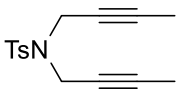
NEW CHALLENGES IN Rh(I)-CATALYSED [2+2+2] CYCLOADDITION REACTION

-SUPPLEMENTARY DATA-

Martí Fernández Wang

SUPPLEMENTARY DATA – CHAPTER 3



1a

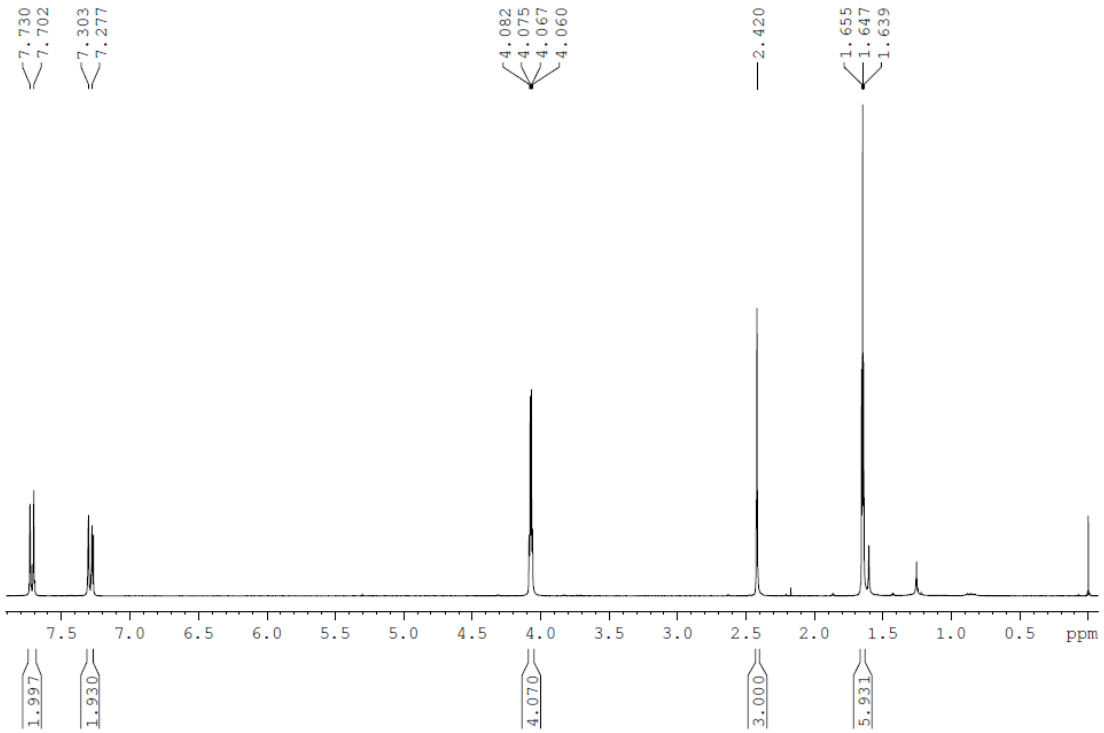


Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **1a**

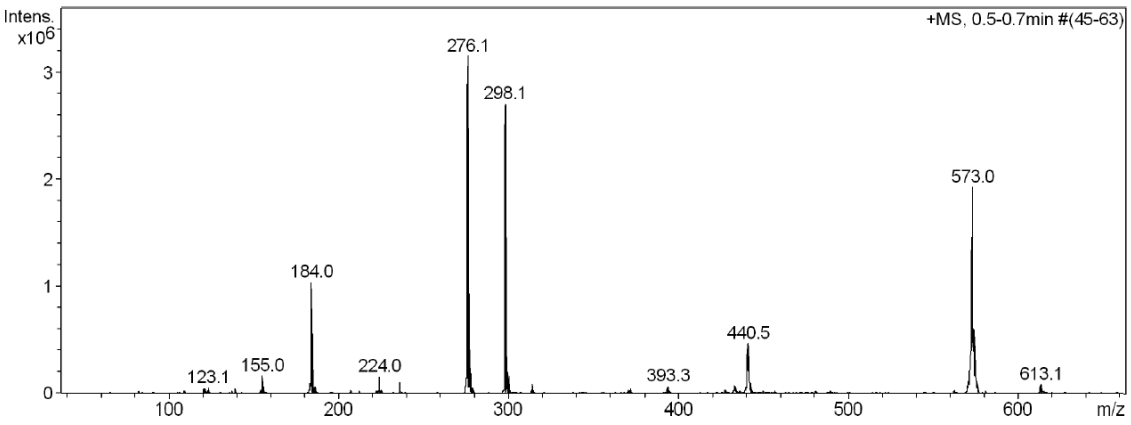


Figure S2: ESI-MS (*m/z*) spectrum of **1a**

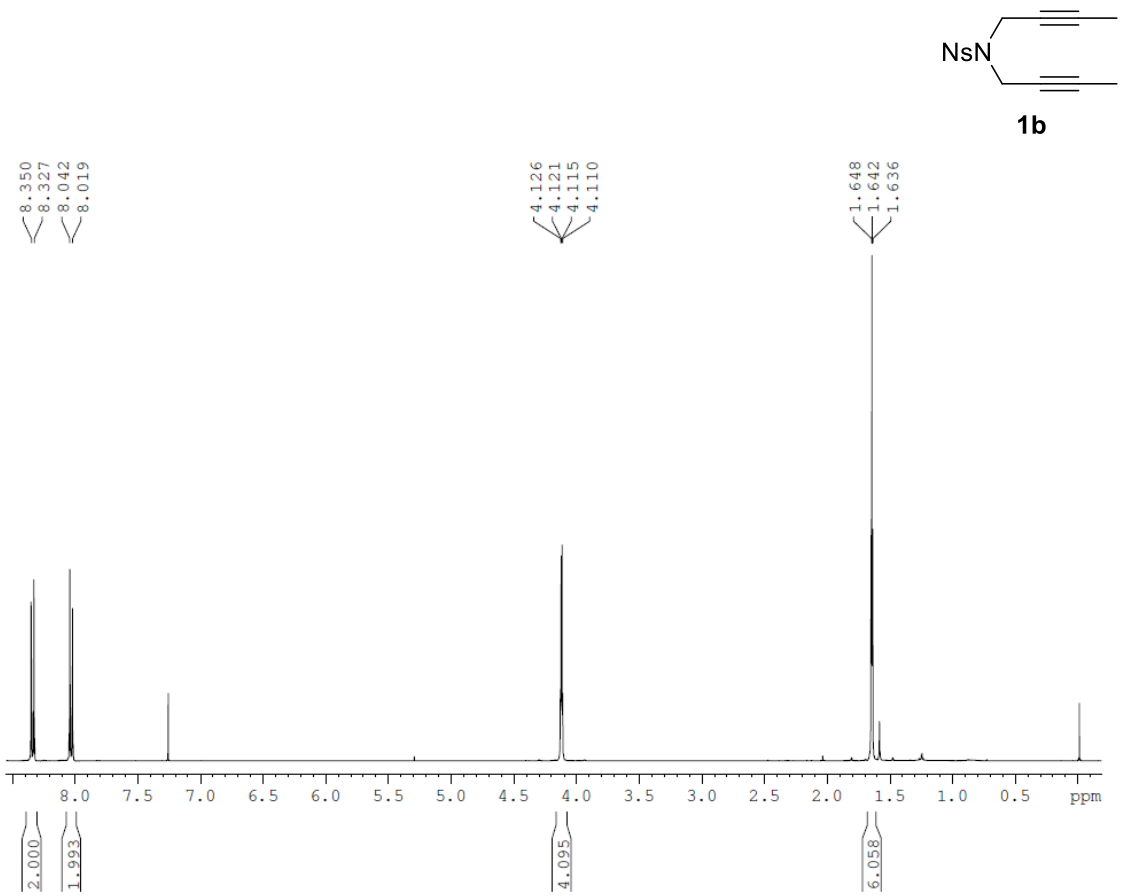


Figure S3: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1b**

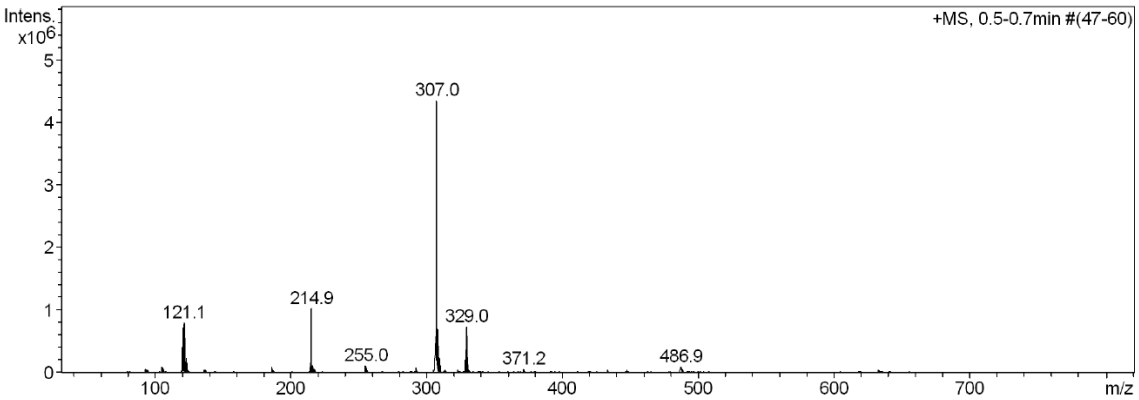
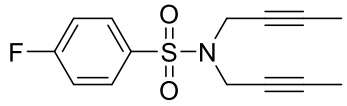


Figure S4: ESI-MS (*m/z*) spectrum of **1b**



1c

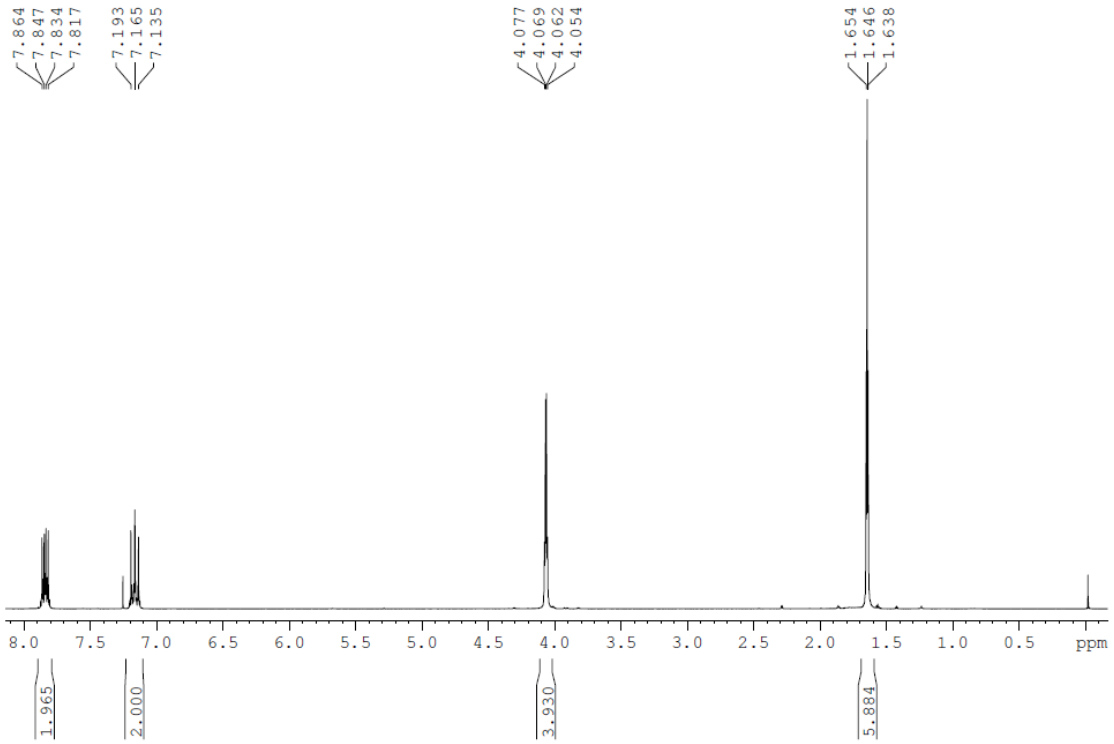


Figure S5: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **1c**

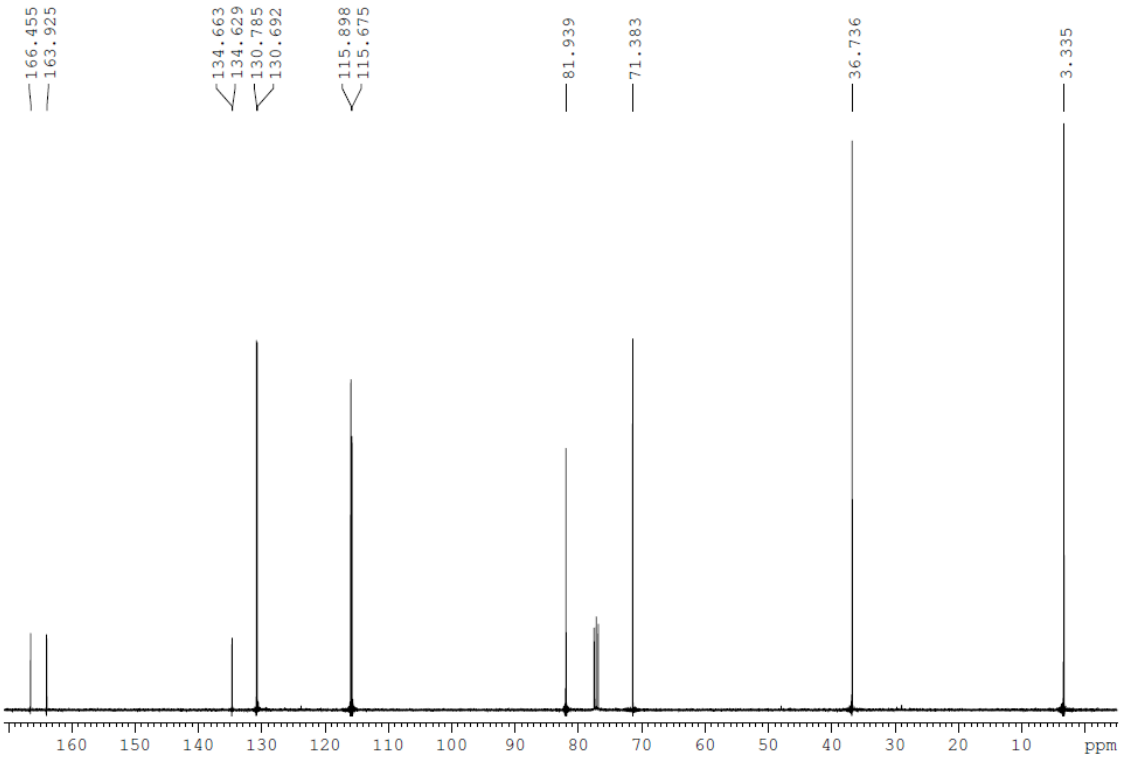


Figure S6: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1c**

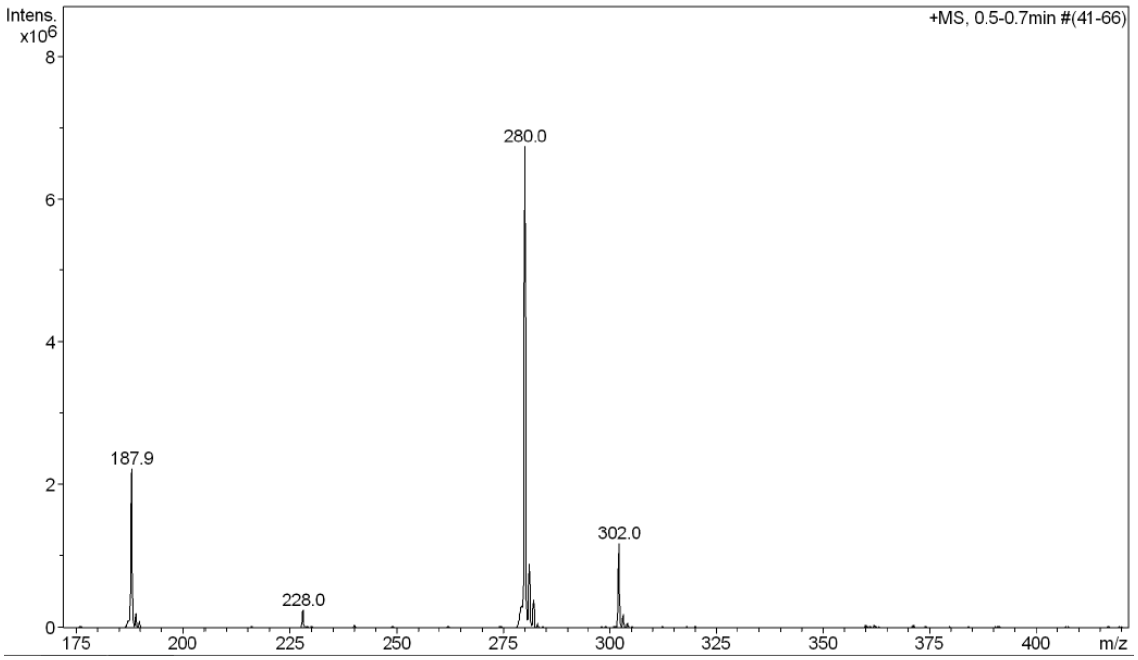


Figure S7: ESI-MS (*m/z*) spectrum of **1c**

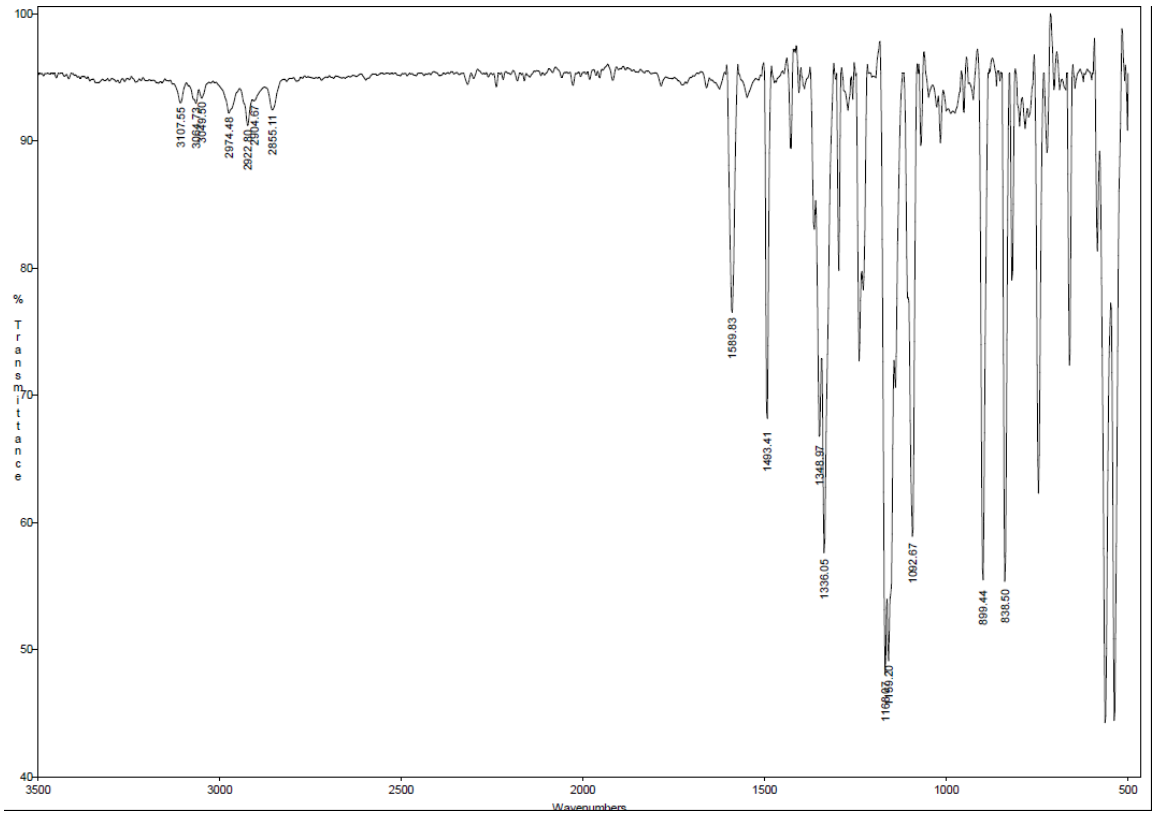


Figure S8: IR (ATR) spectrum of **1c**

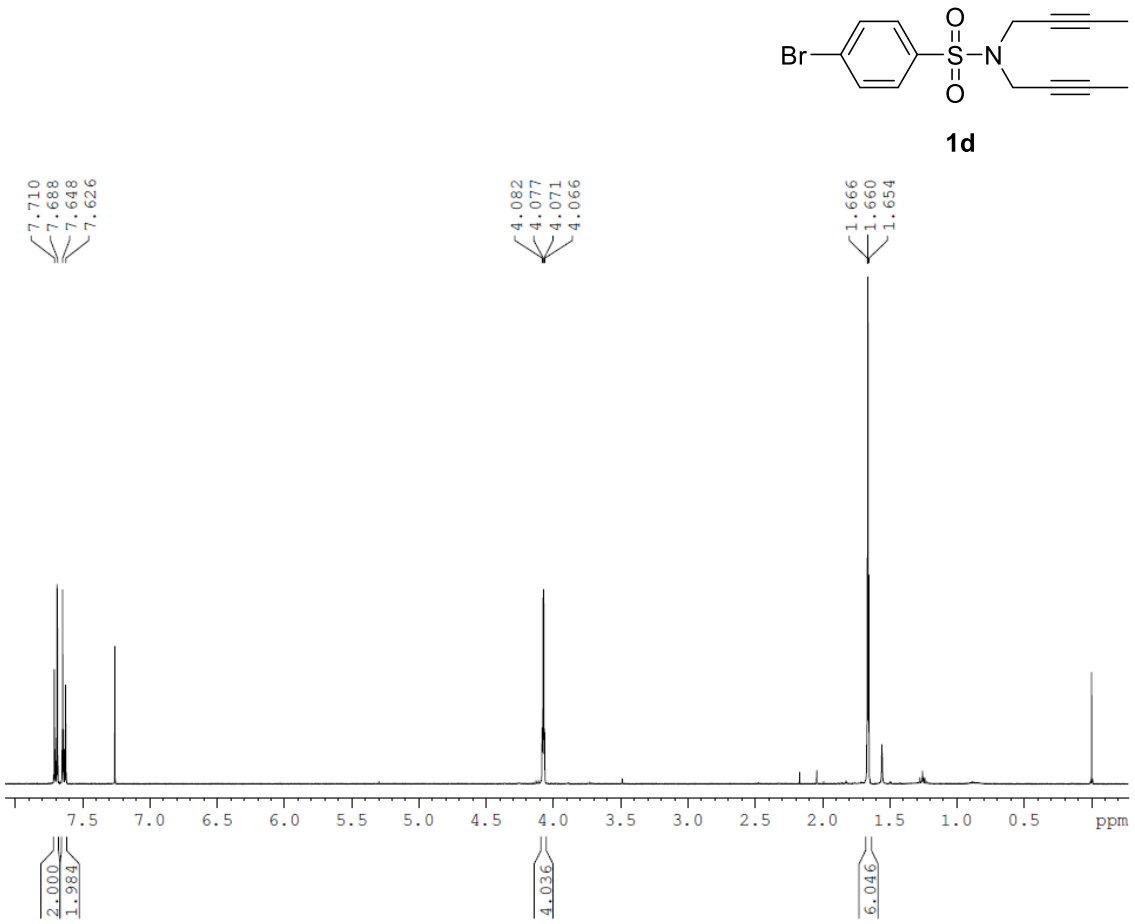


Figure S9: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **1d**

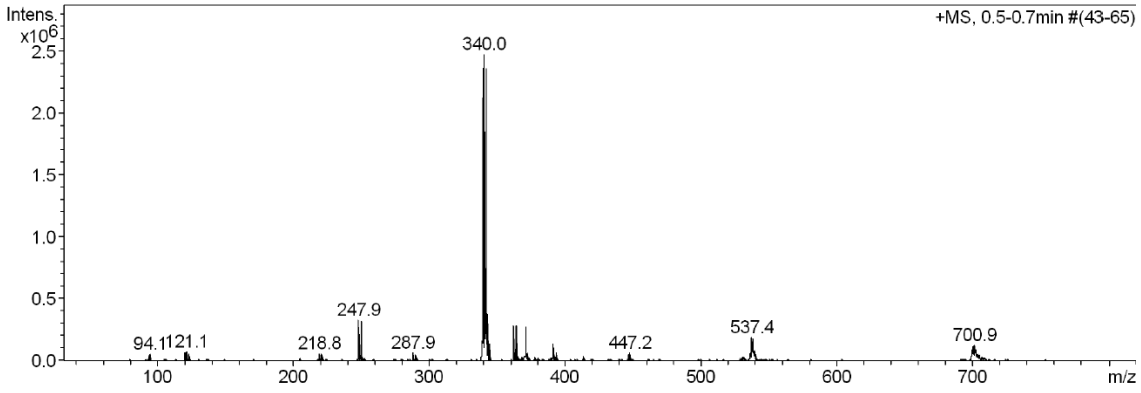
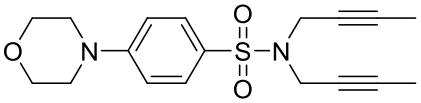


