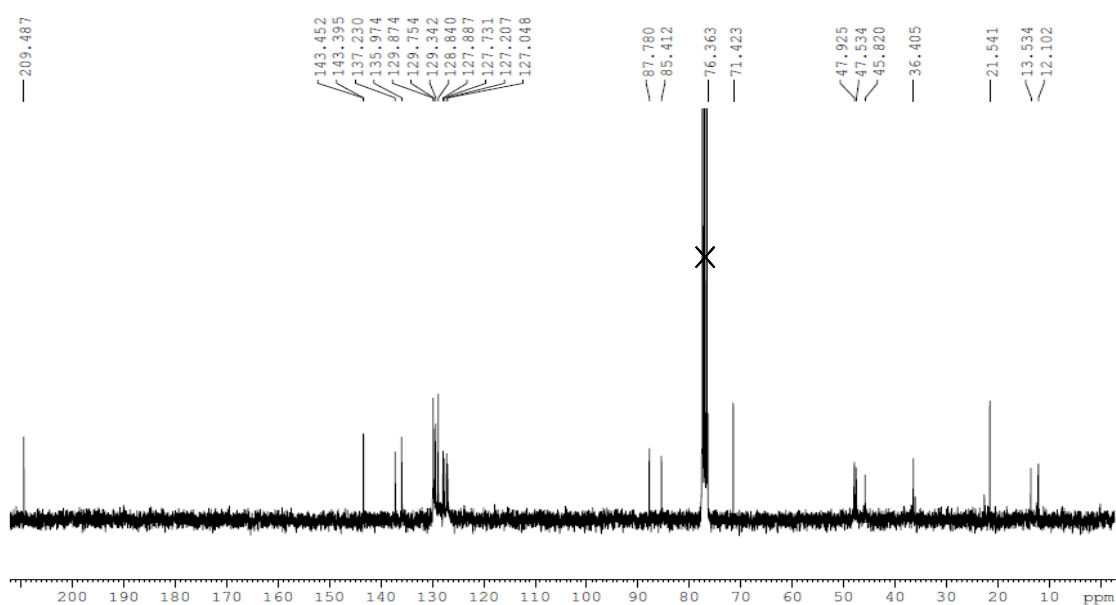


Figure 23. ^1H -decoupled ^{13}C NMR spectrum (75 MHz) of **1c** in CDCl_3 .

Spectra for compound 1d

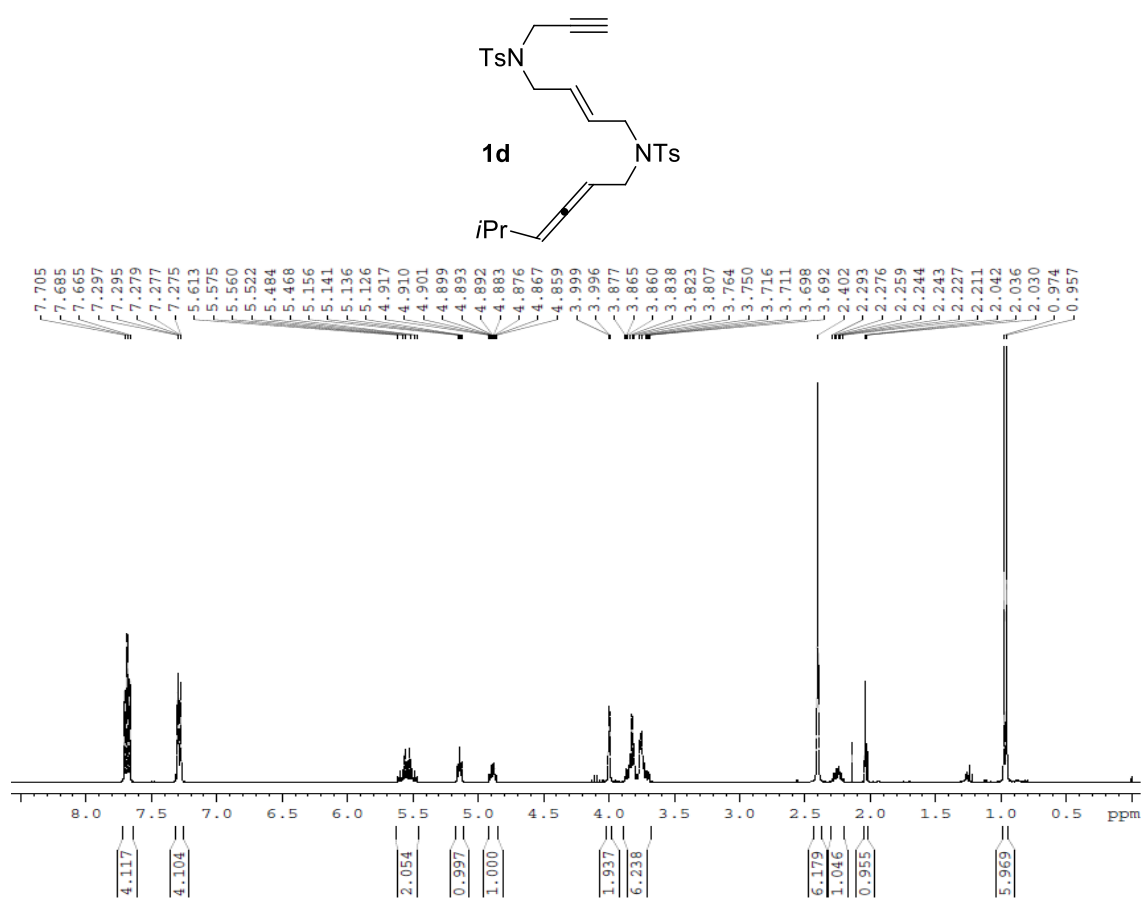


Figure 24. ^1H NMR spectrum (400 MHz) of **1d** in CDCl_3 .

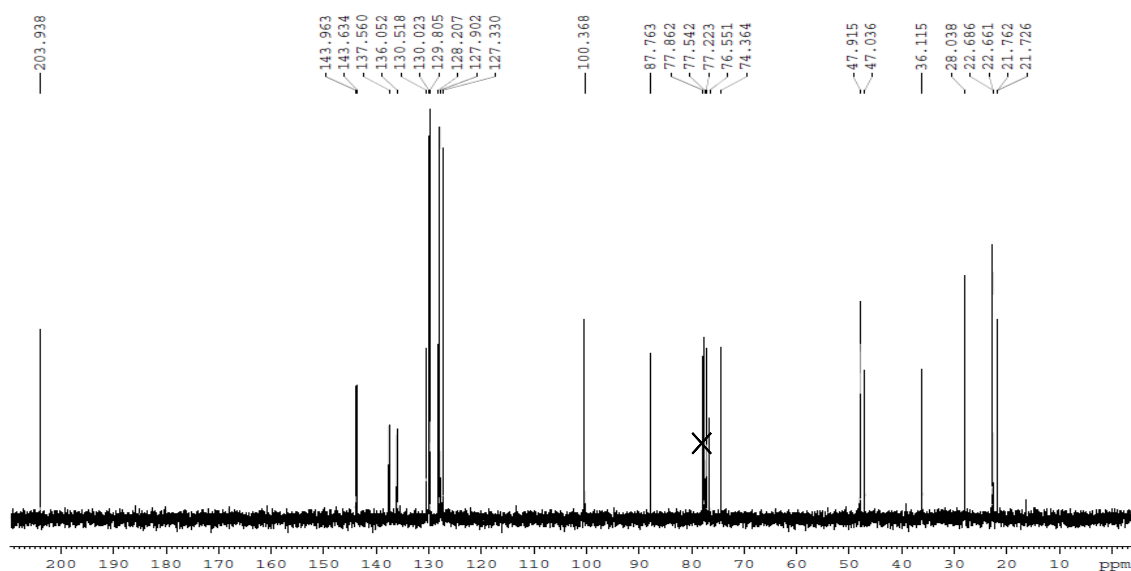


Figure 25. ^1H -decoupled ^{13}C NMR spectrum (100 MHz) of **1d** in CDCl_3 .

Spectra for compound 1e

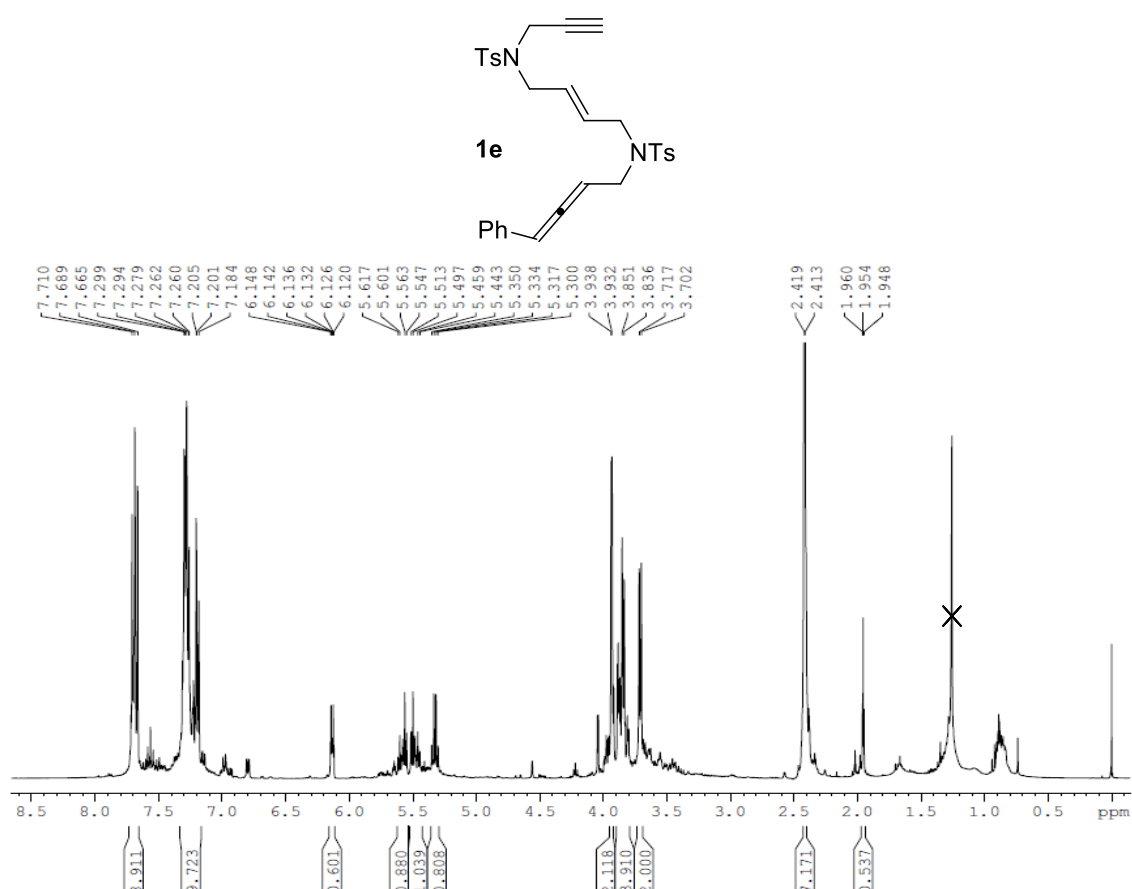


Figure 26. ^1H NMR spectrum (400 MHz) of **1e** in CDCl_3 .

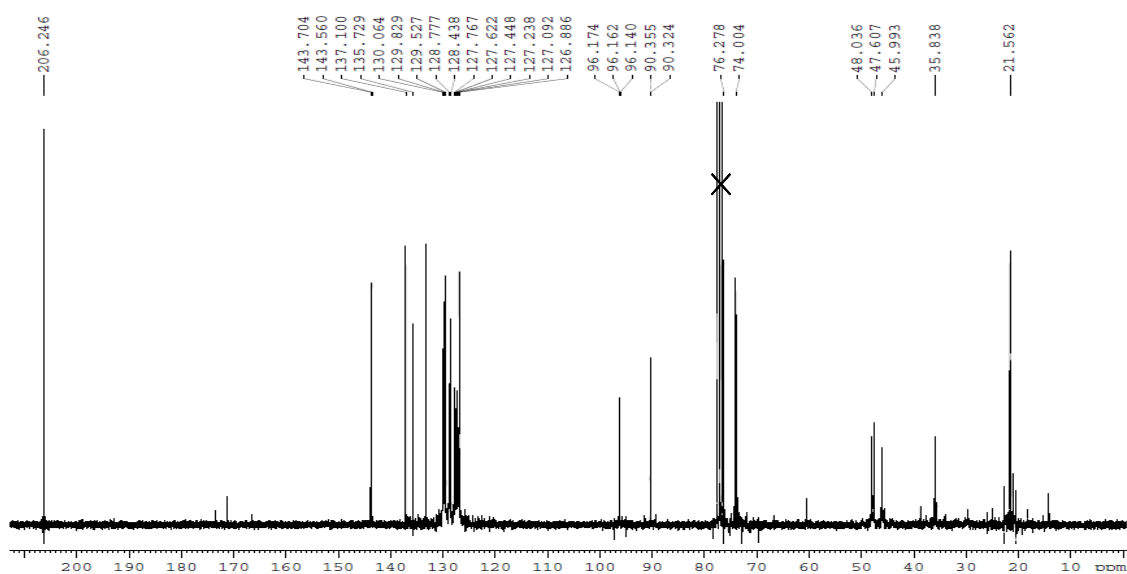
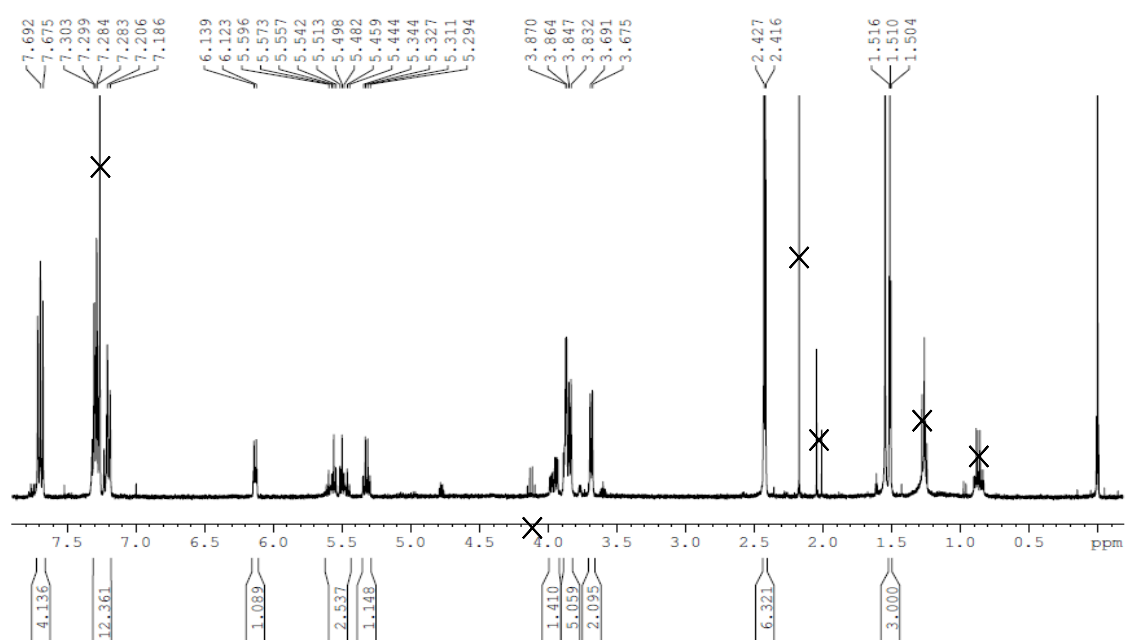
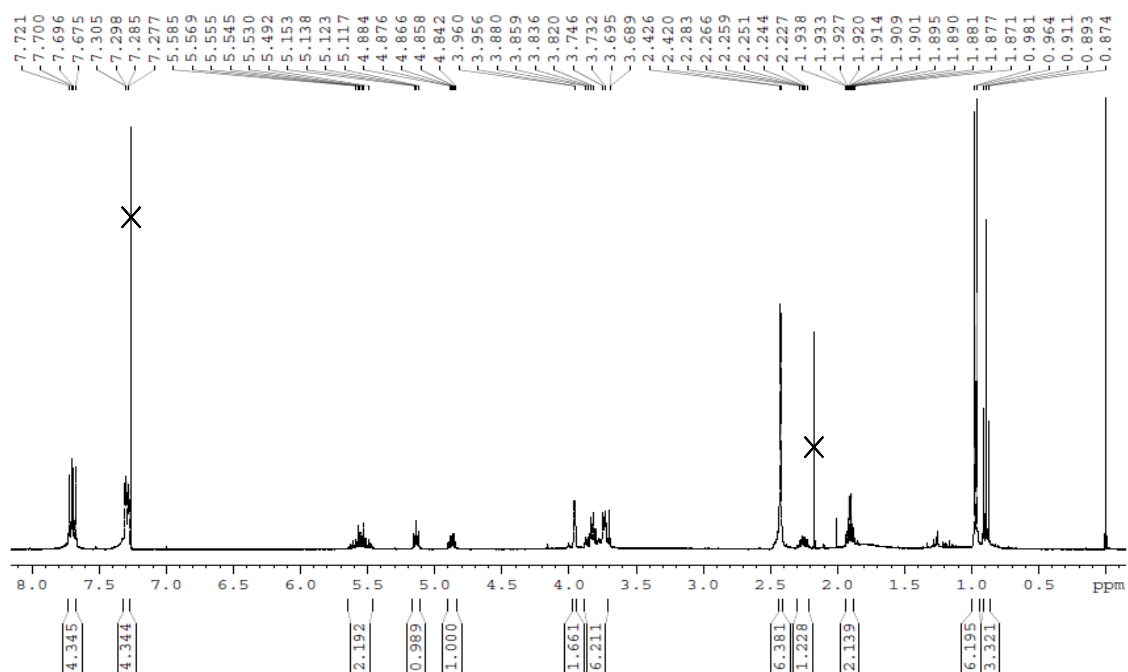


Figure 27. ^1H -decoupled ^{13}C NMR spectrum (75 MHz) of **1e** in CDCl_3 .



Chemical shift (ppm): 206.094, 143.403, 143.231, 137.007, 135.818, 133.189, 129.694, 129.170, 128.616, 127.730, 127.297, 127.055, 126.763, 81.648, 77.105, 71.263, 47.386, 47.442, 45.790, 36.251, 21.419, 21.394, 3.095.

Figure 29. ^1H -decoupled ^{13}C NMR spectrum (75 MHz) of **1f** in CDCl_3 .



13C NMR spectrum of 1,2-dichloroethane in CDCl₃. The x-axis represents chemical shift in ppm, ranging from 200 to 10. The spectrum shows several peaks, with the most prominent one at 77.0 ppm, which is the solvent triplet. Other peaks are labeled with their chemical shift values: 203.716, 143.379, 137.393, 136.054, 130.020, 129.745, 129.352, 128.447, 127.814, 127.137, 100.152, 87.755, 87.427, 71.477, 47.738, 47.533, 46.689, 36.379, 30.924, 27.837, 22.453, 22.404, 21.509, 13.512, and 12.090 ppm.

Figure 31. ^1H -decoupled ^{13}C NMR spectrum (100 MHz) of **1g** in CDCl_3 .

Spectra for compound 1h

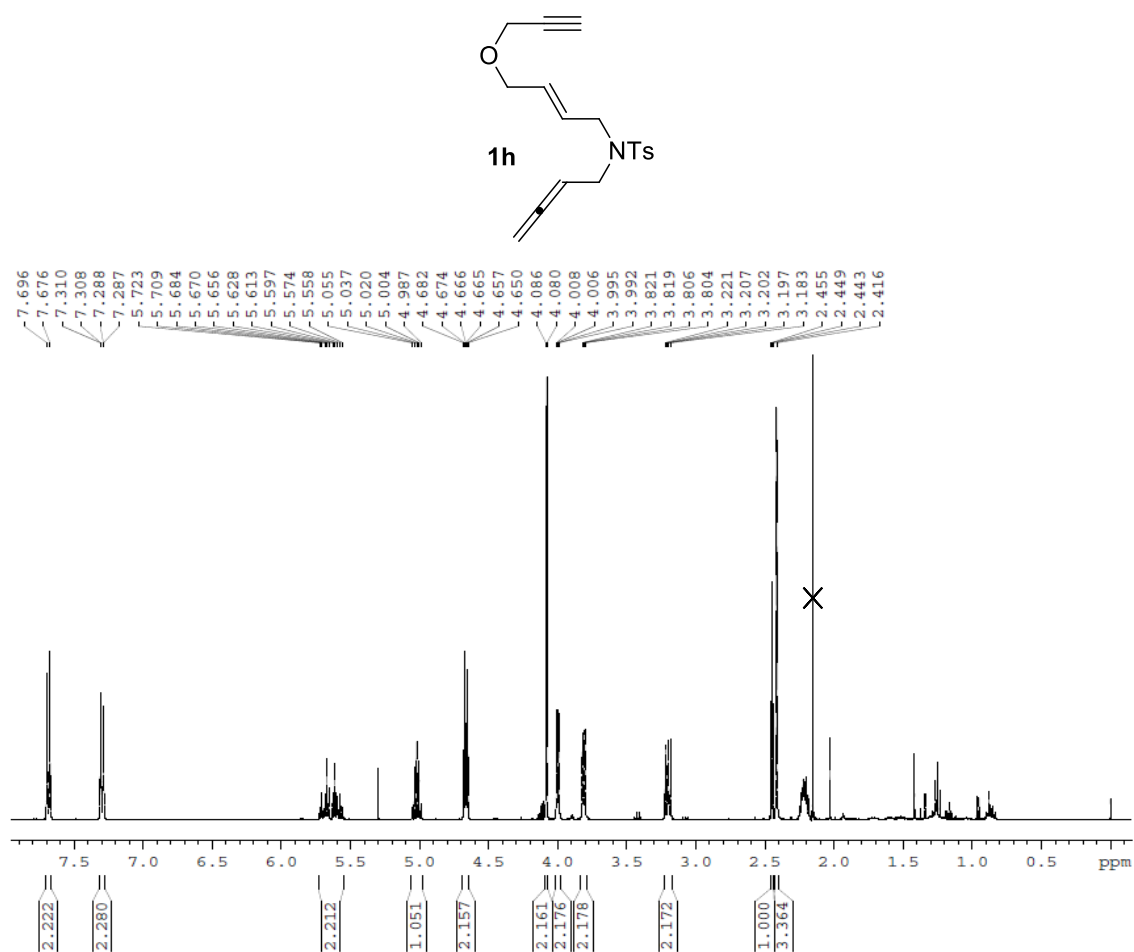


Figure 32. ^1H NMR spectrum (400 MHz) of **1h** in CDCl_3 .

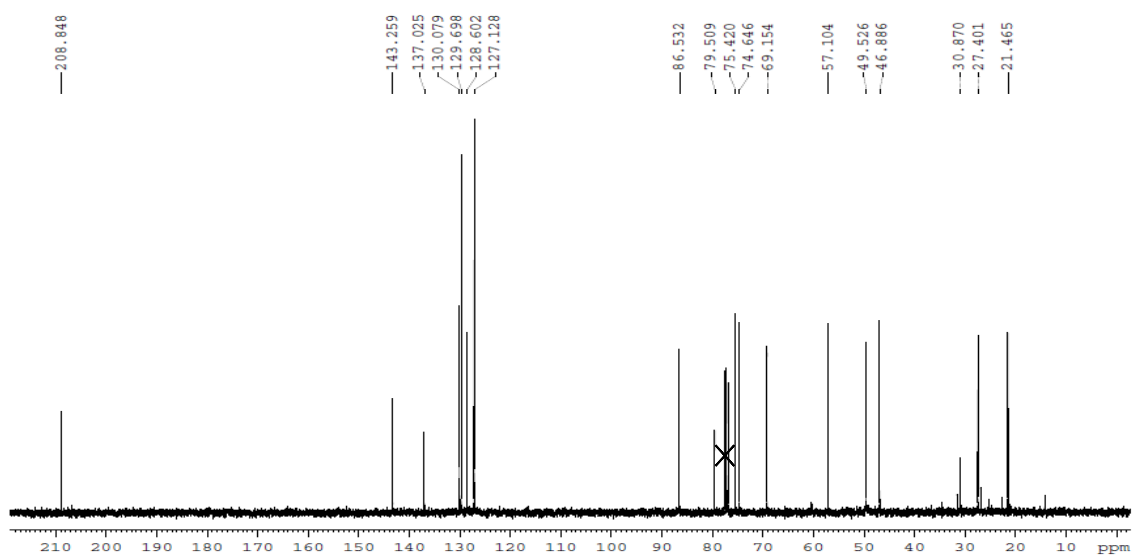


Figure 33. ^1H -decoupled ^{13}C NMR spectrum (100 MHz) of **1h** in CDCl_3 .

Spectra for the cycloisomerised products

Spectra for cycloadduct 5a

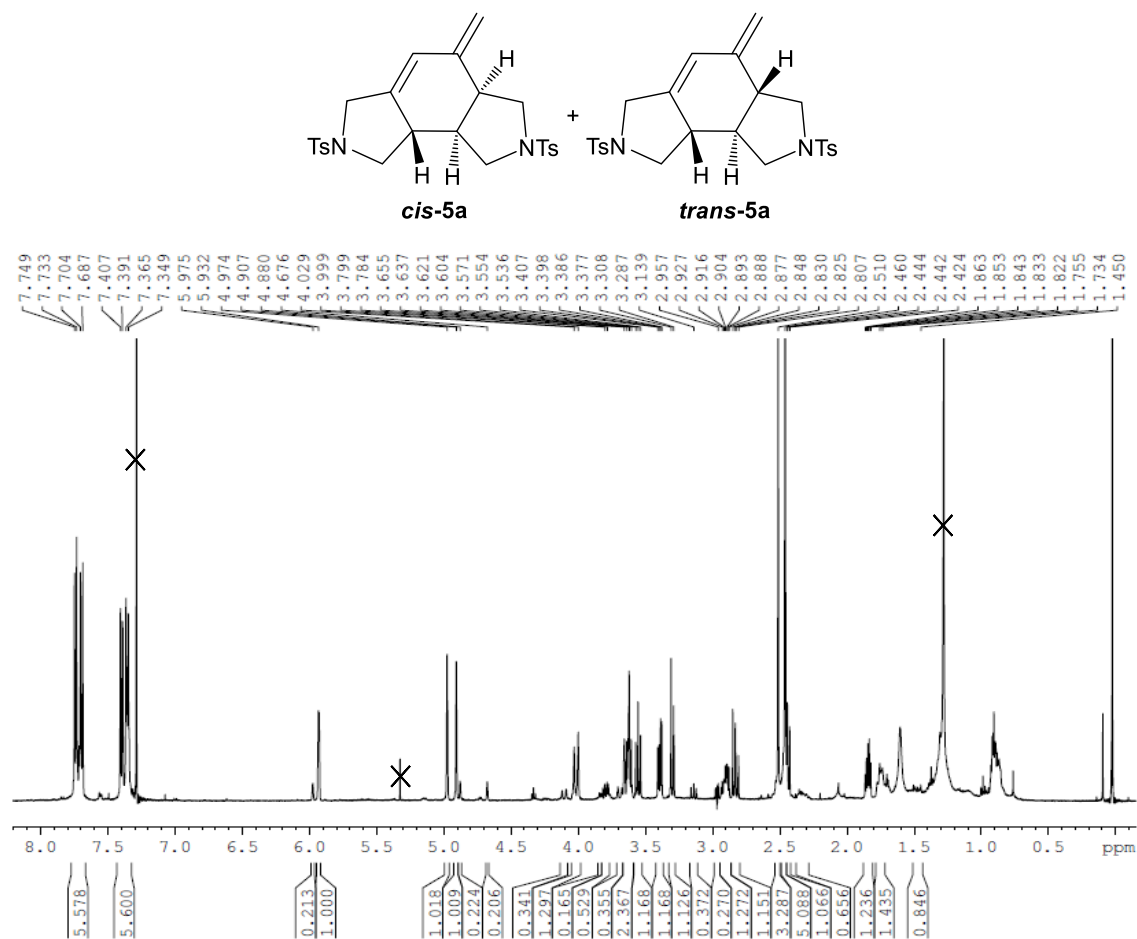


Figure 34. ¹H NMR spectrum (500 MHz) of *cis*-5a and *trans*-5a in CDCl₃.

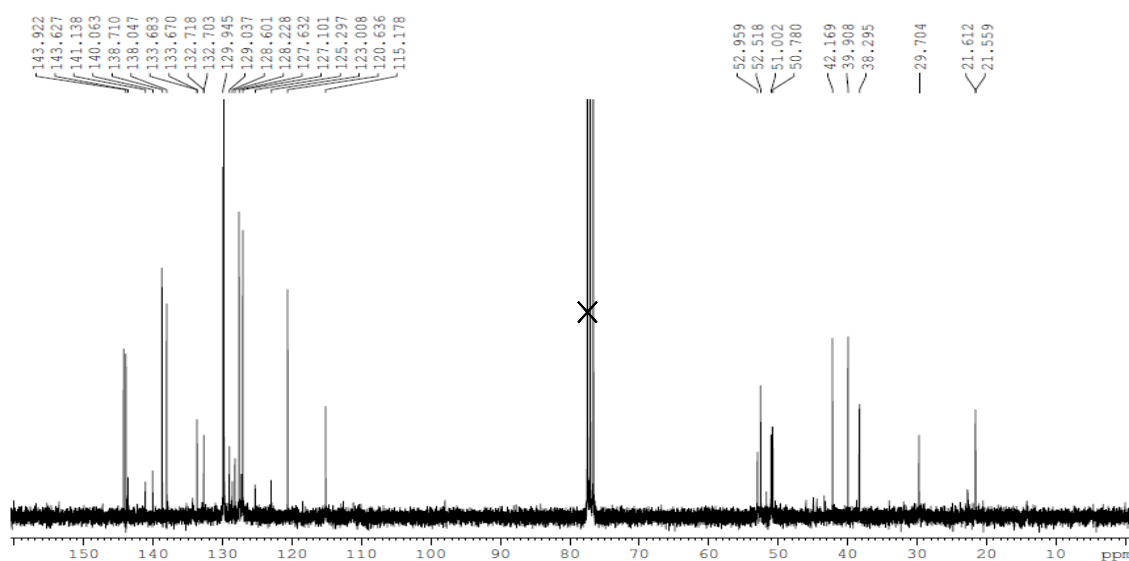


Figure 35. ¹H-decoupled ¹³C NMR spectrum (125 MHz) of *cis*-5a and *trans*-5a in CDCl₃.

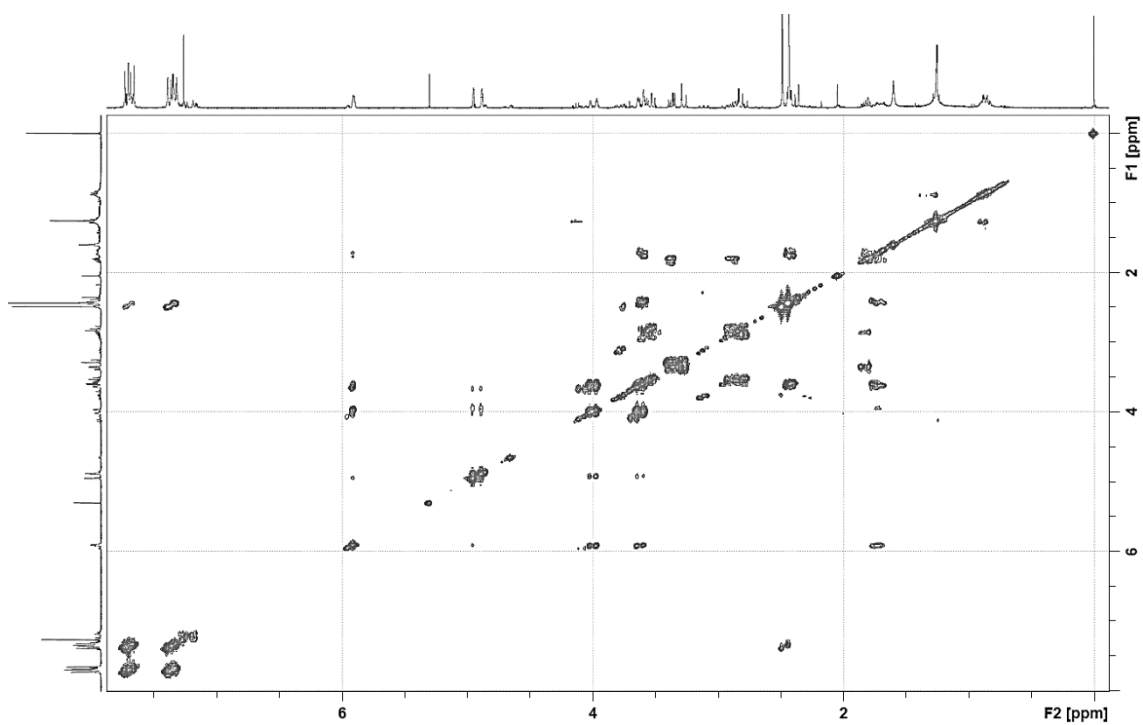


Figure 36. 2D ^1H - ^1H COSY correlation of *cis*-5a and *trans*-5a in CDCl_3 .

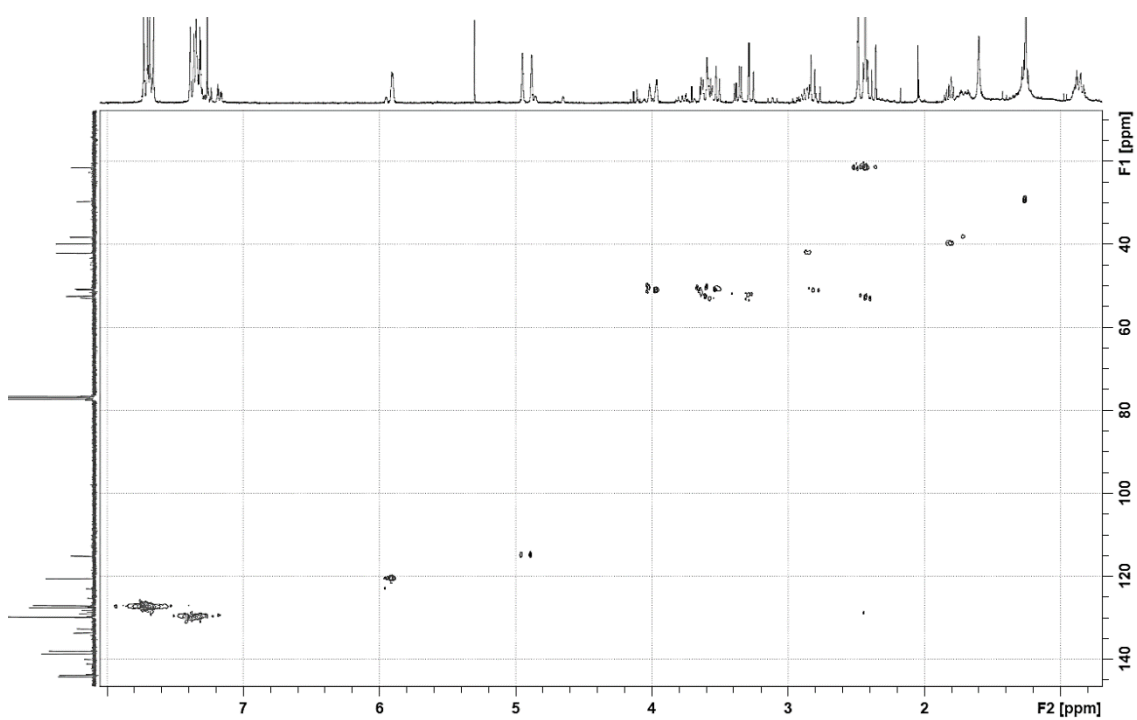


Figure 37. 2D ^1H - ^{13}C HSQC correlation of *cis*-5a and *trans*-5a in CDCl_3 .

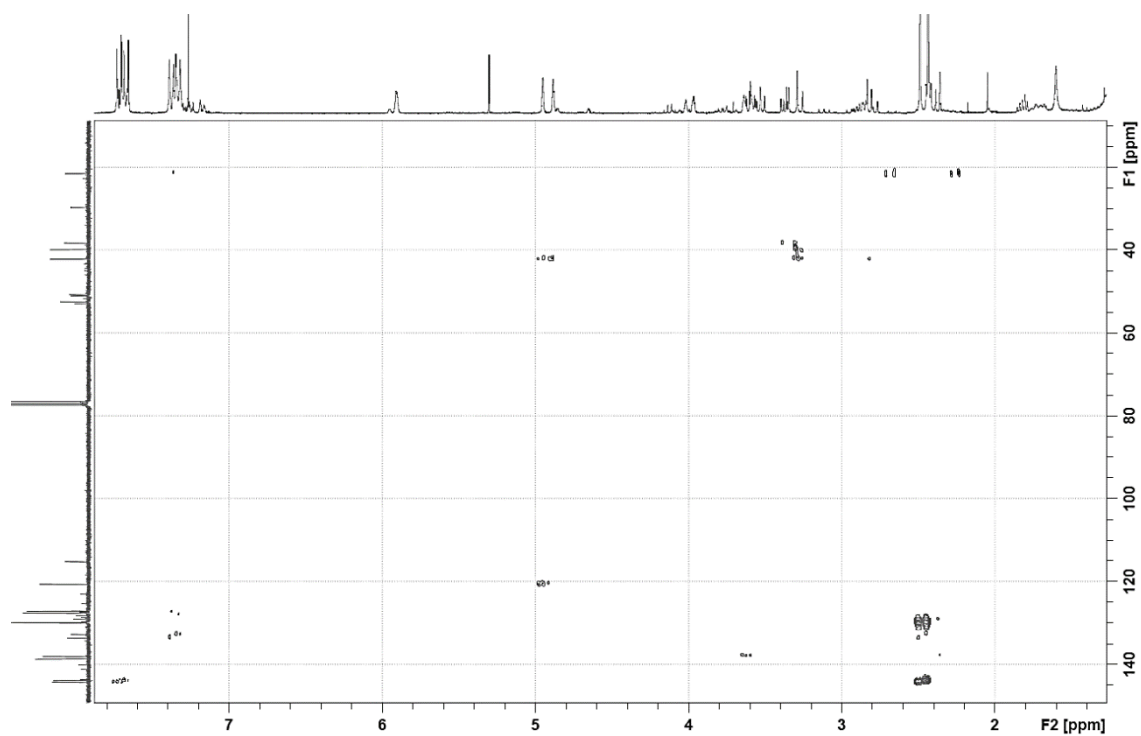


Figure 38. 2D ^1H - ^{13}C HMBC correlation of *cis*-5a and *trans*-5a in CDCl_3 .

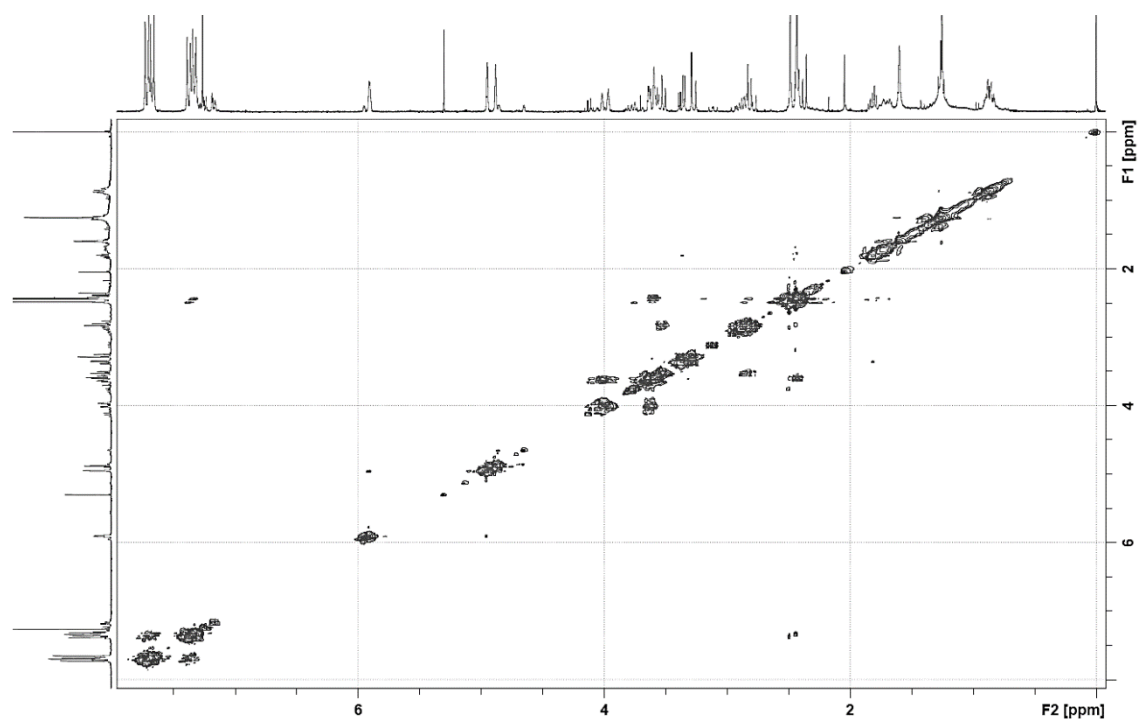


Figure 39. 2D ^1H - ^1H NOESY correlation of *cis*-5a and *trans*-5a in CDCl_3 .

Spectra for cycloadduct **5b**

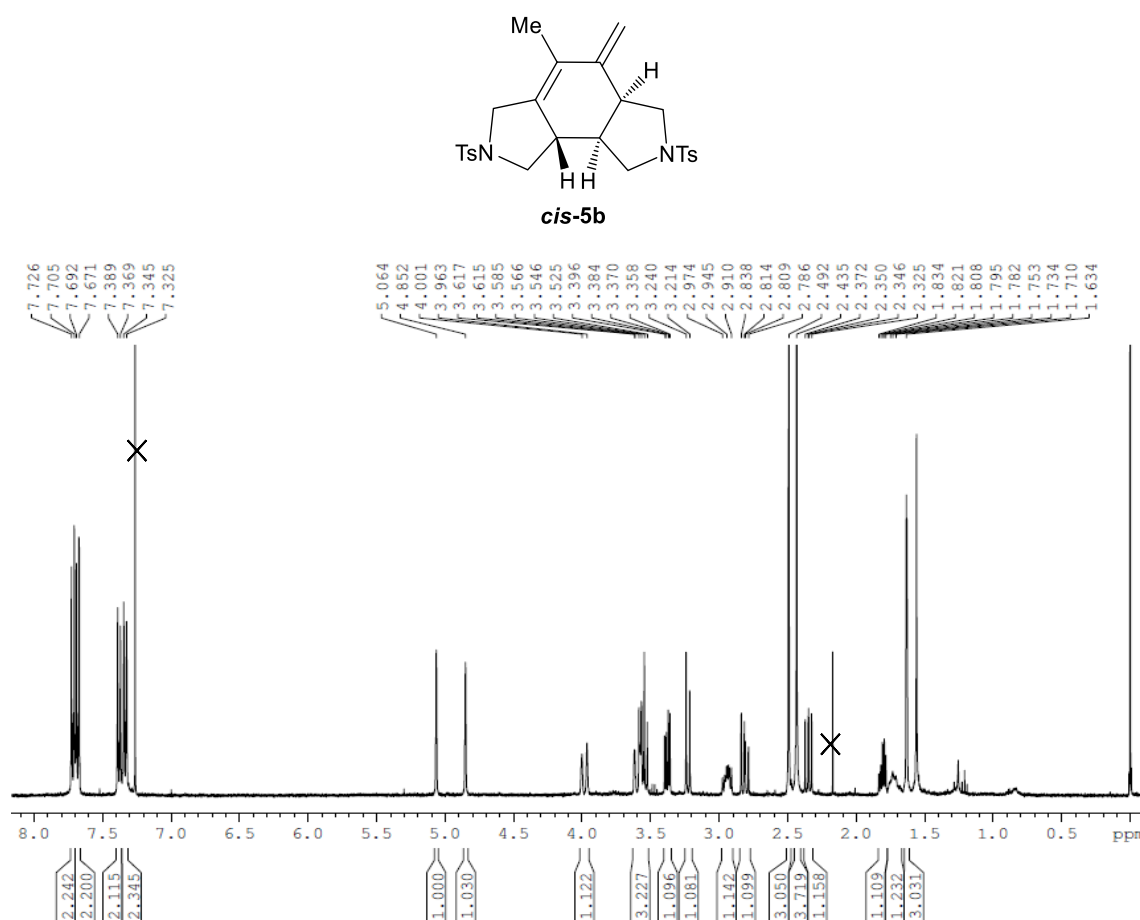


Figure 40. ^1H NMR spectrum (400 MHz) of **cis-5b** in CDCl_3 .

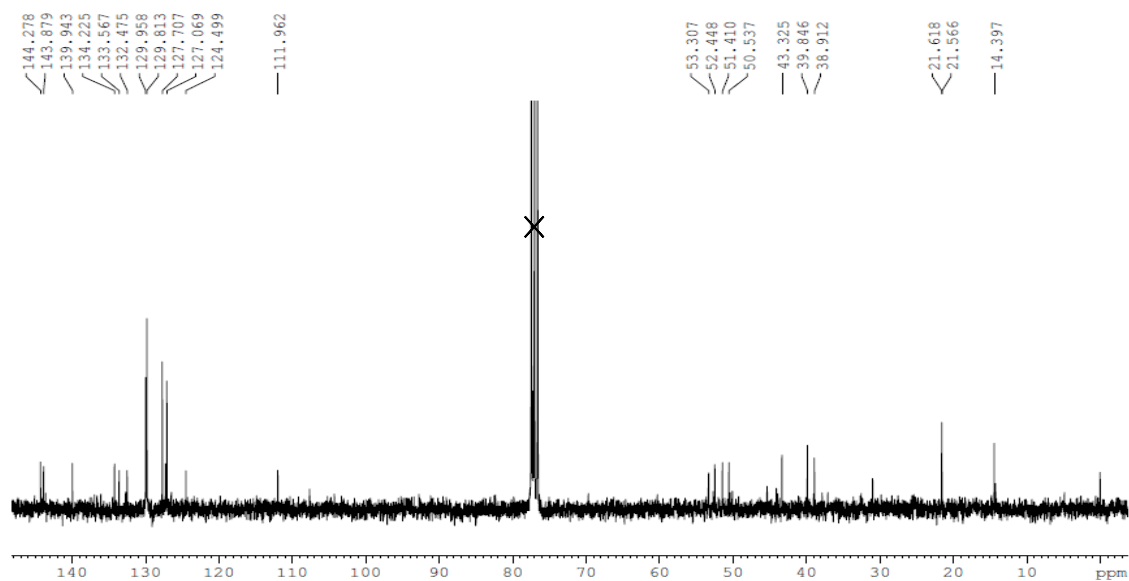


Figure 41. ^1H -decoupled ^{13}C NMR spectrum (100 MHz) of **cis-5b** in CDCl_3 .

Spectra for cycloadduct **5c**

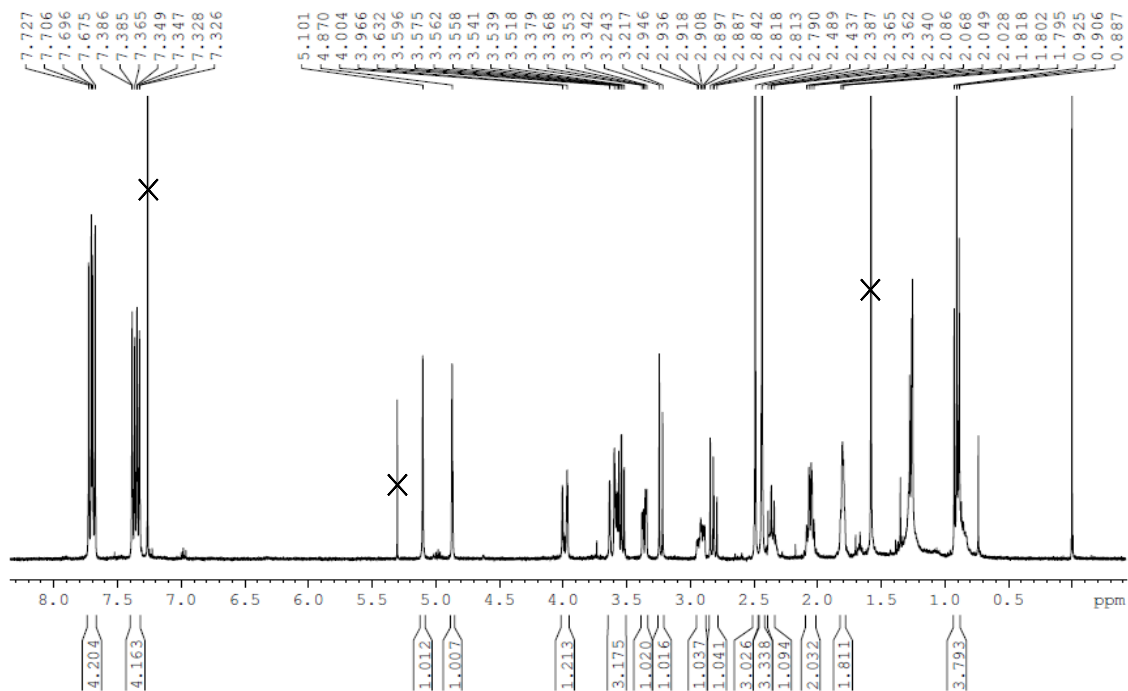
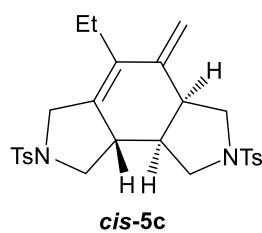


Figure 42. ^1H NMR spectrum (400 MHz) of **cis-5c** in CDCl_3 .

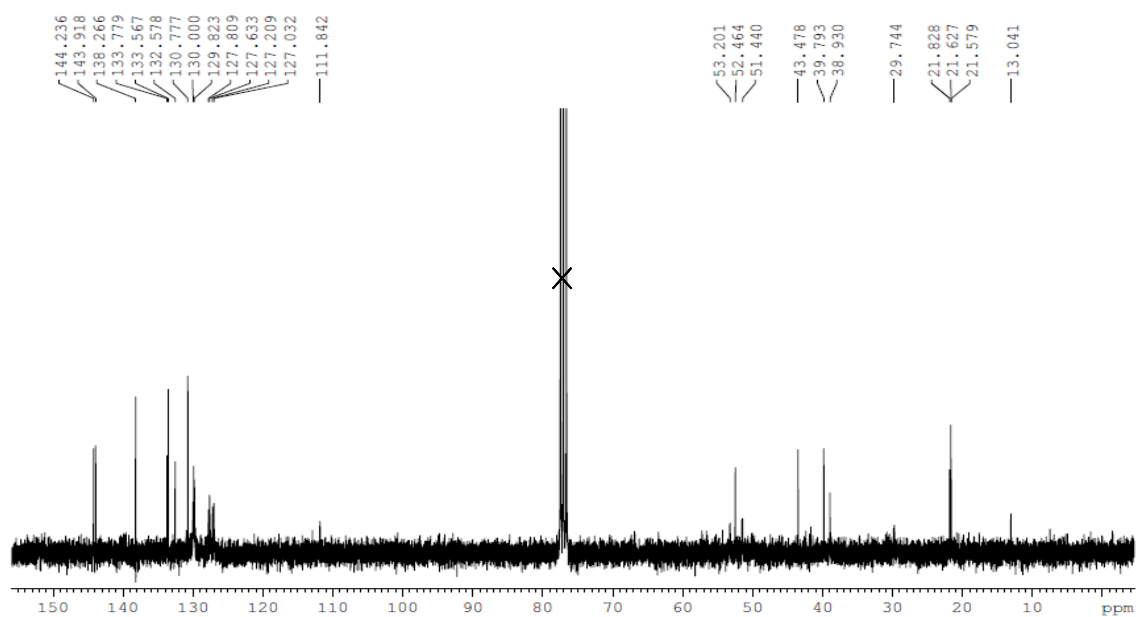


Figure 43. ^1H -decoupled ^{13}C NMR spectrum (100 MHz) of **cis-5c** in CDCl_3 .

Spectra for cycloadduct 5d

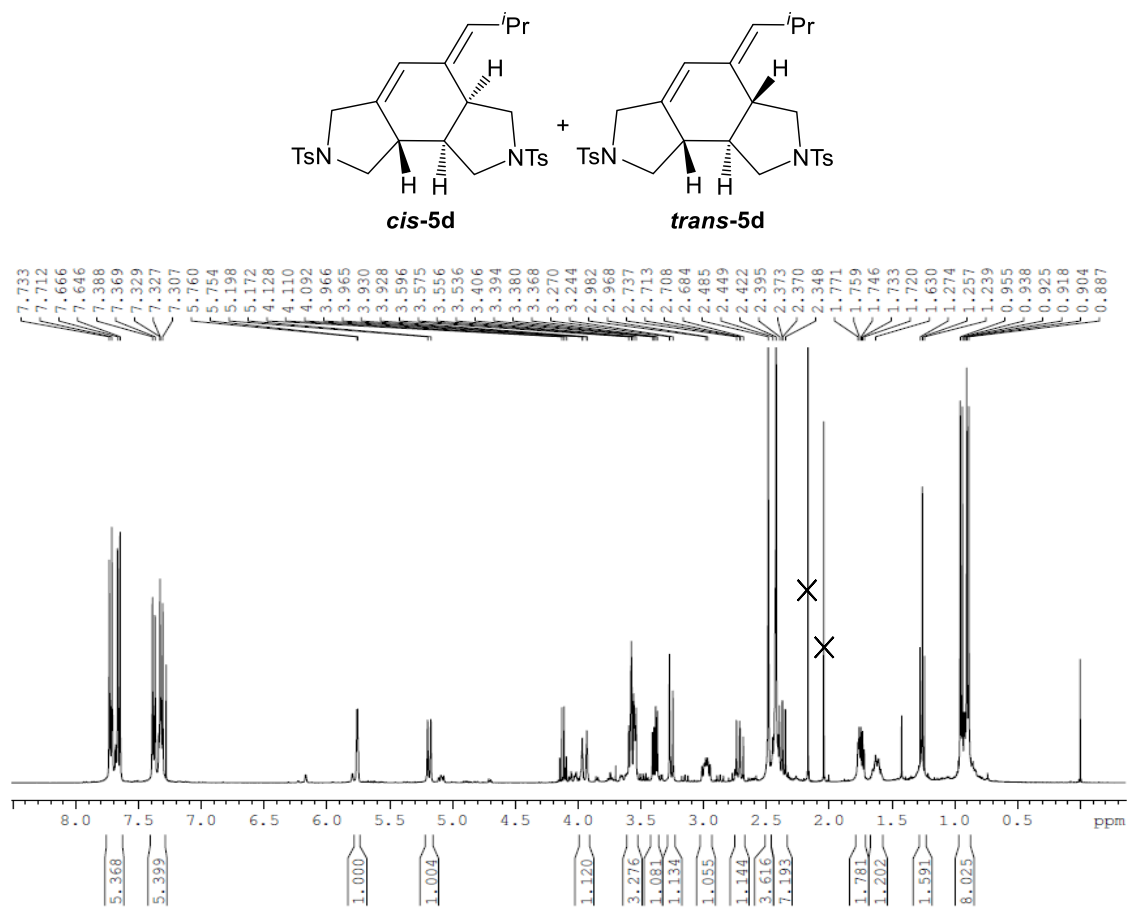


Figure 44. ^1H NMR spectrum (400 MHz) of *cis*-5d and *trans*-5d (*cis:trans* = 9:1) in CDCl_3 .

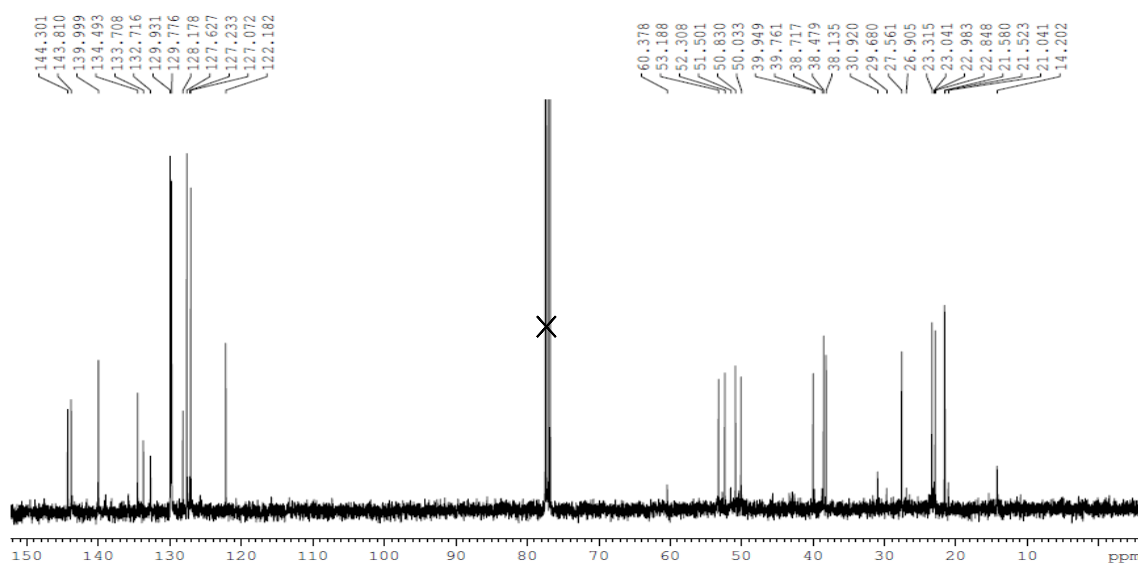


Figure 45. ^1H -decoupled ^{13}C NMR spectrum (100 MHz) of *cis*-5d and *trans*-5d (*cis:trans* = 9:1) in CDCl_3 .

Spectra for cycloadduct 5e

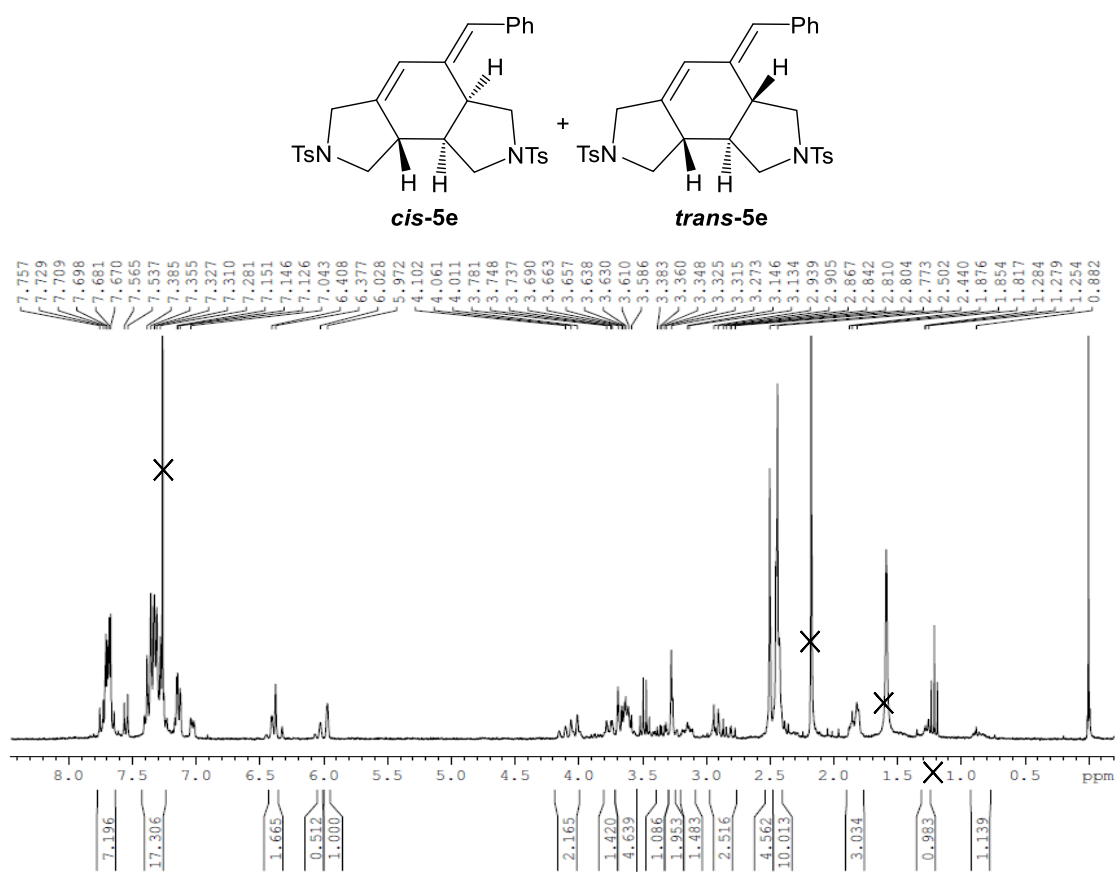


Figure 46. ¹H NMR spectrum (400 MHz) of *cis*-5e and *trans*-5e (*cis:trans* = 7:3) in CDCl₃.

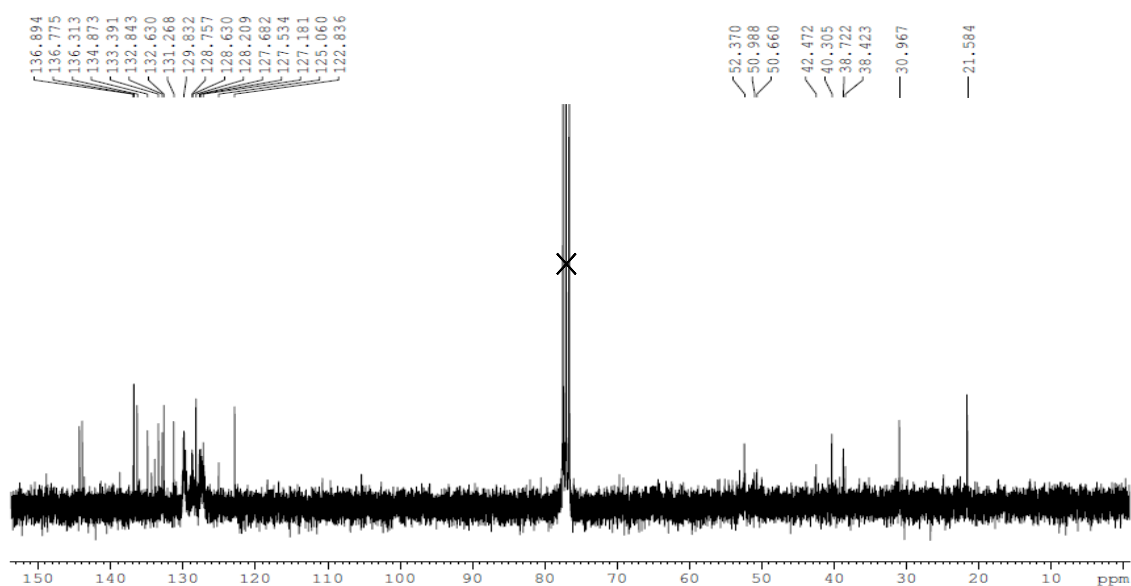


Figure 47. ¹H-decoupled ¹³C NMR spectrum (100 MHz) of *cis*-5e and *trans*-5e (*cis:trans* = 7:3) in CDCl₃.

Spectra for cycloadduct **5g**

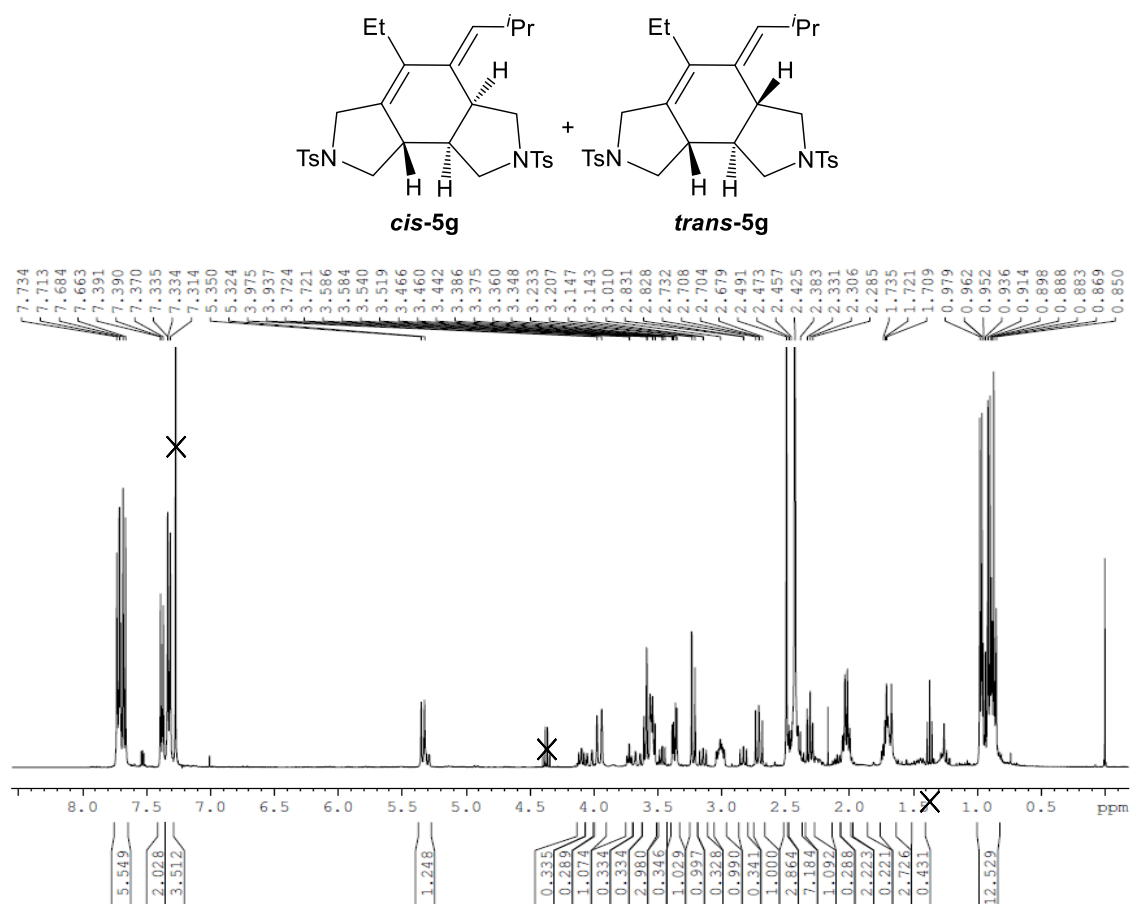


Figure 48. ¹H NMR spectrum (400 MHz) of **cis-5g** and **trans-5g** (*cis:trans* = 6:4) in CDCl₃.

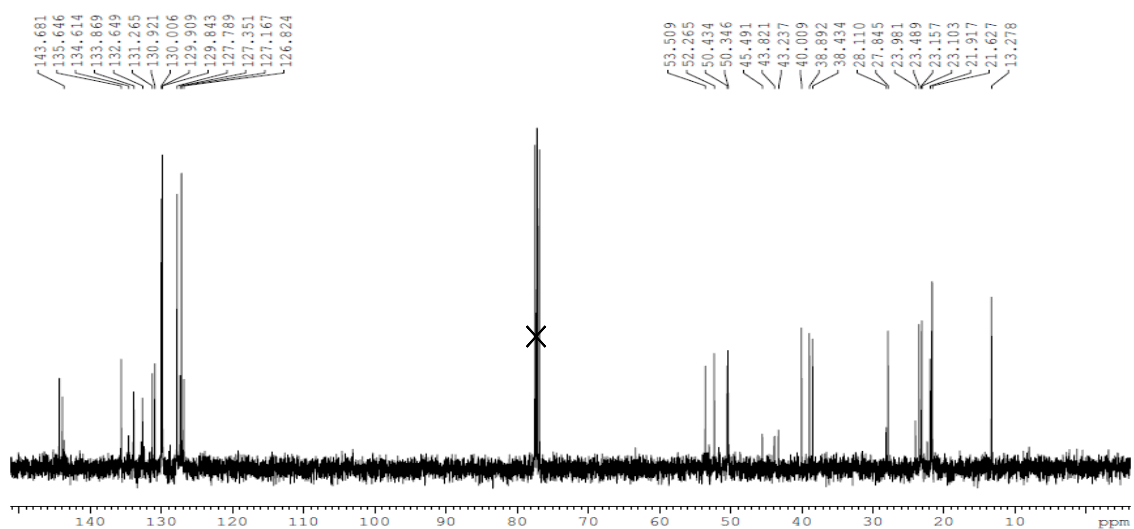


Figure 49. ¹H-decoupled ¹³C NMR spectrum (100 MHz) of **cis-5g** and **trans-5g** (*cis:trans* = 6:4) in CDCl₃.

Spectra for cycloadduct 5h

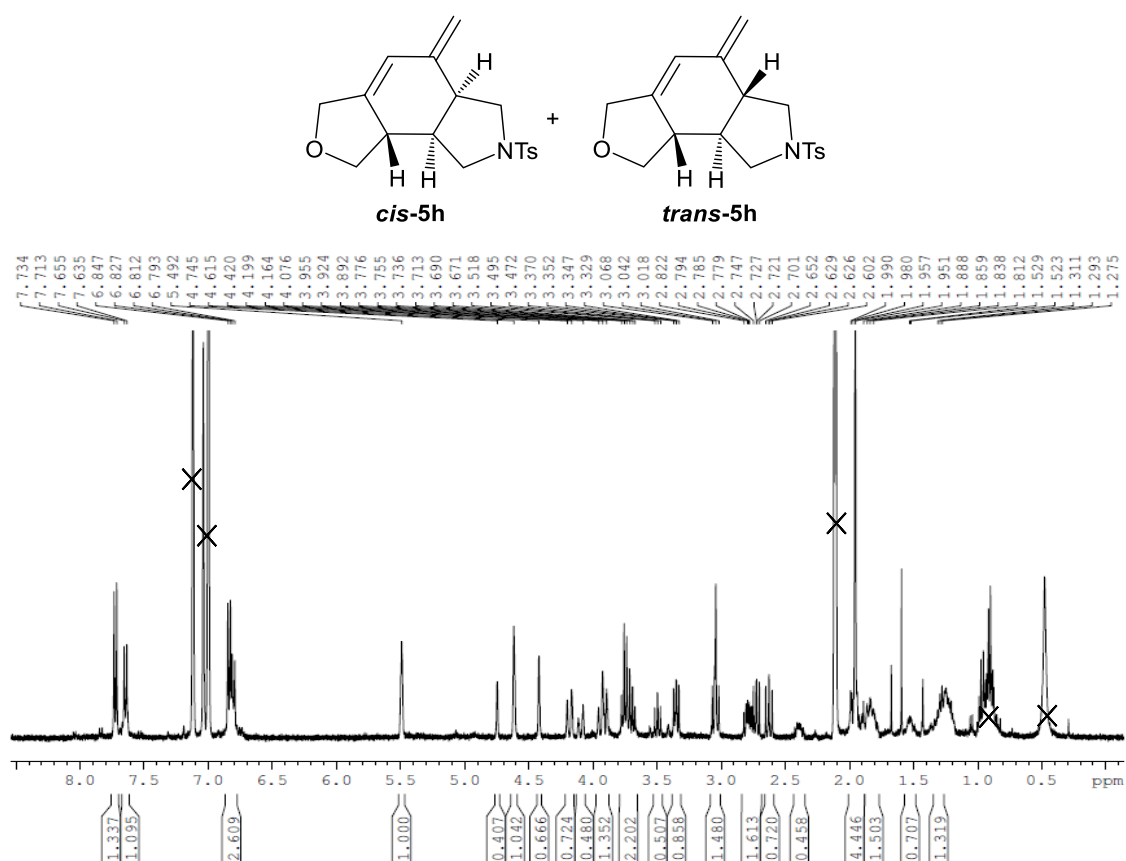


Figure 50. ¹H NMR spectrum (400 MHz) of *cis*-5h and *trans*-5h (*cis:trans* = 3:7) in toluene-*D*₈.

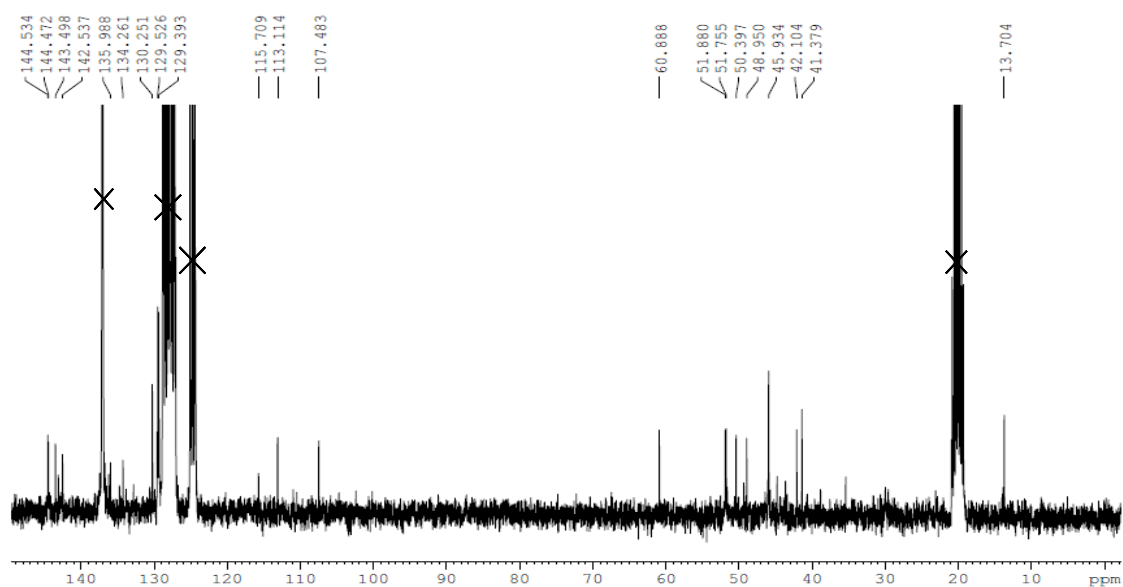


Figure 51. ¹H-decoupled ¹³C NMR spectrum (100 MHz) of *cis*-5h and *trans*-5h (*cis:trans* = 3:7) in toluene-*D*₈.