Figure S10: ESI-MS (*m/z*) spectrum of **1d**



1e

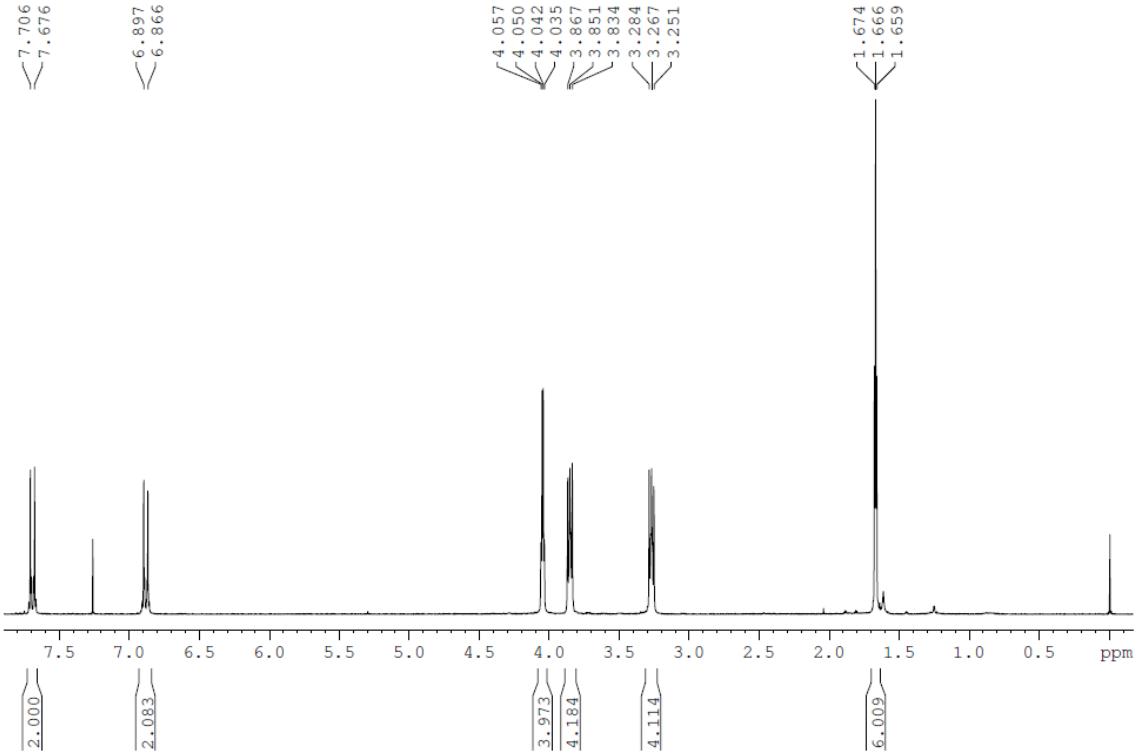


Figure S11: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **1e**

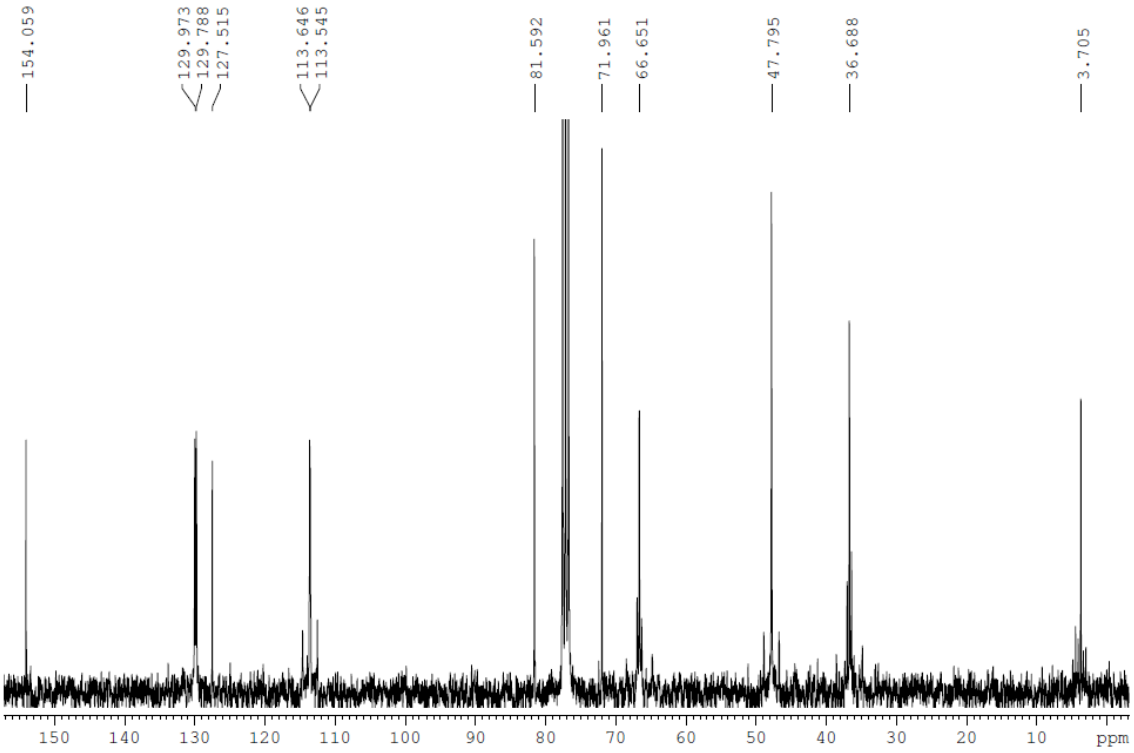


Figure S12: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **1e**

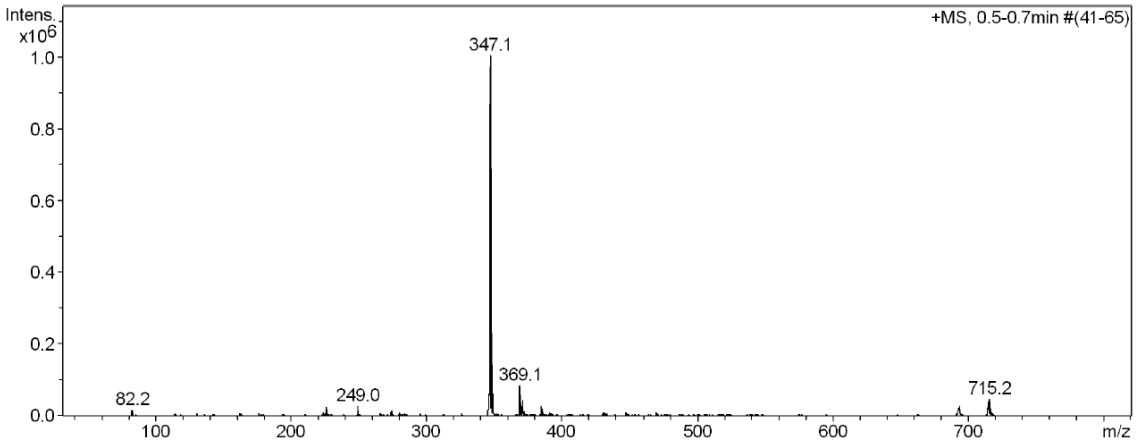


Figure S13: ESI-MS (*m/z*) spectrum of **1e**

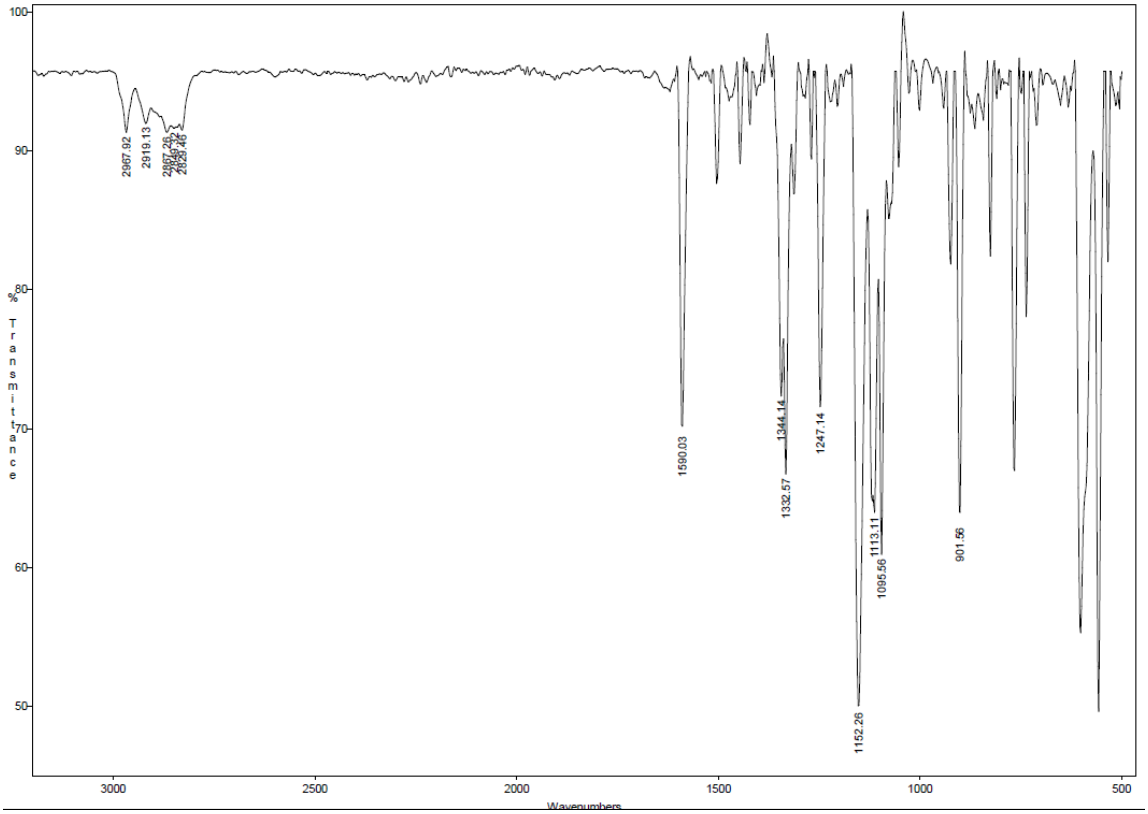


Figure S14: IR (ATR) spectrum of **1e**

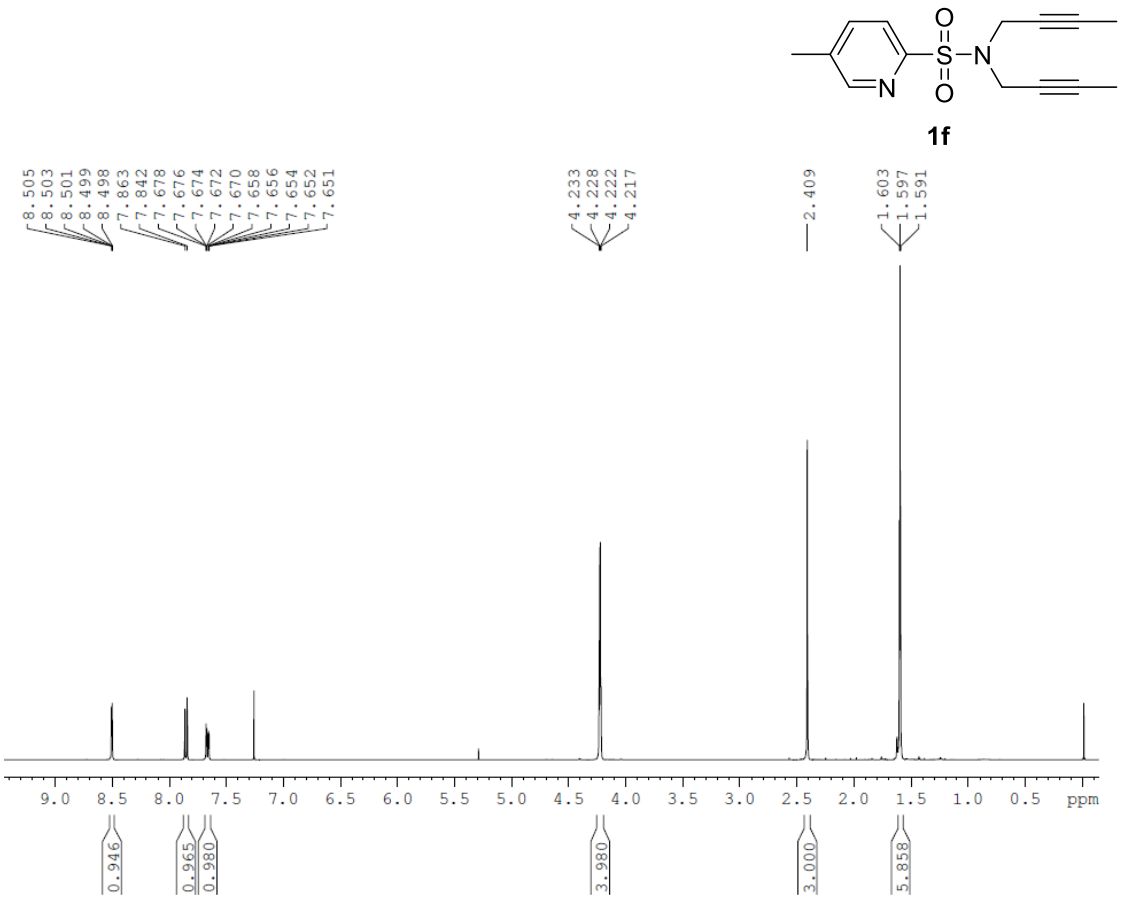


Figure S15: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1f**

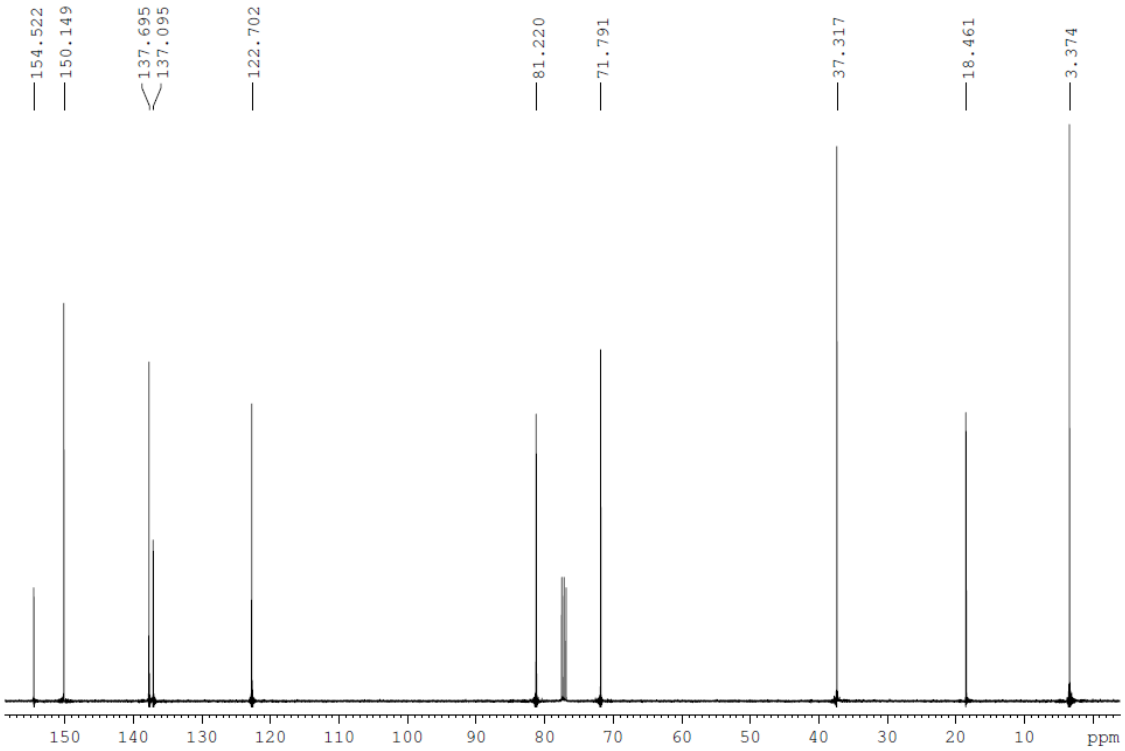


Figure S16: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1f**

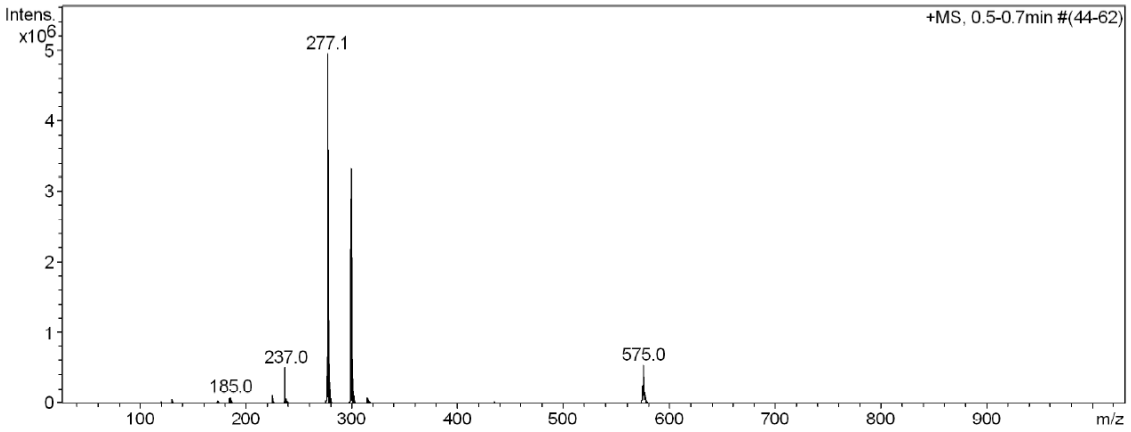
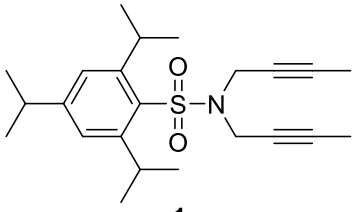


Figure S17: ESI-MS (*m/z*) spectrum of **1f**



1g

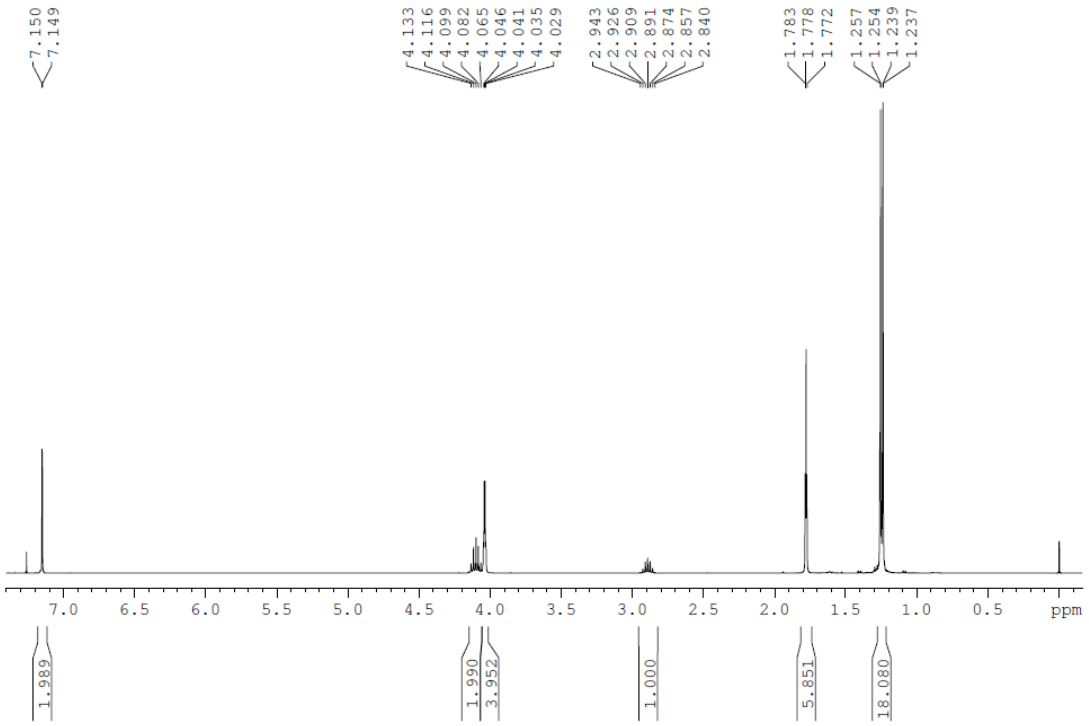


Figure S18: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1g**

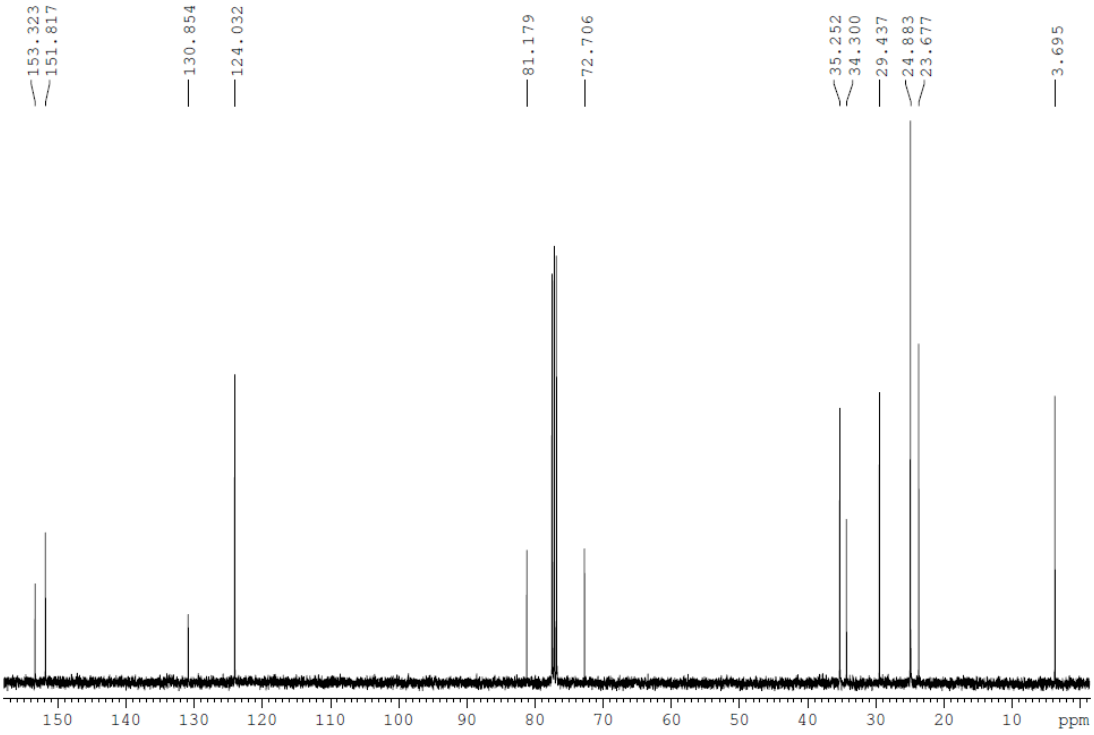


Figure S19: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1g**

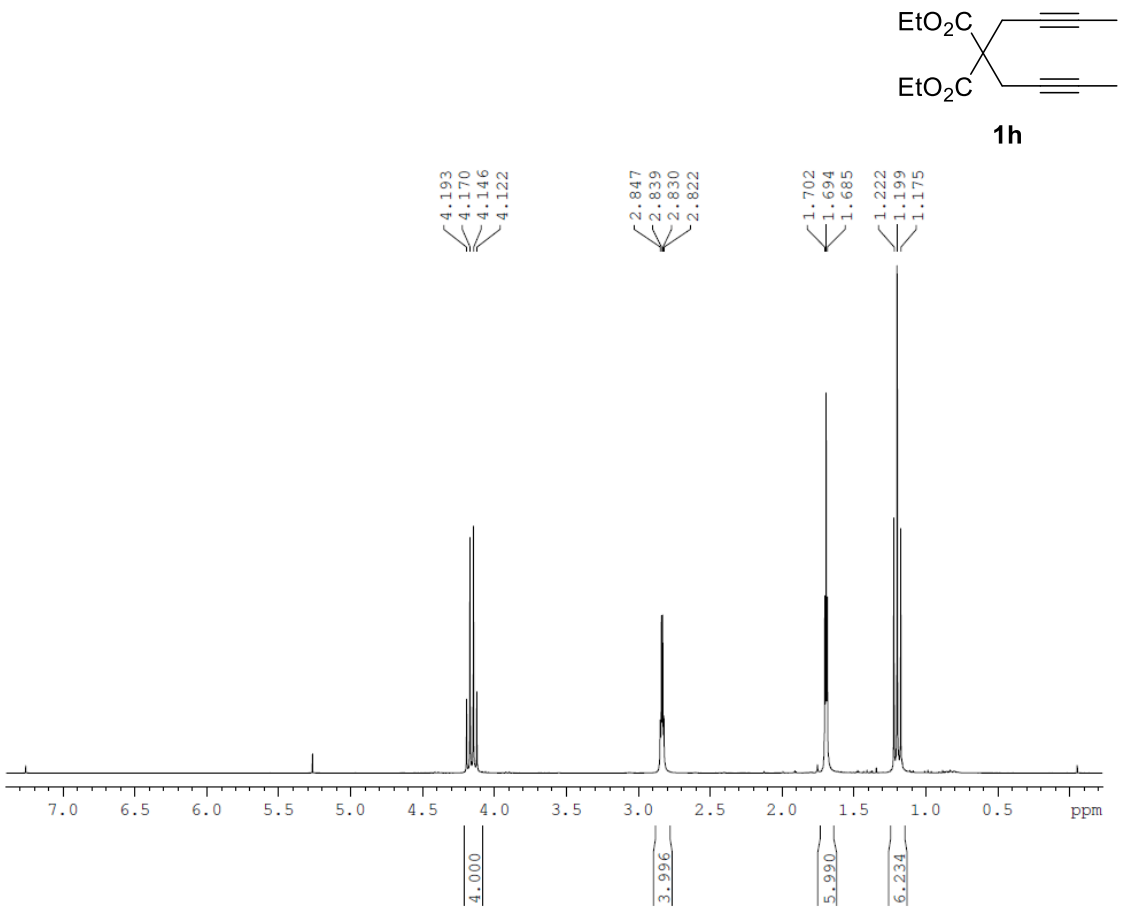


Figure S20: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **1h**

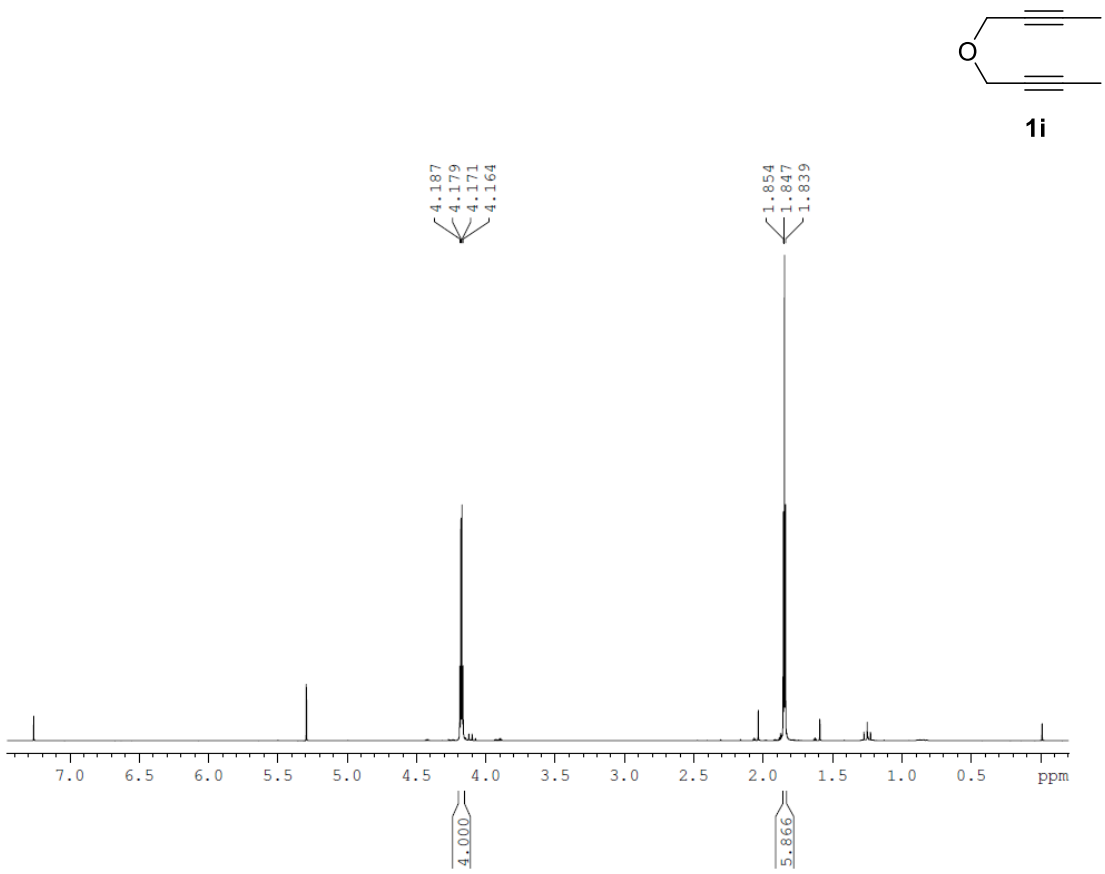
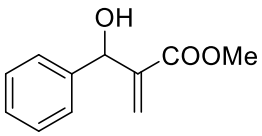


Figure S21: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **1i**



2a

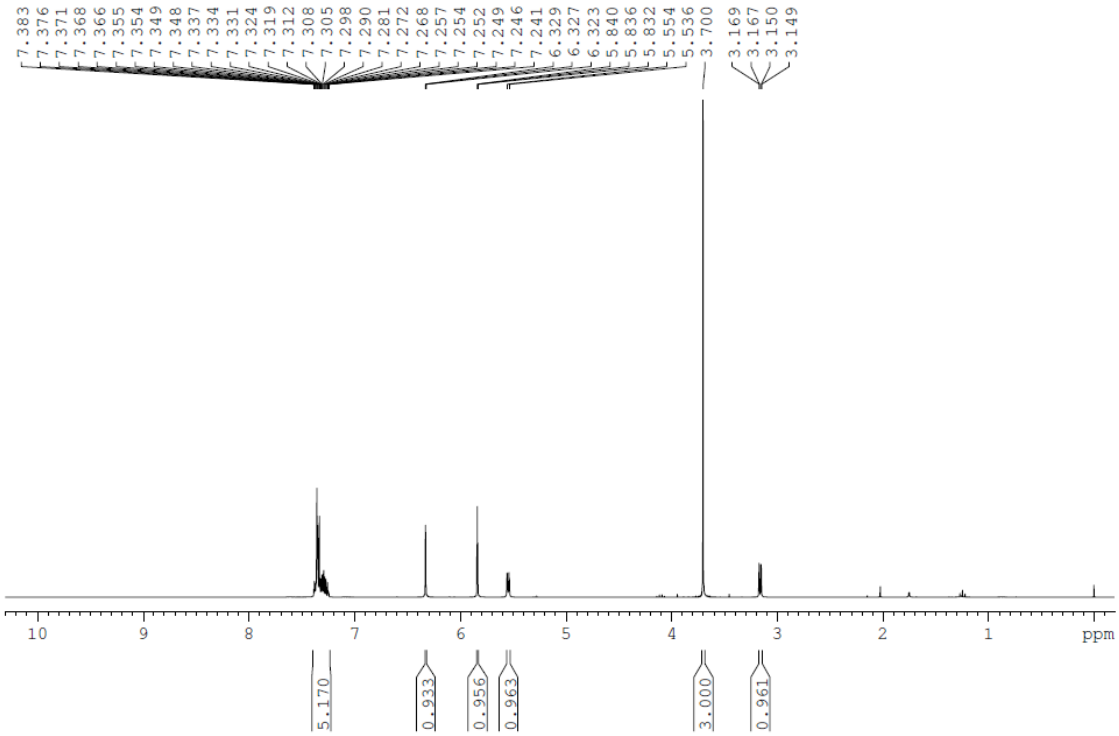


Figure S22: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **2a**

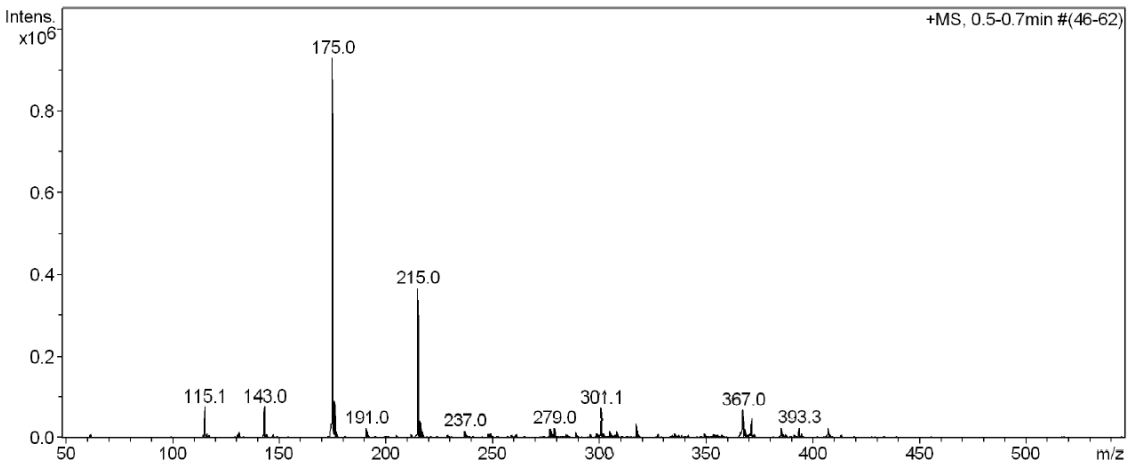


Figure S23: ESI-MS (*m/z*) spectrum of **2a**

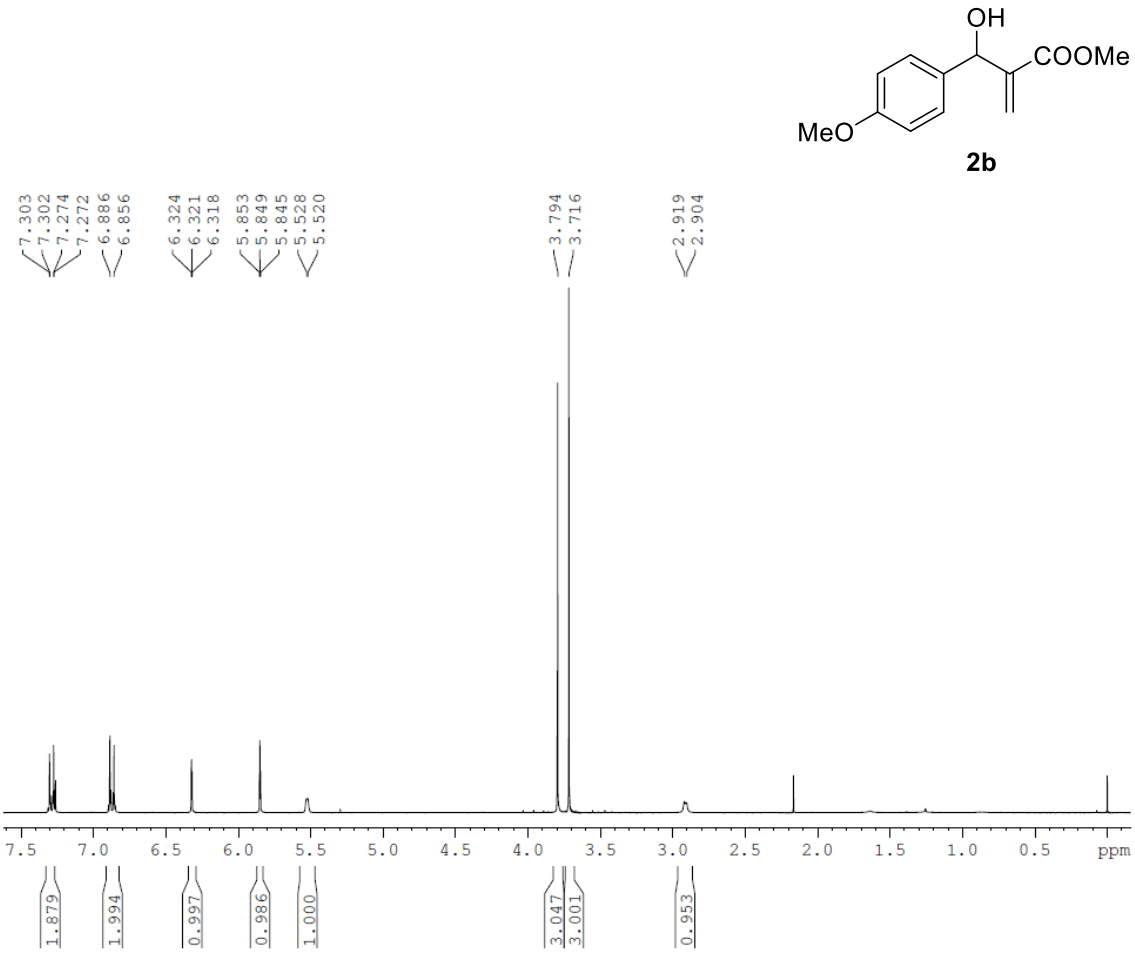


Figure S24: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **2b**

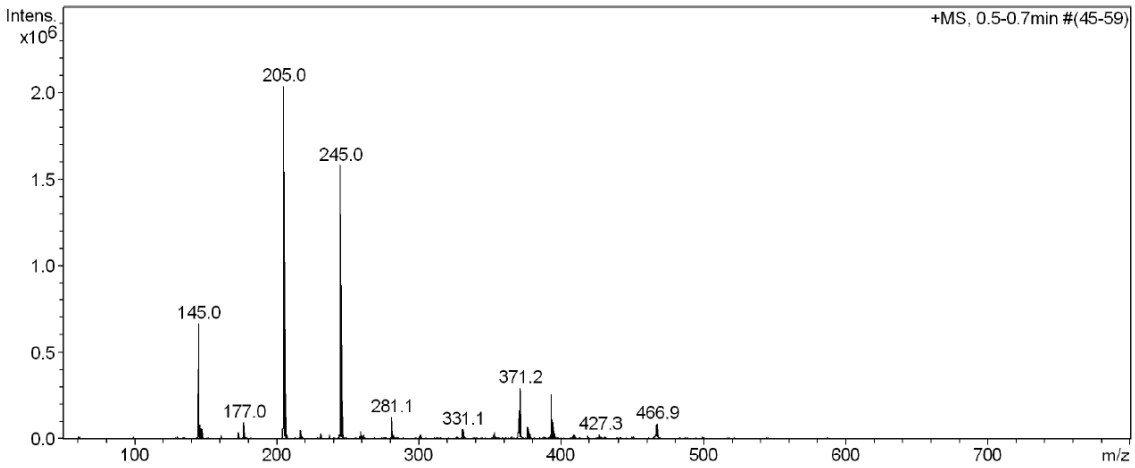
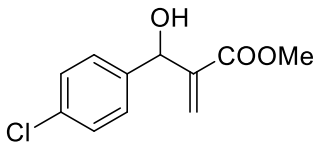