Spectra for the detected catalytic intermediates

D0a and D0b characterization

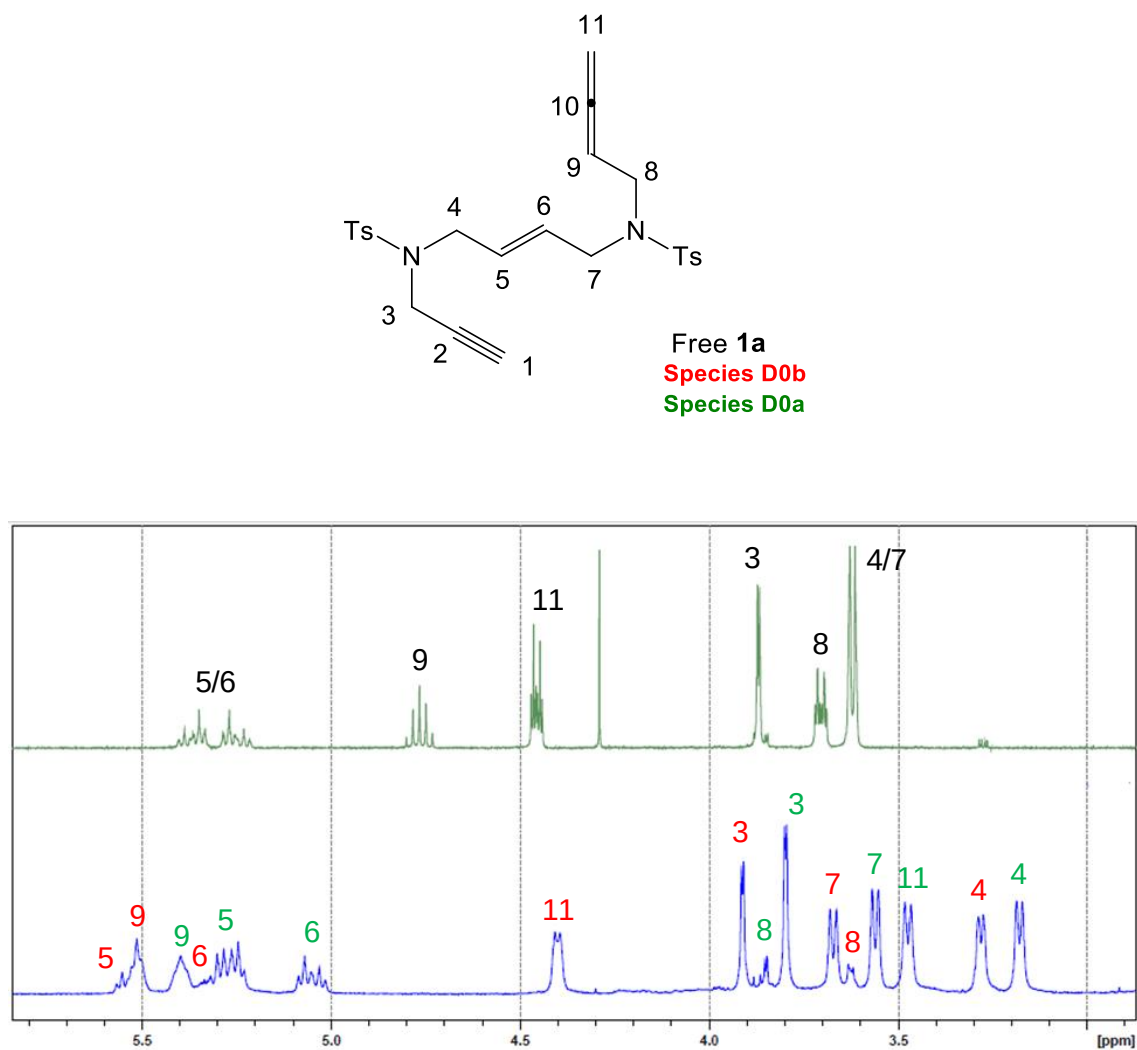


Figure 52. ¹H NMR (400 MHz, toluene-*d*₈, 298 K) proton assignment of free **1a** (top) and species **D0a** and **D0b** (bottom).

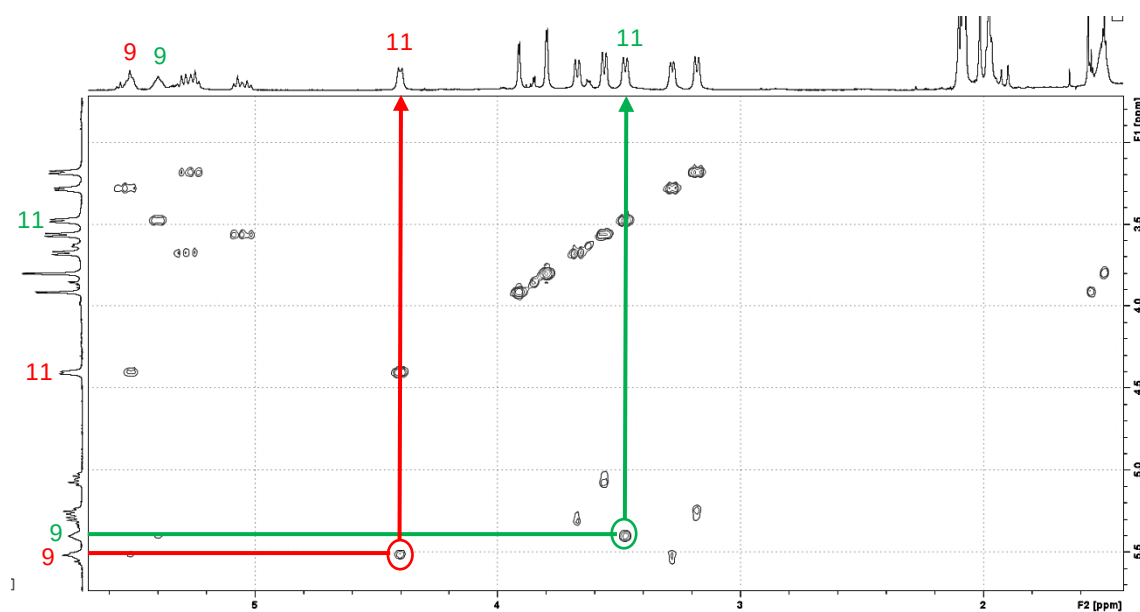


Figure 53. ^1H - ^1H COSY of species **D0a** (green) and **D0b** (red) with selected assignments.

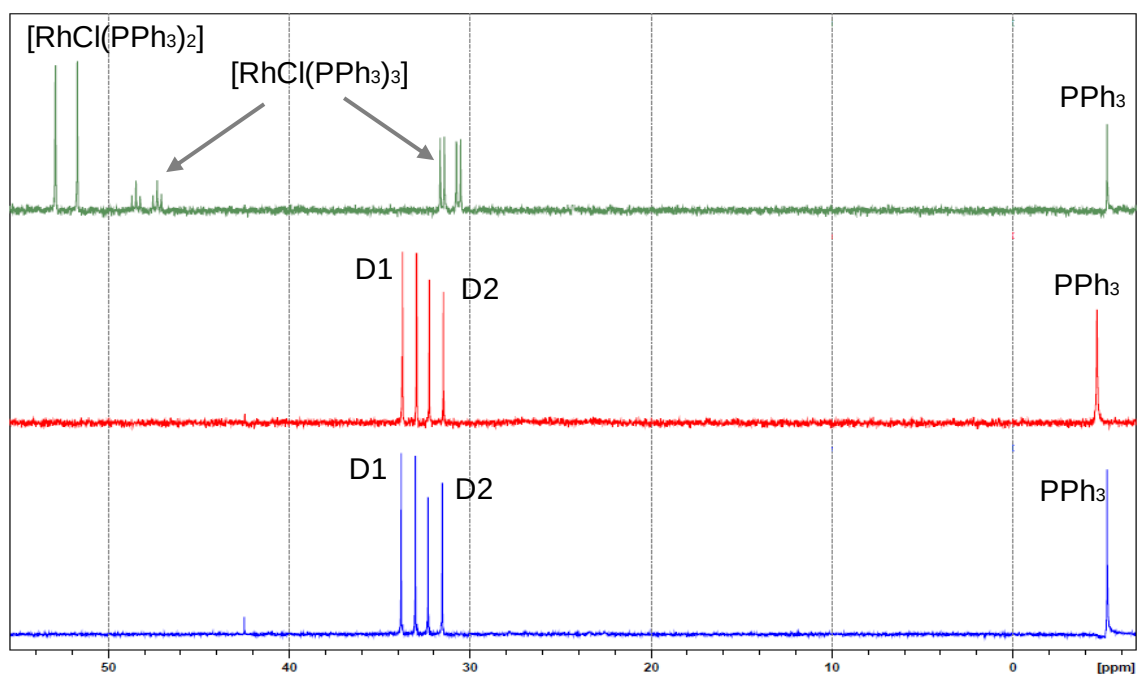


Figure 54. ^{31}P NMR (161.92 MHz, Toluene- d_8 , 298 K) of $[\text{RhCl}(\text{PPh}_3)_3]$ (top), **3a** and $[\text{RhCl}(\text{PPh}_3)_3]$ (50 mol%) (middle) and **3a** and $[\text{RhCl}(\text{PPh}_3)_3]$ (100 mol%) (bottom).

The same species were observed at both catalyst loadings, and the spectra are simpler using a stoichiometric amount of catalyst. The two species formed were characterized by a series of 2D NMR techniques on samples prepared with a stoichiometric amount of catalyst.

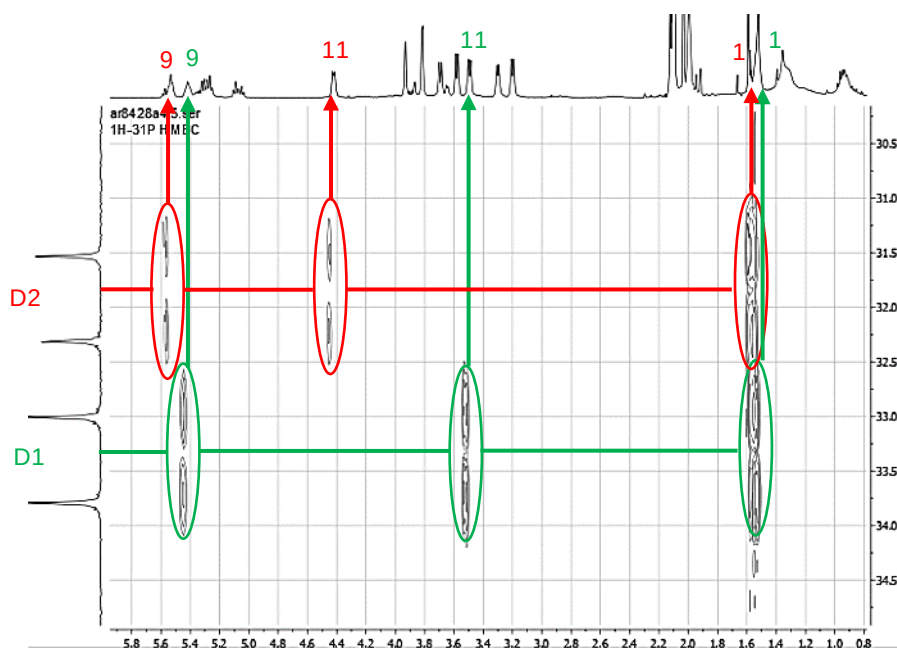


Figure 55. HMBC ^1H - ^{31}P (298K) of species **D0a** (green) and **D0b** (red).

The ^1H - ^{31}P HMBC clearly shows that the rhodium is coordinated to the allene and the triple bond in the two species.

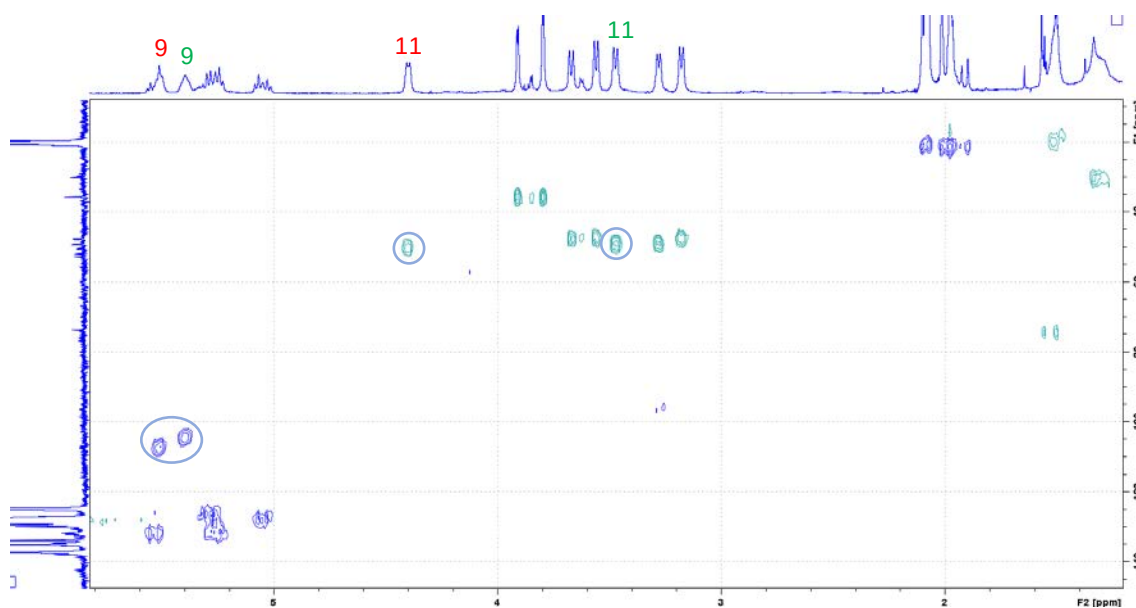


Figure 56. ^1H - ^{13}C HSQC a 298K

A remarkable shift change is appreciated between the allenic protons H₉ and H₁₁ of **D0a** and **D0b** species, while the change appears to be less important for C₉ and C₁₁ (Table 1). When compared to the signals of free **3a**, such differences corroborate the coordination of the allene motif to the rhodium center.

Table 1. Allenic signals comparison

	H ₉	H ₁₁	C ₉	C ₁₁
Free 1a	4.8	4.5	85	76
Species D0b	5.5	4.4	108	50
Species D0a	5.4	3.5	104	50

Last, ¹H-¹H NOESY showed exchange cross peaks between the identified signals for **D0a** and **D0b**, thus indicating the presence of a dynamic equilibrium between them.

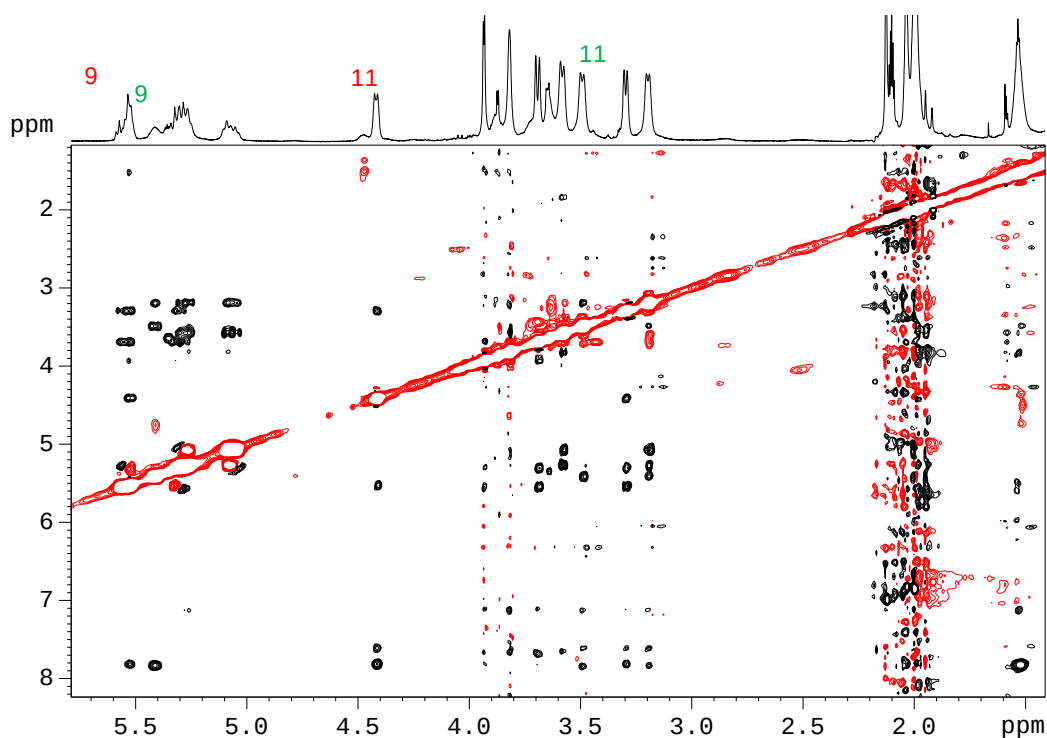


Figure 57. ¹H-¹H NOESY of species **D0a** and **D0b**

ESI-MS study

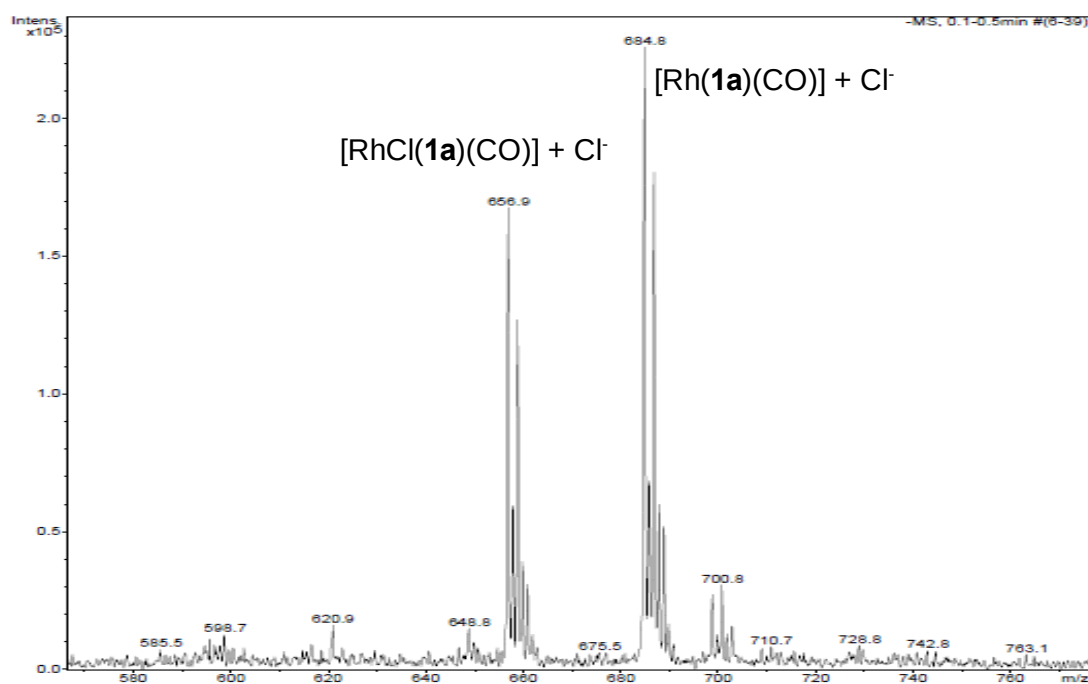


Figure 58. ESI-MS(-) of substrate **1a** + $[\text{RhCl}(\text{CO})_2]_2 + \text{LiCl}$

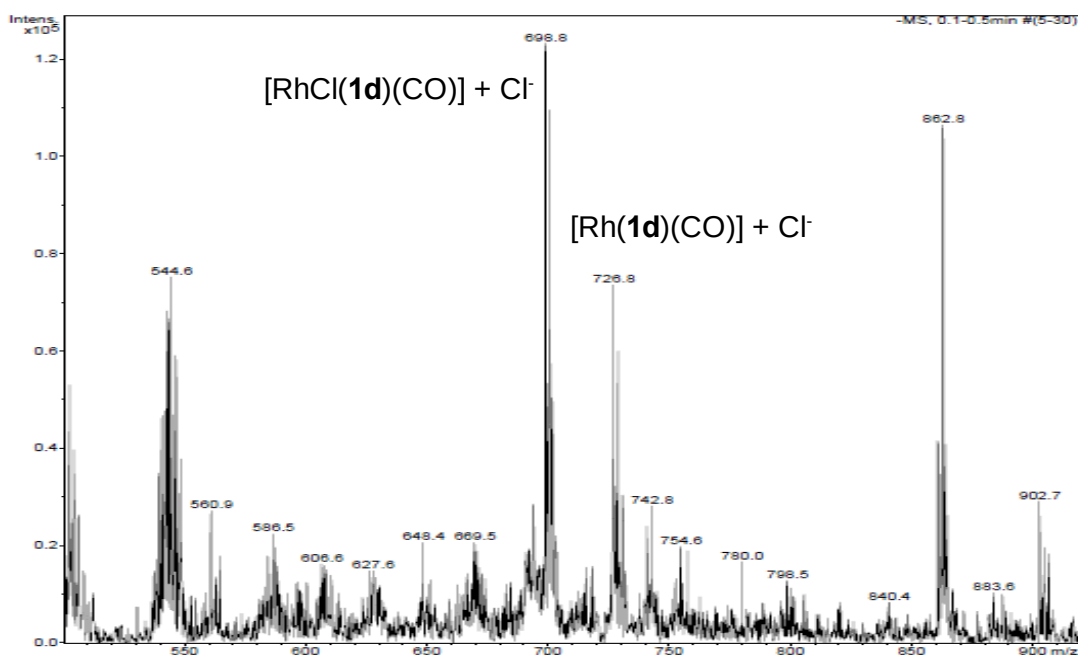
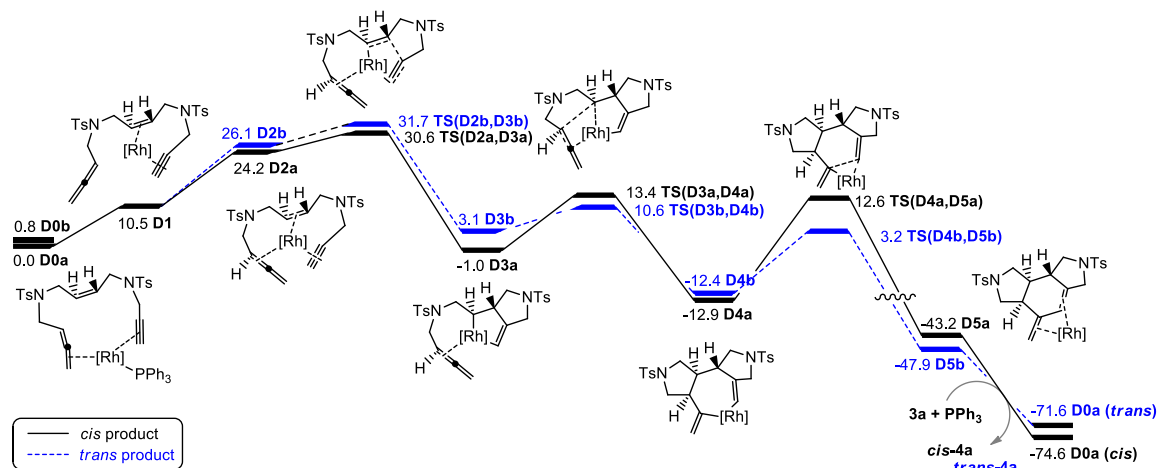


Figure 59. ESI-MS(-) of substrate **1d** + $[\text{RhCl}(\text{CO})_2]_2 + \text{LiCl}$

Annex 3

XYZ coordinates of the catalytic intermediates for the [RhCl(PPh₃)₃]-catalysed [2+2+2] cycloaddition reaction of linear allene-ene-yne substrates



[RhCl(PPh₃)₃]

G = -3679.145751

45	0.024948000	0.467090000	-0.454322000
15	-2.267864000	0.928071000	-0.091677000
15	0.015458000	-1.786246000	-0.104033000
15	2.294253000	0.902204000	-0.022298000
17	0.080727000	2.484776000	-1.818833000
6	-2.388964000	2.664267000	0.565496000
6	-3.548006000	3.439524000	0.412973000
6	-1.302699000	3.193564000	1.280806000
6	-3.617059000	4.721944000	0.966465000
1	-4.400416000	3.052742000	-0.147268000
6	-1.375187000	4.472012000	1.838407000
1	-0.388319000	2.608039000	1.386818000
6	-2.532933000	5.240673000	1.681387000
1	-4.522481000	5.318838000	0.832632000
1	-0.512489000	4.867544000	2.378243000
1	-2.587746000	6.245220000	2.107843000
6	-3.491624000	0.911293000	-1.493627000
6	-4.864676000	0.676774000	-1.308945000
6	-3.010012000	1.135762000	-2.794547000
6	-5.734136000	0.647484000	-2.403982000
1	-5.264193000	0.506452000	-0.308275000
6	-3.881687000	1.110724000	-3.885951000
1	-1.948305000	1.337650000	-2.944339000
6	-5.244964000	0.859458000	-3.696247000
1	-6.798021000	0.457332000	-2.243115000
1	-3.490405000	1.286798000	-4.890742000
1	-5.924096000	0.832679000	-4.551730000
6	-3.153374000	-0.017456000	1.243091000
6	-3.179718000	0.460204000	2.565304000

6	-3.712304000	-1.279010000	0.972946000
6	-3.731332000	-0.313281000	3.590971000
1	-2.762340000	1.439733000	2.801937000
6	-4.260642000	-2.050373000	1.999785000
1	-3.730932000	-1.662380000	-0.045633000
6	-4.267601000	-1.574327000	3.314190000
1	-3.741124000	0.075518000	4.612078000
1	-4.679785000	-3.031519000	1.765495000
1	-4.691341000	-2.181064000	4.117551000
6	-1.418632000	-2.611284000	-0.972176000
6	-2.029658000	-3.785401000	-0.504103000
6	-1.929448000	-1.999926000	-2.129177000
6	-3.139175000	-4.318578000	-1.166593000
1	-1.667731000	-4.273254000	0.400138000
6	-3.041145000	-2.529482000	-2.789353000
1	-1.470558000	-1.081391000	-2.497016000
6	-3.654184000	-3.688759000	-2.304867000
1	-3.612698000	-5.224141000	-0.779844000
1	-3.438636000	-2.015279000	-3.666762000
1	-4.533047000	-4.097309000	-2.808846000
6	-0.022251000	-2.609953000	1.561554000
6	0.436817000	-3.917580000	1.795504000
6	-0.572349000	-1.884873000	2.627799000
6	0.361031000	-4.475875000	3.074831000
1	0.859727000	-4.504878000	0.979009000
6	-0.660403000	-2.446145000	3.903553000
1	-0.927401000	-0.869547000	2.454034000
6	-0.186565000	-3.741655000	4.132535000
1	0.730202000	-5.490080000	3.244371000
1	-1.101140000	-1.865817000	4.716735000
1	-0.245127000	-4.180348000	5.131396000
6	1.454002000	-2.603232000	-0.970717000
6	2.646456000	-2.911836000	-0.295480000
6	1.395893000	-2.814955000	-2.360318000
6	3.753125000	-3.405502000	-0.992895000
1	2.722472000	-2.769394000	0.780699000
6	2.501930000	-3.309758000	-3.054276000
1	0.484307000	-2.587940000	-2.913614000
6	3.688380000	-3.602455000	-2.373991000
1	4.671682000	-3.627472000	-0.445302000
1	2.435131000	-3.463255000	-4.133851000
1	4.555813000	-3.982546000	-2.918151000
6	3.187151000	-0.139103000	1.231057000
6	4.514492000	-0.572806000	1.089641000
6	2.455708000	-0.559502000	2.353481000
6	5.086224000	-1.418614000	2.045028000
1	5.099631000	-0.280954000	0.218038000
6	3.024832000	-1.404564000	3.308459000
1	1.417233000	-0.248779000	2.458808000
6	4.343930000	-1.842194000	3.152708000
1	6.116114000	-1.759097000	1.913761000
1	2.423846000	-1.739192000	4.156583000
1	4.790367000	-2.515242000	3.888262000
6	3.468884000	0.976651000	-1.446356000
6	4.690398000	1.671573000	-1.397232000

6	3.127255000	0.274279000	-2.610127000
6	5.557397000	1.650443000	-2.492371000
1	4.962998000	2.235475000	-0.502853000
6	3.999538000	0.246440000	-3.701631000
1	2.175055000	-0.253934000	-2.654540000
6	5.214968000	0.934042000	-3.645485000
1	6.502942000	2.195863000	-2.445691000
1	3.723047000	-0.311871000	-4.598711000
1	5.894607000	0.918378000	-4.500844000
6	2.427931000	2.598075000	0.745768000
6	2.538773000	3.736586000	-0.071834000
6	2.327291000	2.775059000	2.135602000
6	2.553708000	5.015124000	0.489777000
1	2.598567000	3.624809000	-1.152862000
6	2.336400000	4.056889000	2.694892000
1	2.247698000	1.914987000	2.799841000
6	2.449944000	5.182406000	1.874164000
1	2.638186000	5.886261000	-0.163833000
1	2.258158000	4.170984000	3.778745000
1	2.457447000	6.184072000	2.310257000

PPh3

G = -1036.178925

15	-0.001541000	0.001609000	-1.269027000
6	0.377830000	-1.619533000	-0.438794000
6	-0.210338000	-2.772251000	-0.990520000
6	1.210579000	-1.756997000	0.683877000
6	0.013125000	-4.029374000	-0.423570000
1	-0.853408000	-2.683411000	-1.870543000
6	1.443928000	-3.017858000	1.243648000
1	1.677732000	-0.875535000	1.126817000
6	0.844508000	-4.155767000	0.694931000
1	-0.456713000	-4.913541000	-0.861024000
1	2.095163000	-3.108910000	2.116456000
1	1.027379000	-5.139031000	1.134531000
6	1.214518000	1.138822000	-0.438724000
6	0.924893000	1.912141000	0.697353000
6	2.501053000	1.218834000	-1.002025000
6	1.901766000	2.741526000	1.258596000
1	-0.067881000	1.866473000	1.148779000
6	3.480057000	2.037613000	-0.433554000
1	2.739528000	0.630884000	-1.892720000
6	3.181420000	2.804180000	0.698322000
1	1.660806000	3.338631000	2.141536000
1	4.476174000	2.083286000	-0.880266000
1	3.943066000	3.451374000	1.139405000
6	-1.594552000	0.484265000	-0.436951000
6	-2.310967000	1.555817000	-1.000452000
6	-2.116919000	-0.154526000	0.700055000
6	-3.510931000	1.990153000	-0.431500000
1	-1.923161000	2.056780000	-1.891783000
6	-3.324448000	0.273235000	1.262046000
1	-1.578095000	-0.989556000	1.151474000
6	-4.022468000	1.347232000	0.701139000

1	-4.052138000	2.827422000	-0.878662000
1	-3.718911000	-0.234346000	2.145740000
1	-4.964749000	1.680274000	1.142409000

3a

G = -2175.781461

6	-1.357172000	-1.938581000	-2.071559000
6	-0.410517000	-1.415364000	-1.293867000
6	1.008567000	-1.140208000	-1.709823000
1	1.706260000	-1.796244000	-1.163111000
1	1.164632000	-1.335457000	-2.783115000
6	-2.801560000	-2.119061000	-1.676453000
1	-3.432701000	-1.570223000	-2.392237000
1	-3.097790000	-3.181206000	-1.772040000
1	-1.130520000	-2.222580000	-3.107295000
1	-0.651688000	-1.120412000	-0.274376000
7	1.434384000	0.251802000	-1.457867000
7	-3.134054000	-1.677517000	-0.315222000
6	0.970023000	1.325088000	-2.351182000
6	-3.206675000	-2.709208000	0.741719000
6	-1.854853000	-3.346675000	0.993761000
6	-0.487750000	1.486591000	-2.433564000
6	-1.692766000	1.572049000	-2.530652000
1	-2.767034000	1.564612000	-2.553642000
1	1.368536000	1.102615000	-3.356196000
1	1.433025000	2.263756000	-2.018326000
1	-3.582000000	-2.235627000	1.655208000
1	-3.935545000	-3.487891000	0.450357000
1	-1.515490000	-4.109437000	0.283798000
6	-1.057189000	-2.989866000	1.972614000
6	-0.251360000	-2.587067000	2.924427000
1	0.449799000	-1.767904000	2.731914000
1	-0.257331000	-3.049894000	3.916350000
16	-4.122196000	-0.302339000	-0.124615000
16	1.942783000	0.626775000	0.114096000
8	1.883348000	2.105693000	0.252472000
8	1.248808000	-0.266365000	1.083532000
8	-4.543534000	0.162366000	-1.479494000
8	-5.157237000	-0.618582000	0.895534000
6	3.672040000	0.128708000	0.110908000
6	4.629175000	1.009268000	-0.404613000
6	4.031116000	-1.117691000	0.624366000
6	5.964671000	0.615498000	-0.418758000
1	4.326513000	1.989864000	-0.773925000
6	5.376895000	-1.495858000	0.595599000
1	3.270196000	-1.772485000	1.049760000
6	6.360344000	-0.641840000	0.075985000
1	6.720323000	1.298152000	-0.815659000
1	5.665466000	-2.471380000	0.994016000
6	-3.035604000	0.974705000	0.538512000
6	-3.342245000	2.300763000	0.224531000
6	-1.929064000	0.657951000	1.328603000
6	-2.504984000	3.317974000	0.685996000
1	-4.206404000	2.530090000	-0.399889000

6	-1.101253000	1.686376000	1.771954000
1	-1.686543000	-0.374957000	1.572155000
6	-1.363218000	3.027050000	1.446625000
1	-2.729120000	4.354363000	0.422105000
1	-0.209133000	1.433269000	2.344713000
6	7.815145000	-1.038933000	0.056495000
1	8.238665000	-0.937139000	-0.955955000
1	8.406915000	-0.386389000	0.720340000
1	7.959193000	-2.077837000	0.386286000
6	-0.396372000	4.101019000	1.872963000
1	0.587094000	3.909173000	1.413647000
1	-0.737642000	5.103209000	1.574970000
1	-0.252801000	4.095984000	2.966193000

cis-4a

G = 258.6628996

	0.844416800	0.317228060	2.677770850
1	0.859947160	1.117992190	3.390102460
1	0.619835700	-0.599347430	3.186500860
6	2.027703360	1.179394930	0.783313530
1	2.824203860	1.886529700	0.690641890
1	2.014631170	0.549159880	-0.080858810
6	0.618478800	1.763024090	0.864230180
6	-0.171599270	0.732636650	1.629027420
1	-0.463687040	-0.055433370	0.970759000
7	2.187167080	0.335108060	2.015076190
6	-1.405761490	1.353478290	2.292538490
1	-1.037485420	1.998727470	3.062702940
6	-2.440137060	0.356587900	2.790536620
1	-3.153207010	0.933974240	3.336156590
1	-2.067826630	-0.426120450	3.424932570
6	0.098804680	2.904752040	0.344351970
1	0.718828310	3.623117010	-0.152345200
6	-2.695232240	0.850578310	0.479055610
1	-1.820841510	0.467450880	-0.006358750
1	-3.447092700	1.034195240	-0.258938130
7	-3.117131700	-0.143273640	1.532979670
16	-2.684926290	-1.668415380	0.897738670
16	2.850336820	-1.120481080	1.436982020
8	-2.932508470	-2.720400850	1.893640150
8	-1.260254780	-1.675098550	0.537205780
8	1.949193350	-1.717313870	0.442749520
8	3.037796130	-2.062706830	2.548748210
6	-2.257590970	2.070589050	1.271770640
1	-3.095287880	2.564348540	1.713731820
6	-1.430824580	3.125450640	0.481237200
6	-2.017524930	4.213598340	-0.068290490
1	-1.425633110	4.922686930	-0.610628610
1	-3.069475130	4.363713960	0.039267310
6	-3.694474200	-1.951665300	-0.549940590
6	-5.093596650	-2.018450180	-0.428020260
6	-3.100589430	-2.090149490	-1.812851010
6	-5.897972160	-2.169004640	-1.570185410
1	-5.552040420	-1.955347550	0.538233330

6	-3.903772230	-2.228010260	-2.954630620
1	-2.035748600	-2.087166690	-1.908619430
6	-5.302096040	-2.244847910	-2.837514320
1	-6.964206270	-2.222033450	-1.473721590
1	-3.450960570	-2.316956090	-3.917948260
6	4.424572890	-0.745065960	0.683855260
6	4.627071760	-0.995751390	-0.680732170
6	5.459370560	-0.190737600	1.453694500
6	5.854933090	-0.677429330	-1.277862010
1	3.843027880	-1.426198470	-1.267881410
6	6.687539740	0.124094130	0.856524150
1	5.313218130	-0.008066030	2.497935970
6	6.887282840	-0.118123760	-0.509765860
1	6.002044350	-0.861818110	-2.320845030
1	7.471922430	0.552004560	1.446331260
6	-6.174305030	-2.345711520	-4.107210720
1	-6.347952180	-3.375308110	-4.341901390
1	-7.110568840	-1.856259420	-3.939468120
1	-5.667530710	-1.875189940	-4.924360910
6	8.242232050	0.226800640	-1.164082040
1	8.893576340	-0.617615240	-1.101839720
1	8.088886770	0.483824050	-2.190215040
1	8.684605300	1.055730150	-0.653823460

trans-4a

$G = 248.260906$

6	-2.161142950	0.580429170	-1.696200560
1	-1.743233860	1.052538500	-2.564126790
1	-2.248125380	-0.468392870	-1.896351930
6	-3.007510050	2.598652000	-0.855283980
1	-2.937935700	3.332682710	-1.634437520
1	-3.715259960	2.934133230	-0.128086110
6	-1.596780420	2.356048880	-0.292616600
6	-1.315685250	0.892922880	-0.448094430
1	-1.636578450	0.346286320	0.415798260
7	-3.426591630	1.230565620	-1.333280850
6	0.170813650	0.676877390	-0.658591020
1	0.412312760	1.135894600	-1.594562720
6	0.720477670	-0.755033930	-0.575232250
1	0.331963710	-1.423744970	-1.308955670
1	0.531473590	-1.185219580	0.386955770
6	-0.690651780	3.259109020	0.207015880
1	-0.940355050	4.297604260	0.283888380
6	2.372901200	0.780195570	0.097899990
1	2.881710640	0.597749520	1.020429330
1	2.943999930	1.476484420	-0.478290510
7	2.136757190	-0.426350540	-0.783975440
16	3.288655570	-1.654605240	-0.509019770
16	-4.139197160	0.326843530	-0.069066840
8	4.607702770	-1.193705070	-0.961438110
8	2.915381280	-2.861444040	-1.256291350
8	-5.354644450	1.006274300	0.397752430
8	-3.200927350	0.194255150	1.053035940
6	0.938759270	1.225449030	0.451978260

1	0.628299400	0.709919280	1.336932390
6	0.701963930	2.726673690	0.660970830
6	1.640170210	3.536080800	1.202191150
1	1.431819350	4.576034330	1.332138540
1	2.585539040	3.133555080	1.497703590
6	3.368472950	-2.016858140	1.230991530
6	3.760462970	-1.005786200	2.118522000
6	3.055708920	-3.293239940	1.713520210
6	3.873774320	-1.277974420	3.487115530
1	3.974748920	-0.025141050	1.746545850
6	3.156538680	-3.563268840	3.083840580
1	2.738974150	-4.059003120	1.037567950
6	3.583296150	-2.565287040	3.967457620
1	4.179884670	-0.505174430	4.160146600
1	2.907277060	-4.535257470	3.456415030
6	-4.558067120	-1.281311190	-0.696634960
6	-5.398330240	-1.376861000	-1.810193580
6	-4.058270920	-2.439599670	-0.090966660
6	-5.739494270	-2.632091100	-2.323599420
1	-5.774681940	-0.486939530	-2.273447940
6	-4.402241850	-3.698414210	-0.600224590
1	-3.413870150	-2.362414380	0.760353870
6	-5.244154270	-3.792742440	-1.720920110
1	-6.379745000	-2.701117700	-3.178823610
1	-4.025993850	-4.584181650	-0.135861610
6	-5.627956380	-5.170963360	-2.295408670
1	-6.515891990	-5.523664490	-1.813396550
1	-5.803923700	-5.082865280	-3.347631030
1	-4.830627290	-5.863850240	-2.125361890
6	3.732053550	-2.889831480	5.466132690
1	4.723322790	-3.249587320	5.655243020
1	3.556968420	-2.004957720	6.043667760
1	3.020707990	-3.643574240	5.741328520

D0a

G = -3782.37868

6	1.427012000	1.478798000	-1.580210000
1	0.702977000	1.772117000	-2.347079000
1	2.456756000	1.797122000	-1.768458000
6	-0.521754000	-0.502498000	-2.398204000
6	-0.957523000	-0.708852000	-1.259246000
6	0.994079000	1.257890000	-0.275262000
1	-0.437530000	-0.324380000	-3.456866000
6	0.646605000	1.678261000	0.932676000
1	0.407609000	0.948732000	1.711660000
6	-1.755563000	-1.048898000	-0.067325000
1	-1.792642000	-2.148844000	0.026525000
1	-1.237015000	-0.682540000	0.827759000
6	0.609707000	3.135864000	1.333048000
1	1.280451000	3.283936000	2.200410000
1	0.995819000	3.767722000	0.525340000
45	1.251688000	-0.595018000	-1.070045000
6	-3.506031000	0.246945000	1.171187000
1	-4.507388000	0.657172000	0.977185000

6	-1.393462000	3.094204000	2.892615000
1	-1.995524000	3.893661000	3.352459000
1	-0.604142000	2.850921000	3.627812000
7	-0.720647000	3.639760000	1.714830000
7	-3.085201000	-0.418602000	-0.075265000
6	-2.271483000	1.882304000	2.666590000
1	-2.718639000	1.458461000	3.574825000
1	-3.584916000	-0.462672000	2.017692000
6	-2.554349000	1.371383000	1.467372000
1	-2.092381000	1.806934000	0.582376000
16	-4.287017000	-1.220862000	-0.973469000
16	-1.462823000	4.848903000	0.788892000
8	-2.454697000	5.507230000	1.678483000
8	-0.366684000	5.614494000	0.140515000
8	-3.649567000	-1.598109000	-2.258534000
8	-5.491127000	-0.352844000	-0.919662000
17	1.099579000	-2.992008000	-0.887393000
15	3.402156000	-0.693519000	-0.077194000
6	3.373316000	-1.579019000	1.546434000
6	4.549396000	-2.049522000	2.150995000
6	2.149897000	-1.724152000	2.218520000
6	4.500559000	-2.649586000	3.411694000
1	5.508353000	-1.958895000	1.639423000
6	2.105025000	-2.316762000	3.483242000
1	1.231020000	-1.387920000	1.737639000
6	3.279842000	-2.780464000	4.082428000
1	5.420916000	-3.018087000	3.870133000
1	1.146410000	-2.425955000	3.995275000
1	3.244377000	-3.250463000	5.067846000
6	4.128319000	0.951400000	0.363471000
6	4.744563000	1.734798000	-0.628152000
6	3.959383000	1.490146000	1.648898000
6	5.185193000	3.028665000	-0.337136000
1	4.891393000	1.330483000	-1.632159000
6	4.400473000	2.784702000	1.936966000
1	3.478730000	0.899416000	2.429726000
6	5.011585000	3.558270000	0.945396000
1	5.664515000	3.624140000	-1.117189000
1	4.263504000	3.189827000	2.942067000
1	5.352980000	4.570682000	1.171476000
6	4.731680000	-1.499394000	-1.079013000
6	6.093001000	-1.222057000	-0.851596000
6	4.377770000	-2.416372000	-2.082466000
6	7.079336000	-1.858368000	-1.608781000
1	6.388093000	-0.497065000	-0.091393000
6	5.369858000	-3.048510000	-2.838197000
1	3.327637000	-2.647823000	-2.260353000
6	6.719907000	-2.773261000	-2.604129000
1	8.131934000	-1.634349000	-1.421601000
1	5.080910000	-3.759885000	-3.614910000
1	7.492200000	-3.267425000	-3.197986000
6	-2.368974000	4.006915000	-0.516927000
6	-3.732061000	3.750396000	-0.358995000
6	-1.660041000	3.513335000	-1.616390000
6	-4.381375000	2.948180000	-1.300056000

1	-4.260386000	4.149988000	0.506822000
6	-2.326669000	2.715321000	-2.543346000
1	-0.599966000	3.740475000	-1.728697000
6	-3.690746000	2.406900000	-2.395902000
1	-5.440236000	2.716260000	-1.170276000
1	-1.775660000	2.309395000	-3.395015000
6	-4.636059000	-2.735271000	-0.070531000
6	-3.912990000	-3.892027000	-0.373193000
6	-5.595518000	-2.719515000	0.948547000
6	-4.145831000	-5.046755000	0.378198000
1	-3.193443000	-3.887982000	-1.192533000
6	-5.813728000	-3.883459000	1.682955000
1	-6.169423000	-1.812810000	1.143154000
6	-5.092109000	-5.061337000	1.414248000
1	-3.583518000	-5.954424000	0.147542000
1	-6.565049000	-3.883307000	2.476761000
6	-5.353122000	-6.309401000	2.219723000
1	-5.238714000	-6.113757000	3.298454000
1	-6.385263000	-6.665860000	2.064494000
1	-4.667495000	-7.123243000	1.943831000
6	-4.379727000	1.519484000	-3.399537000
1	-3.839279000	0.566671000	-3.507531000
1	-5.403143000	1.276763000	-3.085140000
1	-4.415367000	2.004572000	-4.389733000

D0b

G = -3782.37745

6	-1.196365000	-3.291267000	1.146932000
1	-1.682506000	-2.866672000	2.030286000
1	-0.906060000	-4.344006000	1.200710000
6	-0.146664000	-0.747180000	2.018335000
6	-0.212397000	-0.218486000	0.882175000
6	-1.315268000	-2.670103000	-0.072686000
1	-0.282961000	-0.818749000	3.087934000
6	-1.906548000	-2.332317000	-1.204695000
1	-1.392735000	-1.679347000	-1.914103000
6	-0.344357000	0.851598000	-0.129228000
1	0.629193000	1.360676000	-0.239457000
1	-0.551757000	0.412110000	-1.112739000
6	-3.273506000	-2.854100000	-1.605944000
1	-3.186635000	-3.369372000	-2.580005000
1	-3.629187000	-3.594900000	-0.880849000
45	0.602976000	-2.168536000	0.626536000
6	-2.388100000	2.059128000	-0.923336000
1	-3.151299000	2.734767000	-0.510775000
6	-4.226695000	-0.847379000	-2.836231000
1	-5.248014000	-0.594299000	-3.161924000
1	-3.754986000	-1.360158000	-3.694367000
7	-4.314595000	-1.823838000	-1.751491000
7	-1.427307000	1.804707000	0.168407000
6	-3.478344000	0.430284000	-2.527160000
1	-3.368219000	1.121183000	-3.372550000
1	-1.912305000	2.560053000	-1.788795000
6	-3.027246000	0.760066000	-1.316170000

1	-3.141903000	0.053472000	-0.495795000
16	-0.983615000	3.138898000	1.121413000
16	-5.628753000	-1.787949000	-0.677409000
8	-6.724361000	-1.072382000	-1.381108000
8	-5.798436000	-3.174162000	-0.171782000
8	-0.166525000	2.592408000	2.236422000
8	-2.229116000	3.906302000	1.372201000
17	1.441566000	-4.135007000	-0.407340000
15	2.786153000	-1.124199000	0.192992000
6	2.576612000	-0.207003000	-1.404101000
6	2.999429000	1.118954000	-1.577328000
6	1.888857000	-0.854810000	-2.448191000
6	2.719742000	1.797443000	-2.768907000
1	3.530424000	1.634239000	-0.775922000
6	1.624920000	-0.177123000	-3.640033000
1	1.556901000	-1.888070000	-2.320558000
6	2.030905000	1.153794000	-3.799856000
1	3.033919000	2.836747000	-2.882357000
1	1.091331000	-0.688897000	-4.444103000
1	1.809308000	1.686806000	-4.727183000
6	4.192682000	-2.273890000	-0.109808000
6	4.471182000	-3.237745000	0.872390000
6	5.006427000	-2.189255000	-1.247324000
6	5.560059000	-4.096646000	0.724205000
1	3.825576000	-3.323114000	1.748940000
6	6.091218000	-3.060462000	-1.398341000
1	4.796747000	-1.447146000	-2.019453000
6	6.371866000	-4.010808000	-0.413380000
1	5.768393000	-4.844536000	1.492303000
1	6.717977000	-2.992475000	-2.290451000
1	7.218982000	-4.689933000	-0.533358000
6	3.541459000	0.133495000	1.330352000
6	4.938702000	0.259806000	1.441005000
6	2.722217000	1.010531000	2.062774000
6	5.498259000	1.244948000	2.259872000
1	5.596570000	-0.410691000	0.887282000
6	3.287009000	1.996222000	2.877977000
1	1.639062000	0.943921000	2.008424000
6	4.675696000	2.117935000	2.979362000
1	6.585001000	1.328265000	2.333689000
1	2.624395000	2.667199000	3.429145000
1	5.116308000	2.886409000	3.618581000
6	0.097678000	4.136290000	0.083359000
6	1.482871000	3.995579000	0.192214000
6	-0.472705000	4.996805000	-0.862003000
6	2.304946000	4.716431000	-0.675908000
1	1.910261000	3.336997000	0.946467000
6	0.366259000	5.701701000	-1.724042000
1	-1.555428000	5.118017000	-0.908585000
6	1.764802000	5.571637000	-1.648717000
1	3.389298000	4.607963000	-0.593443000
1	-0.072286000	6.372333000	-2.467057000
6	-5.110598000	-0.769657000	0.712229000
6	-4.244961000	-1.321720000	1.660976000
6	-5.454888000	0.582690000	0.744546000

6	-3.675955000	-0.485410000	2.618276000
1	-4.007583000	-2.384899000	1.628193000
6	-4.871969000	1.404153000	1.712412000
1	-6.136940000	0.984174000	-0.005066000
6	-3.957188000	0.892002000	2.646237000
1	-2.981321000	-0.903626000	3.350133000
1	-5.109284000	2.469998000	1.726944000
6	2.659131000	6.359201000	-2.572875000
1	2.815111000	7.380359000	-2.183998000
1	3.649039000	5.890147000	-2.675163000
1	2.214716000	6.457046000	-3.575195000
6	-3.279466000	1.782739000	3.654789000
1	-3.494211000	2.842090000	3.463785000
1	-3.599211000	1.530426000	4.679969000
1	-2.186071000	1.660743000	3.603045000

D1

G = -2746.18301

6	-0.006303000	-0.599459000	2.292423000
6	-0.895703000	-1.332941000	1.775683000
1	0.396030000	0.129389000	2.983856000
6	-0.441316000	-0.864049000	-1.064856000
1	0.032666000	-1.277277000	-1.964798000
6	-1.915143000	-1.244882000	-1.031031000
1	-1.999222000	-2.317814000	-1.271245000
1	-2.409992000	-0.700829000	-1.852687000
6	-2.269591000	-1.741797000	1.400409000
1	-2.968547000	-1.515626000	2.216505000
1	-2.321057000	-2.819612000	1.182608000
7	-2.698236000	-1.021380000	0.189643000
45	0.779814000	-1.417485000	0.548972000
16	-3.472812000	0.491640000	0.394622000
8	-2.881010000	1.464850000	-0.557798000
8	-3.517111000	0.777264000	1.853543000
6	0.176123000	0.294170000	-0.505441000
1	-0.434548000	0.929906000	0.140913000
6	1.249500000	1.034400000	-1.277237000
1	0.729581000	1.710078000	-1.988514000
1	1.832652000	0.328868000	-1.880927000
6	1.597989000	3.029276000	0.199136000
1	2.367211000	3.813898000	0.166533000
1	0.730509000	3.381826000	-0.383217000
7	2.170931000	1.815829000	-0.428292000
16	3.731307000	2.045014000	-1.157313000
8	3.625331000	1.977311000	-2.639743000
8	4.339654000	3.241017000	-0.516184000
6	1.204326000	2.794416000	1.643144000
6	0.014058000	3.051579000	2.135490000
1	1.996595000	2.418680000	2.302511000
6	-1.186072000	3.301045000	2.601429000
1	-1.443105000	4.289846000	2.996290000
1	-1.969041000	2.534717000	2.591195000
17	2.337086000	-2.414371000	-0.901242000
6	-5.137029000	0.156632000	-0.140682000

6	-5.997208000	-0.579345000	0.674733000
6	-5.581234000	0.629964000	-1.375261000
6	-7.301070000	-0.842460000	0.255284000
1	-5.646461000	-0.953027000	1.647656000
6	-6.885773000	0.367697000	-1.794551000
1	-4.903467000	1.210197000	-2.017982000
6	-7.745654000	-0.368502000	-0.979594000
1	-7.978933000	-1.423094000	0.897672000
1	-7.235862000	0.741377000	-2.767832000
6	4.615983000	0.605342000	-0.597766000
6	5.008796000	-0.371476000	-1.513188000
6	4.916621000	0.453781000	0.755819000
6	5.701495000	-1.499894000	-1.074938000
1	4.770952000	-0.252065000	-2.580152000
6	5.610389000	-0.674445000	1.194227000
1	4.607254000	1.223655000	1.477425000
6	6.002724000	-1.651299000	0.279150000
1	6.010598000	-2.270178000	-1.796336000
1	5.847650000	-0.793476000	2.261472000
6	6.767668000	-2.897344000	0.762711000
1	6.594703000	-3.707260000	0.085202000
1	7.814880000	-2.680856000	0.799856000
1	6.424908000	-3.169675000	1.739057000
6	-9.185425000	-0.659131000	-1.442404000
1	-9.507793000	-1.595888000	-1.038095000
1	-9.834303000	0.119536000	-1.099570000
1	-9.214540000	-0.702972000	-2.511109000

D2a

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6	1.403879000	-0.042530000	1.701523000
1	1.495021000	-0.999813000	2.238750000
1	0.770006000	0.615588000	2.323245000
6	0.749328000	-0.299641000	0.361572000
1	1.326600000	-0.926269000	-0.323819000
6	-0.664231000	-0.264348000	0.236236000
1	-1.218876000	0.050148000	1.129564000
6	-1.518692000	-1.078996000	-0.700457000
1	-1.700042000	-2.075800000	-0.272109000
1	-1.032700000	-1.207270000	-1.682086000
7	-2.842304000	-0.413616000	-0.788882000
7	2.746883000	0.531385000	1.589127000
6	2.856558000	1.980215000	1.401017000
1	2.183558000	2.510649000	2.096660000
1	3.885194000	2.270272000	1.660879000
6	2.577033000	2.406016000	-0.027861000
1	3.052404000	1.819727000	-0.821612000
6	1.940102000	3.523320000	-0.354993000
6	1.479101000	4.716697000	-0.648214000
1	2.161926000	5.573537000	-0.658842000
1	0.433220000	4.900710000	-0.901132000
6	-2.850558000	0.936325000	-1.403662000
1	-3.848012000	1.381158000	-1.264524000
1	-2.650696000	0.890131000	-2.488288000

6	-1.825925000	1.791699000	-0.751385000
6	-1.351351000	2.734951000	-0.016700000
1	-1.566704000	3.644467000	0.536727000
45	0.154553000	1.467329000	-0.657589000
17	1.339051000	0.450529000	-2.500974000
16	4.052527000	-0.293928000	2.319186000
16	-4.140593000	-1.414378000	-1.336099000
8	3.493244000	-1.364400000	3.183734000
8	4.984016000	0.720364000	2.875226000
8	-3.704394000	-2.822548000	-1.168646000
8	-4.634850000	-0.924030000	-2.648303000
6	-5.389074000	-1.068621000	-0.115383000
6	-6.302278000	-0.034905000	-0.325050000
6	-5.454532000	-1.831153000	1.050725000
6	-7.280263000	0.236583000	0.631538000
1	-6.249924000	0.566574000	-1.244139000
6	-6.433373000	-1.560349000	2.007252000
1	-4.734975000	-2.646035000	1.216055000
6	-7.346095000	-0.526590000	1.797921000
1	-7.999702000	1.051758000	0.466633000
1	-6.485000000	-2.162004000	2.926393000
6	4.868367000	-1.079655000	0.946074000
6	5.733920000	-0.344610000	0.135520000
6	4.642460000	-2.430199000	0.680470000
6	6.372857000	-0.959884000	-0.940778000
1	5.911215000	0.720305000	0.344720000
6	5.282276000	-3.046055000	-0.395526000
1	3.960437000	-3.009723000	1.319318000
6	6.147268000	-2.311132000	-1.206213000
1	7.054624000	-0.380423000	-1.580087000
1	5.104284000	-4.111016000	-0.604455000
6	6.852985000	-2.990218000	-2.394660000
1	6.912429000	-2.304113000	-3.213578000
1	7.839709000	-3.283916000	-2.103080000
1	6.297155000	-3.854457000	-2.693061000
6	-8.426131000	-0.226614000	2.853920000
1	-8.616053000	0.826054000	2.880785000
1	-9.326968000	-0.745202000	2.600032000
1	-8.085788000	-0.552267000	3.814658000

D2b

$G = -2746.15816$

6	1.061298000	1.544898000	-0.400144000
1	1.153723000	2.311472000	0.384188000
1	0.364272000	1.942058000	-1.161771000
6	0.482274000	0.289754000	0.219034000
1	0.962450000	-0.057960000	1.138146000
6	-0.905154000	0.015427000	0.012701000
1	-1.394160000	0.649584000	-0.736138000
6	-1.900288000	-0.561516000	0.986683000
1	-2.275345000	0.260551000	1.618806000
1	-1.446816000	-1.317233000	1.643602000
7	-3.052241000	-1.087506000	0.215580000
7	2.378165000	1.348916000	-1.005272000

6	2.352599000	0.781032000	-2.351980000
1	1.605497000	1.306075000	-2.976183000
1	3.334504000	0.949860000	-2.819138000
6	2.066194000	-0.711639000	-2.348764000
1	1.826451000	-1.127212000	-3.333351000
6	2.507890000	-1.543825000	-1.359743000
6	3.388227000	-2.265317000	-0.690323000
1	3.106716000	-2.807937000	0.214536000
1	4.422621000	-2.335518000	-1.048411000
6	-2.752473000	-2.250364000	-0.661651000
1	-3.656716000	-2.481521000	-1.239495000
1	-2.464677000	-3.143927000	-0.080937000
6	-1.631653000	-1.862058000	-1.549570000
6	-1.052300000	-1.441476000	-2.617749000
1	-1.141965000	-1.231879000	-3.679583000
45	0.297791000	-1.393334000	-1.050734000
17	0.617150000	-2.741102000	1.003131000
16	3.628281000	2.452456000	-0.614397000
16	-4.522414000	-1.224882000	1.108627000
8	3.040274000	3.536071000	0.214603000
8	4.373585000	2.768819000	-1.859533000
8	-4.230274000	-1.251585000	2.563943000
8	-5.314176000	-2.307637000	0.473098000
6	4.699001000	1.487981000	0.430469000
6	5.744784000	0.754207000	-0.130234000
6	4.492629000	1.465851000	1.809769000
6	6.583539000	-0.002035000	0.688185000
1	5.906747000	0.771251000	-1.217763000
6	5.332156000	0.710213000	2.628680000
1	3.668546000	2.044262000	2.251875000
6	6.377417000	-0.023787000	2.068133000
1	7.407471000	-0.580928000	0.246240000
1	5.169452000	0.693282000	3.716207000
6	-5.302515000	0.331077000	0.736027000
6	-5.296122000	1.358307000	1.680077000
6	-5.920100000	0.523456000	-0.499743000
6	-5.907787000	2.577374000	1.388593000
1	-4.809815000	1.206059000	2.654534000
6	-6.531139000	1.743176000	-0.791847000
1	-5.925077000	-0.285993000	-1.243985000
6	-6.525200000	2.770041000	0.152107000
1	-5.903334000	3.386878000	2.132892000
1	-7.017643000	1.894712000	-1.766437000
6	-7.200421000	4.116248000	-0.169455000
1	-7.083740000	4.334107000	-1.210524000
1	-8.242075000	4.058587000	0.068311000
1	-6.744595000	4.891402000	0.410424000
6	7.303778000	-0.858845000	2.971534000
1	7.706001000	-1.676755000	2.411052000
1	8.103211000	-0.243670000	3.328417000
1	6.745761000	-1.236312000	3.802820000

TS(D2a.D3a)

G = -2746.15101

6	-1.336067000	-0.768089000	-1.162371000
1	-1.316494000	-1.862854000	-1.051621000
1	-0.818897000	-0.522001000	-2.109785000
6	-0.615848000	-0.140722000	0.011322000
1	-1.084298000	-0.328964000	0.983216000
6	0.827682000	-0.051637000	-0.018828000
1	1.258882000	-0.423610000	-0.956661000
6	1.756413000	-0.267580000	1.142144000
1	1.817513000	-1.336553000	1.391259000
1	1.419111000	0.285183000	2.034463000
7	3.078773000	0.153290000	0.624826000
7	-2.740514000	-0.349323000	-1.197859000
6	-2.962834000	1.039284000	-1.639943000
1	-2.447420000	1.239843000	-2.595579000
1	-4.040129000	1.174052000	-1.820559000
6	-2.525513000	2.025593000	-0.579522000
1	-3.005160000	1.920935000	0.399655000
6	-1.883476000	3.204290000	-0.875888000
6	-1.823161000	4.454959000	-1.302504000
1	-2.738184000	4.979000000	-1.601613000
1	-0.885544000	5.012361000	-1.351405000
6	3.048203000	1.482529000	-0.022346000
1	3.850353000	1.545466000	-0.774784000
1	3.206629000	2.292885000	0.711143000
6	1.719363000	1.704980000	-0.670450000
6	1.031020000	2.324542000	-1.592302000
1	1.219140000	2.964701000	-2.453313000
45	-0.343486000	1.918946000	-0.148270000
17	-0.946631000	1.978153000	2.201109000
16	-3.877679000	-1.510966000	-1.767250000
16	4.415620000	-0.107530000	1.682594000
8	-3.164336000	-2.807687000	-1.896414000
8	-4.625494000	-0.943708000	-2.918616000
8	3.974263000	-1.114176000	2.677874000
8	4.976748000	1.198576000	2.112747000
6	5.588637000	-0.872480000	0.583830000
6	6.508033000	-0.086702000	-0.111681000
6	5.588775000	-2.257442000	0.418215000
6	7.426881000	-0.685774000	-0.973105000
1	6.507161000	1.005219000	0.018518000
6	6.508484000	-2.856943000	-0.442682000
1	4.864334000	-2.876925000	0.966444000
6	7.427378000	-2.071374000	-1.138420000
1	8.151177000	-0.066423000	-1.521827000
1	6.508628000	-3.948985000	-0.572749000
6	-5.001315000	-1.631741000	-0.392021000
6	-6.065693000	-0.736711000	-0.280248000
6	-4.817813000	-2.621203000	0.573816000
6	-6.945926000	-0.830771000	0.797510000
1	-6.209639000	0.043732000	-1.041451000
6	-5.698803000	-2.716047000	1.651440000
1	-3.979075000	-3.326820000	0.485782000
6	-6.762670000	-1.820969000	1.763503000
1	-7.784536000	-0.124940000	0.886012000
1	-5.554112000	-3.496555000	2.412588000

6	8.442130000	-2.732544000	-2.089594000
1	8.580682000	-2.112281000	-2.950395000
1	9.377214000	-2.855264000	-1.584166000
1	8.073549000	-3.689473000	-2.395103000
6	-7.734826000	-1.924606000	2.953365000
1	-8.062169000	-0.945000000	3.232862000
1	-8.580652000	-2.516646000	2.672352000
1	-7.237118000	-2.384181000	3.781603000

TS(D2b.D3b)

G = -2746.14921

6	1.057772000	1.144257000	-1.226229000
1	1.009954000	2.181850000	-0.862616000
1	0.465827000	1.098410000	-2.160077000
6	0.461288000	0.213962000	-0.185655000
1	0.833079000	0.368349000	0.833452000
6	-0.934866000	-0.163893000	-0.333880000
1	-1.378359000	0.234786000	-1.253931000
6	-1.969132000	-0.282746000	0.749669000
1	-2.254833000	0.727213000	1.087245000
1	-1.600347000	-0.852416000	1.616573000
7	-3.134334000	-0.898685000	0.077131000
7	2.453593000	0.825998000	-1.523558000
6	2.656771000	-0.250470000	-2.494933000
1	2.011313000	-0.087413000	-3.378502000
1	3.698567000	-0.204106000	-2.846536000
6	2.393417000	-1.633888000	-1.919676000
1	2.310831000	-2.411705000	-2.688349000
6	2.763855000	-2.005528000	-0.635171000
6	3.687868000	-2.355446000	0.248607000
1	3.429125000	-2.569304000	1.287121000
1	4.738017000	-2.441820000	-0.055460000
6	-2.772381000	-2.124288000	-0.678394000
1	-3.513019000	-2.293628000	-1.472198000
1	-2.755168000	-3.022207000	-0.034096000
6	-1.405454000	-1.953711000	-1.245083000
6	-0.535673000	-2.236838000	-2.164036000
1	-0.442665000	-2.669049000	-3.157600000
45	0.677432000	-1.796888000	-0.572346000
17	0.732611000	-2.157495000	1.837831000
16	3.616659000	2.076576000	-1.432491000
16	-4.558946000	-1.038991000	1.037598000
8	2.895341000	3.361206000	-1.237762000
8	4.567941000	1.905398000	-2.560012000
8	-4.207625000	-0.952778000	2.476869000
8	-5.311565000	-2.201875000	0.504849000
6	-5.424228000	0.451017000	0.590874000
6	-5.446109000	1.534881000	1.469072000
6	-6.080297000	0.535102000	-0.637153000
6	-6.124500000	2.702282000	1.119525000
1	-4.929427000	1.467997000	2.437477000
6	-6.758110000	1.703144000	-0.987377000
1	-6.063002000	-0.318993000	-1.329506000
6	-6.780428000	2.786616000	-0.109239000

1	-6.142320000	3.556410000	1.811945000
1	-7.274956000	1.769302000	-1.955864000
6	4.487205000	1.710109000	0.076234000
6	5.602090000	0.871702000	0.052228000
6	4.054892000	2.261182000	1.282456000
6	6.284043000	0.583947000	1.234327000
1	5.942204000	0.436790000	-0.898780000
6	4.737532000	1.974228000	2.464856000
1	3.176314000	2.922141000	1.301531000
6	5.851874000	1.135651000	2.441004000
1	7.162440000	-0.077388000	1.215579000
1	4.396689000	2.409197000	3.415699000
6	6.605139000	0.817785000	3.746053000
1	7.104220000	-0.123758000	3.649537000
1	7.325535000	1.585289000	3.938061000
1	5.909035000	0.770969000	4.557316000
6	-7.529327000	4.075801000	-0.494927000
1	-7.437785000	4.239895000	-1.548300000
1	-8.563347000	3.978141000	-0.237703000
1	-7.107186000	4.905098000	0.033243000

D3a

G = -2746.20137

6	1.131498000	0.176366000	1.597164000
1	0.973575000	-0.821947000	2.034799000
1	0.646835000	0.906440000	2.270914000
6	0.482061000	0.224019000	0.216446000
1	0.802131000	-0.633161000	-0.399960000
6	-1.045023000	0.334797000	0.256115000
1	-1.377889000	0.700924000	1.245679000
6	-1.865772000	-0.922671000	-0.082684000
1	-1.998297000	-1.608588000	0.762717000
1	-1.399262000	-1.477599000	-0.916538000
7	-3.173484000	-0.320005000	-0.460908000
7	2.569694000	0.428001000	1.549303000
6	2.988194000	1.833939000	1.568477000
1	2.727327000	2.308605000	2.536099000
1	4.079584000	1.870491000	1.473186000
6	2.369282000	2.683347000	0.452961000
1	3.101014000	3.306595000	-0.078779000
6	1.025015000	3.113462000	0.455429000
6	0.141174000	3.914042000	1.037329000
1	0.471659000	4.583942000	1.838972000
1	-0.910749000	3.944806000	0.752895000
6	-2.948281000	0.974577000	-1.163358000
1	-3.661714000	1.732283000	-0.795974000
1	-3.081639000	0.879703000	-2.252552000
6	-1.523143000	1.310317000	-0.788902000
6	-0.660729000	2.202550000	-1.297162000
1	-0.916367000	3.018984000	-1.984939000
45	1.242882000	1.710044000	-1.005548000
17	3.132195000	0.625329000	-1.937478000
16	3.627067000	-0.681526000	2.314671000
16	-4.315786000	-1.387128000	-1.172269000

8	2.798990000	-1.800541000	2.834758000
8	4.532320000	0.072172000	3.220888000
8	-3.887662000	-2.764550000	-0.822778000
8	-4.552686000	-1.007022000	-2.590612000
6	4.602017000	-1.299353000	0.959620000
6	5.724223000	-0.591610000	0.528082000
6	4.244192000	-2.491064000	0.329276000
6	6.487986000	-1.075196000	-0.534007000
1	6.005616000	0.348277000	1.024743000
6	5.008650000	-2.975443000	-0.732511000
1	3.359852000	-3.049095000	0.669383000
6	6.130327000	-2.267680000	-1.164308000
1	7.372173000	-0.517077000	-0.874613000
1	4.726517000	-3.915295000	-1.229052000
6	-5.789933000	-0.999611000	-0.252964000
6	-6.667214000	-0.021218000	-0.721575000
6	-6.068123000	-1.674120000	0.935815000
6	-7.822058000	0.283007000	-0.001156000
1	-6.447218000	0.510912000	-1.658422000
6	-7.223778000	-1.370615000	1.656063000
1	-5.376888000	-2.445400000	1.305207000
6	-8.100654000	-0.392135000	1.187871000
1	-8.513269000	1.054615000	-0.370132000
1	-7.443068000	-1.902888000	2.593118000
6	-9.375927000	-0.056037000	1.983055000
1	-9.617365000	0.977793000	1.849625000
1	-10.185762000	-0.659846000	1.630235000
1	-9.210719000	-0.252536000	3.021802000
6	6.973913000	-2.801408000	-2.336954000
1	7.435433000	-1.981504000	-2.846520000
1	7.729838000	-3.459389000	-1.962070000
1	6.342594000	-3.334167000	-3.017031000

D3b

$G = -2746.19482$

6	1.330372000	1.250028000	-1.115813000
1	1.407584000	2.242179000	-0.645526000
1	0.736245000	1.384550000	-2.039103000
6	0.584139000	0.309968000	-0.163642000
1	0.868970000	0.480762000	0.883394000
6	-0.924375000	0.417554000	-0.429392000
1	-1.144341000	1.392718000	-0.909541000
6	-1.945623000	0.243935000	0.705753000
1	-2.100587000	1.164692000	1.284821000
1	-1.650857000	-0.560417000	1.397801000
7	-3.190726000	-0.092996000	-0.057297000
7	2.669690000	0.800563000	-1.490640000
6	2.652042000	-0.193283000	-2.562355000
1	1.967440000	0.119314000	-3.372617000
1	3.661477000	-0.267477000	-2.993934000
6	2.251462000	-1.556582000	-2.030194000
1	1.994847000	-2.283058000	-2.811137000
6	2.821603000	-2.027505000	-0.833856000
6	3.848101000	-2.526941000	-0.161456000

1	3.788132000	-2.763506000	0.900879000
1	4.793299000	-2.715103000	-0.685049000
6	-2.866380000	-0.647973000	-1.409492000
1	-3.242276000	0.039016000	-2.188953000
1	-3.321216000	-1.635935000	-1.555125000
6	-1.358335000	-0.683327000	-1.380830000
6	-0.503386000	-1.636180000	-1.787683000
1	-0.722700000	-2.448100000	-2.490526000
45	0.893784000	-1.726640000	-0.382020000
17	1.007811000	-2.212324000	1.928801000
16	3.945133000	1.947213000	-1.464275000
16	-4.431083000	-0.878029000	0.827118000
8	3.367084000	3.312509000	-1.364885000
8	4.881036000	1.600621000	-2.564384000
8	-4.060551000	-0.801369000	2.262169000
8	-4.749246000	-2.186811000	0.195415000
6	-5.820349000	0.200398000	0.552641000
6	-6.667823000	-0.016659000	-0.534164000
6	-6.061833000	1.262379000	1.424094000
6	-7.756119000	0.828529000	-0.749777000
1	-6.476725000	-0.853530000	-1.221457000
6	-7.150989000	2.107325000	1.209119000
1	-5.394096000	1.433491000	2.280818000
6	-7.998027000	1.890666000	0.122325000
1	-8.423787000	0.657882000	-1.606745000
1	-7.341379000	2.944323000	1.896622000
6	4.750941000	1.584740000	0.080939000
6	5.782742000	0.646766000	0.126347000
6	4.350965000	2.238471000	1.246359000
6	6.413914000	0.362156000	1.337066000
1	6.097324000	0.130987000	-0.792485000
6	4.982891000	1.954609000	2.457351000
1	3.537882000	2.977900000	1.210719000
6	6.014133000	1.016525000	2.502910000
1	7.226776000	-0.377613000	1.373047000
1	4.667592000	2.470504000	3.375999000
6	6.711317000	0.702096000	3.839573000
1	7.022202000	-0.321714000	3.847508000
1	7.566251000	1.335342000	3.953536000
1	6.029906000	0.874193000	4.646394000
6	-9.199827000	2.823664000	-0.115985000
1	-9.350738000	2.949325000	-1.167810000
1	-10.076906000	2.394321000	0.321390000
1	-9.006855000	3.775597000	0.332885000

TS(D3a.D4a)

G = -2746.17840

6	-1.693974000	0.681538000	-1.196658000
1	-1.531951000	1.459856000	-1.962751000
1	-1.760302000	1.181239000	-0.220551000
6	-0.558890000	-0.343930000	-1.222627000
1	-0.281602000	-0.510712000	-2.269223000
6	0.775552000	-0.008553000	-0.523452000
1	0.591571000	0.649587000	0.343867000

6	1.822391000	0.668481000	-1.433514000
1	1.741442000	1.760608000	-1.482396000
1	1.749511000	0.262035000	-2.461318000
7	3.094060000	0.288109000	-0.771179000
7	-2.976419000	-0.000395000	-1.524670000
6	-2.686758000	-1.252437000	-2.261437000
1	-3.608806000	-1.841967000	-2.335860000
1	-2.382203000	-0.952395000	-3.276092000
6	-1.564342000	-2.056133000	-1.584244000
1	-0.797462000	-2.432748000	-2.269602000
6	-1.897909000	-3.014349000	-0.545466000
6	-2.494058000	-4.198278000	-0.445354000
1	-2.916700000	-4.687961000	-1.329922000
1	-2.592319000	-4.704564000	0.516097000
6	2.983021000	-1.123959000	-0.313984000
1	3.586498000	-1.271495000	0.595175000
1	3.341562000	-1.828563000	-1.085701000
6	1.496442000	-1.276961000	-0.063546000
6	0.779778000	-2.281531000	0.451985000
1	1.193898000	-3.230101000	0.808690000
45	-1.107988000	-1.733850000	0.658269000
17	-1.183258000	-2.524259000	2.832502000
16	-3.995927000	-0.266102000	-0.159924000
16	4.503383000	0.676340000	-1.673758000
8	-3.158207000	-0.614323000	1.049058000
8	-5.069449000	-1.192333000	-0.579393000
8	4.212486000	1.960404000	-2.360675000
8	4.970754000	-0.494063000	-2.465774000
6	5.680314000	0.969059000	-0.370858000
6	6.593386000	-0.025502000	-0.019263000
6	5.689844000	2.192730000	0.298535000
6	7.515299000	0.203396000	1.001964000
1	6.585110000	-0.990392000	-0.546672000
6	6.612621000	2.422217000	1.319430000
1	4.970389000	2.976775000	0.021431000
6	7.525192000	1.427768000	1.671316000
1	8.234610000	-0.580709000	1.279574000
1	6.620170000	3.387274000	1.846764000
6	-4.682645000	1.350644000	0.128091000
6	-5.015802000	2.169383000	-0.951328000
6	-4.887805000	1.799001000	1.432864000
6	-5.553365000	3.436442000	-0.725923000
1	-4.853219000	1.815917000	-1.979857000
6	-5.426441000	3.066033000	1.658498000
1	-4.625447000	1.153767000	2.283729000
6	-5.759101000	3.884816000	0.579393000
1	-5.815404000	4.082084000	-1.576675000
1	-5.588473000	3.419114000	2.687358000
6	-6.352758000	5.283888000	0.827932000
1	-7.415200000	5.207633000	0.929427000
1	-5.937262000	5.693445000	1.724886000
1	-6.118286000	5.922666000	0.002168000
6	8.543325000	1.680219000	2.798823000
1	8.736611000	0.763996000	3.316583000
1	9.454828000	2.052144000	2.379616000

1	8.145941000	2.399923000	3.483668000

TS(D3b.D4b)

G = -2746.18293

6	-1.469200000	-1.526700000	0.045600000
1	-1.629100000	-2.288800000	0.823500000
1	-1.136100000	-2.066600000	-0.860500000
6	-0.359800000	-0.576300000	0.507400000
1	-0.428800000	-0.361800000	1.582500000
6	0.999700000	-1.136400000	0.065000000
1	0.912500000	-2.230600000	-0.093300000
6	2.264400000	-0.911700000	0.908700000
1	2.364500000	-1.635900000	1.728800000
1	2.294800000	0.104400000	1.332200000
7	3.346400000	-1.136300000	-0.103600000
7	-2.745400000	-0.877300000	-0.247400000
6	-2.720065365	-0.229153340	-1.550623414
1	-2.309665365	-0.924253340	-2.306523414
1	-3.766765365	-0.026653340	-1.822823414
6	-1.588490780	0.584040835	-1.035789874
1	-1.378790780	0.966140835	-2.042489874
6	-2.080390780	1.766640835	-0.454789874
6	-3.005990780	2.710040835	-0.361989874
1	-2.920990780	3.541840835	0.337310126
1	-3.889690780	2.661640835	-1.009889874
6	2.839400000	-0.927900000	-1.496900000
1	2.889400000	-1.881300000	-2.053000000
1	3.432200000	-0.173100000	-2.028700000
6	1.412800000	-0.502500000	-1.251400000
6	0.689400000	0.479200000	-1.814800000
1	0.897700000	0.972100000	-2.771300000
45	-0.026984238	1.484575341	-0.164044376
17	0.479315762	2.623375341	1.844855624
16	-4.179400000	-1.603600000	0.351200000
16	4.882200000	-0.474500000	0.270900000
8	-3.869600000	-2.983600000	0.806900000
8	-5.253800000	-1.359500000	-0.644900000
8	4.837200000	-0.040200000	1.689300000
8	5.297200000	0.472500000	-0.798900000
6	-4.530105230	-0.621171320	1.793503620
6	-5.323033740	0.521447240	1.683237480
6	-4.012325630	-0.993665110	3.033947410
6	-5.597512090	1.291713240	2.813093070
1	-5.730456020	0.815272530	0.705016860
6	-4.287607140	-0.223819990	4.164420090
1	-3.387502610	-1.894295790	3.121065650
6	-5.079946250	0.918800340	4.054172490
1	-6.221981020	2.192699040	2.726146810
1	-3.879563730	-0.517987390	5.142397770
6	5.937804360	-1.903384540	0.159596790
6	6.511832580	-2.253002070	-1.062994970
6	6.191215440	-2.673488430	1.294617040
6	7.338530820	-3.372876020	-1.150596930
1	6.311234430	-1.646104800	-1.957801020

6	7.018934120	-3.793166490	1.207366290
1	5.739016310	-2.397975800	2.258327450
6	7.592478860	-4.143034140	-0.014998660
1	7.790518100	-3.648872260	-2.114355240
1	7.218888410	-4.399934690	2.102533800
6	-5.383274600	1.769479390	5.301544550
1	-5.441277570	2.801261790	5.024126570
1	-6.316121080	1.461107420	5.725341890
1	-4.603179140	1.637124910	6.021845440
6	8.505406820	-5.379457810	-0.112050400
1	8.379901940	-5.841242750	-1.069078720
1	9.525538900	-5.079924400	0.008408240
1	8.245086430	-6.076279530	0.657087280

D4a

G = -2746.22032

6	1.470192000	-1.073240000	0.780811000
1	1.299557000	-2.106646000	0.457135000
1	1.184929000	-0.988651000	1.848701000
6	0.723760000	-0.027587000	-0.059422000
1	0.816190000	-0.320419000	-1.117321000
6	-0.773383000	0.045840000	0.284252000
1	-0.875468000	0.358991000	1.337661000
6	-1.458230000	-1.329791000	0.101833000
1	-1.466067000	-1.942310000	1.010598000
1	-0.953009000	-1.903917000	-0.698512000
7	-2.843859000	-0.970979000	-0.282907000
7	2.878421000	-0.693692000	0.547929000
6	2.946385000	0.778800000	0.688837000
1	3.089883000	1.065566000	1.742001000
1	3.791925000	1.177318000	0.110143000
6	1.585545000	1.280841000	0.129231000
1	1.744731000	1.720490000	-0.862655000
6	0.926216000	2.345718000	0.969826000
6	1.017347000	2.565108000	2.295452000
1	1.593283000	1.915118000	2.964834000
1	0.512171000	3.409193000	2.782580000
6	-2.721593000	0.164352000	-1.223558000
1	-3.669338000	0.714575000	-1.306957000
1	-2.430881000	-0.181619000	-2.234539000
6	-1.614464000	0.983861000	-0.582148000
6	-1.519026000	2.312806000	-0.728513000
1	-2.209982000	2.843202000	-1.404058000
45	-0.348615000	3.566081000	0.190778000
17	0.718516000	4.407816000	-1.609420000
16	4.028321000	-1.580600000	1.471255000
16	-3.794129000	-2.296980000	-0.835340000
8	3.496394000	-2.961299000	1.589401000
8	4.418836000	-0.829735000	2.696544000
8	-3.376803000	-3.473617000	-0.032726000
8	-3.787143000	-2.369554000	-2.321785000
6	-5.418300000	-1.789491000	-0.312922000
6	-6.302305000	-1.225057000	-1.232934000
6	-5.807313000	-1.956183000	1.016150000

6	-7.574773000	-0.826813000	-0.823729000
1	-5.995038000	-1.093069000	-2.280506000
6	-7.080487000	-1.558776000	1.425424000
1	-5.110769000	-2.401191000	1.741355000
6	-7.964163000	-0.994034000	0.505793000
1	-8.271385000	-0.381336000	-1.548697000
1	-7.387077000	-1.690705000	2.473313000
6	5.419814000	-1.589295000	0.361268000
6	6.484590000	-0.712437000	0.570655000
6	5.445793000	-2.472772000	-0.717779000
6	7.574750000	-0.718656000	-0.299250000
1	6.463454000	-0.015511000	1.421002000
6	6.536662000	-2.479801000	-1.587472000
1	4.606749000	-3.164064000	-0.882853000
6	7.601002000	-1.602854000	-1.378472000
1	8.413769000	-0.027102000	-0.134636000
1	6.557058000	-3.176779000	-2.437930000
6	8.804913000	-1.609523000	-2.338761000
1	9.510399000	-2.348649000	-2.021142000
1	8.470075000	-1.838291000	-3.328937000
1	9.270747000	-0.646263000	-2.333417000
6	-9.369286000	-0.554274000	0.957281000
1	-9.697134000	0.266457000	0.354109000
1	-10.051050000	-1.371718000	0.848270000
1	-9.335960000	-0.252014000	1.983160000

D4b

G = -2746.21956

6	1.382057000	-0.744087000	0.361396000
1	1.364859000	-1.325324000	-0.572603000
1	0.935902000	-1.361818000	1.157449000
6	0.655808000	0.606618000	0.220963000
1	0.909319000	1.038952000	-0.759695000
6	-0.865247000	0.506709000	0.337337000
1	-1.134162000	0.320377000	1.395958000
6	-1.488231000	-0.633682000	-0.491477000
1	-1.332718000	-1.625713000	-0.049688000
1	-1.071010000	-0.636734000	-1.514695000
7	-2.928895000	-0.287729000	-0.468803000
7	2.775513000	-0.364649000	0.712262000
6	2.830967000	1.066909000	1.099204000
1	3.446890000	1.205462000	1.994832000
1	3.262987000	1.656365000	0.273664000
6	1.353309000	1.447078000	1.311997000
1	1.042692000	1.051865000	2.298311000
6	1.109018000	2.928951000	1.335994000
6	1.312204000	3.727922000	2.403284000
1	1.210387000	4.818870000	2.357120000
1	1.582049000	3.314363000	3.383823000
6	-3.083100000	1.190271000	-0.440157000
1	-3.786476000	1.470255000	0.363337000
1	-3.474870000	1.578548000	-1.392412000
6	-1.674729000	1.696391000	-0.157608000
6	-1.299859000	2.953416000	-0.429061000

1	-2.023875000	3.639575000	-0.906664000
45	0.328538000	3.961133000	-0.090419000
17	1.516490000	3.498341000	-1.949337000
16	3.660866000	-1.484876000	1.657076000
16	-3.929035000	-1.150140000	-1.560362000
8	2.755614000	-2.589920000	2.072157000
8	4.441289000	-0.734208000	2.676529000
8	-3.178674000	-2.369107000	-1.955642000
8	-4.475966000	-0.234746000	-2.597914000
6	-5.278122000	-1.635252000	-0.505360000
6	-6.400306000	-0.814890000	-0.386279000
6	-5.213480000	-2.835548000	0.202213000
6	-7.457270000	-1.194493000	0.440734000
1	-6.450629000	0.131707000	-0.943651000
6	-6.271109000	-3.215886000	1.028756000
1	-4.329176000	-3.482326000	0.108337000
6	-7.392850000	-2.395544000	1.148226000
1	-8.341548000	-0.547626000	0.535133000
1	-6.220041000	-4.162520000	1.586206000
6	4.808438000	-2.148226000	0.469033000
6	5.967286000	-1.440661000	0.148261000
6	4.549243000	-3.375429000	-0.141164000
6	6.866345000	-1.959936000	-0.783011000
1	6.170960000	-0.472821000	0.628932000
6	5.448963000	-3.895469000	-1.072009000
1	3.636027000	-3.933318000	0.111671000
6	6.607318000	-3.187904000	-1.393106000
1	7.779471000	-1.401986000	-1.036364000
1	5.244540000	-4.863282000	-1.552657000
6	7.600278000	-3.761032000	-2.421286000
1	8.282462000	-4.421764000	-1.928378000
1	7.063242000	-4.299448000	-3.174015000
1	8.145045000	-2.960094000	-2.875851000
6	-8.560125000	-2.814437000	2.061241000
1	-9.019022000	-1.941627000	2.476592000
1	-9.282167000	-3.359336000	1.489716000
1	-8.190215000	-3.433397000	2.851782000

TS(D4a.D5a)

G = -2746.17965

6	1.979169000	-0.512563000	0.669688000
1	2.108681000	-1.604674000	0.666960000
1	1.737173000	-0.196995000	1.701654000
6	0.910000000	-0.045503000	-0.323260000
1	0.996554000	-0.643634000	-1.242955000
6	-0.541130000	-0.147392000	0.189646000
1	-0.570423000	0.177639000	1.242279000
6	-1.130654000	-1.570250000	0.080906000
1	-1.080300000	-2.141097000	1.015123000
1	-0.602842000	-2.145744000	-0.703154000
7	-2.545964000	-1.316891000	-0.281246000
7	3.188907000	0.158596000	0.160455000
6	2.806946000	1.556022000	-0.166183000
1	2.839369000	2.210526000	0.721006000

1	3.490530000	1.969351000	-0.916015000
6	1.359240000	1.417261000	-0.711501000
1	1.345761000	1.525358000	-1.802403000
6	0.442782000	2.422786000	-0.111096000
6	0.192600000	2.904900000	1.216601000
1	1.020047000	3.353668000	1.779492000
1	-0.599953000	2.472991000	1.838671000
6	-2.553404000	-0.181779000	-1.231017000
1	-3.541927000	0.298102000	-1.262356000
1	-2.294990000	-0.508677000	-2.256706000
6	-1.484026000	0.718566000	-0.640506000
6	-1.384266000	2.036679000	-0.870450000
1	-2.076452000	2.447870000	-1.619616000
45	-0.533928000	3.952663000	-0.382960000
17	-0.118102000	6.194346000	-0.099019000
16	4.600763000	0.013970000	1.142000000
16	-3.430469000	-2.711211000	-0.766838000
8	4.220783000	-0.288815000	2.547447000
8	5.446349000	1.193264000	0.832052000
8	-2.836979000	-3.858406000	-0.035265000
8	-3.558129000	-2.754936000	-2.248367000
6	-5.034029000	-2.356896000	-0.080213000
6	-6.052199000	-1.870592000	-0.900768000
6	-5.272760000	-2.565512000	1.278107000
6	-7.308587000	-1.592355000	-0.362905000
1	-5.863444000	-1.705502000	-1.971450000
6	-6.529765000	-2.288173000	1.816097000
1	-4.470449000	-2.948959000	1.924941000
6	-7.547599000	-1.801535000	0.995893000
1	-8.110984000	-1.208449000	-1.009489000
1	-6.717823000	-2.453145000	2.887027000
6	5.357760000	-1.437972000	0.443989000
6	5.383690000	-2.628806000	1.170428000
6	5.924924000	-1.385280000	-0.829234000
6	5.977270000	-3.766461000	0.623964000
1	4.937143000	-2.669814000	2.174498000
6	6.517851000	-2.523457000	-1.376408000
1	5.904418000	-0.446847000	-1.401992000
6	6.544233000	-3.713913000	-0.650010000
1	5.998303000	-4.704958000	1.196746000
1	6.964592000	-2.481725000	-2.380478000
6	-8.935002000	-1.494291000	1.589454000
1	-9.401144000	-0.715853000	1.022316000
1	-9.541743000	-2.374855000	1.552421000
1	-8.826092000	-1.178690000	2.606034000
6	7.199496000	-4.970281000	-1.253143000
1	7.011338000	-5.000144000	-2.306046000
1	8.254987000	-4.940013000	-1.080164000
1	6.787442000	-5.843618000	-0.792280000

TS(D4b.D5b)

G = -2746.19465

6	-1.248659000	-1.090461000	0.576001000
1	-1.260783000	-1.293478000	1.656740000

1	-0.794810000	-1.957207000	0.075343000
6	-0.516210000	0.226632000	0.247609000
1	-0.593604000	0.914140000	1.107014000
6	0.932895000	0.123287000	-0.186500000
1	0.976564000	-0.563417000	-1.056711000
6	1.984930000	-0.366693000	0.817684000
1	1.954958000	-1.454418000	0.974580000
1	1.864645000	0.130785000	1.794398000
7	3.254746000	0.023349000	0.144816000
7	-2.648631000	-0.896156000	0.086710000
6	-2.790231000	0.474387000	-0.450500000
1	-3.519528000	0.502349000	-1.267273000
1	-3.112597000	1.150446000	0.356728000
6	-1.351233000	0.825342000	-0.902167000
1	-1.161446000	0.276191000	-1.842873000
6	-1.095490000	2.263452000	-1.105141000
6	-1.481767000	3.348680000	-1.936115000
1	-0.842786000	3.682834000	-2.761110000
1	-2.551548000	3.551292000	-2.072735000
6	3.019902000	1.145587000	-0.811596000
1	3.262075000	0.811197000	-1.836536000
1	3.648757000	2.012460000	-0.572350000
6	1.539098000	1.431252000	-0.651582000
6	0.977074000	2.645190000	-0.801187000
1	1.607166000	3.421693000	-1.261596000
45	-0.679497000	3.703175000	-0.052790000
17	-1.938369000	5.279798000	1.088753000
16	-3.254772000	-2.149261000	-0.943477000
16	4.648593000	0.108159000	1.138307000
8	-2.411123000	-3.351072000	-0.720007000
8	-3.454961000	-1.627058000	-2.323662000
8	4.250261000	-0.285648000	2.514343000
8	5.343595000	1.398499000	0.889754000
6	5.664193000	-1.191195000	0.468504000
6	5.705923000	-2.437077000	1.095009000
6	6.418218000	-0.963908000	-0.682728000
6	6.502048000	-3.455173000	0.570713000
1	5.111943000	-2.615707000	2.003040000
6	7.213874000	-1.982517000	-1.207872000
1	6.385308000	0.017927000	-1.176740000
6	7.256011000	-3.227978000	-0.581302000
1	6.535477000	-4.437021000	1.064832000
1	7.807964000	-1.803151000	-2.115814000
6	-4.857918000	-2.444996000	-0.228729000
6	-6.009655000	-2.060363000	-0.915774000
6	-4.962769000	-3.061348000	1.018133000
6	-7.265895000	-2.291459000	-0.355704000
1	-5.926629000	-1.573769000	-1.898411000
6	-6.219350000	-3.293478000	1.578069000
1	-4.055129000	-3.364724000	1.559688000
6	-7.370838000	-2.908536000	0.891460000
1	-8.173730000	-1.987748000	-0.896899000
1	-6.301726000	-3.779836000	2.560996000
6	-8.758095000	-3.163635000	1.509556000
1	-9.085621000	-4.150195000	1.255928000

1	-8.696968000	-3.070683000	2.573757000
1	-9.455571000	-2.447271000	1.128438000
6	8.134902000	-4.352369000	-1.160002000
1	8.072330000	-4.340053000	-2.228100000
1	9.150890000	-4.200875000	-0.860472000
1	7.792144000	-5.297412000	-0.793518000

D5a

G = -2746.26856

6	1.694371000	0.022656000	-2.681759000
1	2.223531000	0.327425000	-3.599297000
1	1.224772000	-0.949595000	-2.874770000
6	0.724316000	1.123739000	-2.235827000
1	0.290099000	1.635207000	-3.109689000
6	-0.423644000	0.642961000	-1.333889000
1	-0.043408000	-0.072190000	-0.584492000
6	-1.608044000	-0.013821000	-2.064296000
1	-1.460594000	-1.081923000	-2.262524000
1	-1.806749000	0.497932000	-3.024970000
7	-2.709227000	0.174844000	-1.089900000
7	2.694808000	-0.095495000	-1.586689000
6	2.700921000	1.160854000	-0.785672000
1	2.405015000	0.954299000	0.254990000
1	3.708952000	1.601958000	-0.789472000
6	1.664407000	2.088457000	-1.470899000
1	2.190439000	2.710578000	-2.216891000
6	0.902932000	3.036093000	-0.567453000
6	1.416589000	3.799345000	0.516019000
1	2.451835000	3.652938000	0.836724000
1	0.973081000	4.765774000	0.773851000
6	-2.581925000	1.521245000	-0.483923000
1	-2.920013000	1.502268000	0.564559000
1	-3.186570000	2.277752000	-1.014882000
6	-1.098500000	1.817842000	-0.618636000
6	-0.552956000	3.116551000	-0.652595000
1	-1.128290000	4.040654000	-0.556863000
45	0.050662000	2.319078000	1.180923000
17	0.819347000	2.037779000	3.332665000
16	2.594680000	-1.552894000	-0.674269000
16	-4.280002000	-0.270247000	-1.628231000
8	2.260409000	-2.630792000	-1.640089000
8	1.753204000	-1.385682000	0.546404000
8	-4.094867000	-1.168328000	-2.795377000
8	-5.134735000	0.942307000	-1.739740000
6	-4.868949000	-1.234373000	-0.252729000
6	-5.627799000	-0.628986000	0.749330000
6	-4.571924000	-2.595087000	-0.176690000
6	-6.088910000	-1.384076000	1.827494000
1	-5.861146000	0.443959000	0.689484000
6	-5.033933000	-3.350758000	0.901233000
1	-3.973994000	-3.072424000	-0.966473000
6	-5.792206000	-2.745484000	1.903332000
1	-6.686519000	-0.906839000	2.617687000
1	-4.799934000	-4.423689000	0.960711000

6	4.284445000	-1.744764000	-0.148646000
6	5.326379000	-1.407712000	-1.013077000
6	4.566935000	-2.231959000	1.127438000
6	6.650478000	-1.558490000	-0.601677000
1	5.103341000	-1.024370000	-2.019330000
6	5.891379000	-2.381912000	1.539473000
1	3.745849000	-2.497489000	1.808936000
6	6.933117000	-2.045408000	0.675132000
1	7.471797000	-1.293435000	-1.283202000
1	6.113806000	-2.765679000	2.545814000
6	-6.301573000	-3.578965000	3.093901000
1	-6.329167000	-2.967479000	3.971525000
1	-7.285487000	-3.941345000	2.880605000
1	-5.643977000	-4.407177000	3.256786000
6	8.395258000	-2.211695000	1.129107000
1	8.786492000	-3.129596000	0.742722000
1	8.978058000	-1.392932000	0.761861000
1	8.437125000	-2.228095000	2.198162000

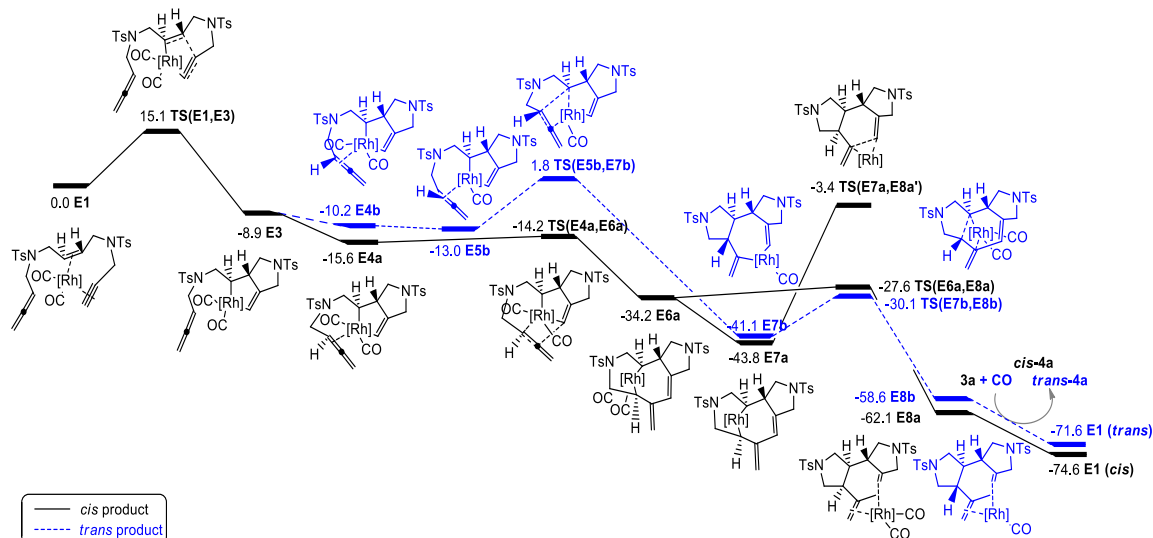
D5b

G = -2746.27613

6	-2.053627000	-0.574484000	-1.662020000
1	-2.013838000	-1.652808000	-1.451862000
1	-2.192371000	-0.439180000	-2.746835000
6	-0.833385000	0.185487000	-1.143376000
1	-0.599105000	-0.177492000	-0.127777000
6	0.466310000	0.209851000	-1.940906000
1	0.232068000	0.435900000	-2.999369000
6	1.375831000	-1.051126000	-1.886894000
1	1.474070000	-1.529848000	-2.871302000
1	1.028242000	-1.805595000	-1.170956000
7	2.746901000	-0.583544000	-1.489606000
7	-3.157941000	0.062892000	-0.883128000
6	-2.713077000	1.351240000	-0.272747000
1	-3.465162000	2.131486000	-0.440417000
1	-2.570079000	1.211217000	0.811262000
6	-1.386872000	1.617774000	-0.984809000
1	-1.623947000	2.004995000	-1.994453000
6	-0.345964000	2.548463000	-0.400937000
6	-0.364507000	3.213741000	0.833888000
1	0.238275000	4.112360000	0.990607000
1	-1.196385000	3.069558000	1.525431000
6	2.780670000	0.874319000	-1.819519000
1	2.953117000	0.946083000	-2.907827000
1	3.597048000	1.393516000	-1.304780000
6	1.393351000	1.322512000	-1.433904000
6	0.960524000	2.612690000	-1.074550000
1	1.557935000	3.524350000	-1.154607000
45	1.168941000	1.668545000	0.766389000
17	0.957778000	1.446058000	3.105200000
16	-4.718473000	-0.001756000	-1.568178000
16	3.105472000	-0.859648000	0.179170000
8	-4.648054000	-0.925951000	-2.730090000
8	-5.259740000	1.374092000	-1.738178000

8	2.360595000	-2.051077000	0.641137000
8	2.987745000	0.444881000	0.957147000
6	4.849712000	-1.213519000	0.150859000
6	5.591155000	-1.161977000	1.331570000
6	5.475266000	-1.542447000	-1.051653000
6	6.957971000	-1.438656000	1.309567000
1	5.097835000	-0.901874000	2.279316000
6	6.842299000	-1.820202000	-1.073670000
1	4.891010000	-1.583290000	-1.982301000
6	7.583721000	-1.768228000	0.106639000
1	7.542572000	-1.397437000	2.240072000
1	7.335171000	-2.079920000	-2.021878000
6	-5.663270000	-0.794062000	-0.284429000
6	-6.362430000	-0.022619000	0.644291000
6	-5.704759000	-2.186121000	-0.206981000
6	-7.102340000	-0.643174000	1.650605000
1	-6.328895000	1.074838000	0.583425000
6	-6.445646000	-2.807030000	0.798985000
1	-5.153915000	-2.794293000	-0.938983000
6	-7.144280000	-2.035832000	1.727803000
1	-7.652942000	-0.035174000	2.383046000
1	-6.478508000	-3.904630000	0.859555000
6	-7.961427000	-2.720718000	2.839020000
1	-7.975677000	-2.096206000	3.707744000
1	-8.963024000	-2.880607000	2.498229000
1	-7.513338000	-3.661201000	3.083165000
6	9.092919000	-2.073754000	0.082703000
1	9.637451000	-1.168427000	-0.086906000
1	9.386280000	-2.495939000	1.021106000
1	9.303626000	-2.769177000	-0.702720000

XYZ coordinates of the catalytic intermediates for the $[\text{RhCl}(\text{CO})_2]_2$ -catalysed $[2+2+2]$ cycloaddition reaction of linear allene-ene-yne substrates



CO

$G = -113.341530$

6	0.000000000	0.000000000	-0.648241000
8	0.000000000	0.000000000	0.486181000

E1

$G = -2511.20911$

6	0.277559000	1.479102000	2.174602000
6	1.394329000	1.598089000	1.671546000
1	-0.557567000	1.310868000	2.830295000
6	1.034719000	0.695176000	-1.261077000
1	0.802660000	0.861941000	-2.322144000
6	2.542482000	0.719929000	-1.072788000
1	2.920176000	1.698110000	-1.410639000
1	2.993786000	-0.039897000	-1.733625000
6	2.813603000	1.527263000	1.284877000
1	3.407311000	1.308862000	2.182399000
7	3.072108000	0.504171000	0.273189000
45	-0.146958000	2.099389000	-0.041811000
16	3.343688000	-1.103337000	0.764089000
8	2.323393000	-2.009395000	0.172611000
8	3.542294000	-1.046628000	2.238467000
6	0.073478000	-0.036762000	-0.521497000
1	0.406628000	-0.510821000	0.401553000
6	-1.051052000	-0.785135000	-1.201409000
1	-0.644231000	-1.757336000	-1.536120000
1	-1.403206000	-0.256244000	-2.096577000
6	-2.079783000	-2.089304000	0.723617000
1	-3.086102000	-2.492958000	0.929284000

1	-1.476453000	-2.922582000	0.334816000
7	-2.220195000	-1.119222000	-0.377519000
16	-3.440787000	0.045619000	-0.200598000
8	-3.451634000	0.627948000	1.172906000
8	-3.340966000	0.938056000	-1.386684000
6	-1.482290000	-1.565072000	2.018035000
6	-0.433290000	-2.086938000	2.608712000
1	-2.009389000	-0.721586000	2.474169000
6	0.619996000	-2.599618000	3.195417000
1	0.518676000	-3.417198000	3.917118000
1	1.624768000	-2.222868000	2.981692000
17	1.358862000	4.163067000	-0.331623000
6	-1.606272000	2.976940000	0.931888000
8	-2.439349000	3.559208000	1.453249000
1	3.117566000	2.499266000	0.869517000
6	-0.956184000	2.536841000	-1.677531000
8	-1.383225000	2.849020000	-2.690048000
6	-4.927707000	-0.955593000	-0.357364000
6	-5.729951000	-1.177669000	0.760408000
6	-5.264054000	-1.470773000	-1.614203000
6	-6.888769000	-1.947220000	0.615894000
1	-5.449957000	-0.747496000	1.722145000
6	-6.422938000	-2.231245000	-1.737736000
1	-4.628672000	-1.268905000	-2.477368000
6	-7.251980000	-2.483886000	-0.627216000
1	-7.521914000	-2.127843000	1.487631000
1	-6.696538000	-2.637016000	-2.714947000
6	4.913739000	-1.478149000	-0.025580000
6	6.082482000	-0.898082000	0.480746000
6	4.942534000	-2.349745000	-1.112942000
6	7.295392000	-1.192395000	-0.134178000
1	6.038789000	-0.235672000	1.346194000
6	6.171923000	-2.629955000	-1.717923000
1	4.017794000	-2.804153000	-1.468965000
6	7.360691000	-2.058134000	-1.243531000
1	8.214573000	-0.746281000	0.253540000
1	6.203560000	-3.310526000	-2.571842000
6	-8.504859000	-3.306879000	-0.791518000
1	-9.017691000	-3.465636000	0.167930000
1	-9.211153000	-2.810211000	-1.477633000
1	-8.274108000	-4.293446000	-1.225845000
6	8.689131000	-2.353813000	-1.892698000
1	9.146442000	-1.430453000	-2.285441000
1	9.397428000	-2.778080000	-1.162125000
1	8.587821000	-3.065140000	-2.724766000

TS(E1.E3)

G = -2511.18505

6	-0.445563000	-3.284878000	-0.117032000
6	-1.195199000	-2.546860000	-0.862180000
1	-0.507205000	-4.292975000	0.283583000
6	-0.853867000	-0.644363000	-1.521897000
1	-0.344974000	-0.950764000	-2.442863000
6	-2.339460000	-0.285890000	-1.728079000

1	-2.505070000	-0.154592000	-2.808670000
1	-2.593582000	0.664308000	-1.242581000
6	-2.575866000	-2.614550000	-1.466493000
1	-3.144742000	-3.430501000	-1.004930000
1	-2.515860000	-2.786977000	-2.553961000
7	-3.264579000	-1.339553000	-1.278650000
45	0.656789000	-1.528310000	0.266055000
16	-3.792305000	-1.089889000	0.363877000
8	-2.717157000	-0.422324000	1.159959000
8	-4.361022000	-2.384645000	0.810334000
6	-0.071858000	0.268180000	-0.706894000
1	-0.658138000	0.806121000	0.043288000
6	0.984432000	1.104303000	-1.401301000
1	0.445427000	1.823581000	-2.053416000
1	1.593841000	0.469947000	-2.052696000
6	1.195134000	2.783370000	0.438912000
1	1.841649000	3.664548000	0.548716000
1	0.247564000	3.132990000	-0.006553000
7	1.862542000	1.836653000	-0.477072000
16	3.335336000	2.403375000	-1.216293000
8	3.236366000	2.148324000	-2.676931000
8	3.603786000	3.772607000	-0.698687000
6	0.944616000	2.177685000	1.805180000
6	-0.237809000	2.114228000	2.370701000
1	1.825859000	1.798387000	2.334906000
6	-1.435006000	2.041963000	2.901191000
1	-1.831807000	2.857067000	3.515642000
1	-2.063375000	1.159560000	2.743160000
6	-0.205780000	-1.404296000	1.952429000
8	-0.617192000	-1.337944000	3.016470000
17	2.095153000	-2.135724000	-1.620020000
6	2.202003000	-0.826447000	1.034125000
8	3.158895000	-0.527111000	1.594519000
6	4.575146000	1.305353000	-0.532944000
6	4.816805000	0.078919000	-1.155822000
6	5.269865000	1.697213000	0.611902000
6	5.754918000	-0.782161000	-0.590688000
1	4.266734000	-0.204411000	-2.051781000
6	6.210691000	0.822190000	1.156484000
1	5.078142000	2.672513000	1.059886000
6	6.460959000	-0.429549000	0.572300000
1	5.936586000	-1.751212000	-1.061196000
1	6.760964000	1.118857000	2.052570000
6	-5.100653000	0.106949000	0.111863000
6	-6.322580000	-0.334384000	-0.407859000
6	-4.888968000	1.440798000	0.460767000
6	-7.342919000	0.593680000	-0.591228000
1	-6.464684000	-1.386837000	-0.655402000
6	-5.927595000	2.356032000	0.266191000
1	-3.933324000	1.752351000	0.884133000
6	-7.162780000	1.950929000	-0.260385000
1	-8.302442000	0.262301000	-0.995660000
1	-5.773283000	3.403374000	0.535153000
6	7.450774000	-1.391292000	1.180419000
1	8.058585000	-0.911921000	1.961653000

1	6.925846000	-2.247143000	1.638247000
1	8.129887000	-1.800772000	0.415658000
6	-8.288442000	2.932630000	-0.465099000
1	-9.157239000	2.664974000	0.159089000
1	-7.987696000	3.958477000	-0.209137000
1	-8.630407000	2.924742000	-1.512974000

E3

G = -2511.22330

6	-0.048898000	-2.978390000	-0.387856000
6	-0.869133000	-2.340691000	-1.234784000
1	-0.136437000	-4.052589000	-0.184439000
6	-0.659615000	-0.878016000	-1.519403000
1	-0.017239000	-0.772453000	-2.410706000
6	-2.095182000	-0.365871000	-1.858231000
1	-2.182885000	-0.106879000	-2.923386000
1	-2.388049000	0.519184000	-1.278361000
6	-2.221561000	-2.735779000	-1.782098000
1	-2.696746000	-3.589602000	-1.285338000
1	-2.176021000	-2.940669000	-2.866266000
7	-3.035732000	-1.497162000	-1.611716000
45	1.155373000	-1.735419000	0.656362000
16	-3.773149000	-1.448205000	-0.044227000
8	-2.785173000	-1.088806000	1.019817000
8	-4.541545000	-2.712902000	0.076047000
6	0.050102000	-0.238079000	-0.331629000
1	-0.665893000	-0.129571000	0.506435000
6	0.709116000	1.068352000	-0.738515000
1	-0.005807000	1.664590000	-1.344427000
1	1.554996000	0.824959000	-1.396387000
6	0.139073000	2.501412000	1.216018000
1	0.445901000	3.530076000	1.456139000
1	-0.802431000	2.556932000	0.644679000
7	1.204159000	1.879871000	0.384965000
16	2.366765000	3.064103000	-0.144436000
8	1.876712000	3.745971000	-1.375165000
8	2.701363000	3.861760000	1.065142000
6	-0.068783000	1.761708000	2.518257000
6	-1.240301000	1.369199000	2.960507000
1	0.824436000	1.608694000	3.132521000
6	-2.417743000	0.983181000	3.388633000
1	-3.044359000	1.647630000	3.993129000
1	-2.808462000	-0.005380000	3.130213000
17	2.687114000	-1.698001000	-1.133106000
6	2.221792000	-0.453529000	1.790905000
8	2.894556000	0.107212000	2.523015000
6	1.952263000	-3.347557000	1.556541000
8	2.394281000	-4.317433000	1.960773000
6	3.773590000	2.043480000	-0.581836000
6	4.007229000	1.736818000	-1.923115000
6	4.630758000	1.604290000	0.429502000
6	5.097089000	0.929437000	-2.246664000
1	3.342291000	2.128066000	-2.693314000
6	5.714236000	0.799069000	0.085342000

1	4.445895000	1.891292000	1.463790000
6	5.954992000	0.436109000	-1.251367000
1	5.281225000	0.673165000	-3.292444000
1	6.386893000	0.443592000	0.869537000
6	-4.894042000	-0.062860000	-0.247812000
6	-4.617922000	1.142529000	0.397455000
6	-6.041385000	-0.232856000	-1.030377000
6	-5.511032000	2.206308000	0.240137000
1	-3.726187000	1.241482000	1.017555000
6	-6.917024000	0.839855000	-1.173119000
1	-6.238837000	-1.191593000	-1.510999000
6	-6.667190000	2.074352000	-0.542866000
1	-5.303524000	3.155007000	0.740584000
1	-7.816518000	0.720195000	-1.782090000
6	7.091302000	-0.489550000	-1.602677000
1	7.454702000	-0.316309000	-2.626691000
1	7.936892000	-0.376273000	-0.907528000
1	6.753675000	-1.539018000	-1.544582000
6	-7.636794000	3.217164000	-0.708325000
1	-7.799176000	3.444537000	-1.774592000
1	-8.620124000	2.959585000	-0.280512000
1	-7.278947000	4.130966000	-0.212896000

E4a

G = -2511.22537

6	2.631289000	0.044795000	0.511870000
1	2.461872000	0.151404000	1.596393000
1	2.891131000	-1.001300000	0.304423000
6	3.163131000	2.289849000	-0.247122000
1	3.490851000	3.049424000	0.477386000
1	3.520054000	2.603945000	-1.239877000
6	1.671438000	2.053285000	-0.191808000
6	1.433575000	0.571771000	-0.293570000
1	1.624499000	0.275984000	-1.343211000
7	3.750505000	0.955572000	0.125410000
6	-0.001925000	0.162216000	0.092537000
1	-0.011463000	-0.418273000	1.028191000
6	-0.615927000	-0.701290000	-1.014487000
1	-0.179797000	-1.709234000	-0.946050000
1	-0.348298000	-0.301788000	-2.007116000
6	0.653131000	2.879181000	0.070520000
1	0.752717000	3.958909000	0.224588000
6	-2.797380000	0.118454000	-1.815954000
1	-2.563657000	-0.107190000	-2.871318000
1	-3.877935000	-0.016602000	-1.669505000
7	-2.089407000	-0.814975000	-0.917498000
16	-2.659092000	-2.449524000	-1.107127000
16	4.752045000	0.300330000	-1.110253000
8	-1.739996000	-3.284928000	-0.292791000
8	-2.881376000	-2.748153000	-2.547940000
8	5.630610000	1.416455000	-1.545995000
8	3.954988000	-0.446728000	-2.128388000
45	-1.155253000	1.927888000	0.466180000
6	-2.480485000	1.592713000	-1.538949000

1	-3.305162000	2.230887000	-1.206027000
6	-1.387652000	2.206091000	-2.019590000
6	-0.474529000	2.742466000	-2.788095000
1	0.508303000	3.032402000	-2.416047000
1	-0.719479000	2.916996000	-3.840959000
6	-2.756976000	0.963667000	1.186719000
8	-3.640802000	0.497429000	1.733206000
17	-2.382148000	4.085959000	0.720130000
6	-0.322355000	2.092614000	2.132609000
8	0.170968000	2.197356000	3.157553000
6	-4.252845000	-2.371024000	-0.290292000
6	-4.301353000	-2.443849000	1.105324000
6	-5.413514000	-2.284829000	-1.059818000
6	-5.542142000	-2.399404000	1.734043000
1	-3.379502000	-2.537748000	1.679546000
6	-6.649043000	-2.238381000	-0.408586000
1	-5.344587000	-2.265893000	-2.147955000
6	-6.732752000	-2.291311000	0.990931000
1	-5.592383000	-2.450081000	2.824301000
1	-7.563472000	-2.166682000	-1.001718000
6	5.703426000	-0.895264000	-0.166512000
6	6.580184000	-0.438390000	0.823891000
6	5.580200000	-2.250855000	-0.465422000
6	7.333081000	-1.370952000	1.531274000
1	6.663148000	0.628910000	1.031644000
6	6.346114000	-3.171500000	0.256403000
1	4.896290000	-2.571293000	-1.251875000
6	7.228968000	-2.749449000	1.260590000
1	8.019168000	-1.027260000	2.309488000
1	6.254546000	-4.236439000	0.030582000
6	-8.062775000	-2.245608000	1.699544000
1	-8.896406000	-2.109280000	0.996070000
1	-8.238069000	-3.178532000	2.260807000
1	-8.089579000	-1.420368000	2.429797000
6	8.062849000	-3.736510000	2.038150000
1	9.137650000	-3.566338000	1.858650000
1	7.896142000	-3.625597000	3.122171000
1	7.831833000	-4.774648000	1.759652000

E4b

$G = -2511.23397$

6	0.573527000	2.883145000	-0.644588000
6	1.260401000	2.018754000	-1.392663000
1	0.931266000	3.894159000	-0.418775000
6	0.735823000	0.602737000	-1.541144000
1	0.118191000	0.501334000	-2.446273000
6	2.040257000	-0.243183000	-1.672885000
1	2.155075000	-0.641766000	-2.692042000
1	2.087791000	-1.087388000	-0.972509000
6	2.692862000	2.040985000	-1.851019000
1	3.308972000	2.831504000	-1.409339000
1	2.790313000	2.080934000	-2.950011000
7	3.183908000	0.689135000	-1.440522000
45	-1.237136000	2.143750000	0.056571000

16	3.815252000	0.629499000	0.167724000
8	2.797285000	0.199927000	1.174654000
8	4.552467000	1.904835000	0.371916000
6	-0.089560000	0.384602000	-0.276236000
1	0.645454000	0.433989000	0.533450000
6	-0.863696000	-0.906987000	-0.127506000
1	-0.158413000	-1.761304000	-0.130716000
1	-1.587262000	-1.049956000	-0.944826000
6	-0.944900000	-0.172378000	2.268529000
1	-1.410666000	-0.508948000	3.204398000
1	0.130561000	-0.401750000	2.313468000
7	-1.617604000	-0.880646000	1.159193000
16	-2.253122000	-2.425089000	1.611058000
8	-1.224122000	-3.485405000	1.431575000
8	-2.898200000	-2.224582000	2.936152000
6	-1.159958000	1.343753000	2.199578000
6	-0.145316000	2.241906000	2.017041000
1	-2.096419000	1.703248000	2.637141000
6	0.957237000	2.868936000	2.365370000
1	1.328266000	2.749340000	3.387956000
1	1.538386000	3.482187000	1.678617000
17	-1.997396000	2.253683000	-2.262688000
6	-1.906226000	4.046028000	0.352218000
8	-2.117808000	5.158730000	0.462940000
6	-3.075187000	1.299659000	0.236544000
8	-4.154538000	0.937215000	0.218700000
6	-3.521728000	-2.650851000	0.364873000
6	-4.768109000	-2.044849000	0.548356000
6	-3.248696000	-3.440221000	-0.752182000
6	-5.745156000	-2.216808000	-0.428145000
1	-4.960568000	-1.452573000	1.442472000
6	-4.242216000	-3.598638000	-1.721454000
1	-2.276111000	-3.922618000	-0.852099000
6	-5.497738000	-2.988708000	-1.578647000
1	-6.721145000	-1.742919000	-0.298432000
1	-4.036774000	-4.210246000	-2.602925000
6	4.989188000	-0.720394000	-0.005824000
6	4.750794000	-1.926101000	0.650832000
6	6.142342000	-0.519823000	-0.772961000
6	5.684066000	-2.959903000	0.520817000
1	3.852657000	-2.045317000	1.257152000
6	7.060043000	-1.559556000	-0.887271000
1	6.311935000	0.438220000	-1.265627000
6	6.845878000	-2.795458000	-0.246107000
1	5.503826000	-3.909169000	1.030749000
1	7.964646000	-1.413585000	-1.483014000
6	7.853010000	-3.908168000	-0.394749000
1	7.917607000	-4.239606000	-1.444837000
1	8.860340000	-3.569892000	-0.101570000
1	7.591072000	-4.780375000	0.221216000
6	-6.572644000	-3.152524000	-2.623258000
1	-7.462352000	-3.644495000	-2.196198000
1	-6.898839000	-2.171526000	-3.005966000
1	-6.225593000	-3.754304000	-3.475274000

E5b

G = -2397.88830

6	-0.195052000	-2.157283000	0.095877000
6	-0.991824000	-1.595602000	-0.815892000
1	-0.346282000	-3.142135000	0.548515000
6	-0.732437000	-0.169256000	-1.276550000
1	-0.099359000	-0.174572000	-2.176718000
6	-2.161250000	0.348731000	-1.625932000
1	-2.293382000	0.452301000	-2.713671000
1	-2.402351000	1.309082000	-1.155128000
6	-2.369131000	-1.993891000	-1.273686000
1	-2.844301000	-2.778670000	-0.676773000
1	-2.393073000	-2.284690000	-2.338363000
7	-3.121632000	-0.706614000	-1.178614000
45	1.329286000	-0.942450000	0.654049000
16	-3.843268000	-0.411914000	0.367291000
8	-3.168078000	0.717494000	1.070816000
8	-3.989222000	-1.729705000	1.048458000
6	0.008019000	0.489827000	-0.109558000
1	-0.739020000	0.717916000	0.662357000
6	0.964281000	1.659707000	-0.292010000
1	0.503525000	2.663814000	-0.257763000
1	1.533899000	1.556496000	-1.226316000
6	1.317565000	1.506956000	2.202333000
1	1.976525000	2.037905000	2.899058000
1	0.344239000	2.015263000	2.175353000
7	1.936003000	1.496852000	0.845296000
16	3.403570000	2.442739000	0.693372000
8	3.084264000	3.716304000	-0.002224000
8	4.015998000	2.443515000	2.048670000
6	1.195624000	0.048571000	2.641221000
6	0.061545000	-0.692397000	2.558298000
1	2.059973000	-0.347893000	3.184114000
6	-1.130486000	-1.161407000	2.845229000
1	-1.598021000	-0.872254000	3.791983000
1	-1.702745000	-1.794938000	2.167746000
17	2.318412000	-1.246952000	-1.494524000
6	2.519088000	-2.437873000	1.303098000
8	3.103468000	-3.379500000	1.577960000
6	-5.479300000	0.156680000	-0.115471000
6	-6.410837000	-0.778196000	-0.579791000
6	-5.798840000	1.507584000	0.002937000
6	-7.677987000	-0.335382000	-0.947605000
1	-6.143935000	-1.833831000	-0.641610000
6	-7.077258000	1.932466000	-0.373521000
1	-5.059906000	2.208658000	0.391510000
6	-8.030963000	1.024823000	-0.855018000
1	-8.413766000	-1.057495000	-1.310641000
1	-7.335918000	2.990245000	-0.284987000
6	4.377452000	1.408941000	-0.386934000
6	5.066077000	0.324949000	0.164437000
6	4.427673000	1.698185000	-1.748976000
6	5.796868000	-0.499705000	-0.683934000
1	5.026989000	0.140364000	1.238396000

6	5.164769000	0.855483000	-2.582431000
1	3.899329000	2.566869000	-2.142129000
6	5.846519000	-0.257091000	-2.068373000
1	6.334026000	-1.355510000	-0.268457000
1	5.204974000	1.064927000	-3.653722000
6	-9.408382000	1.477922000	-1.269939000
1	-9.572550000	1.295626000	-2.345306000
1	-10.187947000	0.919416000	-0.726319000
1	-9.559555000	2.550306000	-1.080410000
6	6.588350000	-1.201199000	-2.978769000
1	7.516947000	-1.565445000	-2.512726000
1	5.961961000	-2.083935000	-3.195316000
1	6.841456000	-0.728356000	-3.939039000

TS(E4a.E6a)

G = -2511.23174

6	-1.435322000	-0.344722000	-1.868403000
1	-1.510146000	0.222562000	-2.811504000
1	-1.138511000	-1.375838000	-2.091601000
6	-2.889698000	0.982264000	-0.536199000
1	-3.340838000	1.704480000	-1.236723000
1	-3.546899000	0.921871000	0.342216000
6	-1.463308000	1.368598000	-0.212153000
6	-0.532763000	0.361891000	-0.838463000
1	-0.321295000	-0.386850000	-0.059093000
7	-2.789824000	-0.326675000	-1.240510000
6	0.793061000	0.993027000	-1.278373000
1	0.754306000	1.286677000	-2.339624000
6	1.972403000	0.030242000	-1.100071000
1	2.905180000	0.465008000	-1.500493000
1	1.768334000	-0.888047000	-1.672683000
6	-0.953061000	2.407060000	0.459543000
1	-1.523116000	3.170779000	0.994523000
6	2.805354000	0.604572000	1.193643000
1	3.080075000	0.084536000	2.122188000
1	3.731269000	1.004339000	0.743090000
7	2.177244000	-0.350243000	0.298189000
16	2.003839000	-1.963299000	0.770024000
16	-3.039955000	-1.657385000	-0.155805000
8	0.915384000	-2.524251000	-0.068861000
8	1.937667000	-1.954287000	2.253088000
8	-2.470077000	-1.370814000	1.195071000
8	-2.628261000	-2.872953000	-0.900133000
45	1.031820000	2.830893000	-0.160720000
6	1.874665000	1.766579000	1.561590000
1	2.350174000	2.595484000	2.097853000
6	0.563083000	1.477862000	1.888089000
6	-0.285184000	0.770192000	2.600245000
1	-1.346108000	0.652922000	2.398401000
1	0.154546000	0.220876000	3.441924000
6	2.843431000	3.175322000	-0.788889000
8	3.902893000	3.397292000	-1.152464000
6	0.128049000	3.821043000	-1.575093000
8	-0.445728000	4.399642000	-2.372396000

17	1.091878000	4.918125000	1.231066000
6	-4.831054000	-1.609796000	-0.015731000
6	-5.411955000	-1.332319000	1.220191000
6	-5.608587000	-1.891814000	-1.144609000
6	-6.806734000	-1.323153000	1.322145000
1	-4.776992000	-1.133102000	2.083908000
6	-6.994745000	-1.876278000	-1.022755000
1	-5.128377000	-2.115862000	-2.097647000
6	-7.615855000	-1.590949000	0.209011000
1	-7.270866000	-1.105805000	2.286978000
1	-7.612754000	-2.091578000	-1.898103000
6	3.534746000	-2.776419000	0.287503000
6	4.619714000	-2.768261000	1.167630000
6	3.620958000	-3.389199000	-0.966236000
6	5.818746000	-3.359568000	0.766092000
1	4.516402000	-2.323539000	2.157992000
6	4.828055000	-3.974663000	-1.348060000
1	2.746503000	-3.423521000	-1.616691000
6	5.945442000	-3.964418000	-0.495300000
1	6.669134000	-3.361610000	1.452220000
1	4.900569000	-4.461389000	-2.323885000
6	-9.120422000	-1.580621000	0.310868000
1	-9.539023000	-2.561599000	0.031207000
1	-9.459003000	-1.342611000	1.329360000
1	-9.555419000	-0.837104000	-0.377505000
6	7.249193000	-4.581806000	-0.935755000
1	7.909590000	-4.789584000	-0.081205000
1	7.081559000	-5.523209000	-1.481784000
1	7.789497000	-3.902228000	-1.617526000

TS(E5b.E6b)

G = -2397.86471

6	-1.710524000	-3.005304000	-0.537210000
6	-2.054897000	-2.039568000	-1.394459000
1	-2.392701000	-3.736249000	-0.095223000
6	-1.033169000	-0.939398000	-1.671724000
1	-0.372525000	-1.160514000	-2.527094000
6	-1.939958000	0.283240000	-2.007912000
1	-1.950877000	0.462425000	-3.094532000
1	-1.624738000	1.214934000	-1.525085000
6	-3.416468000	-1.554712000	-1.849449000
1	-4.261634000	-1.985145000	-1.297659000
1	-3.587052000	-1.705522000	-2.928633000
7	-3.322949000	-0.080431000	-1.627682000
45	0.284685000	-2.887621000	-0.204641000
16	-3.842491000	0.356297000	-0.014623000
8	-3.045982000	-0.315773000	1.054980000
8	-5.311957000	0.149279000	-0.038939000
6	-0.241622000	-0.850118000	-0.369190000
1	-0.977684000	-0.668257000	0.419194000
6	0.861026000	0.171601000	-0.268752000
1	0.421947000	1.176027000	-0.416605000
1	1.645450000	0.016991000	-1.021486000
6	0.794568000	-0.710596000	2.100003000

1	1.348321000	-0.582395000	3.042051000
1	-0.247867000	-0.401725000	2.277489000
7	1.480562000	0.105963000	1.084535000
16	2.014544000	1.623427000	1.658077000
8	0.963649000	2.675838000	1.498023000
8	2.582578000	1.382626000	3.010337000
6	0.861701000	-2.182627000	1.754341000
6	-0.272754000	-3.005037000	1.788368000
1	1.857249000	-2.630837000	1.842848000
6	-1.212678000	-3.582048000	2.515014000
1	-1.179463000	-3.497809000	3.605766000
1	-2.033891000	-4.148132000	2.074131000
17	2.467894000	-2.568398000	-1.199317000
6	0.572453000	-4.905657000	-0.179538000
8	0.689241000	-6.034234000	-0.093562000
6	-3.442009000	2.103653000	0.020228000
6	-2.283747000	2.522552000	0.682090000
6	-4.297037000	3.011966000	-0.608857000
6	-1.965863000	3.880410000	0.688247000
1	-1.630012000	1.807129000	1.179220000
6	-3.967563000	4.366959000	-0.580523000
1	-5.204681000	2.658007000	-1.098992000
6	-2.799133000	4.820122000	0.058923000
1	-1.048636000	4.195685000	1.189204000
1	-4.632024000	5.089080000	-1.061233000
6	3.320189000	1.960445000	0.472379000
6	4.297294000	0.987038000	0.233650000
6	3.350417000	3.199550000	-0.165100000
6	5.319237000	1.274593000	-0.666305000
1	4.236238000	0.015399000	0.723968000
6	4.390501000	3.470802000	-1.058764000
1	2.567362000	3.931355000	0.034781000
6	5.385568000	2.518495000	-1.322715000
1	6.079365000	0.516895000	-0.871375000
1	4.423452000	4.439347000	-1.563154000
6	-2.434848000	6.283521000	0.046237000
1	-1.817937000	6.552412000	0.916416000
1	-1.852026000	6.527513000	-0.859275000
1	-3.330442000	6.923153000	0.041122000
6	6.504712000	2.800715000	-2.293334000
1	6.497989000	2.072803000	-3.121540000
1	6.427646000	3.809439000	-2.723920000
1	7.485423000	2.713884000	-1.797004000

E6a

G = -2511.26361

6	0.707137000	2.776359000	-0.599986000
6	1.433663000	1.768103000	-1.090896000
1	1.151320000	3.778074000	-0.633837000
6	1.098185000	0.285144000	-1.219977000
1	0.466547000	0.146126000	-2.112538000
6	2.482942000	-0.388576000	-1.470054000
1	2.577071000	-0.715584000	-2.515837000
1	2.662707000	-1.266034000	-0.834237000

6	2.864459000	1.928020000	-1.582027000
1	3.406335000	2.774625000	-1.145285000
1	2.903599000	2.018710000	-2.682344000
7	3.526151000	0.642594000	-1.247657000
45	-1.165044000	2.763047000	0.276279000
16	4.188736000	0.622180000	0.350626000
8	3.168104000	0.276075000	1.386635000
8	4.964733000	1.881688000	0.480702000
6	0.355509000	-0.302498000	-0.020748000
1	1.012713000	-0.236444000	0.855511000
6	-0.088279000	-1.777964000	-0.218634000
1	0.497862000	-2.450083000	0.428940000
1	0.023327000	-2.119276000	-1.256843000
6	-1.813398000	-0.651883000	1.025537000
1	-2.886216000	-0.417493000	1.034230000
1	-1.463551000	-0.834749000	2.057751000
7	-1.534282000	-1.780937000	0.128004000
16	-2.193658000	-3.288529000	0.594397000
8	-1.569788000	-4.278610000	-0.318848000
8	-2.108915000	-3.460392000	2.070838000
6	-0.975502000	0.420159000	0.315576000
6	-1.653307000	1.126675000	-0.788441000
1	-0.696543000	1.203296000	1.158749000
6	-2.308874000	0.768407000	-1.882242000
1	-2.749088000	1.517567000	-2.543248000
1	-2.415493000	-0.291475000	-2.138746000
17	-1.784071000	4.388252000	-1.356742000
6	-3.072171000	2.817774000	0.976363000
8	-4.171830000	2.858558000	1.263557000
6	-0.413749000	4.114583000	1.582793000
8	0.057610000	4.864507000	2.296560000
6	-3.913264000	-3.035420000	0.151494000
6	-4.858122000	-2.835186000	1.156186000
6	-4.270724000	-3.049646000	-1.201300000
6	-6.191968000	-2.625837000	0.792341000
1	-4.548772000	-2.848984000	2.201697000
6	-5.603469000	-2.839729000	-1.542370000
1	-3.512868000	-3.228761000	-1.964925000
6	-6.583356000	-2.621110000	-0.554254000
1	-6.940243000	-2.466604000	1.572131000
1	-5.895677000	-2.847477000	-2.595367000
6	5.309088000	-0.773838000	0.204070000
6	5.048836000	-1.938986000	0.923369000
6	6.441445000	-0.651487000	-0.609199000
6	5.938106000	-3.012272000	0.811108000
1	4.167290000	-1.996314000	1.562368000
6	7.314757000	-1.730681000	-0.706226000
1	6.627385000	0.275464000	-1.152673000
6	7.077770000	-2.926884000	-0.001091000
1	5.740560000	-3.930483000	1.369082000
1	8.201327000	-1.647888000	-1.339915000
6	8.044261000	-4.078234000	-0.120398000
1	8.198083000	-4.356106000	-1.175906000
1	9.031429000	-3.802982000	0.287358000
1	7.688994000	-4.966869000	0.420690000

6	-8.018788000	-2.389564000	-0.953663000
1	-8.109967000	-1.484567000	-1.577112000
1	-8.400839000	-3.232825000	-1.552158000
1	-8.671899000	-2.267494000	-0.077797000

E7a

G = -2397.93308

6	2.083159000	0.326270000	0.111889000
1	2.458352000	1.358055000	0.017556000
1	2.414933000	-0.085457000	1.073530000
6	1.540154000	-0.595968000	-2.087692000
1	1.952378000	-0.327007000	-3.068590000
1	1.126912000	-1.615828000	-2.142686000
6	0.507948000	0.373454000	-1.579559000
6	0.563143000	0.249900000	-0.080583000
1	0.305488000	-0.806408000	0.128807000
7	2.609717000	-0.490159000	-1.029309000
6	-0.364237000	1.068908000	0.800646000
1	0.043419000	1.121854000	1.822286000
6	-1.760308000	0.428208000	0.871931000
1	-2.413884000	0.983100000	1.564376000
1	-1.654901000	-0.592075000	1.274756000
6	-0.097818000	1.321597000	-2.295352000
1	0.040582000	1.351512000	-3.381340000
6	-3.050052000	1.537429000	-0.967549000
1	-3.507056000	1.286412000	-1.936329000
1	-3.854434000	1.874133000	-0.287043000
7	-2.401475000	0.342341000	-0.443895000
16	-2.691364000	-1.165411000	-1.136813000
16	3.230081000	-2.014400000	-0.552233000
8	-1.484553000	-1.996219000	-0.887881000
8	-3.183720000	-0.901486000	-2.512485000
8	3.407741000	-2.780426000	-1.812337000
8	2.439428000	-2.601864000	0.568556000
45	-0.689524000	3.055352000	0.346016000
6	-2.075203000	2.677703000	-1.158258000
1	-2.577134000	3.645081000	-1.305528000
6	-0.758495000	2.527951000	-1.727599000
6	0.067734000	3.665981000	-1.522178000
1	1.134870000	3.595346000	-1.749940000
1	-0.356653000	4.680607000	-1.546640000
17	-1.015990000	3.585767000	2.588461000
6	-4.034398000	-1.880006000	-0.176857000
6	-5.353352000	-1.524933000	-0.481579000
6	-3.740497000	-2.750306000	0.874128000
6	-6.385268000	-2.036976000	0.301943000
1	-5.561578000	-0.869197000	-1.327993000
6	-4.790268000	-3.251363000	1.648557000
1	-2.707210000	-3.039032000	1.068255000
6	-6.122332000	-2.903148000	1.379507000
1	-7.418659000	-1.766336000	0.070654000
1	-4.566887000	-3.932213000	2.473239000
6	4.834916000	-1.532637000	0.097512000
6	5.103176000	-1.698241000	1.454797000

6	5.800409000	-1.034349000	-0.784469000
6	6.364485000	-1.339461000	1.941117000
1	4.334517000	-2.106024000	2.112004000
6	7.049470000	-0.682959000	-0.281243000
1	5.569266000	-0.928986000	-1.845033000
6	7.351222000	-0.827032000	1.087060000
1	6.583065000	-1.464382000	3.004228000
1	7.811270000	-0.292146000	-0.960584000
6	-7.258391000	-3.455961000	2.203338000
1	-7.934784000	-2.652161000	2.535911000
1	-7.863166000	-4.161905000	1.609080000
1	-6.894318000	-3.990147000	3.092749000
6	8.710579000	-0.430781000	1.606463000
1	9.510781000	-0.944387000	1.048849000
1	8.876104000	0.652726000	1.482472000
1	8.826140000	-0.672001000	2.672881000

E7b

G = -2284.59585

6	-1.038183000	-2.301587000	0.743929000
6	-1.236134000	-1.619736000	-0.458629000
1	-1.556165000	-3.267473000	0.785420000
6	-0.852433000	-0.181745000	-0.807383000
1	-0.528414000	-0.147873000	-1.860426000
6	-2.230003000	0.507375000	-0.701411000
1	-2.352891000	1.357099000	-1.385508000
1	-2.416754000	0.834482000	0.331847000
6	-2.423401000	-1.865212000	-1.357372000
1	-3.036056000	-2.739209000	-1.110663000
1	-2.166225000	-1.893596000	-2.425845000
7	-3.191467000	-0.592476000	-1.095360000
45	0.964024000	-2.027857000	-0.233458000
16	-4.439210000	-0.841700000	0.085983000
8	-3.885697000	-0.853288000	1.472057000
8	-5.213350000	-2.011157000	-0.401908000
6	0.296119000	-0.013615000	0.130969000
1	-0.162600000	0.029833000	1.124371000
6	1.467079000	0.911976000	0.151191000
1	1.096753000	1.939798000	0.344167000
1	2.041501000	0.915094000	-0.787551000
6	1.753593000	-0.396263000	2.337198000
1	2.593785000	-0.647514000	2.992627000
1	1.023735000	0.177339000	2.940628000
7	2.338786000	0.453785000	1.259682000
16	3.422808000	1.655213000	1.800621000
8	2.715942000	2.952797000	2.012248000
8	4.196333000	1.052644000	2.916524000
6	1.081337000	-1.697284000	1.822907000
6	-0.399153000	-1.868057000	2.050124000
1	1.649396000	-2.581872000	2.151077000
6	-1.113018000	-1.729500000	3.172157000
1	-0.629972000	-1.439414000	4.108937000
1	-2.195689000	-1.876626000	3.168760000
17	3.312180000	-2.151417000	-0.330426000

6	0.914198000	-2.372306000	-2.224451000
8	0.954321000	-2.492980000	-3.358837000
6	4.478009000	1.835745000	0.358498000
6	5.278547000	0.758318000	-0.035917000
6	4.498105000	3.051259000	-0.323783000
6	6.103991000	0.912751000	-1.146113000
1	5.235194000	-0.184749000	0.507209000
6	5.337752000	3.186817000	-1.433392000
1	3.866012000	3.872139000	0.015838000
6	6.148407000	2.125078000	-1.860650000
1	6.725344000	0.074260000	-1.470248000
1	5.361337000	4.135776000	-1.974593000
6	-5.380552000	0.667000000	-0.131601000
6	-5.417427000	1.600727000	0.903032000
6	-6.083566000	0.862198000	-1.325975000
6	-6.167413000	2.767195000	0.727489000
1	-4.871788000	1.409162000	1.827402000
6	-6.822852000	2.031112000	-1.480192000
1	-6.047854000	0.107960000	-2.112706000
6	-6.876004000	3.001069000	-0.459959000
1	-6.203222000	3.505445000	1.531779000
1	-7.376583000	2.197320000	-2.407467000
6	7.057555000	2.264634000	-3.056110000
1	8.114303000	2.158517000	-2.758576000
1	6.853087000	1.478035000	-3.800976000
1	6.939550000	3.241397000	-3.547258000
6	-7.684011000	4.258809000	-0.655996000
1	-8.734447000	4.017893000	-0.887710000
1	-7.667999000	4.898072000	0.238202000
1	-7.293928000	4.846293000	-1.503843000

TS(E7b.E8b)

G = -2511.25310

6	2.265252000	-0.484613000	-0.417940000
1	2.168636000	-1.086361000	-1.335057000
1	2.380970000	0.571413000	-0.694635000
6	2.972524000	-2.175960000	1.064387000
1	3.200162000	-3.060869000	0.447397000
1	3.508948000	-2.280026000	2.017187000
6	1.467954000	-2.030425000	1.206932000
6	1.061016000	-0.746066000	0.519688000
1	1.129082000	0.030110000	1.302102000
7	3.442630000	-0.979651000	0.322464000
6	-0.286961000	-0.575666000	-0.184737000
1	-0.116826000	-0.625212000	-1.286143000
6	-0.971687000	0.747966000	0.140477000
1	-1.497363000	1.155840000	-0.734644000
1	-0.212895000	1.484976000	0.460814000
6	0.698844000	-2.945834000	1.810494000
1	1.185295000	-3.817678000	2.258717000
6	-1.539090000	-0.565429000	2.097686000
1	-0.563595000	-0.383858000	2.579325000
1	-2.290302000	-0.675504000	2.893004000
7	-1.961963000	0.523855000	1.215866000

16	-2.496408000	1.953658000	2.016017000
16	4.185278000	0.220771000	1.317930000
8	-1.352553000	2.867753000	2.279085000
8	-3.358961000	1.481548000	3.129010000
8	5.119962000	-0.518007000	2.204851000
8	3.181768000	1.152979000	1.912773000
45	-1.582944000	-2.122171000	-1.130517000
6	-1.550276000	-1.840843000	1.273230000
1	-2.589645000	-2.127726000	1.096360000
6	-0.757903000	-2.986812000	1.776101000
6	-1.433517000	-4.076241000	2.214179000
1	-0.905899000	-4.916787000	2.671379000
1	-2.520212000	-4.146974000	2.136259000
6	-3.093105000	-1.017707000	-1.192533000
8	-4.030477000	-0.366394000	-1.319355000
17	0.357054000	-3.487579000	-1.469948000
6	-2.465889000	-3.426239000	-2.215110000
8	-2.978567000	-4.240974000	-2.832452000
6	5.108655000	1.128653000	0.073207000
6	6.135808000	0.479066000	-0.620676000
6	4.809548000	2.471202000	-0.151134000
6	6.861084000	1.197262000	-1.566517000
1	6.353460000	-0.570466000	-0.420455000
6	5.551576000	3.175328000	-1.104863000
1	4.011019000	2.949867000	0.416555000
6	6.581247000	2.553450000	-1.824942000
1	7.663622000	0.700473000	-2.117459000
1	5.324277000	4.227981000	-1.288492000
6	-3.513036000	2.676280000	0.727734000
6	-4.770389000	2.121774000	0.468331000
6	-3.040014000	3.781306000	0.021051000
6	-5.554230000	2.683002000	-0.535080000
1	-5.119701000	1.265465000	1.045415000
6	-3.842736000	4.329993000	-0.983129000
1	-2.063455000	4.202383000	0.261712000
6	-5.104398000	3.791671000	-1.277071000
1	-6.535745000	2.254349000	-0.751490000
1	-3.480954000	5.194549000	-1.544426000
6	-5.978470000	4.384657000	-2.353284000
1	-6.888407000	4.828508000	-1.915357000
1	-5.456219000	5.170759000	-2.917305000
1	-6.308367000	3.610294000	-3.064706000
6	7.381368000	3.305383000	-2.858837000
1	7.258651000	2.850697000	-3.856082000
1	7.075510000	4.359390000	-2.924644000
1	8.457506000	3.274469000	-2.621543000

TS(E7a.E8a)

G = -2397.91555

6	-1.193877000	-1.270202000	-1.785315000
1	-1.164971000	-1.303226000	-2.887075000
1	-1.253421000	-2.295942000	-1.406235000
6	-2.016955000	0.913465000	-1.573069000
1	-2.160639000	1.177547000	-2.635469000

1	-2.651925000	1.577032000	-0.972345000
6	-0.545424000	0.965813000	-1.189362000
6	-0.007447000	-0.462275000	-1.221678000
1	0.211597000	-0.824088000	-0.202957000
7	-2.410474000	-0.508102000	-1.418274000
6	1.268202000	-0.466362000	-2.062454000
1	1.023097000	-0.034098000	-3.045810000
6	2.028009000	-1.801026000	-2.282628000
1	2.081770000	-2.040488000	-3.354810000
1	1.553736000	-2.656319000	-1.786644000
6	0.163570000	2.099819000	-1.006489000
1	-0.314867000	3.058497000	-1.229469000
6	3.664328000	-0.140986000	-1.749413000
1	4.467230000	0.100237000	-1.043931000
1	3.979857000	0.170569000	-2.758861000
7	3.402688000	-1.591806000	-1.776143000
16	3.832791000	-2.539158000	-0.403330000
16	-2.967604000	-0.861235000	0.191977000
8	5.060873000	-1.910650000	0.142414000
8	3.803154000	-3.937751000	-0.893452000
8	-2.333617000	0.054998000	1.186083000
8	-2.843154000	-2.333330000	0.357354000
45	1.741720000	2.241943000	0.361409000
6	2.303126000	0.471211000	-1.392954000
1	2.203247000	0.268666000	-0.281305000
6	1.995714000	1.924337000	-1.616178000
6	2.389736000	2.729288000	-2.617102000
1	2.076892000	3.773260000	-2.662703000
1	3.021463000	2.348712000	-3.424680000
17	2.937416000	2.093134000	2.379431000
6	1.578705000	4.046362000	0.486832000
8	1.474793000	5.190297000	0.520839000
6	-4.696219000	-0.407376000	0.043951000
6	-5.532833000	-1.182531000	-0.767243000
6	-5.179208000	0.682486000	0.766202000
6	-6.877533000	-0.837809000	-0.860404000
1	-5.131366000	-2.038334000	-1.310931000
6	-6.534204000	1.010954000	0.658426000
1	-4.504629000	1.254237000	1.404046000
6	-7.399328000	0.263192000	-0.152902000
1	-7.541565000	-1.434108000	-1.491058000
1	-6.923210000	1.862874000	1.220688000
6	2.501151000	-2.372615000	0.799801000
6	2.533835000	-1.320309000	1.719182000
6	1.424965000	-3.267476000	0.762945000
6	1.452795000	-1.145811000	2.584258000
1	3.388118000	-0.644059000	1.763680000
6	0.349300000	-3.071024000	1.630236000
1	1.442966000	-4.110573000	0.071675000
6	0.344340000	-2.010583000	2.552846000
1	1.479368000	-0.315159000	3.291827000
1	-0.506179000	-3.747807000	1.587582000
6	-0.827266000	-1.792653000	3.472806000
1	-1.373263000	-2.729819000	3.656933000
1	-0.504241000	-1.375920000	4.438848000

1	-1.530121000	-1.081490000	3.011088000
6	-8.859472000	0.617602000	-0.278495000
1	-9.135643000	1.451036000	0.382976000
1	-9.102950000	0.908564000	-1.314156000
1	-9.496753000	-0.246331000	-0.028756000

E8a

G = -2511.30808

6	0.122329000	-1.691747000	0.596396000
1	0.893218000	-1.426187000	1.344112000
1	-0.504992000	-2.491766000	1.008724000
6	0.794914000	-0.991381000	-1.655399000
1	1.807677000	-0.821403000	-2.039649000
1	0.147367000	-1.205272000	-2.522802000
6	0.226157000	0.169941000	-0.872483000
6	-0.658370000	-0.443664000	0.179664000
1	-1.519860000	-0.778005000	-0.424640000
7	0.714879000	-2.119714000	-0.689523000
6	-1.192567000	0.470768000	1.289064000
1	-0.592166000	0.304436000	2.192282000
6	-2.681180000	0.166890000	1.636780000
1	-2.822997000	0.113364000	2.726721000
1	-3.048349000	-0.777534000	1.211944000
6	0.135841000	1.496162000	-1.200346000
1	0.525959000	1.853007000	-2.154455000
6	-2.602738000	2.478630000	1.344375000
1	-2.982620000	3.329758000	0.770371000
1	-2.646265000	2.741467000	2.413001000
7	-3.486981000	1.311517000	1.167202000
16	-4.105388000	1.157225000	-0.442156000
16	2.002294000	-3.214324000	-0.634562000
8	-3.128680000	0.501562000	-1.363941000
8	-4.648125000	2.495808000	-0.784795000
8	2.321149000	-3.530603000	-2.047236000
8	1.586623000	-4.248038000	0.345563000
45	2.329134000	1.377905000	-0.181417000
6	-1.171552000	2.013810000	0.967563000
1	-0.458923000	2.495948000	1.654265000
6	-0.720380000	2.415055000	-0.436140000
6	-1.015674000	3.609548000	-0.981463000
1	-0.622042000	3.886627000	-1.961588000
1	-1.656238000	4.339147000	-0.484783000
17	3.112634000	1.561472000	-2.430825000
6	4.046940000	1.957596000	0.309311000
8	5.082895000	2.356764000	0.586702000
6	1.913872000	1.164621000	1.611302000
8	1.761803000	1.016831000	2.744322000
6	3.403862000	-2.328485000	0.063602000
6	4.311950000	-1.694129000	-0.789672000
6	3.562357000	-2.284294000	1.452583000
6	5.388956000	-1.003669000	-0.234801000
1	4.181146000	-1.752675000	-1.869857000
6	4.639751000	-1.577146000	1.988295000
1	2.864674000	-2.819777000	2.096782000