Figure S25: ESI-MS (*m/z*) spectrum of **2b**



2c

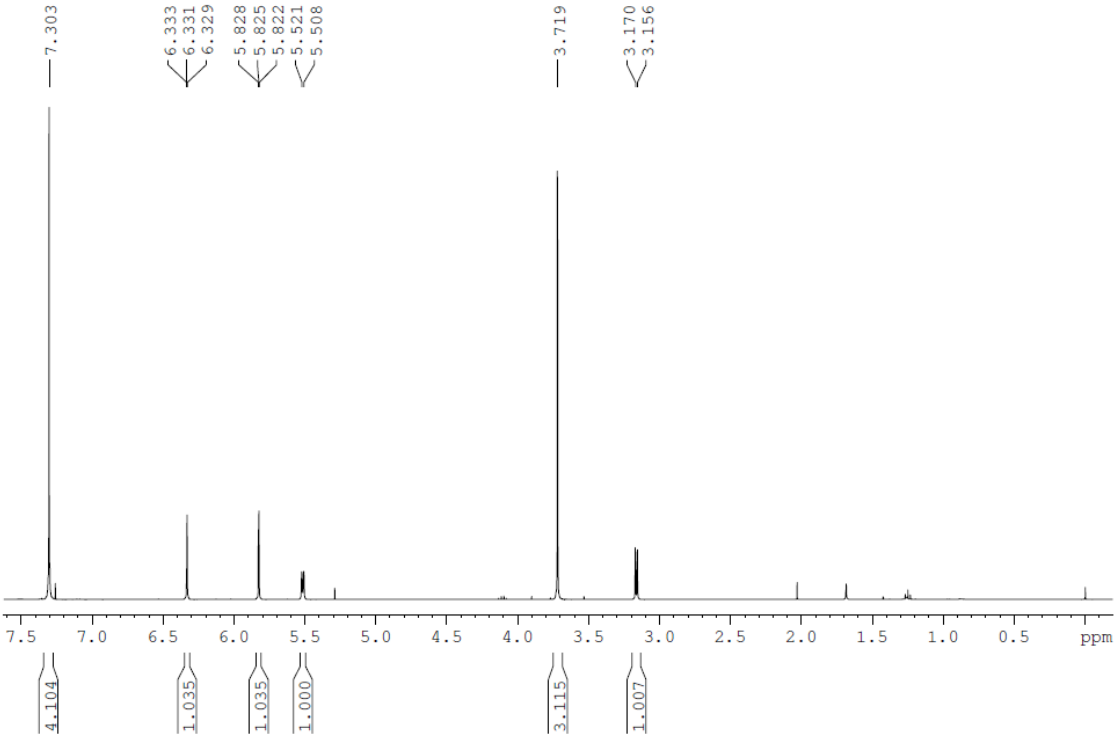


Figure S26: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2c**

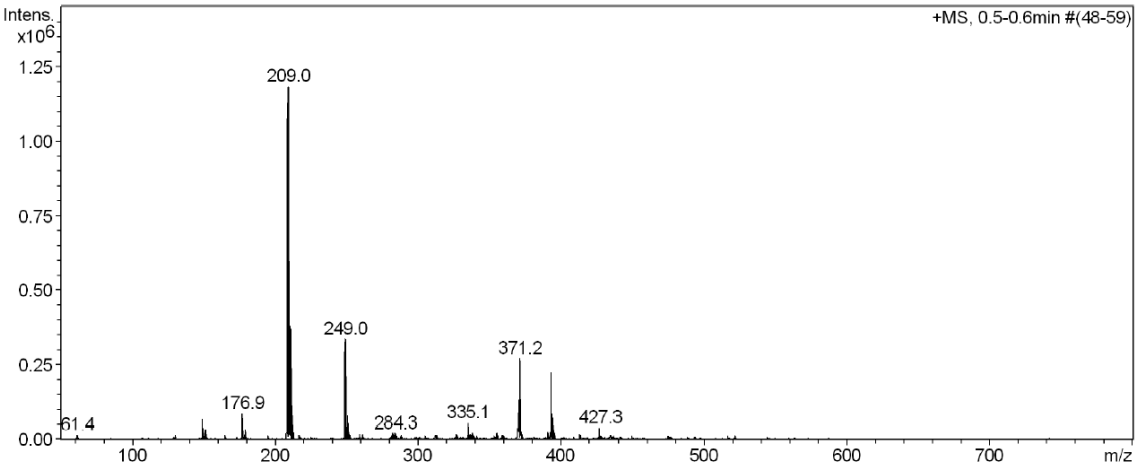


Figure S27: ESI-MS (*m/z*) spectrum of **2c**

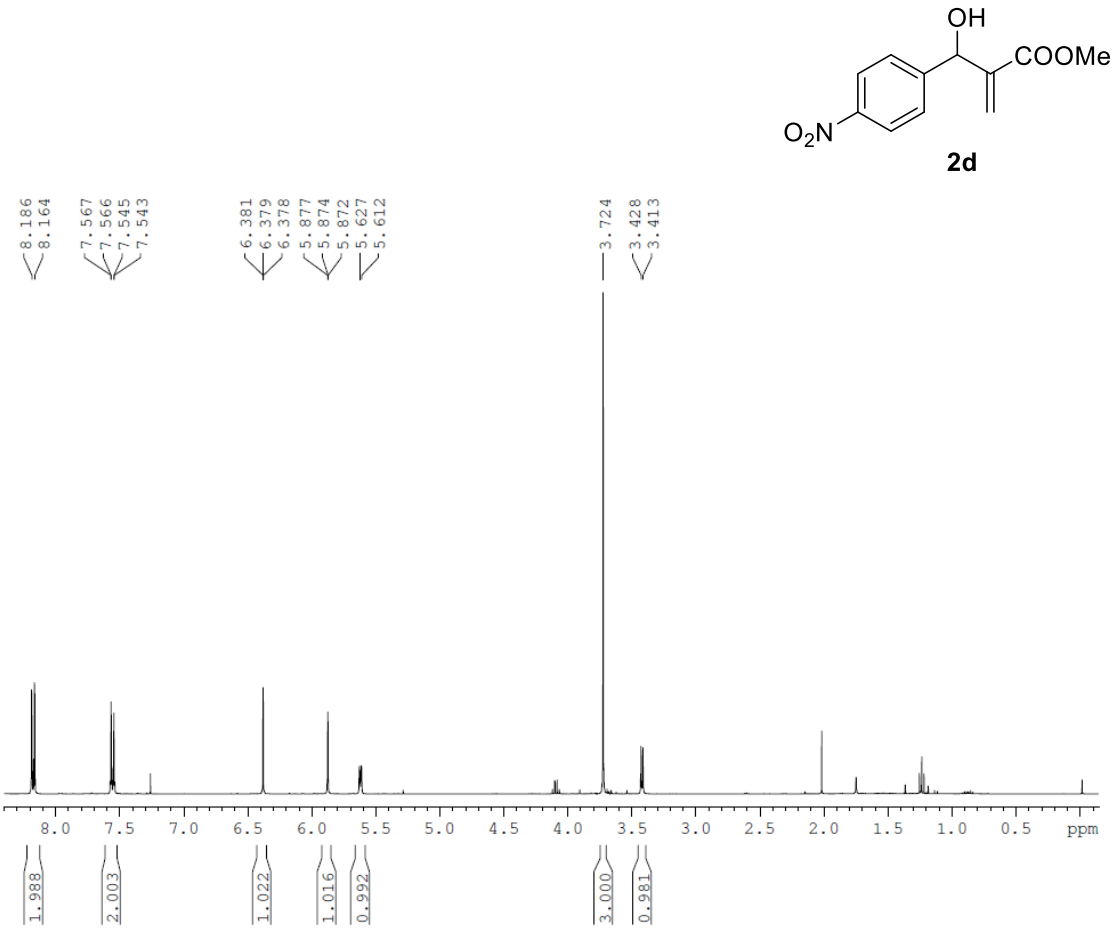


Figure S28: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2d**

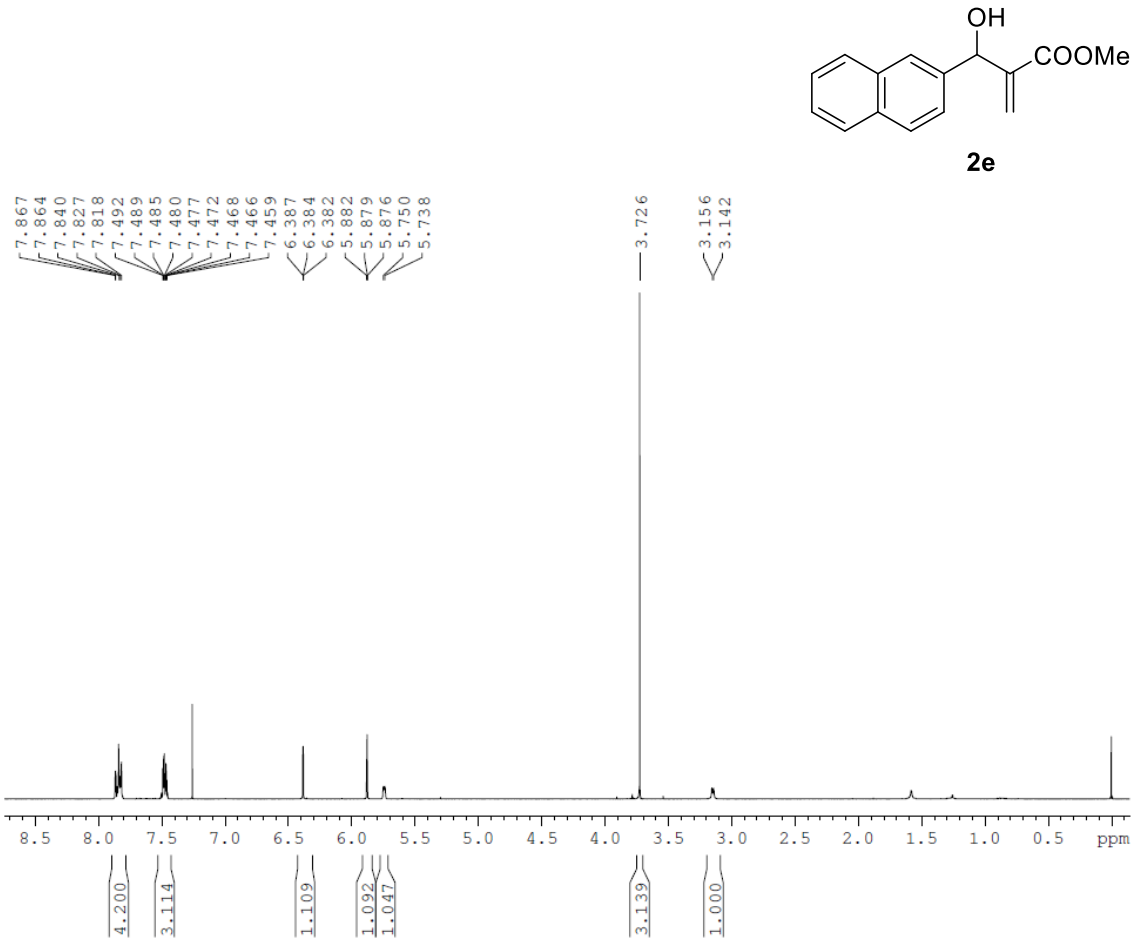


Figure S29: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2e**

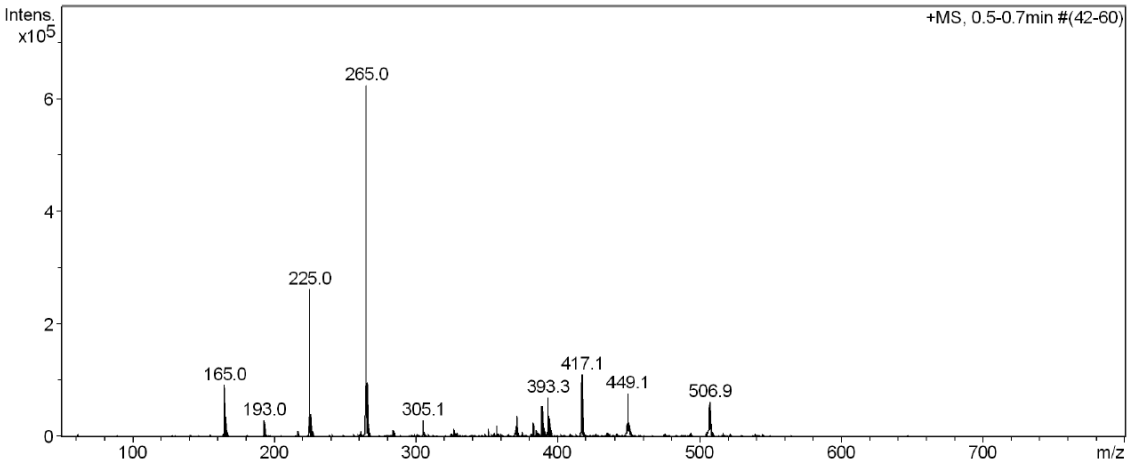


Figure S30: ESI-MS (*m/z*) spectrum of **2e**

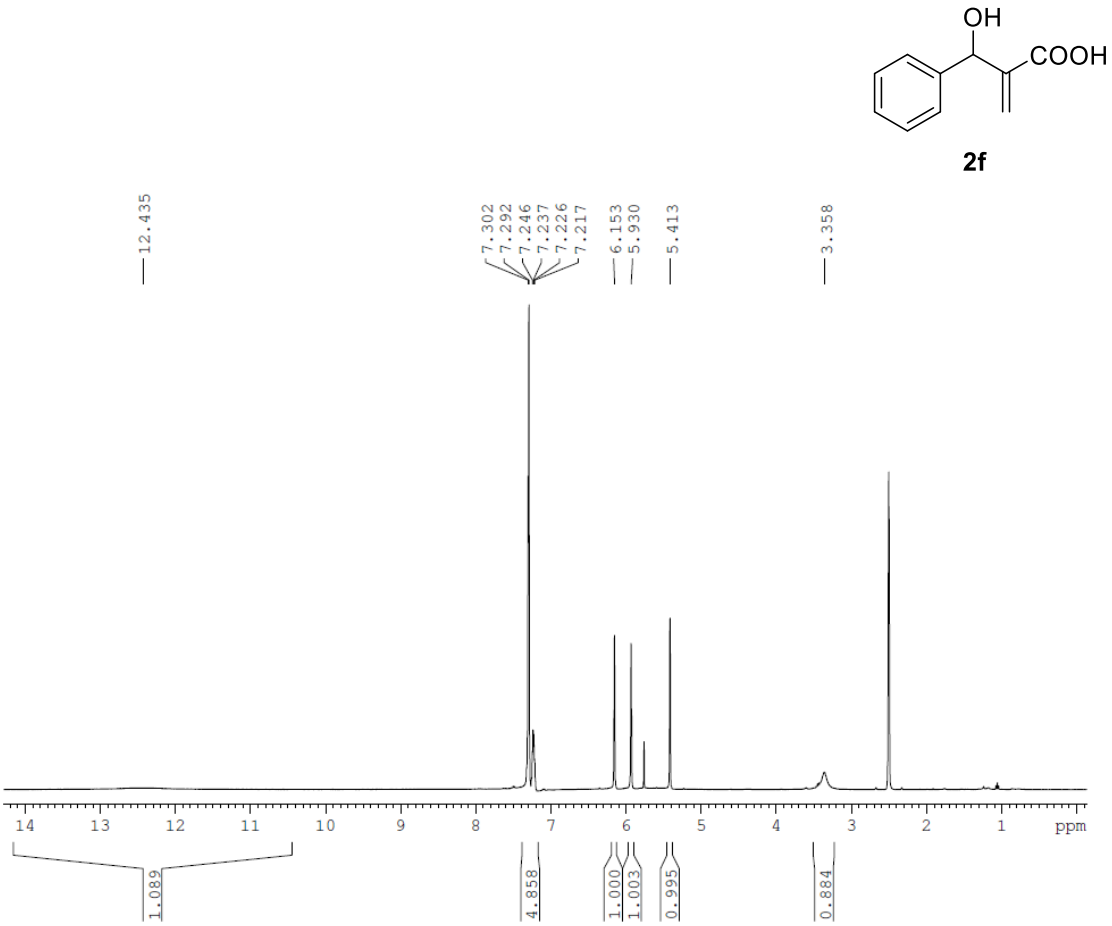


Figure S31: ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of **2f**

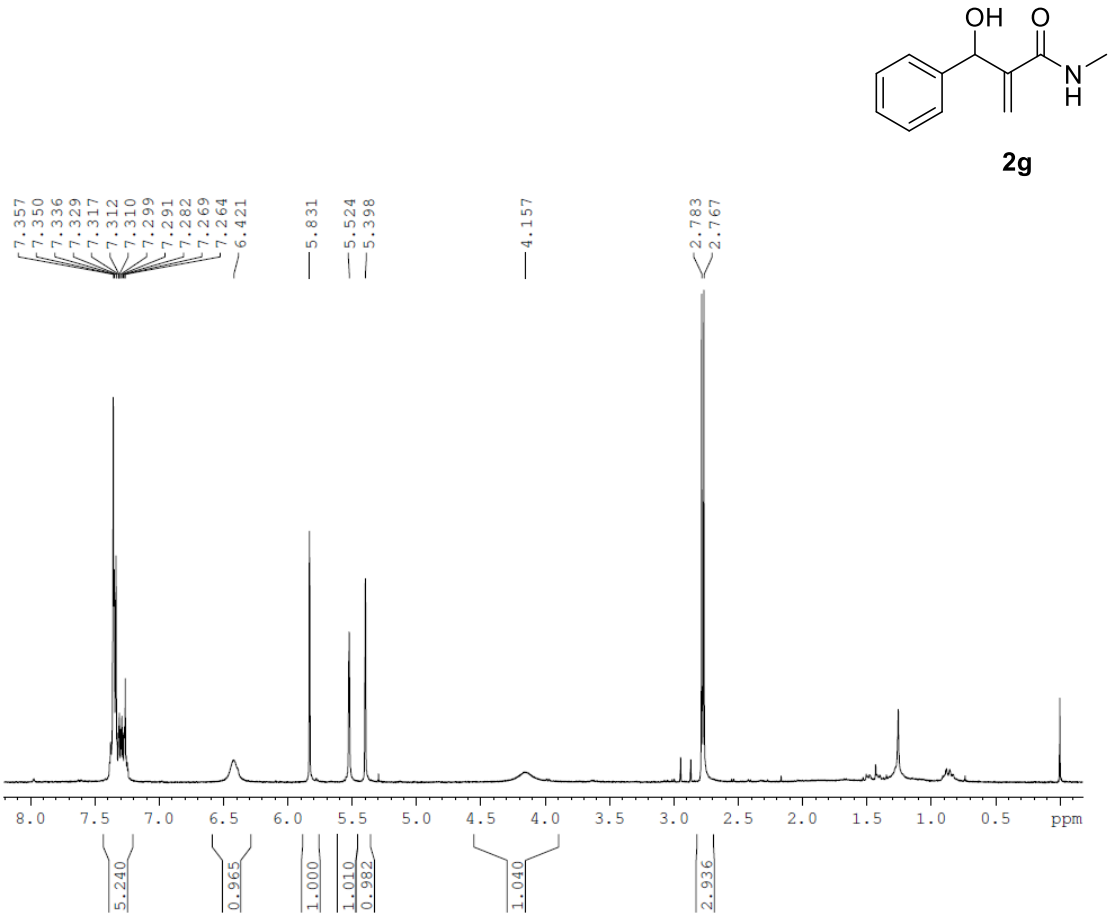


Figure S32: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **2g**

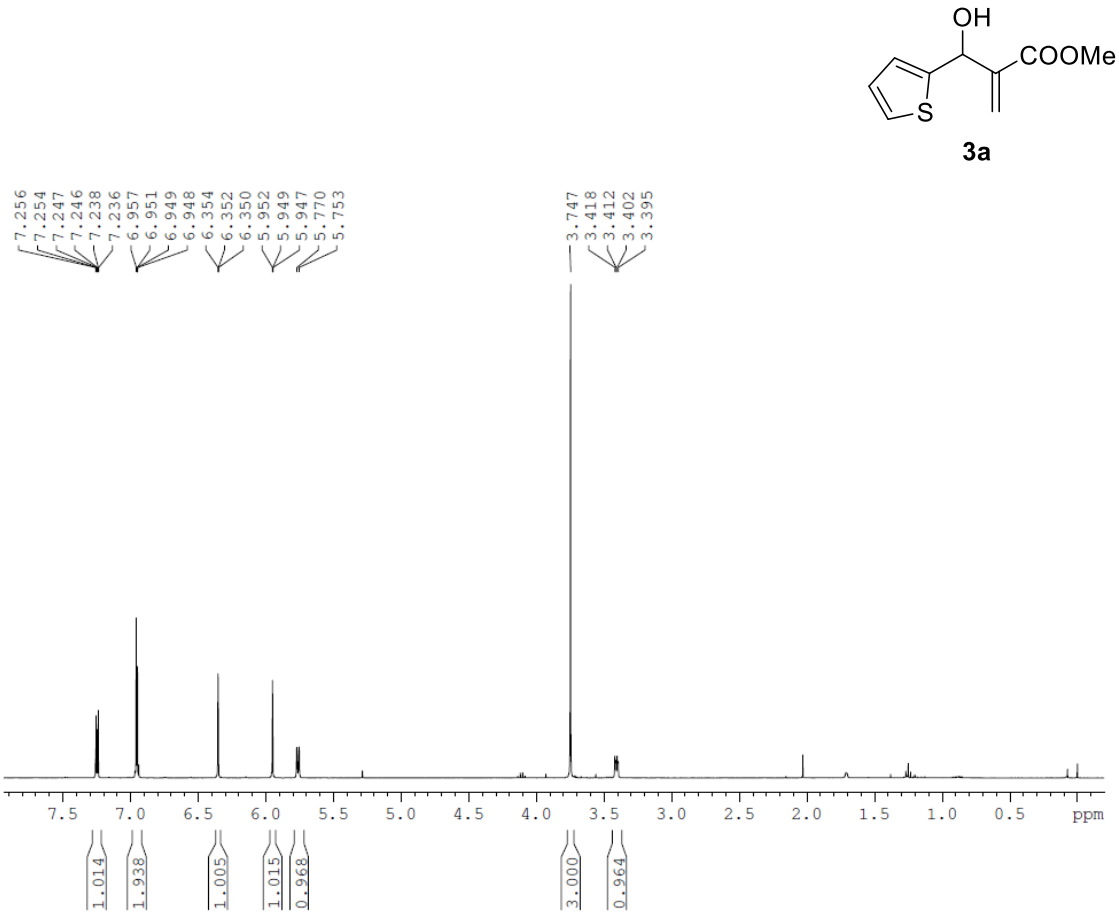


Figure S33: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3a**

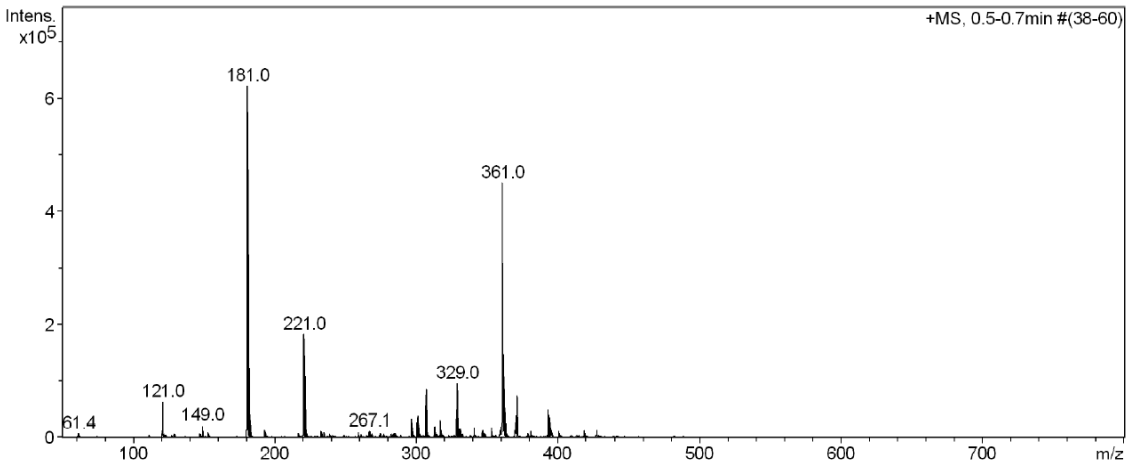


Figure S34: ESI-MS (*m/z*) spectrum of **3a**

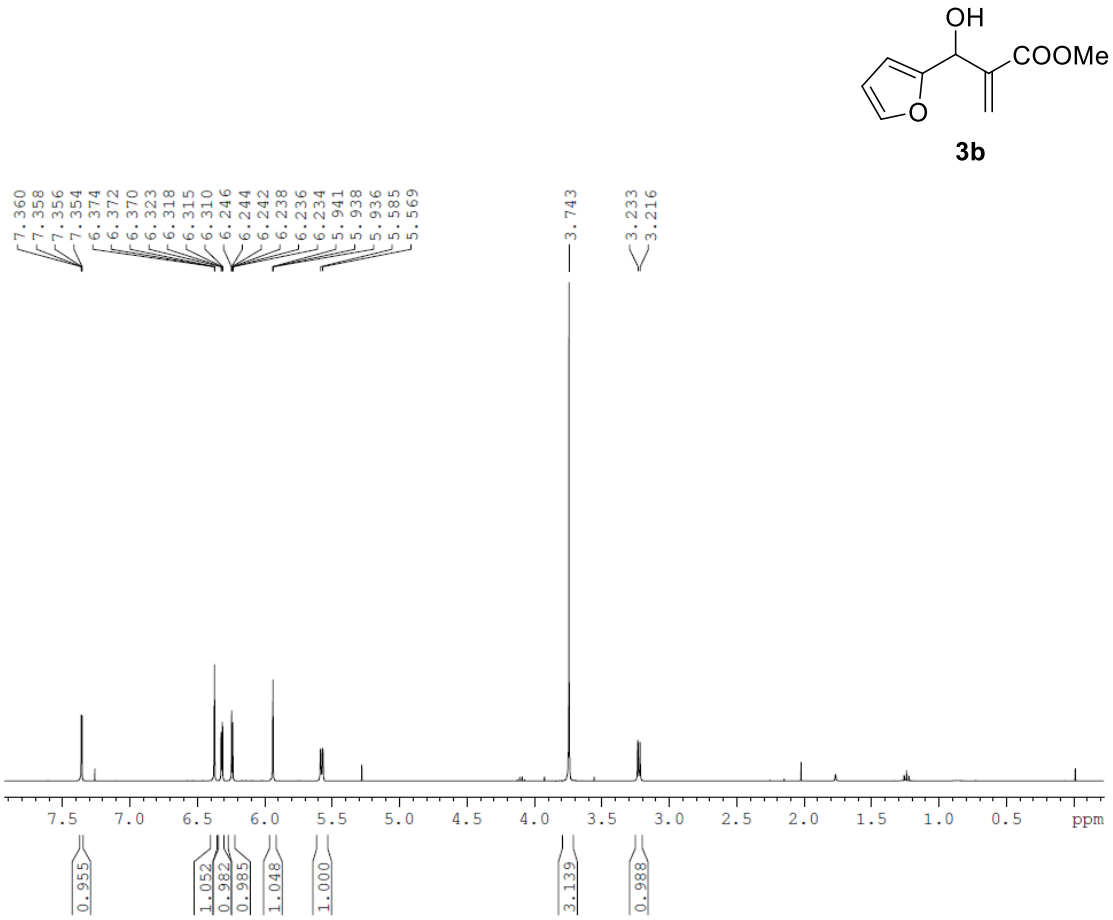


Figure S35: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3b**

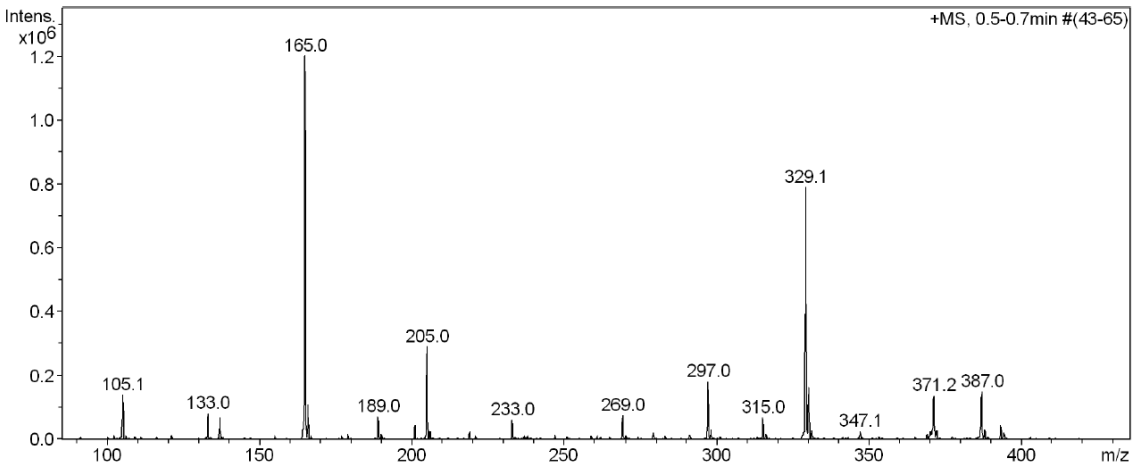
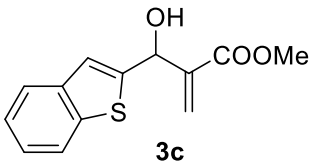


Figure S36: ESI-MS (*m/z*) spectrum of **3b**



3c

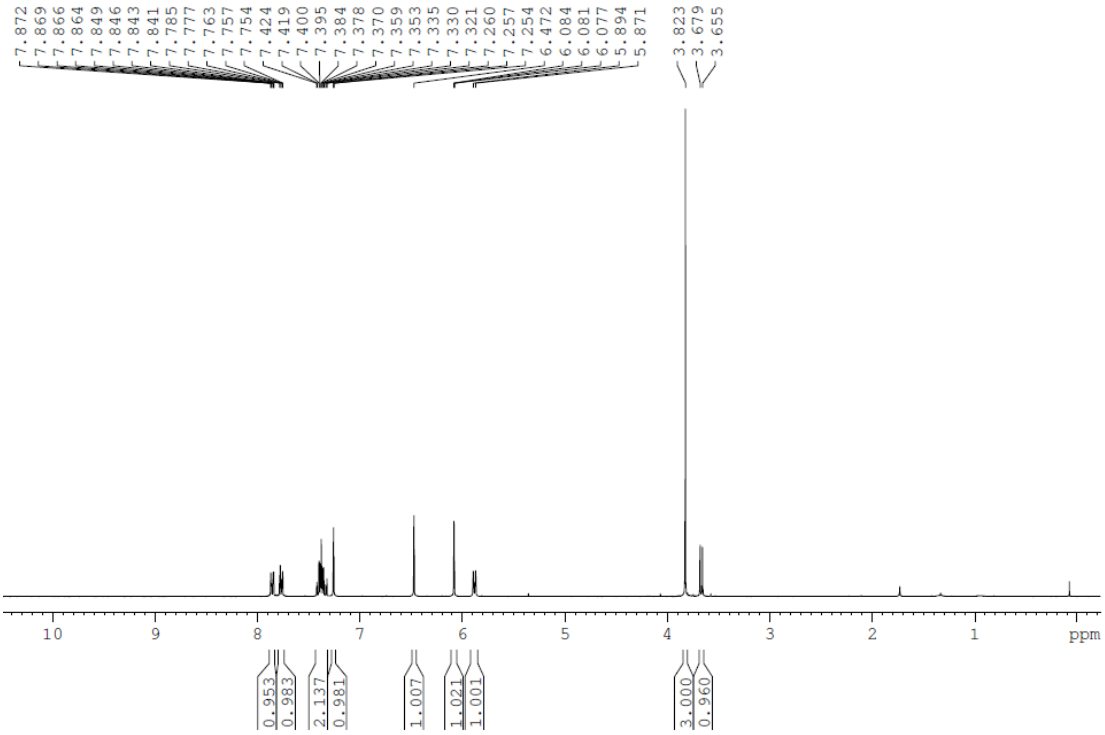


Figure S37: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **3c**

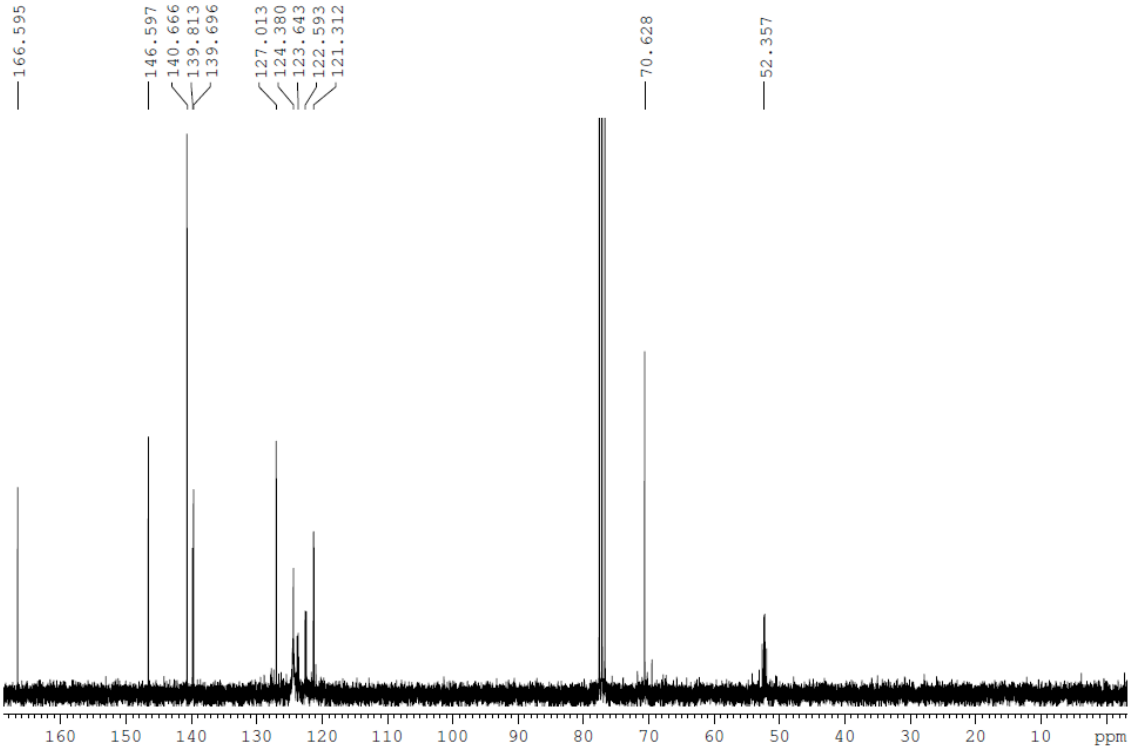


Figure S38: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **3c**

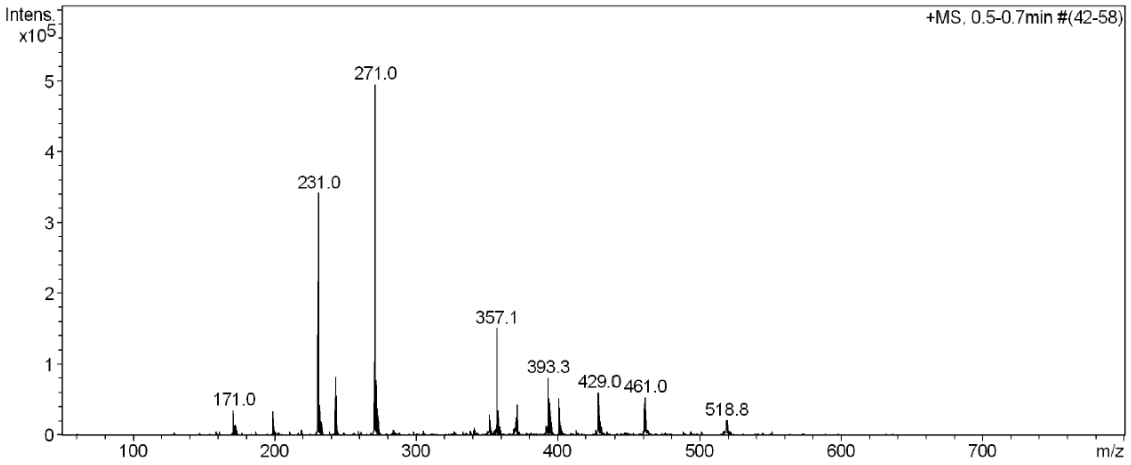


Figure S39: ESI-MS (*m/z*) spectrum of 3**c**

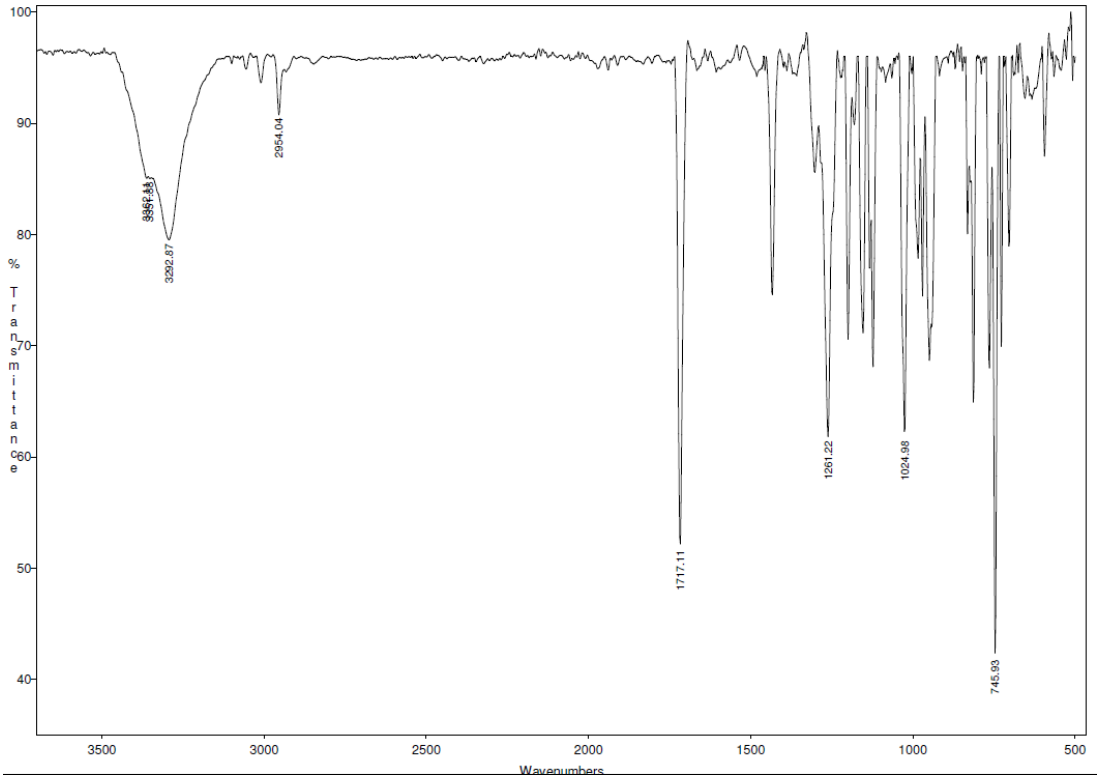


Figure S40: IR (ATR) spectrum of **3c**

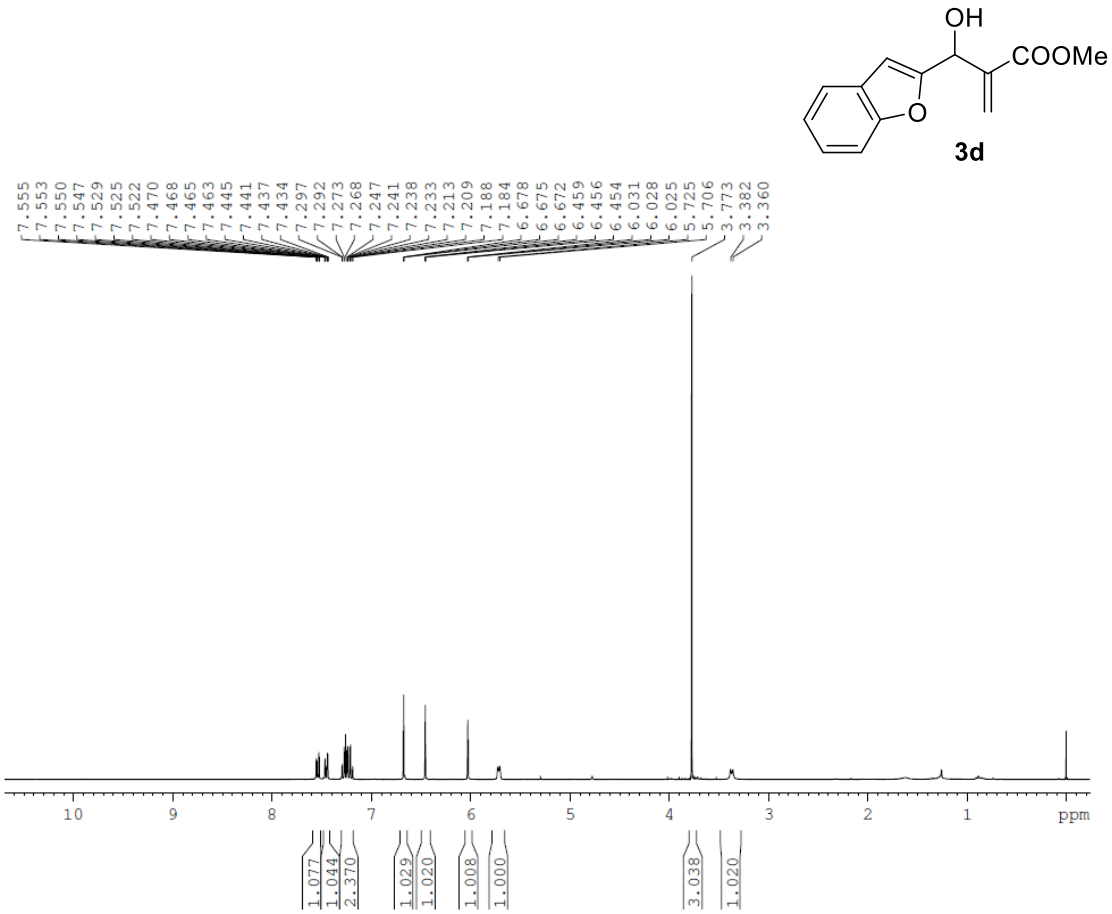


Figure S41: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **3d**

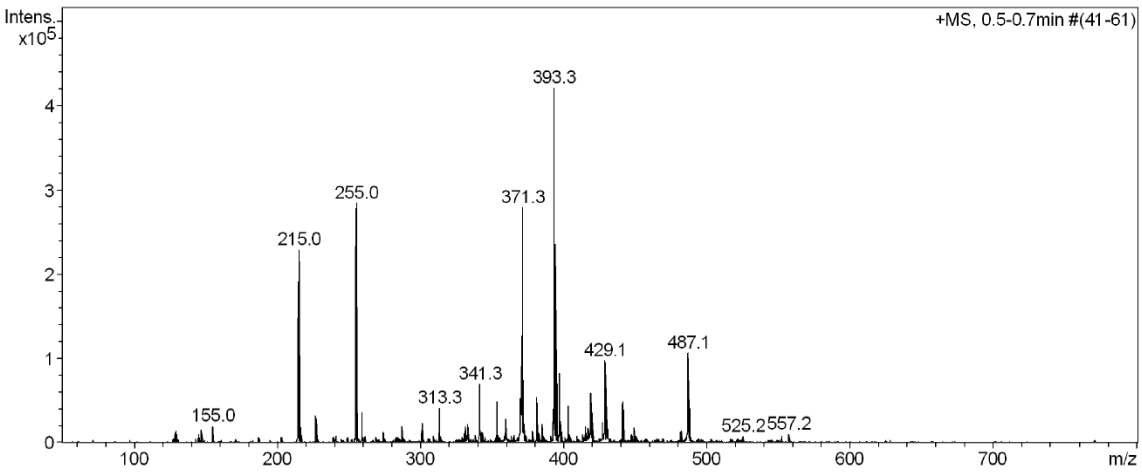
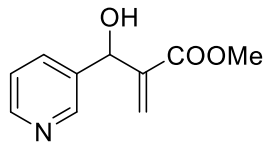


Figure S42: ESI-MS (*m/z*) spectrum of **3d**



3f

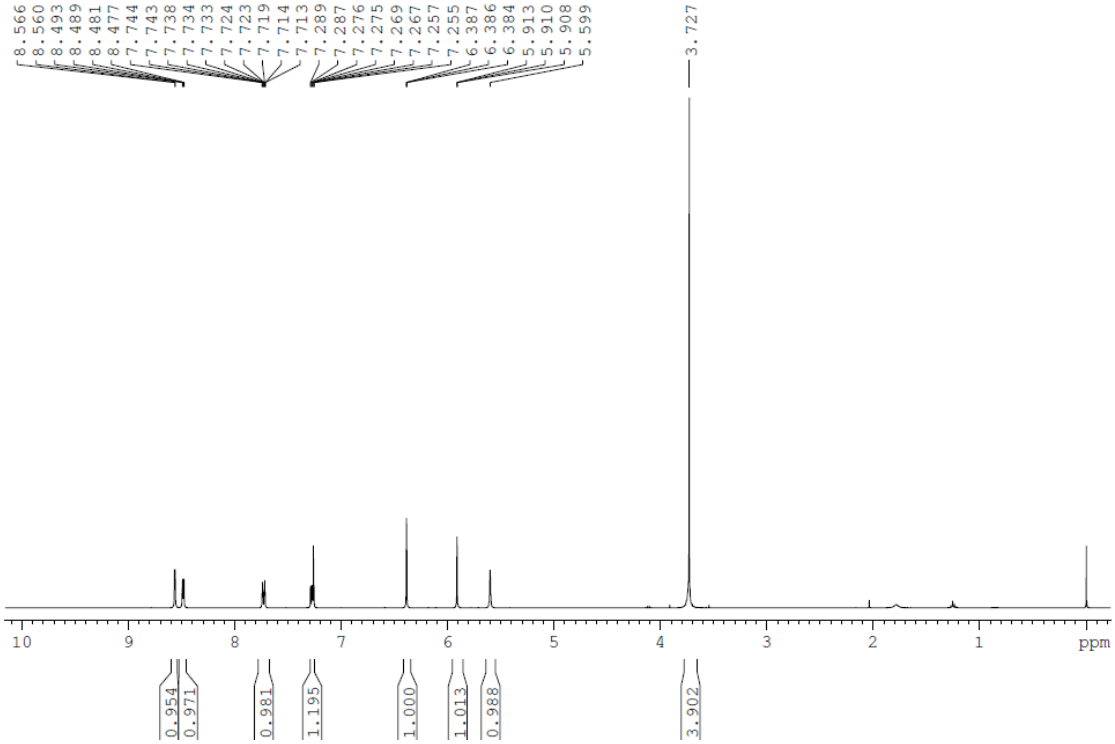
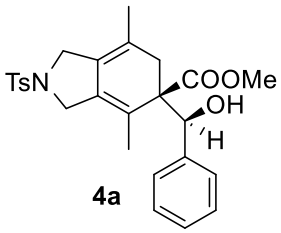