6	5.572868000	-0.935654000	1.156795000
1	6.098215000	-0.503312000	-0.898028000
1	4.768061000	-1.538163000	3.072676000
6	-5.446772000	0.001474000	-0.150122000
6	-5.401646000	-1.259352000	-0.742837000
6	-6.530816000	0.404561000	0.638187000
6	-6.464534000	-2.141989000	-0.527241000
1	-4.550423000	-1.537029000	-1.364959000
6	-7.577741000	-0.489428000	0.840950000
1	-6.545095000	1.400645000	1.081681000
6	-7.562143000	-1.774572000	0.264047000
1	-6.437391000	-3.132803000	-0.986393000
1	-8.428715000	-0.188116000	1.456911000
6	-8.714549000	-2.719248000	0.494344000
1	-8.897018000	-2.862852000	1.571886000
1	-9.644068000	-2.312815000	0.061724000
1	-8.531393000	-3.704441000	0.042309000
6	6.765595000	-0.217990000	1.736277000
1	6.608685000	0.041633000	2.793706000
1	7.664068000	-0.856390000	1.679275000
1	6.984210000	0.706232000	1.181208000

E8b

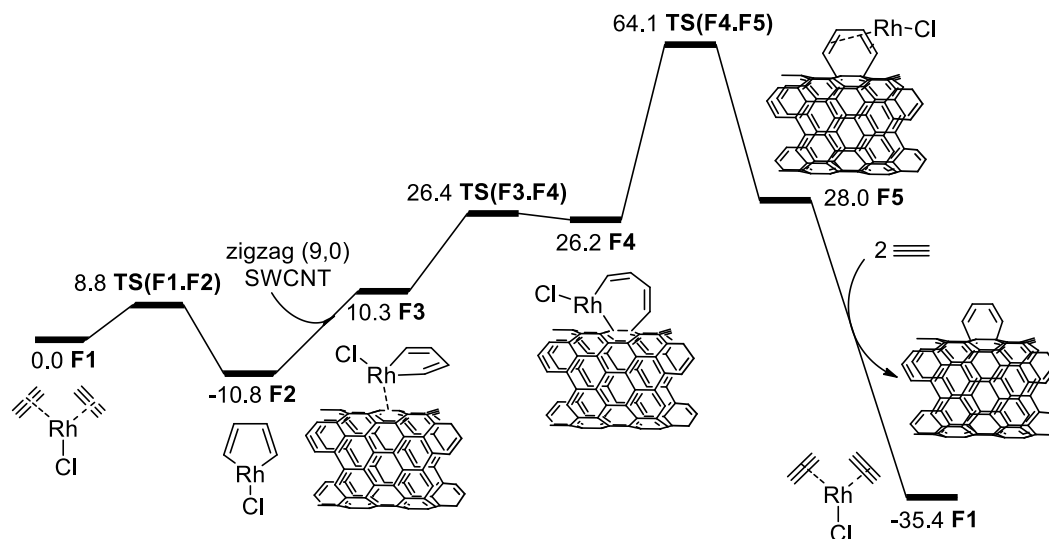
$G = -2397.96097$

6	-1.097632000	-0.658002000	-1.815415000
1	-1.069632000	-0.887917000	-2.893018000
1	-1.439975000	-1.554161000	-1.283267000
6	-1.263663000	1.657355000	-2.016438000
1	-1.233211000	1.674931000	-3.120014000
1	-1.754903000	2.572933000	-1.674296000
6	0.137476000	1.398703000	-1.466160000
6	0.270520000	-0.135636000	-1.320853000
1	0.367590000	-0.425299000	-0.258477000
7	-2.051836000	0.463146000	-1.643349000
6	1.531774000	-0.570922000	-2.059341000
1	1.449586000	-0.244599000	-3.111077000
6	1.952214000	-2.057186000	-2.032807000
1	1.841150000	-2.526152000	-3.021000000
1	1.355549000	-2.649591000	-1.327635000
6	1.274519000	2.215729000	-1.691940000
1	1.140690000	3.184150000	-2.183735000
6	3.917093000	-0.686478000	-1.766432000
1	4.792906000	-0.560010000	-1.119661000
1	4.235372000	-0.525408000	-2.810554000
7	3.390008000	-2.066705000	-1.650627000
16	3.751085000	-2.943859000	-0.219875000
16	-2.693042000	0.558753000	-0.024065000
8	5.154157000	-2.600436000	0.121402000
8	3.319560000	-4.333016000	-0.508649000
8	-3.169691000	1.956078000	0.136423000
8	-1.745903000	-0.036098000	0.967660000
45	0.661318000	2.336067000	0.388676000
6	2.714481000	0.184811000	-1.412305000
1	2.588320000	0.103452000	-0.317339000

6	2.645331000	1.647049000	-1.771521000
6	3.698604000	2.383834000	-2.163770000
1	3.585952000	3.441124000	-2.415130000
1	4.699487000	1.955091000	-2.240371000
17	0.904240000	2.647212000	2.683365000
6	-0.229726000	3.861917000	0.085451000
8	-0.800639000	4.838922000	-0.131771000
6	2.670676000	-2.309016000	1.075212000
6	3.069085000	-1.201635000	1.829636000
6	1.409459000	-2.889097000	1.258296000
6	2.168641000	-0.641167000	2.738746000
1	4.071223000	-0.788887000	1.704424000
6	0.522041000	-2.309659000	2.163727000
1	1.142633000	-3.789507000	0.704146000
6	0.877244000	-1.171462000	2.908216000
1	2.464893000	0.234439000	3.317400000
1	-0.468461000	-2.749858000	2.300312000
6	-4.097484000	-0.548815000	-0.152486000
6	-4.085345000	-1.748276000	0.557512000
6	-5.201926000	-0.157601000	-0.917456000
6	-5.206202000	-2.580996000	0.487533000
1	-3.217325000	-2.013633000	1.161302000
6	-6.307022000	-1.001262000	-0.973409000
1	-5.191139000	0.794071000	-1.449705000
6	-6.328426000	-2.223517000	-0.273313000
1	-5.208233000	-3.521651000	1.042924000
1	-7.177086000	-0.706249000	-1.565100000
6	-0.117412000	-0.542799000	3.846725000
1	-0.593532000	-1.306692000	4.482731000
1	0.349788000	0.216349000	4.486995000
1	-0.909930000	-0.049722000	3.261463000
6	-7.542485000	-3.114500000	-0.347077000
1	-8.446078000	-2.572862000	-0.022566000
1	-7.721429000	-3.447951000	-1.382847000
1	-7.432368000	-4.007218000	0.284862000

Annex 4

XYZ coordinates of the catalytic intermediates for the transition metal-catalysed [2+2+2] cycloaddition involving SWCNTs



Acetylene

G = -77.32218

6	0.000000000	0.000000000	0.602769000
6	0.000000000	0.000000000	-0.602769000
1	0.000000000	0.000000000	1.668725000
1	0.000000000	0.000000000	-1.668725000

Zigzag (9,0) SWCNT

G = -4129.61329

6	4.595667000	-2.482752000	-2.534354000
6	4.634866000	-3.621664000	-0.339211000
6	6.010236000	-3.873552000	-0.258658000
6	6.671804000	-3.768510000	0.967034000
6	4.634898000	-3.006790000	2.038572000
6	6.010407000	-3.266006000	2.089935000
6	4.595452000	-0.950368000	3.413618000
6	4.634992000	1.520460000	3.306819000
6	6.010703000	1.715049000	3.483844000
6	6.672450000	2.724568000	2.781035000
6	4.634980000	3.274591000	1.587883000
6	6.010718000	3.447492000	1.785890000
6	4.595339000	3.432615000	-0.880204000
6	4.634801000	2.100065000	-2.964402000
6	6.010283000	2.156838000	-3.222600000
6	6.671729000	1.044528000	-3.748050000
6	4.634847000	-0.264601000	-3.627900000
6	6.010207000	-0.178787000	-3.878173000
6	3.918307000	-1.504883000	-3.283100000
6	0.350813000	-2.490451000	-2.542230000

6	1.787187000	-2.497549000	-2.549468000
6	2.499335000	-3.238165000	-1.563365000
6	3.918292000	-3.251272000	-1.572050000
6	0.360949000	-3.557938000	-0.346665000
6	1.774777000	-3.544481000	-0.351164000
6	2.484455000	-3.382373000	0.867179000
6	3.919512000	-3.383311000	0.867600000
6	0.360919000	-2.947410000	2.013692000
6	1.774786000	-2.933270000	2.011067000
6	2.499299000	-2.079109000	2.924020000
6	3.918245000	-2.086627000	2.938780000
6	0.350788000	-0.952602000	3.421534000
6	1.787025000	-0.955312000	3.431422000
6	2.499273000	0.268444000	3.583413000
6	3.918167000	0.267117000	3.599701000
6	0.360818000	1.483153000	3.255932000
6	1.774753000	1.472528000	3.246531000
6	2.484440000	2.448308000	2.499185000
6	3.919610000	2.448511000	2.499355000
6	0.360799000	3.224333000	1.549633000
6	1.774718000	3.215128000	1.538758000
6	2.499190000	3.576953000	0.341942000
6	3.918081000	3.593292000	0.340918000
6	0.350700000	3.440569000	-0.882168000
6	1.786931000	3.450530000	-0.884734000
6	2.499180000	2.966343000	-2.018759000
6	3.918133000	2.981259000	-2.026028000
6	0.360801000	2.073815000	-2.905331000
6	1.774669000	2.070976000	-2.891358000
6	2.484381000	0.936526000	-3.363722000
6	3.919451000	0.937008000	-3.364729000
6	0.360916000	-0.273463000	-3.564433000
6	1.774745000	-0.278195000	-3.551033000
6	2.499334000	-1.496492000	-3.269879000
6	-0.360818000	-1.483153000	-3.255932000
6	-3.919610000	-2.448511000	-2.499355000
6	-2.484440000	-2.448308000	-2.499185000
6	-1.774718000	-3.215128000	-1.538758000
6	-0.360799000	-3.224333000	-1.549633000
6	-3.918081000	-3.593292000	-0.340918000
6	-2.499190000	-3.576953000	-0.341942000
6	-1.786931000	-3.450530000	0.884734000
6	-0.350700000	-3.440569000	0.882168000
6	-3.918133000	-2.981259000	2.026028000
6	-2.499180000	-2.966343000	2.018759000
6	-1.774669000	-2.070976000	2.891358000
6	-0.360801000	-2.073815000	2.905331000
6	-3.919451000	-0.937008000	3.364729000
6	-2.484381000	-0.936526000	3.363722000
6	-1.774745000	0.278195000	3.551033000
6	-0.360916000	0.273463000	3.564433000
6	-3.918307000	1.504883000	3.283100000
6	-2.499334000	1.496492000	3.269879000
6	-1.787187000	2.497549000	2.549468000
6	-0.350813000	2.490451000	2.542230000

6	-3.918292000	3.251272000	1.572050000
6	-2.499335000	3.238165000	1.563365000
6	-1.774777000	3.544481000	0.351164000
6	-0.360949000	3.557938000	0.346665000
6	-3.919512000	3.383311000	-0.867600000
6	-2.484455000	3.382373000	-0.867179000
6	-1.774786000	2.933270000	-2.011067000
6	-0.360919000	2.947410000	-2.013692000
6	-3.918245000	2.086627000	-2.938780000
6	-2.499299000	2.079109000	-2.924020000
6	-1.787025000	0.955312000	-3.431422000
6	-0.350788000	0.952602000	-3.421534000
6	-3.918167000	-0.267117000	-3.599701000
6	-2.499273000	-0.268444000	-3.583413000
6	-1.774753000	-1.472528000	-3.246531000
6	-4.634992000	-1.520460000	-3.306819000
6	-6.672450000	-2.724568000	-2.781035000
6	-6.010718000	-3.447492000	-1.785890000
6	-4.634980000	-3.274591000	-1.587883000
6	-4.595339000	-3.432615000	0.880204000
6	-6.010283000	-2.156838000	3.222600000
6	-4.634801000	-2.100065000	2.964402000
6	-6.671729000	-1.044528000	3.748050000
6	-6.010207000	0.178787000	3.878173000
6	-4.634847000	0.264601000	3.627900000
6	-4.595667000	2.482752000	2.534354000
6	-6.010236000	3.873552000	0.258658000
6	-4.634866000	3.621664000	0.339211000
6	-6.671804000	3.768510000	-0.967034000
6	-6.010407000	3.266006000	-2.089935000
6	-4.634898000	3.006790000	-2.038572000
6	-4.595452000	0.950368000	-3.413618000
6	-6.010703000	-1.715049000	-3.483844000
1	5.674119000	-2.410093000	-2.460178000
1	6.568424000	-4.118826000	-1.156921000
1	7.731584000	-3.997704000	1.026240000
1	6.568717000	-3.044866000	2.994401000
1	5.674244000	-0.923259000	3.317119000
1	6.569144000	1.057964000	4.143419000
1	7.732549000	2.889227000	2.949042000
1	6.569088000	4.120284000	1.142290000
1	5.674124000	3.335475000	-0.855012000
1	6.568481000	3.056667000	-2.983014000
1	7.731493000	1.108501000	-3.976029000
1	6.568437000	-1.071794000	-4.141883000
1	-7.732549000	-2.889227000	-2.949042000
1	-6.569088000	-4.120284000	-1.142290000
1	-5.674124000	-3.335475000	0.855012000
1	-6.568481000	-3.056667000	2.983014000
1	-7.731493000	-1.108501000	3.976029000
1	-6.568437000	1.071794000	4.141883000
1	-5.674119000	2.410093000	2.460178000
1	-6.568424000	4.118826000	1.156921000
1	-7.731584000	3.997704000	-1.026240000
1	-6.568717000	3.044866000	-2.994401000

1	-5.674244000	0.923259000	-3.317119000
1	-6.569144000	-1.057964000	-4.143419000

F1

G = -725.49197

45	-0.000026000	0.358859000	-0.000004000
6	1.879816000	1.000956000	-0.508712000
6	2.025009000	0.218050000	0.469879000
6	-1.879841000	1.000680000	0.508892000
6	-2.024956000	0.218112000	-0.470005000
17	0.000068000	-1.952130000	-0.000015000
1	-2.184917000	1.649377000	1.311677000
1	-2.545374000	-0.444175000	-1.137258000
1	2.545378000	-0.444454000	1.136950000
1	2.184753000	1.650014000	-1.311257000

TS(F1.F2)

G = -725.47791

45	-0.181320000	-0.126563000	0.000000000
6	1.095612000	-1.480169000	0.991774000
6	1.095612000	-0.280581000	1.487623000
6	1.095612000	-1.480169000	-0.991774000
6	1.095612000	-0.280581000	-1.487623000
17	-1.393267000	1.825325000	0.000000000
1	1.275532000	-2.520351000	-1.216889000
1	1.499606000	0.417248000	-2.204956000
1	1.499606000	0.417248000	2.204956000
1	1.275532000	-2.520351000	1.216889000

F2

G = -725.48460

45	0.000000000	0.170298000	0.000000000
6	-0.754322000	-2.257164000	0.000000000
6	-1.465820000	-1.119685000	0.000000000
6	0.745325000	-2.259861000	0.000000000
6	1.461066000	-1.125086000	0.000000000
17	0.005832000	2.427352000	0.000000000
1	1.245945000	-3.227174000	0.000000000
1	2.532378000	-0.958406000	0.000000000
1	-2.536579000	-0.949346000	0.000000000
1	-1.258383000	-3.222663000	0.000000000

F3

G = -4855.08891

6	-4.768312000	0.926466000	2.329890000
6	-4.360037000	-1.175539000	3.571013000
6	-5.692468000	-1.526443000	3.824922000
6	-6.083306000	-2.867221000	3.790658000
6	-3.857313000	-3.532940000	3.096296000

6	-5.195540000	-3.854896000	3.356244000
6	-3.505929000	-4.983874000	1.124461000
6	-3.538402000	-5.012605000	-1.347546000
6	-4.844658000	-5.483989000	-1.535179000
6	-5.627635000	-4.984404000	-2.578382000
6	-3.880405000	-3.415569000	-3.181475000
6	-5.181756000	-3.905615000	-3.347135000
6	-4.356781000	-1.002621000	-3.454675000
6	-4.843612000	1.096024000	-2.232110000
6	-6.246916000	1.064627000	-2.305301000
6	-7.012920000	1.531056000	-1.239483000
6	-5.017086000	1.920833000	0.079476000
6	-6.407527000	1.883664000	-0.023841000
6	-4.254318000	1.779065000	1.338693000
6	-0.612306000	1.818318000	2.327744000
6	-2.026571000	1.527185000	2.335467000
6	-2.522121000	0.445914000	3.120331000
6	-3.911523000	0.159155000	3.137277000
6	-0.180949000	-0.280874000	3.504317000
6	-1.564655000	-0.571913000	3.488481000
6	-2.002889000	-1.918180000	3.400705000
6	-3.406609000	-2.217976000	3.401466000
6	0.318797000	-2.621247000	3.039871000
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6	1.978280000	3.355750000	0.087151000
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6	-0.390911000	0.788793000	3.131002000
6	-3.423396000	2.965904000	2.608718000
6	-2.072390000	2.498879000	2.578009000
6	-1.146893000	3.049659000	1.653448000
6	0.212769000	2.606718000	1.633823000
6	-3.021986000	4.150145000	0.509748000
6	-1.686612000	3.725985000	0.509430000
6	-1.021641000	3.365356000	-0.743880000
6	-3.730521000	4.301300000	-0.778100000
6	-5.764459000	4.629341000	-2.054145000
6	-5.409941000	3.595818000	-2.920640000
6	-4.176085000	2.942344000	-2.775652000
6	-4.900476000	0.664009000	-3.444190000
6	-7.064971000	-1.325643000	-2.747021000

6	-5.684589000	-1.540478000	-2.636090000
6	-7.933801000	-1.836537000	-1.779843000
6	-7.432073000	-2.424270000	-0.615040000
6	-6.056971000	-2.650768000	-0.479558000
6	-5.808212000	-2.043736000	1.900590000
6	-6.511454000	0.287305000	3.689486000
6	-5.216003000	-0.175111000	3.415421000
6	-6.749898000	1.652980000	3.847238000
6	-5.741222000	2.586308000	3.587608000
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6	-3.827400000	3.896630000	1.652726000
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1	6.783415000	-3.238374000	-4.048306000
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1	6.473144000	-0.607708000	3.524010000
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1	-6.708067000	5.148289000	-2.194264000
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1	-5.923191000	1.009613000	-3.349748000
1	-7.455381000	-0.731864000	-3.567979000
1	-9.004683000	-1.694179000	-1.890996000
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1	-4.877382000	4.159248000	1.601063000
1	-5.326459000	5.625270000	-0.190211000
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6	1.174469000	4.746895000	0.882611000
6	3.105596000	4.808782000	-1.560760000
1	0.869067000	4.998266000	1.893621000
6	1.476634000	5.740206000	0.034899000
1	3.527493000	4.715093000	-2.564862000
6	2.043369000	5.585726000	-1.305663000
1	1.327150000	6.761151000	0.385157000
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6	5.248887000	4.074928000	3.711868000

6	2.997599000	4.357305000	2.855756000
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6	2.556536000	5.561985000	0.744794000
6	2.747180000	5.280174000	-1.695712000
6	3.992860000	5.893926000	-1.885054000
6	4.913354000	5.347395000	-2.782301000
6	3.436004000	3.471105000	-3.206375000
6	4.672428000	4.106373000	-3.378785000
6	4.234309000	1.121655000	-3.117799000
6	4.954367000	-0.778313000	-1.712908000
6	6.341974000	-0.503482000	-1.738124000
6	7.122263000	-0.716532000	-0.611972000
6	5.163618000	-1.329543000	0.667689000
6	6.517217000	-1.032357000	0.623150000
6	4.270526000	-1.108296000	1.823909000
6	0.583783000	-1.524434000	2.550013000
6	1.951753000	-1.030422000	2.579617000
6	2.227608000	0.228489000	3.194370000
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6	-0.200853000	0.654764000	3.386459000
6	1.125423000	1.136588000	3.389425000
6	1.376100000	2.518777000	3.207519000
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6	0.327595000	3.342673000	2.722905000
6	0.715370000	4.432271000	1.857561000
6	2.043217000	4.932997000	1.891093000
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6	-0.092448000	4.619913000	0.699482000
6	0.576664000	4.931475000	-0.519826000
6	1.905025000	5.429442000	-0.495098000
6	-1.262139000	3.782188000	-1.734347000
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6	1.051076000	3.694870000	-2.553291000
6	2.404054000	4.176662000	-2.524108000
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6	3.201277000	2.025967000	-3.371880000
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6	1.584840000	0.184106000	-3.109945000
6	2.613284000	-0.615947000	-2.511621000
6	3.971254000	-0.155775000	-2.565512000
6	0.866572000	-2.130388000	-1.634949000
6	2.212614000	-1.654556000	-1.632974000
6	3.105785000	-2.053640000	-0.580431000
6	4.444358000	-1.498076000	-0.572374000
6	1.167141000	-3.239965000	0.693766000
6	2.593813000	-2.603122000	0.709748000
6	2.956724000	-1.639181000	1.804692000
6	0.228405000	-2.633831000	1.767009000
6	-3.442794000	-2.935234000	2.555475000
6	-2.090727000	-2.445080000	2.551543000
6	-1.782837000	-1.213455000	3.174163000
6	-0.451055000	-0.741819000	3.151048000

6	-4.218092000	-0.796449000	3.458961000
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6	-1.285908000	1.559820000	3.226783000
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6	-1.109848000	-3.062568000	1.735476000
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6	-4.457070000	-2.235656000	3.263858000
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6	-7.512391000	2.242498000	-0.586352000
6	-6.134176000	2.484575000	-0.633530000
6	-5.615328000	1.296622000	-2.734190000
6	-6.091146000	-1.442252000	-3.913506000
6	-4.839884000	-0.877221000	-3.630305000
6	-6.302469000	-2.809202000	-3.725403000
6	-5.326491000	-3.602437000	-3.115054000
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6	-5.044201000	-4.652756000	1.944528000
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1	5.865984000	2.059912000	4.160954000
1	6.213911000	4.503027000	3.966325000
1	4.480524000	5.922888000	2.909840000
1	3.604343000	5.838178000	0.741353000
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1	5.456885000	3.618492000	-3.949335000
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1	7.095015000	-0.975100000	1.540430000
1	-6.899821000	-4.601051000	3.037039000
1	-6.461948000	-2.386313000	4.051130000
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1	-8.093506000	2.242473000	-1.503610000
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6	1.156065000	-4.776063000	0.824765000
6	3.992596000	-4.003584000	1.289137000
1	0.248875000	-5.244997000	0.470659000
6	2.092567000	-5.557523000	1.382036000
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6	2.371535000	5.650784000	0.474490000
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6	4.875098000	5.199299000	-2.928203000
6	3.447967000	3.267806000	-3.263004000
6	4.680535000	3.911265000	-3.433536000
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6	6.385518000	-0.552040000	-1.430845000
6	7.121585000	-0.628706000	-0.262421000
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6	1.844505000	-0.787837000	2.781011000
6	2.067352000	0.521589000	3.308444000

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6	1.163800000	2.783005000	3.121329000
6	2.491537000	3.321156000	3.175309000
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6	0.116246000	3.539485000	2.536440000
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6	2.377099000	4.001774000	-2.677117000
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6	0.785453000	2.212990000	-3.277603000
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6	2.680654000	-0.769411000	-2.313053000
6	4.026097000	-0.293282000	-2.351019000
6	0.920935000	-2.230003000	-1.350781000
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6	1.173488000	-3.176441000	1.065992000
6	2.655449000	-2.579903000	1.119836000
6	2.888824000	-1.431735000	2.105428000
6	0.197580000	-2.537794000	2.085790000
6	-3.506224000	-2.828883000	2.758952000
6	-2.162373000	-2.314435000	2.765166000
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6	-5.056735000	-4.619454000	2.224507000
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1	5.920089000	4.944291000	3.903880000
1	4.196640000	6.237030000	2.680160000
1	3.412735000	5.950490000	0.490057000
1	4.131884000	6.724206000	-1.598268000
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1	7.008610000	-0.655342000	1.902244000
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1	-6.586835000	-2.227932000	4.100203000
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1	-9.292215000	1.600511000	0.267939000
1	-8.113686000	1.913564000	-1.889508000
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1	-5.296487000	-5.541181000	1.702656000

17	6.001522000	-5.441792000	-1.027080000
6	1.171858000	-4.704841000	1.037216000
6	3.776621000	-3.633559000	1.312308000
1	0.201900000	-5.177340000	1.104592000
6	2.240345000	-5.473157000	0.756588000
1	4.544574000	-3.415995000	2.047564000
6	3.587066000	-4.960893000	0.872397000
1	2.106800000	-6.537067000	0.583189000
1	4.358980000	-5.689248000	1.098818000
45	4.526215000	-3.684604000	-0.626542000

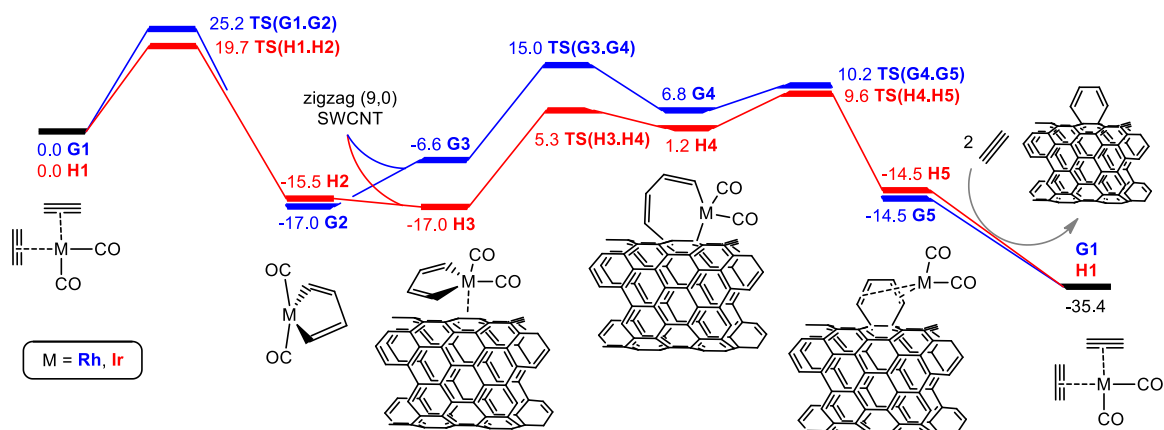
Cycloadduct (zigzag (9,0) + 2 acetylenes)

G = -4284.31404

6	-4.764059000	-2.825253000	2.251147000
6	-4.852865000	-3.771282000	-0.029566000
6	-6.238131000	-3.941432000	-0.137904000
6	-6.885256000	-3.666412000	-1.345689000
6	-4.805085000	-2.890202000	-2.319861000
6	-6.192192000	-3.071415000	-2.401959000
6	-4.656409000	-0.680314000	-3.425699000
6	-4.599195000	1.768885000	-3.057485000
6	-5.965233000	2.029372000	-3.241132000
6	-6.602390000	3.011134000	-2.482486000
6	-4.563747000	3.415028000	-1.237288000
6	-5.928551000	3.646083000	-1.434560000
6	-4.533133000	3.328167000	1.233860000
6	-4.603641000	1.725109000	3.116005000
6	-5.968524000	1.810367000	3.411160000
6	-6.671715000	0.673860000	3.821191000
6	-4.694783000	-0.697349000	3.519415000
6	-6.062930000	-0.581056000	3.803363000
6	-4.039402000	-1.933052000	3.063896000
6	-0.523837000	-3.038746000	2.244844000
6	-1.959465000	-2.974726000	2.255011000
6	-2.704688000	-3.611646000	1.224420000
6	-4.124067000	-3.550423000	1.233056000
6	-0.578333000	-3.940155000	-0.015266000
6	-1.989848000	-3.853349000	-0.009039000
6	-2.684427000	-3.519531000	-1.202016000
6	-4.117761000	-3.442187000	-1.202828000
6	-0.532870000	-3.044431000	-2.277075000
6	-1.944971000	-2.963450000	-2.276609000
6	-2.620498000	-1.956060000	-3.062727000
6	-4.037359000	-1.897524000	-3.091668000
6	-0.422425000	-0.858534000	-3.354229000
6	-1.854950000	-0.802415000	-3.392850000
6	-2.509066000	0.459306000	-3.403072000
6	-3.926619000	0.520570000	-3.452055000
6	-0.332480000	1.542370000	-2.877314000
6	-1.742931000	1.589048000	-2.927858000
6	-2.428163000	2.549145000	-2.150057000
6	-3.864690000	2.609858000	-2.178819000
6	-0.291542000	3.301817000	-1.190168000

6	-1.699895000	3.287153000	-1.187318000
6	-2.442849000	3.604486000	0.030161000
6	-3.843331000	3.632783000	0.031493000
6	-0.283647000	3.295787000	1.205827000
6	-1.716490000	3.298021000	1.227339000
6	-2.438496000	2.621438000	2.244049000
6	-3.866995000	2.688359000	2.278345000
6	-0.333396000	1.519824000	2.876406000
6	-1.742979000	1.583931000	2.942869000
6	-2.498911000	0.433368000	3.322061000
6	-3.931947000	0.494781000	3.364331000
6	-0.429179000	-0.871008000	3.357806000
6	-1.846521000	-0.816332000	3.377591000
6	-2.623228000	-1.985680000	3.036564000
6	0.233565000	-2.097739000	2.999297000
6	3.746734000	-3.184135000	2.204838000
6	2.311735000	-3.124722000	2.202782000
6	1.570356000	-3.802134000	1.202103000
6	0.155134000	-3.745315000	1.211926000
6	3.701002000	-4.165578000	-0.023398000
6	2.284301000	-4.092294000	-0.022102000
6	1.583430000	-3.793349000	-1.226166000
6	0.147602000	-3.719814000	-1.223230000
6	3.742677000	-3.252387000	-2.287409000
6	2.325018000	-3.183868000	-2.278970000
6	1.644902000	-2.133851000	-2.999537000
6	0.234933000	-2.076681000	-3.019443000
6	3.834446000	-1.030214000	-3.302537000
6	2.402520000	-0.967083000	-3.280401000
6	1.746304000	0.287512000	-3.276496000
6	0.337131000	0.341963000	-3.297455000
6	3.927585000	1.395869000	-2.962109000
6	2.512490000	1.445556000	-2.889315000
6	1.857554000	2.457889000	-2.121386000
6	0.401957000	2.495139000	-2.101900000
6	4.020648000	3.139570000	-1.258595000
6	2.612675000	3.247235000	-1.238950000
6	1.993004000	3.960665000	-0.001971000
6	0.384371000	4.029752000	0.004087000
6	4.025731000	2.975552000	1.152414000
6	2.597108000	3.100084000	1.143589000
6	1.857613000	2.405174000	2.074108000
6	0.403127000	2.489392000	2.096408000
6	3.938950000	1.337861000	2.946630000
6	2.525216000	1.392087000	2.869853000
6	1.765229000	0.259153000	3.267159000
6	0.329351000	0.321802000	3.264703000
6	3.840344000	-1.060378000	3.409704000
6	2.417431000	-0.994161000	3.367603000
6	1.644085000	-2.150335000	2.988538000
6	4.500488000	-2.332765000	3.060466000
6	6.481570000	-3.600441000	2.473017000
6	5.792866000	-4.232836000	1.435891000
6	4.426832000	-3.984638000	1.246791000
6	4.393316000	-3.884727000	-1.215331000

6	5.868963000	-2.345112000	-3.361141000
6	4.498750000	-2.269563000	-3.084655000
6	6.572652000	-1.198281000	-3.737354000
6	5.960768000	0.056560000	-3.704027000
6	4.591592000	0.165420000	-3.427189000
6	4.654600000	2.316540000	-2.201700000
6	6.154367000	3.510948000	0.107132000
6	4.780880000	3.363465000	0.000385000
6	6.806781000	3.154753000	1.305697000
6	6.110937000	2.496652000	2.306012000
6	4.709421000	2.329825000	2.211675000
6	4.563782000	0.131292000	3.343046000
6	5.863825000	-2.600343000	3.229431000
1	-5.838193000	-2.697662000	2.187945000
1	-6.814354000	-4.250438000	0.728857000
1	-7.955003000	-3.832173000	-1.431311000
1	-6.733023000	-2.716110000	-3.273709000
1	-5.734848000	-0.618592000	-3.342027000
1	-6.533953000	1.444402000	-3.957352000
1	-7.653652000	3.223471000	-2.652374000
1	-6.471579000	4.293618000	-0.752768000
1	-5.614606000	3.273012000	1.200633000
1	-6.489328000	2.755179000	3.289713000
1	-7.723495000	0.757394000	4.077949000
1	-6.653344000	-1.473456000	3.986708000
1	7.532321000	-3.822464000	2.633589000
1	6.322792000	-4.888705000	0.751904000
1	5.474900000	-3.834086000	-1.174767000
1	6.390795000	-3.291411000	-3.256074000
1	7.627737000	-1.273419000	-3.983037000
1	6.552807000	0.951420000	-3.868642000
1	5.726925000	2.185511000	-2.122270000
1	6.735897000	3.833662000	-0.751423000
1	7.877228000	3.308883000	1.401324000
1	6.641164000	2.096497000	3.164417000
1	5.643641000	0.074281000	3.278981000
1	6.450315000	-2.004933000	3.922380000
6	2.648922000	5.349062000	0.104847000
6	2.014987000	6.522007000	0.121540000
1	3.727854000	5.347393000	0.165164000
1	2.587807000	7.442482000	0.191071000
6	0.568643000	6.585928000	0.039529000
6	-0.158205000	5.469859000	-0.015301000
1	0.075606000	7.553688000	0.018904000
1	-1.233848000	5.555143000	-0.078283000



CO

G = -113.32356

6	0.000000000	0.000000000	-0.650254000
8	0.000000000	0.000000000	0.487691000

G1

G = -491.71709

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6	1.600942000	-1.649404000	-0.611631000
6	1.601765000	-1.648399000	0.612190000
1	1.732984000	-1.771015000	-1.669481000
1	1.735052000	-1.767761000	1.670135000
6	-1.596667000	-1.653075000	0.612355000
6	-1.596807000	-1.653366000	-0.611481000
1	-1.729440000	-1.774578000	-1.669304000
1	-1.728947000	-1.773778000	1.670280000
6	-1.372760000	1.295980000	0.000029000
8	-2.202576000	2.074644000	0.000258000
6	1.369305000	1.299460000	-0.000172000
8	2.197456000	2.079888000	0.000111000

TS(G1.G2)

G = -491.67692

45	-0.057246000	-0.049563000	-0.180035000
6	-1.628995000	1.237350000	0.710533000
6	-0.762482000	0.828121000	1.554500000
6	-2.230734000	-0.245748000	-0.612468000
6	-1.617307000	-1.359703000	-0.471718000
1	-3.068977000	0.322928000	-0.982549000
1	-1.712875000	-2.427354000	-0.595316000
1	-0.377852000	0.734039000	2.558385000
1	-2.355411000	2.010092000	0.507442000
6	1.309165000	1.420934000	-0.325266000
8	2.084016000	2.239346000	-0.463548000
6	1.248245000	-1.485137000	0.200904000
8	1.938962000	-2.337383000	0.497886000

G2 $G = -491.74418$

45	0.000673000	-0.648987000	0.000000000
6	-0.000851000	0.900492000	-1.332999000
6	-0.002374000	2.094519000	-0.731871000
1	-0.000034000	0.630079000	-2.386187000
1	-0.003604000	3.017065000	-1.309416000
6	-0.002229000	2.094524000	0.731853000
6	-0.000583000	0.900501000	1.332987000
1	0.000446000	0.630092000	2.386176000
1	-0.003346000	3.017074000	1.309392000
6	1.984966000	-0.557163000	-0.000237000
8	3.112849000	-0.456454000	-0.000327000
6	-1.984013000	-0.559395000	0.000256000
8	-3.112004000	-0.459894000	0.000342000

G3 $G = -4621.34081$

6	4.755581000	0.947605000	-2.379330000
6	4.382026000	-1.163466000	-3.617836000
6	5.718768000	-1.484982000	-3.883414000
6	6.137442000	-2.818041000	-3.854235000
6	3.932796000	-3.528981000	-3.134341000
6	5.275447000	-3.822471000	-3.407618000
6	3.629082000	-4.983837000	-1.158035000
6	3.681590000	-5.001512000	1.313075000
6	4.998188000	-5.439434000	1.494191000
6	5.778681000	-4.916461000	2.530767000
6	3.997532000	-3.391662000	3.142729000
6	5.315494000	-3.845688000	3.296507000
6	4.416891000	-0.966054000	3.422644000
6	4.855783000	1.143558000	2.206836000
6	6.255652000	1.138292000	2.272370000
6	7.008552000	1.598323000	1.189342000
6	4.996212000	1.931555000	-0.119619000
6	6.392185000	1.915469000	-0.025982000
6	4.230670000	1.778909000	-1.371073000
6	0.574777000	1.741341000	-2.339722000
6	1.993916000	1.480423000	-2.358923000
6	2.508069000	0.413947000	-3.144578000
6	3.908115000	0.159062000	-3.172636000
6	0.181769000	-0.361860000	-3.519098000
6	1.571283000	-0.622201000	-3.513079000
6	2.041489000	-1.957197000	-3.427125000
6	3.451695000	-2.224981000	-3.437085000
6	-0.262122000	-2.710752000	-3.048703000
6	1.127536000	-2.973089000	-3.042831000
6	1.665111000	-4.051998000	-2.246648000
6	3.055945000	-4.330226000	-2.263490000
6	-0.543110000	-4.199197000	-1.135259000
6	0.865115000	-4.476290000	-1.146955000
6	1.533530000	-4.819765000	0.063159000

6	2.925158000	-5.099073000	0.052469000
6	-0.509980000	-4.158719000	1.303866000
6	0.881018000	-4.411598000	1.284649000
6	1.716537000	-3.856847000	2.292011000
6	3.125408000	-4.117521000	2.281373000
6	-0.197508000	-2.569791000	3.127347000
6	1.194096000	-2.819733000	3.106998000
6	2.127092000	-1.795032000	3.510676000
6	3.521219000	-2.053269000	3.517578000
6	0.246745000	-0.192034000	3.452483000
6	1.652578000	-0.452559000	3.446988000
6	2.567962000	0.555315000	3.013072000
6	3.969424000	0.301621000	3.029085000
6	0.628646000	1.849789000	2.182899000
6	2.022431000	1.579045000	2.171204000
6	2.833637000	2.021115000	1.081423000
6	4.240240000	1.742706000	1.073046000
6	0.786787000	2.762209000	-0.109754000
6	2.185633000	2.432965000	-0.122539000
6	2.838329000	2.033843000	-1.359731000
6	0.006573000	2.553880000	-1.328673000
6	-3.626786000	2.500615000	-2.292454000
6	-2.217201000	2.230529000	-2.298235000
6	-1.696533000	1.188093000	-3.106825000
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6	-0.748231000	-1.439386000	-3.471637000
6	-4.468688000	-1.919232000	-3.057066000
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6	-2.528116000	-3.219827000	-2.210308000
6	-1.142300000	-3.499265000	-2.223264000
6	-4.728082000	-3.341068000	-1.088465000
6	-3.319063000	-3.610311000	-1.097847000
6	-2.659788000	-3.989733000	0.100661000
6	-1.273621000	-4.268398000	0.086213000
6	-4.718797000	-3.386145000	1.351803000
6	-3.322639000	-3.637662000	1.334539000
6	-2.490943000	-3.114159000	2.366302000
6	-1.080690000	-3.375531000	2.350528000
6	-4.405598000	-1.794739000	3.182054000
6	-3.009828000	-2.049910000	3.159539000
6	-2.073484000	-1.010903000	3.514876000
6	-0.683791000	-1.272544000	3.517903000
6	-3.953568000	0.594754000	3.430175000
6	-2.545070000	0.327739000	3.420876000
6	-1.632059000	1.341536000	3.025603000
6	-0.244204000	1.074051000	3.018898000
6	-3.560530000	2.695671000	2.247431000
6	-2.167896000	2.414874000	2.228833000
6	-1.369975000	2.859718000	1.134555000
6	0.030179000	2.582521000	1.120117000
6	-3.419116000	3.490171000	-0.071088000
6	-2.032858000	3.216251000	-0.081381000

6	-1.378649000	2.802277000	-1.305665000
6	-4.178995000	3.394321000	-1.332363000
6	-6.274367000	3.310384000	-2.545372000
6	-5.809776000	2.240186000	-3.312630000
6	-4.495980000	1.777138000	-3.155264000
6	-4.918312000	-0.644539000	-3.442633000
6	-6.751271000	-2.749191000	-2.286995000
6	-5.352442000	-2.754838000	-2.225288000
6	-7.503423000	-3.201803000	-1.199340000
6	-6.882652000	-3.513383000	0.012705000
6	-5.484758000	-3.529272000	0.102111000
6	-5.247933000	-2.575932000	2.372887000
6	-6.217019000	-0.145341000	3.882444000
6	-4.881128000	-0.469537000	3.615197000
6	-6.637578000	1.186782000	3.844471000
6	-5.779211000	2.192323000	3.392001000
6	-4.437497000	1.897905000	3.121307000
6	-4.124963000	3.352633000	1.142941000
6	-5.495676000	3.833231000	-1.508086000
1	5.802626000	0.675330000	-2.322994000
1	6.436638000	-0.696234000	-4.086904000
1	7.166307000	-3.063046000	-4.098871000
1	5.652979000	-4.827637000	-3.246930000
1	4.706344000	-5.097770000	-1.135383000
1	5.426128000	-6.164646000	0.808958000
1	6.786700000	-5.289409000	2.683135000
1	5.982354000	-3.350571000	3.995594000
1	5.474201000	-1.185910000	3.336407000
1	6.755959000	0.747557000	3.152693000
1	8.091463000	1.620918000	1.261717000
1	6.997581000	2.110743000	-0.905511000
1	-7.282670000	3.682274000	-2.698731000
1	-6.476711000	1.747415000	-4.013182000
1	-5.974876000	-0.425288000	-3.344604000
1	-7.253160000	-2.366316000	-3.170254000
1	-8.586411000	-3.228166000	-1.269931000
1	-7.484490000	-3.717481000	0.892940000
1	-6.296198000	-2.307322000	2.318242000
1	-6.934145000	-0.933313000	4.090275000
1	-7.667393000	1.430318000	4.086726000
1	-6.160224000	3.194974000	3.224270000
1	-5.202420000	3.466328000	1.116515000
1	-5.923935000	4.557048000	-0.821310000
6	0.102891000	5.873534000	-0.135333000
6	1.890976000	5.016301000	-1.897542000
1	-0.483948000	6.141263000	0.737707000
6	-0.187210000	6.070004000	-1.427776000
1	2.722291000	4.626830000	-2.479469000
6	0.799884000	5.612689000	-2.405125000
1	-1.128115000	6.527510000	-1.731117000
1	0.631666000	5.738469000	-3.472756000
45	1.851298000	4.845241000	0.177625000
6	1.686277000	4.840276000	2.200203000
8	1.579657000	4.965113000	3.329032000
6	2.830534000	6.457689000	0.007961000

8	3.395707000	7.442763000	-0.129326000

TS(G3.G4)

G = -4621.30647

6	-4.704811000	-0.043795000	-2.346454000
6	-3.940195000	1.976260000	-3.552727000
6	-5.193003000	2.539177000	-3.826084000
6	-5.357873000	3.926689000	-3.800467000
6	-3.063125000	4.220624000	-3.074057000
6	-4.326550000	4.756805000	-3.353940000
6	-2.499851000	5.588780000	-1.094010000
6	-2.562562000	5.569833000	1.373966000
6	-3.782323000	6.231362000	1.561206000
6	-4.654774000	5.827804000	2.576949000
6	-3.182099000	3.990504000	3.150734000
6	-4.398715000	4.668515000	3.311212000
6	-4.033523000	1.671905000	3.394666000
6	-4.856275000	-0.313911000	2.173990000
6	-6.231056000	-0.015902000	2.245269000
6	-7.066126000	-0.300300000	1.169593000
6	-5.163122000	-1.041042000	-0.139493000
6	-6.518467000	-0.721265000	-0.051464000
6	-4.362775000	-1.009480000	-1.383315000
6	-0.758579000	-1.630759000	-2.299382000
6	-2.106977000	-1.100543000	-2.317920000
6	-2.397635000	0.070731000	-3.072828000
6	-3.720996000	0.585692000	-3.118002000
6	0.027203000	0.405044000	-3.426157000
6	-1.286409000	0.920778000	-3.422137000
6	-1.499252000	2.319803000	-3.346549000
6	-2.832762000	2.847682000	-3.366759000
6	0.902583000	2.635190000	-2.977878000
6	-0.412130000	3.151849000	-2.972369000
6	-0.738010000	4.317581000	-2.184548000
6	-2.054373000	4.847058000	-2.201874000
6	1.460518000	4.054104000	-1.075341000
6	0.127037000	4.586820000	-1.085412000
6	-0.471272000	5.035204000	0.127763000
6	-1.790284000	5.559791000	0.118998000
6	1.412661000	3.988344000	1.360814000
6	0.087439000	4.489252000	1.342408000
6	-0.844052000	4.065338000	2.326459000
6	-2.184739000	4.573243000	2.317192000
6	0.798220000	2.430760000	3.129186000
6	-0.526871000	2.922988000	3.104545000
6	-1.631605000	2.067207000	3.462106000
6	-2.960450000	2.575974000	3.483313000
6	-0.067594000	0.165728000	3.376132000
6	-1.407658000	0.668810000	3.365361000
6	-2.489869000	-0.158410000	2.925733000
6	-3.822557000	0.348394000	2.972042000
6	-0.805061000	-1.763310000	2.076643000
6	-2.158447000	-1.273134000	2.086688000

6	-3.066310000	-1.637484000	1.056636000
6	-4.383251000	-1.045846000	1.053677000
6	-1.201385000	-2.848780000	-0.148999000
6	-2.576616000	-2.268289000	-0.172634000
6	-3.058804000	-1.549897000	-1.377289000
6	-0.371017000	-2.620955000	-1.366988000
6	3.231157000	-3.155312000	-2.324105000
6	1.893784000	-2.632473000	-2.315027000
6	1.579507000	-1.472692000	-3.068661000
6	0.260275000	-0.964468000	-3.047423000
6	4.006331000	-1.156775000	-3.503811000
6	2.684429000	-0.637928000	-3.476387000
6	2.474487000	0.767652000	-3.401209000
6	1.139867000	1.291145000	-3.388809000
6	4.883434000	1.071096000	-2.999762000
6	3.562043000	1.586719000	-2.985764000
6	3.225864000	2.716665000	-2.150249000
6	1.916664000	3.251724000	-2.161208000
6	5.411428000	2.425723000	-1.037757000
6	4.078745000	2.956338000	-1.042977000
6	3.502113000	3.449670000	0.158330000
6	2.190731000	3.978764000	0.146528000
6	5.412612000	2.459550000	1.400976000
6	4.084245000	2.964725000	1.387415000
6	3.164883000	2.579267000	2.403764000
6	1.822916000	3.090516000	2.387308000
6	4.800157000	0.912458000	3.190077000
6	3.475153000	1.417289000	3.167701000
6	2.363044000	0.550849000	3.480114000
6	1.036727000	1.057398000	3.477828000
6	3.922777000	-1.361437000	3.373449000
6	2.587095000	-0.840893000	3.359957000
6	1.506609000	-1.664713000	2.930821000
6	0.189289000	-1.154686000	2.919515000
6	3.164733000	-3.346958000	2.159233000
6	1.842427000	-2.808099000	2.135745000
6	0.968926000	-3.116606000	1.060444000
6	-0.358905000	-2.592268000	1.047529000
6	2.847319000	-4.147011000	-0.136059000
6	1.533567000	-3.642537000	-0.142820000
6	0.954107000	-3.094277000	-1.360371000
6	3.611015000	-4.166508000	-1.396475000
6	5.692245000	-4.423503000	-2.608530000
6	5.429559000	-3.262031000	-3.338821000
6	4.222285000	-2.572636000	-3.161594000
6	5.085380000	-0.263134000	-3.399080000
6	7.283982000	1.457489000	-2.237573000
6	5.910175000	1.726945000	-2.172980000
6	8.110945000	1.767621000	-1.155647000
6	7.562651000	2.195114000	0.057416000
6	6.193415000	2.470432000	0.150462000
6	5.779749000	1.549280000	2.404909000
6	6.279761000	-1.051851000	3.853223000
6	5.024367000	-0.486344000	3.587112000
6	6.453104000	-2.435184000	3.793018000

6	5.428627000	-3.261709000	3.319269000
6	4.165827000	-2.726530000	3.045905000
6	3.586159000	-4.120269000	1.075411000
6	4.829586000	-4.828479000	-1.586253000
1	-5.677120000	0.428104000	-2.273845000
1	-6.042858000	1.896751000	-4.035456000
1	-6.322695000	4.356974000	-4.050513000
1	-4.511767000	5.815211000	-3.198758000
1	-3.538723000	5.895629000	-1.071026000
1	-4.066208000	7.040568000	0.895388000
1	-5.581473000	6.370496000	2.735041000
1	-5.151494000	4.280364000	3.990337000
1	-5.035773000	2.076142000	3.326756000
1	-6.632652000	0.462475000	3.132893000
1	-8.130113000	-0.099294000	1.242132000
1	-7.143767000	-0.764599000	-0.937810000
1	6.617874000	-4.965112000	-2.776624000
1	6.176433000	-2.875724000	-4.025380000
1	6.083952000	-0.674786000	-3.313302000
1	7.702120000	0.983478000	-3.120254000
1	9.179585000	1.591113000	-1.228705000
1	8.194350000	2.283363000	0.936043000
1	6.761311000	1.094392000	2.346679000
1	7.124159000	-0.409789000	4.083660000
1	7.419439000	-2.865885000	4.036173000
1	5.623430000	-4.314106000	3.137659000
1	4.623740000	-4.430635000	1.040479000
1	5.118465000	-5.636157000	-0.920563000
6	-1.519399000	-4.717507000	0.255610000
6	-3.335912000	-4.998235000	-1.590213000
1	-0.988637000	-4.873277000	1.189278000
6	-1.181952000	-5.521999000	-0.835480000
1	-4.204710000	-5.119725000	-2.235301000
6	-2.113733000	-5.538193000	-1.899621000
1	-0.270021000	-6.114968000	-0.855397000
1	-1.898460000	-5.975431000	-2.872497000
45	-3.558887000	-4.237622000	0.249848000
6	-3.846530000	-5.869214000	1.292897000
8	-3.919289000	-6.887836000	1.810151000
6	-5.492911000	-3.901487000	-0.125697000
8	-6.598328000	-3.971738000	-0.407534000

G4

$G = -4621.31960$

6	-4.816432000	-0.299471000	-1.730723000
6	-4.071136000	1.519553000	-3.238656000
6	-5.329091000	2.078878000	-3.495865000
6	-5.453982000	3.455278000	-3.701007000
6	-3.091404000	3.770972000	-3.237118000
6	-4.362113000	4.302232000	-3.498081000
6	-2.308197000	5.450219000	-1.605761000
6	-2.164874000	5.829505000	0.824282000
6	-3.342681000	6.566318000	0.998106000

6	-4.151434000	6.345301000	2.117221000
6	-2.709476000	4.534525000	2.837175000
6	-3.884838000	5.283829000	2.984798000
6	-3.619492000	2.306928000	3.449226000
6	-4.585249000	0.157131000	2.658263000
6	-5.949027000	0.466129000	2.777376000
6	-6.903359000	-0.077094000	1.901816000
6	-5.130966000	-1.137591000	0.634421000
6	-6.492633000	-0.788648000	0.778341000
6	-4.421532000	-1.167067000	-0.680378000
6	-0.889649000	-2.013056000	-1.745213000
6	-2.209806000	-1.442884000	-1.762472000
6	-2.529433000	-0.350663000	-2.594013000
6	-3.858345000	0.209667000	-2.599993000
6	-0.143128000	-0.174226000	-3.198304000
6	-1.438149000	0.391831000	-3.165169000
6	-1.608005000	1.790915000	-3.306158000
6	-2.926006000	2.360180000	-3.299413000
6	0.825436000	2.061598000	-3.213801000
6	-0.472192000	2.627926000	-3.184365000
6	-0.690557000	3.929374000	-2.596839000
6	-1.987509000	4.504000000	-2.594718000
6	1.591144000	3.763171000	-1.647392000
6	0.278974000	4.347290000	-1.640840000
6	-0.198983000	5.015358000	-0.476454000
6	-1.495813000	5.592849000	-0.467952000
6	1.740324000	4.082785000	0.761922000
6	0.437138000	4.636272000	0.764121000
6	-0.434381000	4.394191000	1.858399000
6	-1.754174000	4.955916000	1.869392000
6	1.203925000	2.811508000	2.766320000
6	-0.101817000	3.354029000	2.762597000
6	-1.207974000	2.602539000	3.304440000
6	-2.514533000	3.167167000	3.344183000
6	0.286569000	0.639054000	3.377101000
6	-1.036391000	1.196421000	3.387615000
6	-2.170615000	0.362578000	3.163884000
6	-3.478311000	0.924622000	3.228821000
6	-0.605660000	-1.454665000	2.472036000
6	-1.939068000	-0.898361000	2.505559000
6	-2.941959000	-1.429488000	1.692950000
6	-4.224922000	-0.848394000	1.719263000
6	-1.279742000	-3.100192000	0.589417000
6	-2.641218000	-2.350680000	0.562376000
6	-3.099254000	-1.730655000	-0.689013000
6	-0.489156000	-2.914608000	-0.735357000
6	3.032472000	-3.662681000	-1.840437000
6	1.713455000	-3.092517000	-1.808791000
6	1.383501000	-2.037072000	-2.691105000
6	0.086251000	-1.479311000	-2.642524000
6	3.770949000	-1.887246000	-3.358163000
6	2.471970000	-1.317401000	-3.307873000
6	2.305836000	0.088518000	-3.449912000
6	0.990909000	0.660689000	-3.410612000
6	4.748593000	0.356003000	-3.308835000

6	3.446440000	0.920804000	-3.273293000
6	3.216094000	2.187467000	-2.618481000
6	1.926265000	2.768938000	-2.612995000
6	5.480092000	1.989327000	-1.649527000
6	4.168143000	2.570057000	-1.638923000
6	3.708308000	3.272210000	-0.493117000
6	2.418698000	3.853542000	-0.490665000
6	5.677256000	2.396408000	0.745092000
6	4.369961000	2.953058000	0.750907000
6	3.516025000	2.755069000	1.872119000
6	2.194388000	3.319041000	1.875466000
6	5.148250000	1.146847000	2.776979000
6	3.842030000	1.698308000	2.770265000
6	2.728034000	0.931667000	3.276742000
6	1.420933000	1.487336000	3.284431000
6	4.215046000	-1.035978000	3.367893000
6	2.898470000	-0.468564000	3.356682000
6	1.763071000	-1.304620000	3.137926000
6	0.468525000	-0.745009000	3.117073000
6	3.303420000	-3.166245000	2.566395000
6	1.995065000	-2.586803000	2.546879000
6	1.015737000	-3.069324000	1.638703000
6	-0.300895000	-2.517961000	1.637211000
6	2.772011000	-4.335934000	0.483370000
6	1.476104000	-3.808788000	0.497812000
6	0.820355000	-3.411734000	-0.750217000
6	3.446460000	-4.556276000	-0.812559000
6	5.427371000	-5.052430000	-2.115169000
6	5.146751000	-3.994885000	-2.979441000
6	3.973468000	-3.240709000	-2.818576000
6	4.879102000	-1.031604000	-3.491945000
6	7.216394000	0.764184000	-2.817367000
6	5.861349000	1.097233000	-2.690412000
6	8.138655000	1.206773000	-1.866010000
6	7.705243000	1.841356000	-0.698017000
6	6.357132000	2.185753000	-0.546232000
6	6.087797000	1.623158000	1.842829000
6	6.610141000	-0.754165000	3.631916000
6	5.356191000	-0.185353000	3.365510000
6	6.735452000	-2.135216000	3.784746000
6	5.652222000	-2.982196000	3.526413000
6	4.389763000	-2.445342000	3.256024000
6	3.613101000	-4.134329000	1.613869000
6	4.626712000	-5.282037000	-0.989703000
1	-5.784351000	0.180514000	-1.660803000
1	-6.211182000	1.446384000	-3.522064000
1	-6.424695000	3.877359000	-3.941020000
1	-4.501875000	5.378674000	-3.521253000
1	-3.330754000	5.804081000	-1.549850000
1	-3.645326000	7.288028000	0.245481000
1	-5.042981000	6.947315000	2.262465000
1	-4.599600000	5.025453000	3.760142000
1	-4.611330000	2.738947000	3.388542000
1	-6.274822000	1.158465000	3.547957000
1	-7.953463000	0.154872000	2.044403000

1	-7.197872000	-1.020475000	-0.014474000
1	6.322455000	-5.647479000	-2.267448000
1	5.849976000	-3.738395000	-3.765608000
1	5.870104000	-1.463683000	-3.420548000
1	7.545977000	0.137625000	-3.640442000
1	9.191915000	0.975636000	-1.991586000
1	8.408817000	2.037105000	0.105378000
1	7.046964000	1.122730000	1.783789000
1	7.488524000	-0.119839000	3.698963000
1	7.703362000	-2.562706000	4.027435000
1	5.799387000	-4.057677000	3.509470000
1	4.635199000	-4.488954000	1.553880000
1	4.940595000	-6.000657000	-0.238652000
6	-1.425166000	-4.588677000	0.971151000
6	-3.526522000	-4.658320000	-1.417880000
1	-1.056881000	-4.838205000	1.961875000
6	-1.863675000	-5.584272000	0.191176000
1	-3.932850000	-4.628911000	-2.426310000
6	-2.474218000	-5.429177000	-1.130760000
1	-1.778289000	-6.602416000	0.570255000
1	-2.072171000	-6.046668000	-1.938172000
45	-4.510009000	-3.399408000	-0.130266000
6	-6.175122000	-3.815526000	-1.109640000
8	-7.196634000	-4.023926000	-1.580025000
6	-4.582600000	-4.657534000	1.343389000
8	-4.665124000	-5.408154000	2.202928000

TS(G4.G5)

G = -4621.31411

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6	-4.844648000	4.655450000	-3.661285000
6	-2.615664000	4.743508000	-2.708819000
6	-3.838687000	5.362990000	-2.999257000
6	-2.179499000	5.771814000	-0.503980000
6	-2.451797000	5.348275000	1.909013000
6	-3.665141000	6.014294000	2.110988000
6	-4.639271000	5.468492000	2.955940000
6	-3.272559000	3.497076000	3.299622000
6	-4.483910000	4.184381000	3.476886000
6	-4.204917000	1.209045000	3.036293000
6	-4.988010000	-0.515367000	1.448147000
6	-6.350995000	-0.177684000	1.457901000
6	-7.107650000	-0.273110000	0.289660000
6	-5.124186000	-0.879358000	-0.962222000
6	-6.476736000	-0.526770000	-0.933971000
6	-4.202573000	-0.667784000	-2.090581000
6	-0.519028000	-1.240268000	-2.737337000
6	-1.858336000	-0.680542000	-2.789352000
6	-2.047247000	0.620397000	-3.331610000
6	-3.350678000	1.188062000	-3.418671000
6	0.406496000	0.929780000	-3.427372000

6	-0.892879000	1.479000000	-3.436171000
6	-1.079227000	2.854561000	-3.156226000
6	-2.393405000	3.427569000	-3.199219000
6	1.293744000	3.030405000	-2.570457000
6	-0.006792000	3.582071000	-2.579321000
6	-0.366838000	4.623061000	-1.645719000
6	-1.664909000	5.193999000	-1.678142000
6	1.730001000	4.109572000	-0.430053000
6	0.415335000	4.686308000	-0.456311000
6	-0.272319000	4.952548000	0.763602000
6	-1.572613000	5.523092000	0.738502000
6	1.466524000	3.629265000	1.942407000
6	0.163135000	4.182654000	1.904501000
6	-0.866196000	3.628646000	2.713390000
6	-2.186149000	4.182781000	2.682751000
6	0.649258000	1.802526000	3.330869000
6	-0.653366000	2.349825000	3.285277000
6	-1.807344000	1.491869000	3.377048000
6	-3.117494000	2.041140000	3.377214000
6	-0.298065000	-0.431077000	3.081049000
6	-1.609997000	0.125588000	3.042830000
6	-2.667063000	-0.565674000	2.367923000
6	-3.993633000	-0.019340000	2.400132000
6	-0.979738000	-2.119684000	1.440520000
6	-2.293288000	-1.549841000	1.412572000
6	-3.166460000	-1.785132000	0.290974000
6	-4.453136000	-1.112033000	0.271497000
6	-1.254597000	-2.996057000	-0.984861000
6	-2.610744000	-2.242186000	-0.993789000
6	-2.920547000	-1.272495000	-2.062374000
6	-0.239018000	-2.384561000	-1.979348000
6	3.424608000	-2.871167000	-2.691361000
6	2.104382000	-2.305646000	-2.698056000
6	1.881431000	-1.028992000	-3.270086000
6	0.577144000	-0.487996000	-3.267654000
6	4.341824000	-0.735733000	-3.460530000
6	3.035164000	-0.180254000	-3.451522000
6	2.853187000	1.202389000	-3.171423000
6	1.532740000	1.760935000	-3.170847000
6	5.228979000	1.354433000	-2.548990000
6	3.923119000	1.908300000	-2.552598000
6	3.545842000	2.899541000	-1.571210000
6	2.255105000	3.477148000	-1.595064000
6	5.620159000	2.339560000	-0.351518000
6	4.307739000	2.917862000	-0.374604000
6	3.640027000	3.220345000	0.842717000
6	2.350386000	3.800496000	0.815747000
6	5.400597000	1.939447000	2.042602000
6	4.094484000	2.498674000	2.007894000
6	3.074606000	1.976647000	2.853146000
6	1.756167000	2.541448000	2.816135000
6	4.581639000	0.126694000	3.464864000
6	3.279621000	0.683929000	3.416439000
6	2.120419000	-0.174309000	3.473593000
6	0.816729000	0.381992000	3.438648000

6	3.623068000	-2.109828000	3.201098000
6	2.311595000	-1.537141000	3.148079000
6	1.247410000	-2.240077000	2.501848000
6	-0.041359000	-1.669703000	2.437253000
6	2.916864000	-3.858187000	1.641109000
6	1.611272000	-3.274755000	1.589152000
6	0.812537000	-3.415035000	0.417682000
6	-0.507125000	-2.886933000	0.370358000
6	2.803238000	-4.238443000	-0.774837000
6	1.511925000	-3.703572000	-0.807623000
6	1.066633000	-2.899634000	-1.940001000
6	3.693710000	-4.045311000	-1.934357000
6	5.869991000	-4.165474000	-2.989906000
6	5.698812000	-2.888995000	-3.528654000
6	4.496362000	-2.194290000	-3.335013000
6	5.430011000	0.092038000	-3.136079000
6	7.565940000	1.520138000	-1.544223000
6	6.198749000	1.826917000	-1.546410000
6	8.300817000	1.603025000	-0.359202000
6	7.657679000	1.831039000	0.861297000
6	6.293301000	2.141702000	0.886853000
6	5.646552000	0.847914000	2.891148000
6	5.934552000	-1.980380000	3.925126000
6	4.726929000	-1.325564000	3.642894000
6	6.068042000	-3.345613000	3.670724000
6	5.065115000	-4.047963000	2.992857000
6	3.851959000	-3.421675000	2.694341000
6	3.420829000	-4.457975000	0.489604000
6	4.909478000	-4.708395000	-2.131055000
1	-5.392180000	0.947586000	-2.836567000
1	-5.548658000	2.720194000	-4.294194000
1	-5.773565000	5.155516000	-3.916956000
1	-4.012739000	6.389027000	-2.689820000
1	-3.208791000	6.110181000	-0.511541000
1	-3.867186000	6.941512000	1.583493000
1	-5.561691000	6.012729000	3.132176000
1	-5.306229000	3.709428000	4.002864000
1	-5.186982000	1.659383000	2.966967000
1	-6.808720000	0.190159000	2.370604000
1	-8.168348000	-0.045614000	0.313260000
1	-7.023948000	-0.400993000	-1.863183000
1	6.794033000	-4.705279000	-3.171811000
1	6.510336000	-2.421604000	-4.077685000
1	6.407955000	-0.364380000	-3.039951000
1	8.048707000	1.190092000	-2.458870000
1	9.366997000	1.399273000	-0.373721000
1	8.210064000	1.735298000	1.791071000
1	6.617144000	0.369255000	2.837566000
1	6.773644000	-1.419447000	4.324299000
1	6.993758000	-3.850811000	3.928118000
1	5.242332000	-5.070422000	2.673860000
1	4.447126000	-4.805668000	0.497491000
1	5.117915000	-5.631833000	-1.599277000
6	-1.352284000	-4.505122000	-1.300892000
6	-4.202212000	-3.664822000	-1.651495000

1	-0.464305000	-5.053658000	-1.014922000
6	-2.295228000	-5.158686000	-1.989348000
1	-5.034810000	-3.119201000	-2.091299000
6	-3.532484000	-4.547088000	-2.425814000
1	-2.094823000	-6.187978000	-2.282474000
1	-3.915134000	-4.828616000	-3.408473000
45	-4.295819000	-3.745442000	0.504698000
6	-5.089294000	-5.430123000	0.260795000
8	-5.556179000	-6.466433000	0.091017000
6	-4.378570000	-3.816713000	2.410841000
8	-4.416208000	-3.853129000	3.558787000

G5

G = -4621.35355

6	-4.327491000	0.660019000	-2.979762000
6	-3.352737000	2.859334000	-3.580191000
6	-4.546752000	3.533332000	-3.866739000
6	-4.663922000	4.898486000	-3.593207000
6	-2.452068000	4.926938000	-2.600558000
6	-3.657187000	5.574481000	-2.898831000
6	-2.052478000	5.872029000	-0.354684000
6	-2.411441000	5.334075000	2.020495000
6	-3.621914000	6.008279000	2.216884000
6	-4.635302000	5.428674000	2.988457000
6	-3.312772000	3.416412000	3.261900000
6	-4.518797000	4.111920000	3.435158000
6	-4.265876000	1.154495000	2.854875000
6	-5.039682000	-0.515101000	1.200586000
6	-6.399424000	-0.132871000	1.187959000
6	-7.131842000	-0.194959000	0.010312000
6	-5.136342000	-0.831969000	-1.209556000
6	-6.471097000	-0.440583000	-1.208342000
6	-4.153140000	-0.551292000	-2.289771000
6	-0.463920000	-1.128255000	-2.835314000
6	-1.788852000	-0.528988000	-2.863440000
6	-1.942268000	0.809638000	-3.334893000
6	-3.230285000	1.399045000	-3.430141000
6	0.513321000	1.074211000	-3.361660000
6	-0.774418000	1.649638000	-3.376219000
6	-0.942549000	3.020058000	-3.062157000
6	-2.244468000	3.617314000	-3.116359000
6	1.418352000	3.133546000	-2.422600000
6	0.131061000	3.711936000	-2.444241000
6	-0.230344000	4.732963000	-1.489530000
6	-1.516677000	5.329459000	-1.535315000
6	1.822878000	4.133052000	-0.239165000
6	0.520390000	4.737186000	-0.278359000
6	-0.198800000	4.964056000	0.931459000
6	-1.487512000	5.557731000	0.893544000
6	1.477610000	3.549361000	2.097792000
6	0.184647000	4.126898000	2.044407000
6	-0.882623000	3.543955000	2.777528000
6	-2.193664000	4.119938000	2.730264000

6	0.581383000	1.659579000	3.341671000
6	-0.710300000	2.228710000	3.275764000
6	-1.877339000	1.385452000	3.266918000
6	-3.181586000	1.954301000	3.257635000
6	-0.383488000	-0.540771000	2.923714000
6	-1.686826000	0.038861000	2.864743000
6	-2.732459000	-0.610923000	2.137889000
6	-4.053308000	-0.053149000	2.171405000
6	-1.039433000	-2.157539000	1.195568000
6	-2.358890000	-1.586079000	1.164308000
6	-3.249162000	-1.873545000	0.079507000
6	-4.506523000	-1.133633000	0.037474000
6	-1.267029000	-3.028896000	-1.257824000
6	-2.731051000	-2.373632000	-1.320434000
6	-2.882240000	-1.166057000	-2.257266000
6	-0.232169000	-2.359972000	-2.200811000
6	3.463434000	-2.806865000	-2.803171000
6	2.147300000	-2.229058000	-2.818438000
6	1.955629000	-0.911425000	-3.297678000
6	0.656580000	-0.353947000	-3.277892000
6	4.425747000	-0.640661000	-3.412938000
6	3.125060000	-0.069794000	-3.400357000
6	2.957652000	1.298832000	-3.053352000
6	1.646275000	1.876657000	-3.054368000
6	5.320726000	1.387293000	-2.373632000
6	4.024477000	1.962446000	-2.384404000
6	3.642501000	2.925536000	-1.377252000
6	2.364829000	3.530384000	-1.411659000
6	5.672425000	2.277382000	-0.128511000
6	4.372892000	2.883723000	-0.162386000
6	3.678004000	3.152170000	1.047818000
6	2.401114000	3.758849000	1.009649000
6	5.377826000	1.783208000	2.239042000
6	4.083089000	2.367590000	2.190880000
6	3.026397000	1.821509000	2.972449000
6	1.718230000	2.409922000	2.917951000
6	4.481915000	-0.083295000	3.538243000
6	3.190796000	0.496883000	3.470693000
6	2.018812000	-0.345345000	3.431772000
6	0.724453000	0.232385000	3.371090000
6	3.504148000	-2.287678000	3.118726000
6	2.203630000	-1.690581000	3.042718000
6	1.155856000	-2.343546000	2.322618000
6	-0.122734000	-1.752645000	2.234166000
6	2.833622000	-3.951414000	1.452156000
6	1.538809000	-3.343964000	1.380507000
6	0.774174000	-3.431443000	0.185793000
6	-0.546248000	-2.892336000	0.117449000
6	2.782044000	-4.254639000	-0.975413000
6	1.496433000	-3.708048000	-1.025794000
6	1.077774000	-2.869943000	-2.145884000
6	3.702539000	-4.022828000	-2.103389000
6	5.907188000	-4.107349000	-3.100104000
6	5.762313000	-2.801365000	-3.570509000
6	4.560803000	-2.105236000	-3.371411000

6	5.516725000	0.152304000	-3.017782000
6	7.632702000	1.464388000	-1.301153000
6	6.272147000	1.799303000	-1.327393000
6	8.336923000	1.486366000	-0.095026000
6	7.665666000	1.679914000	1.116357000
6	6.307461000	2.017009000	1.118311000
6	5.577897000	0.648119000	3.040870000
6	5.786977000	-2.231352000	3.938364000
6	4.599838000	-1.545037000	3.643892000
6	5.913411000	-3.583299000	3.618730000
6	4.928000000	-4.234506000	2.868454000
6	3.735245000	-3.575783000	2.556411000
6	3.365359000	-4.517316000	0.296360000
6	4.917460000	-4.686459000	-2.299595000
1	-5.288759000	1.154445000	-2.912915000
1	-5.389579000	2.992278000	-4.285650000
1	-5.579605000	5.420621000	-3.852881000
1	-3.819472000	6.595997000	-2.568573000
1	-3.075645000	6.227756000	-0.376785000
1	-3.789266000	6.968867000	1.739282000
1	-5.556311000	5.976091000	3.162464000
1	-5.368481000	3.619971000	3.898294000
1	-5.242112000	1.616951000	2.784537000
1	-6.862926000	0.235255000	2.097549000
1	-8.185523000	0.064268000	0.011158000
1	-6.982787000	-0.251479000	-2.147333000
1	6.831869000	-4.645109000	-3.284907000
1	6.593424000	-2.311901000	-4.068620000
1	6.485215000	-0.323924000	-2.922266000
1	8.133695000	1.159996000	-2.214887000
1	9.398868000	1.261019000	-0.089592000
1	8.190372000	1.535639000	2.055893000
1	6.541852000	0.155441000	2.995901000
1	6.616559000	-1.703426000	4.398068000
1	6.821938000	-4.114695000	3.884575000
1	5.103405000	-5.242365000	2.505033000
1	4.388080000	-4.874756000	0.320172000
1	5.103313000	-5.637199000	-1.809078000
6	-1.277774000	-4.544318000	-1.490814000
6	-3.837791000	-3.386575000	-1.693516000
1	-0.304521000	-5.014571000	-1.505814000
6	-2.354512000	-5.333264000	-1.605197000
1	-4.759706000	-2.978105000	-2.087890000
6	-3.667988000	-4.743406000	-1.736166000
1	-2.245253000	-6.408392000	-1.699281000
1	-4.491875000	-5.363992000	-2.079697000
45	-4.375888000	-3.795995000	0.486184000
6	-4.462894000	-3.573104000	2.367503000
8	-4.498498000	-3.418268000	3.503116000
6	-5.420892000	-5.380479000	0.528345000
8	-6.059232000	-6.334357000	0.556521000

H1

G = -485.53334

6	-0.000073000	-2.030924000	0.627822000
6	-0.000044000	-2.031152000	-0.627244000
1	-0.000086000	-2.434931000	1.626308000
1	-0.000053000	-2.435477000	-1.625597000
6	0.623502000	2.162771000	0.000170000
6	-0.623403000	2.162797000	0.000155000
1	-1.616907000	2.574276000	0.000112000
1	1.617023000	2.574207000	0.000189000
6	-1.965922000	-0.115250000	-0.000222000
8	-3.091244000	-0.273775000	-0.000367000
6	1.965923000	-0.115335000	-0.000131000
8	3.091245000	-0.273862000	-0.000411000
77	0.000002000	0.050722000	0.000025000

TS(H1.H2)

G = -485.50191

6	2.091564000	-0.986162000	-0.077716000
6	1.211953000	-1.531677000	-0.834872000
1	2.931559000	-1.190725000	0.570412000
1	0.944795000	-2.468406000	-1.300171000
6	1.211814000	1.531811000	0.834833000
6	2.091491000	0.986264000	0.077764000
1	2.931561000	1.190850000	-0.570263000
1	0.944610000	2.468518000	1.300151000
6	-1.338377000	-1.309301000	0.261641000
8	-2.134139000	-2.086550000	0.515714000
6	-1.338531000	1.309167000	-0.261632000
8	-2.134370000	2.086351000	-0.515664000
77	0.036572000	0.000010000	-0.000008000

H2

G = -485.55802

6	-2.740319000	-0.647528000	0.240695000
6	-1.416845000	-1.222587000	0.341953000
1	-3.648790000	-1.198488000	0.472229000
1	-1.366273000	-2.281234000	0.607623000
6	-1.417398000	1.222274000	-0.341355000
6	-2.740690000	0.646813000	-0.240047000
1	-3.649372000	1.197552000	-0.471199000
1	-1.367197000	2.281214000	-0.605972000
6	1.479548000	-1.481903000	-0.090106000
8	2.228375000	-2.322328000	-0.246187000
6	1.478824000	1.482471000	0.090421000
8	2.227024000	2.323298000	0.247384000
77	0.084801000	-0.000052000	-0.000281000