Figure S43: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3f**



4a

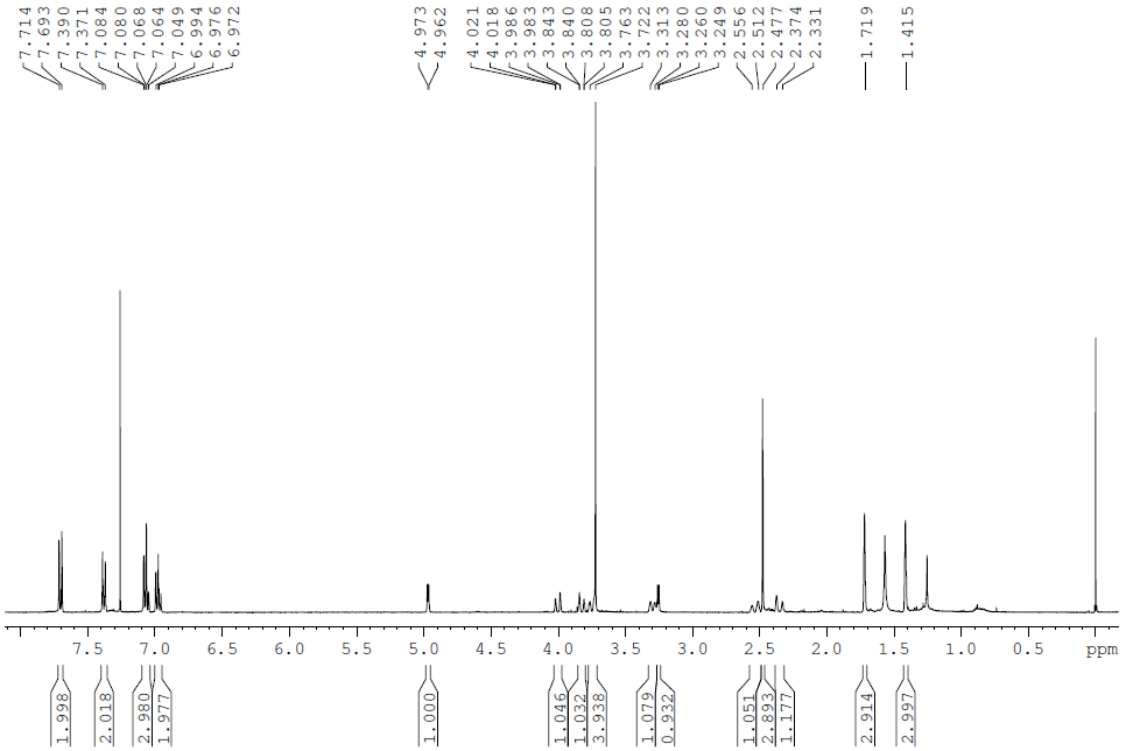


Figure S44: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4a**

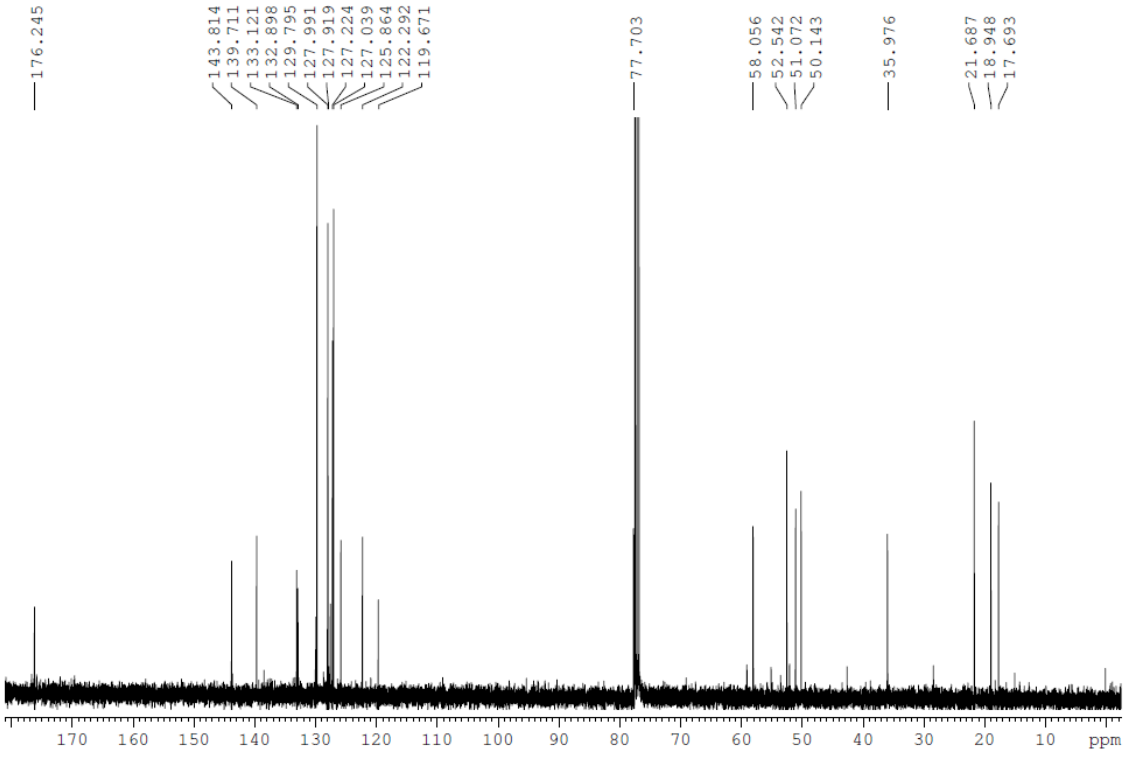


Figure S45: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4a**

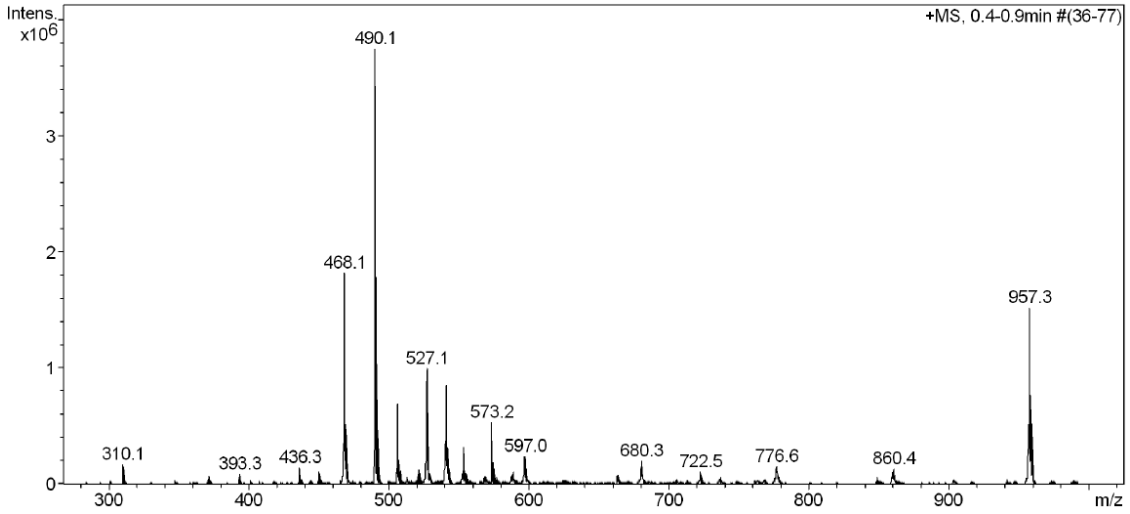


Figure S46: ESI-MS (*m/z*) spectrum of **4a**

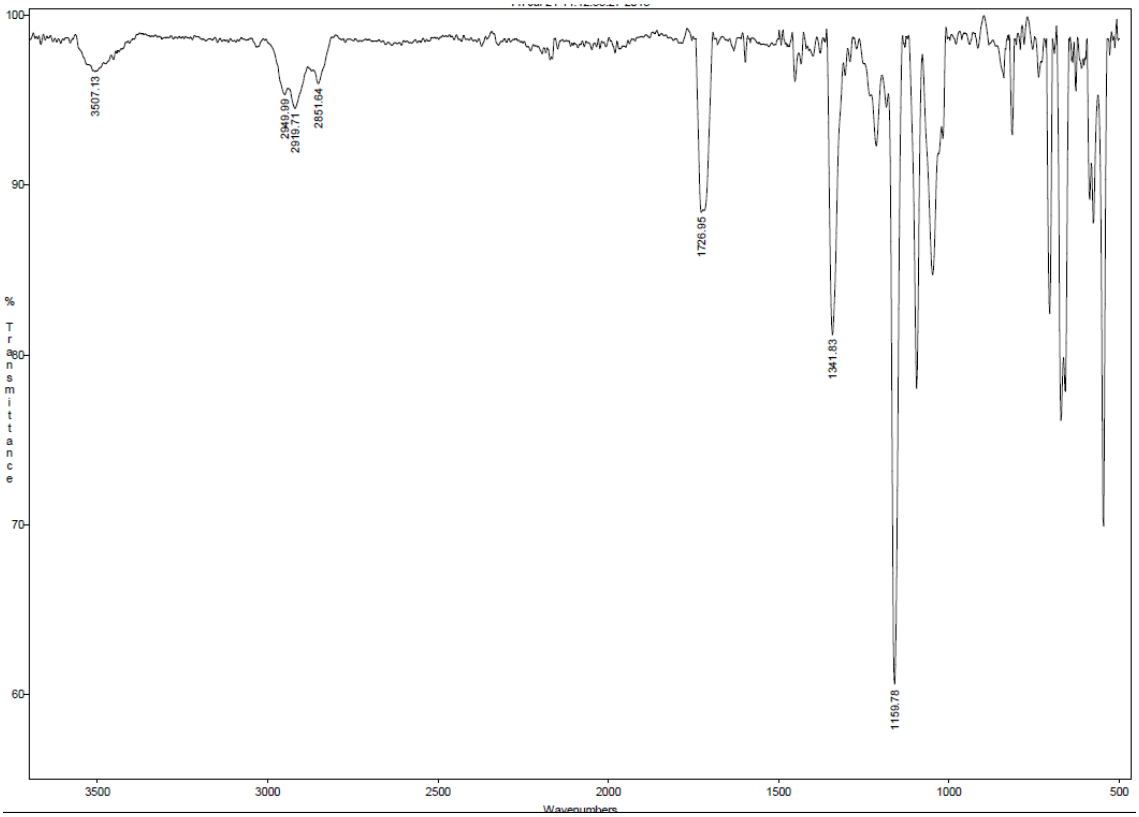


Figure S47: IR (ATR) spectrum of **4a**

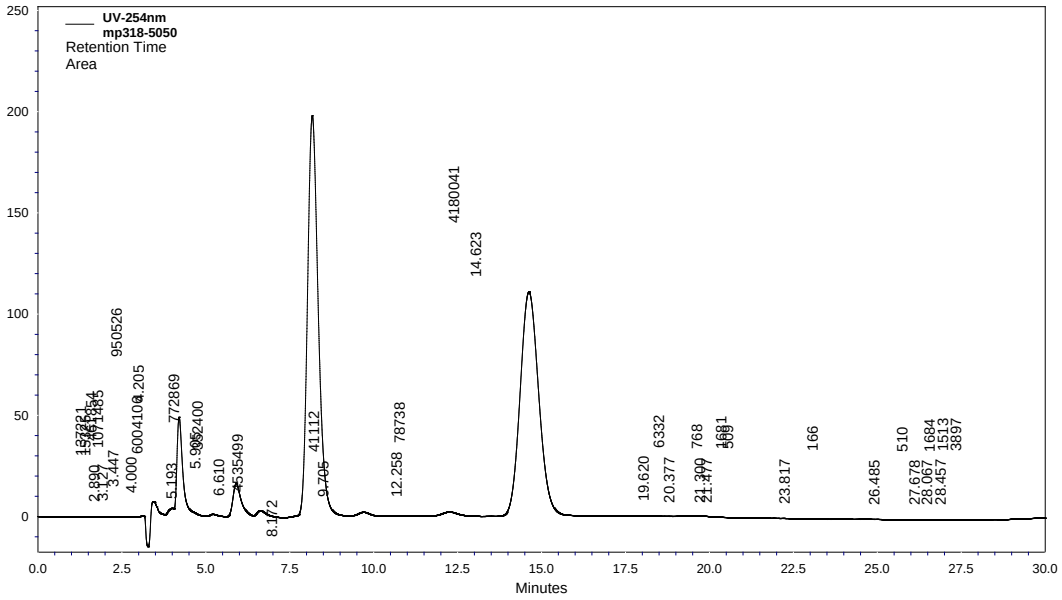


Figure S48: HPLC chromatogram of *rac*-**4a**

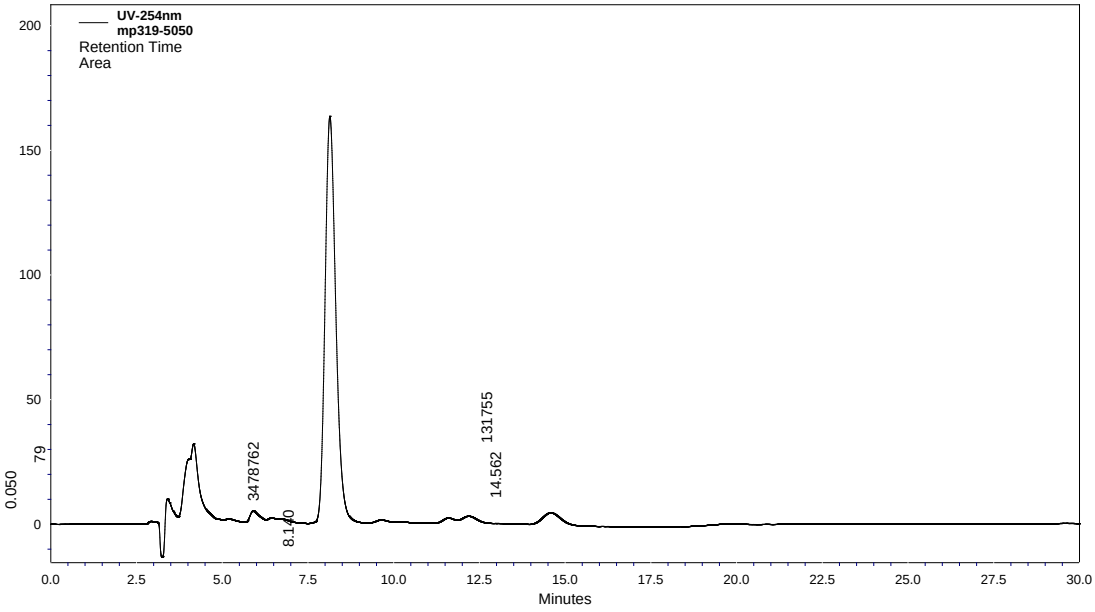


Figure S49: HPLC chromatogram of (*R*,*S*)-**4a**

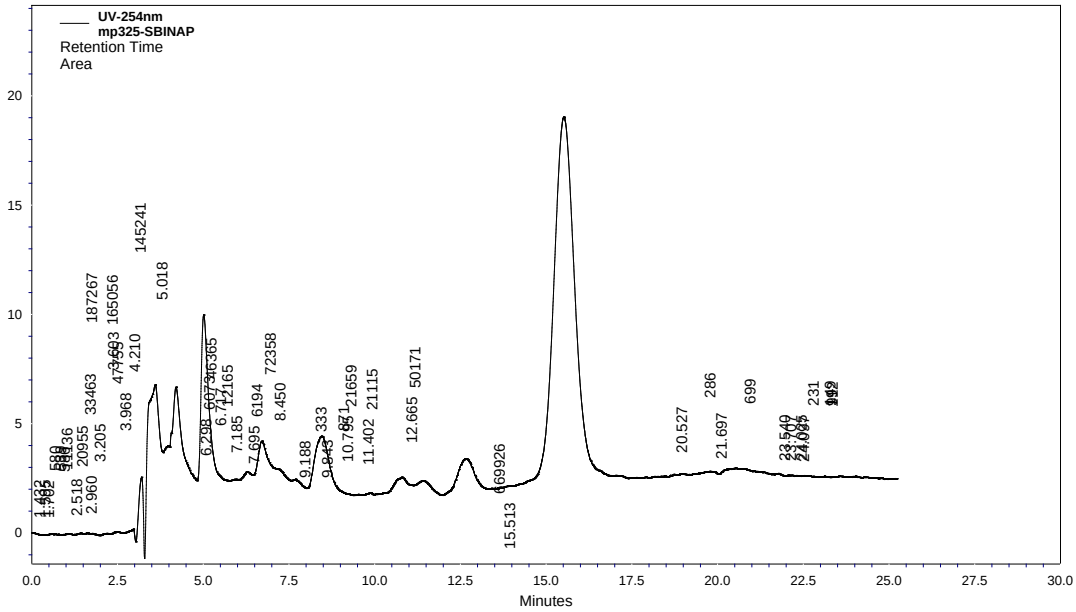


Figure S50: HPLC chromatogram of (*S*,*R*)-**4a**

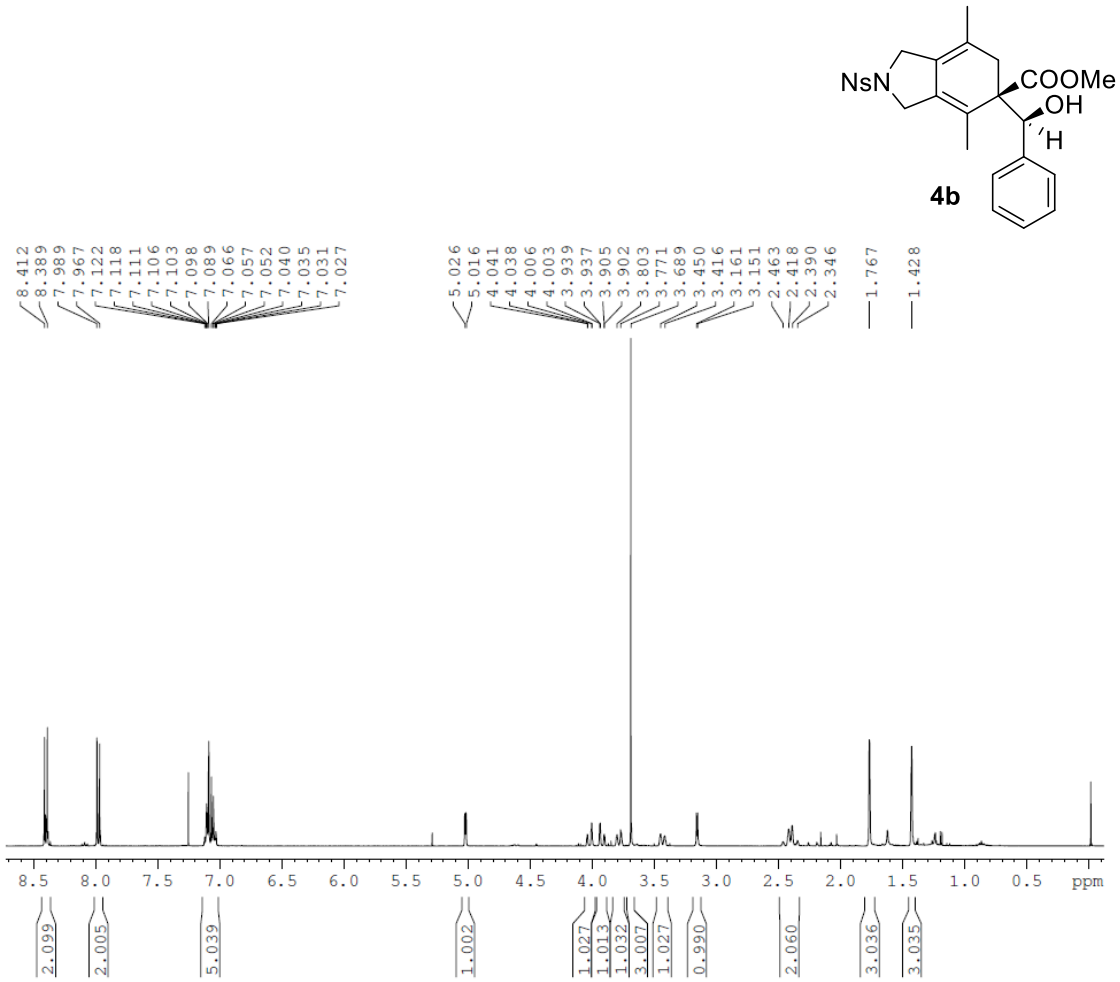


Figure S51: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4b**

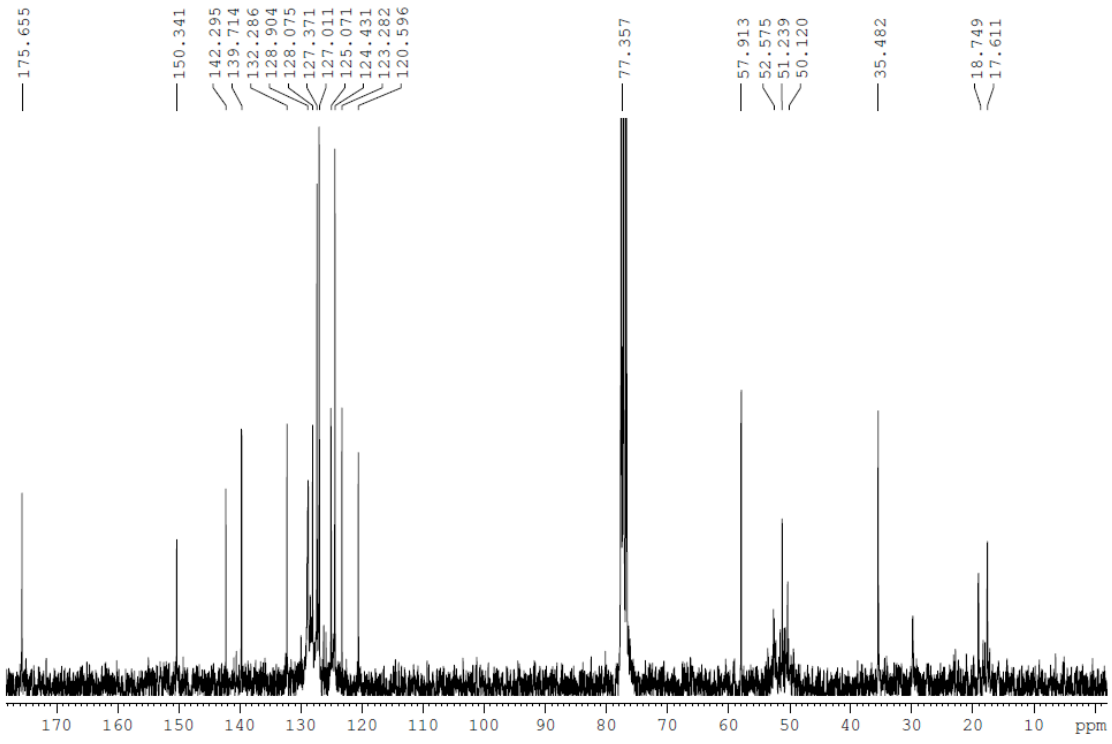


Figure S52: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **4b**

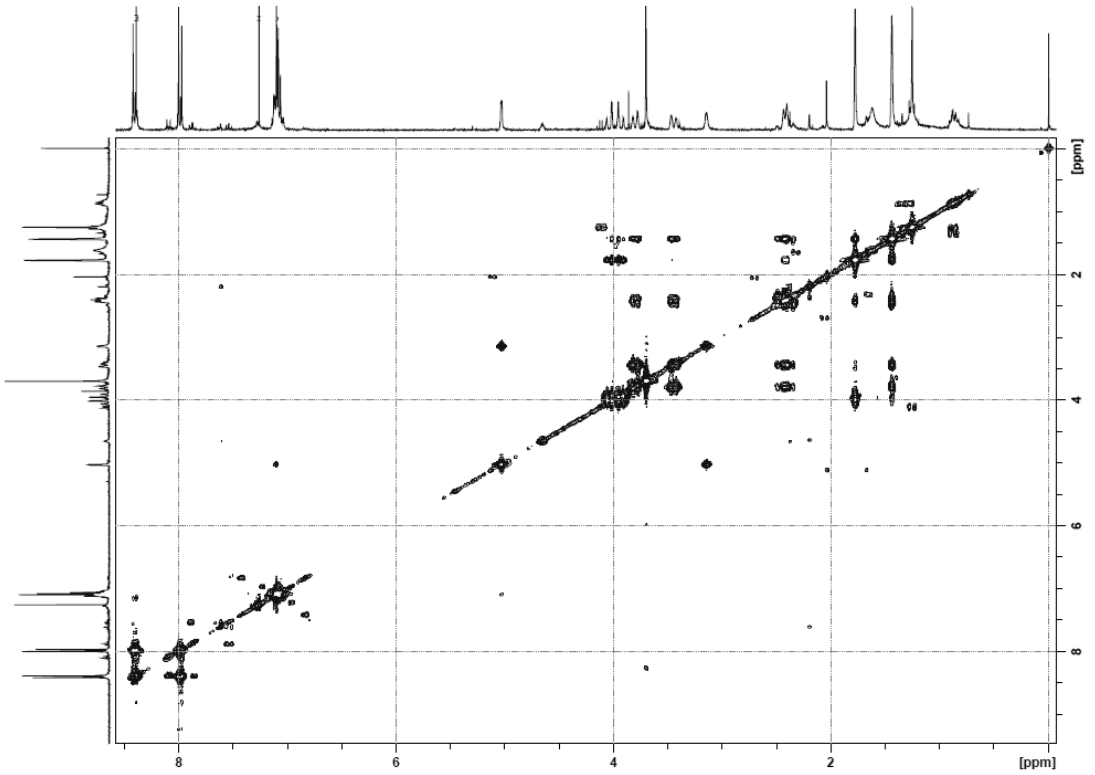


Figure S53: COSY spectrum ($CDCl_3$, 300 MHz) of **4b**

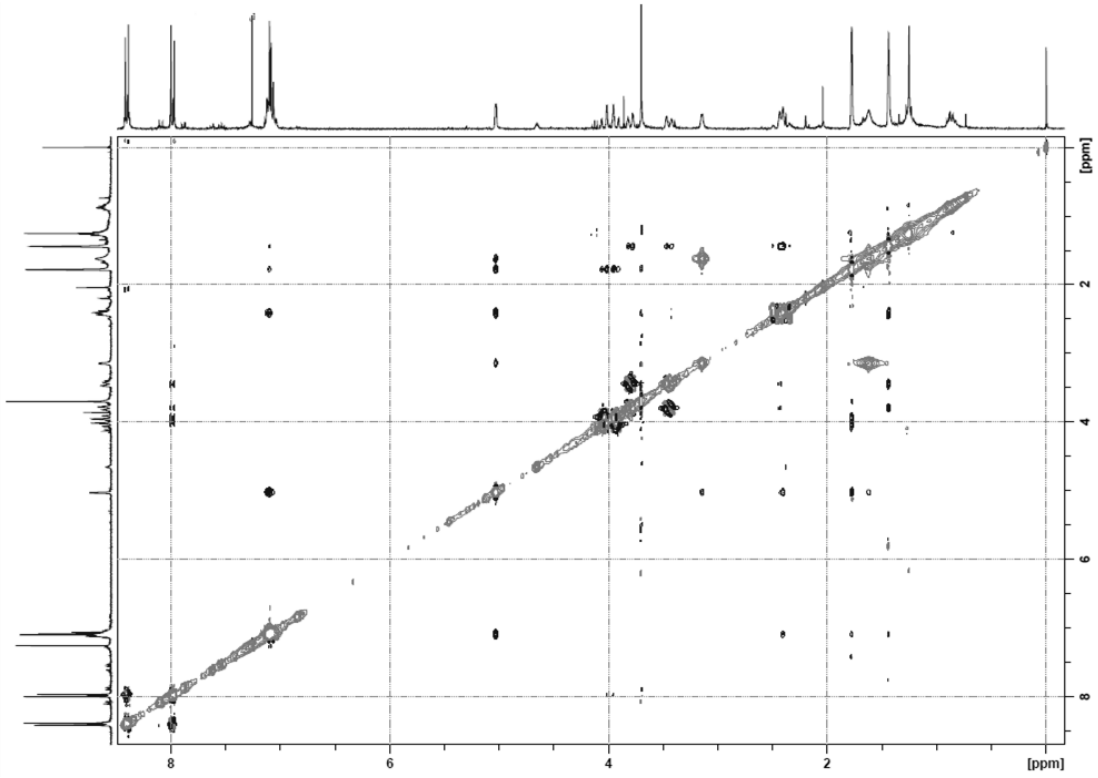


Figure S54: NOESY spectrum ($CDCl_3$, 300 MHz) of **4b**

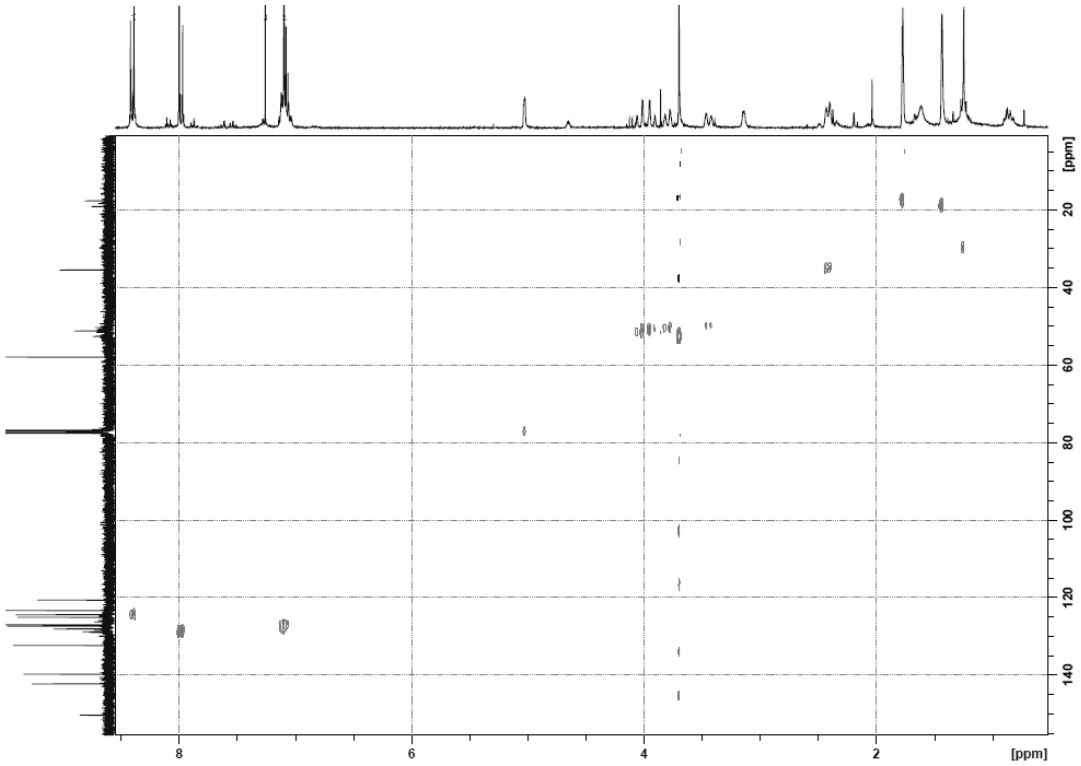


Figure S55: HSQC spectrum ($CDCl_3$, 300 MHz) of **4b**

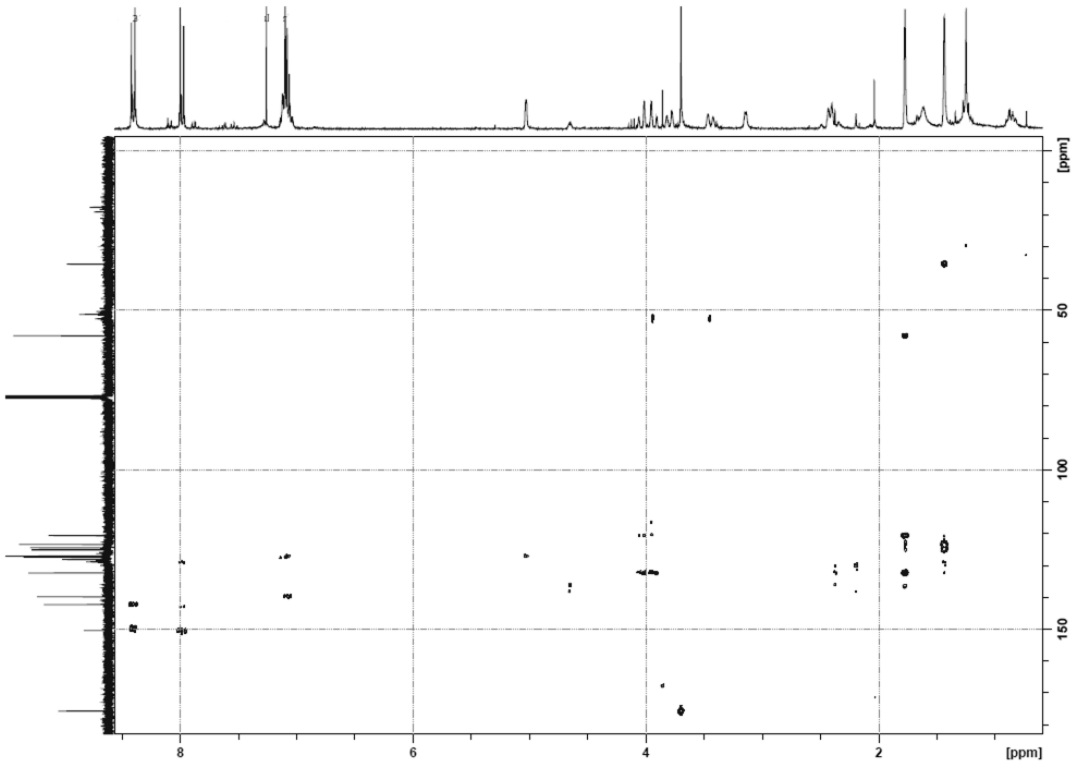


Figure S56: HMBC spectrum ($CDCl_3$, 300 MHz) of **4b**

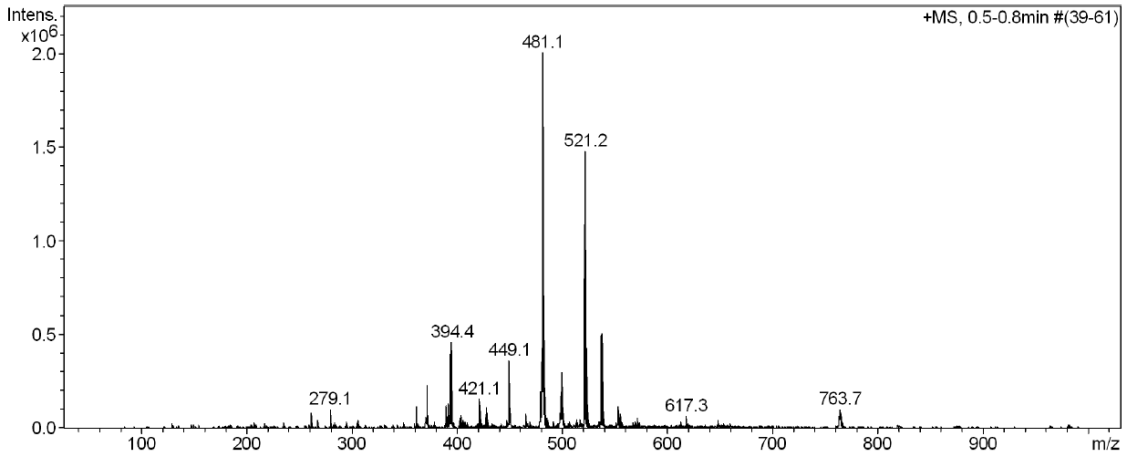


Figure S57: ESI-MS (*m/z*) spectrum of **4b**

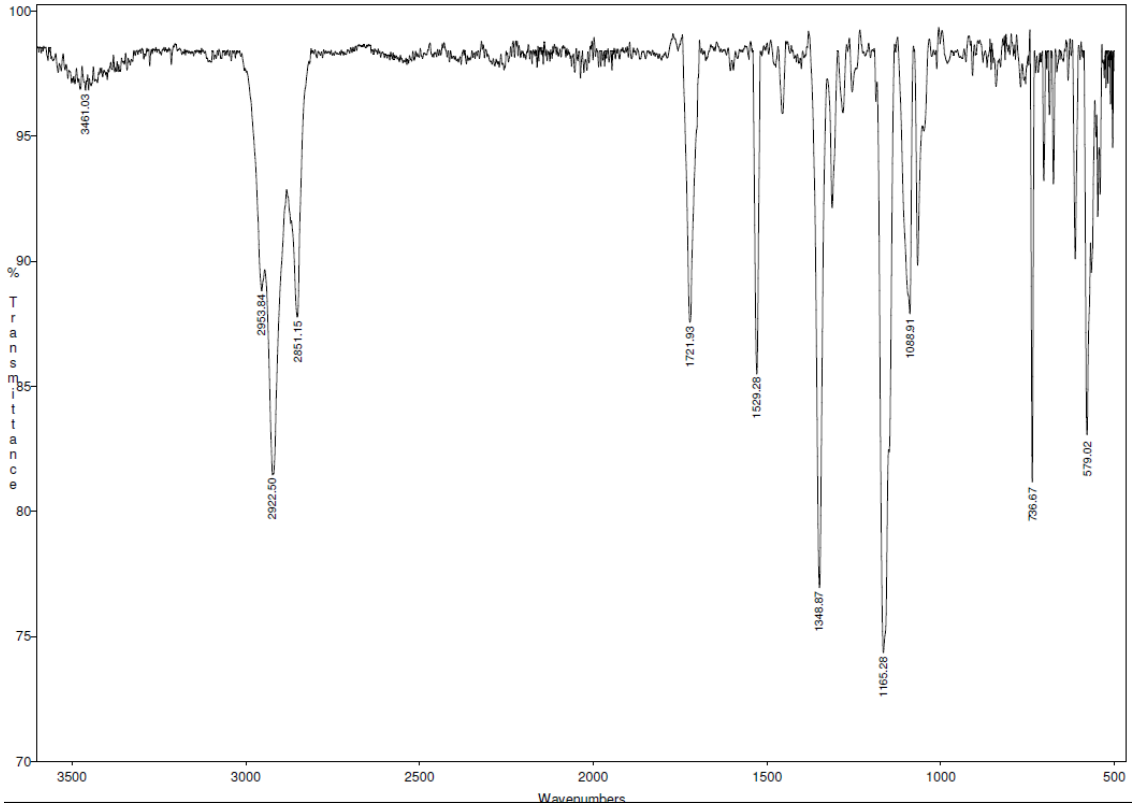


Figure S58: IR (ATR) spectrum of **4b**

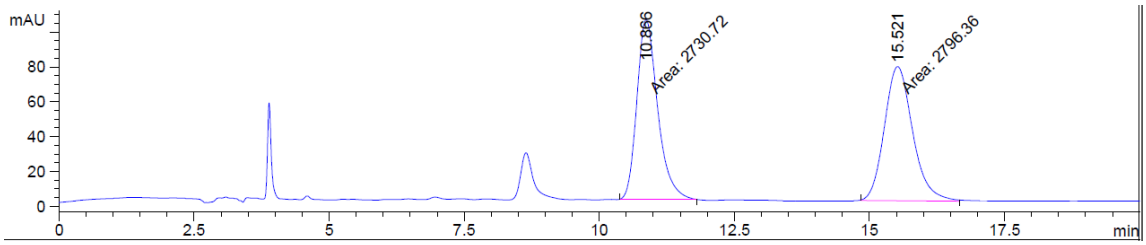


Figure S59: HPLC chromatogram of *rac*-**4b**

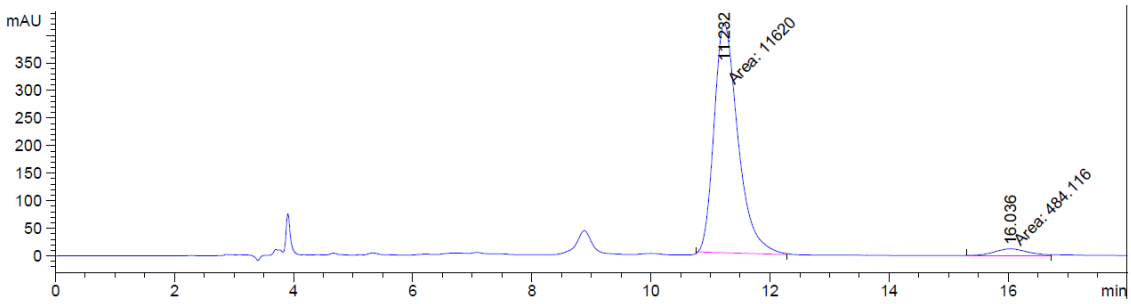


Figure S60: HPLC chromatogram of (*R*,*S*)-**4b**

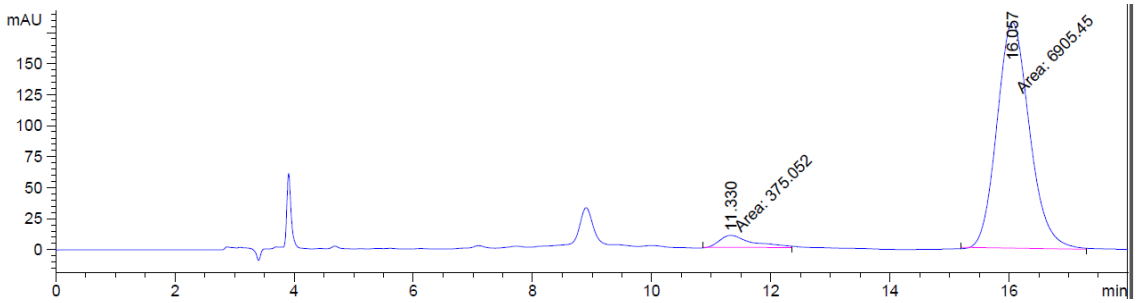


Figure S61: HPLC chromatogram of (*S*,*R*)-**4b**

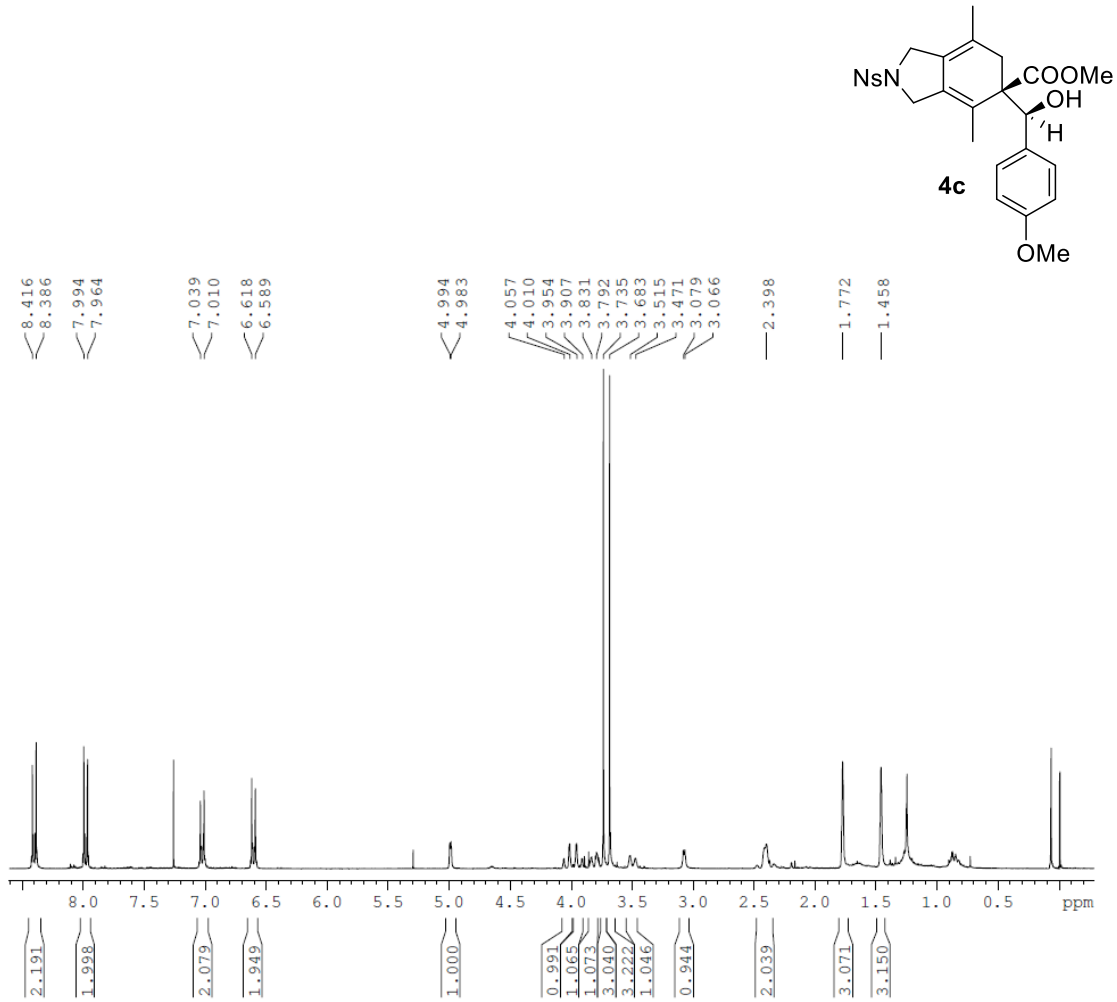


Figure S62: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **4c**

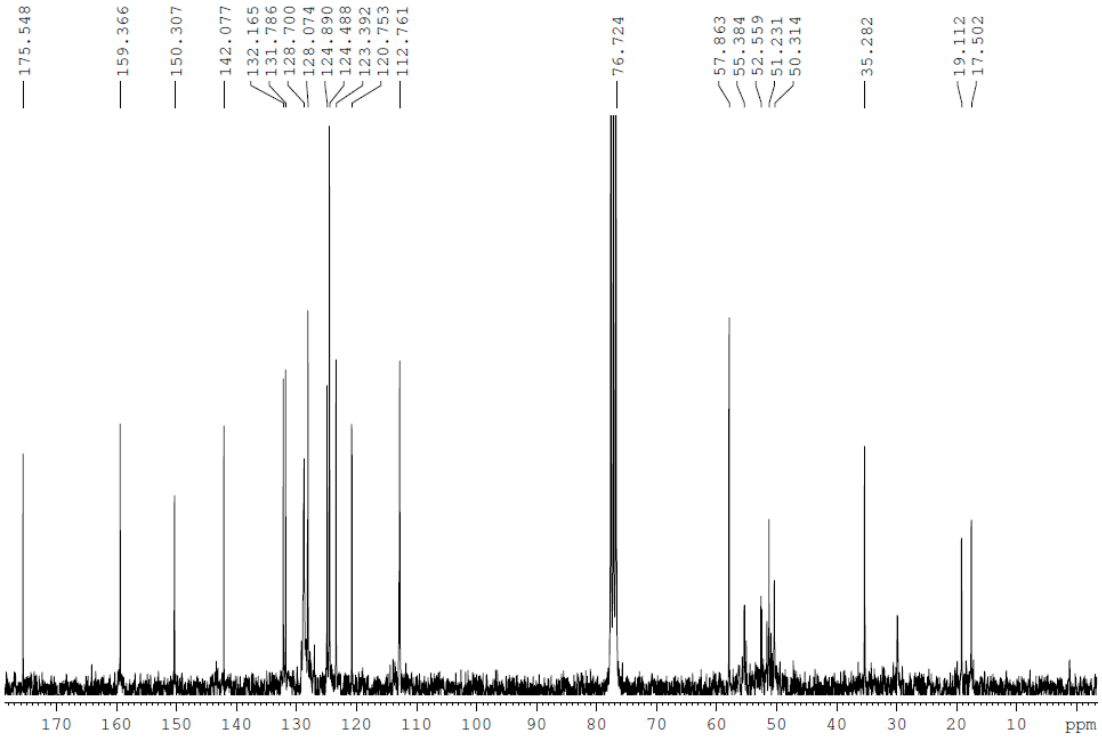


Figure S63: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **4c**

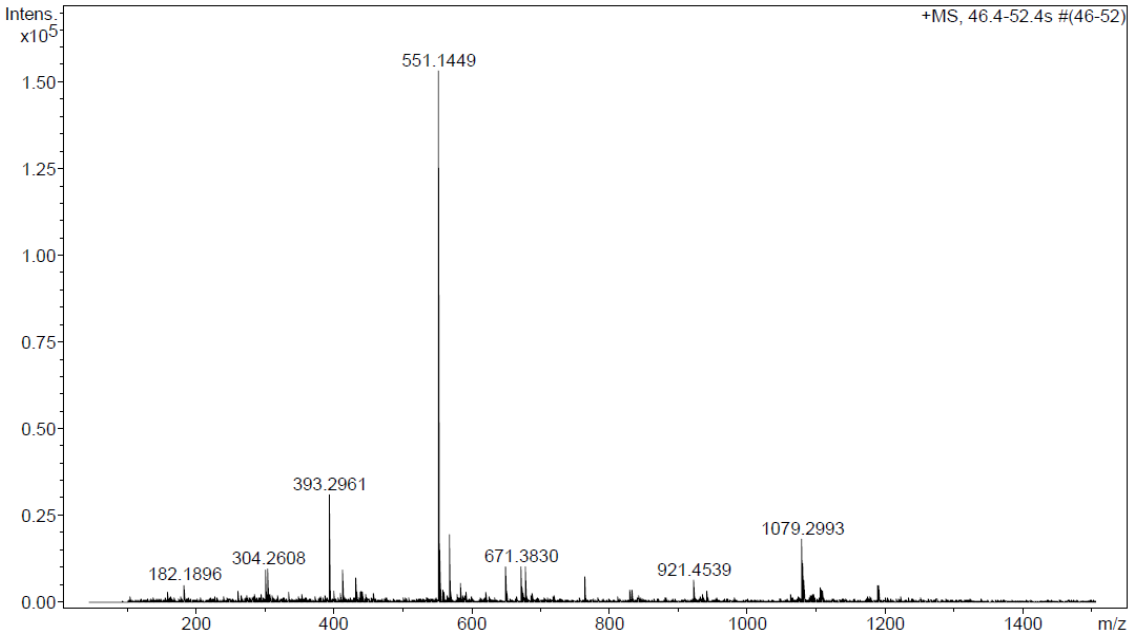


Figure S64: ESI-HRMS (*m/z*) spectrum of **4c**

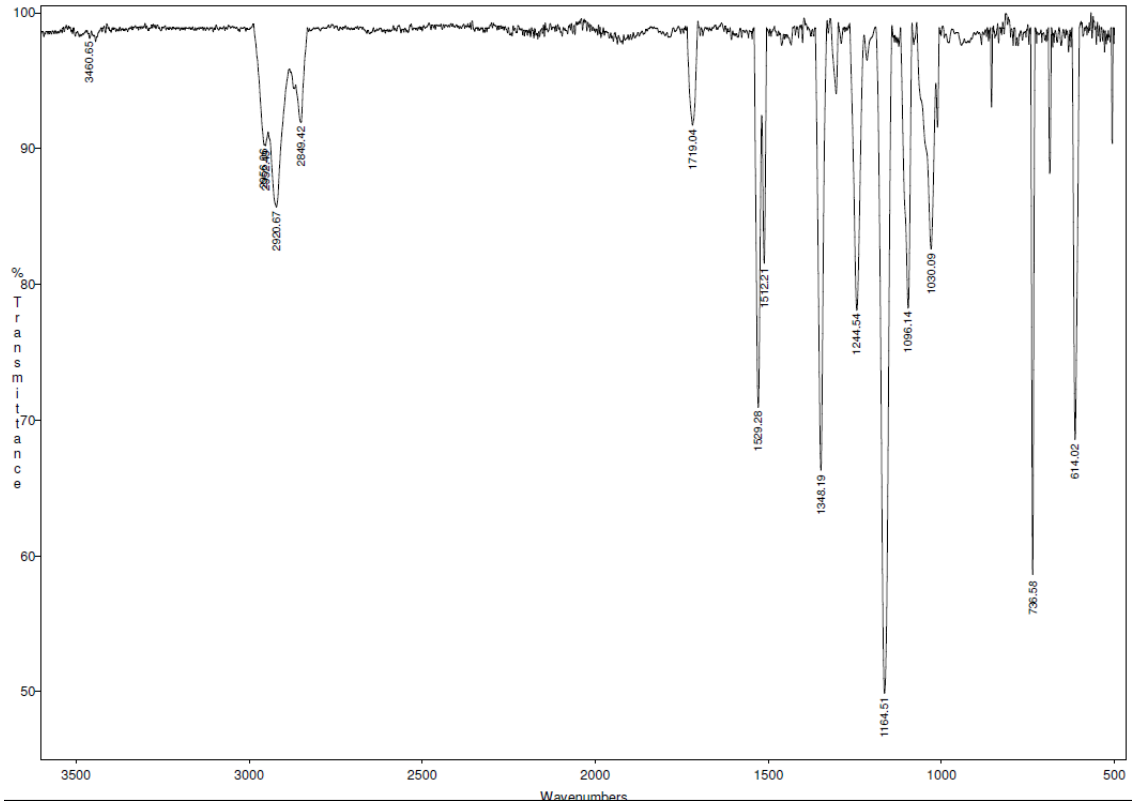


Figure S65: IR(ATR) spectrum of **4c**

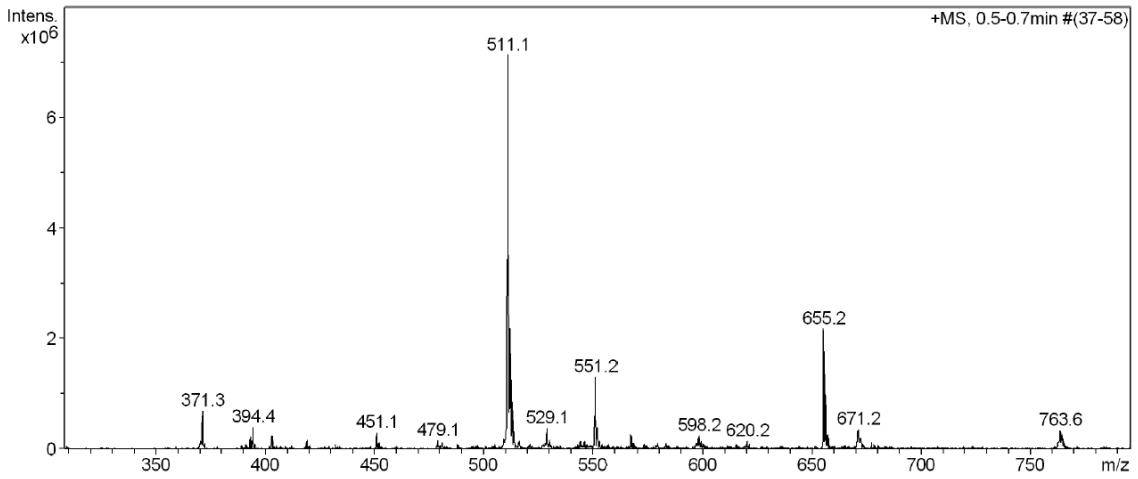


Figure S66: ESI-MS (*m/z*) spectrum of **4c**

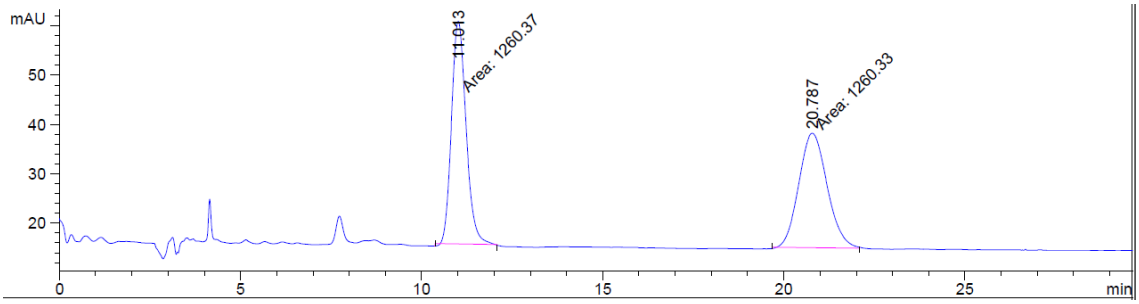


Figure S67: HPLC chromatogram of *rac*-**4c**

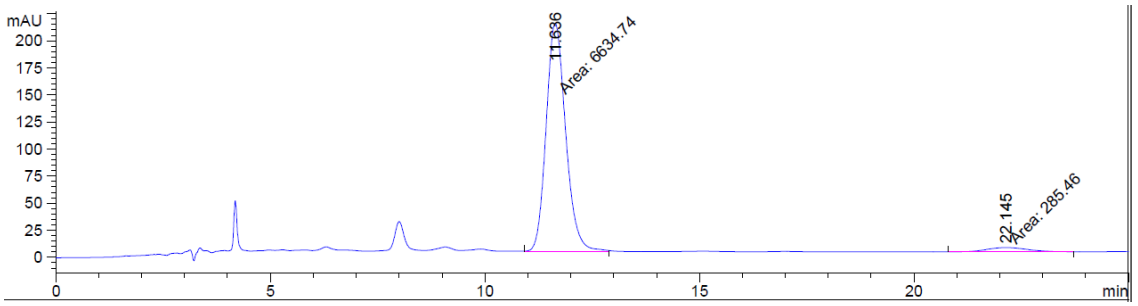


Figure S68: HPLC chromatogram of (*R,S*)-**4c**

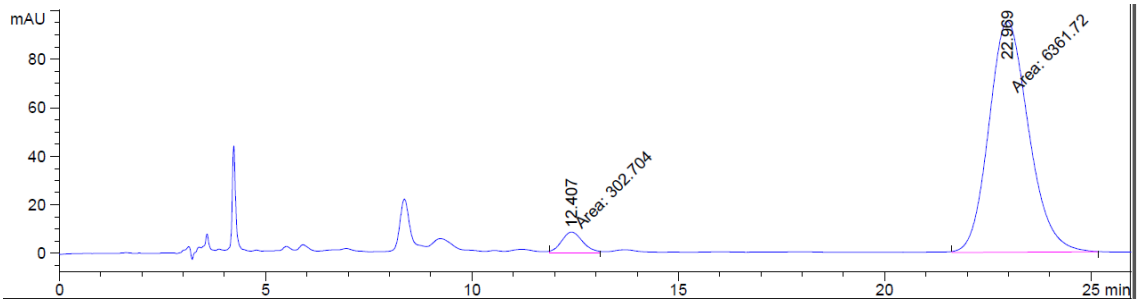


Figure S69: HPLC chromatogram of (*S,R*)-**4c**