H3

G = -4615.17367

6	4.739340000	-0.017829000	-2.383999000
6	4.025341000	-2.047984000	-3.609414000

6	5.291664000	-2.581773000	-3.877951000
6	5.488931000	-3.965029000	-3.849780000
6	3.199772000	-4.310154000	-3.125951000
6	4.476511000	-4.817077000	-3.402180000
6	2.666880000	-5.695672000	-1.148357000
6	2.720247000	-5.713755000	1.321825000
6	3.950414000	-6.355309000	1.502381000
6	4.808952000	-5.957083000	2.533096000
6	3.297125000	-4.163102000	3.139192000
6	4.526229000	-4.821279000	3.292394000
6	4.102138000	-1.834767000	3.410396000
6	4.876211000	0.175218000	2.193141000
6	6.256986000	-0.056367000	2.258372000
6	7.073758000	0.277045000	1.175550000
6	5.141775000	0.930456000	-0.133332000
6	6.516353000	0.689602000	-0.040179000
6	4.359391000	0.898169000	-1.383545000
6	0.740798000	1.442215000	-2.341646000
6	2.100087000	0.954742000	-2.360564000
6	2.432265000	-0.186653000	-3.137897000
6	3.772846000	-0.664806000	-3.168140000
6	0.010420000	-0.577670000	-3.506042000
6	1.339481000	-1.059335000	-3.499501000
6	1.587913000	-2.452393000	-3.413059000
6	2.936144000	-2.944842000	-3.425749000
6	-0.807181000	-2.824014000	-3.035758000
6	0.521709000	-3.307454000	-3.030252000
6	0.877822000	-4.460564000	-2.236500000
6	2.205560000	-4.959418000	-2.254205000
6	-1.324278000	-4.248975000	-1.123511000
6	0.020347000	-4.750522000	-1.136096000
6	0.625886000	-5.195502000	0.074251000
6	1.954773000	-5.694303000	0.062805000
6	-1.281176000	-4.207650000	1.314703000
6	0.050330000	-4.682459000	1.295031000
6	0.967797000	-4.262189000	2.297077000
6	2.316365000	-4.745548000	2.285492000
6	-0.711099000	-2.677044000	3.125757000
6	0.622012000	-3.148176000	3.104464000
6	1.708905000	-2.285050000	3.498920000
6	3.042962000	-2.764171000	3.507334000
6	0.112117000	-0.400570000	3.437562000
6	1.456554000	-0.883727000	3.430415000
6	2.522665000	-0.036713000	2.995716000
6	3.865363000	-0.512700000	3.014535000
6	0.817032000	1.552141000	2.166717000
6	2.150125000	1.062067000	2.156125000
6	3.024422000	1.371228000	1.068777000
6	4.365929000	0.867613000	1.060174000
6	1.124440000	2.448268000	-0.122683000
6	2.456686000	1.893179000	-0.135419000
6	3.028208000	1.376318000	-1.372401000
6	0.315367000	2.348814000	-1.341881000
6	-3.282306000	2.871744000	-2.297483000
6	-1.934671000	2.378021000	-2.303482000

6	-1.591892000	1.258092000	-3.101872000
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6	-4.010679000	0.889363000	-3.529119000
6	-2.678240000	0.402079000	-3.519537000
6	-2.430725000	-0.998874000	-3.459453000
6	-1.081181000	-1.490414000	-3.456956000
6	-4.830294000	-1.362455000	-3.042902000
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6	-3.968713000	-3.219088000	-1.084867000
6	-3.378411000	-3.698829000	0.113629000
6	-2.055237000	-4.197276000	0.098582000
6	-5.309468000	-2.764341000	1.364941000
6	-3.972991000	-3.238985000	1.347058000
6	-3.064340000	-2.849551000	2.373754000
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6	-1.494894000	1.416213000	3.010940000
6	-0.168561000	0.927685000	3.002154000
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6	-0.990713000	2.875450000	1.122450000
6	0.343039000	2.373127000	1.106230000
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6	-1.010309000	2.817863000	-1.318637000
6	-3.680056000	3.850227000	-1.343458000
6	-5.766920000	4.094085000	-2.549443000
6	-5.483046000	2.957851000	-3.309211000
6	-4.259768000	2.290948000	-3.151943000
6	-5.068124000	-0.032632000	-3.429926000
6	-7.216610000	-1.812303000	-2.271176000
6	-5.837211000	-2.044463000	-2.210769000
6	-8.031344000	-2.136564000	-1.182538000
6	-7.467980000	-2.543396000	0.029207000
6	-6.090907000	-2.785773000	0.116978000
6	-5.697785000	-1.871816000	2.381472000
6	-6.257075000	0.691533000	3.879429000
6	-4.992219000	0.155051000	3.610069000
6	-6.456777000	2.074239000	3.838979000
6	-5.448473000	2.927250000	3.383240000
6	-4.172512000	2.419452000	3.110226000
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1	-6.689230000	-1.438204000	2.326590000
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1	-7.433055000	2.481437000	4.083044000
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1	0.430731000	6.064069000	0.647779000
6	0.685091000	5.857766000	-1.504617000
1	3.293138000	3.945390000	-2.573184000
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TS(H3.H4)

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6	2.140648000	4.880563000	3.001922000
6	3.301821000	5.612344000	3.282370000
6	1.424540000	6.073040000	0.958492000
6	1.546778000	5.974835000	-1.505447000
6	2.655626000	6.807013000	-1.697802000
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6	2.438844000	4.444962000	-3.208642000
6	3.543650000	5.293644000	-3.372902000
6	3.636541000	2.275611000	-3.349311000
6	4.723622000	0.490309000	-2.034293000
6	6.035058000	0.998122000	-2.090668000
6	6.874585000	0.893122000	-0.985487000
6	5.075151000	-0.087759000	0.313128000

6	6.365523000	0.441202000	0.239502000
6	4.254845000	-0.145129000	1.541655000
6	0.764558000	-1.274134000	2.419630000
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6	2.109408000	0.680892000	3.153628000
6	3.338019000	1.392238000	3.204062000
6	-0.346058000	0.656399000	3.452458000
6	0.874668000	1.364236000	3.450725000
6	0.875416000	2.775896000	3.323968000
6	2.112794000	3.500805000	3.346602000
6	-1.536923000	2.709466000	2.898617000
6	-0.315523000	3.418887000	2.896433000
6	-0.150206000	4.589950000	2.067607000
6	1.070078000	5.313497000	2.087193000
6	-2.257326000	3.956065000	0.930767000
6	-1.019834000	4.683989000	0.943279000
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6	0.756223000	5.892997000	-0.264603000
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6	-0.909066000	4.505868000	-1.477431000
6	0.098046000	4.194398000	-2.429386000
6	1.345400000	4.899394000	-2.416303000
6	-1.259424000	2.302674000	-3.197403000
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6	2.198743000	-0.871380000	-1.965649000
6	3.136004000	-1.065858000	-0.905881000
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6	1.429585000	-2.469255000	0.323565000
6	2.713051000	-1.706672000	0.347177000
6	3.050190000	-0.879803000	1.532925000
6	0.548115000	-2.336917000	1.512488000
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6	-1.708158000	-2.664465000	2.423728000
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6	-0.360718000	-0.745479000	3.124447000
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6	-2.819091000	0.642522000	3.370525000
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6	-2.370018000	-4.379184000	0.285677000
6	-1.150842000	-3.677646000	0.296052000
6	-0.689052000	-3.008092000	1.501315000
6	-3.151681000	-4.470873000	1.531368000
6	-5.196338000	-5.001546000	2.716053000
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6	-4.037365000	-2.930632000	3.226657000
6	-5.243602000	-0.771823000	3.360419000
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6	-6.329177000	1.022812000	2.040590000
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6	-7.979821000	1.152197000	-0.236538000
6	-6.666043000	1.628374000	-0.316035000
6	-6.064881000	0.700925000	-2.525799000
6	-6.132515000	-1.994162000	-3.885369000
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1	5.317380000	5.546391000	4.032315000
1	3.329438000	6.679974000	3.087042000
1	2.405625000	6.532582000	0.942314000
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1	-5.943100000	-3.497921000	4.065045000
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1	-6.967518000	0.104520000	-2.467532000

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6	4.076103000	-4.304857000	1.660383000
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1	4.988460000	-4.330585000	2.255551000
6	2.938089000	-4.970768000	2.093303000
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H4

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6	-0.957514000	5.258969000	1.857269000
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6	-0.695666000	2.854300000	3.287224000
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6	-0.640495000	-2.730747000	-0.714604000
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6	8.063592000	1.044025000	-0.712052000
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6	6.435729000	1.024760000	1.831757000
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6	5.463969000	-3.494949000	3.527191000
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H5

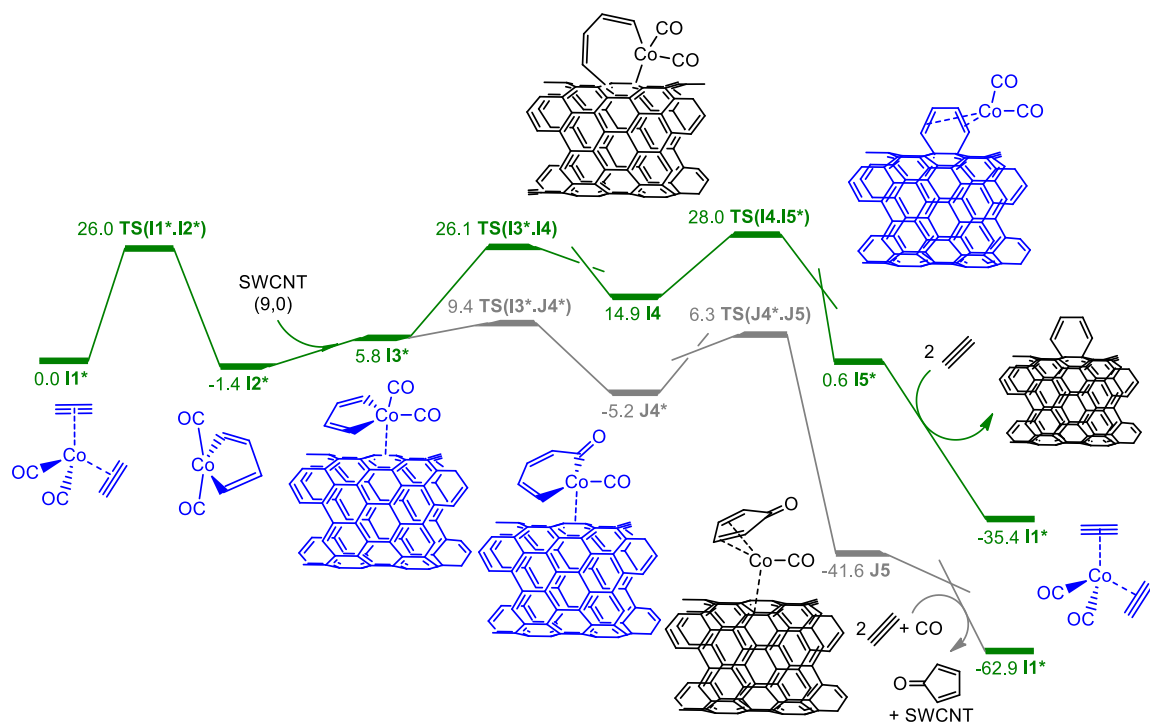
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6	4.082422000	-4.037333000	1.858814000
1	2.892850000	-5.877044000	1.887494000
1	4.982707000	-4.532489000	2.214505000
77	4.671519000	-3.088183000	-0.389055000
6	4.805241000	-2.814131000	-2.246756000
8	4.860996000	-2.616896000	-3.378813000
6	5.840320000	-4.575901000	-0.416868000
8	6.548262000	-5.484495000	-0.428452000



I1*

G = -1763.75738

6	-0.006017000	-1.551095000	-1.599199000
6	-0.940332000	-0.793442000	-1.869418000
1	0.715416000	-2.346902000	-1.648060000
1	-1.764018000	-0.268066000	-2.310657000
6	0.936983000	-0.791306000	1.871186000
6	-0.001714000	-1.544915000	1.605000000
1	-0.727653000	-2.336426000	1.656396000
1	1.763209000	-0.268581000	2.310848000
6	-1.433118000	1.035766000	0.303693000
8	-2.277444000	1.736963000	0.589901000
6	1.438384000	1.028161000	-0.307378000
8	2.285144000	1.726146000	-0.594188000
27	-0.000506000	-0.251256000	0.000091000

TS(I1*.I2*)

G = -1763.71595

6	1.902196000	0.300774000	-0.936699000
6	0.954557000	-0.193584000	-1.678753000
1	2.887806000	0.706549000	-1.115828000
1	0.785330000	-0.480257000	-2.706151000
6	0.954277000	-0.195634000	1.678607000
6	1.902087000	0.299402000	0.937254000
1	2.887786000	0.704688000	1.116990000
1	0.784785000	-0.483701000	2.705572000
6	-1.032366000	-1.478950000	-0.000830000
8	-1.693940000	-2.401241000	-0.000616000
6	-1.321584000	1.449697000	0.000564000
8	-2.089785000	2.278267000	0.000732000
27	0.102559000	-0.020508000	-0.000088000

I2*

G = -1763.75953

6	-2.558648000	-0.710211000	0.002720000
6	-1.284536000	-1.266413000	-0.001027000
1	-3.474676000	-1.298219000	0.005436000
1	-1.194639000	-2.353233000	-0.002075000
6	-1.283341000	1.267712000	-0.001657000
6	-2.557974000	0.712525000	0.002269000
1	-3.473543000	1.301258000	0.004595000
1	-1.192730000	2.354482000	-0.002988000
6	1.414008000	-1.409937000	-0.000057000
8	2.110915000	-2.303509000	0.002585000
6	1.416506000	1.408297000	0.000072000
8	2.115745000	2.300050000	0.003070000
27	0.172082000	0.000428000	-0.002375000

I3*

G = -5893.36139

6	4.763756000	0.933450000	-2.263191000
6	4.271999000	-1.103208000	-3.592470000
6	5.591121000	-1.488706000	-3.867208000
6	5.928947000	-2.842624000	-3.915291000
6	3.678569000	-3.464374000	-3.254563000
6	5.003036000	-3.819568000	-3.538283000
6	3.272452000	-5.020272000	-1.377427000
6	3.312814000	-5.186922000	1.087811000
6	4.598816000	-5.720700000	1.243281000
6	5.408106000	-5.303791000	2.302891000
6	3.731742000	-3.695045000	2.992700000
6	5.013413000	-4.242698000	3.122915000
6	4.304599000	-1.316919000	3.386276000
6	4.856619000	0.833787000	2.276541000
6	6.261733000	0.768488000	2.345176000
6	7.040741000	1.299126000	1.321410000
6	5.060405000	1.824843000	0.029066000
6	6.447677000	1.752687000	0.129635000
6	4.286278000	1.766689000	-1.236944000
6	0.643678000	1.956894000	-2.184774000
6	2.038916000	1.612806000	-2.215282000
6	2.493221000	0.550555000	-3.044786000
6	3.874715000	0.219577000	-3.086342000
6	0.127802000	-0.058748000	-3.458881000
6	1.498622000	-0.404788000	-3.466414000
6	1.886980000	-1.768315000	-3.459181000
6	3.278460000	-2.116999000	-3.478980000
6	-0.461616000	-2.399492000	-3.130804000
6	0.909893000	-2.747635000	-3.138895000
6	1.375067000	-3.904880000	-2.410100000
6	2.747881000	-4.265383000	-2.439986000
6	-0.843629000	-3.979406000	-1.310823000
6	0.545151000	-4.343962000	-1.339006000

6	1.185516000	-4.798438000	-0.150346000
6	2.555491000	-5.164891000	-0.176057000
6	-0.814905000	-4.072199000	1.127720000
6	0.557830000	-4.413870000	1.093836000
6	1.424640000	-3.964708000	2.123229000
6	2.815631000	-4.317560000	2.098514000
6	-0.402849000	-2.593155000	3.018852000
6	0.969401000	-2.932619000	2.986272000
6	1.965731000	-1.989252000	3.431391000
6	3.346170000	-2.340183000	3.427263000
6	0.186756000	-0.265877000	3.447891000
6	1.578445000	-0.621512000	3.428574000
6	2.553632000	0.338181000	3.044017000
6	3.930063000	-0.000721000	3.045635000
6	0.690796000	1.819026000	2.292119000
6	2.073975000	1.444925000	2.251953000
6	2.894977000	1.909567000	1.223535000
6	4.277050000	1.553297000	1.195008000
6	0.894352000	2.820266000	0.081802000
6	2.299030000	2.567142000	0.050237000
6	2.907341000	2.083258000	-1.202296000
6	0.125727000	2.767289000	-1.132500000
6	-3.503976000	2.978412000	-2.102643000
6	-2.113291000	2.625336000	-2.120455000
6	-1.655694000	1.583486000	-2.968305000
6	-0.279585000	1.241113000	-2.990520000
6	-4.020991000	1.000692000	-3.444068000
6	-2.644819000	0.649238000	-3.446553000
6	-2.257883000	-0.721913000	-3.464475000
6	-0.866437000	-1.077109000	-3.476123000
6	-4.611182000	-1.344764000	-3.092892000
6	-3.233955000	-1.691882000	-3.101210000
6	-2.759257000	-2.814473000	-2.325419000
6	-1.392920000	-3.180175000	-2.354768000
6	-4.965994000	-2.859731000	-1.212288000
6	-3.576945000	-3.217967000	-1.238045000
6	-2.946698000	-3.704367000	-0.062876000
6	-1.581094000	-4.069769000	-0.093802000
6	-4.966171000	-3.035327000	1.221947000
6	-3.588077000	-3.374230000	1.189560000
6	-2.726731000	-2.954676000	2.241947000
6	-1.334674000	-3.305313000	2.210792000
6	-4.555695000	-1.556848000	3.123457000
6	-3.177938000	-1.897261000	3.084236000
6	-2.179409000	-0.933352000	3.478831000
6	-0.805125000	-1.282691000	3.465266000
6	-3.957743000	0.784774000	3.492404000
6	-2.567399000	0.432414000	3.460170000
6	-1.596300000	1.406384000	3.110026000
6	-0.223234000	1.053383000	3.085546000
6	-3.442632000	2.920674000	2.423073000
6	-2.066008000	2.560654000	2.385094000
6	-1.241064000	3.022349000	1.324071000
6	0.147729000	2.655995000	1.285230000
6	-3.250911000	3.843666000	0.166526000

6	-1.878773000	3.494012000	0.141460000
6	-1.248473000	3.098524000	-1.099276000
6	-4.006756000	3.855759000	-1.100295000
6	-6.100028000	3.952923000	-2.318035000
6	-5.696673000	2.893694000	-3.133736000
6	-4.412360000	2.348010000	-2.997702000
6	-4.980323000	-0.025658000	-3.409935000
6	-6.944553000	-2.068137000	-2.370999000
6	-5.548375000	-2.169149000	-2.311429000
6	-7.727515000	-2.534575000	-1.312137000
6	-7.130004000	-2.954462000	-0.120681000
6	-5.736517000	-3.064814000	-0.033529000
6	-5.446212000	-2.246803000	2.282732000
6	-6.263049000	0.159426000	3.911285000
6	-4.948209000	-0.228678000	3.624871000
6	-6.604512000	1.514002000	3.944151000
6	-5.685980000	2.486715000	3.542627000
6	-4.362350000	2.128387000	3.255298000
6	-3.968251000	3.683844000	1.368534000
6	-5.294940000	4.379118000	-1.257115000
1	5.793318000	0.599625000	-2.210918000
1	6.356550000	-0.734113000	-4.020580000
1	6.944000000	-3.134464000	-4.166391000
1	5.319795000	-4.853133000	-3.437280000
1	4.340210000	-5.203267000	-1.358627000
1	4.977855000	-6.437376000	0.521220000
1	6.389369000	-5.748684000	2.436251000
1	5.711309000	-3.826130000	3.842947000
1	5.347940000	-1.593462000	3.288401000
1	6.737740000	0.293365000	3.197173000
1	8.122763000	1.277018000	1.405905000
1	7.067972000	1.987507000	-0.730178000
1	-7.084270000	4.390227000	-2.454184000
1	-6.389275000	2.473431000	-3.856391000
1	-6.021814000	0.252219000	-3.301359000
1	-7.417930000	-1.602630000	-3.230048000
1	-8.809753000	-2.487506000	-1.382715000
1	-7.745597000	-3.168054000	0.747777000
1	-6.475758000	-1.911902000	2.243980000
1	-7.025118000	-0.595017000	4.080730000
1	-7.618068000	1.805956000	4.200797000
1	-6.005485000	3.518030000	3.428210000
1	-5.037103000	3.859454000	1.349076000
1	-5.681804000	5.092519000	-0.535727000
6	1.251771000	5.592478000	0.406374000
6	2.407110000	4.984416000	-1.777021000
1	1.041017000	5.899861000	1.431247000
6	0.548440000	5.909671000	-0.695283000
1	3.142627000	4.741908000	-2.554927000
6	1.191631000	5.526092000	-1.959100000
1	-0.417428000	6.407259000	-0.638519000
1	0.721575000	5.662412000	-2.931239000
27	2.959422000	4.742243000	0.016292000
6	3.477088000	6.447255000	-0.010318000
8	3.754667000	7.573894000	0.040930000

6	4.014034000	4.446936000	1.698714000
8	4.776545000	4.426797000	2.540075000

TS(I3*.I4)

G = -5893.32343

6	-4.828259000	0.964272000	2.028210000
6	-4.373798000	-0.998091000	3.461525000
6	-5.694872000	-1.371055000	3.731372000
6	-6.036986000	-2.724637000	3.823989000
6	-3.777683000	-3.371012000	3.229968000
6	-5.109634000	-3.716163000	3.499923000
6	-3.335176000	-4.978140000	1.405704000
6	-3.320804000	-5.193844000	-1.054352000
6	-4.605629000	-5.716076000	-1.233396000
6	-5.383769000	-5.310492000	-2.323744000
6	-3.673050000	-3.734275000	-3.003528000
6	-4.958790000	-4.273159000	-3.154922000
6	-4.204557000	-1.363676000	-3.501208000
6	-4.795786000	0.819495000	-2.507999000
6	-6.192057000	0.730642000	-2.618161000
6	-7.010042000	1.248527000	-1.612663000
6	-5.068978000	1.804216000	-0.280085000
6	-6.456220000	1.705906000	-0.410412000
6	-4.326153000	1.766871000	0.988647000
6	-0.712790000	2.037237000	2.013954000
6	-2.112333000	1.687121000	2.027330000
6	-2.582606000	0.644748000	2.877468000
6	-3.963363000	0.304505000	2.908269000
6	-0.233980000	0.046163000	3.365693000
6	-1.603279000	-0.297504000	3.354909000
6	-1.992779000	-1.662894000	3.398269000
6	-3.381620000	-2.016080000	3.407974000
6	0.358781000	-2.311642000	3.161713000
6	-1.010577000	-2.657091000	3.148835000
6	-1.460265000	-3.840486000	2.454955000
6	-2.831532000	-4.197695000	2.464219000
6	0.783631000	-3.963325000	1.418791000
6	-0.603356000	-4.319550000	1.420477000
6	-1.218138000	-4.800956000	0.226327000
6	-2.593172000	-5.154916000	0.226697000
6	0.820285000	-4.130730000	-1.012907000
6	-0.555342000	-4.455781000	-1.006005000
6	-1.395595000	-4.016818000	-2.069224000
6	-2.787337000	-4.349565000	-2.070987000
6	0.470147000	-2.692944000	-2.953063000
6	-0.906453000	-3.011937000	-2.944100000
6	-1.879223000	-2.070022000	-3.441801000
6	-3.256114000	-2.406222000	-3.472786000
6	-0.088902000	-0.374446000	-3.455290000
6	-1.478044000	-0.703211000	-3.468057000
6	-2.455801000	0.293318000	-3.155848000
6	-3.837201000	-0.039636000	-3.213375000
6	-0.613395000	1.753528000	-2.381570000

6	-2.004619000	1.435143000	-2.410141000
6	-2.875674000	1.960490000	-1.417620000
6	-4.255016000	1.571675000	-1.427866000
6	-0.928491000	3.075158000	-0.269549000
6	-2.345108000	2.640944000	-0.258035000
6	-2.957113000	2.133300000	0.986410000
6	-0.173546000	2.861908000	0.997885000
6	3.435185000	3.039444000	2.056714000
6	2.045019000	2.688822000	2.038851000
6	1.559017000	1.665875000	2.895859000
6	0.187994000	1.330267000	2.870649000
6	3.909129000	1.092684000	3.460753000
6	2.533122000	0.744691000	3.428115000
6	2.144520000	-0.625049000	3.480738000
6	0.756373000	-0.973175000	3.458942000
6	4.504853000	-1.269239000	3.210286000
6	3.129665000	-1.612632000	3.189322000
6	2.674714000	-2.764072000	2.445954000
6	1.308248000	-3.124066000	2.449136000
6	4.910375000	-2.859275000	1.401204000
6	3.522672000	-3.212968000	1.399212000
6	2.922420000	-3.742699000	0.222765000
6	1.554719000	-4.098468000	0.226331000
6	4.981306000	-3.131037000	-1.022330000
6	3.600124000	-3.458360000	-1.017599000
6	2.768927000	-3.063091000	-2.107692000
6	1.376963000	-3.396927000	-2.102954000
6	4.631250000	-1.703414000	-2.978189000
6	3.252299000	-2.031326000	-2.966397000
6	2.273077000	-1.072665000	-3.416130000
6	0.898111000	-1.405973000	-3.425168000
6	4.061474000	0.633109000	-3.415257000
6	2.672087000	0.289986000	-3.414532000
6	1.694205000	1.281773000	-3.115792000
6	0.323458000	0.944774000	-3.113797000
6	3.525575000	2.811125000	-2.431639000
6	2.149086000	2.448469000	-2.417068000
6	1.285229000	2.965890000	-1.411857000
6	-0.092882000	2.620865000	-1.405641000
6	3.248986000	3.853583000	-0.229374000
6	1.879413000	3.517821000	-0.232033000
6	1.201708000	3.161272000	1.001762000
6	3.970160000	3.898022000	1.053836000
6	6.024318000	4.020551000	2.331545000
6	5.594234000	2.978123000	3.157505000
6	4.317013000	2.427950000	2.992331000
6	4.865402000	0.063577000	3.485382000
6	6.856077000	-2.029228000	2.588263000
6	5.461915000	-2.124577000	2.490072000
6	7.666829000	-2.543162000	1.573287000
6	7.105475000	-3.010246000	0.381008000
6	5.715745000	-3.116105000	0.254712000
6	5.492977000	-2.376036000	-2.091436000
6	6.373404000	-0.017330000	-3.758141000
6	5.048490000	-0.391097000	-3.495989000

6	6.721052000	1.333483000	-3.818848000
6	5.797934000	2.325025000	-3.470698000
6	4.467859000	1.983547000	-3.204311000
6	4.012202000	3.623531000	-1.399878000
6	5.254716000	4.423668000	1.237452000
1	-5.855170000	0.625655000	1.960096000
1	-6.462070000	-0.610774000	3.841346000
1	-7.057198000	-3.003473000	4.068753000
1	-5.425024000	-4.752835000	3.433306000
1	-4.403317000	-5.156506000	1.369061000
1	-5.013788000	-6.412666000	-0.507667000
1	-6.366231000	-5.747874000	-2.471830000
1	-5.632484000	-3.868319000	-3.903650000
1	-5.253195000	-1.628216000	-3.434392000
1	-6.636257000	0.234656000	-3.475357000
1	-8.088958000	1.206664000	-1.724627000
1	-7.098962000	1.940916000	0.432033000
1	7.003889000	4.460612000	2.490304000
1	6.263765000	2.574980000	3.910965000
1	5.910803000	0.335963000	3.401301000
1	7.306772000	-1.531602000	3.441313000
1	8.746668000	-2.498045000	1.675243000
1	7.747560000	-3.261615000	-0.457522000
1	6.524309000	-2.048508000	-2.036359000
1	7.135664000	-0.779036000	-3.888898000
1	7.742367000	1.613573000	-4.057457000
1	6.122313000	3.357095000	-3.380535000
1	5.079664000	3.803601000	-1.350934000
1	5.663505000	5.122770000	0.514291000
6	-1.048155000	4.928805000	-0.785852000
6	-2.056436000	5.690354000	1.446513000
1	-0.866151000	4.841333000	-1.854704000
6	-0.245217000	5.796912000	-0.037559000
1	-2.524511000	5.878262000	2.414379000
6	-0.758706000	6.105336000	1.245495000
1	0.696140000	6.195046000	-0.411042000
1	-0.171444000	6.637407000	1.992772000
27	-2.871874000	4.756169000	-0.060459000
6	-3.296457000	6.068515000	-1.252404000
8	-3.434511000	6.978429000	-1.934666000
6	-4.463059000	4.720663000	0.805351000
8	-5.429518000	4.837825000	1.408740000

I4

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6	-5.830289000	2.894042000	-3.663644000
6	-3.501887000	3.411139000	-3.212159000
6	-4.815014000	3.831771000	-3.467766000
6	-2.865220000	5.150961000	-1.582070000
6	-2.764555000	5.520047000	0.849880000

6	-4.001290000	6.150758000	1.025919000
6	-4.797128000	5.842363000	2.134731000
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6	-3.930788000	1.841247000	3.394870000
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6	-4.390295000	-1.685589000	-0.704317000
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6	-2.166047000	-1.720087000	-1.775326000
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6	-2.071551000	5.355448000	-0.441209000
6	1.274262000	4.112246000	0.790978000
6	-0.070651000	4.552411000	0.791149000
6	-0.924818000	4.222640000	1.877645000
6	-2.286976000	4.668717000	1.885557000
6	0.838211000	2.775071000	2.777886000
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6	-2.311863000	0.036238000	3.129199000
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6	-2.530902000	-2.703698000	0.530075000
6	-3.027471000	-2.109575000	-0.713650000
6	-0.333300000	-3.052674000	-0.762784000
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6	1.464164000	-1.990282000	-2.697904000
6	0.123824000	-1.547225000	-2.648409000
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6	2.486590000	-1.173680000	-3.305727000
6	2.197541000	0.213442000	-3.440832000
6	0.837415000	0.669068000	-3.400263000

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6	2.919898000	2.378743000	-2.595781000
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6	5.340827000	2.771182000	0.779486000
6	3.990321000	3.212265000	0.783078000
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6	3.032053000	-4.196301000	0.458392000
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6	1.014210000	-3.434024000	-0.776688000
6	3.731761000	-4.339627000	-0.834693000
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6	4.149596000	-2.962464000	-2.825043000
6	4.859765000	-0.677695000	-3.481319000
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6	5.650128000	1.522969000	-2.665004000
6	7.906426000	1.822066000	-1.829651000
6	7.415546000	2.406898000	-0.658329000
6	6.042248000	2.632574000	-0.510111000
6	5.811050000	2.024722000	1.872070000
6	6.529434000	-0.313479000	3.646324000
6	5.232261000	0.145960000	3.375718000
6	6.772846000	-1.679155000	3.793844000
6	5.768685000	-2.616191000	3.526332000
6	4.466271000	-2.189661000	3.250110000
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6	2.845774000	-5.403942000	-0.750905000
6	3.023401000	-5.109080000	1.687900000
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6	5.193471000	-5.071815000	2.776088000
6	3.629185000	-3.269407000	3.199157000
6	4.901089000	-3.841961000	3.363637000
6	4.330889000	-0.883835000	3.113361000
6	4.976531000	1.047048000	1.700584000
6	6.366720000	0.853974000	1.736492000
6	7.144640000	1.124920000	0.609650000
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6	0.574935000	1.583899000	-2.550685000
6	1.960898000	1.148927000	-2.581856000
6	2.292674000	-0.092676000	-3.197560000
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6	2.903737000	-2.857150000	-3.256287000
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6	2.189427000	-5.297255000	0.486645000
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6	0.304988000	-4.209304000	1.683506000
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6	2.627602000	-4.023410000	2.520287000
6	-0.446071000	-1.983309000	3.237791000
6	0.906464000	-2.393955000	3.191126000
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6	2.187032000	1.773010000	1.626228000
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6	4.418149000	1.677270000	0.552644000
6	1.080636000	3.311299000	-0.687690000
6	2.528612000	2.729587000	-0.701399000
6	2.936727000	1.796173000	-1.800972000
6	0.171046000	2.671747000	-1.764565000
6	-3.508111000	2.827363000	-2.554605000
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6	-1.777435000	1.176683000	-3.178514000
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6	-1.162483000	-1.570261000	-3.239656000
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6	-3.078010000	4.118117000	-0.539100000
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6	-4.492162000	2.087246000	-3.265186000
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6	-7.986265000	-2.263064000	-0.654028000
6	-7.357171000	-2.523904000	0.567316000
6	-5.970370000	-2.704290000	0.615963000
6	-5.503633000	-1.498404000	2.719927000
6	-6.095656000	1.216696000	3.909951000
6	-4.822690000	0.703234000	3.623262000
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1	6.008067000	-1.769789000	-4.168821000
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1	4.784515000	-5.685978000	-2.918212000
1	3.902849000	-5.641410000	-0.749633000
1	4.596690000	-6.532510000	1.306279000
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1	7.110706000	1.402372000	-1.531922000
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6	1.844457000	5.609951000	-1.597534000
1	4.670170000	3.760331000	-2.008754000
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1	3.392367000	5.493198000	-3.145100000
27	3.914662000	4.048017000	0.504065000
6	4.568188000	5.653225000	0.372158000
8	4.973656000	6.725310000	0.278648000
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6	-4.409584000	4.915383000	-2.933947000
6	-2.813334000	5.455779000	-0.425447000
6	-3.073311000	4.937249000	1.967516000
6	-4.351233000	5.472888000	2.168490000
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6	-3.727864000	2.962741000	3.272795000
6	-5.001961000	3.519555000	3.451454000
6	-4.416433000	0.594005000	2.942331000
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6	-0.464717000	-1.378963000	-2.776803000
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6	-2.164508000	0.368897000	-3.289911000
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6	5.423398000	1.236775000	2.954767000
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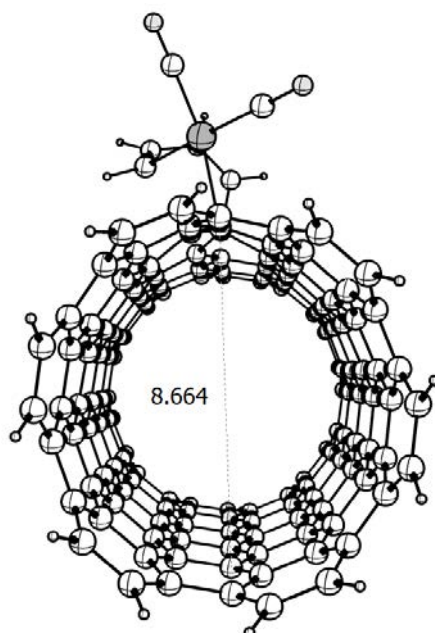
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1	-6.130270000	4.287720000	-1.210158000
6	0.396806000	6.559731000	-0.085888000
6	2.368424000	6.024863000	-1.167333000
1	-0.311077000	6.947042000	0.634719000
6	0.079348000	5.763776000	-1.209212000
1	3.418477000	5.930677000	-1.410355000
6	1.296824000	5.428519000	-1.879477000
1	-0.902226000	5.400428000	-1.480784000
1	1.377261000	4.779553000	-2.741805000
27	1.329132000	4.704913000	0.013724000
6	2.102725000	4.968862000	1.632279000
8	2.579254000	5.208910000	2.642958000
6	1.810872000	7.058048000	-0.231604000
8	2.383329000	7.934884000	0.380543000



Armchair (6,6) SWCNT

G = -5501.63814

6	-7.603379000	-2.296519000	0.442957000
6	-7.306653000	-3.076552000	-0.654845000
6	-5.962982000	-3.405840000	-0.975366000
6	-5.492740000	-3.523384000	-2.349911000
6	-6.344506000	-3.316608000	-3.467164000
6	-5.870515000	-2.730351000	-4.621792000
6	-4.516509000	-2.315411000	-4.727285000
6	-4.118683000	-1.123379000	-5.465766000
6	-5.056174000	-0.291883000	-6.133806000
6	-4.878711000	1.074363000	-6.190015000
6	-3.753254000	1.690144000	-5.581226000
6	-3.825564000	3.000116000	-4.946505000
6	-5.027085000	3.754930000	-4.889836000
6	-5.323309000	4.534905000	-3.791858000
6	-4.435632000	4.606544000	-2.685734000
6	-4.906101000	4.724114000	-1.311269000
6	-6.285955000	4.775018000	-0.979714000
6	-6.760332000	4.188806000	0.174778000
6	-5.882801000	3.516195000	1.065942000
6	-6.280304000	2.324126000	1.804535000
6	-7.573910000	1.750250000	1.687060000
6	-7.751521000	0.384020000	1.743217000
6	-6.645896000	-0.489378000	1.919938000
6	-6.573761000	-1.799330000	1.285155000
6	-5.308160000	-2.432194000	1.192473000
6	-5.000084000	-3.242242000	0.052564000
6	-3.632060000	-3.608867000	-0.180309000
6	-3.173869000	-3.723366000	-1.519394000
6	-4.096194000	-3.468480000	-2.589248000
6	-3.604019000	-2.859542000	-3.788059000
6	-2.209183000	-2.530157000	-3.868711000
6	-1.821682000	-1.368964000	-4.588479000
6	-2.839503000	-0.568650000	-5.207910000

6	-2.655333000	0.850122000	-5.265945000
6	-1.460420000	1.411504000	-4.702823000
6	-1.530923000	2.687606000	-4.084021000
6	-2.794398000	3.367778000	-4.045187000
6	-3.101988000	4.177769000	-2.905107000
6	-2.133989000	4.274659000	-1.849777000
6	-2.592263000	4.389167000	-0.510721000
6	-4.006062000	4.404029000	-0.263360000
6	-4.498606000	3.795134000	0.935321000
6	-3.557350000	3.196005000	1.838455000
6	-3.944839000	2.034811000	2.558227000
6	-5.262952000	1.504221000	2.355232000
6	-5.447272000	0.085467000	2.413214000
6	-4.306188000	-0.745647000	2.672541000
6	-4.235661000	-2.021752000	2.053747000
6	-2.992739000	-2.708273000	2.018599000
6	-2.683195000	-3.522001000	0.872918000
6	-1.333158000	-3.888726000	0.634151000
6	-0.872658000	-4.003873000	-0.711588000
6	-1.777089000	-3.749001000	-1.775156000
6	-1.282411000	-3.137316000	-2.979924000
6	0.095163000	-2.807304000	-3.068533000
6	0.484515000	-1.640343000	-3.791878000
6	-0.516325000	-0.840994000	-4.402982000
6	-0.331113000	0.584694000	-4.461560000
6	0.847034000	1.148928000	-3.906868000
6	0.776222000	2.431351000	-3.284969000
6	-0.470442000	3.108159000	-3.237901000
6	-0.779746000	3.921858000	-2.092135000
6	0.170980000	4.022920000	-1.043325000
6	-0.289531000	4.138068000	0.302410000
6	-1.685862000	4.148860000	0.555936000
6	-2.180753000	3.537200000	1.760628000
6	-1.257646000	2.941533000	2.659251000
6	-1.647115000	1.774585000	3.382556000
6	-2.946996000	1.240895000	3.183630000
6	-3.132265000	-0.184785000	3.242189000
6	-2.009699000	-1.014678000	3.497522000
6	-1.938772000	-2.297114000	2.875663000
6	-0.677810000	-2.975898000	2.826749000
6	-0.370809000	-3.782729000	1.690352000
6	0.977285000	-4.158171000	1.454181000
6	1.441649000	-4.274249000	0.097269000
6	0.537629000	-4.010240000	-0.964390000
6	1.028288000	-3.403700000	-2.159272000
6	2.407142000	-3.080813000	-2.253936000
6	2.799715000	-1.904299000	-2.983495000
6	1.796257000	-1.101871000	-3.586220000
6	1.979986000	0.312058000	-3.644333000
6	3.161381000	0.877946000	-3.098245000
6	3.089990000	2.170958000	-2.471068000
6	1.840293000	2.841669000	-2.417467000
6	1.533408000	3.648485000	-1.281029000
6	2.486037000	3.758269000	-0.234829000
6	2.021729000	3.874341000	1.122103000

6	0.625036000	3.875990000	1.373736000
6	0.134262000	3.269463000	2.568578000
6	1.056039000	2.680928000	3.473238000
6	0.663226000	1.504441000	4.202713000
6	-0.634080000	0.967678000	3.995396000
6	-0.817798000	-0.446254000	4.053511000
6	0.301570000	-1.277805000	4.317465000
6	0.373174000	-2.570842000	3.690364000
6	1.629075000	-3.231275000	3.626856000
6	1.934495000	-4.034131000	2.496046000
6	3.299610000	-4.413810000	2.267007000
6	3.761798000	-4.529040000	0.916708000
6	2.840106000	-4.260625000	-0.150302000
6	3.328389000	-3.657096000	-1.339274000
6	4.725134000	-3.338420000	-1.429051000
6	5.115744000	-2.167790000	-2.155362000
6	4.093985000	-1.362915000	-2.762253000
6	4.276815000	0.044010000	-2.819994000
6	5.476567000	0.607841000	-2.269606000
6	5.405516000	1.894434000	-1.645249000
6	4.137458000	2.565427000	-1.596600000
6	3.832026000	3.368285000	-0.465794000
6	4.802844000	3.478238000	0.585671000
6	4.340807000	3.593451000	1.936021000
6	2.926502000	3.594768000	2.180584000
6	2.438195000	2.991242000	3.369548000
6	3.377424000	2.402837000	4.281764000
6	2.986329000	1.232262000	5.007905000
6	1.672064000	0.697122000	4.792339000
6	1.489316000	-0.709812000	4.850109000
6	2.625689000	-1.543390000	5.122213000
6	2.697110000	-2.830025000	4.497987000
6	3.923399000	-3.542084000	4.490857000
6	4.236820000	-4.365879000	3.329955000
6	5.554546000	-4.811605000	3.044525000
6	5.999590000	-4.922909000	1.744206000
6	5.153260000	-4.594798000	0.652175000
6	5.654547000	-3.975757000	-0.568327000
6	7.025448000	-3.654759000	-0.753258000
6	7.401582000	-2.527358000	-1.452656000
6	6.429324000	-1.654380000	-2.008747000
6	6.617071000	-0.210234000	-2.068013000
6	7.785586000	0.427372000	-1.573494000
6	7.717247000	1.666530000	-0.972371000
6	6.475912000	2.341301000	-0.829512000
6	6.162169000	3.165131000	0.331275000
6	7.075538000	3.353239000	1.402221000
6	6.630642000	3.464525000	2.702592000
6	5.245891000	3.394032000	3.009113000
6	4.744778000	2.774971000	4.229676000
6	5.605016000	2.196348000	5.200138000
6	5.228380000	1.069006000	5.899359000
6	3.969291000	0.453676000	5.669845000
6	3.781770000	-0.990496000	5.729192000
6	4.844875000	-1.885781000	6.020372000

6	4.913600000	-3.124985000	5.419385000
1	-6.581161000	-2.463187000	-5.396431000
1	-7.411208000	-3.489863000	-3.374539000
1	-8.104139000	-3.318568000	-1.349059000
1	-8.623795000	-1.952806000	0.573265000
1	-8.730707000	-0.020714000	1.511333000
1	-8.419740000	2.371436000	1.413050000
1	-7.833270000	4.127587000	0.321460000
1	-7.002590000	5.154191000	-1.700209000
1	-6.308934000	4.982813000	-3.725434000
1	-5.790252000	3.617163000	-5.648101000
1	-5.682875000	1.685017000	-6.586005000
1	-5.993581000	-0.707164000	-6.487631000
1	5.689374000	-1.549724000	6.612264000
1	5.809721000	-3.719723000	5.559788000
1	6.270754000	-4.936863000	3.849347000
1	8.142568000	3.272590000	1.225232000
1	7.049992000	-5.131701000	1.572601000
1	8.448203000	-2.242622000	-1.452047000
1	7.789657000	-4.216805000	-0.227466000
1	8.724424000	-0.114604000	-1.537516000
1	8.604709000	2.055322000	-0.484817000
1	7.363591000	3.467398000	3.502070000
1	6.624390000	2.552448000	5.302301000
1	5.964871000	0.578379000	6.526539000

G3 (armchair (6,6))

G = -5993.34763

6	-6.933017000	0.331554000	4.204191000
6	-7.166366000	-0.998181000	3.937821000
6	-6.106056000	-1.862673000	3.542272000
6	-6.295904000	-2.941473000	2.590316000
6	-7.557181000	-3.215934000	1.986119000
6	-7.634002000	-3.651650000	0.683993000
6	-6.454968000	-3.844848000	-0.093029000
6	-6.404140000	-3.556670000	-1.512850000
6	-7.531921000	-3.068807000	-2.237032000
6	-7.373431000	-2.167796000	-3.262887000
6	-6.077661000	-1.701364000	-3.634214000
6	-5.839920000	-0.347421000	-4.088667000
6	-6.885704000	0.616011000	-4.213923000
6	-6.655853000	1.943394000	-3.945828000
6	-5.364733000	2.396520000	-3.539264000
6	-5.183037000	3.472716000	-2.589725000
6	-6.281789000	4.156545000	-1.985136000
6	-6.208058000	4.593069000	-0.685336000
6	-5.029325000	4.381459000	0.092954000
6	-5.073887000	4.095502000	1.510744000
6	-6.299395000	4.017840000	2.238610000
6	-6.449044000	3.116685000	3.263875000
6	-5.385021000	2.237730000	3.631104000
6	-5.624029000	0.880454000	4.087397000
6	-4.540297000	-0.035728000	4.075697000

6	-4.783596000	-1.420196000	3.802779000
6	-3.669892000	-2.264086000	3.483501000
6	-3.855411000	-3.319920000	2.555746000
6	-5.150118000	-3.503979000	1.969911000
6	-5.230652000	-3.959421000	0.614639000
6	-4.012805000	-4.210995000	-0.097106000
6	-3.963374000	-3.930541000	-1.485433000
6	-5.133153000	-3.409201000	-2.127238000
6	-4.968315000	-2.470437000	-3.196395000
6	-3.640623000	-2.091648000	-3.577105000
6	-3.408296000	-0.766049000	-4.018826000
6	-4.509103000	0.147310000	-4.078108000
6	-4.269382000	1.531987000	-3.798809000
6	-2.938554000	1.945369000	-3.468857000
6	-2.758974000	3.005595000	-2.548181000
6	-3.914185000	3.622863000	-1.970299000
6	-3.838252000	4.084988000	-0.616224000
6	-2.608541000	3.916285000	0.097098000
6	-2.651369000	3.626920000	1.480270000
6	-3.924687000	3.527899000	2.124214000
6	-4.085283000	2.584834000	3.193009000
6	-2.960974000	1.774246000	3.565909000
6	-3.193145000	0.449495000	4.015338000
6	-2.103020000	-0.465440000	4.079594000
6	-2.346218000	-1.851236000	3.807017000
6	-1.247040000	-2.699204000	3.498789000
6	-1.434090000	-3.762598000	2.565955000
6	-2.713612000	-3.942926000	1.974313000
6	-2.793031000	-4.392903000	0.617183000
6	-1.590791000	-4.656335000	-0.095782000
6	-1.541253000	-4.374076000	-1.493608000
6	-2.696180000	-3.844718000	-2.132273000
6	-2.530000000	-2.900639000	-3.193166000
6	-1.215618000	-2.527401000	-3.589447000
6	-0.981588000	-1.190284000	-4.029729000
6	-2.069504000	-0.275387000	-4.073140000
6	-1.829996000	1.101505000	-3.782761000
6	-0.508167000	1.525013000	-3.467488000
6	-0.325061000	2.593690000	-2.538745000
6	-1.471911000	3.209066000	-1.961149000
6	-1.395977000	3.683830000	-0.620633000
6	-0.170796000	3.557866000	0.097636000
6	-0.221738000	3.230236000	1.492739000
6	-1.477590000	3.109112000	2.120566000
6	-1.645801000	2.155370000	3.182155000
6	-0.539584000	1.350950000	3.562667000
6	-0.771172000	0.022172000	4.027219000
6	0.324470000	-0.897327000	4.077027000
6	0.083257000	-2.276251000	3.809574000
6	1.184071000	-3.122880000	3.500832000
6	0.996554000	-4.187373000	2.560136000
6	-0.284840000	-4.372455000	1.970514000
6	-0.364846000	-4.824466000	0.620526000
6	0.838553000	-5.084250000	-0.093242000
6	0.889799000	-4.794086000	-1.492483000

6	-0.267836000	-4.270044000	-2.134814000
6	-0.102951000	-3.331220000	-3.194457000
6	1.213940000	-2.952120000	-3.582829000
6	1.448858000	-1.612714000	-4.010017000
6	0.358174000	-0.696512000	-4.062178000
6	0.596341000	0.676412000	-3.769669000
6	1.920020000	1.095857000	-3.440757000
6	2.102392000	2.150119000	-2.509285000
6	0.957403000	2.790492000	-1.946118000
6	1.044029000	3.323903000	-0.621964000
6	2.304035000	3.295495000	0.109221000
6	2.216835000	2.819427000	1.503020000
6	0.950789000	2.672644000	2.111178000
6	0.781411000	1.723553000	3.159206000
6	1.889038000	0.931332000	3.561879000
6	1.656637000	-0.406894000	4.023715000
6	2.747053000	-1.318278000	4.057072000
6	2.507977000	-2.691984000	3.791400000
6	3.623495000	-3.539188000	3.486546000
6	3.435662000	-4.609404000	2.554454000
6	2.142779000	-4.783547000	1.960829000
6	2.063118000	-5.235090000	0.618845000
6	3.277809000	-5.505050000	-0.091684000
6	3.328225000	-5.222527000	-1.494521000
6	2.162008000	-4.682144000	-2.126598000
6	2.327009000	-3.747275000	-3.178489000
6	3.652831000	-3.378433000	-3.574242000
6	3.888916000	-2.036333000	-4.015034000
6	2.788398000	-1.120357000	-4.039245000
6	3.026768000	0.242253000	-3.745680000
6	4.360309000	0.666223000	-3.451398000
6	4.550195000	1.739193000	-2.523072000
6	3.396320000	2.341838000	-1.919195000
6	3.490841000	2.845126000	-0.610638000
6	4.717649000	2.678327000	0.098738000
6	4.657040000	2.391189000	1.504577000
6	3.356710000	2.258549000	2.114913000
6	3.195981000	1.303840000	3.157249000
6	4.322208000	0.510992000	3.559436000
6	4.092484000	-0.826824000	4.012402000
6	5.181835000	-1.731609000	4.119403000
6	4.937500000	-3.138378000	3.842624000
6	5.988056000	-4.057895000	3.566609000
6	5.808197000	-5.086590000	2.669408000
6	4.566065000	-5.260950000	1.996096000
6	4.484326000	-5.723760000	0.623523000
6	5.640084000	-6.048568000	-0.145124000
6	5.688760000	-5.774438000	-1.491768000
6	4.583181000	-5.166270000	-2.155003000
6	4.752541000	-4.207584000	-3.227774000
6	6.036522000	-3.809728000	-3.705936000
6	6.261885000	-2.521602000	-4.128123000
6	5.218170000	-1.549154000	-4.108169000
6	5.463092000	-0.152383000	-3.818999000
6	6.766592000	0.364822000	-3.555778000

6	6.946215000	1.393479000	-2.662759000
6	5.836892000	1.978131000	-1.981499000
6	5.921339000	2.447865000	-0.615225000
6	7.119049000	2.359785000	0.158815000
6	7.058810000	2.096930000	1.504413000
6	5.803295000	1.906929000	2.163083000
6	5.637135000	0.929885000	3.232883000
6	6.706471000	0.124369000	3.705766000
6	6.485476000	-1.169086000	4.133162000
1	-8.609734000	-3.724466000	0.216356000
1	-8.474228000	-2.957936000	2.504127000
1	-8.191634000	-1.350508000	3.910872000
1	-7.781553000	0.983768000	4.378692000
1	-7.428691000	2.997156000	3.713381000
1	-7.164342000	4.581140000	1.906375000
1	-7.101316000	4.992382000	-0.217701000
1	-7.230879000	4.223073000	-2.505229000
1	-7.498686000	2.625579000	-3.930190000
1	-7.902800000	0.289877000	-4.400995000
1	-8.257515000	-1.721482000	-3.704777000
1	-8.535433000	-3.304308000	-1.900391000
1	7.729969000	0.470086000	3.611882000
1	7.343579000	-1.792953000	4.358190000
1	6.982840000	-3.878928000	3.959405000
1	7.639783000	-0.133401000	-3.961846000
1	6.667571000	-5.683957000	2.385220000
1	6.627633000	-5.911214000	-2.017107000
1	6.541794000	-6.391303000	0.350231000
1	6.880268000	-4.485148000	-3.618340000
1	7.277080000	-2.221390000	-4.363262000
1	7.957207000	1.677966000	-2.391745000
1	8.085876000	2.369768000	-0.332112000
1	7.983302000	1.911797000	2.040456000
45	2.048791000	5.558768000	-0.247194000
6	1.555188000	5.821396000	1.762606000
6	3.918823000	5.905750000	0.571068000
6	3.914545000	6.088493000	1.900634000
6	2.612718000	6.050841000	2.562150000
1	2.525678000	6.188811000	3.639132000
1	0.526123000	5.781787000	2.114334000
1	4.836311000	6.250779000	2.459813000
1	4.794789000	5.906105000	-0.072229000
6	1.477030000	7.391823000	-0.250419000
8	1.226732000	8.508479000	-0.176766000
6	2.790954000	5.497970000	-2.093761000
8	3.296817000	5.562221000	-3.118730000

TS(G3.G4) (armchair (6,6))

G = -5993.32270

6	6.908530000	0.547957000	-4.234206000
6	7.168697000	-0.784308000	-4.005083000
6	6.128711000	-1.675480000	-3.616797000
6	6.347621000	-2.773754000	-2.692233000

6	7.617879000	-3.035572000	-2.103776000
6	7.714452000	-3.496235000	-0.810556000
6	6.546922000	-3.724719000	-0.027795000
6	6.502774000	-3.463283000	1.399675000
6	7.623718000	-2.962602000	2.120692000
6	7.454801000	-2.083113000	3.166216000
6	6.155714000	-1.651551000	3.557434000
6	5.895490000	-0.309962000	4.049920000
6	6.918956000	0.665830000	4.197026000
6	6.659042000	2.000264000	3.970012000
6	5.362086000	2.440260000	3.589111000
6	5.151940000	3.542404000	2.663387000
6	6.232366000	4.249300000	2.062388000
6	6.142561000	4.708345000	0.767400000
6	4.966494000	4.489231000	-0.004205000
6	5.007405000	4.225881000	-1.433587000
6	6.226189000	4.179084000	-2.168088000
6	6.385597000	3.301080000	-3.216242000
6	5.337426000	2.414222000	-3.593676000
6	5.592900000	1.071963000	-4.088015000
6	4.525725000	0.137859000	-4.086153000
6	4.795917000	-1.248681000	-3.851034000
6	3.701004000	-2.120058000	-3.541042000
6	3.914973000	-3.196208000	-2.642607000
6	5.218557000	-3.369111000	-2.072712000
6	5.319238000	-3.849722000	-0.727749000
6	4.112291000	-4.138911000	-0.011027000
6	4.069277000	-3.884705000	1.383497000
6	5.233539000	-3.348673000	2.024619000
6	5.058908000	-2.432874000	3.111310000
6	3.726121000	-2.089492000	3.510123000
6	3.471236000	-0.774325000	3.978806000
6	4.553829000	0.159767000	4.051704000
6	4.284618000	1.546660000	3.819024000
6	2.941249000	1.947947000	3.516315000
6	2.728707000	3.043305000	2.633370000
6	3.878615000	3.681470000	2.056198000
6	3.788113000	4.153743000	0.707730000
6	2.554626000	3.969714000	0.001551000
6	2.593738000	3.708068000	-1.388495000
6	3.867437000	3.644639000	-2.044479000
6	4.034138000	2.726535000	-3.130152000
6	2.920731000	1.905916000	-3.508481000
6	3.170566000	0.597614000	-3.996019000
6	2.096822000	-0.333489000	-4.068596000
6	2.366934000	-1.722537000	-3.840388000
6	1.287836000	-2.597195000	-3.542691000
6	1.502494000	-3.681373000	-2.640277000
6	2.790761000	-3.852055000	-2.063943000
6	2.891569000	-4.333814000	-0.718313000
6	1.700295000	-4.631198000	-0.000702000
6	1.657324000	-4.377101000	1.402568000
6	2.806769000	-3.834796000	2.040615000
6	2.632527000	-2.913930000	3.123523000
6	1.312931000	-2.570633000	3.530701000

6	1.057812000	-1.247250000	3.995867000
6	2.126473000	-0.311616000	4.049380000
6	1.859010000	1.072401000	3.798000000
6	0.526161000	1.472334000	3.485835000
6	0.310388000	2.577549000	2.610159000
6	1.440721000	3.259552000	2.074678000
6	1.350610000	3.731516000	0.717750000
6	0.128558000	3.616896000	0.021946000
6	0.174650000	3.271974000	-1.351893000
6	1.431348000	3.179695000	-2.013456000
6	1.602779000	2.254082000	-3.095663000
6	0.507977000	1.444114000	-3.483259000
6	0.757291000	0.131446000	-3.980739000
6	-0.319653000	-0.804105000	-4.039940000
6	-0.052877000	-2.185065000	-3.822191000
6	-1.137010000	-3.056313000	-3.520254000
6	-0.920978000	-4.146547000	-2.621408000
6	0.370367000	-4.323452000	-2.047942000
6	0.471041000	-4.806899000	-0.710599000
6	-0.722938000	-5.098554000	0.007793000
6	-0.765781000	-4.843507000	1.414133000
6	0.386457000	-4.308287000	2.054817000
6	0.213025000	-3.390732000	3.132521000
6	-1.107735000	-3.039171000	3.531915000
6	-1.361220000	-1.711064000	3.987971000
6	-0.290944000	-0.780798000	4.045516000
6	-0.555909000	0.594646000	3.776661000
6	-1.883657000	0.995171000	3.461438000
6	-2.085851000	2.090564000	2.572803000
6	-0.978133000	2.764524000	2.033676000
6	-1.118884000	3.576971000	0.807383000
6	-2.363276000	3.317101000	0.005329000
6	-2.257009000	2.824835000	-1.351940000
6	-0.986897000	2.713036000	-1.981549000
6	-0.811958000	1.786596000	-3.044727000
6	-1.909501000	0.976054000	-3.450386000
6	-1.661288000	-0.335590000	-3.954558000
6	-2.737913000	-1.265875000	-4.009131000
6	-2.473264000	-2.640851000	-3.790127000
6	-3.568860000	-3.515800000	-3.501814000
6	-3.353033000	-4.608847000	-2.602760000
6	-2.052236000	-4.776487000	-2.025947000
6	-1.951482000	-5.260113000	-0.697393000
6	-3.154771000	-5.565810000	0.017088000
6	-3.198372000	-5.310071000	1.425331000
6	-2.036708000	-4.760916000	2.057506000
6	-2.210026000	-3.847082000	3.125812000
6	-3.539723000	-3.504431000	3.534561000
6	-3.794258000	-2.172684000	3.996387000
6	-2.710053000	-1.239944000	4.026242000
6	-2.972186000	0.124247000	3.765505000
6	-4.318397000	0.537240000	3.506902000
6	-4.535425000	1.638517000	2.613930000
6	-3.407762000	2.284157000	2.016588000
6	-3.531326000	2.825005000	0.728709000

6	-4.756099000	2.620239000	0.023855000
6	-4.697835000	2.358261000	-1.381408000
6	-3.400047000	2.251643000	-1.983748000
6	-3.227420000	1.322864000	-3.039287000
6	-4.339402000	0.524558000	-3.463571000
6	-4.089293000	-0.799129000	-3.947499000
6	-5.163023000	-1.721723000	-4.066154000
6	-4.893769000	-3.125876000	-3.831924000
6	-5.928717000	-4.070814000	-3.568997000
6	-5.722240000	-5.120573000	-2.705881000
6	-4.468103000	-5.289856000	-2.047844000
6	-4.364105000	-5.788498000	-0.692022000
6	-5.509186000	-6.147471000	0.079662000
6	-5.551320000	-5.901192000	1.430777000
6	-4.450519000	-5.281790000	2.094156000
6	-4.627911000	-4.344261000	3.183140000
6	-5.917184000	-3.971732000	3.670397000
6	-6.160951000	-2.696112000	4.117381000
6	-5.131157000	-1.707275000	4.106869000
6	-5.398025000	-0.307649000	3.861764000
6	-6.720610000	0.193679000	3.631763000
6	-6.933195000	1.241028000	2.775634000
6	-5.837913000	1.856653000	2.088269000
6	-5.949429000	2.348723000	0.740469000
6	-7.153746000	2.244483000	-0.027104000
6	-7.101972000	2.014299000	-1.376709000
6	-5.843120000	1.854889000	-2.043225000
6	-5.662442000	0.910785000	-3.124914000
6	-6.722972000	0.094173000	-3.616422000
6	-6.481887000	-1.180580000	-4.071689000
1	8.695374000	-3.557364000	-0.352260000
1	8.525723000	-2.748121000	-2.622597000
1	8.200241000	-1.118813000	-3.998882000
1	7.743840000	1.218882000	-4.401930000
1	7.366861000	3.204016000	-3.667590000
1	7.087066000	4.743661000	-1.827074000
1	7.029267000	5.123362000	0.300736000
1	7.187667000	4.314589000	2.571436000
1	7.491262000	2.695725000	3.961490000
1	7.945570000	0.356698000	4.359397000
1	8.333696000	-1.622857000	3.604055000
1	8.629412000	-3.165095000	1.769261000
1	-7.750530000	0.428259000	-3.525064000
1	-7.326376000	-1.812967000	-4.322237000
1	-6.929268000	-3.899371000	-3.950297000
1	-7.576075000	-0.324297000	4.050870000
1	-6.566297000	-5.743677000	-2.431751000
1	-6.481822000	-6.066207000	1.962614000
1	-6.407824000	-6.499071000	-0.415147000
1	-6.750397000	-4.659391000	3.576786000
1	-7.178816000	-2.416349000	4.365202000
1	-7.951123000	1.525618000	2.533007000
1	-8.115664000	2.230896000	0.473343000
1	-8.025530000	1.825343000	-1.912305000
45	-2.768895000	5.639504000	-0.133655000

6	-1.491636000	5.333093000	1.557355000
6	-0.963812000	6.275465000	-0.873820000
6	-0.076724000	6.636363000	0.112491000
6	-0.442619000	6.244463000	1.435740000
1	0.095976000	6.625932000	2.304469000
1	-1.860871000	5.086551000	2.550625000
1	0.863893000	7.151660000	-0.079277000
1	-0.740283000	6.539072000	-1.908313000
6	-3.604351000	5.869033000	-1.842893000
8	-4.059975000	5.955518000	-2.894072000
6	-4.379073000	5.673400000	1.002334000
8	-5.261806000	5.832550000	1.718412000

G4 (armchair (6,6))

G = -5993.32673

6	6.771855000	1.312077000	-4.218961000
6	7.074533000	-0.029597000	-4.185613000
6	6.073590000	-0.996520000	-3.881895000
6	6.357795000	-2.206972000	-3.133475000
6	7.656587000	-2.505793000	-2.630465000
6	7.815926000	-3.134704000	-1.416894000
6	6.684914000	-3.498665000	-0.631237000
6	6.685593000	-3.422970000	0.819258000
6	7.813616000	-2.970086000	1.558759000
6	7.655277000	-2.228844000	2.709223000
6	6.359038000	-1.891031000	3.187250000
6	6.074772000	-0.629532000	3.855255000
6	7.069299000	0.350563000	4.101337000
6	6.761858000	1.697292000	4.076320000
6	5.444728000	2.141303000	3.797435000
6	5.170194000	3.366113000	3.051716000
6	6.215229000	4.173033000	2.518928000
6	6.076607000	4.799488000	1.299893000
6	4.882279000	4.650965000	0.542057000
6	4.881222000	4.568424000	-0.910755000
6	6.076308000	4.637065000	-1.681661000
6	6.220969000	3.896593000	-2.833267000
6	5.182888000	3.030110000	-3.279033000
6	5.450040000	1.773191000	-3.954548000
6	4.408126000	0.815654000	-4.036155000
6	4.721482000	-0.581867000	-4.005924000
6	3.663366000	-1.520976000	-3.780089000
6	3.940910000	-2.706667000	-3.055226000
6	5.270455000	-2.916590000	-2.562907000
6	5.435678000	-3.572396000	-1.300852000
6	4.265079000	-3.993885000	-0.589320000
6	4.266420000	-3.922663000	0.827074000
6	5.436320000	-3.426871000	1.491781000
6	5.271739000	-2.651540000	2.683708000
6	3.943330000	-2.405307000	3.161354000
6	3.665185000	-1.163431000	3.793446000
6	4.720319000	-0.209001000	3.950494000
6	4.401902000	1.185900000	3.916289000

6	3.037445000	1.579786000	3.709119000
6	2.758041000	2.796904000	3.014491000
6	3.878750000	3.551138000	2.509483000
6	3.733974000	4.201540000	1.243389000
6	2.480222000	4.089916000	0.560254000
6	2.484369000	3.987640000	-0.848907000
6	3.737656000	4.030201000	-1.548100000
6	3.888369000	3.246240000	-2.735549000
6	2.784922000	2.441910000	-3.167272000
6	3.046972000	1.217621000	-3.829794000
6	1.994787000	0.269640000	-3.981345000
6	2.307113000	-1.126593000	-3.971878000
6	1.263957000	-2.066339000	-3.760442000
6	1.542198000	-3.262915000	-3.034304000
6	2.857265000	-3.470314000	-2.532168000
6	3.024783000	-4.136703000	-1.275688000
6	1.869632000	-4.562911000	-0.564532000
6	1.871291000	-4.493929000	0.860636000
6	3.027041000	-3.993592000	1.523544000
6	2.864857000	-3.218281000	2.717978000
6	1.550217000	-2.966528000	3.197892000
6	1.272119000	-1.715220000	3.819754000
6	2.313462000	-0.757857000	3.954331000
6	1.996828000	0.639684000	3.891930000
6	0.644892000	1.029799000	3.663241000
6	0.361960000	2.244555000	2.973874000
6	1.454898000	3.056168000	2.540999000
6	1.294698000	3.769275000	1.284202000
6	0.058812000	3.725896000	0.622774000
6	0.075672000	3.486665000	-0.773842000
6	1.318629000	3.486734000	-1.482892000
6	1.471835000	2.698027000	-2.666018000
6	0.386722000	1.905372000	-3.104331000
6	0.647160000	0.677758000	-3.780966000
6	-0.405006000	-0.272164000	-3.924595000
6	-0.097137000	-1.658456000	-3.924056000
6	-1.147624000	-2.596548000	-3.705219000
6	-0.867349000	-3.799093000	-2.995286000
6	0.452094000	-4.015673000	-2.498956000
6	0.618323000	-4.680211000	-1.249410000
6	-0.540572000	-5.100160000	-0.535749000
6	-0.536404000	-5.038833000	0.892442000
6	0.622386000	-4.547376000	1.556001000
6	0.460458000	-3.771159000	2.741729000
6	-0.854078000	-3.508790000	3.217329000
6	-1.129000000	-2.250995000	3.838510000
6	-0.086390000	-1.303223000	3.966940000
6	-0.400234000	0.087939000	3.874626000
6	-1.743896000	0.482710000	3.667175000
6	-2.010534000	1.700457000	2.960672000
6	-0.959815000	2.485843000	2.502557000
6	-1.201602000	3.630856000	1.494592000
6	-2.471505000	3.349067000	0.650988000
6	-2.362811000	3.017933000	-0.767518000
6	-1.077080000	2.957846000	-1.429074000

6	-0.923053000	2.152258000	-2.575436000
6	-2.016873000	1.349941000	-3.035718000
6	-1.757973000	0.140909000	-3.722747000
6	-2.815661000	-0.807358000	-3.874181000
6	-2.507357000	-2.188401000	-3.869190000
6	-3.566230000	-3.129815000	-3.674997000
6	-3.285001000	-4.335070000	-2.954577000
6	-1.958433000	-4.542148000	-2.455060000
6	-1.791699000	-5.205917000	-1.214636000
6	-2.958083000	-5.642858000	-0.507548000
6	-2.955876000	-5.573148000	0.922895000
6	-1.786209000	-5.071255000	1.580177000
6	-1.947225000	-4.297089000	2.755080000
6	-3.271045000	-4.045345000	3.243671000
6	-3.545444000	-2.786727000	3.870985000
6	-2.486384000	-1.829080000	3.973358000
6	-2.795009000	-0.452302000	3.897119000
6	-4.165666000	-0.050764000	3.762113000
6	-4.455155000	1.162581000	3.052370000
6	-3.375389000	1.934854000	2.512976000
6	-3.578141000	2.675876000	1.352512000
6	-4.821633000	2.523582000	0.672514000
6	-4.794642000	2.443186000	-0.774214000
6	-3.509768000	2.400837000	-1.413534000
6	-3.341528000	1.612163000	-2.565059000
6	-4.445753000	0.846944000	-3.056170000
6	-4.175428000	-0.396047000	-3.712923000
6	-5.228251000	-1.329305000	-3.917044000
6	-4.914429000	-2.737945000	-3.896501000
6	-5.913625000	-3.746089000	-3.736350000
6	-5.644426000	-4.901612000	-3.045788000
6	-4.359463000	-5.121311000	-2.460944000
6	-4.187993000	-5.804704000	-1.197850000
6	-5.293601000	-6.297036000	-0.441286000
6	-5.290820000	-6.231030000	0.930755000
6	-4.183595000	-5.663691000	1.629954000
6	-4.347006000	-4.872823000	2.833034000
6	-5.626343000	-4.600587000	3.401765000
6	-5.887564000	-3.397180000	4.012914000
6	-4.887584000	-2.382896000	4.089704000
6	-5.203050000	-0.968915000	4.046032000
6	-6.548400000	-0.488285000	3.941905000
6	-6.831531000	0.661594000	3.254403000
6	-5.786627000	1.409339000	2.623283000
6	-5.971445000	2.093426000	1.370276000
6	-7.197660000	2.051356000	0.624961000
6	-7.188426000	2.009795000	-0.743427000
6	-5.946501000	1.969263000	-1.463325000
6	-5.768718000	1.158309000	-2.640572000
6	-6.823731000	0.370572000	-3.200747000
6	-6.563760000	-0.828030000	-3.814910000
1	8.814801000	-3.226045000	-1.004698000
1	8.535954000	-2.123130000	-3.136919000
1	8.113000000	-0.331286000	-4.266000000
1	7.582338000	2.024265000	-4.328333000

1	7.188122000	3.882005000	-3.323326000
1	6.935283000	5.179611000	-1.301771000
1	6.940402000	5.290803000	0.865614000
1	7.185432000	4.192380000	3.003215000
1	7.573960000	2.413099000	4.140486000
1	8.110703000	0.059475000	4.184719000
1	8.534455000	-1.791887000	3.169778000
1	8.812031000	-3.090315000	1.152624000
1	-7.856147000	0.665480000	-3.049136000
1	-7.397693000	-1.446713000	-4.127182000
1	-6.931906000	-3.555282000	-4.057025000
1	-7.368120000	-1.090171000	4.318207000
1	-6.457809000	-5.587769000	-2.837728000
1	-6.195448000	-6.492652000	1.468375000
1	-6.200768000	-6.609115000	-0.947152000
1	-6.445043000	-5.295442000	3.250155000
1	-6.903202000	-3.182571000	4.326039000
1	-7.867526000	0.941001000	3.095648000
1	-8.141576000	1.936979000	1.147053000
1	-8.123987000	1.861799000	-1.270810000
45	-3.410570000	4.962266000	-0.561945000
6	-1.369764000	4.916683000	2.331984000
6	-1.812930000	6.197855000	-0.574470000
6	-1.085222000	6.578017000	0.482474000
6	-1.264704000	6.173836000	1.881434000
1	-1.295084000	6.980178000	2.613854000
1	-1.533889000	4.749726000	3.393290000
1	-0.290315000	7.304046000	0.291417000
1	-1.573728000	6.575116000	-1.566102000
6	-3.955223000	5.645255000	-2.349993000
8	-4.347116000	6.031931000	-3.355324000
6	-4.259667000	6.029941000	0.836475000
8	-4.728818000	6.681073000	1.654638000

TS(G4.G5) (armchair (6,6))

G = -5993.31474

6	7.110938000	1.013830000	-4.127354000
6	7.521697000	-0.248013000	-3.759301000
6	6.583683000	-1.218443000	-3.308723000
6	6.899252000	-2.194038000	-2.278383000
6	8.164140000	-2.233615000	-1.627712000
6	8.261895000	-2.557979000	-0.292608000
6	7.099992000	-2.860218000	0.471077000
6	6.958853000	-2.469239000	1.864862000
6	7.970414000	-1.756743000	2.564554000
6	7.643955000	-0.804175000	3.506458000
6	6.286683000	-0.505226000	3.802826000
6	5.837804000	0.837773000	4.146180000
6	6.720065000	1.941814000	4.240439000
6	6.309718000	3.212117000	3.879378000
6	4.996745000	3.448932000	3.404995000
6	4.701606000	4.437714000	2.369741000
6	5.726062000	5.196433000	1.739200000

6	5.651769000	5.518513000	0.400445000
6	4.545285000	5.098082000	-0.385268000
6	4.675652000	4.703997000	-1.781912000
6	5.921383000	4.724838000	-2.468230000
6	6.225134000	3.770115000	-3.413672000
6	5.306055000	2.728309000	-3.720585000
6	5.738157000	1.384220000	-4.067218000
6	4.791783000	0.331882000	-3.991951000
6	5.218625000	-0.982936000	-3.616952000
6	4.227374000	-1.953401000	-3.256572000
6	4.537033000	-2.914806000	-2.260945000
6	5.828079000	-2.868620000	-1.638839000
6	5.929692000	-3.207989000	-0.251786000
6	4.737689000	-3.584153000	0.450949000
6	4.599896000	-3.201448000	1.810433000
6	5.656567000	-2.454076000	2.428269000
6	5.317580000	-1.460072000	3.400913000
6	3.933461000	-1.250968000	3.710996000
6	3.495136000	0.065944000	4.020509000
6	4.450446000	1.131597000	4.037605000
6	4.026403000	2.445490000	3.661701000
6	2.660006000	2.647089000	3.270935000
6	2.353732000	3.646358000	2.294783000
6	3.455536000	4.369149000	1.706543000
6	3.379444000	4.702702000	0.317601000
6	2.205586000	4.322399000	-0.408929000
6	2.335236000	3.919240000	-1.757984000
6	3.639160000	3.930829000	-2.359810000
6	3.956594000	2.926142000	-3.327598000
6	2.964113000	1.937776000	-3.635504000
6	3.387901000	0.628160000	-3.976604000
6	2.438779000	-0.431574000	-3.979002000
6	2.867902000	-1.753947000	-3.627672000
6	1.894799000	-2.727970000	-3.282028000
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6	3.481088000	-3.655719000	-1.658570000
6	3.585643000	-4.004276000	-0.271191000
6	2.409319000	-4.380230000	0.433115000
6	2.271092000	-3.995570000	1.799913000
6	3.312706000	-3.246768000	2.413708000
6	2.973670000	-2.244143000	3.382739000
6	1.602520000	-2.026128000	3.691465000
6	1.164605000	-0.702512000	3.985974000
6	2.106338000	0.359938000	3.981630000
6	1.684954000	1.671636000	3.579182000
6	0.331118000	1.867556000	3.169178000
6	0.015639000	2.876455000	2.211192000
6	1.084733000	3.667891000	1.684587000
6	0.995998000	4.052508000	0.286291000
6	-0.161076000	3.725877000	-0.433101000
6	-0.021021000	3.209374000	-1.734516000
6	1.271614000	3.184591000	-2.344297000
6	1.597158000	2.163631000	-3.296478000
6	0.625663000	1.181228000	-3.602379000
6	1.050376000	-0.131052000	-3.964355000

6	0.099974000	-1.195714000	-3.964287000
6	0.524457000	-2.511081000	-3.630683000
6	-0.455504000	-3.484163000	-3.286166000
6	-0.140314000	-4.468509000	-2.299129000
6	1.138482000	-4.429919000	-1.673367000
6	1.242333000	-4.778644000	-0.294737000
6	0.063369000	-5.151036000	0.410106000
6	-0.073633000	-4.766776000	1.782843000
6	0.970378000	-4.022635000	2.396307000
6	0.632091000	-3.019261000	3.352945000
6	-0.737613000	-2.794230000	3.658752000
6	-1.173064000	-1.461828000	3.945646000
6	-0.231255000	-0.407467000	3.930774000
6	-0.648345000	0.890729000	3.500390000
6	-1.995435000	1.095448000	3.113405000
6	-2.299980000	2.108562000	2.141541000
6	-1.274952000	2.886144000	1.605333000
6	-1.483520000	3.737599000	0.337952000
6	-2.654042000	3.179395000	-0.507856000
6	-2.375422000	2.421613000	-1.710271000
6	-1.075813000	2.403788000	-2.288949000
6	-0.741528000	1.392714000	-3.224844000
6	-1.713583000	0.410409000	-3.568699000
6	-1.290864000	-0.893117000	-3.954754000
6	-2.243307000	-1.949517000	-3.959114000
6	-1.821785000	-3.260859000	-3.626186000
6	-2.813338000	-4.237844000	-3.297234000
6	-2.498657000	-5.224050000	-2.308437000
6	-1.208949000	-5.181615000	-1.683427000
6	-1.104169000	-5.532135000	-0.313771000
6	-2.292470000	-5.917117000	0.388687000
6	-2.431938000	-5.526265000	1.759256000
6	-1.375364000	-4.772204000	2.365493000
6	-1.711294000	-3.772785000	3.311860000
6	-3.092178000	-3.553490000	3.626973000
6	-3.526940000	-2.219493000	3.916975000
6	-2.566102000	-1.161357000	3.878343000
6	-2.977390000	0.129552000	3.467552000
6	-4.351369000	0.347465000	3.137541000
6	-4.668481000	1.352362000	2.157192000
6	-3.629146000	2.119923000	1.569658000
6	-3.821187000	2.674689000	0.264684000
6	-4.958207000	2.181476000	-0.485087000
6	-4.760398000	1.708315000	-1.826631000
6	-3.413147000	1.649961000	-2.312596000
6	-3.080037000	0.633159000	-3.244013000
6	-4.067728000	-0.327418000	-3.628832000
6	-3.641392000	-1.648748000	-3.976574000
6	-4.591640000	-2.703399000	-4.043778000
6	-4.164087000	-4.039925000	-3.692348000
6	-5.085410000	-5.083651000	-3.382142000
6	-4.783557000	-6.031911000	-2.434371000
6	-3.543789000	-5.990035000	-1.728853000
6	-3.433712000	-6.355779000	-0.331692000
6	-4.559791000	-6.777456000	0.435508000

6	-4.693384000	-6.403150000	1.751075000
6	-3.709344000	-5.581753000	2.376265000
6	-4.052503000	-4.556016000	3.341797000
6	-5.399603000	-4.292267000	3.730420000
6	-5.817032000	-3.014948000	4.019461000
6	-4.913277000	-1.914553000	3.932763000
6	-5.331080000	-0.586712000	3.540326000
6	-6.698812000	-0.272067000	3.241792000
6	-7.014621000	0.666140000	2.299430000
6	-5.979853000	1.349960000	1.581922000
6	-6.124205000	1.743556000	0.220014000
6	-7.266546000	1.403662000	-0.578146000
6	-7.110413000	1.061841000	-1.891511000
6	-5.794344000	0.976599000	-2.465119000
6	-5.444702000	-0.066505000	-3.395676000
6	-6.376430000	-1.056620000	-3.832993000
6	-5.965311000	-2.329333000	-4.145349000
1	9.221103000	-2.445060000	0.200612000
1	9.050228000	-1.877071000	-2.141419000
1	8.585163000	-0.450353000	-3.694785000
1	7.865434000	1.762337000	-4.343017000
1	7.229430000	3.745677000	-3.821933000
1	6.697186000	5.418623000	-2.162791000
1	6.513884000	5.976274000	-0.072135000
1	6.646475000	5.410453000	2.271272000
1	7.052863000	4.000961000	3.836998000
1	7.768372000	1.782514000	4.468146000
1	8.437461000	-0.190282000	3.918269000
1	9.008830000	-1.857945000	2.268651000
1	-7.439399000	-0.843167000	-3.820367000
1	-6.715541000	-3.080987000	-4.364128000
1	-6.084820000	-5.068046000	-3.803027000
1	-7.496541000	-0.847989000	3.697802000
1	-5.554256000	-6.733049000	-2.134019000
1	-5.620398000	-6.628066000	2.266834000
1	-5.385680000	-7.287182000	-0.048388000
1	-6.140155000	-5.083165000	3.684173000
1	-6.872588000	-2.839464000	4.194495000
1	-8.051429000	0.810473000	2.017298000
1	-8.241568000	1.305203000	-0.113802000
1	-7.969398000	0.711699000	-2.452092000
45	-4.946478000	4.625915000	0.028207000
6	-1.660749000	5.217527000	0.761707000
6	-3.462307000	4.826244000	-1.522137000
6	-2.581743000	5.860251000	-1.394858000
6	-2.052419000	6.189079000	-0.080792000
1	-1.931799000	7.232837000	0.205021000
1	-1.271212000	5.460476000	1.745103000
1	-2.246980000	6.439281000	-2.256769000
1	-3.737488000	4.479294000	-2.518591000
6	-6.143555000	4.519747000	1.518869000
8	-6.836400000	4.490767000	2.435297000
6	-5.599730000	6.314492000	-0.513107000
8	-5.977510000	7.338765000	-0.872029000

G5 (armchair (6,6)) $G = -5993.34631$

6	7.161012000	-1.008029000	4.081892000
6	7.599486000	0.228689000	3.655988000
6	6.683832000	1.204577000	3.181535000
6	7.012654000	2.133560000	2.107688000
6	8.266229000	2.111382000	1.439632000
6	8.351686000	2.375973000	0.088609000
6	7.189003000	2.679714000	-0.669110000
6	7.009520000	2.221875000	-2.041212000
6	7.985064000	1.445278000	-2.720414000
6	7.613240000	0.454647000	-3.606749000
6	6.244285000	0.183180000	-3.865207000
6	5.749421000	-1.161998000	-4.136050000
6	6.596530000	-2.294278000	-4.208976000
6	6.160383000	-3.539646000	-3.793236000
6	4.854819000	-3.721872000	-3.278321000
6	4.558735000	-4.666825000	-2.202807000
6	5.578321000	-5.419429000	-1.561149000
6	5.523523000	-5.684272000	-0.206910000
6	4.440944000	-5.213365000	0.579866000
6	4.602630000	-4.755372000	1.956992000
6	5.856543000	-4.769104000	2.621970000
6	6.196431000	-3.771481000	3.512492000
6	5.308993000	-2.695273000	3.779283000
6	5.781612000	-1.343843000	4.054381000
6	4.860785000	-0.272511000	3.938057000
6	5.316661000	1.014917000	3.508254000
6	4.346627000	2.000687000	3.126167000
6	4.669859000	2.919354000	2.093063000
6	5.951044000	2.811059000	1.455883000
6	6.040821000	3.090267000	0.054965000
6	4.847625000	3.472462000	-0.645425000
6	4.673390000	3.027031000	-1.982309000
6	5.696720000	2.216228000	-2.578643000
6	5.310582000	1.182781000	-3.490553000
6	3.914430000	0.998090000	-3.761887000
6	3.433281000	-0.320066000	-3.993804000
6	4.358640000	-1.412183000	-3.983990000
6	3.907209000	-2.698698000	-3.546856000
6	2.545744000	-2.846094000	-3.117625000
6	2.232297000	-3.811404000	-2.109059000
6	3.326455000	-4.545468000	-1.519314000
6	3.270673000	-4.827327000	-0.119315000
6	2.115436000	-4.402351000	0.612508000
6	2.277471000	-3.921942000	1.933862000
6	3.594100000	-3.925921000	2.509278000
6	3.950602000	-2.877288000	3.413634000
6	2.984917000	-1.847768000	3.681338000
6	3.448418000	-0.531958000	3.951784000
6	2.530019000	0.550081000	3.922206000
6	2.990176000	1.851362000	3.517569000
6	2.039637000	2.838383000	3.148242000

6	2.365079000	3.769744000	2.118033000
6	3.630172000	3.670695000	1.480650000
6	3.722280000	3.958071000	0.074361000
6	2.545594000	4.335857000	-0.627076000
6	2.371542000	3.888687000	-1.970732000
6	3.379508000	3.083242000	-2.565542000
6	2.990349000	2.034425000	-3.468341000
6	1.609186000	1.839401000	-3.736647000
6	1.129092000	0.513363000	-3.947071000
6	2.039730000	-0.572804000	-3.914025000
6	1.591106000	-1.852857000	-3.440458000
6	0.245142000	-1.991622000	-2.993324000
6	-0.081181000	-2.960800000	-1.994911000
6	0.975147000	-3.781255000	-1.473130000
6	0.901560000	-4.148589000	-0.070629000
6	-0.241857000	-3.775412000	0.658543000
6	-0.059522000	-3.160309000	1.905187000
6	1.242138000	-3.127396000	2.489130000
6	1.612872000	-2.053648000	3.371621000
6	0.673009000	-1.025668000	3.625609000
6	1.136163000	0.287487000	3.926176000
6	0.211341000	1.378430000	3.899063000
6	0.666725000	2.672407000	3.519382000
6	-0.288205000	3.661526000	3.162104000
6	0.041617000	4.606962000	2.133291000
6	1.307580000	4.509372000	1.493876000
6	1.400487000	4.800351000	0.100205000
6	0.224227000	5.181330000	-0.601786000
6	0.049269000	4.728788000	-1.953626000
6	1.059125000	3.923527000	-2.544464000
6	0.672959000	2.877282000	-3.434594000
6	-0.706509000	2.676938000	-3.705238000
6	-1.184997000	1.340270000	-3.898928000
6	-0.272202000	0.261103000	-3.844804000
6	-0.714608000	-1.001251000	-3.341124000
6	-2.059370000	-1.154384000	-2.925000000
6	-2.379853000	-2.127180000	-1.913226000
6	-1.358852000	-2.915452000	-1.368342000
6	-1.568994000	-3.773336000	-0.107833000
6	-2.786034000	-3.305345000	0.796736000
6	-2.395215000	-2.315155000	1.895621000
6	-1.093115000	-2.278347000	2.413319000
6	-0.705691000	-1.215761000	3.279896000
6	-1.644091000	-0.201840000	3.589918000
6	-1.180594000	1.114220000	3.919385000
6	-2.103185000	2.189078000	3.891318000
6	-1.653053000	3.479949000	3.514192000
6	-2.628094000	4.469926000	3.163506000
6	-2.298934000	5.417749000	2.143060000
6	-1.015062000	5.323098000	1.506337000
6	-0.920585000	5.618409000	0.121669000
6	-2.112418000	6.004488000	-0.579028000
6	-2.287384000	5.552530000	-1.926259000
6	-1.261047000	4.739993000	-2.511649000
6	-1.644001000	3.697264000	-3.392807000

6	-3.037827000	3.498257000	-3.665464000
6	-3.514449000	2.163070000	-3.867020000
6	-2.579813000	1.081857000	-3.789761000
6	-3.015436000	-0.177355000	-3.304045000
6	-4.385703000	-0.341367000	-2.940792000
6	-4.718021000	-1.305548000	-1.931593000
6	-3.695972000	-2.103072000	-1.332890000
6	-3.946345000	-2.717278000	-0.056436000
6	-5.025962000	-2.088212000	0.709232000
6	-4.771930000	-1.547076000	2.012383000
6	-3.391150000	-1.482466000	2.446344000
6	-3.013479000	-0.405155000	3.295142000
6	-3.973033000	0.598965000	3.655157000
6	-3.509565000	1.922711000	3.936655000
6	-4.432795000	2.999803000	3.991277000
6	-3.975863000	4.320468000	3.583864000
6	-4.873366000	5.370593000	3.249092000
6	-4.558022000	6.283593000	2.266064000
6	-3.329320000	6.195072000	1.554728000
6	-3.228372000	6.506642000	0.137539000
6	-4.352406000	6.924799000	-0.628897000
6	-4.520554000	6.490849000	-1.924674000
6	-3.572388000	5.616227000	-2.525139000
6	-3.964765000	4.542465000	-3.423225000
6	-5.322606000	4.293896000	-3.771790000
6	-5.781066000	3.011955000	-3.979903000
6	-4.907922000	1.896022000	-3.850646000
6	-5.351411000	0.596964000	-3.381646000
6	-6.713062000	0.317710000	-3.068927000
6	-7.047919000	-0.596436000	-2.098433000
6	-6.034122000	-1.278288000	-1.370653000
6	-6.185168000	-1.640520000	0.012135000
6	-7.291832000	-1.204766000	0.805524000
6	-7.090966000	-0.809380000	2.099735000
6	-5.761258000	-0.749107000	2.633097000
6	-5.359296000	0.351518000	3.493617000
6	-6.252684000	1.378799000	3.901739000
6	-5.804635000	2.662045000	4.137726000
1	9.299014000	2.210089000	-0.412789000
1	9.149426000	1.747017000	1.952900000
1	8.667157000	0.397113000	3.566434000
1	7.900221000	-1.766625000	4.314625000
1	7.209149000	-3.748160000	3.899620000
1	6.614556000	-5.491121000	2.337782000
1	6.389409000	-6.132289000	0.268267000
1	6.487696000	-5.667446000	-2.097384000
1	6.882727000	-4.346952000	-3.740755000
1	7.642869000	-2.174195000	-4.468125000
1	8.381488000	-0.204166000	-3.996784000
1	9.031023000	1.527089000	-2.445719000
1	-7.320769000	1.194198000	3.926371000
1	-6.536070000	3.439169000	4.330452000
1	-5.872454000	5.387231000	3.670995000
1	-7.502450000	0.904534000	-3.525902000
1	-5.320779000	6.984758000	1.945709000

1	-5.454076000	6.711591000	-2.430766000
1	-5.158957000	7.473353000	-0.154813000
1	-6.042577000	5.104686000	-3.751506000
1	-6.845557000	2.858668000	-4.119677000
1	-8.086097000	-0.700076000	-1.804228000
1	-8.265174000	-1.063555000	0.348617000
1	-7.918601000	-0.383772000	2.654520000
45	-5.169611000	-4.660642000	-0.001547000
6	-1.744150000	-5.203609000	-0.638240000
6	-3.457663000	-4.503088000	1.516974000
6	-3.355064000	-5.796472000	1.069648000
6	-2.560076000	-6.125157000	-0.104864000
1	-2.604856000	-7.133379000	-0.502515000
1	-1.106763000	-5.465822000	-1.474830000
1	-3.742720000	-6.603320000	1.686940000
1	-3.921838000	-4.291255000	2.475998000
6	-6.308962000	-4.316363000	-1.479481000
8	-6.981531000	-4.143300000	-2.392937000
6	-6.008433000	-6.349100000	0.244765000
8	-6.470302000	-7.394883000	0.334165000

H3 (armchair (6,6))

$G = -4615.17367$

6	-6.968678000	0.666205000	4.203740000
6	-7.304909000	-0.639256000	3.929422000
6	-6.314657000	-1.581423000	3.527280000
6	-6.586890000	-2.635291000	2.568764000
6	-7.865623000	-2.806218000	1.961439000
6	-7.974030000	-3.224383000	0.656367000
6	-6.811823000	-3.502991000	-0.121441000
6	-6.736288000	-3.207387000	-1.537473000
6	-7.822040000	-2.626485000	-2.258875000
6	-7.592313000	-1.732514000	-3.276449000
6	-6.262766000	-1.365219000	-3.642581000
6	-5.920011000	-0.032205000	-4.087308000
6	-6.888253000	1.010814000	-4.209455000
6	-6.556634000	2.314191000	-3.934437000
6	-5.234119000	2.663357000	-3.522877000
6	-4.971935000	3.715756000	-2.567602000
6	-6.016997000	4.477590000	-1.958904000
6	-5.912586000	4.896268000	-0.656158000
6	-4.753722000	4.588654000	0.121692000
6	-4.821550000	4.294530000	1.535498000
6	-6.050834000	4.305883000	2.262877000
6	-6.270256000	3.411351000	3.280247000
6	-5.276807000	2.449119000	3.640322000
6	-5.620532000	1.112505000	4.087709000
6	-4.611308000	0.114721000	4.071475000
6	-4.961874000	-1.245311000	3.791458000
6	-3.917501000	-2.171588000	3.467571000
6	-4.183705000	-3.203924000	2.533478000
6	-5.487932000	-3.282487000	1.945693000
6	-5.601503000	-3.720082000	0.586783000
6	-4.405974000	-4.059405000	-0.125780000

6	-4.332389000	-3.770960000	-1.511031000
6	-5.456543000	-3.154771000	-2.149651000
6	-5.217249000	-2.222421000	-3.210368000
6	-3.863833000	-1.944490000	-3.585858000
6	-3.528654000	-0.638375000	-4.017807000
6	-4.554694000	0.357681000	-4.073670000
6	-4.208280000	1.718216000	-3.786708000
6	-2.850555000	2.025358000	-3.452546000
6	-2.590969000	3.064048000	-2.527030000
6	-3.695481000	3.765224000	-1.946767000
6	-3.587000000	4.210079000	-0.589140000
6	-2.375546000	3.941810000	0.123833000
6	-2.442061000	3.642820000	1.503165000
6	-3.719355000	3.635806000	2.145274000
6	-3.953963000	2.697896000	3.205217000
6	-2.896273000	1.798821000	3.570179000
6	-3.230921000	0.493915000	4.011771000
6	-2.215192000	-0.503881000	4.071883000
6	-2.565408000	-1.864574000	3.793196000
6	-1.535274000	-2.794710000	3.481911000
6	-1.803515000	-3.834823000	2.542598000
6	-3.092761000	-3.910421000	1.948400000
6	-3.204498000	-4.341464000	0.588425000
6	-2.025043000	-4.692559000	-0.125614000
6	-1.951147000	-4.402025000	-1.520611000
6	-3.060368000	-3.777704000	-2.155614000
6	-2.819412000	-2.840504000	-3.206430000
6	-1.479139000	-2.567702000	-3.599036000
6	-1.141169000	-1.249617000	-4.028827000
6	-2.155017000	-0.252340000	-4.066877000
6	-1.809688000	1.098733000	-3.768625000
6	-0.458894000	1.416868000	-3.449767000
6	-0.193931000	2.464245000	-2.516236000
6	-1.292307000	3.163408000	-1.936239000
6	-1.182763000	3.623904000	-0.595393000
6	0.029814000	3.401891000	0.122695000
6	-0.049119000	3.058775000	1.513164000
6	-1.310992000	3.027428000	2.137419000
6	-1.555079000	2.078387000	3.187968000
6	-0.515155000	1.187027000	3.561982000
6	-0.849460000	-0.121425000	4.020967000
6	0.171007000	-1.123472000	4.068238000
6	-0.176693000	-2.478172000	3.795301000
6	0.855576000	-3.406405000	3.482584000
6	0.587159000	-4.446444000	2.535399000
6	-0.704745000	-4.528212000	1.943943000
6	-0.817384000	-4.961755000	0.590359000
6	0.363917000	-5.307566000	-0.124789000
6	0.440092000	-5.009199000	-1.519917000
6	-0.672736000	-4.391447000	-2.159359000
6	-0.433493000	-3.458635000	-3.209729000
6	0.910021000	-3.178807000	-3.592697000
6	1.248411000	-1.859998000	-4.008897000
6	0.232187000	-0.861043000	-4.056738000
6	0.576131000	0.487386000	-3.755335000

6	1.927969000	0.800568000	-3.419839000
6	2.190722000	1.833605000	-2.486397000
6	1.098809000	2.561258000	-1.923613000
6	1.226370000	3.092344000	-0.599759000
6	2.489679000	2.976493000	0.139501000
6	2.352145000	2.460152000	1.523800000
6	1.076300000	2.401188000	2.123598000
6	0.830755000	1.457709000	3.160887000
6	1.873026000	0.580096000	3.560993000
6	1.537294000	-0.737702000	4.015808000
6	2.553966000	-1.730907000	4.047304000
6	2.208952000	-3.080768000	3.775788000
6	3.255524000	-4.010063000	3.466996000
6	2.986252000	-5.057012000	2.528391000
6	1.684579000	-5.126500000	1.932892000
6	1.572310000	-5.559828000	0.587510000
6	2.763313000	-5.916983000	-0.124017000
6	2.838026000	-5.626176000	-1.524140000
6	1.718767000	-4.991013000	-2.152213000
6	1.957804000	-4.062268000	-3.194584000
6	3.308241000	-3.794230000	-3.586536000
6	3.648212000	-2.471428000	-4.017642000
6	2.622677000	-1.472456000	-4.034561000
6	2.966019000	-0.135295000	-3.731578000
6	4.328106000	0.181880000	-3.435955000
6	4.600502000	1.231264000	-2.501156000
6	3.497216000	1.918440000	-1.892339000
6	3.632152000	2.408445000	-0.585766000
6	4.839733000	2.141017000	0.122874000
6	4.752956000	1.846484000	1.526848000
6	3.441504000	1.804967000	2.129948000
6	3.205053000	0.853647000	3.161241000
6	4.265961000	-0.026000000	3.560182000
6	3.933021000	-1.344625000	4.004591000
6	4.949242000	-2.331690000	4.107944000
6	4.596705000	-3.713328000	3.824333000
6	5.573170000	-4.710829000	3.544789000
6	5.315132000	-5.717144000	2.641851000
6	4.063645000	-5.790144000	1.966028000
6	3.948606000	-6.233607000	0.590537000
6	5.077169000	-6.641237000	-0.180272000
6	5.149262000	-6.359407000	-1.523709000
6	4.095140000	-5.660322000	-2.182549000
6	4.340116000	-4.708899000	-3.245574000
6	5.652063000	-4.408613000	-3.721172000
6	5.976731000	-3.139624000	-4.134765000
6	5.011330000	-2.088372000	-4.107692000
6	5.364057000	-0.717752000	-3.809795000
6	6.704790000	-0.304940000	-3.544423000
6	6.963289000	0.700121000	-2.645137000
6	5.901803000	1.364577000	-1.958781000
6	6.021910000	1.817155000	-0.590944000
6	7.208395000	1.629033000	0.184227000
6	7.124209000	1.362379000	1.526868000
6	5.854507000	1.266736000	2.181645000

6	5.610123000	0.293419000	3.239921000
6	6.613177000	-0.595962000	3.707513000
6	6.292405000	-1.871691000	4.124923000
1	-8.951742000	-3.218360000	0.187205000
1	-8.760445000	-2.482137000	2.481153000
1	-8.354404000	-0.911048000	3.902291000
1	-7.763562000	1.381092000	4.384979000
1	-7.255620000	3.365670000	3.730801000
1	-6.868473000	4.938760000	1.936166000
1	-6.772738000	5.360110000	-0.186138000
1	-6.956647000	4.621209000	-2.480485000
1	-7.343117000	3.060628000	-3.918252000
1	-7.926811000	0.765625000	-4.402025000
1	-8.438136000	-1.216068000	-3.716776000
1	-8.841413000	-2.787439000	-1.926087000
1	7.660437000	-0.329664000	3.617570000
1	7.099568000	-2.561661000	4.345556000
1	6.578217000	-4.611452000	3.939685000
1	7.536339000	-0.865742000	-3.956139000
1	6.125448000	-6.378683000	2.355616000
1	6.074905000	-6.565254000	-2.049981000
1	5.947919000	-7.059148000	0.312605000
1	6.440212000	-5.148865000	-3.639853000
1	7.011864000	-2.917711000	-4.369928000
1	7.993175000	0.905543000	-2.373765000
1	8.173900000	1.567518000	-0.305538000
1	8.029828000	1.102999000	2.064284000
77	2.407855000	5.232118000	-0.178698000
6	1.882957000	5.488779000	1.848997000
6	4.276921000	5.455000000	0.709534000
6	4.252208000	5.597462000	2.046262000
6	2.935905000	5.633669000	2.678167000
1	2.835621000	5.772324000	3.753218000
1	0.853669000	5.531604000	2.201364000
1	5.170399000	5.682162000	2.626439000
1	5.173320000	5.436786000	0.095883000
6	1.920583000	7.082070000	-0.251718000
8	1.671346000	8.204345000	-0.226665000
6	3.182625000	5.119236000	-1.987049000
8	3.710430000	5.128446000	-3.007141000

TS(H3.H4) (armchair (6,6))

G = -4615.13813

6	6.904432000	-1.060159000	4.237912000
6	7.288294000	0.244166000	4.027940000
6	6.337097000	1.233341000	3.644923000
6	6.661956000	2.317260000	2.737499000
6	7.955601000	2.467412000	2.157828000
6	8.101085000	2.932229000	0.871808000
6	6.962620000	3.277964000	0.086710000
6	6.900644000	3.036159000	-1.341541000
6	7.974360000	2.439500000	-2.064367000
6	7.728856000	1.589557000	-3.117549000

6	6.395275000	1.283112000	-3.515884000
6	6.014288000	-0.020915000	-4.023704000
6	6.945132000	-1.085975000	-4.182467000
6	6.561890000	-2.392529000	-3.978069000
6	5.226540000	-2.715834000	-3.606704000
6	4.912570000	-3.806255000	-2.700204000
6	5.923288000	-4.615945000	-2.103946000
6	5.786535000	-5.078695000	-0.815737000
6	4.629888000	-4.761744000	-0.045902000
6	4.687570000	-4.516172000	1.384326000
6	5.902660000	-4.589071000	2.125342000
6	6.136179000	-3.740800000	3.182586000
6	5.171103000	-2.763798000	3.563855000
6	5.546068000	-1.458280000	4.075018000
6	4.569593000	-0.429290000	4.081352000
6	4.968869000	0.929395000	3.867681000
6	3.962208000	1.902775000	3.564935000
6	4.280207000	2.966506000	2.683631000
6	5.597014000	3.025361000	2.122357000
6	5.748871000	3.511366000	0.784098000
6	4.578031000	3.919287000	0.066249000
6	4.517637000	3.683429000	-1.330138000
6	5.629043000	3.047519000	-1.972630000
6	5.374119000	2.160554000	-3.067450000
6	4.017427000	1.945140000	-3.472357000
6	3.643862000	0.665029000	-3.955448000
6	4.634903000	-0.364011000	-4.038296000
6	4.236624000	-1.723484000	-3.827455000
6	2.861532000	-2.003375000	-3.534093000
6	2.544376000	-3.089276000	-2.672304000
6	3.627752000	-3.838966000	-2.101464000
6	3.489071000	-4.316397000	-0.759046000
6	2.275235000	-4.027397000	-0.055281000
6	2.331564000	-3.780004000	1.334972000
6	3.601834000	-3.839363000	1.996684000
6	3.847074000	-2.949664000	3.090688000
6	2.812055000	-2.033064000	3.470435000
6	3.179034000	-0.760109000	3.975556000
6	2.195379000	0.266155000	4.055834000
6	2.594136000	1.625799000	3.850357000
6	1.602543000	2.602643000	3.563129000
6	1.921995000	3.675060000	2.678005000
6	3.224278000	3.732455000	2.109071000
6	3.375870000	4.218275000	0.771645000
6	2.220851000	4.635337000	0.052874000
6	2.160519000	4.399422000	-1.352891000
6	3.257284000	3.756135000	-1.991766000
6	3.002486000	2.864947000	-3.080792000
6	1.658305000	2.650186000	-3.496418000
6	1.283211000	1.360397000	-3.974264000
6	2.261146000	0.329510000	-4.034207000
6	1.865357000	-1.025053000	-3.803666000
6	0.499844000	-1.303674000	-3.501585000
6	0.177142000	-2.397340000	-2.644713000
6	1.237927000	-3.194665000	-2.120090000

6	1.098918000	-3.677132000	-0.772582000
6	-0.114718000	-3.466092000	-0.082449000
6	-0.039518000	-3.123220000	1.288758000
6	1.217658000	-3.150014000	1.956576000
6	1.469760000	-2.251637000	3.044447000
6	0.452016000	-1.347754000	3.436831000
6	0.818901000	-0.071199000	3.953474000
6	-0.166398000	0.958995000	4.024010000
6	0.228443000	2.312161000	3.829469000
6	-0.768802000	3.284974000	3.536153000
6	-0.448155000	4.361855000	2.654860000
6	0.858452000	4.428019000	2.090502000
6	1.010348000	4.916431000	0.760121000
6	-0.148764000	5.325000000	0.039911000
6	-0.208986000	5.088523000	-1.367211000
6	0.892205000	4.454630000	-2.009924000
6	0.638543000	3.565752000	-3.095126000
6	-0.708497000	3.339945000	-3.499947000
6	-1.081685000	2.047121000	-3.968406000
6	-0.101635000	1.021607000	-4.032696000
6	-0.494395000	-0.326002000	-3.782287000
6	-1.854630000	-0.605684000	-3.472863000
6	-2.162155000	-1.693093000	-2.606873000
6	-1.124243000	-2.476040000	-2.077292000
6	-1.352289000	-3.323817000	-0.884351000
6	-2.585284000	-2.979997000	-0.063513000
6	-2.420150000	-2.458126000	1.290083000
6	-1.148159000	-2.462894000	1.919735000
6	-0.890516000	-1.561634000	2.987895000
6	-1.909932000	-0.658693000	3.400912000
6	-1.544727000	0.617670000	3.922025000
6	-2.531724000	1.642406000	3.987983000
6	-2.139879000	2.990082000	3.792576000
6	-3.147889000	3.966669000	3.513594000
6	-2.826867000	5.048486000	2.632476000
6	-1.513178000	5.103646000	2.064197000
6	-1.361144000	5.592610000	0.742933000
6	-2.526848000	6.016673000	0.027502000
6	-2.587825000	5.779359000	-1.383384000
6	-1.479997000	5.130403000	-2.016365000
6	-1.733370000	4.244537000	-3.091562000
6	-3.086693000	4.029157000	-3.507461000
6	-3.461136000	2.731128000	-3.982882000
6	-2.468206000	1.702669000	-4.016731000
6	-2.856818000	0.366529000	-3.771816000
6	-4.236559000	0.075433000	-3.526692000
6	-4.560425000	-1.015514000	-2.654509000
6	-3.502093000	-1.776173000	-2.061056000
6	-3.687637000	-2.331346000	-0.790397000
6	-4.889408000	-2.015411000	-0.088885000
6	-4.809842000	-1.769145000	1.318945000
6	-3.505750000	-1.782471000	1.920764000
6	-3.251714000	-0.878308000	2.981009000
6	-4.287387000	0.013537000	3.412339000
6	-3.919344000	1.302830000	3.912694000

6	-4.904484000	2.318756000	4.040841000
6	-4.505569000	3.694498000	3.829385000
6	-5.447637000	4.735974000	3.577715000
6	-5.140424000	5.774637000	2.732305000
6	-3.871462000	5.836993000	2.081989000
6	-3.714819000	6.340340000	0.734784000
6	-4.818177000	6.814077000	-0.037873000
6	-4.876973000	6.585422000	-1.390597000
6	-3.835375000	5.870561000	-2.055989000
6	-4.094591000	4.963006000	-3.151545000
6	-5.411300000	4.715719000	-3.647707000
6	-5.769167000	3.472964000	-4.108274000
6	-4.834829000	2.392035000	-4.103530000
6	-5.231860000	1.021508000	-3.878114000
6	-6.597524000	0.641322000	-3.666387000
6	-6.910852000	-0.393790000	-2.827339000
6	-5.881737000	-1.118525000	-2.143078000
6	-6.047075000	-1.617297000	-0.804324000
6	-7.240197000	-1.409251000	-0.039161000
6	-7.171738000	-1.201168000	1.312472000
6	-5.903748000	-1.166478000	1.982036000
6	-5.639060000	-0.247598000	3.068234000
6	-6.622279000	0.658515000	3.564215000
6	-6.267611000	1.901339000	4.032731000
1	9.085886000	2.909526000	0.418319000
1	8.829936000	2.092178000	2.678051000
1	8.346147000	0.482735000	4.034516000
1	7.672158000	-1.807452000	4.405048000
1	7.118236000	-3.741419000	3.642520000
1	6.708392000	-5.229635000	1.783874000
1	6.628664000	-5.579061000	-0.350309000
1	6.870121000	-4.762518000	-2.611748000
1	7.324617000	-3.163581000	-3.980955000
1	7.996037000	-0.870203000	-4.339954000
1	8.562783000	1.055502000	-3.559475000
1	8.993228000	2.547474000	-1.709245000
1	-7.675641000	0.420666000	3.466725000
1	-7.051780000	2.605867000	4.286795000
1	-6.461648000	4.651768000	3.952697000
1	-7.398149000	1.240415000	-4.085529000
1	-5.921336000	6.477919000	2.465006000
1	-5.784472000	6.843622000	-1.925097000
1	-5.681053000	7.245655000	0.457135000
1	-6.177379000	5.477150000	-3.551877000
1	-6.806845000	3.290787000	-4.364521000
1	-7.952325000	-0.589136000	-2.596284000
1	-8.194557000	-1.300937000	-0.542512000
1	-8.075292000	-0.935370000	1.849488000
77	-3.138216000	-5.213958000	0.136624000
6	-1.903388000	-4.972235000	-1.604774000
6	-1.388600000	-6.115928000	0.702908000
6	-0.550699000	-6.487273000	-0.344315000
6	-0.880841000	-5.950213000	-1.604486000
1	-0.338966000	-6.229785000	-2.507214000
1	-2.308327000	-4.671742000	-2.569484000

1	0.328398000	-7.114356000	-0.205470000
1	-1.138506000	-6.466156000	1.705439000
6	-3.906253000	-5.337078000	1.894521000
8	-4.319718000	-5.363615000	2.969984000
6	-4.786989000	-5.113911000	-0.901513000
8	-5.715813000	-5.219358000	-1.575869000

H4 (armchair (6,6))

G = -4615.14471

6	-6.712182000	-1.866124000	-4.212903000
6	-7.140521000	-0.558697000	-4.205995000
6	-6.237403000	0.503527000	-3.914678000
6	-6.639535000	1.693756000	-3.187922000
6	-7.963575000	1.874396000	-2.694639000
6	-8.188884000	2.502548000	-1.491166000
6	-7.102001000	2.983805000	-0.706525000
6	-7.103822000	2.930256000	0.745016000
6	-8.187741000	2.383168000	1.486524000
6	-7.966606000	1.679983000	2.650541000
6	-6.647186000	1.476703000	3.141014000
6	-6.247740000	0.259716000	3.832744000
6	-7.145691000	-0.806590000	4.091482000
6	-6.711064000	-2.118043000	4.090618000
6	-5.356004000	-2.438745000	3.824331000
6	-4.962001000	-3.644322000	3.101026000
6	-5.923319000	-4.554490000	2.577221000
6	-5.720097000	-5.183789000	1.368763000
6	-4.541334000	-4.934319000	0.613299000
6	-4.540863000	-4.874167000	-0.840518000
6	-5.719765000	-5.067873000	-1.614844000
6	-5.927388000	-4.363341000	-2.779451000
6	-4.973658000	-3.409753000	-3.235595000
6	-5.354429000	-2.195358000	-3.934206000
6	-4.407116000	-1.145119000	-4.028154000
6	-4.851268000	0.216692000	-4.024492000
6	-3.888272000	1.255613000	-3.810065000
6	-4.281426000	2.421673000	-3.106764000
6	-5.627952000	2.511986000	-2.623698000
6	-5.861815000	3.166953000	-1.372022000
6	-4.740653000	3.708307000	-0.662158000
6	-4.743658000	3.659161000	0.755153000
6	-5.864949000	3.064889000	1.422810000
6	-5.634543000	2.329188000	2.629128000
6	-4.291834000	2.219499000	3.117426000
6	-3.899896000	1.020069000	3.771200000
6	-4.859935000	-0.028155000	3.940127000
6	-4.409533000	-1.386548000	3.930438000
6	-3.012621000	-1.651881000	3.734433000
6	-2.614632000	-2.848958000	3.062864000
6	-3.655891000	-3.714986000	2.567013000
6	-3.443869000	-4.368481000	1.311982000
6	-2.202908000	-4.149016000	0.631826000
6	-2.210393000	-4.068386000	-0.778641000

6	-3.450072000	-4.240247000	-1.481907000
6	-3.667647000	-3.493450000	-2.683039000
6	-2.642769000	-2.595667000	-3.123782000
6	-3.015305000	-1.412759000	-3.808590000
6	-2.056727000	-0.371936000	-3.971144000
6	-2.499464000	0.988370000	-3.987970000
6	-1.551045000	2.025810000	-3.787257000
6	-1.945992000	3.202638000	-3.083039000
6	-3.278210000	3.292349000	-2.590667000
6	-3.515690000	3.958730000	-1.345385000
6	-2.410540000	4.503463000	-0.636059000
6	-2.414534000	4.457514000	0.789956000
6	-3.521408000	3.860303000	1.455873000
6	-3.293500000	3.124567000	2.664825000
6	-1.964243000	3.008205000	3.155392000
6	-1.571236000	1.798701000	3.797970000
6	-2.516530000	0.747861000	3.943272000
6	-2.067224000	-0.613920000	3.904124000
6	-0.683372000	-0.876390000	3.685261000
6	-0.281457000	-2.070864000	3.019272000
6	-1.290319000	-2.990576000	2.598027000
6	-1.056206000	-3.706997000	1.354924000
6	0.174652000	-3.559602000	0.698554000
6	0.140163000	-3.342453000	-0.701995000
6	-1.094177000	-3.469109000	-1.415270000
6	-1.314672000	-2.718047000	-2.612123000
6	-0.307215000	-1.833299000	-3.058546000
6	-0.677817000	-0.647101000	-3.756745000
6	0.281170000	0.395154000	-3.910431000
6	-0.156080000	1.745752000	-3.935757000
6	0.799780000	2.782151000	-3.727176000
6	0.402063000	3.965058000	-3.040608000
6	-0.935470000	4.063682000	-2.554713000
6	-1.171838000	4.729095000	-1.316921000
6	-0.062680000	5.268707000	-0.604958000
6	-0.070419000	5.231357000	0.824063000
6	-1.181274000	4.642652000	1.490243000
6	-0.953676000	3.905971000	2.690476000
6	0.376509000	3.779086000	3.177144000
6	0.767071000	2.562445000	3.818499000
6	-0.180400000	1.520690000	3.956071000
6	0.265391000	0.164804000	3.884254000
6	1.641115000	-0.102134000	3.686517000
6	2.026502000	-1.300677000	3.001550000
6	1.060129000	-2.194260000	2.556086000
6	1.415377000	-3.337344000	1.578277000
6	2.675724000	-2.980533000	0.736270000
6	2.530545000	-2.671750000	-0.708684000
6	1.239906000	-2.720268000	-1.363818000
6	1.016831000	-1.948217000	-2.520783000
6	2.033477000	-1.053634000	-2.988313000
6	1.666004000	0.114702000	-3.695161000
6	2.630750000	1.156010000	-3.856011000
6	2.193477000	2.501427000	-3.875911000
6	3.157557000	3.541431000	-3.692246000

6	2.758229000	4.727490000	-2.995849000
6	1.414263000	4.816828000	-2.507412000
6	1.177119000	5.482353000	-1.279332000
6	2.292006000	6.039922000	-0.574164000
6	2.286543000	5.995376000	0.857162000
6	1.165610000	5.395567000	1.517291000
6	1.392112000	4.660654000	2.706678000
6	2.730726000	4.545035000	3.206106000
6	3.121021000	3.327745000	3.853351000
6	2.157640000	2.274274000	3.964298000
6	2.596541000	0.932918000	3.906762000
6	4.000445000	0.663482000	3.784525000
6	4.408513000	-0.525154000	3.093629000
6	3.409555000	-1.406544000	2.560960000
6	3.691671000	-2.151240000	1.424164000
6	4.919434000	-1.894415000	0.748465000
6	4.894758000	-1.856089000	-0.703945000
6	3.612916000	-1.938781000	-1.350077000
6	3.376000000	-1.184707000	-2.511393000
6	4.405600000	-0.325717000	-3.008332000
6	4.022528000	0.877281000	-3.683284000
6	4.983825000	1.902547000	-3.896549000
6	4.538550000	3.275097000	-3.899544000
6	5.436868000	4.375690000	-3.751464000
6	5.054404000	5.512406000	-3.083582000
6	3.749992000	5.620098000	-2.510269000
6	3.505712000	6.306476000	-1.260855000
6	4.554241000	6.914739000	-0.507693000
6	4.547837000	6.873602000	0.865326000
6	3.494788000	6.215900000	1.568791000
6	3.724952000	5.465233000	2.786940000
6	5.020764000	5.325853000	3.365840000
6	5.392604000	4.162183000	3.996581000
6	4.494182000	3.057988000	4.084185000
6	4.944005000	1.680022000	4.062070000
6	6.328884000	1.328446000	3.971759000
6	6.724386000	0.200925000	3.301986000
6	5.759786000	-0.652044000	2.677981000
6	6.016863000	-1.339666000	1.438748000
6	7.238520000	-1.197740000	0.697740000
6	7.235175000	-1.189806000	-0.671100000
6	5.999368000	-1.283606000	-1.397243000
6	5.750486000	-0.508011000	-2.585348000
6	6.729000000	0.368555000	-3.152982000
6	6.360139000	1.529551000	-3.783208000
1	-9.194181000	2.503861000	-1.084574000
1	-8.799527000	1.401776000	-3.198662000
1	-8.202228000	-0.357957000	-4.297183000
1	-7.450849000	-2.653805000	-4.313074000
1	-6.888770000	-4.448486000	-3.273706000
1	-6.525682000	-5.683276000	-1.229761000
1	-6.531576000	-5.760682000	0.938866000
1	-6.889919000	-4.657352000	3.058125000
1	-7.451336000	-2.907216000	4.163576000
1	-8.210479000	-0.614653000	4.165982000

1	-8.802769000	1.167901000	3.113829000
1	-9.190404000	2.399930000	1.073564000
1	7.783974000	0.173702000	-2.995336000
1	7.133819000	2.219246000	-4.101739000
1	6.471018000	4.276820000	-4.062814000
1	7.085589000	2.011106000	4.342131000
1	5.797822000	6.275833000	-2.883067000
1	5.419633000	7.229613000	1.403078000
1	5.431136000	7.302764000	-1.014323000
1	5.770050000	6.093441000	3.206351000
1	6.422296000	4.050894000	4.317457000
1	7.783320000	0.019491000	3.152256000
1	8.163525000	-0.981616000	1.221511000
1	8.155543000	-0.964266000	-1.197721000
77	3.733924000	-4.502180000	-0.443339000
6	1.682597000	-4.583393000	2.447166000
6	2.222722000	-5.884730000	-0.430377000
6	1.533512000	-6.305350000	0.638553000
6	1.681475000	-5.855969000	2.027077000
1	1.776522000	-6.639467000	2.778326000
1	1.831354000	-4.378917000	3.504234000
1	0.803362000	-7.099290000	0.464201000
1	2.008212000	-6.308514000	-1.408899000
6	4.363117000	-5.212933000	-2.164132000
8	4.782454000	-5.603352000	-3.160394000
6	4.693428000	-5.465834000	0.930463000
8	5.235280000	-6.045558000	1.761528000

TS(H4.H5) (armchair (6,6))

G = -4615.13137

6	-7.153979000	-1.593888000	-4.122622000
6	-7.692483000	-0.383405000	-3.746714000
6	-6.859086000	0.676388000	-3.292017000
6	-7.271361000	1.606808000	-2.253780000
6	-8.531025000	1.509499000	-1.599248000
6	-8.657299000	1.812293000	-0.261374000
6	-7.530773000	2.229156000	0.501169000
6	-7.344673000	1.846983000	1.892247000
6	-8.273811000	1.029137000	2.590861000
6	-7.846506000	0.111279000	3.526996000
6	-6.464343000	-0.045926000	3.817723000
6	-5.876450000	-1.336016000	4.153407000
6	-6.638088000	-2.526775000	4.245496000
6	-6.098732000	-3.745625000	3.876867000
6	-4.770366000	-3.841433000	3.395893000
6	-4.378603000	-4.787487000	2.353137000
6	-5.321275000	-5.644859000	1.721047000
6	-5.220110000	-5.948475000	0.379747000
6	-4.167216000	-5.409302000	-0.407246000
6	-4.343037000	-5.022609000	-1.800756000
6	-5.582609000	-5.168330000	-2.483096000
6	-5.986185000	-4.246004000	-3.423147000
6	-5.180088000	-3.113708000	-3.728013000

6	-5.750069000	-1.819998000	-4.067069000
6	-4.917710000	-0.675596000	-3.987707000
6	-5.477734000	0.585645000	-3.604264000
6	-4.591707000	1.651783000	-3.240126000
6	-4.996926000	2.569411000	-2.237422000
6	-6.274012000	2.384635000	-1.612245000
6	-6.405744000	2.702089000	-0.222556000
6	-5.257321000	3.196788000	0.479312000
6	-5.075576000	2.822525000	1.835918000
6	-6.046116000	1.964869000	2.451847000
6	-5.601671000	1.006912000	3.418120000
6	-4.202167000	0.942015000	3.723013000
6	-3.627594000	-0.323277000	4.024450000
6	-4.466409000	-1.482934000	4.039729000
6	-3.908716000	-2.743669000	3.655780000
6	-2.530555000	-2.799139000	3.258447000
6	-2.126290000	-3.755177000	2.275067000
6	-3.149600000	-4.584871000	1.685911000
6	-3.045740000	-4.899549000	0.294392000
6	-1.921268000	-4.394825000	-0.433619000
6	-2.096144000	-4.000606000	-1.779927000
6	-3.393753000	-4.143867000	-2.377905000
6	-3.816358000	-3.172742000	-3.339515000
6	-2.932346000	-2.085100000	-3.644302000
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6	-1.965489000	1.957162000	3.701212000
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6	0.370270000	-3.555638000	-0.461216000
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H5 (armchair (6,6))

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Cycloadduct (armchair (6,6) SWCNT + 2 acetylenes)

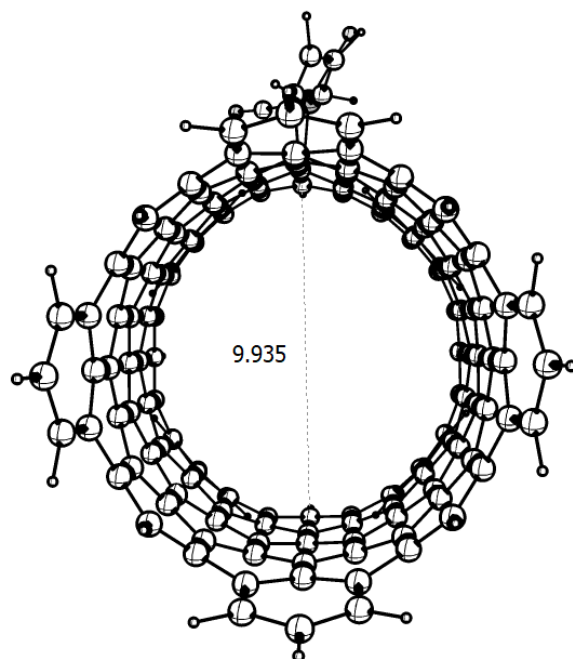
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6	-6.680940000	3.870702000	-1.726504000
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6	-5.493767000	4.159730000	0.377436000
6	-5.487860000	3.766198000	1.783243000
6	-6.676551000	3.447644000	2.490697000
6	-6.687184000	2.454022000	3.447126000
6	-5.512510000	1.713728000	3.744720000
6	-5.550219000	0.301346000	4.103985000
6	-4.349639000	-0.447347000	4.019701000
6	-4.398848000	-1.835999000	3.672341000
6	-3.179577000	-2.502976000	3.314926000
6	-3.220098000	-3.534151000	2.339909000
6	-4.481308000	-3.859426000	1.737723000
6	-4.500151000	-4.241300000	0.358089000
6	-3.256812000	-4.283470000	-0.358342000
6	-3.246498000	-3.896828000	-1.724362000
6	-4.478774000	-3.482530000	-2.333443000
6	-4.442759000	-2.443982000	-3.318405000
6	-3.175210000	-1.859183000	-3.649092000
6	-3.127312000	-0.475191000	-3.972082000

6	-4.344404000	0.280762000	-3.985377000
6	-4.300840000	1.667034000	-3.630451000
6	-3.040757000	2.248338000	-3.259849000
6	-3.016002000	3.313734000	-2.308008000
6	-4.269618000	3.716496000	-1.718292000
6	-4.273842000	4.093387000	-0.339221000
6	-3.029592000	4.081935000	0.373007000
6	-3.019874000	3.666606000	1.724905000
6	-4.267294000	3.316264000	2.346376000
6	-4.278541000	2.270967000	3.322286000
6	-3.042704000	1.600561000	3.617848000
6	-3.082381000	0.226784000	3.978193000
6	-1.880382000	-0.526914000	3.984616000
6	-1.928593000	-1.927146000	3.659540000
6	-0.727495000	-2.599487000	3.314587000
6	-0.766565000	-3.640346000	2.339595000
6	-2.008964000	-3.968426000	1.736209000
6	-2.027361000	-4.353590000	0.350677000
6	-0.801565000	-4.394397000	-0.366403000
6	-0.791464000	-4.005613000	-1.739340000
6	-2.006990000	-3.591741000	-2.347473000
6	-1.972904000	-2.541560000	-3.329135000
6	-0.722848000	-1.951179000	-3.656093000
6	-0.677135000	-0.560392000	-3.964071000
6	-1.877642000	0.195622000	-3.957583000
6	-1.835742000	1.579396000	-3.570717000
6	-0.589282000	2.146732000	-3.176001000
6	-0.556002000	3.215002000	-2.233518000
6	-1.796578000	3.702638000	-1.715921000
6	-1.805860000	4.155689000	-0.335863000
6	-0.587444000	4.196469000	0.369603000
6	-0.562543000	3.644493000	1.661246000
6	-1.784415000	3.262846000	2.291188000
6	-1.802281000	2.189843000	3.250490000
6	-0.592857000	1.514213000	3.543574000
6	-0.632732000	0.144664000	3.933262000
6	0.579695000	-0.614955000	3.943166000
6	0.534153000	-2.005319000	3.639934000
6	1.739460000	-2.678073000	3.307436000
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6	0.458287000	-4.056537000	1.722091000
6	0.440484000	-4.440650000	0.348306000
6	1.666526000	-4.485427000	-0.369136000
6	1.676292000	-4.090358000	-1.750112000
6	0.460272000	-3.675197000	-2.354408000
6	0.493163000	-2.628441000	-3.323893000
6	1.739851000	-2.032481000	-3.652110000
6	1.780919000	-0.631526000	-3.950452000
6	0.581838000	0.114531000	-3.929031000
6	0.622255000	1.481258000	-3.513303000
6	1.859154000	2.061127000	-3.144481000
6	1.875664000	3.132514000	-2.189878000
6	0.689163000	3.594358000	-1.646256000
6	0.668657000	4.551061000	-0.438566000
6	1.990062000	4.510317000	0.449964000

6	1.916705000	3.551616000	1.652420000
6	0.694447000	3.160500000	2.206825000
6	0.658941000	2.091750000	3.151264000
6	1.862881000	1.435161000	3.503344000
6	1.825093000	0.059516000	3.911503000
6	3.030333000	-0.686939000	3.916210000
6	2.987840000	-2.072318000	3.612408000
6	4.212969000	-2.740828000	3.283404000
6	4.175743000	-3.792735000	2.312883000
6	2.916418000	-4.123461000	1.706950000
6	2.898834000	-4.508025000	0.341191000
6	4.142492000	-4.553367000	-0.374424000
6	4.152898000	-4.155213000	-1.749849000
6	2.918717000	-3.735419000	-2.348545000
6	2.951272000	-2.691153000	-3.306608000
6	4.213799000	-2.095029000	-3.641108000
6	4.254250000	-0.696647000	-3.949925000
6	3.032130000	0.049810000	-3.899984000
6	3.069979000	1.404833000	-3.503043000
6	4.336819000	2.013988000	-3.211734000
6	4.379515000	3.083834000	-2.260077000
6	3.161421000	3.522553000	-1.623590000
6	3.216029000	4.071797000	-0.357504000
6	4.455596000	3.979798000	0.346627000
6	4.414092000	3.513824000	1.707492000
6	3.125805000	3.090663000	2.219904000
6	3.102969000	2.017544000	3.149849000
6	4.328192000	1.374869000	3.534689000
6	4.291732000	-0.006849000	3.904632000
6	5.497135000	-0.750655000	3.989919000
6	5.455793000	-2.169844000	3.660400000
6	6.623697000	-2.916590000	3.349862000
6	6.589486000	-3.929317000	2.415433000
6	5.385220000	-4.252894000	1.733090000
6	5.366730000	-4.652563000	0.334062000
6	6.553480000	-4.749977000	-0.443842000
6	6.563338000	-4.365028000	-1.765987000
6	5.386330000	-3.863229000	-2.386747000
6	5.418826000	-2.788348000	-3.366747000
6	6.629461000	-2.161492000	-3.774546000
6	6.666899000	-0.819842000	-4.082954000
6	5.496114000	-0.015320000	-4.000725000
6	5.533455000	1.391679000	-3.639086000
6	6.754610000	2.086213000	-3.380778000
6	6.802598000	3.106187000	-2.465895000
6	5.632493000	3.495589000	-1.744321000
6	5.675338000	3.920175000	-0.365266000
6	6.873710000	3.900285000	0.413740000
6	6.836398000	3.528012000	1.731926000
6	5.606344000	3.113322000	2.337962000
6	5.570176000	2.011346000	3.293808000
6	6.737635000	1.331149000	3.726471000
6	6.703823000	-0.008611000	4.058294000
1	-7.876792000	-4.426365000	-0.052633000
1	-7.844259000	-3.787563000	2.275871000

1	-7.777824000	-2.254848000	3.788051000
1	-7.694287000	0.080003000	4.395705000
1	-7.639869000	2.150923000	3.867664000
1	-7.620952000	3.888091000	2.189235000
1	-7.634056000	4.424893000	0.088942000
1	-7.632562000	3.796576000	-2.241476000
1	-7.642866000	2.309071000	-3.778913000
1	-7.715311000	-0.030459000	-4.371295000
1	-7.797517000	-2.099735000	-3.796246000
1	-7.860252000	-3.843039000	-2.127733000
1	7.701373000	1.826228000	3.681377000
1	7.641834000	-0.516342000	4.255463000
1	7.586045000	-2.605706000	3.742025000
1	7.679564000	1.738033000	-3.827469000
1	7.526280000	-4.377738000	2.102890000
1	7.513938000	-4.316033000	-2.286041000
1	7.496846000	-4.990238000	0.034601000
1	7.565475000	-2.706683000	-3.719389000
1	7.630937000	-0.357005000	-4.263488000
1	7.763871000	3.535946000	-2.204767000
1	7.835369000	4.052311000	-0.064653000
1	7.771262000	3.407414000	2.267842000
6	0.419664000	5.949375000	-1.034676000
6	2.322627000	5.888182000	1.052532000
6	1.857413000	7.048580000	0.581808000
6	0.950101000	7.078421000	-0.557067000
1	0.698798000	8.033181000	-1.010429000
1	-0.275109000	5.973459000	-1.867024000
1	2.159678000	7.984190000	1.043989000
1	3.014515000	5.867163000	1.887266000



Zigzag (12,0) SWCNT

$G = -5506.47443$

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6	1.775889000	-2.692725000	3.883260000
6	3.920772000	-1.586930000	4.420339000
6	2.485408000	-1.580649000	4.402921000
6	1.775917000	-0.391960000	4.709312000
6	3.918753000	0.860413000	4.695983000
6	2.498557000	0.852308000	4.674838000
6	1.787299000	2.016802000	4.275831000
6	3.918818000	3.076634000	3.650875000
6	2.498561000	3.065461000	3.631073000
6	1.775926000	3.883261000	2.692706000
6	3.920805000	4.420336000	1.586909000
6	2.485444000	4.402925000	1.580633000
6	1.775945000	4.709335000	0.391950000
6	3.918776000	4.695995000	-0.860434000
6	2.498582000	4.674854000	-0.852323000
6	1.787313000	4.275849000	-2.016809000
6	3.918824000	3.650876000	-3.076650000
6	2.498569000	3.631080000	-3.065467000
6	1.775924000	2.692708000	-3.883256000
6	3.920795000	1.586897000	-4.420331000
6	2.485433000	1.580628000	-4.402913000
6	1.775932000	0.391942000	-4.709311000
6	3.918758000	-0.860448000	-4.695974000
6	2.498564000	-0.852331000	-4.674831000
6	1.787290000	-2.016818000	-4.275830000
6	3.918795000	-3.076669000	-3.650869000
6	2.498539000	-3.065485000	-3.631070000
6	1.775897000	-3.883278000	-2.692707000
6	3.920770000	-4.420364000	-1.586901000
6	2.485408000	-4.402947000	-1.580629000

6	1.775904000	-4.709349000	-0.391947000
6	3.918731000	-4.696020000	0.860439000
6	2.498539000	-4.674872000	0.852327000
6	1.787269000	-4.275861000	2.016813000
6	0.352095000	-4.269103000	2.013622000
6	-0.359768000	-3.615878000	3.056539000
6	-1.776012000	-3.606749000	3.052736000
6	-2.498659000	-2.702815000	3.908358000
6	0.359703000	-2.695545000	3.892600000
6	-0.352192000	-1.594941000	4.442827000
6	-1.787316000	-1.597433000	4.449825000
6	-2.498582000	-0.400106000	4.735372000
6	0.359716000	-0.395694000	4.718358000
6	-0.359745000	0.846314000	4.658451000
6	-1.775926000	0.841682000	4.649760000
6	-2.485433000	1.995368000	4.230456000
6	0.352126000	2.013625000	4.269082000
6	-0.359734000	3.056553000	3.615866000
6	-1.775979000	3.052760000	3.606748000
6	-2.498622000	3.908399000	2.702822000
6	0.359740000	3.892610000	2.695539000
6	-0.352156000	4.442857000	1.594941000
6	-1.787275000	4.449863000	1.597444000
6	-2.498557000	4.735422000	0.400121000
6	0.359749000	4.718389000	0.395691000
6	-0.359725000	4.658489000	-0.846314000
6	-1.775903000	4.649797000	-0.841672000
6	-2.485420000	4.230489000	-1.995351000
6	0.352139000	4.269102000	-2.013623000
6	-0.359729000	3.615882000	-3.056544000
6	-1.775973000	3.606767000	-3.052740000
6	-2.498623000	2.702837000	-3.908369000
6	0.359738000	2.695543000	-3.892594000
6	-0.352163000	1.594944000	-4.442831000
6	-1.787286000	1.597452000	-4.449829000
6	-2.498569000	0.400131000	-4.735386000
6	0.359733000	0.395690000	-4.718356000
6	-0.359743000	-0.846312000	-4.658461000
6	-1.775922000	-0.841664000	-4.649763000
6	-2.485442000	-1.995347000	-4.230468000
6	0.352115000	-2.013626000	-4.269079000
6	-0.359752000	-3.056550000	-3.615870000
6	-1.775997000	-3.052743000	-3.606751000
6	-2.498651000	-3.908375000	-2.702832000
6	0.359711000	-3.892614000	-2.695536000
6	-0.352195000	-4.442854000	-1.594945000
6	-1.787315000	-4.449848000	-1.597447000
6	-2.498599000	-4.735401000	-0.400128000
6	0.359708000	-4.718391000	-0.395693000
6	-0.359769000	-4.658486000	0.846310000
6	-1.775946000	-4.649782000	0.841666000
6	-2.485463000	-4.230468000	1.995344000
6	-3.920878000	-4.247271000	2.003172000
6	-4.634976000	-3.693406000	3.103837000
6	-6.010505000	-3.943301000	3.199519000

6	-3.918859000	-2.712208000	3.929289000
6	-4.593777000	-1.597593000	4.450273000
6	-3.918797000	-0.406244000	4.757664000
6	-4.634929000	0.875956000	4.744687000
6	-6.010504000	1.007831000	4.977347000
6	-3.920852000	2.003204000	4.247264000
6	-4.634942000	3.103883000	3.693414000
6	-6.010471000	3.199564000	3.943296000
6	-3.918820000	3.929341000	2.712223000
6	-4.593746000	4.450334000	1.597618000
6	-3.918763000	4.757721000	0.406265000
6	-4.634907000	4.744733000	-0.875929000
6	-6.010484000	4.977384000	-1.007792000
6	-3.920838000	4.247297000	-2.003178000
6	-4.634938000	3.693434000	-3.103843000
6	-6.010469000	3.943305000	-3.199512000
6	-3.918823000	2.712240000	-3.929300000
6	-4.593754000	1.597636000	-4.450287000
6	-3.918779000	0.406281000	-4.757679000
6	-4.634922000	-0.875912000	-4.744704000
6	-6.010499000	-1.007772000	-4.977362000
6	-3.920858000	-2.003170000	-4.247278000
6	-4.634964000	-3.103839000	-3.693427000
6	-6.010495000	-3.199502000	-3.943307000
6	-3.918850000	-3.929305000	-2.712236000
6	-4.593783000	-4.450294000	-1.597633000
6	-3.918808000	-4.757689000	-0.406277000
6	-4.634950000	-4.744705000	0.875924000
6	-6.010520000	-4.977384000	1.007803000
6	4.634920000	2.735426000	-3.974541000
6	4.634984000	0.416980000	-4.806461000
6	4.593734000	-2.016643000	-4.275398000
1	5.673534000	-1.979885000	-4.197408000
6	4.634893000	-3.974566000	-2.735429000
6	4.593759000	4.275414000	-2.016623000
1	5.673558000	4.197436000	-1.979857000
6	4.635001000	4.806477000	0.417000000
6	4.634921000	3.974529000	2.735438000
6	4.593742000	2.016601000	4.275410000
1	5.673542000	1.979823000	4.197428000
6	4.634970000	-0.417021000	4.806469000
6	4.634887000	-2.735468000	3.974553000
6	4.593714000	-4.275444000	2.016632000
1	5.673514000	-4.197462000	1.979871000
6	4.634961000	-4.806500000	-0.416987000
6	-6.674712000	-4.633290000	2.185261000
1	-7.733862000	-4.849708000	2.287353000
6	-6.674689000	2.185294000	4.633261000
1	-7.733844000	2.287386000	4.849658000
6	-6.674681000	4.633278000	-2.185244000
1	-7.733838000	4.849668000	-2.287323000
6	-6.674700000	-2.185226000	-4.633273000
1	-7.733855000	-2.287300000	-4.849675000
1	-6.565238000	-3.589487000	4.062700000
1	-6.565188000	-5.418606000	0.185782000

1	-5.673659000	-1.568837000	4.370346000
1	-6.565179000	0.185798000	5.418537000
1	-6.565204000	4.062749000	3.589490000
1	-5.673629000	4.370426000	1.568878000
1	-6.565152000	5.418581000	-0.185757000
1	-6.565212000	3.589476000	-4.062682000
1	-5.673636000	1.568894000	-4.370361000
1	-6.565160000	-0.185731000	-5.418555000
1	-6.565236000	-4.062678000	-3.589492000
1	-5.673665000	-4.370380000	-1.568895000
6	6.010640000	5.050285000	0.525714000
1	6.565254000	5.410058000	-0.335075000
6	6.674946000	4.820908000	1.730749000
1	7.734200000	5.045674000	1.811464000
6	6.010584000	4.231777000	2.806629000
1	6.565168000	3.961885000	3.699724000
6	6.010625000	0.525684000	-5.050269000
1	6.565233000	-0.335114000	-5.410029000
6	6.674939000	1.730717000	-4.820912000
1	7.734192000	1.811424000	-5.045683000
6	6.010582000	2.806609000	-4.231795000
1	6.565167000	3.699710000	-3.961922000
6	6.010604000	-5.050297000	-0.525688000
1	6.565216000	-5.410050000	0.335111000
6	6.674916000	-4.820923000	-1.730719000
1	7.734172000	-5.045679000	-1.811427000
6	6.010556000	-4.231804000	-2.806610000
1	6.565148000	-3.961914000	-3.699702000
6	6.010612000	-0.525735000	5.050272000
1	6.565231000	0.335059000	5.410025000
6	6.674915000	-1.730772000	4.820911000
1	7.734169000	-1.811489000	5.045676000
6	6.010547000	-2.806663000	4.231798000
1	6.565127000	-3.699764000	3.961917000

G3 (zigzag (12,0))

G = -5998.17347

6	3.872382000	-3.344404000	-4.088491000
6	3.584266000	-1.953370000	-4.088047000
6	2.303481000	-1.473981000	-4.533638000
6	1.515388000	-3.816820000	-4.630098000
6	1.239074000	-2.409000000	-4.627491000
6	-0.095715000	-1.946150000	-4.512088000
6	-0.834143000	-4.270171000	-4.051648000
6	-1.091322000	-2.873242000	-4.046761000
6	-2.173558000	-2.352715000	-3.282975000
6	-2.541466000	-4.586291000	-2.319717000
6	-2.794533000	-3.189366000	-2.318553000
6	-3.390127000	-2.556993000	-1.174481000
6	-3.097564000	-4.665419000	0.080999000
6	-3.366323000	-3.261551000	0.063560000
6	-3.389768000	-2.529607000	1.284731000

6	-2.523901000	-4.524418000	2.474873000
6	-2.780406000	-3.129211000	2.440543000
6	-2.150519000	-2.265314000	3.375005000
6	-0.800409000	-4.159818000	4.181340000
6	-1.059267000	-2.763217000	4.140661000
6	-0.059653000	-1.823281000	4.569654000
6	1.554140000	-3.689707000	4.724949000
6	1.276725000	-2.282536000	4.685139000
6	2.339704000	-1.350440000	4.555450000
6	3.905830000	-3.231933000	4.149013000
6	3.616910000	-1.841679000	4.112302000
6	4.423046000	-0.967879000	3.332245000
6	5.606764000	-2.920241000	2.412345000
6	5.315848000	-1.530320000	2.379030000
6	5.621336000	-0.748638000	1.210136000
6	6.157486000	-2.845253000	0.014510000
6	5.865422000	-1.440551000	-0.003558000
6	5.612460000	-0.781833000	-1.233787000
6	5.588273000	-2.985326000	-2.376043000
6	5.297954000	-1.594978000	-2.378678000
6	4.397289000	-1.058566000	-3.339539000
6	4.116470000	0.347858000	-3.352047000
6	3.022573000	0.849726000	-4.109019000
6	2.741157000	2.237727000	-4.118401000
6	1.477188000	2.719586000	-4.608429000
6	2.030094000	-0.084696000	-4.559608000
6	0.691190000	0.377023000	-4.699278000
6	0.413231000	1.782344000	-4.720503000
6	-0.924036000	2.245950000	-4.578524000
6	-0.367888000	-0.555951000	-4.533746000
6	-1.626469000	-0.064963000	-4.051303000
6	-1.894983000	1.324248000	-4.058893000
6	-2.969971000	1.847066000	-3.285448000
6	-2.439842000	-0.945848000	-3.282489000
6	-3.330560000	-0.385917000	-2.327662000
6	-3.609392000	1.008800000	-2.342900000
6	-4.277170000	1.633777000	-1.232356000
6	-3.681334000	-1.179759000	-1.195450000
6	-4.093970000	-0.519026000	0.026240000
6	-4.322992000	0.918862000	0.005562000
6	-4.270872000	1.668508000	1.225387000
6	-3.679940000	-1.150695000	1.268830000
6	-3.319100000	-0.323873000	2.376450000
6	-3.591228000	1.073195000	2.349304000
6	-2.945029000	1.936243000	3.261722000
6	-2.417688000	-0.858444000	3.337551000
6	-1.595626000	0.044192000	4.070640000
6	-1.863235000	1.433630000	4.040141000
6	-0.888560000	2.369021000	4.525836000
6	-0.332091000	-0.433134000	4.554494000
6	0.728134000	0.504128000	4.684046000
6	0.450087000	1.909311000	4.668679000
6	1.512718000	2.843265000	4.521674000
6	2.066002000	0.039020000	4.545228000
6	3.054256000	0.960654000	4.060720000

6	2.772638000	2.348355000	4.034445000
6	3.563028000	3.217607000	3.241500000
6	4.141844000	0.438270000	3.308499000
6	4.753050000	1.272205000	2.331654000
6	4.472718000	2.660169000	2.305964000
6	4.825556000	3.451471000	1.157214000
6	5.359701000	0.643003000	1.191797000
6	5.363359000	1.354007000	-0.039648000
6	5.093920000	2.762768000	-0.057740000
6	4.816965000	3.418315000	-1.288972000
6	5.350905000	0.609856000	-1.251380000
6	4.735659000	1.208034000	-2.403331000
6	4.455606000	2.596216000	-2.413318000
6	3.538225000	3.128174000	-3.356087000
6	3.271734000	4.537520000	-3.385680000
6	2.247925000	5.054086000	-4.230840000
6	2.178163000	6.440507000	-4.425590000
6	1.202621000	4.112225000	-4.648308000
6	-0.133430000	4.535925000	-4.757708000
6	-1.202142000	3.639103000	-4.621923000
6	-2.522293000	4.112677000	-4.185288000
6	-2.991921000	5.417681000	-4.385032000
6	-3.264709000	3.252219000	-3.326830000
6	-4.249865000	3.800036000	-2.457416000
6	-4.689476000	5.111499000	-2.681277000
6	-4.561929000	3.025265000	-1.249923000
6	-4.792019000	3.681162000	-0.029060000
6	-4.553695000	3.060294000	1.207818000
6	-4.232249000	3.866791000	2.392386000
6	-4.670138000	5.183575000	2.584574000
6	-3.239564000	3.342733000	3.267408000
6	-2.490730000	4.225208000	4.096462000
6	-2.958769000	5.535321000	4.265530000
6	-1.166595000	3.763235000	4.533728000
6	-0.097259000	4.663120000	4.636127000
6	1.238093000	4.236399000	4.525979000
6	2.279389000	5.166491000	4.074259000
6	2.210696000	6.557824000	4.231716000
6	3.296321000	4.627119000	3.234964000
6	3.995386000	5.481200000	2.334309000
6	3.900888000	6.866285000	2.521508000
6	4.573261000	4.849293000	1.140952000
6	4.552191000	5.517681000	-0.093054000
6	4.564813000	4.816078000	-1.308732000
6	3.978160000	5.415607000	-2.514414000
6	3.882383000	6.795223000	-2.738411000
6	0.483598000	-4.629401000	4.716878000
6	2.901445000	-4.151794000	4.698678000
6	4.965502000	-3.721958000	3.370399000
1	5.120339000	-4.793420000	3.328949000
6	6.270202000	-3.535238000	1.255418000
6	-1.608281000	-5.018153000	3.417474000
1	-1.345767000	-6.068526000	3.377913000
6	-2.923265000	-5.344329000	1.325281000
6	-2.933026000	-5.376195000	-1.146509000

6	-1.637011000	-5.106834000	-3.257562000
1	-1.376393000	-6.156438000	-3.193226000
6	0.444554000	-4.755347000	-4.585416000
6	2.862751000	-4.278828000	-4.603170000
6	4.938565000	-3.813132000	-3.305866000
1	5.093207000	-4.883098000	-3.235513000
6	6.260765000	-3.568662000	-1.208028000
6	3.034452000	7.293468000	-3.729121000
1	2.997438000	8.362211000	-3.916343000
6	-4.101783000	5.887041000	-3.680993000
1	-4.473872000	6.888805000	-3.871923000
6	-4.074293000	5.985719000	3.558487000
1	-4.444929000	6.992278000	3.725479000
6	3.060972000	7.391400000	3.505240000
1	3.025256000	8.464853000	3.663489000
1	1.452377000	6.854890000	-5.118139000
1	4.464770000	7.483195000	-2.133788000
1	-0.340487000	5.597469000	-4.696316000
1	-2.485547000	6.072735000	-5.086514000
1	-5.485554000	5.529424000	-2.073192000
1	-4.911725000	4.757800000	-0.043693000
1	-5.470614000	5.585383000	1.971417000
1	-2.446694000	6.208518000	4.945336000
1	-0.304999000	5.722635000	4.548232000
1	1.490681000	6.990921000	4.918811000
1	4.477981000	7.537626000	1.893566000
1	4.264370000	6.561964000	-0.106275000
6	-2.929132000	-6.744642000	1.322221000
1	-2.865925000	-7.289615000	2.258310000
6	-2.999378000	-7.445310000	0.116683000
1	-3.034799000	-8.530394000	0.130793000
6	-2.939410000	-6.775825000	-1.107165000
1	-2.883562000	-7.344834000	-2.029337000
6	3.147565000	-5.500293000	4.988950000
1	4.168584000	-5.863906000	5.043768000
6	2.087576000	-6.383345000	5.199887000
1	2.293908000	-7.417145000	5.459276000
6	0.769042000	-5.970632000	5.005157000
1	-0.036722000	-6.694646000	5.073361000
6	6.790249000	-4.865546000	-1.172773000
1	6.944524000	-5.412797000	-2.097288000
6	7.113764000	-5.462568000	0.046435000
1	7.557744000	-6.453231000	0.058187000
6	6.799637000	-4.832585000	1.251447000
1	6.961174000	-5.354400000	2.189307000
6	0.727217000	-6.104504000	-4.838357000
1	-0.079216000	-6.829816000	-4.878940000
6	2.043595000	-6.523168000	-5.033777000
1	2.247301000	-7.563947000	-5.265901000
6	3.105828000	-5.634935000	-4.857643000
1	4.126194000	-6.000546000	-4.911619000
45	-6.414881000	-0.431163000	0.131634000
6	-6.503368000	-0.715638000	-1.936328000
6	-6.755394000	-2.451612000	0.052529000
6	-6.682695000	-1.998477000	-2.293141000

6	-6.797387000	-2.951901000	-1.191527000
1	-6.394814000	0.114263000	-2.630419000
1	-6.716701000	-2.330308000	-3.329113000
1	-6.886507000	-4.023514000	-1.368128000
1	-6.863353000	-2.998579000	0.984543000
6	-6.487850000	-0.401370000	2.152050000
8	-6.651121000	-0.465837000	3.279380000
6	-8.240656000	-0.028152000	-0.187174000
8	-9.344124000	0.172133000	-0.416577000

TS(G3.G4) (zigzag (12,0))

G = -5998.12454

6	-4.888784000	-2.404465000	3.826395000
6	-4.337732000	-1.095830000	3.812170000
6	-3.031624000	-0.849548000	4.362759000
6	-2.727293000	-3.289703000	4.613834000
6	-2.184068000	-1.963098000	4.590835000
6	-0.777058000	-1.769338000	4.593111000
6	-0.463314000	-4.211825000	4.307279000
6	0.058074000	-2.890498000	4.275294000
6	1.298545000	-2.629083000	3.621267000
6	1.328731000	-4.948389000	2.801914000
6	1.845902000	-3.626194000	2.773239000
6	2.695363000	-3.194645000	1.700649000
6	2.127507000	-5.274273000	0.494952000
6	2.679867000	-3.962453000	0.496177000
6	2.959165000	-3.301277000	-0.742242000
6	1.796870000	-5.138344000	-1.941462000
6	2.316240000	-3.817292000	-1.920213000
6	1.935577000	-2.889097000	-2.922790000
6	0.321145000	-4.527259000	-3.805161000
6	0.838791000	-3.205446000	-3.776851000
6	0.088528000	-2.115372000	-4.332415000
6	-1.833946000	-3.643675000	-4.609999000
6	-1.293310000	-2.315667000	-4.584578000
6	-2.159017000	-1.191438000	-4.609520000
6	-4.098620000	-2.712407000	-4.327433000
6	-3.548537000	-1.403112000	-4.304116000
6	-4.247171000	-0.348767000	-3.654429000
6	-5.882338000	-1.984997000	-2.812829000
6	-5.329863000	-0.676591000	-2.792877000
6	-5.595104000	0.210288000	-1.690768000
6	-6.644683000	-1.681484000	-0.493455000
6	-6.087409000	-0.358880000	-0.488830000
6	-5.831484000	0.301258000	0.740182000
6	-6.342264000	-1.808492000	1.945338000
6	-5.788810000	-0.499821000	1.934975000
6	-4.891984000	-0.099377000	2.962843000
6	-4.345044000	1.226786000	2.960477000
6	-3.244266000	1.545996000	3.802725000
6	-2.70096000	2.853609000	3.797255000
6	-1.412405000	3.107063000	4.386416000
6	-2.495031000	0.462119000	4.370431000

6	-1.109537000	0.665747000	4.622280000
6	-0.565386000	1.990478000	4.624247000
6	0.844348000	2.182223000	4.596389000
6	-0.241937000	-0.457890000	4.590912000
6	1.128158000	-0.244017000	4.223740000
6	1.660577000	1.069121000	4.208116000
6	2.892244000	1.333509000	3.543742000
6	1.830559000	-1.304349000	3.591980000
6	2.921557000	-0.985310000	2.722843000
6	3.458618000	0.341886000	2.713051000
6	4.362180000	0.758425000	1.680941000
6	3.250188000	-1.902337000	1.702972000
6	4.064089000	-1.474863000	0.539268000
6	4.470351000	-0.047730000	0.509918000
6	4.681192000	0.620733000	-0.739892000
6	3.524941000	-2.014960000	-0.737122000
6	3.374344000	-1.171226000	-1.870118000
6	3.925275000	0.141247000	-1.883302000
6	3.532606000	1.068704000	-2.862028000
6	2.461423000	-1.561685000	-2.894069000
6	1.902973000	-0.556058000	-3.728587000
6	2.437548000	0.753421000	-3.717821000
6	1.719730000	1.832671000	-4.329041000
6	0.624877000	-0.804739000	-4.329889000
6	-0.209291000	0.309969000	-4.608036000
6	0.338233000	1.633621000	-4.604850000
6	-0.527299000	2.761450000	-4.611118000
6	-1.619506000	0.118432000	-4.611296000
6	-2.452923000	1.238350000	-4.278226000
6	-1.906515000	2.545405000	-4.262621000
6	-2.592802000	3.592669000	-3.599103000
6	-3.698573000	0.976729000	-3.643832000
6	-4.235449000	1.964779000	-2.772656000
6	-3.691673000	3.272386000	-2.760006000
6	-4.001138000	4.177312000	-1.684770000
6	-5.068806000	1.525023000	-1.688135000
6	-5.056525000	2.286812000	-0.487528000
6	-4.520078000	3.617233000	-0.485035000
6	-4.242692000	4.270320000	0.747524000
6	-5.306779000	1.616380000	0.741331000
6	-4.697645000	2.142545000	1.931147000
6	-4.154852000	3.450860000	1.926925000
6	-3.240114000	3.842872000	2.938310000
6	-2.707402000	5.174598000	2.951459000
6	-1.679025000	5.525410000	3.872762000
6	-1.357803000	6.880966000	4.031933000
6	-0.876417000	4.421974000	4.410910000
6	0.502264000	4.587663000	4.634599000
6	1.383051000	3.498662000	4.626897000
6	2.806198000	3.688253000	4.319046000
6	3.497435000	4.888233000	4.528509000
6	3.448653000	2.657670000	3.574815000
6	4.606372000	2.960904000	2.806534000
6	5.266967000	4.176740000	3.034276000
6	4.898478000	2.071396000	1.679999000

6	5.429474000	2.590519000	0.484911000
6	5.208733000	1.952126000	-0.740771000
6	5.142167000	2.738378000	-1.980951000
6	5.851068000	3.928694000	-2.185852000
6	4.116608000	2.384813000	-2.901437000
6	3.622359000	3.355192000	-3.817305000
6	4.359255000	4.534303000	-3.997670000
6	2.270437000	3.143989000	-4.354693000
6	1.416440000	4.226815000	-4.598112000
6	0.017799000	4.072591000	-4.625733000
6	-0.862214000	5.208700000	-4.331736000
6	-0.502623000	6.550308000	-4.523701000
6	-2.054315000	4.922206000	-3.605774000
6	-2.666438000	5.943135000	-2.823402000
6	-2.280570000	7.271777000	-3.042419000
6	-3.481795000	5.499383000	-1.685110000
6	-3.455518000	6.215627000	-0.478367000
6	-3.725289000	5.593041000	0.750147000
6	-3.148651000	6.128602000	1.990200000
6	-2.806994000	7.473579000	2.181315000
6	-0.973802000	-4.769097000	-4.453046000
6	-3.241200000	-3.837286000	-4.722628000
6	-5.312150000	-2.946292000	-3.662357000
1	-5.677234000	-3.964362000	-3.601470000
6	-6.767242000	-2.400092000	-1.716609000
6	0.881541000	-5.488082000	-2.946066000
1	0.420372000	-6.467417000	-2.901849000
6	1.932060000	-5.969107000	-0.740638000
6	1.684763000	-5.867773000	1.718786000
6	0.243449000	-5.230353000	3.646973000
1	-0.204059000	-6.215696000	3.597182000
6	-1.859370000	-4.415632000	4.713885000
6	-4.130928000	-3.487318000	4.465735000
6	-5.952157000	-2.698721000	2.958047000
1	-6.304297000	-3.721913000	2.905471000
6	-7.003857000	-2.309393000	0.733231000
6	-1.968680000	7.847636000	3.233437000
1	-1.741352000	8.897342000	3.391564000
6	4.743867000	5.101503000	3.936597000
1	5.282585000	6.022565000	4.135998000
6	5.495325000	4.785983000	-3.228017000
1	6.074246000	5.687236000	-3.403737000
6	-1.248168000	7.570620000	-3.933576000
1	-0.983737000	8.606771000	-4.120815000
1	-0.627557000	7.181268000	4.776659000
1	-3.187945000	8.230202000	1.502685000
1	0.915752000	5.586262000	4.563119000
1	3.059417000	5.662623000	5.149853000
1	6.188751000	4.401310000	2.507130000
1	5.756997000	3.622507000	0.472719000
1	6.674311000	4.189062000	-1.528008000
1	4.042613000	5.260217000	-4.739540000
1	1.819898000	5.229410000	-4.523190000
1	0.361640000	6.798265000	-5.131634000
1	-2.780375000	8.075018000	-2.510398000

1	-2.971274000	7.184602000	-0.467056000
6	1.657962000	-7.339676000	-0.691437000
1	1.573243000	-7.910419000	-1.610285000
6	1.467553000	-7.974883000	0.539050000
1	1.286614000	-9.045146000	0.564238000
6	1.414220000	-7.242031000	1.725886000
1	1.146637000	-7.738093000	2.652939000
6	-3.715291000	-5.127799000	-4.992331000
1	-4.776238000	-5.292505000	-5.150759000
6	-2.832976000	-6.207673000	-5.051310000
1	-3.210095000	-7.195749000	-5.296350000
6	-1.486224000	-6.044599000	-4.726011000
1	-0.835371000	-6.912072000	-4.682096000
6	-7.769346000	-3.481794000	0.683429000
1	-8.115218000	-3.942207000	1.603438000
6	-8.083046000	-4.067723000	-0.543884000
1	-8.707920000	-4.955097000	-0.571278000
6	-7.536419000	-3.571494000	-1.728043000
1	-7.703296000	-4.101084000	-2.660748000
6	-2.422310000	-5.670435000	4.982128000
1	-1.780715000	-6.532769000	5.132924000
6	-3.807795000	-5.820411000	5.052691000
1	-4.230742000	-6.789898000	5.297209000
6	-4.655816000	-4.757558000	4.738557000
1	-5.728272000	-4.919350000	4.700294000
45	6.716309000	-0.912229000	-0.308836000
6	7.161685000	-0.320982000	1.606556000
6	5.697017000	-2.512576000	0.854068000
6	6.902204000	-1.263664000	2.552425000
6	6.310580000	-2.488615000	2.083559000
1	7.533295000	0.674762000	1.844130000
1	7.100393000	-1.111988000	3.612696000
1	6.381859000	-3.408427000	2.665265000
1	5.373343000	-3.444325000	0.399959000
6	6.390426000	-1.608593000	-2.138698000
8	6.261176000	-2.057533000	-3.183710000
6	8.484886000	-1.522671000	-0.190451000
8	9.545048000	-1.954891000	-0.105366000

G4 (zigzag (12,0))

G = -5998.14770

6	5.726788000	-1.600721000	-3.264867000
6	5.000309000	-0.380896000	-3.292343000
6	3.760863000	-0.287554000	-4.016069000
6	3.837556000	-2.734396000	-4.367858000
6	3.116654000	-1.495608000	-4.389480000
6	1.710418000	-1.493838000	-4.586300000
6	1.704364000	-3.965990000	-4.399804000
6	1.006168000	-2.730017000	-4.413797000
6	-0.338206000	-2.665446000	-3.939340000
6	-0.165571000	-5.001384000	-3.191621000
6	-0.856983000	-3.762016000	-3.205851000
6	-1.919024000	-3.501213000	-2.279125000

6	-1.275623000	-5.545589000	-1.056655000
6	-2.000227000	-4.326285000	-1.108849000
6	-2.572386000	-3.776279000	0.083691000
6	-1.349709000	-5.490021000	1.399432000
6	-2.033772000	-4.248248000	1.329118000
6	-1.924786000	-3.317292000	2.393666000
6	-0.241314000	-4.767651000	3.466496000
6	-0.918437000	-3.521434000	3.386782000
6	-0.399192000	-2.367833000	4.059578000
6	1.651958000	-3.648229000	4.579432000
6	0.949680000	-2.401102000	4.504404000
6	1.647174000	-1.178831000	4.683946000
6	3.792065000	-2.424123000	4.648663000
6	3.081667000	-1.196491000	4.582765000
6	3.721068000	-0.029969000	4.080178000
6	5.665268000	-1.399023000	3.444560000
6	4.952315000	-0.171744000	3.383539000
6	5.256989000	0.800018000	2.366770000
6	6.718920000	-0.874185000	1.283778000
6	5.994805000	0.363864000	1.236613000
6	5.834052000	1.048788000	0.004825000
6	6.801374000	-0.909165000	-1.174072000
6	6.075500000	0.311350000	-1.206870000
6	5.285349000	0.638793000	-2.343256000
6	4.561673000	1.876315000	-2.380791000
6	3.552422000	2.083602000	-3.362062000
6	2.830691000	3.302090000	-3.395073000
6	1.612292000	3.405832000	-4.153286000
6	3.050367000	0.936858000	-4.061840000
6	1.696312000	0.962368000	-4.503375000
6	0.974225000	2.196803000	-4.544918000
6	-0.439169000	2.192705000	-4.721892000
6	1.001219000	-0.268346000	-4.628474000
6	-0.423553000	-0.258074000	-4.462617000
6	-1.136351000	0.962884000	-4.497060000
6	-2.488789000	1.020631000	-4.031337000
6	-1.050066000	-1.431209000	-3.963657000
6	-2.296270000	-1.303563000	-3.271380000
6	-3.030296000	-0.076606000	-3.341390000
6	-4.148213000	0.162398000	-2.447410000
6	-2.633145000	-2.299595000	-2.337359000
6	-3.774235000	-2.093185000	-1.341211000
6	-4.281318000	-0.665175000	-1.321831000
6	-4.760701000	-0.090719000	-0.114630000
6	-3.316648000	-2.586605000	0.026758000
6	-3.419194000	-1.765370000	1.168171000
6	-4.122050000	-0.520171000	1.120382000
6	-3.975827000	0.420794000	2.155352000
6	-2.606374000	-2.067814000	2.307978000
6	-2.296236000	-1.027743000	3.225957000
6	-2.983740000	0.207527000	3.158637000
6	-2.512506000	1.337272000	3.900200000
6	-1.095807000	-1.136277000	4.002556000
6	-0.464004000	0.060417000	4.431602000
6	-1.174296000	1.301317000	4.382317000

6	-0.478038000	2.528014000	4.560942000
6	0.943830000	0.050079000	4.642264000
6	1.660214000	1.281674000	4.477043000
6	0.953402000	2.507921000	4.422498000
6	1.583868000	3.667823000	3.908141000
6	3.009066000	1.213807000	4.030698000
6	3.531526000	2.307271000	3.285931000
6	2.826195000	3.534243000	3.234696000
6	3.163265000	4.525657000	2.248170000
6	4.565654000	2.035122000	2.326866000
6	4.624969000	2.850402000	1.162972000
6	3.918672000	4.097951000	1.121364000
6	3.728823000	4.767775000	-0.119263000
6	5.138436000	2.281514000	-0.034840000
6	4.635692000	2.780260000	-1.284855000
6	3.919484000	4.001344000	-1.321611000
6	3.103886000	4.313408000	-2.441218000
6	2.394327000	5.558333000	-2.491776000
6	1.457520000	5.807583000	-3.536575000
6	0.969524000	7.112390000	-3.699405000
6	0.902412000	4.633120000	-4.215624000
6	-0.441196000	4.619815000	-4.638509000
6	-1.149280000	3.424064000	-4.799816000
6	-2.617181000	3.400761000	-4.727625000
6	-3.428273000	4.503603000	-5.025791000
6	-3.219202000	2.259537000	-4.127027000
6	-4.520644000	2.363928000	-3.563734000
6	-5.302510000	3.484006000	-3.877581000
6	-4.858925000	1.399578000	-2.510621000
6	-5.609283000	1.804103000	-1.400381000
6	-5.458275000	1.161965000	-0.155955000
6	-5.643765000	1.917769000	1.093585000
6	-6.526306000	2.999334000	1.224271000
6	-4.720252000	1.652335000	2.142351000
6	-4.502168000	2.632349000	3.151530000
6	-5.405711000	3.697440000	3.256149000
6	-3.229684000	2.566714000	3.882128000
6	-2.576263000	3.732867000	4.294800000
6	-1.189096000	3.756212000	4.535712000
6	-0.436135000	5.008678000	4.421565000
6	-0.997045000	6.281561000	4.600883000
6	0.877495000	4.915262000	3.877436000
6	1.454195000	6.045703000	3.230413000
6	0.866137000	7.300618000	3.432209000
6	2.475761000	5.768054000	2.212435000
6	2.520029000	6.531614000	1.035614000
6	3.038453000	6.008497000	-0.159076000
6	2.563951000	6.518075000	-1.452574000
6	2.063404000	7.810734000	-1.652040000
6	0.975389000	-4.867045000	4.282317000
6	3.044126000	-3.664984000	4.886024000
6	5.109634000	-2.467887000	4.165327000
1	5.612910000	-3.426592000	4.130129000
6	6.752436000	-1.636986000	2.486044000
6	-0.546971000	-5.759081000	2.519702000

1	0.038780000	-6.670526000	2.523869000
6	-1.185514000	-6.273391000	0.174101000
6	-0.558547000	-6.011529000	-2.207180000
6	1.059781000	-5.097270000	-3.868951000
1	1.627336000	-6.015744000	-3.778298000
6	3.156602000	-3.962901000	-4.611096000
6	5.222554000	-2.746425000	-4.032254000
6	6.687944000	-1.791583000	-2.259987000
1	7.168168000	-2.759819000	-2.186163000
6	7.339619000	-1.383042000	0.107619000
6	1.325930000	8.114975000	-2.798355000
1	0.974115000	9.129706000	-2.956565000
6	-4.773601000	4.513987000	-4.654577000
1	-5.398968000	5.359095000	-4.924854000
6	-6.440478000	3.843262000	2.330224000
1	-7.152681000	4.654459000	2.443742000
6	-0.316118000	7.418129000	4.166155000
1	-0.741268000	8.400806000	4.345310000
1	0.309068000	7.344633000	-4.528724000
1	2.239927000	8.580249000	-0.907251000
1	-0.998113000	5.548287000	-4.603618000
1	-3.008576000	5.358068000	-5.546576000
1	-6.322962000	3.551724000	-3.514128000
1	-6.082267000	2.778060000	-1.420632000
1	-7.278015000	3.179735000	0.462383000
1	-5.300645000	4.417926000	4.060634000
1	-3.094498000	4.678513000	4.192872000
1	-1.966881000	6.384632000	5.077035000
1	1.325834000	8.187783000	3.008328000
1	1.913513000	7.427658000	0.982614000
6	-0.724815000	-7.593697000	0.129733000
1	-0.712651000	-8.196147000	1.031941000
6	-0.253983000	-8.131644000	-1.070298000
1	0.072858000	-9.166670000	-1.098419000
6	-0.107785000	-7.335820000	-2.209706000
1	0.373427000	-7.744533000	-3.091966000
6	3.641912000	-4.894363000	5.193242000
1	4.683155000	-4.929055000	5.497134000
6	2.908530000	-6.078556000	5.106409000
1	3.374666000	-7.019299000	5.382576000
6	1.608544000	-6.076035000	4.599752000
1	1.089175000	-7.017219000	4.449911000
6	8.242272000	-2.447131000	0.236492000
1	8.781937000	-2.808437000	-0.633216000
6	8.444777000	-3.053193000	1.477140000
1	9.173633000	-3.852194000	1.571836000
6	7.663240000	-2.697765000	2.577567000
1	7.758471000	-3.251768000	3.506096000
6	3.920236000	-5.117850000	-4.827280000
1	3.431532000	-6.052315000	-5.083981000
6	5.309916000	-5.075120000	-4.710983000
1	5.893175000	-5.967266000	-4.916966000
6	5.951798000	-3.920693000	-4.259936000
1	7.021690000	-3.937000000	-4.078553000
45	-6.949383000	-1.061381000	0.421413000

6	-6.769180000	-3.010436000	0.851539000
6	-4.917127000	-2.954841000	-1.961807000
6	-6.165320000	-3.911623000	0.056264000
6	-5.829680000	-3.731667000	-1.367770000
1	-7.082887000	-3.333220000	1.842350000
1	-6.037613000	-4.924285000	0.448170000
1	-6.456819000	-4.307483000	-2.052837000
1	-4.916343000	-2.904373000	-3.047414000
6	-7.236350000	-0.700996000	2.289864000
8	-7.540607000	-0.452560000	3.371967000
6	-7.827052000	-1.445460000	-1.243916000
8	-8.488260000	-1.610706000	-2.172200000

TS(G4.G5) (zigzag (12,0))

G = -5998.07966

6	-5.340145000	-1.042608000	4.072808000
6	-4.403886000	0.023677000	4.025491000
6	-3.050619000	-0.175328000	4.470449000
6	-3.521797000	-2.592626000	4.678312000
6	-2.587833000	-1.507081000	4.620961000
6	-1.195195000	-1.769735000	4.514186000
6	-1.696626000	-4.173694000	4.189962000
6	-0.785856000	-3.085468000	4.128024000
6	0.430159000	-3.211581000	3.389948000
6	-0.336384000	-5.392042000	2.551439000
6	0.573404000	-4.303246000	2.499539000
6	1.466976000	-4.140677000	1.392600000
6	0.186229000	-5.881797000	0.198085000
6	1.132620000	-4.825236000	0.180586000
6	1.548615000	-4.248685000	-1.065788000
6	-0.220448000	-5.564857000	-2.205009000
6	0.689634000	-4.474615000	-2.191506000
6	0.565371000	-3.432173000	-3.143625000
6	-1.536879000	-4.445704000	-3.946591000
6	-0.631761000	-3.352294000	-3.920650000
6	-1.037983000	-2.061853000	-4.390312000
6	-3.356466000	-2.904394000	-4.567172000
6	-2.427730000	-1.813339000	-4.550891000
6	-2.899978000	-0.476680000	-4.497376000
6	-5.196390000	-1.328459000	-4.105719000
6	-4.265457000	-0.256420000	-4.103633000
6	-4.562285000	0.942822000	-3.399770000
6	-6.570198000	-0.131691000	-2.465661000
6	-5.639465000	0.941391000	-2.471518000
6	-5.549958000	1.836723000	-1.348452000
6	-7.057857000	0.327848000	-0.098116000
6	-6.118448000	1.412518000	-0.120229000
6	-5.590997000	1.923178000	1.093684000
6	-6.656559000	0.041209000	2.312227000
6	-5.721304000	1.109955000	2.273609000
6	-4.673342000	1.172939000	3.232931000
6	-3.735124000	2.256948000	3.199683000
6	-2.528065000	2.179393000	3.949223000

6	-1.595483000	3.244497000	3.909581000
6	-0.252605000	3.053032000	4.388017000
6	-2.123737000	0.895308000	4.441709000
6	-0.729555000	0.639014000	4.580108000
6	0.208247000	1.717517000	4.545853000
6	1.601225000	1.448720000	4.416203000
6	-0.270354000	-0.698462000	4.474460000
6	1.070830000	-0.921675000	4.015186000
6	1.996603000	0.146215000	3.972707000
6	3.228869000	0.004890000	3.255972000
6	1.358136000	-2.132081000	3.332690000
6	2.461900000	-2.167829000	2.414863000
6	3.421277000	-1.102865000	2.403857000
6	4.404738000	-1.009746000	1.351452000
6	2.433991000	-3.118656000	1.385514000
6	3.387635000	-3.062107000	0.176227000
6	4.244750000	-1.788698000	0.147442000
6	4.381579000	-1.024443000	-1.061943000
6	2.510386000	-3.225896000	-1.080795000
6	2.547267000	-2.312405000	-2.151140000
6	3.467200000	-1.212303000	-2.152166000
6	3.311248000	-0.164603000	-3.081991000
6	1.481113000	-2.340232000	-3.112006000
6	1.205717000	-1.169689000	-3.872045000
6	2.118210000	-0.089832000	-3.866827000
6	1.737593000	1.178100000	-4.412143000
6	-0.119945000	-0.984137000	-4.388819000
6	-0.580723000	0.341929000	-4.595904000
6	0.349898000	1.427568000	-4.608434000
6	-0.120994000	2.768418000	-4.557870000
6	-1.979203000	0.598832000	-4.515197000
6	-2.402816000	1.911390000	-4.122943000
6	-1.477579000	2.983354000	-4.131674000
6	-1.767119000	4.175776000	-3.423723000
6	-3.630333000	2.032311000	-3.414275000
6	-3.782910000	3.115435000	-2.504901000
6	-2.860844000	4.189932000	-2.518833000
6	-2.807012000	5.115745000	-1.419089000
6	-4.643431000	2.924295000	-1.370717000
6	-4.318366000	3.608780000	-0.167177000
6	-3.394395000	4.705573000	-0.190223000
6	-2.839724000	5.195487000	1.024837000
6	-4.681996000	3.008624000	1.069772000
6	-3.854849000	3.275096000	2.213875000
6	-2.927374000	4.344906000	2.181594000
6	-1.858542000	4.387432000	3.115090000
6	-0.929688000	5.479398000	3.099110000
6	0.228964000	5.446786000	3.928326000
6	0.978065000	6.623295000	4.076046000
6	0.675579000	4.126439000	4.381771000
6	2.047776000	3.835638000	4.501361000
6	2.531985000	2.525064000	4.424488000
6	3.923761000	2.256277000	4.044940000
6	4.959043000	3.180102000	4.218885000
6	4.177684000	1.081772000	3.276386000

6	5.337104000	1.015799000	2.456731000
6	6.340364000	1.985346000	2.632343000
6	5.306316000	0.071684000	1.344924000
6	5.976444000	0.389508000	0.123990000
6	5.297478000	0.050831000	-1.087414000
6	5.377495000	0.911375000	-2.257296000
6	6.407286000	1.843793000	-2.475626000
6	4.254357000	0.916454000	-3.128513000
6	4.039497000	2.027663000	-3.994804000
6	5.086588000	2.934346000	-4.189355000
6	2.664837000	2.257742000	-4.456456000
6	2.179292000	3.555830000	-4.645395000
6	0.802288000	3.845123000	-4.596743000
6	0.337244000	5.190892000	-4.249285000
6	1.085619000	6.358973000	-4.455633000
6	-0.843714000	5.271919000	-3.456097000
6	-1.062085000	6.412764000	-2.631630000
6	-0.295879000	7.561057000	-2.867162000
6	-1.902483000	6.210523000	-1.444138000
6	-1.570165000	6.840889000	-0.235222000
6	-1.932550000	6.288249000	1.002812000
6	-1.120438000	6.563912000	2.195376000
6	-0.354027000	7.722289000	2.374561000
6	-2.881319000	-4.246374000	-4.500712000
6	-4.758802000	-2.647176000	-4.579868000
6	-6.379209000	-1.196180000	-3.360961000
1	-7.039181000	-2.052200000	-3.287551000
6	-7.471952000	-0.283269000	-1.316077000
6	-1.255168000	-5.570054000	-3.151893000
1	-1.994411000	-6.360461000	-3.100795000
6	-0.289988000	-6.438790000	-1.032780000
6	-0.357347000	-6.342294000	1.440695000
6	-1.398188000	-5.341155000	3.468497000
1	-2.137174000	-6.133131000	3.444327000
6	-3.052633000	-3.938348000	4.700374000
6	-4.922354000	-2.330067000	4.640885000
6	-6.499652000	-0.958139000	3.285295000
1	-7.160416000	-1.815969000	3.249791000
6	-7.517860000	-0.192510000	1.145193000
6	0.643632000	7.766440000	3.350999000
1	1.205947000	8.682581000	3.502580000
6	6.176231000	3.012683000	3.554914000
1	6.979894000	3.724327000	3.715937000
6	6.281000000	2.804497000	-3.473691000
1	7.096997000	3.495174000	-3.662389000
6	0.727019000	7.546101000	-3.818078000
1	1.289393000	8.453420000	-4.015607000
1	1.824011000	6.645844000	4.755515000
1	-0.527669000	8.588875000	1.744481000
1	2.752934000	4.652620000	4.411023000
1	4.813140000	4.042691000	4.860753000
1	7.254172000	1.938801000	2.053834000
1	6.551400000	1.305804000	0.110384000
1	7.307155000	1.807456000	-1.869761000
1	4.971862000	3.750603000	-4.895183000

1	2.877696000	4.381515000	-4.585606000
1	1.950071000	6.340065000	-5.111589000
1	-0.489711000	8.466353000	-2.300637000
1	-0.805922000	7.608468000	-0.250496000
6	-0.979269000	-7.654349000	-0.984033000
1	-1.292155000	-8.140250000	-1.902255000
6	-1.292380000	-8.234543000	0.248836000
1	-1.801401000	-9.193356000	0.271800000
6	-1.046935000	-7.560713000	1.447094000
1	-1.407541000	-7.976739000	2.381888000
6	-5.627615000	-3.714516000	-4.841114000
1	-6.694858000	-3.535900000	-4.923738000
6	-5.130848000	-5.010257000	-4.990747000
1	-5.811902000	-5.821292000	-5.229439000
6	-3.782213000	-5.286907000	-4.764857000
1	-3.433331000	-6.314320000	-4.791585000
6	-8.611803000	-1.067970000	1.137753000
1	-9.026329000	-1.425045000	2.075210000
6	-9.166329000	-1.493330000	-0.070383000
1	-10.036343000	-2.142671000	-0.062669000
6	-8.565878000	-1.158308000	-1.284848000
1	-8.945307000	-1.584380000	-2.208245000
6	-3.964835000	-4.958002000	5.002536000
1	-3.622306000	-5.983700000	5.095641000
6	-5.317080000	-4.663127000	5.181014000
1	-6.007783000	-5.456181000	5.450409000
6	-5.803143000	-3.376658000	4.944171000
1	-6.871032000	-3.188919000	4.990318000
45	7.979326000	-1.171172000	-0.044311000
6	6.546762000	-2.572684000	-0.435719000
6	4.206005000	-4.388146000	0.313305000
6	6.416378000	-3.872352000	-0.745771000
6	5.432572000	-4.725007000	-0.106242000
1	7.026277000	-1.990081000	-1.356038000
1	7.063896000	-4.340396000	-1.490462000
1	5.706670000	-5.773123000	0.006763000
1	3.620189000	-5.180500000	0.762733000
6	9.673642000	-1.488889000	-0.800674000
8	10.678408000	-1.729132000	-1.308216000
6	8.744684000	-0.229599000	1.392343000
8	9.250275000	0.287044000	2.289064000

G5 (zigzag (12,0))

G = -5998.15423

6	-5.017916000	-1.434057000	4.243100000
6	-4.137658000	-0.321917000	4.180220000
6	-2.746055000	-0.475787000	4.508562000
6	-3.090855000	-2.918368000	4.646860000
6	-2.213661000	-1.788656000	4.563446000
6	-0.822913000	-1.980198000	4.341980000
6	-1.232961000	-4.393746000	3.979233000
6	-0.379194000	-3.262348000	3.891160000
6	0.796883000	-3.313271000	3.081001000

6	0.073153000	-5.505381000	2.225986000
6	0.937543000	-4.378627000	2.160251000
6	1.780168000	-4.161758000	1.027139000
6	0.482797000	-5.896300000	-0.164388000
6	1.399773000	-4.816469000	-0.188899000
6	1.731183000	-4.172750000	-1.423655000
6	-0.076748000	-5.473915000	-2.513697000
6	0.793481000	-4.350927000	-2.492062000
6	0.557753000	-3.246142000	-3.346486000
6	-1.546458000	-4.306103000	-4.091628000
6	-0.691724000	-3.171774000	-4.038888000
6	-1.185692000	-1.877843000	-4.395087000
6	-3.469892000	-2.822024000	-4.516388000
6	-2.592814000	-1.689805000	-4.479842000
6	-3.124421000	-0.383388000	-4.340995000
6	-5.357350000	-1.362351000	-3.887945000
6	-4.480782000	-0.245813000	-3.883232000
6	-4.804878000	0.910695000	-3.122331000
6	-6.704977000	-0.303410000	-2.135122000
6	-5.833963000	0.819099000	-2.145757000
6	-5.732462000	1.676382000	-0.994129000
6	-7.078728000	0.033853000	0.272508000
6	-6.203097000	1.170589000	0.244699000
6	-5.626835000	1.655893000	1.446493000
6	-6.507721000	-0.337773000	2.635250000
6	-5.632341000	0.780154000	2.588517000
6	-4.520414000	0.849979000	3.472000000
6	-3.639784000	1.980959000	3.428032000
6	-2.373046000	1.924082000	4.072898000
6	-1.495544000	3.034134000	4.018820000
6	-0.109221000	2.882464000	4.369474000
6	-1.872441000	0.637741000	4.458840000
6	-0.462359000	0.442355000	4.469421000
6	0.420963000	1.564591000	4.414380000
6	1.809325000	1.367739000	4.168947000
6	0.046881000	-0.865688000	4.270884000
6	1.361771000	-1.010779000	3.715754000
6	2.232320000	0.101363000	3.650760000
6	3.433769000	0.030885000	2.879008000
6	1.671563000	-2.191715000	2.992736000
6	2.739523000	-2.167381000	2.028633000
6	3.654064000	-1.057763000	1.992139000
6	4.665831000	-0.960090000	0.993824000
6	2.729263000	-3.118269000	1.004804000
6	3.655543000	-3.075060000	-0.237654000
6	4.704430000	-1.858031000	-0.282173000
6	4.472878000	-0.843939000	-1.423509000
6	2.677094000	-3.127207000	-1.437887000
6	2.562863000	-2.110705000	-2.400276000
6	3.423800000	-0.955890000	-2.369615000
6	3.139841000	0.151707000	-3.206156000
6	1.421739000	-2.112612000	-3.278789000
6	1.037136000	-0.907000000	-3.927363000
6	1.893546000	0.218704000	-3.899998000
6	1.427326000	1.491139000	-4.358582000

6	-0.320374000	-0.757926000	-4.366713000
6	-0.852759000	0.551201000	-4.490359000
6	0.023324000	1.680593000	-4.491415000
6	-0.508707000	2.993535000	-4.379922000
6	-2.256829000	0.736071000	-4.348931000
6	-2.728888000	2.011893000	-3.897282000
6	-1.858819000	3.128911000	-3.904883000
6	-2.181718000	4.284773000	-3.152573000
6	-3.931764000	2.047980000	-3.138685000
6	-4.099454000	3.091969000	-2.187506000
6	-3.236771000	4.214843000	-2.205541000
6	-3.177311000	5.104414000	-1.076290000
6	-4.889248000	2.813554000	-1.020001000
6	-4.530398000	3.465801000	0.192103000
6	-3.668820000	4.612501000	0.164849000
6	-3.058764000	5.074472000	1.364362000
6	-4.779582000	2.790191000	1.418541000
6	-3.885522000	3.043173000	2.514642000
6	-3.016444000	4.160572000	2.474575000
6	-1.877092000	4.205686000	3.320285000
6	-1.003008000	5.341925000	3.294768000
6	0.225091000	5.318812000	4.017386000
6	0.930765000	6.520748000	4.173579000
6	0.767741000	3.998200000	4.348570000
6	2.155734000	3.767049000	4.342114000
6	2.689651000	2.485230000	4.166228000
6	4.068042000	2.287554000	3.708971000
6	5.073345000	3.243510000	3.865197000
6	4.339497000	1.134576000	2.908464000
6	5.489091000	1.110522000	2.075167000
6	6.468104000	2.110584000	2.244013000
6	5.511360000	0.147074000	0.990221000
6	6.213902000	0.500871000	-0.266787000
6	5.338522000	0.245109000	-1.444778000
6	5.228766000	1.238884000	-2.484858000
6	6.193008000	2.247749000	-2.698711000
6	4.030453000	1.265792000	-3.252857000
6	3.704918000	2.428029000	-4.017648000
6	4.692484000	3.394758000	-4.214189000
6	2.299754000	2.616434000	-4.392340000
6	1.746279000	3.895448000	-4.514354000
6	0.360046000	4.115325000	-4.414304000
6	-0.159845000	5.426821000	-4.018034000
6	0.521833000	6.636493000	-4.216230000
6	-1.316159000	5.427079000	-3.185802000
6	-1.560492000	6.531730000	-2.320893000
6	-0.863128000	7.724203000	-2.550179000
6	-2.333444000	6.246370000	-1.104686000
6	-1.961757000	6.843177000	0.109741000
6	-2.210815000	6.213486000	1.338895000
6	-1.320790000	6.466137000	2.480062000
6	-0.596216000	7.649890000	2.666641000
6	-2.929025000	-4.139775000	-4.556994000
6	-4.881646000	-2.633755000	-4.446071000
6	-6.506486000	-1.321189000	-3.081388000

1	-7.117660000	-2.213147000	-3.011193000
6	-7.531704000	-0.548911000	-0.945517000
6	-1.169429000	-5.464255000	-3.393876000
1	-1.870903000	-6.288722000	-3.350614000
6	-0.047884000	-6.410584000	-1.390347000
6	0.020934000	-6.419614000	1.085386000
6	-0.930904000	-5.526459000	3.204643000
1	-1.635480000	-6.349456000	3.201643000
6	-2.560418000	-4.239621000	4.585273000
6	-4.501125000	-2.722051000	4.721346000
6	-6.234148000	-1.372078000	3.544278000
1	-6.854355000	-2.259957000	3.513096000
6	-7.431174000	-0.565043000	1.515439000
6	0.480885000	7.686754000	3.554933000
1	1.012327000	8.619650000	3.715511000
6	6.283096000	3.125913000	3.171689000
1	7.064761000	3.863098000	3.326424000
6	5.943752000	3.276105000	-3.595088000
1	6.708105000	4.023039000	-3.785473000
6	0.125018000	7.787021000	-3.535514000
1	0.633517000	8.726936000	-3.726493000
1	1.832771000	6.545700000	4.776608000
1	-0.863723000	8.541831000	2.108952000
1	2.816264000	4.619930000	4.244974000
1	4.916060000	4.092420000	4.522399000
1	7.381853000	2.080449000	1.663387000
1	6.540954000	1.533165000	-0.256944000
1	7.142840000	2.207169000	-2.176583000
1	4.492136000	4.252964000	-4.847208000
1	2.405248000	4.752556000	-4.450286000
1	1.363971000	6.678773000	-4.899545000
1	-1.080954000	8.602110000	-1.950148000
1	-1.239014000	7.649656000	0.083859000
6	-0.701012000	-7.647643000	-1.357302000
1	-1.054604000	-8.102573000	-2.276667000
6	-0.927039000	-8.287291000	-0.135496000
1	-1.408817000	-9.260290000	-0.125508000
6	-0.633777000	-7.656441000	1.076823000
1	-0.934366000	-8.120767000	2.010171000
6	-5.712490000	-3.727360000	-4.722761000
1	-6.789750000	-3.597218000	-4.741157000
6	-5.164376000	-4.985807000	-4.973864000
1	-5.818458000	-5.815213000	-5.224580000
6	-3.793403000	-5.206562000	-4.837310000
1	-3.399039000	-6.211832000	-4.946318000
6	-8.475336000	-1.499419000	1.532894000
1	-8.810483000	-1.919772000	2.475812000
6	-9.080213000	-1.902596000	0.341524000
1	-9.912341000	-2.599260000	0.370885000
6	-8.573656000	-1.483960000	-0.889990000
1	-8.984234000	-1.892786000	-1.807860000
6	-3.401613000	-5.312218000	4.911188000
1	-3.006671000	-6.322656000	4.942649000
6	-4.749372000	-5.089702000	5.194111000
1	-5.382214000	-5.924203000	5.479972000

6	-5.309136000	-3.819963000	5.043501000
1	-6.378177000	-3.685223000	5.172912000
45	7.860524000	-0.852265000	0.059628000
6	6.152643000	-2.357014000	-0.582633000
6	4.344547000	-4.458161000	-0.138179000
6	6.562249000	-3.647264000	-0.521605000
6	5.659309000	-4.706680000	-0.176852000
1	6.735271000	-1.744972000	-1.305580000
1	7.566780000	-3.901971000	-0.844924000
1	6.026879000	-5.722122000	-0.069958000
1	3.674470000	-5.294761000	-0.005964000
6	9.215536000	-2.144722000	0.490655000
8	10.034998000	-2.909319000	0.745549000
6	9.019523000	0.599533000	0.136234000
8	9.714274000	1.519659000	0.163031000

H3 (zigzag (12,0))

G = -4615.21573

6	4.013086000	-3.416600000	-4.079410000
6	3.753744000	-2.019891000	-4.079812000
6	2.483580000	-1.514519000	-4.526783000
6	1.647543000	-3.840779000	-4.624093000
6	1.400195000	-2.427577000	-4.621909000
6	0.075200000	-1.937345000	-4.508592000
6	-0.712373000	-4.245812000	-4.051288000
6	-0.940505000	-2.843886000	-4.046400000
6	-2.014310000	-2.301384000	-3.285919000
6	-2.432375000	-4.527081000	-2.325852000
6	-2.656364000	-3.125382000	-2.325171000
6	-3.245891000	-2.481425000	-1.184506000
6	-2.998448000	-4.594118000	0.073160000
6	-3.241048000	-3.186151000	0.054668000
6	-3.247487000	-2.452820000	1.276456000
6	-2.421888000	-4.463896000	2.467327000
6	-2.648592000	-3.063632000	2.431336000
6	-2.001703000	-2.212179000	3.365090000
6	-0.692601000	-4.133752000	4.175146000
6	-0.922040000	-2.732167000	4.132765000
6	0.095900000	-1.812877000	4.563033000
6	1.670221000	-3.712200000	4.723250000
6	1.422053000	-2.299654000	4.682394000
6	2.504587000	-1.389643000	4.555651000
6	4.032563000	-3.303041000	4.153871000
6	3.772697000	-1.907064000	4.116522000
6	4.599158000	-1.050058000	3.339024000
6	5.744867000	-3.026470000	2.422419000
6	5.482853000	-1.630848000	2.388321000
6	5.807319000	-0.855689000	1.220184000
6	6.302429000	-2.963126000	0.025969000
6	6.039430000	-1.552726000	0.007105000
6	5.802226000	-0.889251000	-1.223681000
6	5.734268000	-3.092196000	-2.365331000
6	5.472590000	-1.696174000	-2.368713000

6	4.584248000	-1.141686000	-3.330760000
6	4.332350000	0.270176000	-3.344042000
6	3.249773000	0.794124000	-4.102236000
6	2.996937000	2.187634000	-4.112475000
6	1.743575000	2.695083000	-4.603815000
6	2.238858000	-0.119961000	-4.553421000
6	0.909878000	0.369208000	-4.694770000
6	0.660827000	1.779750000	-4.716783000
6	-0.666886000	2.270686000	-4.577021000
6	-0.168322000	-0.541723000	-4.530609000
6	-1.417102000	-0.024878000	-4.050453000
6	-1.657202000	1.369321000	-4.058957000
6	-2.724781000	1.914184000	-3.289621000
6	-2.251038000	-0.889318000	-3.284455000
6	-3.133302000	-0.311811000	-2.333027000
6	-3.385049000	1.089324000	-2.349976000
6	-4.048027000	1.728023000	-1.245477000
6	-3.508868000	-1.100140000	-1.206679000
6	-3.930778000	-0.436070000	0.015781000
6	-4.124340000	1.013131000	-0.006345000
6	-4.042209000	1.764559000	1.213557000
6	-3.507200000	-1.069298000	1.259488000
6	-3.128225000	-0.248129000	2.362712000
6	-3.372861000	1.155419000	2.335080000
6	-2.709331000	2.005187000	3.247155000
6	-2.239231000	-0.800346000	3.325137000
6	-1.399525000	0.085930000	4.058884000
6	-1.638393000	1.480376000	4.027160000
6	-0.646302000	2.395368000	4.515598000
6	-0.147763000	-0.417297000	4.546401000
6	0.931174000	0.497828000	4.678983000
6	0.682186000	1.908194000	4.662717000
6	1.764309000	2.820135000	4.519408000
6	2.259640000	0.005083000	4.544464000
6	3.268160000	0.906214000	4.063358000
6	3.015378000	2.299454000	4.036428000
6	3.825890000	3.152275000	3.246008000
6	4.347079000	0.361544000	3.314559000
6	4.978200000	1.182738000	2.339489000
6	4.726541000	2.576151000	2.312975000
6	5.098210000	3.359893000	1.165010000
6	5.574489000	0.541043000	1.201139000
6	5.595113000	1.251589000	-0.030428000
6	5.354710000	2.665572000	-0.049291000
6	5.093115000	3.326329000	-1.281086000
6	5.569369000	0.507518000	-1.242021000
6	4.968058000	1.117849000	-2.394947000
6	4.716483000	2.511466000	-2.405652000
6	3.811239000	3.061839000	-3.349627000
6	3.573382000	4.476282000	-3.379869000
6	2.561121000	5.013437000	-4.226161000
6	2.519946000	6.400988000	-4.421290000
6	1.497416000	4.092959000	-4.644627000
6	0.170348000	4.543775000	-4.756877000
6	-0.916635000	3.669138000	-4.622606000

6	-2.228534000	4.169442000	-4.190944000
6	-2.671026000	5.483461000	-4.393457000
6	-2.991321000	3.324974000	-3.334490000
6	-3.968773000	3.893280000	-2.469938000
6	-4.381151000	5.213048000	-2.696194000
6	-4.301822000	3.125207000	-1.263930000
6	-4.517470000	3.786186000	-0.043281000
6	-4.294253000	3.161664000	1.194785000
6	-3.955499000	3.962178000	2.378087000
6	-4.366437000	5.287736000	2.569657000
6	-2.974993000	3.417443000	3.253891000
6	-2.209425000	4.284048000	4.084466000
6	-2.650545000	5.603407000	4.253156000
6	-0.895755000	3.795029000	4.523814000
6	0.191430000	4.672556000	4.629645000
6	1.518218000	4.218505000	4.523071000
6	2.579612000	5.127085000	4.074733000
6	2.539010000	6.519612000	4.231912000
6	3.587934000	4.566887000	3.238666000
6	4.306951000	5.406365000	2.339969000
6	4.240452000	6.793071000	2.526886000
6	4.874586000	4.762565000	1.148057000
6	4.869452000	5.430994000	-0.086087000
6	4.869568000	4.728927000	-1.301568000
6	4.296727000	5.339986000	-2.508095000
6	4.229470000	6.721186000	-2.732545000
6	0.580462000	-4.629568000	4.713009000
6	3.007824000	-4.201974000	4.700617000
6	5.084209000	-3.814810000	3.378523000
1	5.216982000	-4.889240000	3.337463000
6	6.398449000	-3.655061000	1.267195000
6	-1.517567000	-4.975741000	3.410891000
1	-1.277618000	-6.031565000	3.373046000
6	-2.838141000	-5.275852000	1.318231000
6	-2.844529000	-5.308510000	-1.154121000
6	-1.535209000	-5.065979000	-3.260200000
1	-1.297059000	-6.120894000	-3.195648000
6	0.557547000	-4.757090000	-4.581639000
6	2.985137000	-4.330278000	-4.595135000
6	5.068648000	-3.906813000	-3.295653000
1	5.201339000	-4.979703000	-3.224950000
6	6.393057000	-3.688822000	-1.196220000
6	3.392896000	7.236387000	-3.724236000
1	3.377984000	8.305599000	-3.911822000
6	-3.773875000	5.975735000	-3.694098000
1	-4.125061000	6.984551000	-3.887396000
6	-3.755415000	6.077062000	3.544472000
1	-4.105459000	7.090968000	3.711357000
6	3.408549000	7.335419000	3.508118000
1	3.394464000	8.409378000	3.666286000
1	1.803603000	6.830048000	-5.114721000
1	4.825221000	7.397289000	-2.127559000
1	-0.015157000	5.609381000	-4.697179000
1	-2.149005000	6.127615000	-5.093552000
1	-5.171696000	5.646863000	-2.092042000

1	-4.613812000	4.865188000	-0.058750000
1	-5.158396000	5.705604000	1.956206000
1	-2.125826000	6.265787000	4.933936000
1	0.005810000	5.736175000	4.542065000
1	1.826026000	6.967539000	4.916821000
1	4.833034000	7.452381000	1.900632000
1	4.603221000	6.480979000	-0.100024000
6	-2.872577000	-6.675661000	1.315544000
1	-2.821286000	-7.221679000	2.251721000
6	-2.955557000	-7.374901000	0.109951000
1	-3.013067000	-8.459037000	0.124375000
6	-2.879509000	-6.707511000	-1.114270000
1	-2.832793000	-7.278059000	-2.035978000
6	3.225365000	-5.555136000	4.991728000
1	4.238499000	-5.939802000	5.049192000
6	2.146817000	-6.416039000	5.200332000
1	2.331153000	-7.453767000	5.460561000
6	0.837561000	-5.976315000	5.002493000
1	0.016987000	-6.683561000	5.069672000
6	6.896014000	-4.996164000	-1.159724000
1	7.040921000	-5.546635000	-2.083826000
6	7.205119000	-5.599330000	0.060221000
1	7.628920000	-6.598771000	0.072990000
6	6.901389000	-4.962888000	1.264525000
1	7.050463000	-5.487668000	2.202783000
6	0.812990000	-6.111731000	-4.834315000
1	-0.008000000	-6.820374000	-4.877034000
6	2.120866000	-6.557270000	-5.027289000
1	2.303586000	-7.601970000	-5.259233000
6	3.200813000	-5.691054000	-4.849231000
1	4.213533000	-6.077542000	-4.901626000
77	-6.241658000	-0.285018000	0.106864000
6	-6.301085000	-0.574960000	-1.985918000
6	-6.629046000	-2.311404000	-0.005248000
6	-6.500482000	-1.856091000	-2.351141000
6	-6.650853000	-2.809246000	-1.254917000
1	-6.190876000	0.235745000	-2.703015000
1	-6.541611000	-2.184718000	-3.387270000
1	-6.758197000	-3.878099000	-1.433975000
1	-6.787338000	-2.876354000	0.908715000
6	-6.308676000	-0.275335000	2.096105000
8	-6.449091000	-0.345452000	3.230160000
6	-8.039479000	0.237862000	-0.166136000
8	-9.130111000	0.533190000	-0.371534000

TS(H3.H4) (zigzag (12,0))

G = -4615.17987

6	-5.025161000	-2.581524000	3.798715000
6	-4.529633000	-1.250855000	3.786127000
6	-3.239748000	-0.948690000	4.347031000
6	-2.835006000	-3.373365000	4.606154000
6	-2.347981000	-2.025089000	4.584686000
6	-0.950453000	-1.772192000	4.598258000

6	-0.531683000	-4.199826000	4.320578000
6	-0.066177000	-2.857760000	4.289954000
6	1.167646000	-2.545541000	3.645706000
6	1.302427000	-4.863072000	2.831880000
6	1.763655000	-3.520311000	2.804529000
6	2.603189000	-3.055389000	1.738088000
6	2.133638000	-5.159400000	0.532403000
6	2.630208000	-3.825465000	0.535268000
6	2.891829000	-3.155468000	-0.702271000
6	1.818113000	-5.042178000	-1.906985000
6	2.281166000	-3.700370000	-1.884393000
6	1.870198000	-2.790960000	-2.892206000
6	0.333712000	-4.497394000	-3.784304000
6	0.794951000	-3.154886000	-3.754667000
6	0.004136000	-2.098466000	-4.318933000
6	-1.849833000	-3.706969000	-4.609084000
6	-1.365862000	-2.357307000	-4.582158000
6	-2.277925000	-1.270616000	-4.616862000
6	-4.154033000	-2.871445000	-4.347522000
6	-3.659817000	-1.540086000	-4.322579000
6	-4.407703000	-0.514887000	-3.681127000
6	-5.979516000	-2.216976000	-2.849496000
6	-5.482845000	-0.886410000	-2.827896000
6	-5.794495000	-0.009398000	-1.730046000
6	-6.773492000	-1.941440000	-0.537253000
6	-6.272495000	-0.596516000	-0.530971000
6	-6.054978000	0.076167000	0.698636000
6	-6.486555000	-2.050934000	1.904259000
6	-5.988662000	-0.720120000	1.895552000
6	-5.118198000	-0.280271000	2.929956000
6	-4.627617000	1.067760000	2.929152000
6	-3.548403000	1.434690000	3.779827000
6	-3.059782000	2.764064000	3.775938000
6	-1.788924000	3.072692000	4.375243000
6	-2.758979000	0.384441000	4.356212000
6	-1.385466000	0.646766000	4.619146000
6	-0.897647000	1.993257000	4.622655000
6	0.502941000	2.244197000	4.606122000
6	-0.471062000	-0.439361000	4.597556000
6	0.891852000	-0.168631000	4.241341000
6	1.368586000	1.165749000	4.227188000
6	2.593575000	1.480548000	3.572513000
6	1.643602000	-1.199618000	3.617861000
6	2.727476000	-0.836537000	2.757133000
6	3.208206000	0.512095000	2.748819000
6	4.102083000	0.964379000	1.723341000
6	3.103035000	-1.740842000	1.742115000
6	3.907982000	-1.281663000	0.584276000
6	4.253988000	0.161266000	0.555088000
6	4.447004000	0.835636000	-0.694429000
6	3.402844000	-1.846440000	-0.695341000
6	3.226387000	-1.011967000	-1.831459000
6	3.721623000	0.322534000	-1.843016000
6	3.298490000	1.230747000	-2.827078000
6	2.339390000	-1.442511000	-2.862103000

6	1.746120000	-0.462910000	-3.703522000
6	2.224939000	0.867955000	-3.691259000
6	1.467465000	1.914822000	-4.310884000
6	0.484749000	-0.766388000	-4.314898000
6	-0.393269000	0.311637000	-4.602513000
6	0.097954000	1.657194000	-4.597754000
6	-0.814243000	2.747525000	-4.613791000
6	-1.794085000	0.060824000	-4.617101000
6	-2.676723000	1.145253000	-4.293527000
6	-2.186020000	2.474204000	-4.276321000
6	-2.921389000	3.492875000	-3.620920000
6	-3.915547000	0.832572000	-3.668953000
6	-4.500898000	1.798775000	-2.804522000
6	-4.012823000	3.128162000	-2.790295000
6	-4.369190000	4.021290000	-1.719726000
6	-5.324098000	1.326355000	-1.725997000
6	-5.354042000	2.090274000	-0.527055000
6	-4.874165000	3.442126000	-0.523098000
6	-4.634939000	4.108675000	0.710252000
6	-5.586175000	1.412236000	0.701187000
6	-5.009800000	1.965877000	1.894849000
6	-4.522594000	3.295898000	1.892195000
6	-3.633741000	3.728046000	2.910284000
6	-3.157740000	5.081065000	2.924864000
6	-2.152858000	5.476668000	3.853916000
6	-1.890386000	6.844860000	4.012694000
6	-1.309037000	4.409071000	4.401233000
6	0.059505000	4.633150000	4.636037000
6	0.985425000	3.582228000	4.638144000
6	2.401865000	3.831048000	4.341745000
6	3.040140000	5.059494000	4.554251000
6	3.093419000	2.827042000	3.605230000
6	4.243768000	3.177337000	2.845948000
6	4.850608000	4.420368000	3.076441000
6	4.582575000	2.298783000	1.723903000
6	5.101281000	2.837545000	0.532114000
6	4.917971000	2.188077000	-0.693920000
6	4.828792000	2.968457000	-1.936387000
6	5.488615000	4.187202000	-2.138060000
6	3.826835000	2.570224000	-2.864592000
6	3.299877000	3.517159000	-3.786742000
6	3.987934000	4.725935000	-3.963622000
6	1.962631000	3.248136000	-4.334908000
6	1.065853000	4.293537000	-4.587889000
6	-0.324766000	4.080446000	-4.626825000
6	-1.254311000	5.179012000	-4.342748000
6	-0.949959000	6.534216000	-4.534741000
6	-2.439359000	4.843912000	-3.626107000
6	-3.100524000	5.839624000	-2.851178000
6	-2.769145000	7.182929000	-3.069974000
6	-3.906025000	5.364073000	-1.718725000
6	-3.920120000	6.083089000	-0.513428000
6	-4.173765000	5.452031000	0.714198000
6	-3.630674000	6.013787000	1.957803000
6	-3.347610000	7.372331000	2.148718000

6	-0.944390000	-4.794834000	-4.442417000
6	-3.246681000	-3.959937000	-4.733007000
6	-5.362193000	-3.155003000	-3.692062000
1	-5.684560000	-4.187438000	-3.631920000
6	-6.855353000	-2.666907000	-1.759758000
6	0.926831000	-5.432102000	-2.918394000
1	0.506977000	-6.429918000	-2.875810000
6	1.978060000	-5.864211000	-0.703199000
6	1.705994000	-5.768698000	1.753841000
6	0.222905000	-5.188917000	3.668494000
1	-0.182256000	-6.192340000	3.617201000
6	-1.921290000	-4.461518000	4.715986000
6	-4.227771000	-3.630249000	4.446801000
6	-6.067836000	-2.921995000	2.922197000
1	-6.376099000	-3.959219000	2.869000000
6	-7.116218000	-2.581588000	0.687812000
6	-2.534697000	7.783397000	3.206947000
1	-2.353138000	8.842052000	3.364590000
6	4.281424000	5.323981000	3.972274000
1	4.779158000	6.267310000	4.174077000
6	5.105865000	5.026744000	-3.185092000
1	5.647761000	5.951261000	-3.358015000
6	-1.742776000	7.523321000	-3.953163000
1	-1.520667000	8.569338000	-4.140533000
1	-1.179744000	7.177095000	4.762803000
1	-3.754368000	8.110929000	1.465225000
1	0.431141000	5.648151000	4.565750000
1	2.564664000	5.815918000	5.170167000
1	5.766522000	4.682585000	2.556494000
1	5.385125000	3.882395000	0.520320000
1	6.294584000	4.483292000	-1.473963000
1	3.647253000	5.436441000	-4.709746000
1	1.426065000	5.312388000	-4.511872000
1	-0.091817000	6.817220000	-5.136004000
1	-3.306814000	7.965404000	-2.543958000
1	-3.477243000	7.071634000	-0.500270000
6	1.761545000	-7.245019000	-0.653186000
1	1.708695000	-7.820578000	-1.571416000
6	1.587704000	-7.885338000	0.577103000
1	1.451812000	-8.962226000	0.603202000
6	1.493541000	-7.153122000	1.761793000
1	1.239292000	-7.658252000	2.687702000
6	-3.663689000	-5.269798000	-5.003735000
1	-4.715382000	-5.479378000	-5.170633000
6	-2.736195000	-6.311634000	-5.052911000
1	-3.069271000	-7.315193000	-5.298852000
6	-1.400299000	-6.091320000	-4.716761000
1	-0.713868000	-6.930503000	-4.665458000
6	-7.831184000	-3.785305000	0.634279000
1	-8.165093000	-4.258130000	1.552411000
6	-8.109565000	-4.386276000	-0.594279000
1	-8.696244000	-5.299250000	-0.624876000
6	-7.574370000	-3.869708000	-1.774957000
1	-7.710919000	-4.407640000	-2.707821000
6	-2.433104000	-5.738419000	4.982362000

1	-1.757040000	-6.572655000	5.140454000
6	-3.811585000	-5.946525000	5.041707000
1	-4.195356000	-6.932509000	5.284881000
6	-4.700956000	-4.920961000	4.718108000
1	-5.765282000	-5.127885000	4.671268000
77	6.541195000	-0.609359000	-0.242949000
6	6.945107000	0.003788000	1.674748000
6	5.580469000	-2.249025000	0.915030000
6	6.717611000	-0.947186000	2.620550000
6	6.182094000	-2.196878000	2.149538000
1	7.272419000	1.014762000	1.913161000
1	6.900290000	-0.785269000	3.682091000
1	6.287158000	-3.111756000	2.733897000
1	5.300178000	-3.194453000	0.460346000
6	6.260374000	-1.322331000	-2.073886000
8	6.158966000	-1.778313000	-3.118922000
6	8.332860000	-1.144487000	-0.108438000
8	9.409536000	-1.531475000	-0.013537000

H4 (zigzag (12,0))

G = -4615.21101

6	-5.840052000	-1.873203000	3.283124000
6	-5.177035000	-0.617727000	3.308757000
6	-3.937334000	-0.463217000	4.021571000
6	-3.885874000	-2.911608000	4.366825000
6	-3.229041000	-1.637657000	4.385436000
6	-1.822973000	-1.564800000	4.570077000
6	-1.692535000	-4.033454000	4.379059000
6	-1.058318000	-2.763159000	4.390428000
6	0.278270000	-2.630183000	3.908598000
6	0.221943000	-4.972216000	3.161153000
6	0.849430000	-3.699157000	3.173251000
6	1.896005000	-3.386051000	2.245691000
6	1.357933000	-5.461241000	1.026529000
6	2.023455000	-4.209055000	1.078986000
6	2.570827000	-3.631707000	-0.113352000
6	1.420490000	-5.395411000	-1.428343000
6	2.043121000	-4.121873000	-1.356859000
6	1.874052000	-3.189375000	-2.412151000
6	0.257904000	-4.717599000	-3.480584000
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TS(H4.H5) (zigzag (12,0))

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6	-8.406796000	-2.715603000	0.756134000
1	-8.782912000	-3.162490000	1.670999000
6	-8.787254000	-3.243626000	-0.479127000
1	-9.493622000	-4.067207000	-0.516069000

6	-8.205196000	-2.780043000	-1.659618000
1	-8.426998000	-3.274924000	-2.599838000
6	-3.212698000	-5.575356000	4.794357000
1	-2.668007000	-6.508046000	4.900983000
6	-4.602396000	-5.569966000	4.925424000
1	-5.121249000	-6.491520000	5.170563000
6	-5.336842000	-4.411215000	4.673848000
1	-6.421309000	-4.448706000	4.685974000
77	6.775214000	-0.423549000	-0.141850000
6	5.928547000	-1.920665000	-1.147379000
6	4.950499000	-3.463381000	0.974760000
6	5.999763000	-3.264496000	-1.086650000
6	5.936474000	-3.926730000	0.206601000
1	5.762347000	-1.577166000	-2.170991000
1	5.826647000	-3.852845000	-1.989470000
1	6.586552000	-4.741625000	0.513530000
1	4.779903000	-3.826298000	1.981834000
6	8.324141000	0.021011000	-1.334330000
8	9.245183000	0.334407000	-1.941672000
6	7.738817000	-1.203610000	1.292408000
8	8.305286000	-1.758487000	2.126968000

H5 (zigzag (12,0))

$G = -4615.18333$

6	-5.260215000	-1.552622000	4.217013000
6	-4.419406000	-0.410468000	4.153419000
6	-3.025763000	-0.512884000	4.493620000
6	-3.285579000	-2.964996000	4.646520000
6	-2.448208000	-1.805533000	4.561521000
6	-1.049553000	-1.949377000	4.352726000
6	-1.371338000	-4.378836000	4.004770000
6	-0.557233000	-3.218129000	3.915309000
6	0.627640000	-3.234172000	3.116993000
6	-0.009021000	-5.457440000	2.273264000
6	0.815903000	-4.301653000	2.207059000
6	1.664121000	-4.065596000	1.081682000
6	0.444214000	-5.855267000	-0.108121000
6	1.323708000	-4.744818000	-0.131719000
6	1.648473000	-4.100538000	-1.369102000
6	-0.102639000	-5.471108000	-2.467122000
6	0.727567000	-4.318122000	-2.445151000
6	0.460744000	-3.227298000	-3.308584000
6	-1.597469000	-4.365530000	-4.066252000
6	-0.784357000	-3.201175000	-4.012498000
6	-1.320951000	-1.927547000	-4.380235000
6	-3.568628000	-2.953697000	-4.516670000
6	-2.733003000	-1.790671000	-4.479001000
6	-3.312476000	-0.503301000	-4.354020000
6	-5.513337000	-1.558767000	-3.915896000
6	-4.677491000	-0.411425000	-3.910832000
6	-5.051036000	0.738382000	-3.162606000
6	-6.916576000	-0.535810000	-2.185495000
6	-6.086791000	0.617509000	-2.196397000

6	-6.029694000	1.487643000	-1.051374000
6	-7.329819000	-0.192007000	0.214668000
6	-6.495813000	0.975657000	0.186530000
6	-5.950864000	1.491692000	1.390239000
6	-6.772413000	-0.522720000	2.586559000
6	-5.937126000	0.625593000	2.539506000
6	-4.837132000	0.741900000	3.433059000
6	-3.996738000	1.903144000	3.388273000
6	-2.734087000	1.895781000	4.043939000
6	-1.895838000	3.035838000	3.988780000
6	-0.507513000	2.935542000	4.350289000
6	-2.191452000	0.630666000	4.442578000
6	-0.775531000	0.485432000	4.465774000
6	0.068312000	1.637732000	4.408661000
6	1.464899000	1.488497000	4.175292000
6	-0.219188000	-0.805181000	4.280593000
6	1.104768000	-0.908061000	3.738366000
6	1.936081000	0.233978000	3.671234000
6	3.146928000	0.199056000	2.911905000
6	1.462670000	-2.082863000	3.028504000
6	2.540100000	-2.029276000	2.076204000
6	3.414266000	-0.888549000	2.037983000
6	4.435810000	-0.766691000	1.052431000
6	2.576489000	-2.988579000	1.061806000
6	3.517945000	-2.923956000	-0.170151000
6	4.526482000	-1.672711000	-0.213605000
6	4.268853000	-0.676548000	-1.364141000
6	2.556656000	-3.022749000	-1.381768000
6	2.414517000	-2.015587000	-2.350830000
6	3.231634000	-0.830282000	-2.317843000
6	2.916741000	0.262454000	-3.161969000
6	1.282762000	-2.063093000	-3.239873000
6	0.861155000	-0.875031000	-3.898043000
6	1.675826000	0.281173000	-3.868274000
6	1.169034000	1.533742000	-4.338096000
6	-0.496693000	-0.777092000	-4.350530000
6	-1.074349000	0.511354000	-4.487417000
6	-0.239327000	1.671516000	-4.487089000
6	-0.819440000	2.965210000	-4.391353000
6	-2.485559000	0.646514000	-4.361482000
6	-3.008022000	1.907815000	-3.924807000
6	-2.178821000	3.055505000	-3.932379000
6	-2.551759000	4.205123000	-3.193735000
6	-4.219524000	1.906409000	-3.179315000
6	-4.435560000	2.951548000	-2.239187000
6	-3.614227000	4.104989000	-2.257789000
6	-3.599947000	5.005673000	-1.135889000
6	-5.227972000	2.654485000	-1.078071000
6	-4.906809000	3.329613000	0.132058000
6	-4.086973000	4.506541000	0.104106000
6	-3.506667000	4.999952000	1.305914000
6	-5.144785000	2.655571000	1.361588000
6	-4.271525000	2.949074000	2.464486000
6	-3.442483000	4.096545000	2.423707000
6	-2.312995000	4.188266000	3.278902000

6	-1.479448000	5.354547000	3.252123000
6	-0.256744000	5.379734000	3.983780000
6	0.404901000	6.606934000	4.136767000
6	0.329876000	4.081410000	4.327429000
6	1.725336000	3.899783000	4.332074000
6	2.305752000	2.636677000	4.169373000
6	3.694217000	2.483961000	3.724748000
6	4.664979000	3.475273000	3.879472000
6	4.013107000	1.333262000	2.939023000
6	5.171527000	1.339772000	2.117184000
6	6.115657000	2.373614000	2.285376000
6	5.240129000	0.365936000	1.048296000
6	5.971906000	0.711365000	-0.203443000
6	5.096169000	0.439916000	-1.384144000
6	4.959263000	1.426075000	-2.426755000
6	5.889749000	2.466856000	-2.636856000
6	3.767198000	1.407732000	-3.204830000
6	3.407833000	2.554087000	-3.978198000
6	4.362378000	3.554586000	-4.169389000
6	2.000911000	2.689585000	-4.369172000
6	1.403173000	3.946859000	-4.506802000
6	0.008820000	4.117251000	-4.424971000
6	-0.562586000	5.412358000	-4.046299000
6	0.077425000	6.644121000	-4.247351000
6	-1.727863000	5.377845000	-3.227461000
6	-2.022112000	6.480337000	-2.375406000
6	-1.365749000	7.695307000	-2.607503000
6	-2.797900000	6.177358000	-1.165246000
6	-2.461427000	6.797326000	0.047875000
6	-2.700085000	6.168610000	1.279633000
6	-1.830078000	6.461133000	2.426794000
6	-1.149376000	7.671057000	2.610598000
6	-2.980771000	-4.251404000	-4.544843000
6	-4.986841000	-2.815808000	-4.460778000
6	-6.671416000	-1.553123000	-3.121314000
1	-7.250944000	-2.465951000	-3.050749000
6	-7.747119000	-0.801456000	-1.003010000
6	-1.186218000	-5.505516000	-3.357602000
1	-1.858711000	-6.353825000	-3.315520000
6	-0.053642000	-6.397943000	-1.335826000
6	-0.016094000	-6.382340000	1.140744000
6	-1.022127000	-5.505719000	3.242468000
1	-1.697151000	-6.353119000	3.239919000
6	-2.708427000	-4.267162000	4.599175000
6	-4.702291000	-2.818042000	4.708985000
6	-6.471362000	-1.539355000	3.506631000
1	-7.059043000	-2.449113000	3.477133000
6	-7.674740000	-0.792534000	1.458915000
6	-0.081264000	7.752120000	3.506861000
1	0.415551000	8.704327000	3.664898000
6	5.885999000	3.391499000	3.199944000
1	6.640504000	4.156224000	3.355616000
6	5.611803000	3.482522000	-3.539229000
1	6.350937000	4.255174000	-3.726426000
6	-0.368892000	7.785397000	-3.581890000

1	0.107515000	8.741442000	-3.775514000
1	1.300883000	6.667881000	4.746157000
1	-1.443675000	8.549040000	2.044298000
1	2.355704000	4.775017000	4.233433000
1	4.472663000	4.325309000	4.525829000
1	7.037357000	2.366737000	1.716278000
1	6.264267000	1.755200000	-0.196699000
1	6.836508000	2.459249000	-2.107777000
1	4.137422000	4.402685000	-4.807768000
1	2.029976000	4.827686000	-4.441672000
1	0.925668000	6.710953000	-4.921096000
1	-1.622291000	8.569895000	-2.018028000
1	-1.767921000	7.629103000	0.022594000
6	-0.664654000	-7.655818000	-1.299366000
1	-0.991817000	-8.130409000	-2.218584000
6	-0.884844000	-8.291990000	-0.074229000
1	-1.333735000	-9.280550000	-0.061360000
6	-0.629038000	-7.640871000	1.135412000
1	-0.925973000	-8.106711000	2.069161000
6	-5.775286000	-3.940011000	-4.738679000
1	-6.856262000	-3.848538000	-4.767986000
6	-5.180244000	-5.179512000	-4.977222000
1	-5.801878000	-6.033157000	-5.229131000
6	-3.803666000	-5.350157000	-4.826790000
1	-3.372401000	-6.341139000	-4.926483000
6	-8.684801000	-1.763695000	1.473113000
1	-9.015653000	-2.187670000	2.415910000
6	-9.260632000	-2.199057000	0.278628000
1	-10.067348000	-2.925115000	0.304944000
6	-8.755089000	-1.773328000	-0.950807000
1	-9.139759000	-2.204901000	-1.869477000
6	-3.513667000	-5.366260000	4.927016000
1	-3.083603000	-6.361864000	4.969215000
6	-4.870724000	-5.189430000	5.198118000
1	-5.475890000	-6.043597000	5.485801000
6	-5.473638000	-3.941485000	5.033507000
1	-6.547707000	-3.843498000	5.154015000
77	7.686889000	-0.597197000	0.024875000
6	6.000050000	-2.125681000	-0.502516000
6	4.248749000	-4.279573000	-0.037577000
6	6.436651000	-3.412937000	-0.431839000
6	5.572431000	-4.488882000	-0.057681000
1	6.534657000	-1.558758000	-1.311490000
1	7.438774000	-3.652144000	-0.773948000
1	5.971483000	-5.489810000	0.069521000
1	3.605713000	-5.136153000	0.100745000
6	9.100876000	-1.858647000	0.282454000
8	9.954722000	-2.621077000	0.424069000
6	8.793613000	0.870718000	0.267790000
8	9.442596000	1.817455000	0.410735000

Cycloadduct (zigzag (12,0) SWCNT + 2 acetylenes)

G = -5661.13214

6	4.329722000	-1.963636000	4.067344000
6	2.928068000	-2.190324000	4.040153000
6	2.015935000	-1.153392000	4.442878000
6	3.920074000	0.411968000	4.587438000
6	2.507736000	0.170107000	4.538958000
6	1.604668000	1.256406000	4.388505000
6	3.519927000	2.783635000	4.033748000
6	2.124544000	2.524885000	3.976805000
6	1.267019000	3.381215000	3.223472000
6	3.252924000	4.557811000	2.365229000
6	1.852126000	4.306278000	2.325143000
6	1.057438000	4.747118000	1.218361000
6	3.160899000	5.199881000	-0.000019000
6	1.752648000	5.005044000	-0.000016000
6	1.057425000	4.747098000	-1.218473000
6	3.252967000	4.557725000	-2.365273000
6	1.852149000	4.306185000	-2.325195000
6	1.267058000	3.381141000	-3.223539000
6	3.519965000	2.783537000	-4.033773000
6	2.124610000	2.524800000	-3.976855000
6	1.604737000	1.256298000	-4.388549000
6	3.920140000	0.411872000	-4.587401000
6	2.507805000	0.170013000	-4.538948000
6	2.015999000	-1.153505000	-4.442855000
6	4.329788000	-1.963723000	-4.067237000
6	2.928132000	-2.190415000	-4.040070000
6	2.397832000	-3.285200000	-3.304180000
6	4.639339000	-3.719807000	-2.386951000
6	3.237336000	-3.950586000	-2.370881000
6	2.608390000	-4.547891000	-1.221292000
6	4.744302000	-4.304108000	0.000084000
6	3.328023000	-4.541221000	0.000075000
6	2.608369000	-4.547873000	1.221435000
6	4.639305000	-3.719763000	2.387109000
6	3.237291000	-3.950541000	2.371018000
6	2.397778000	-3.285132000	3.304285000
6	0.982307000	-3.526287000	3.294652000
6	0.108367000	-2.661355000	4.007141000
6	-1.288516000	-2.891612000	3.993244000
6	-2.197203000	-1.866783000	4.431991000
6	0.618054000	-1.388985000	4.433653000
6	-0.288274000	-0.301305000	4.519794000
6	-1.701468000	-0.539646000	4.515191000
6	-2.602434000	0.545742000	4.347605000
6	0.209187000	1.019095000	4.352453000
6	-0.679985000	2.027994000	3.855359000
6	-2.081372000	1.785940000	3.837277000
6	-2.939249000	2.638432000	3.112553000
6	-0.138468000	3.132899000	3.157213000
6	-0.963035000	3.853782000	2.221047000
6	-2.390076000	3.614320000	2.206896000
6	-3.211229000	4.165670000	1.219176000
6	-0.349108000	4.610767000	1.219633000
6	-1.092538000	5.213830000	-0.000054000
6	-2.685166000	4.970152000	-0.000056000

6	-3.211267000	4.165691000	-1.219358000
6	-0.349040000	4.610745000	-1.219797000
6	-0.963023000	3.853742000	-2.221242000
6	-2.390019000	3.614299000	-2.207108000
6	-2.939174000	2.638412000	-3.112685000
6	-0.138435000	3.132851000	-3.157334000
6	-0.679951000	2.027923000	-3.855527000
6	-2.081277000	1.785884000	-3.837458000
6	-2.602346000	0.545657000	-4.347707000
6	0.209258000	1.018988000	-4.352531000
6	-0.288198000	-0.301403000	-4.519840000
6	-1.701384000	-0.539739000	-4.515250000
6	-2.197127000	-1.866884000	-4.432016000
6	0.618140000	-1.389097000	-4.433653000
6	0.108439000	-2.661447000	-4.007093000
6	-1.288446000	-2.891700000	-3.993213000
6	-1.820009000	-3.978298000	-3.255062000
6	0.982365000	-3.526357000	-3.294568000
6	0.418690000	-4.433842000	-2.357312000
6	-0.978356000	-4.670057000	-2.348390000
6	-1.598671000	-5.317527000	-1.221805000
6	1.215649000	-4.806111000	-1.220682000
6	0.541229000	-5.083445000	0.000057000
6	-0.871893000	-5.339776000	0.000048000
6	-1.598693000	-5.317506000	1.221890000
6	1.215630000	-4.806091000	1.220806000
6	0.418653000	-4.433792000	2.357413000
6	-0.978402000	-4.670007000	2.348471000
6	-1.820066000	-3.978235000	3.255110000
6	-3.233708000	-4.230069000	3.265071000
6	-4.097915000	-3.430158000	4.065986000
6	-5.421355000	-3.854171000	4.245266000
6	-3.598717000	-2.104972000	4.455948000
6	-4.465520000	-1.006795000	4.537433000
6	-4.001275000	0.312091000	4.395359000
6	-4.902442000	1.391366000	3.991517000
6	-6.287521000	1.365329000	4.195004000
6	-4.351355000	2.426059000	3.176608000
6	-5.212231000	3.206364000	2.360047000
6	-6.595446000	3.149352000	2.587198000
6	-4.602080000	3.878044000	1.217651000
6	-5.308666000	3.908047000	-0.000055000
6	-4.601978000	3.878069000	-1.217842000
6	-5.212143000	3.206226000	-2.360109000
6	-6.595396000	3.149129000	-2.587174000
6	-4.351276000	2.425987000	-3.176718000
6	-4.902370000	1.391279000	-3.991624000
6	-6.287428000	1.365196000	-4.195062000
6	-4.001187000	0.311992000	-4.395455000
6	-4.465432000	-1.006876000	-4.537479000
6	-3.598624000	-2.105072000	-4.455977000
6	-4.097839000	-3.430233000	-4.065981000
6	-5.421283000	-3.854245000	-4.245274000
6	-3.233649000	-4.230133000	-3.265039000
6	-3.784404000	-5.226521000	-2.410652000

6	-5.112350000	-5.623239000	-2.617739000
6	-2.994382000	-5.580719000	-1.223756000
6	-3.639178000	-5.816707000	0.000027000
6	-2.994402000	-5.580697000	1.223821000
6	-3.784445000	-5.226472000	2.410693000
6	-5.112398000	-5.623192000	2.617767000
6	4.414838000	1.747738000	-4.565333000
6	4.831638000	-0.683623000	-4.582678000
6	5.163207000	-2.803992000	-3.312034000
1	6.217506000	-2.561919000	-3.253045000
6	5.441268000	-4.142145000	-1.230744000
6	4.036768000	3.858771000	-3.294122000
1	5.111717000	3.987380000	-3.256938000
6	3.879466000	5.244834000	-1.232943000
6	3.879449000	5.244852000	1.232902000
6	4.036728000	3.858847000	3.294128000
1	5.111675000	3.987471000	3.256941000
6	4.414778000	1.747833000	4.565368000
6	4.831563000	-0.683530000	4.582751000
6	5.163156000	-2.803937000	3.312176000
1	6.217458000	-2.561871000	3.253206000
6	5.441250000	-4.142131000	1.230922000
6	-5.899782000	-4.978609000	3.572026000
1	-6.916986000	-5.316297000	3.746156000
6	-7.116806000	2.275365000	3.538283000
1	-8.185109000	2.266481000	3.732707000
6	-7.116748000	2.275174000	-3.538252000
1	-8.185058000	2.266223000	-3.732633000
6	-5.899720000	-4.978667000	-3.572023000
1	-6.916923000	-5.316358000	-3.746161000
1	-6.082286000	-3.299539000	4.903664000
1	-5.535073000	-6.427232000	2.023630000
1	-5.531540000	-1.185674000	4.467022000
1	-6.720928000	0.628966000	4.863990000
1	-7.261908000	3.791687000	2.020501000
1	-6.345436000	3.598142000	-0.000092000
1	-7.261859000	3.791418000	-2.020429000
1	-6.720844000	0.628823000	-4.864032000
1	-5.531452000	-1.185756000	-4.467059000
1	-6.082198000	-3.299626000	-4.903698000
1	-5.535040000	-6.427265000	-2.023593000
1	-4.718066000	-5.913182000	0.000018000
6	5.199441000	5.711904000	-1.213578000
1	5.747990000	5.825123000	-2.143204000
6	5.824479000	6.006805000	-0.000001000
1	6.837420000	6.397993000	-0.000023000
6	5.199457000	5.711932000	1.213549000
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6	6.179672000	-0.430050000	-4.867843000
1	6.882384000	-1.254473000	-4.934405000
6	6.626581000	0.877515000	-5.059293000
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6	5.770027000	1.959022000	-4.854847000
1	6.158892000	2.970510000	-4.913276000
6	6.842145000	-4.165329000	1.211843000

1	7.396206000	-4.111245000	2.143557000
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6	6.842165000	-4.165338000	-1.211643000
1	7.396238000	-4.111261000	-2.143349000
6	5.769953000	1.959116000	4.854910000
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6	6.626506000	0.877602000	5.059384000
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6	6.179601000	-0.429955000	4.867940000
1	6.882308000	-1.254380000	4.934536000
6	-3.493839000	6.288654000	0.000021000
6	-0.709410000	6.712670000	-0.000130000
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1	-3.659829000	8.377829000	0.000183000
1	-1.170950000	8.756578000	-0.000028000
1	0.352959000	6.910228000	-0.000319000

Cyclizations

Rhodium-Catalyzed [2+2+2] Cycloaddition Reactions of Linear Allene–Ene–Ynes to afford Fused Tricyclic Scaffolds: Insights into the Mechanism

Daniel Cassú,^[a] Teodor Parella,^[b] Miquel Solà,^{*,[a]} Anna Pla-Quintana,^{*,[a]} and Anna Roglans^{*,[a]}

Abstract: Allene-(E)-ene-yne *N*-tosyl-tethered substrates **3a–3h** were efficiently prepared and their rhodium-catalyzed [2+2+2] cycloaddition reactions were evaluated. The cycloadditions are chemoselective as only the proximal double bond of the allene reacted to afford exocyclic double bonds in the fused-tricyclic scaffolds. The stereoselectivity depend-

ed on the catalytic system used. Reactivity between allene, alkene, and alkyne was studied for the first time by density functional theory calculations. This mechanistic study determines the order in which the unsaturated groups take part in the catalytic cycle.

Introduction

The development of efficient and sustainable syntheses for organic molecules of all shapes and sizes is having a tremendous impact on a wide range of scientific areas, including biomedicine and the production of new drugs, agrochemical products, and new materials. The transition-metal-catalyzed [2+2+2] cycloaddition reaction of three unsaturated partners^[1] offers efficient, atom-economical pathways to a variety of complex carbocyclic and heterocyclic derivatives.

Among the range of unsaturated groups that can be involved in [2+2+2] cycloadditions, allenes^[2,3] have shown great versatility.^[4] They are less reactive than alkynes, but allow sp³-containing six-membered rings to be constructed, opening the door to the enantioselective synthesis of compounds with central chirality. Furthermore, after cycloaddition there is still one unreacted double bond that can be used in subsequent reactions. Despite the progress achieved in this field,^[4] there is still room for improvement, especially regarding the control of selectivity. By obtaining a better understanding of aspects governing the selectivity of these processes, we should be able to apply rational criteria to improve them.

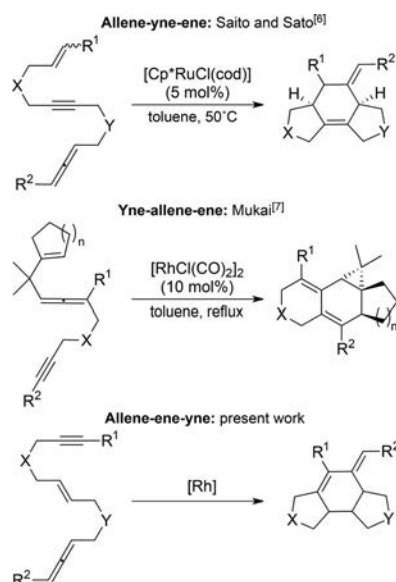
Our research group has explored the rhodium-catalyzed [2+2+2] cycloaddition reaction of linear allene–ene–allene and allene–yne–allene derivatives.^[5] Wilkinson's complex was able to promote the cycloaddition chemoselectively, involving only the internal double bonds of the two allenes, and diastereoselectively.^[5a] The reaction mechanism was studied for the allene–ene–allene substrate by means of DFT calculations. The process involved an initial oxidative addition between the proximal double bond of the allene and the alkene, undergoing *cis* ring fusion. Although allenes are more reactive than alkenes in [2+2+2] cycloaddition reactions, entropically favored allene–alkene oxidative addition was preferred. Furthermore, the proximal double bond of the allene, which has a molecular orbital with greater energy, was selectively reacted in this first step. The reaction continued by the insertion of the proximal double bond of the second allene unit to afford a rhodacycloheptane intermediate that evolved, by reductive elimination, to the final cyclohexane adduct. When optically active substrates, bearing a substituent in the α position of the allene, were reacted with Wilkinson's complex as catalyst, a highly diastereoselective reaction occurred resulting in the production of enantiomerically pure polycycles.^[5b]

Since the chemoselectivity of the [2+2+2] cycloaddition reaction is especially compromised when three different unsaturated groups are combined in a reaction, we were interested in studying [2+2+2] cycloaddition reactions using three different carbon-based functionalities: an allene, an alkene, and an alkyne. Only two previous examples have been reported evaluating this type of processes (Scheme 1), both in a completely intramolecular manner. Saito, Ichimaru, and Sato^[6] have described the intramolecular [Cp**Ru*Cl(cod)]-catalyzed [2+2+2] cycloaddition reaction of allene–yne–enes, which diastereoselectively affords fused-tricyclic skeletons with two stereogenic centers. Mukai et al.^[7] have reported the stereospecific and stereoselective [RhCl(CO)₂]₂-catalyzed intramolecular [2+2+2] cycloaddition of linear yne–allene–ene derivatives to produce

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<https://doi.org/10.1002/chem.201703194>.



Scheme 1. Transition-metal-catalyzed [2+2+2] cycloaddition reactions of allenes, alkynes, and alkenes.

polycyclic products with three contiguous stereogenic centers. In both studies,^[6,7] a plausible mechanism is proposed involving oxidative addition between the allene and the alkyne, which are in contiguous—and thus entropically favored—positions in the linear substrate.

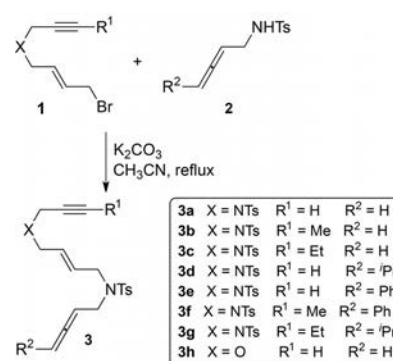
In the course of our ongoing program based on the synthesis of polycyclic structures,^[8] we designed the present project aimed at reacting allene–ene–yne substrates in which the oxidative addition of the alkyne and the allene is not geometrically favored (Scheme 1). Apart from the synthetic interest in the tricyclic scaffolds with three contiguous stereogenic centers, we also wanted to study the process mechanistically, paying special attention to the order of reactivity of the three unsaturated groups in the [2+2+2] cycloaddition reaction.

Abstract in Catalan: *S'ha preparat satisfactòriament una sèrie de substrats 3a–3h de cadena oberta contenint un al·lè, un doble enllaç i un alquí i s'ha avaluat la seva reacció de cicloaddició [2+2+2] catalitzada per rodi. La cicloaddició és quimioselectiva degut a què només el doble enllaç intern de l'al·lè reacciona per donar un sistema tricíclic fusionat amb un doble enllaç exocíclic. L'estereoselectivitat del procés depèn del sistema catalític emprat. La diferent reactivitat entre l'al·lè, l'alquí i l'alquí s'ha estudiat per primer cop mitjançant càlculs teòrics basats en la teoria del funcional de la densitat. Aquest estudi mecanístic permet determinar l'ordre en què les insaturacions participen en el cicle catalític.*

Results and Discussion

Synthesis of allene–ene–yne substrates

To evaluate the reactivity of allene–ene–yne scaffolds in the fully intramolecular [2+2+2] cycloaddition reaction, a synthesis for eight model substrates (**3**) was designed. This was based on the nucleophilic substitution of bromoallyl derivatives (**1**) with *N*-tosyllallenes (**2**) using potassium carbonate as a base in refluxing acetonitrile (Scheme 2). Variations were introduced at the tether [*N*-tosyl (NTs) or oxygen (O)] and either at the terminal position of the triple bond ($R^1 = \text{H, Me, Et}$) or the allene ($R^2 = \text{H, } ^i\text{Pr, Ph}$), or both (Scheme 2; see the Supporting Information for details on the synthesis of **3**).



Scheme 2. Allene–ene–yne substrates used in this study (Ts = *p*-toluenesulfonyl).

Cycloaddition reactions

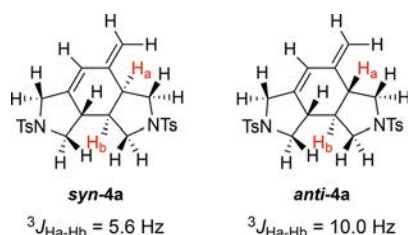
After preparation of the substrates, the feasibility of the cycloaddition was assessed with allene–ene–yne **3a** (Table 1). The substrate was first treated with Wilkinson's catalyst (**A**) in toluene at 100 °C. A mixture of two inseparable diastereoisomers in 8:2 ratio was isolated with an overall yield of 56% (Entry 1, Table 1). The reaction was completely chemoselective with cycloaddition taking place only on the internal double bond of the allene. The two diastereoisomers differ in the 6:5 ring fusions that can either be *cis* or *trans* (*syn* or *anti* relative orientation of H_a and H_b in Figure 1). After a complete chemical shift assignment (see the Supporting Information), it could be inferred that the protons placed in *syn* orientation display a smaller coupling constant ($^3J_{H_a-H_b} = 5.6 \text{ Hz}$) than in the *anti* orientation ($^3J_{H_a-H_b} = 10 \text{ Hz}$) (Figure 1), which provided a straightforward identification of the two diastereoisomers.

Ethanol was tested as a more polar reaction solvent (Entry 2, Table 1), but it only caused the degradation of the substrate. *p*-Xylene was also tested to increase the reaction temperature to 130 °C. However, owing to decomposition processes, the yield of the cycloadduct was lower (Entry 3, Table 1). Given that no improvement could be achieved by changing the reaction media, further optimization was again attempted in toluene. Neither the use of a microwave heating source, nor the addition of AgBF_4 to the reaction mixture to render the catalytic system cationic, led to any improvement. The addition of an

Table 1. Optimization of conditions for the [2+2+2] cycloaddition of **3a**.^[a]

Entry	Catalytic system ^[b]	Solvent	T [°C]	Time [h]	Yield 4 [%] ^[c]	d.r. ^[d]
1	A	toluene	100	5	56 ^[e]	8:2
2	A	ethanol	70	22	0	–
3	A	<i>p</i> -xylene	130	2.5	36	10:0
4	A ^[f]	toluene	100	4	33	9:1
5	B	dichloroethane	60	5	31	7:3
6	B	dichloroethane	80	4	22	5:5
7	C	toluene	0–5	1	38	0:10
8	C	toluene	60	0.33	49	1:9

[a] A solution of the catalytic system (10 mol%) was added to **3a** (0.03 M) and the reaction was heated to the temperature noted. [b] **A**: [RhCl(PPh₃)₃]; **B**: [Rh(cod)₂]BF₄, (*R*)-DTBM-SegPhos [(*R*)-5,5'-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole]; **C**: [RhCl(CO)₂]₂. [c] The two diastereoisomers were obtained as an inseparable mixture and their ratio was determined by ¹H NMR spectroscopy. [d] Diastereomeric ratio (**syn-4a**:**anti-4a**). [e] At the end of the reaction 8% of starting material was recovered. [f] With Et₃N (1.8 equiv).

**Figure 1.** Cycloadducts obtained upon [2+2+2] cycloaddition of allene–ene–yne **3a**, showing the characteristic coupling constants between H_a and H_b in the two diastereoisomers.

excess of triethylamine^[8i,9] to stabilize the catalyst or generate more active species also proved unsuccessful (Entry 4, Table 1).

The combination of bisphosphine ligands and a cationic rhodium source was then studied as the catalytic system for the cycloaddition of **3a**. Phosphines such as (*R*)-H₈-BINAP, (*R*)-BINAP, and (*R*)-tol-BINAP in combination with cationic rhodium complex [Rh(cod)₂]BF₄ were tested in several solvents (dichloroethane and chlorobenzene) and temperatures were raised from room temperature to 100 °C but in no cases did a reaction take place. However, when (*R*)-DTBM-SegPhos was tested in dichloroethane at 60 °C, cycloaddition took place giving a 31% yield of the **syn-4a/anti-4a** diastereoisomeric mixture in a 7:3 ratio (Entry 5, Table 1). Lower yields of the cycloadducts (**4**) were obtained with lower diastereoselectivities when the reaction temperature was increased (Entry 6, Table 1). We also checked the enantioselectivity of the process using chiral HPLC. Unfortunately, no enantioinduction was obtained for the major diastereoisomer **syn-4a** and consequently the enantioselectivity study was abandoned.

The dimeric rhodium complex [RhCl(CO)₂]₂ (**C**) was then tested in our model cycloaddition reaction to see the effect of a change from phosphine to carbonyl ligands on rhodium. By

performing the reaction in toluene at different temperatures (Entries 7 and 8, Table 1), the diastereoisomeric mixture of cycloadducts **4a** was efficiently obtained. Surprisingly, the major diastereoisomer formed was now the one with a *trans* 5,6-ring fusion (**anti-4a**). The yield increased with the temperature but concurrent with a slight decrease in the diastereoselectivity. Further increases in the temperature did not improve the reaction.

Since the rhodium sources gave complementary results in terms of selectivity, we decided to ascertain the scope of the process using the three catalytic systems. The optimized conditions found for each catalytic system were applied to the array of allene–ene–yne scaffolds synthesized (Scheme 3).

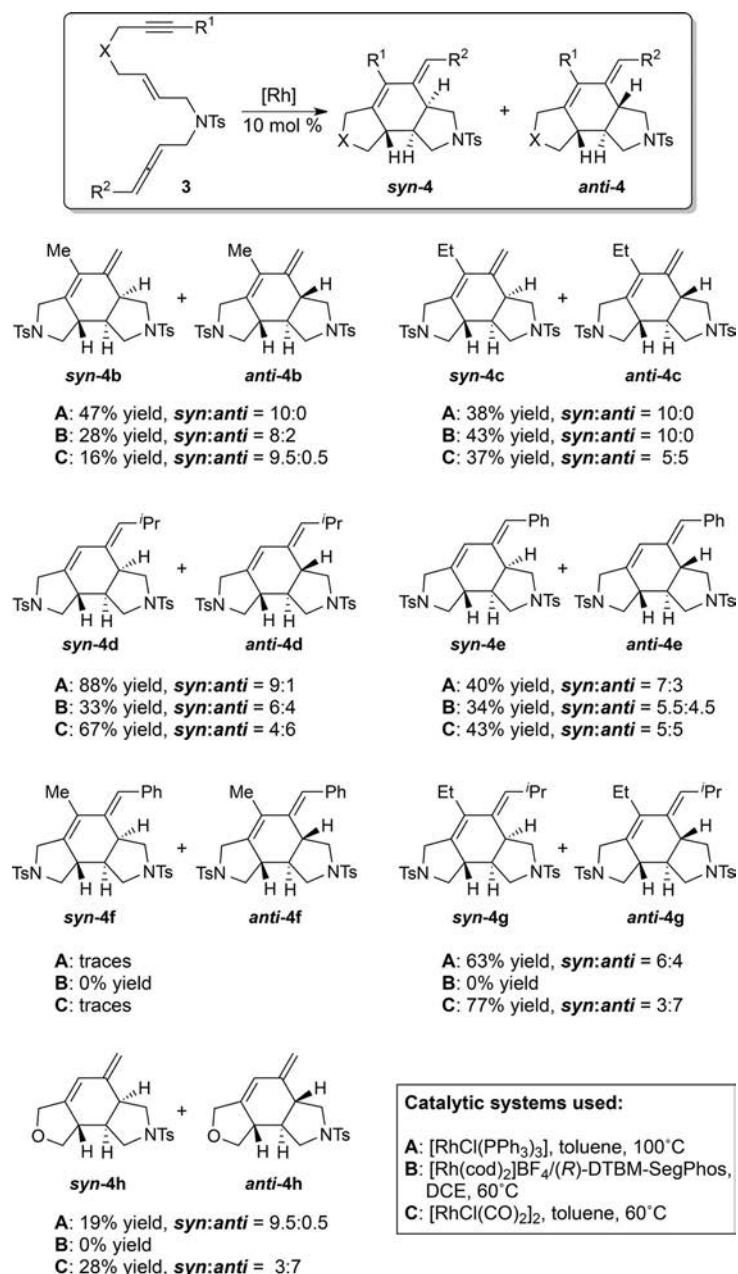
All compounds except for **3f** react in the cycloisomerization reaction under the influence of at least one of the catalysts tested. The lack of reaction of **3f** is unexplained since **3g**, which was also substituted both in the alkyne and allene ends, reacted with great efficiency. The best results in terms of yields were obtained for the substrate featuring an *iso*-propyl substituent at the allene end (**3d** and **3g**).

When comparing the results for the three different catalytic systems, it is seen that the neutral rhodium catalytic systems (**A** and **C**) react more efficiently than the cationic one (**B**). System **B** only affords moderate yields of the cycloadducts that are substituted only in one of the alkyne (**4b** and **4c**) or allene (**4d** and **4e**) termini. The substrates substituted at both ends (**3f** and **3g**) as well as the compound with an oxygen tether (**3h**) failed to react under the catalysis of a mixture of [Rh(cod)₂]BF₄ and (*R*)-DTBM-SegPhos, most likely owing to steric hindrance.

As a general trend, Wilkinson's catalyst (catalytic system **A**) displays a higher selectivity for the *cis*-ring fused cycloadduct. When methyl and ethyl substituents were placed at the terminus of the alkyne group (**4b** and **4c**), pure *cis*-ring fused diastereoisomers were obtained in moderate yields. It seems that stereoselectivity is reduced when the steric hindrance of the groups on the unsaturated ends is increased. On the other hand, the [RhCl(CO)₂]₂ is only moderately selective towards the *trans*-ring fused cycloadduct in most cases, although there are some exceptions. As noted (Entry 8, Table 1) [RhCl(CO)₂]₂ is highly selective toward **anti-4a** when the unsubstituted substrate **3a** is reacted and, quite surprisingly, is highly selective for the **syn-4b** cycloadduct when a methyl substituent is placed at the alkyne terminus (**3b**).

Mechanistic study

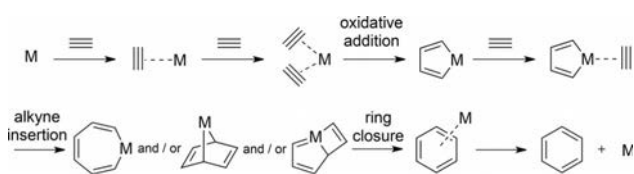
After exploring the reactivity of the allene–ene–yne substrates from the experimental point of view, we decided to computationally investigate the reaction mechanism of the [2+2+2] cycloaddition reaction of **3a** catalyzed by [RhCl(PPh₃)₃] and [RhCl(CO)₂]₂ to yield diastereoisomers **syn-4a** and **anti-4a**. To this end, we performed density functional theory (DFT) calcula-



Scheme 3. Scope of the [2+2+2] cycloaddition reactions of substrates **3** (the results reported are an average of two runs).

tions at the B3LYP-D3/cc-pVDZ-PP level (see Computational Methods for more details).

The mechanism postulated for the [2+2+2] cycloaddition reaction of three alkynes entails several key steps (Scheme 4).^[8f,10] First, oxidative addition takes place between



Scheme 4. Generally accepted mechanism for the [2+2+2] cycloaddition reaction involving three alkynes (M = transition metal complex).

two of the alkyne ligands initially coordinated to the metal center. Second, the insertion of the last alkyne coordinated to the metal generates a metallacycloheptatriene intermediate in a Schore-type mechanism.^[11] Depending on the catalyst used, type of unsaturated groups, and experimental conditions, this second key step can also proceed through a metal-mediated [4+2] cycloaddition to yield a metallanorbornadiene intermediate or a [2+2] cycloaddition to give a metallabicyclo[3.2.0]heptatriene. In a subsequent step, the intermediate formed undergoes ring closure through a reductive elimination process. Finally, the catalytic cycle is completed with the recovery of the catalyst and release of the product.

For [2+2+2] cycloaddition reactions in which unsaturated groups other than alkynes participate, the same general mechanism is postulated to take place, only with some notable features. In our specific case, it was necessary to determine the order in which the unsaturated groups participate in the catalytic cycle (i.e., whether the oxidative addition occurs between the alkyne and the alkene, between the alkyne and the allene, or between the alkene and the allene). Moreover, it is important to discuss the diastereoselectivity experimentally found when C(sp²)-containing unsaturated groups are involved. To shed more light on what catalytic species participated in each of the processes catalyzed by $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{RhCl}(\text{CO})_2]_2$, we undertook several empirical tests intended to determine the ligands present in the rhodium coordination sphere.

Firstly, the mechanism for the cyclization catalyzed by $[\text{RhCl}(\text{PPh}_3)_3]$ will be considered. Active species in the cycloaddition reaction catalyzed by Wilkinson's catalyst are generated after PPh_3 release. To determine how many PPh_3 units are coordinated to the Rh center in the catalytically relevant species, we took advantage of the presence of phosphorus atoms in Wilkinson's catalyst to monitor and detect these species by NMR spectroscopy. When either catalytic or stoichiometric mixtures of substrate **3a** and Wilkinson's catalyst in $[\text{D}_8]\text{toluene}$ were introduced into the NMR spectrometer and analyzed at room temperature

in a sealed NMR tube, the formation of two new products (in a 1:0.8 ratio) was observed both by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (see Figure 2a and the Supporting Information for full experimental details and spectra). Each species gave a doublet in the ^{31}P NMR spectra, at 31.93 ($^1J_{\text{P-Rh}} = 126.6$ Hz) and 33.40 ppm ($^1J_{\text{P-Rh}} = 127.0$ Hz), respectively. We postulated that these peaks corresponded to species containing only one triphenylphosphine ligand and carried out 2D NMR experiments such as ^1H - ^1H COSY, DOSY and ^1H - ^{31}P HMBC to fully characterize them. Key to the assignment was the analysis of the ^1H - ^{31}P HMBC, which showed cross-peaks between the P and both the terminal alkyne and the allenic protons in the two species (see Spectra SII-5 in the Supporting Information), allowing us to conclude that both species correspond to rhodium complexes

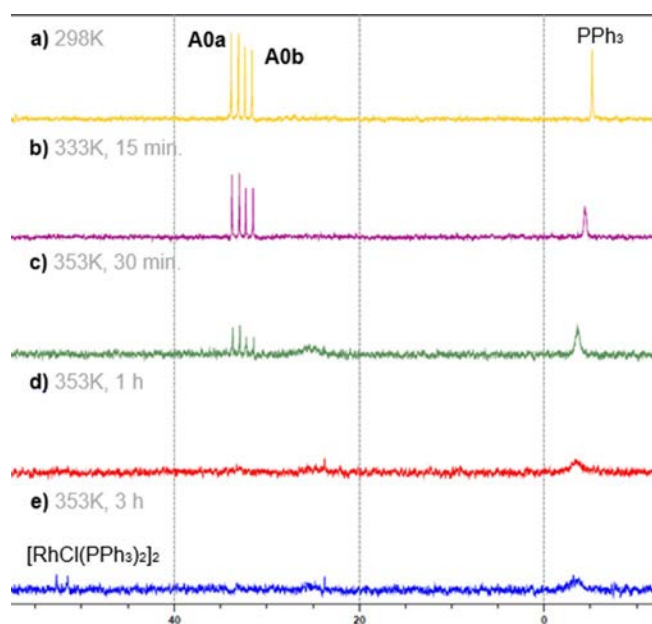
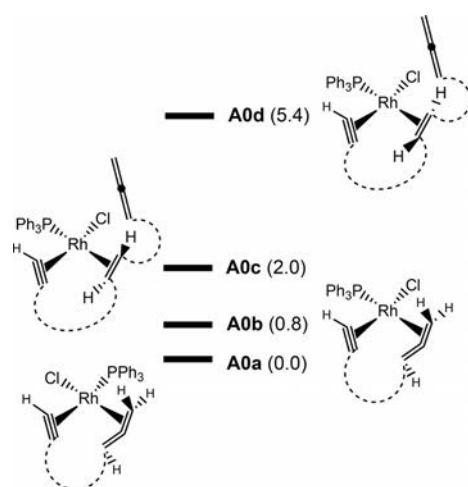


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy monitoring of the [2+2+2] cycloaddition reaction of **3a** using catalytic system **A**.

containing one triphenylphosphine ligand in which the rhodium is coordinated to the alkyne and the two double bonds of the allene moieties of the substrate.

To shed more light on the identity of these metal complexes, B3LYP-D3/cc-pVDZ-PP calculations were undertaken to find the most stable coordination species incorporating one PPh_3 unit. As a result of these calculations, we were able to establish the relative stability order of the coordinated species (Scheme 5). The two lowest-energy species (**A0a** and **A0b**) both consist of compounds in which the rhodium atom is coordinated to the alkyne and to the distal double bond of the allene. These two new ligands replace two of the triphenylphosphine ligands of the initial Wilkinson's catalyst. Attempts to optimize complexes in which the allene was coordinated with the proximal double



Scheme 5. Most stable coordination intermediates computed by DFT calculations. Energies in kcal mol^{-1} .

bond invariably led to the isomerization to complexes coordinated to the distal double bond. Species **A0a** and **A0b** differ in the relative orientation of the ligands in the square-planar coordination sphere of the coordination compound (Figure 3). The next two species **A0c** and **A0d** are 2.0 and 5.4 kcal mol^{-1} higher in energy, respectively, compared to the lowest energy **A0a** species. These geometries consist of the coordination of the alkyne and allene motifs to the rhodium center and are differentiated by the opposite configuration of the allene.

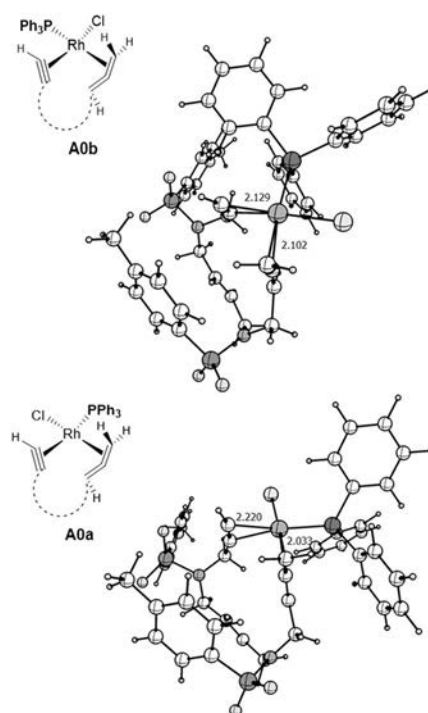
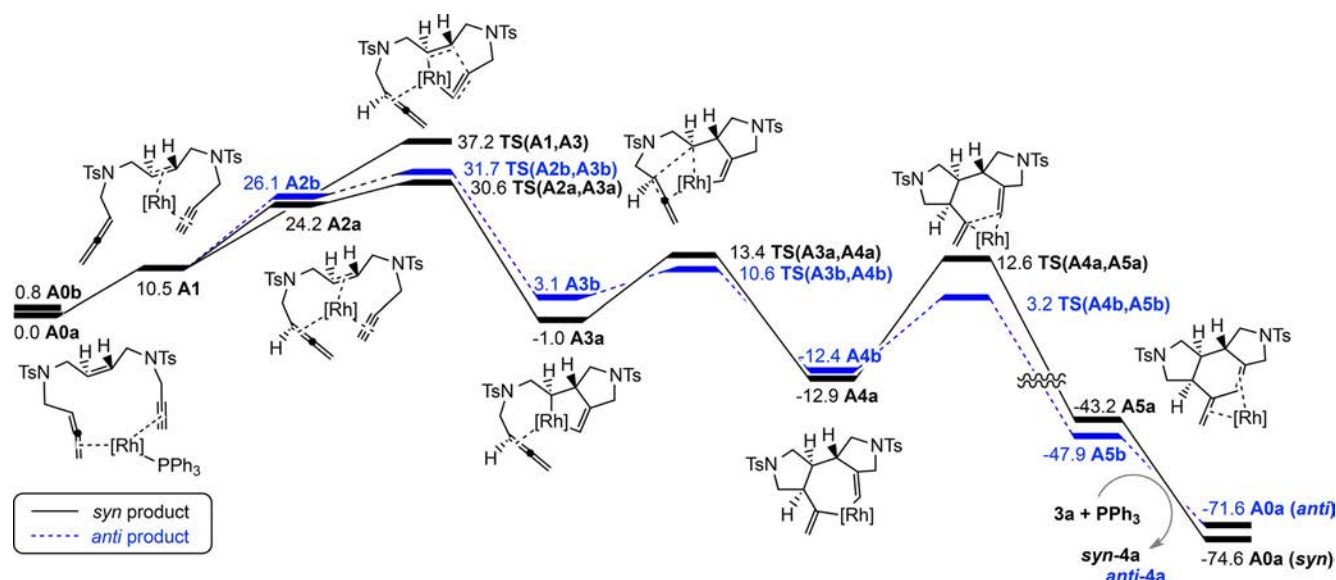


Figure 3. Coordination compounds **A0a** and **A0b** observed by NMR experiments when **3a** was mixed with stoichiometric amounts of Wilkinson's catalyst. Geometries from B3LYP-D3/cc-pVDZ-PP optimizations. Distances are given in Å.

Taking the experimental and computational data together, **A0a** and **A0b** were assigned as the two species that are experimentally detected. The calculated small energy difference of 0.8 kcal mol^{-1} between **A0a** and **A0b** concurs with the ratio of these compounds that are detected experimentally. Furthermore, analysis of the NOESY spectra gave exchange cross-peaks indicating that these species interconvert in a slow equilibrium on the NMR timescale (see the Supporting Information for spectra and scheme of the equilibrium).

The sample was then heated inside the NMR spectrometer to 353 K and periodically monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Figure 2). No change was observed from 298 K to 333 K, but when the reaction was gradually heated to 353 K, the two doublets corresponding to **A0a** and **A0b** gradually disappeared, the PPh_3 signal broadened, and no distinct signal appeared. Our interpretation of these results is that the catalytically active species might not have coordinated phosphine, and that $[\text{RhCl}(\text{PPh}_3)_2]_2$, which is detected in the reaction media



Scheme 6. Gibbs energy profile (kcal mol^{-1}) at 373.15 K for the most favorable route of the $[\text{RhCl}(\text{PPh}_3)_3]$ -catalyzed [2+2+2] cycloaddition of allene-ene-yne **3a** leading to **syn-4a** and **anti-4a**. Energies are relative to complex **A0a**. Only drawings of the structures for the *syn* path are depicted. $[\text{Rh}] = \text{RhCl}$.

toward the end of the reaction, is a resting-state species for rhodium.

Based on the precedents in our research group^[10d] and the results of the NMR study, we decided to analyze catalytically active species containing one or no triphenylphosphine ligands coordinated to the rhodium center. In Scheme 6, the Gibbs free energy profiles of the most favorable pathways leading to **syn-4a** and **anti-4a** from **3a** under $[\text{RhCl}(\text{PPh}_3)_3]$ catalysis are depicted. Oxidative addition from either **A0a** or **A0b** would lead to a cycloadduct that is regioisomeric to those that were isolated and, therefore, direct oxidative addition was not considered from these experimentally detected intermediates. Oxidative addition from either **A0c** or **A0d** was evaluated but high energy barriers ($\Delta G^\ddagger = 49.2$ and $39.7 \text{ kcal mol}^{-1}$, respectively) were found, which ruled out these pathways. Instead, the endergonic loss of the PPh_3 ligand from **A0a** and **A0b** was considered to generate **A1**, from which a somewhat lower barrier for the oxidative addition was calculated to be $37.2 \text{ kcal mol}^{-1}$.

Although **A1** has a lower energy barrier in the oxidative addition than **A0d**, the barrier obtained is still too high to explain the experimental outcome. However, a lower energy pathway for the oxidative addition was found by the coordination of the allene moiety to the metal center to yield **A2a** or **A2b**. The main difference between **A2a** and **A2b** is the orientation of the allene group that is approximately perpendicular to the $\text{Rh}-\text{Cl}$ bond in **A2a** and parallel in **A2b** (see Figure 4). As expected from the molecular orbitals of a $d^8 \text{ ML}_4$ fragment,^[12] these two orientations lead to complexes with small energy differences. The different orientation of the allene fragment is important because it places the H atom of the internal allene in the right position to provide **syn-4a** (**A2a**) or **anti-4a** (**A2b**) products. Oxidative addition from **A2a** via transition state (TS) **TS(A2a,A3a)** and from **A2b** via **TS(A2b,A3b)** have Gibbs energy barriers of 30.6 and $31.7 \text{ kcal mol}^{-1}$, respectively. The

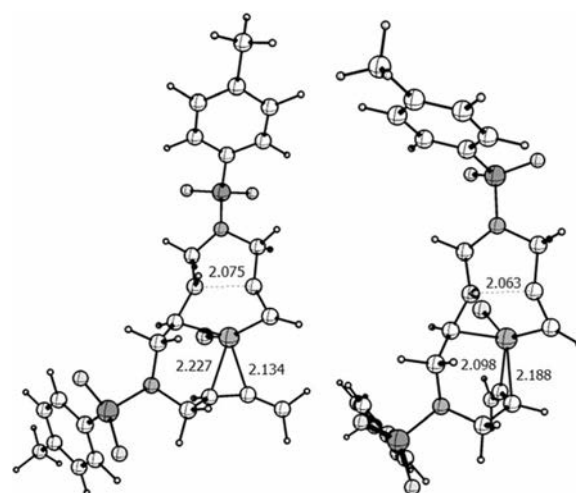


Figure 4. Optimized structures (B3LYP-D3/cc-pVDZ-PP) for **TS(A2a,A3a)** (left) and **TS(A2b,A3b)** (right). Relevant distances are given in Å.

two oxidative addition processes leading to **A3a** and **A3b** are exergonic by $1.0 \text{ kcal mol}^{-1}$ and endergonic by $3.1 \text{ kcal mol}^{-1}$, respectively.

We then proceeded to evaluate the insertion step. From intermediates **A3a** and **A3b**, several possibilities emerge for the insertion of the internal double bond of the allene group. Attacks leading to rhodacycloheptene were computed for the insertion of the allene into $\text{Rh}-\text{C}(\text{sp}^3)$ or $\text{Rh}-\text{C}(\text{sp}^2)$ bonds. Moreover, a rhodanorbornane intermediate could also be generated through a Diels-Alder-like TS. However, despite many attempts, we were unable to locate either the TS or the rhodanorbornane intermediate for a Diels-Alder-like attack. By comparing the energy barriers for the remaining cases, we observed a clear preference for the insertion taking place on the $\text{Rh}-\text{C}(\text{sp}^3)$ bond. **TS(A3a,A4a)** and **TS(A3b,A4b)**, leading to

rhodacycloheptenes **A4a** and **A4b**, respectively, had the two lowest energy barriers with $\Delta G^\ddagger = 14.4$ and $7.5 \text{ kcal mol}^{-1}$, respectively.

The subsequent step involves reductive elimination and formation of the C–C bond that affords the final cyclohexene ring η^4 -coordinated to RhCl. The energy barriers found for such process were computed to be $\Delta G^\ddagger = 25.5$ and $15.6 \text{ kcal mol}^{-1}$ for **TS(A4a,A5a)** and **TS(A4b,A5b)**, respectively. In both pathways, the highest energy barriers are associated with the oxidative addition step and so the rate-determining step for this route takes place at the beginning of the process.

The overall reaction is exergonic by 71.6 – $74.6 \text{ kcal mol}^{-1}$ and the energy span between the turnover frequency (TOF)-determining intermediate (TDI) and TOF-determining TS (TDTS)^[13] is 30.6 and $31.7 \text{ kcal mol}^{-1}$ for pathways leading to **syn-4a** and **anti-4a**, respectively.

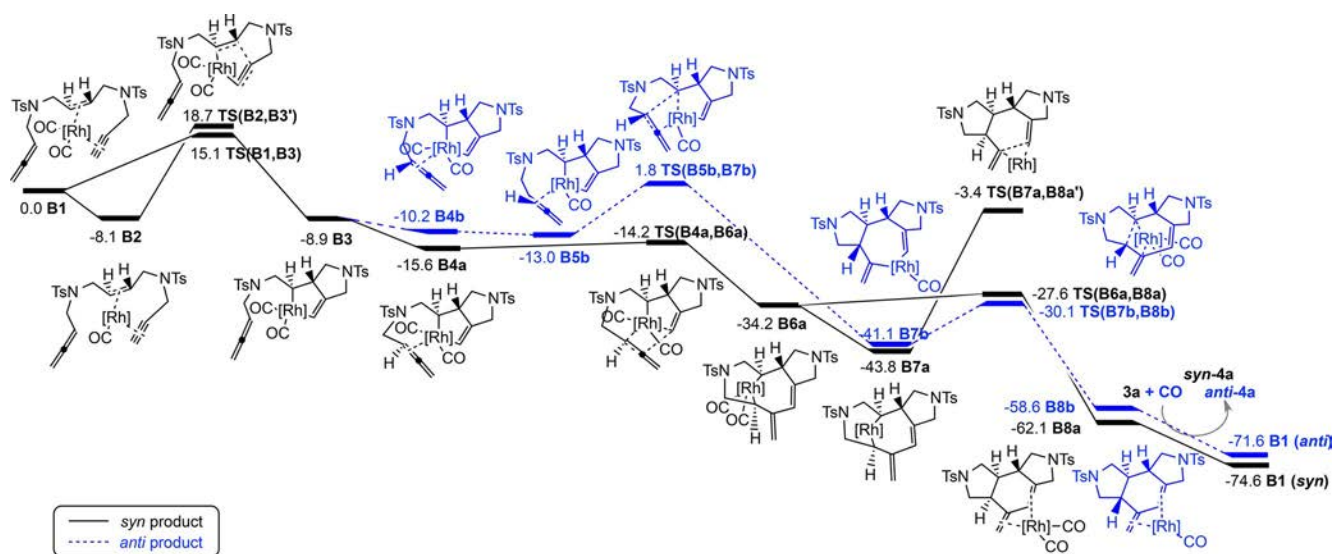
Further support for the mechanism being comprised of phosphine-free intermediates was gained by performing the cycloaddition reaction using $[\text{RhCl}(\text{ethylene})_2]_2$ as a catalyst. Compounds **syn-4a** and **anti-4a** were obtained in a 41% yield [2.5:7.5 diastereomeric ratio (d.r.)] after heating a solution of **3a** in toluene to 100°C for 1 h with this catalyst. This result indicated that the reaction can take place in the absence of PPh_3 ligands and probably through the same catalytic intermediates, since the ethylene ligand can easily be released owing to their lability when the substrate enters the coordination sphere of the rhodium center.

We then turned our attention to the $[\text{RhCl}(\text{CO})_2]_2$ catalyst, which was observed to afford the opposite diastereoisomeric ratio when **3a** is employed. Once again, the study firstly involved an empirical test to obtain more information about the coordination sphere of the metal center. In the case of $[\text{RhCl}(\text{CO})_2]_2$, we decided to use electrospray ionization mass spectrometry (ESI-MS) to propose a structure for the catalytically active species.^[14] We set up the reactions that afford **4a**

and **4d** under the optimized conditions and several aliquots were sequentially taken from the crude reaction mixture and analyzed by ESI-MS. After some optimization, we found that the best sensitivity was obtained by mixing the aliquots taken from the reactions with a solution of 0.01 M LiCl in methanol prior to injection and analysis in the negative ion mode.^[15] When **3a** was employed, two peaks at $m/z = 684.8$ and $m/z = 656.9$ were detected, which were assigned to $[\text{RhCl}(\text{3a})(\text{CO}) + \text{Cl}]^-$ and $[\text{RhCl}(\text{3a}) + \text{Cl}]^-$. Analogously, when **3d** was used, peaks were observed at $m/z = 726.9$ ($[\text{RhCl}(\text{3d})(\text{CO}) + \text{Cl}]^-$) and $m/z = 698.8$ ($[\text{RhCl}(\text{3d}) + \text{Cl}]^-$). Furthermore, CID fragmentation of $[\text{RhCl}(\text{3a})(\text{CO}) + \text{Cl}]^-$ or $[\text{RhCl}(\text{3d})(\text{CO}) + \text{Cl}]^-$ showed the formation of a peak at $[\text{M}-28]^-$ corresponding to the loss of the CO group forming $[\text{RhCl}(\text{3a}) + \text{Cl}]^-$ or $[\text{RhCl}(\text{3d}) + \text{Cl}]^-$, respectively. It seems from these results that at least one carbon monoxide ligand may be present in the catalytically active species.

At this point we performed a similar computational analysis of the different possible pathways that could lead to the observed compounds. Taking into account literature precedent^[16] and the ESI-MS results, we considered the monomeric form of the catalyst, in other words, $[\text{RhCl}(\text{CO})_2]$. Different possibilities regarding the coordination of the allene, alkene, and alkyne moieties to the rhodium center were explored. We also computed the different intermediates and TSs that can intervene, depending on the number of carbonyl ligands involved: none, one, or two.

The proposed mechanism (Scheme 7) starts with the coordination of the alkyne and alkene unsaturated groups to the rhodium center with two carbonyl ligands and the chloride (**B1**). From this point onwards, the intermediate can afford the rhodacyclopentene intermediate **B3** surmounting an energy barrier of $\Delta G^\ddagger = 15.1 \text{ kcal mol}^{-1}$ for this oxidative addition process. As in the previous case, the oxidative addition between the alkene and the alkyne was the most favorable. Even



Scheme 7. Gibbs free energy profile (kcal mol^{-1}) at 333.15 K for the most favorable routes of the $[\text{RhCl}(\text{CO})_2]$ -catalyzed $[2+2+2]$ cycloaddition of allene-ene-yne **3a** leading to **syn-4a** and **anti-4a**. In this scheme $[\text{Rh}] = \text{RhCl}$. Drawings of the structures for the syn path are in black and for the anti path in blue.

though **B2**, which could be obtained from **B1** after releasing a CO ligand, is a more stable intermediate by $8.1 \text{ kcal mol}^{-1}$, we computed that the corresponding **TS(B2,B3')** is located at $\Delta G^\ddagger = 26.8 \text{ kcal mol}^{-1}$, allowing this alternative path to be excluded. This is not an unexpected result given that the σ donation of Rh to C in the Rh–CO bond is higher than the π -backdonation of the CO ligand.^[17] Thus, the presence of CO favors the oxidation of Rh^I to Rh^{III} and the barrier of the oxidative addition step is lower when catalyzed by $[\text{RhCl}(\text{CO})_2]$ than by $[\text{RhCl}(\text{CO})]$.

Having reached rhodacyclopentene intermediate **B3**, this intermediate rearranges to **B4a** or **B4b**, in which the allene moiety coordinates to the rhodium center. This gives rise to the two possible orientations of the protons for the generation of the *syn-4a* and *anti-4a* diastereoisomers. For the synthesis of the *anti-4a* cycloadduct, loss of a CO ligand in **B4b** occurs, releasing $2.8 \text{ kcal mol}^{-1}$ to yield **B5b**. From **B5b**, insertion of the internal double bond of the allene into the Rh–C(sp³) bond generates rhodacycloheptene intermediate **B7b** with a *trans*-ring fusion in a process with a $14.8 \text{ kcal mol}^{-1}$ energy barrier (Figure 5). On the other hand, **B4a** evolves into the cycloadduct with *cis*-ring fusion, through a pathway that differs from that of **B4b** in two aspects. Firstly, there is no CO dissociation, and, secondly, the insertion of the allene takes place on the Rh–C(sp²) bond of **B4a**. The energy barrier for the formation of **B6a** is only $1.4 \text{ kcal mol}^{-1}$ (Figure 5).

The ring closure in **B7b** toward the *anti-4a* diastereoisomer was computed to be possible by passing over an energy barrier of $11.0 \text{ kcal mol}^{-1}$ to give **B8b**. In the pathway leading to the *syn-4a* diastereoisomer we observed that the stability of **B6a** significantly increased by $9.6 \text{ kcal mol}^{-1}$ when the two carbonyl ligands were lost to yield **B7a**. However, looking at the final step, the ring-closure process was observed to be more favorable if the carbonyl ligands were recovered, since **TS(B6a,B8a)** was located at $\Delta G^\ddagger = 16.2 \text{ kcal mol}^{-1}$ with respect to the most stable intermediate **B7b**. This is a much more plausible value than the corresponding reductive elimination via **TS(B7a,B8a')**: $\Delta G^\ddagger = 40.4 \text{ kcal mol}^{-1}$.

Overall, the catalytic cycle showed itself to be exergonic by $71.6\text{--}74.6 \text{ kcal mol}^{-1}$ and the energetic difference between TDI and TDTS was $15.1 \text{ kcal mol}^{-1}$ (oxidative addition) for the *anti* pathway, and $16.2 \text{ kcal mol}^{-1}$ (ring closure) for the *syn* pathway. The generation of the two diastereoisomers that have been experimentally detected could be justified by looking at the low differences in energy ($1.1 \text{ kcal mol}^{-1}$) of the rate-determining steps between the pathways leading to *syn-4a* and *anti-4a* (favoring the *anti-4a* diastereoisomer), which matches the empirical results. The results of the empirical tests carried out using ESI-MS to detect reaction intermediates support the type of intermediates proposed for this catalytic cycle. We were able to observe peaks corresponding to $[\text{RhCl}(\mathbf{3})(\text{CO})]$ species, which corroborate the proposed coordination sphere of the intermediates depicted in Scheme 7.

Comparison of the two proposed catalytic cycles allowed us to explain computationally the experimental detection of two diastereoisomers, since very small energetic differences were found between similar potential energy surfaces leading to the

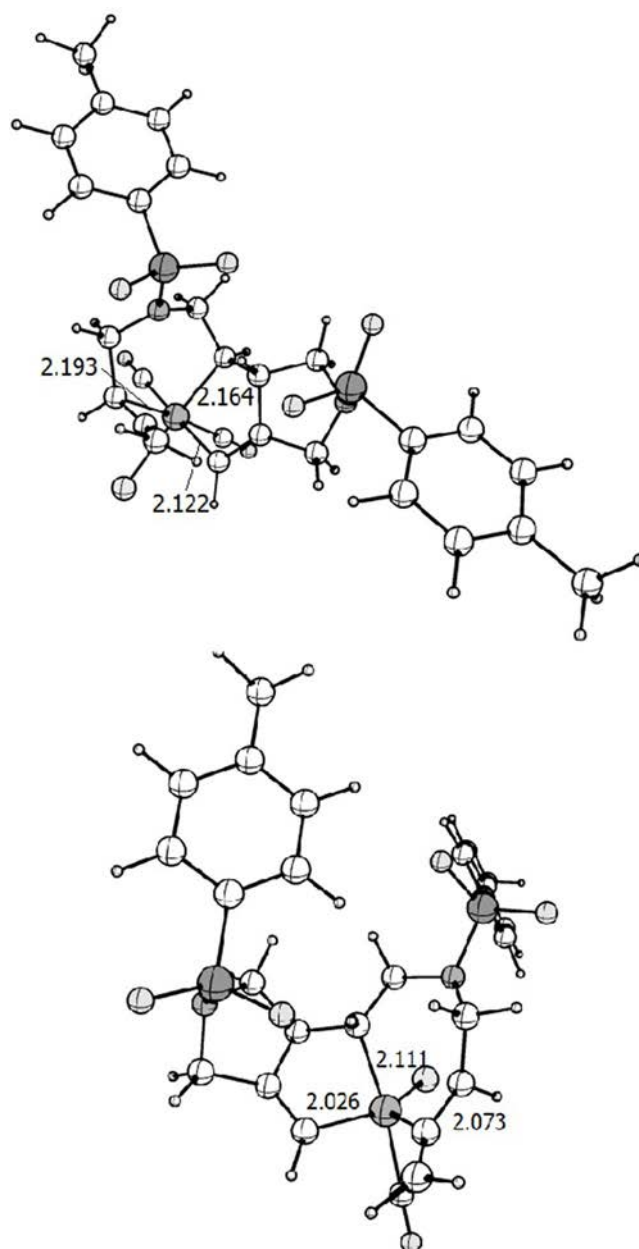


Figure 5. Optimized structures (B3LYP-D3/cc-pVDZ-PP) for **TS(B4a,B6a)** (top) and **TS(B5b,B7b)** (bottom). The most relevant distances given in Å.

syn-4 and the *anti-4* diastereoisomers. Furthermore, the difference in selectivity of the two catalytic systems can be attributed to the variation in the coordination sphere of the catalytically-active species: the $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst cycle involves a catalytic species with only a chloride ligand, whereas the outcome for the $[\text{RhCl}(\text{CO})_2]$ catalyst relies on the number of carbonyl units coordinated to the metallic center. On the other hand, the requirement for heating the system to 100°C when the $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst is employed and to just 60°C when $[\text{RhCl}(\text{CO})_2]$ is used is in accordance with the energy barriers found, since the first system requires about 30 kcal mol^{-1} to complete the cycle and only approximately 15 kcal mol^{-1} for the second system.

Conclusion

The reactivity of linear allene–(E)–ene–yne substrates bearing an *N*-tosyl tether was evaluated in the rhodium-catalyzed [2+2+2] cycloaddition reaction. Three catalytic systems were tested: the neutral Wilkinson's complex, cationic [Rh(cod)₂]BF₄ in combination with a biphosphine ligand, and the dimeric complex [RhCl(CO)₂]₂. All three catalysts were able to promote the cycloaddition regioselectively involving the internal double bonds of the allene, allowing for the preparation of scaffolds featuring an exocyclic double bond. However, the diastereoselectivity of the process seems to be catalyst-dependent. Regarding the mechanism operating in these transformations, it is important to highlight that oxidative addition always takes place between the alkyne and the alkene and that the diastereoselectivity is defined later during the allene insertion step. The allene inserts with the inner double bond preferentially at the Rh–C(sp³) bond. The variable and low diastereoselectivity of the process can be ascribed to the small differences in the rate-determining energy barriers.

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. All reactions requiring anhydrous conditions were conducted in oven-dried glassware under a dry nitrogen atmosphere. The solvents were removed under reduced pressure with a rotary evaporator. Crude reaction mixtures were purified by chromatography on a silica gel column (230–400 mesh) by using mixtures of hexane/ethyl acetate as the eluent.

¹H and ¹³C NMR spectra were measured on a 400 or a 300 MHz NMR spectrometer. ¹H and ¹³C chemical shifts (δ) are referenced to internal solvent resonances and reported relative to SiMe₄. The chemical shifts were assigned on the basis of 2D COSY, NOESY, DOSY, ¹H–¹³C HSQC, ¹H–¹³C HMBC, and ¹H–³¹P HMBC experiments performed under routine conditions. Electrospray mass spectrometry analyses were recorded on an Esquire 6000 ion trap mass spectrometer (Bruker) equipped with an electrospray ion source, operated in positive ESI(+) and negative ESI(–) ion modes. IR spectra were recorded with an FTIR instrument using a single reflection ATR system as a sampling accessory.

Rh^I-catalyzed [2+2+2] cycloaddition reaction of allene–ene–yne derivative **3a**

General procedure using catalytic system A (Entry 1, Table 1)

In a 10 mL two-necked round-bottom flask, a mixture of **3a** (24.6 mg, 0.050 mmol) and tris(triphenylphosphine)rhodium(I) chloride (5.6 mg, 0.006 mmol, 10 mol%) was dissolved in anhydrous toluene (3 mL) and heated to 100 °C. The mixture was stirred for 5 h until completion (TLC monitoring). The solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel using a mixture of hexanes/ethyl acetate (8:2) as the eluent to afford **4a** (13.8 mg, 56% yield) as a colorless solid.

General procedure using catalytic system B (Entry 5, Table 1)

In a 10 mL two-necked round-bottom flask, a mixture of bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (2.1 mg, 0.0052 mmol, 10 mol%) and (*R*)-DTBM-SegPhos (6.6 mg, 0.0056 mmol) was dissolved in anhydrous dichloromethane (3 mL) and hydrogenated for 30 min. The solvent was then removed under vacuum, anhydrous dichloroethane (3 mL) was introduced, and the reaction mixture was heated to 60 °C. Allene–ene–yne **3a** (25.4 mg, 0.052 mmol) was slowly added to the previous mixture. The mixture was stirred for 5 h until completion (TLC monitoring). The solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (8:2) as the eluent to afford **4a** (7.8 mg, 31% yield) as a colorless solid.

General procedure using catalytic system C (Entry 8, Table 1)

In a 10 mL two-necked round-bottom flask, **3a** (24.2 mg, 0.050 mmol) was dissolved in anhydrous toluene (3 mL) and heated to 60 °C. Di-μ-chloro-tetracarbonyldirrhodium(I) (2.37 mg, 0.006 mmol, 10 mol%) was slowly added to the previous solution. The mixture was stirred for 20 min until completion (TLC monitoring). The solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel using a mixture of hexane/EtOAc (8:2) as the eluent to afford **4a** (11.8 mg, 49% yield) as a colorless solid.

Cycloadduct 4a was obtained as an inseparable mixture of the two diastereoisomers *syn* and *anti*. ¹H NMR (500 MHz, CDCl₃, TMS): δ(ppm) 1.48 (m, 1H_{anti}), 1.74 (m, 1H_{syn}), 1.84 (m, 1H_{syn}), 2.34 (m, 1H_{anti}), 2.43 (m, 1H_{syn}), 2.46 (s, 3H_{syn} + 3H_{anti}), 2.46–2.52 (m, 2H_{anti}), 2.51 (s, 3H_{syn} + 3H_{anti}), 2.83 (dd, ²J_{H–H} = 11.5 Hz, ³J_{H–H} = 8.8 Hz, 1H_{syn}), 2.90 (m, 1H_{syn}), 2.97 (m, 1H_{anti}), 3.14 (dd, ²J_{H–H} = ³J_{H–H} = 10.5 Hz, 1H_{anti}), 3.30 (d, ²J_{H–H} = 10.5 Hz, 1H_{syn}), 3.39 (dd, ²J_{H–H} = 10.5 Hz, ³J_{H–H} = 4.5 Hz, 1H_{syn}), 3.55 (m, 1H_{syn}), 3.60–3.66 (m, 2H_{syn} + 1H_{anti}), 3.69 (d, ²J_{H–H} = 15.0 Hz, 1H_{anti}), 3.76–3.84 (m, 2H_{anti}), 4.01 (d, ²J_{H–H} = 15.0 Hz, 1H_{syn}), 4.10 (d, ²J_{H–H} = 15.0 Hz, 1H_{syn}), 4.68 (s, 1H_{anti}), 4.88 (s, 1H_{anti}), 4.91 (s, 1H_{syn}), 4.97 (s, 1H_{syn}), 5.93 (s, 1H_{syn}), 5.98 (s, 1H_{anti}), 7.35 (d, ³J_{H–H} = 8.0 Hz, 2H_{syn} + 2H_{anti}), 7.40 (d, ³J_{H–H} = 8.0 Hz, 2H_{syn} + 2H_{anti}), 7.69 (d, ³J_{H–H} = 8.0 Hz, 2H_{syn} + 2H_{anti}), 7.74 (d, ³J_{H–H} = 8.0 Hz, 2H_{syn} + 2H_{anti}); ¹³C NMR (75 MHz, CDCl₃, TMS, *syn*): δ(ppm) 21.6, 29.7, 38.3, 39.9, 42.2, 50.8, 51.0, 52.5, 52.9, 115.2, 120.6, 127.1, 127.6, 129.9, 138.0, 138.7, 143.9, 144.3; HRMS calcd For [C₂₅H₂₈N₂O₄S₂ + Na]⁺: 507.1388. Found: 507.1388.

Cycloadduct 4b was obtained as pure *syn* diastereoisomer. IR(ATR): $\tilde{\nu}$ (cm^{–1}) 2922, 1334, 1153; ¹H NMR (400 MHz, CDCl₃, TMS): δ(ppm) 1.63 (br, 3H), 1.73 (m, 1H), 1.81 (m, 1H), 2.35 (dd, ²J_{H–H} = 10.4 Hz, ³J_{H–H} = 8.6 Hz, 1H), 2.44 (s, 3H), 2.49 (s, 3H), 2.81 (dd, ²J_{H–H} = 11.6 Hz, ³J_{H–H} = 9.6 Hz, 1H), 2.94 (s, 1H), 3.23 (d, ²J_{H–H} = 10.4 Hz, 1H), 3.38 (dd, ²J_{H–H} = 10.4 Hz, ³J_{H–H} = 4.8 Hz, 1H), 3.52–3.62 (m, 3H), 3.98 (d, ²J_{H–H} = 15.2 Hz, 1H), 4.85 (s, 1H), 5.06 (s, 1H), 7.33 (d, ³J_{H–H} = 8.4 Hz, 2H), 7.38 (d, ³J_{H–H} = 8.4 Hz, 2H), 7.68 (d, ³J_{H–H} = 8.4 Hz, 2H), 7.72 (d, ³J_{H–H} = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ(ppm) 21.6, 30.9, 38.3, 40.0, 42.2, 50.8, 51.0, 52.5, 53.0, 115.2, 120.6, 127.1, 127.6, 129.8, 129.9, 138.1, 138.8, 144.2, HRMS calcd For [C₂₆H₃₀N₂O₄S₂ + Na]⁺: 521.1539. Found: 521.1548.

Cycloadduct 4c was obtained as pure *syn* diastereoisomer. IR(ATR): $\tilde{\nu}$ (cm^{–1}) 2925, 1339, 1155; ¹H NMR (400 MHz, CDCl₃, TMS): δ(ppm) 0.91 (t, ³J_{H–H} = 7.6 Hz, 3H), 1.79–1.82 (m, 2H), 2.06 (q, ³J_{H–H} = 7.6 Hz, 2H), 2.36 (m, 1H), 2.44 (s, 3H), 2.49 (s, 3H), 2.82 (dd, ²J_{H–H} = 11.6 Hz, ³J_{H–H} = 9.6 Hz, 3H), 2.92 (m, 1H), 3.23 (d, ²J_{H–H} = 10.4 Hz, 1H), 3.36 (dd, ²J_{H–H} = 10.4 Hz, ³J_{H–H} = 4.4 Hz, 1H), 3.52–3.63 (m, 3H), 3.98 (m, 1H), 4.87 (s, 1H), 5.10 (s, 1H), 7.34 (d, ³J_{H–H} = 8.4 Hz, 2H), 7.38 (d, ³J_{H–H} = 8.4 Hz, 2H), 7.68 (d, ³J_{H–H} = 8.4 Hz, 2H), 7.72 (d, ³J_{H–H} = 8.4 Hz, 2H).

2H); ^{13}C NMR (100 MHz, CDCl_3 , TMS): $\delta(\text{ppm})$ 13.0, 21.6, 21.8, 29.7, 38.9, 39.8, 43.5, 51.4, 52.5, 53.2, 111.8, 127.1, 127.7, 130.8, 132.6, 133.6, 133.8, 138.3, 143.9, 144.2; HRMS calcd For $[\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 535.1696. Found: 535.1675.

Cycloadduct 4d was obtained as an inseparable mixture of the two diastereoisomers *syn* and *anti*. ^1H NMR (400 MHz, CDCl_3 , TMS, *syn*): $\delta(\text{ppm})$ 0.90 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H), 0.95 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H), 1.63 (m, 1H), 1.75 (m, 1H), 2.35–2.45 (m, 1H + 1H), 2.42 (s, 3H), 2.48 (s, 3H), 2.71 (dd, $^2J_{\text{H-H}} = 11.6$ Hz, $^3J_{\text{H-H}} = 9.6$ Hz, 1H), 2.98 (m, 1H), 3.26 (d, $^2J_{\text{H-H}} = 10.4$ Hz, 1H), 3.38 (dd, $^2J_{\text{H-H}} = 10.4$ Hz, $^3J_{\text{H-H}} = 4.8$ Hz, 1H), 3.54–3.60 (m, 1H + 1H + 1H), 3.95 (m, 1H), 5.19 (d, $^3J_{\text{H-H}} = 10.4$ Hz, 1H), 5.76 (d, $^3J_{\text{H-H}} = 2.4$ Hz, 1H), 7.32 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 2H), 7.38 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 2H), 7.66 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 2H), 7.72 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , TMS, *syn*): $\delta(\text{ppm})$ 21.6, 23.0, 23.3, 27.6, 38.1, 38.5, 39.9, 50.0, 50.8, 52.3, 53.2, 122.2, 127.1, 127.6, 128.2, 129.8, 129.9, 132.7, 133.7, 134.5, 140.0, 143.8, 144.3; HRMS calcd For $[\text{C}_{28}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 549.1858. Found: 549.1855.

Cycloadduct 4e was obtained as an inseparable mixture of the two diastereoisomers *syn* and *anti*. ^1H NMR (300 MHz, CDCl_3 , TMS): $\delta(\text{ppm})$ 1.28 (m, 1H_{*anti*}), 1.82–1.88 (m, 2H_{*syn*}), 2.38 (m, 1H_{*anti*}), 2.42–2.48 (m, 1H_{*syn*} + 2H_{*anti*}), 2.44 (s, 3H_{*syn*} + 3H_{*anti*}), 2.50 (s, 3H_{*syn*} + 3H_{*anti*}), 2.77–2.94 (m, 2H_{*syn*} + 1H_{*anti*}), 3.01 (m, 1H_{*anti*}), 3.14 (m, 1H_{*anti*}), 3.27–3.38 (m, 2H_{*syn*}), 3.59–3.78 (m, 3H_{*syn*} + 4H_{*anti*}), 4.04 (d, $^2J_{\text{H-H}} = 15.0$ Hz, 1H_{*syn*}), 4.13 (d, $^2J_{\text{H-H}} = 15.3$ Hz, 1H_{*anti*}), 5.97 (s, 1H_{*syn*}), 6.03 (s, 1H_{*anti*}), 6.38 (s, 1H_{*syn*}), 6.41 (s, 1H_{*anti*}), 7.13–7.38 (m, 9H_{*syn*} + 9H_{*anti*}), 7.54–7.75 (m, 4H_{*syn*} + 4H_{*anti*}); ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta(\text{ppm})$ 21.6, 38.4, 38.7, 40.3, 42.5, 50.7, 51.0, 52.4, 122.8, 125.1, 127.2, 127.5, 127.7, 128.2, 128.6, 128.8, 129.8, 131.3, 132.6, 132.8, 133.4, 134.9, 136.8, 136.9, 143.9, 144.3; HRMS calcd For $[\text{C}_{31}\text{H}_{32}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 583.1701. Found: 583.1697.

Cycloadduct 4g: was obtained as an inseparable mixture of the two diastereoisomers *syn* and *anti*. ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta(\text{ppm})$ 0.86–0.97 (m, 6H_{*syn*} + 3H_{*syn*} + 6H_{*anti*} + 3H_{*anti*}), 1.47 (m, 1H_{*anti*}), 1.67–1.74 (m, 2H_{*syn*}), 1.90 (m, 1H_{*syn*}), 1.98–2.05 (m, 2H_{*syn*}), 2.07–2.11 (m, 2H_{*anti*}), 2.30 (m, 1H_{*anti*}), 2.35–2.43 (m, 1H_{*syn*} + 2H_{*anti*}), 2.43 (s, 6H_{*syn*} + 6H_{*anti*}), 2.70 (dd, $^2J_{\text{H-H}} = 11.6$ Hz, $^3J_{\text{H-H}} = 10.0$ Hz, 1H_{*anti*}), 2.82 (dd, $^2J_{\text{H-H}} = 10.8$ Hz, $^3J_{\text{H-H}} = 9.6$ Hz, 1H_{*syn*}), 3.01 (m, 1H_{*anti*}), 3.01 (m, 1H_{*anti*}), 3.15 (dd, $^2J_{\text{H-H}} = 10.8$ Hz, $^3J_{\text{H-H}} = 9.2$ Hz, 1H_{*syn*}), 3.21 (d, $^3J_{\text{H-H}} = 10.8$ Hz, 1H_{*anti*}), 3.70 (dd, $^2J_{\text{H-H}} = 10.4$ Hz, $^4J_{\text{H-H}} = 4.4$ Hz, 1H_{*syn*}), 3.46 (dd, $^2J_{\text{H-H}} = 9.2$ Hz, $^3J_{\text{H-H}} = 7.2$ Hz, 1H_{*syn*}), 3.51–3.74 (m, 6H_{*syn*} + 6H_{*anti*}), 3.94–4.12 (m, 1H_{*syn*} + 1H_{*anti*}), 5.30 (dd, $^2J_{\text{H-H}} = 10.4$ Hz, $^3J_{\text{H-H}} = 2.4$ Hz, 1H_{*syn*}), 5.34 (d, $^2J_{\text{H-H}} = 10.0$ Hz, 1H_{*anti*}), 7.32–7.39 (m, 4H_{*syn*} + 4H_{*anti*}), 7.68–7.72 (m, 4H_{*syn*} + 4H_{*anti*}); ^{13}C NMR (100 MHz, CDCl_3 , TMS): $\delta(\text{ppm})$ 13.3, 21.6, 21.9, 23.1, 23.2, 23.5, 23.9, 27.8, 28.1, 38.4, 38.9, 40.0, 43.2, 43.8, 45.5, 50.3, 50.4, 52.3, 53.5, 126.8, 127.2, 127.4, 127.8, 129.8, 129.9, 130.0, 130.9, 131.3, 132.6, 133.9, 134.6, 143.7, 143.9, 144.0, 144.3; HRMS calcd For $[\text{C}_{30}\text{H}_{38}\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$: 577.2171. Found: 577.2171.

Cycloadduct 4h was obtained as an inseparable mixture of the two diastereoisomers *syn* and *anti*. ^1H NMR (400 MHz, toluene- D_8 , TMS): $\delta(\text{ppm})$ 1.53 (m, 1H_{*syn*}), 1.81 (m, 1H_{*anti*}), 1.95–1.99 (m, 2H_{*syn*} + 2H_{*anti*}), 1.95 (s, 3H_{*syn*} + 3H_{*anti*}), 2.39 (m, 1H_{*syn*}), 2.63 (dd, $^2J_{\text{H-H}} = 10.4$ Hz, $^3J_{\text{H-H}} = 9.2$ Hz, 1H_{*anti*}), 2.72 (dd, $^2J_{\text{H-H}} = 10.4$ Hz, $^3J_{\text{H-H}} = 8.0$ Hz, 1H_{*anti*}), 2.78–2.82 (m, 1H_{*syn*} + 1H_{*anti*}), 3.04 (m, 1H_{*syn*}), 3.35 (dd, $^2J_{\text{H-H}} = 9.2$ Hz, $^3J_{\text{H-H}} = 7.2$ Hz, 1H_{*anti*}), 3.50 (t, $^2J_{\text{H-H}} = 9.5$ Hz, 1H_{*anti*}), 3.67–3.78 (m, 1H_{*syn*} + 3H_{*anti*}), 3.89–3.96 (m, 2H_{*syn*}), 4.08 (d, $^3J_{\text{H-H}} = 14.8$ Hz, 1H_{*anti*}), 4.18 (d, $^3J_{\text{H-H}} = 14.0$ Hz, 1H_{*syn*}), 4.42 (s, 1H_{*syn*}), 4.62 (s, 1H_{*anti*}), 4.74 (s, 1H_{*syn*}), 5.49 (s, 1H_{*anti*}), 6.80 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H_{*syn*}), 6.84 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H_{*anti*}), 7.64 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H_{*syn*}), 7.72 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H_{*anti*}); ^{13}C NMR (100 MHz, toluene- D_8 , TMS): $\delta(\text{ppm})$ 13.7, 41.4, 42.1, 45.9, 48.9, 50.4, 51.6, 51.9, 60.9, 107.5, 113.1, 115.7, 129.4,

129.5, 130.2, 134.3, 136.0, 142.5, 143.5, 144.5, 144.5; HRMS calcd For $[\text{C}_{18}\text{H}_{21}\text{NO}_3\text{S} + \text{Na}]^+$: 354.1140. Found: 354.1134.

Computational details

All geometry optimizations were performed without symmetry constraints using the hybrid DFT B3LYP^[18] method with the all-electron cc-pVDZ basis set for P, Cl, O, C, and H^[19] and the cc-pVDZ-PP basis set containing an effective core relativistic pseudopotential for Rh.^[20] The D3 Grimme energy corrections for dispersion with their original damping functions^[21] were added in all B3LYP/cc-pVDZ-PP calculations. Analytical Hessians were computed at the B3LYP-D3/cc-pVDZ level of theory to determine the nature of stationary points (one or zero imaginary frequencies for transition states and energy minima, respectively), and to calculate unscaled zero-point energies (ZPEs) as well as thermal corrections and entropy effects by using the standard statistical-mechanics relationships for an ideal gas.^[22] These last two terms were computed at 373.15 K (for the $[\text{RhCl}(\text{PPh}_3)_3]$ catalytic cycle) or 333.15 K (for the $[\text{RhCl}(\text{CO})_2]_2$ catalytic cycle) and at 1 atm to provide the reported relative Gibbs free energies. Furthermore, the connectivity between stationary points was established by intrinsic reaction path calculations.^[23] All calculations were performed with the Gaussian 09^[24] program package. Previous studies found that solvent effects attributed to toluene in [2+2+2] cycloadditions are minor, likely owing to the absence of charged or polarized intermediates and transition states in the reaction mechanism.^[10a,25] Because the reactions studied are carried out in toluene solution, solvent effects have not been included in the present calculations.

Supporting Information

The Supporting Information contains experimental procedures for the synthesis of the substrates and full spectroscopic data for all new compounds and intermediates, Gibbs free energy profiles for all possible pathways not included in the main paper, and Cartesian coordinates of all reactants, intermediates, transition states, and products of the reactions.

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Conflict of interest

The authors declare no conflict of interest.

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