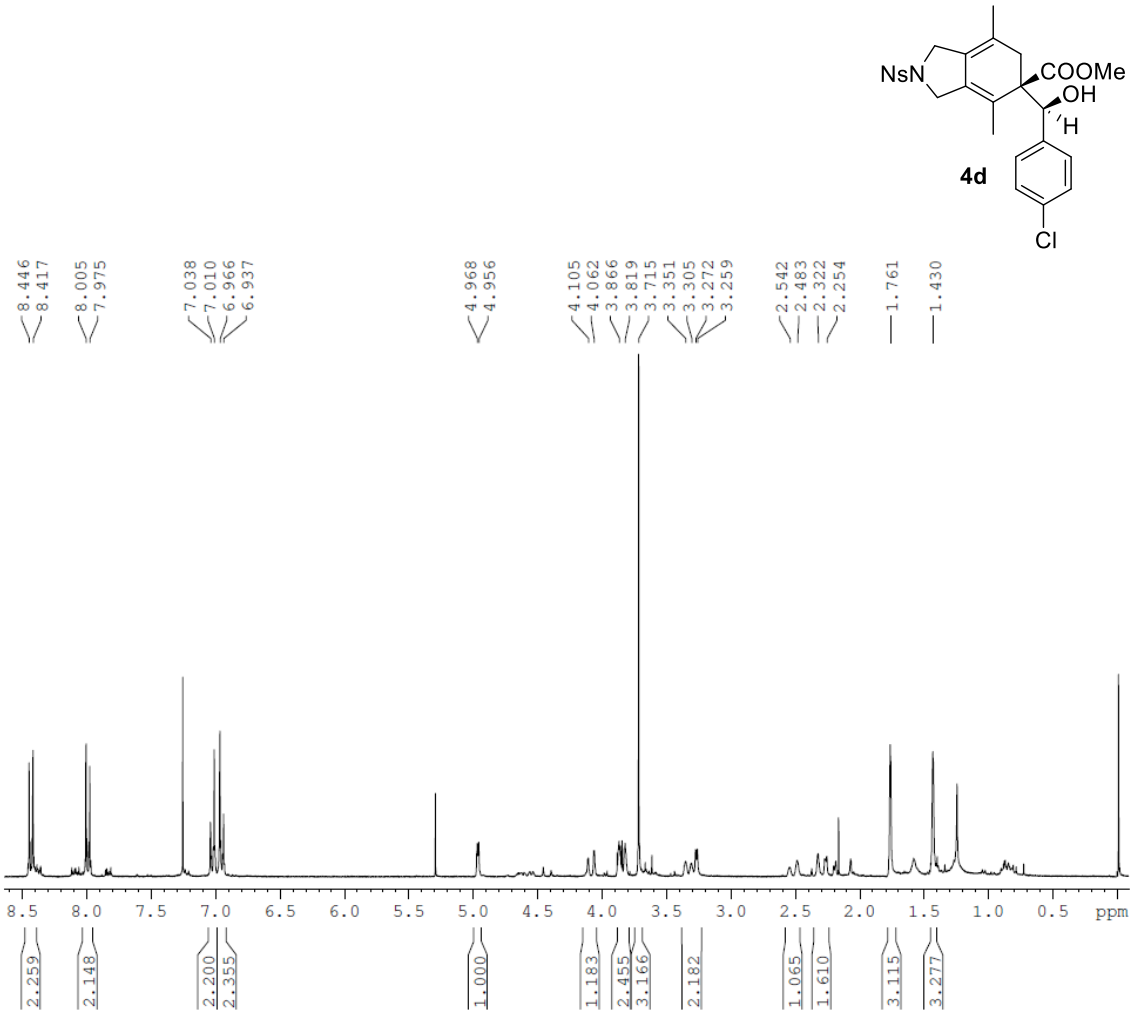


Figure S70: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **4d**

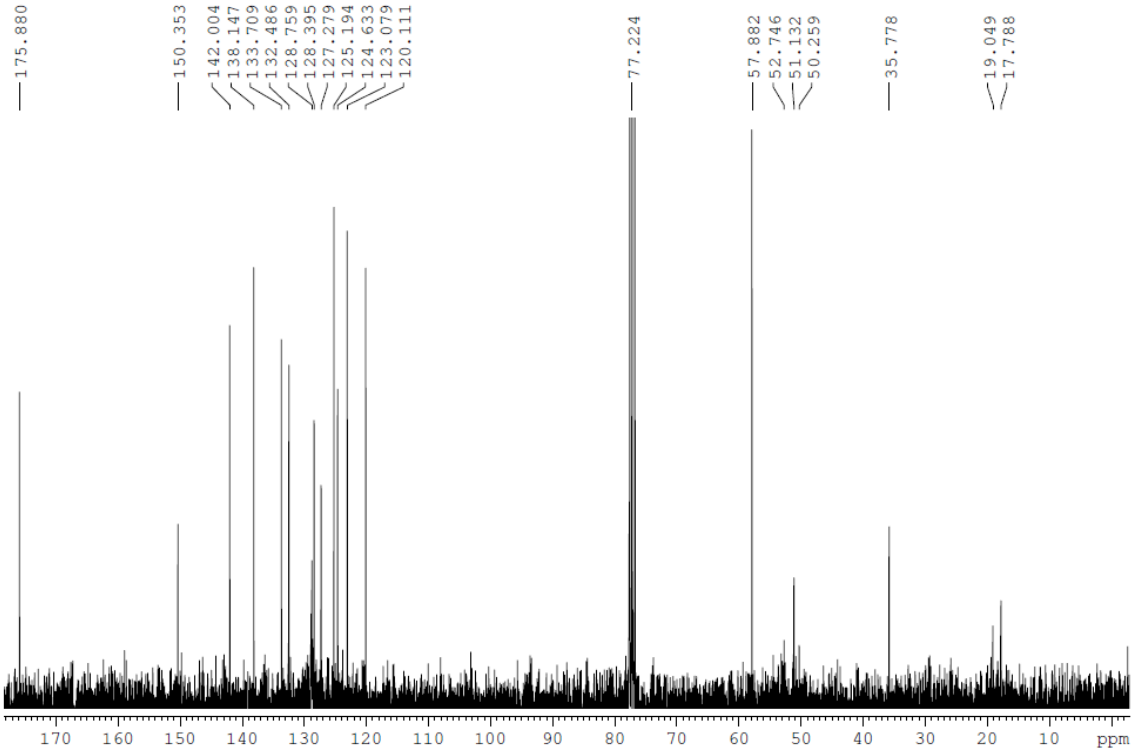


Figure S71: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **4d**

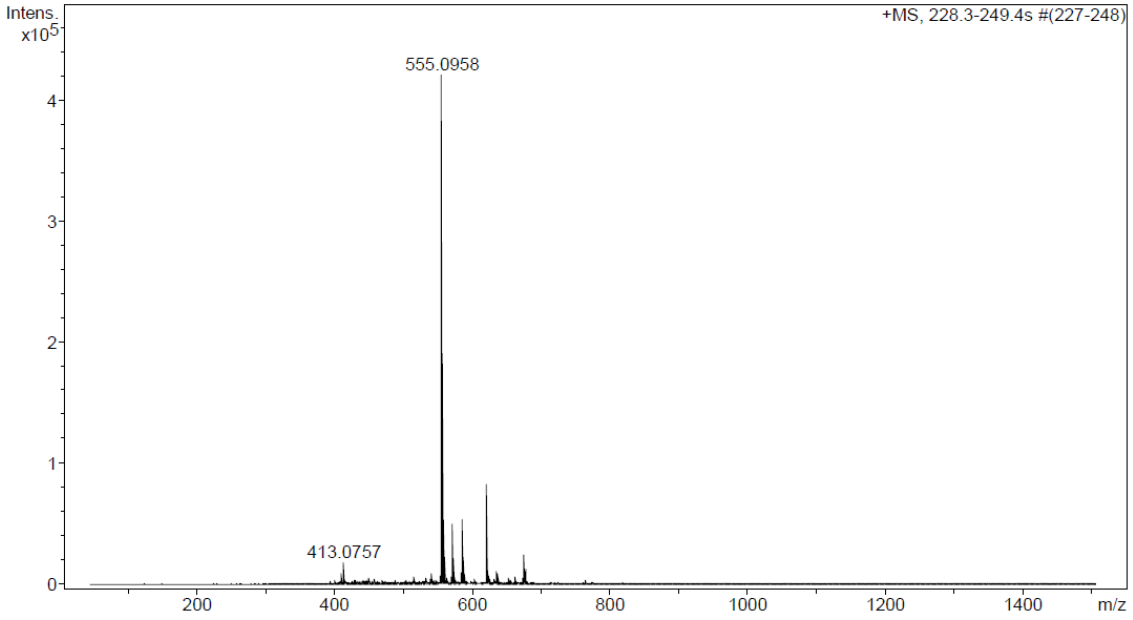


Figure S72: ESI-HRMS (*m/z*) spectrum of **4d**

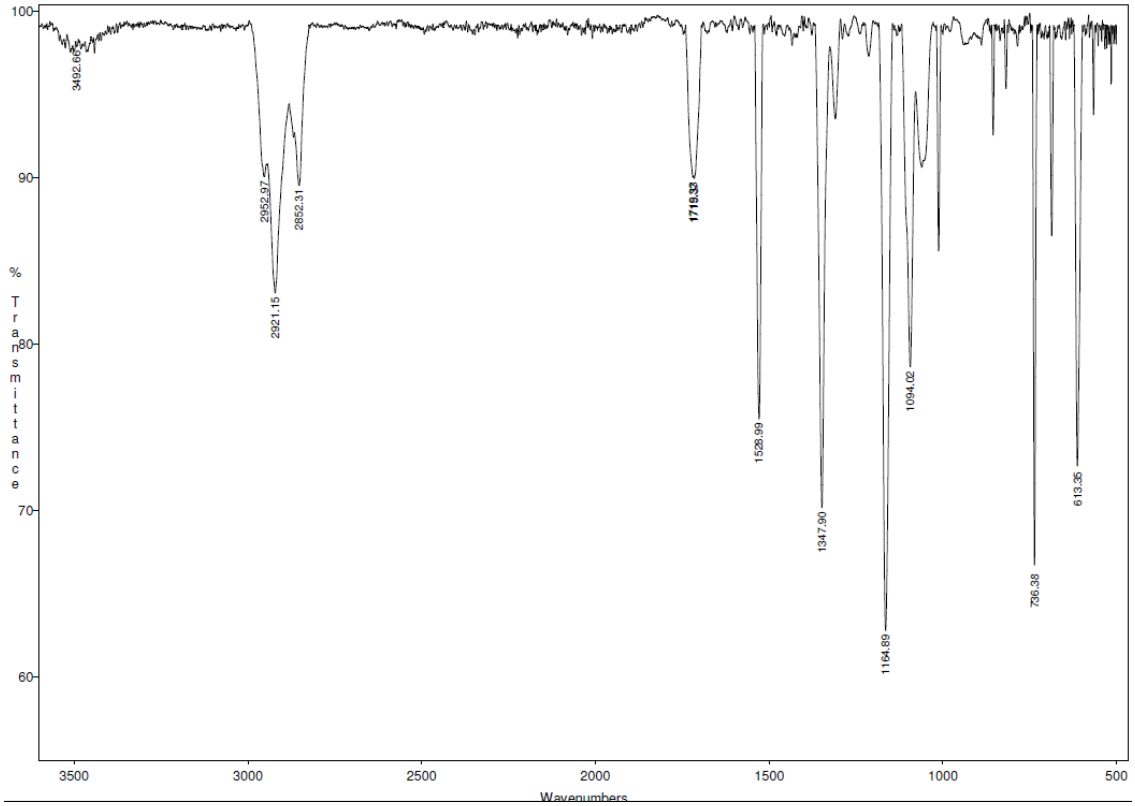


Figure S73: IR (ATR) spectrum of **4d**

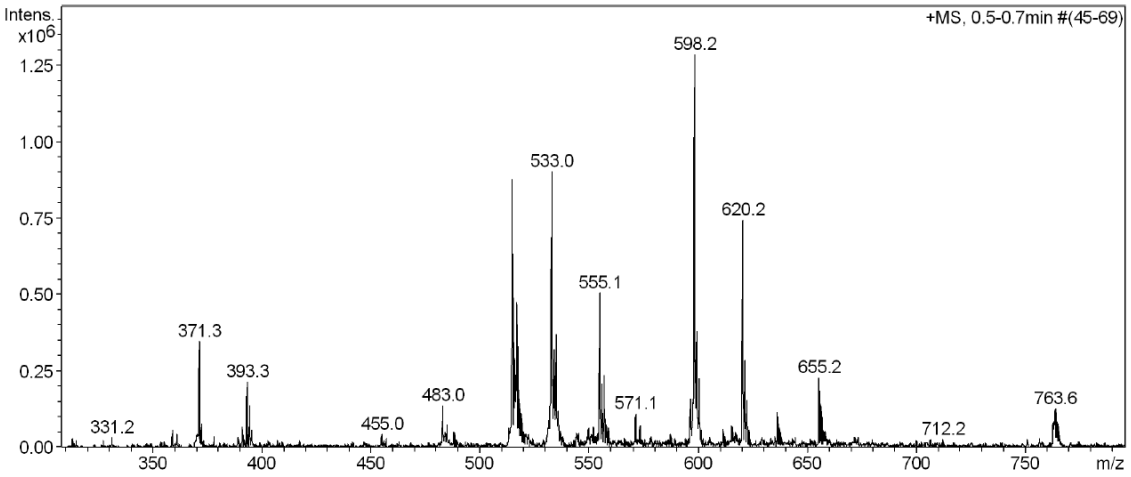


Figure S74: ESI-MS (*m/z*) spectrum of **4d**

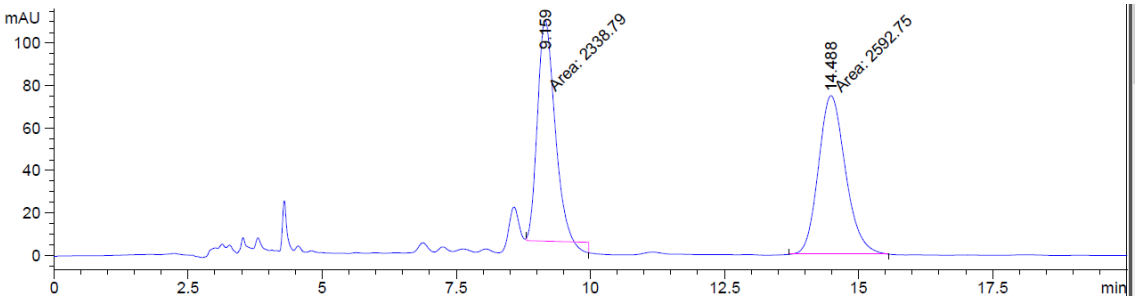


Figure S75: HPLC chromatogram of *rac*-**4d**

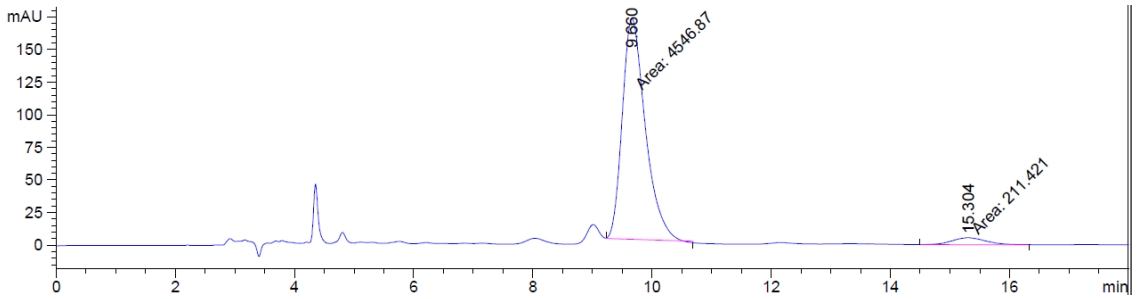


Figure S76: HPLC chromatogram of (*R*,*S*)-**4d**

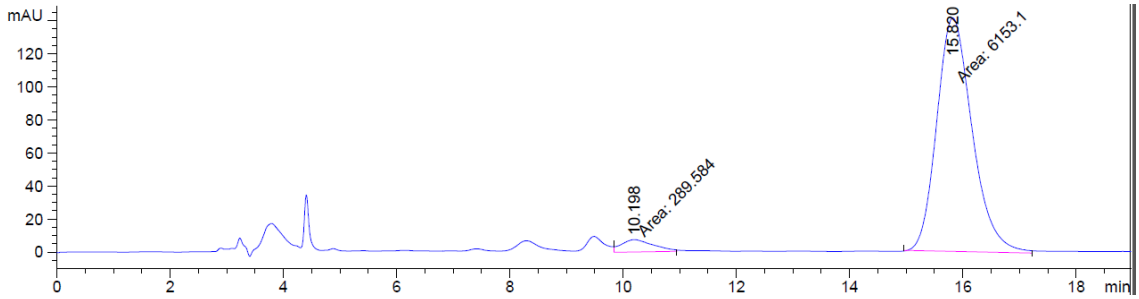


Figure S77: HPLC chromatogram of (*S*,*R*)-**4d**

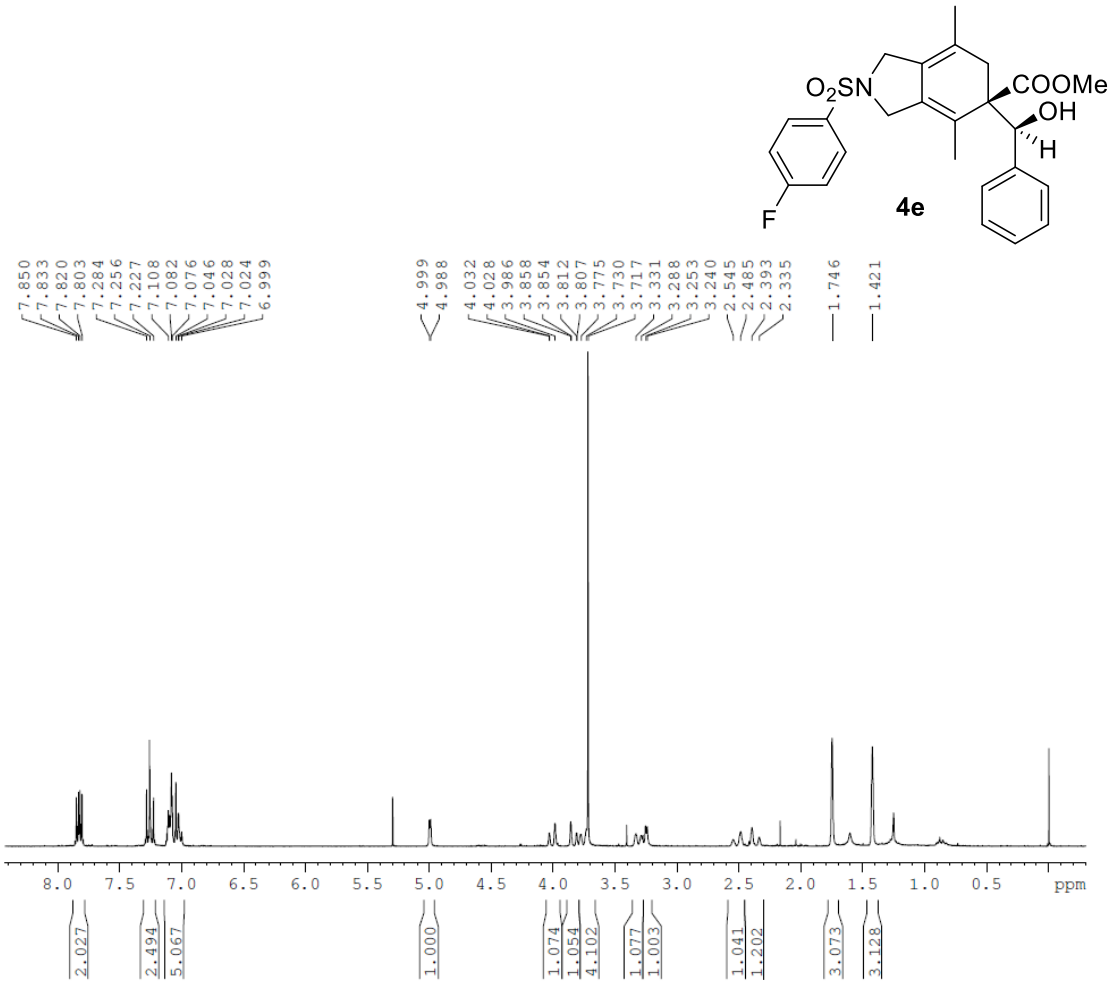


Figure S78: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **4e**

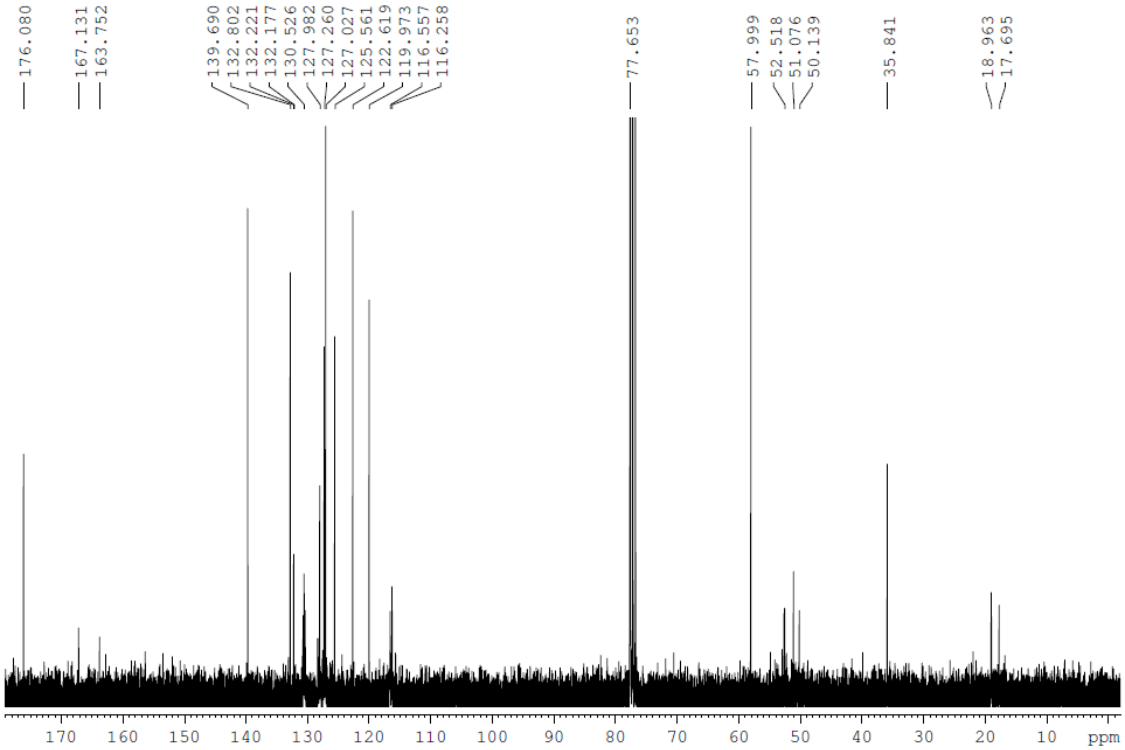


Figure S79: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **4e**

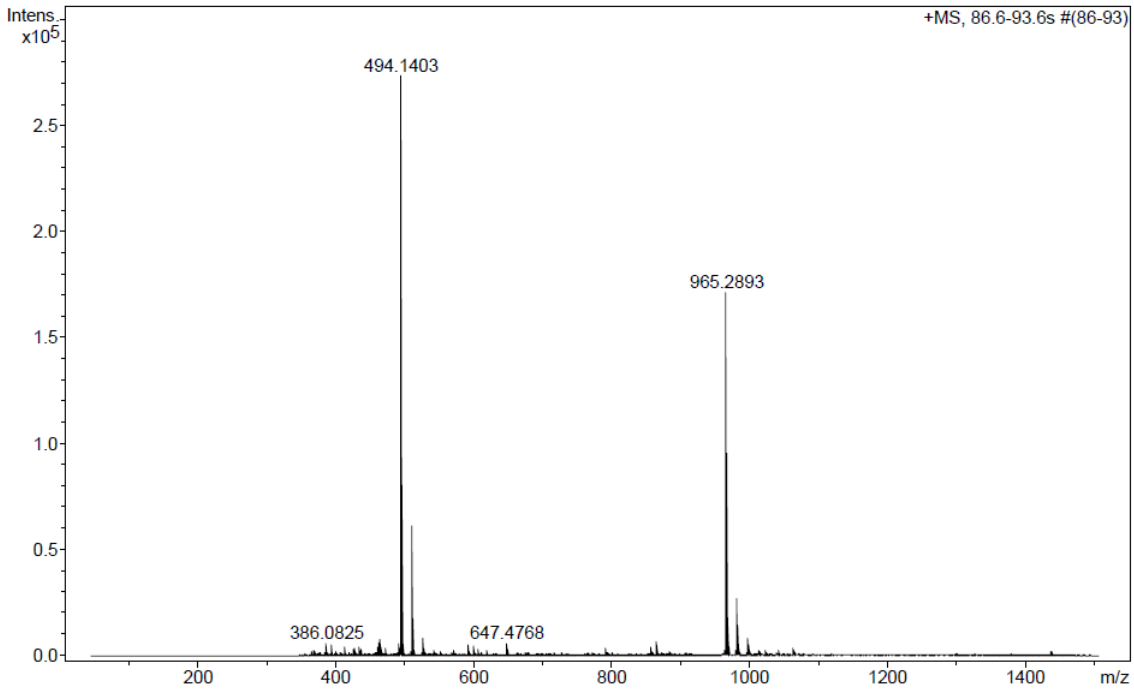


Figure S80: ESI-HRMS (*m/z*) spectrum of **4e**

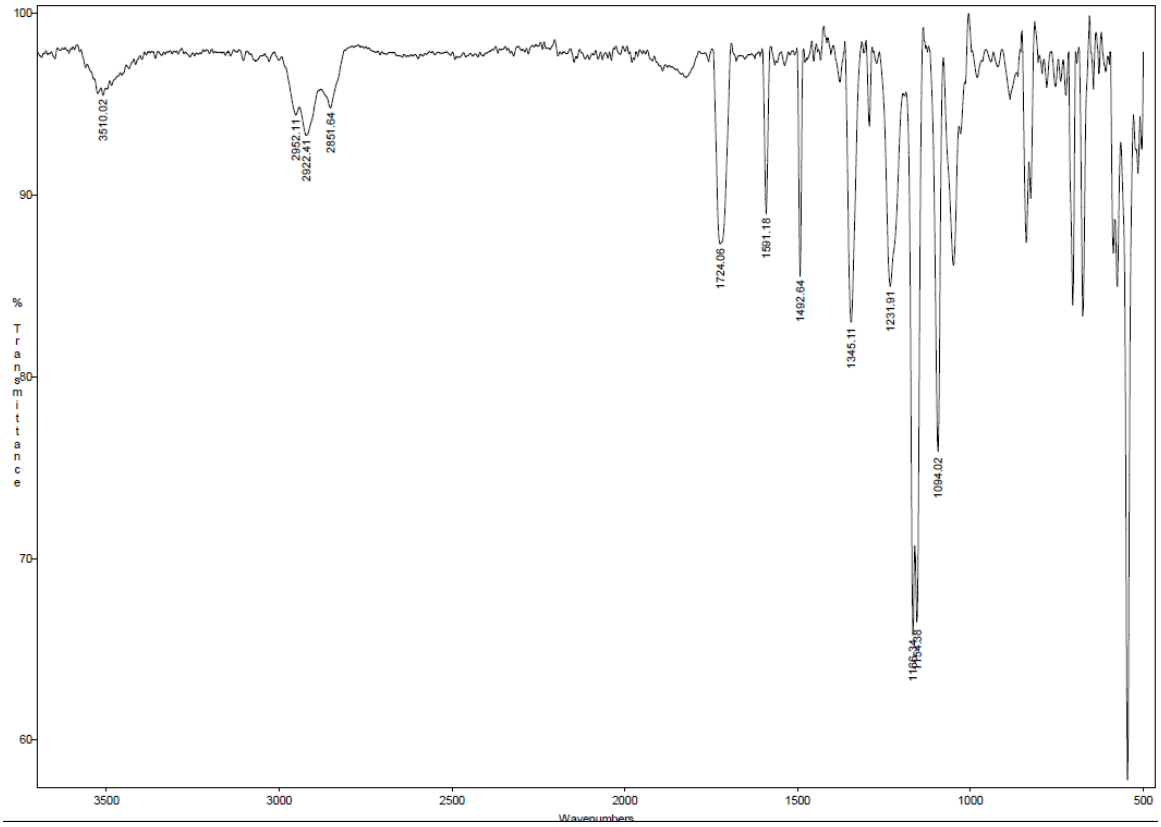


Figure S81: IR(ATR) spectrum of **4e**

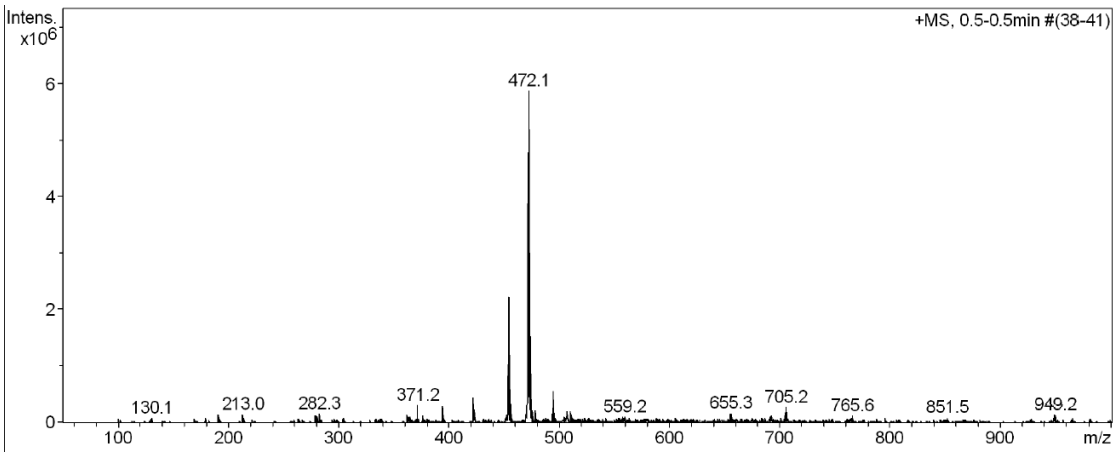


Figure S82: ESI-MS (*m/z*) spectrum of **4e**

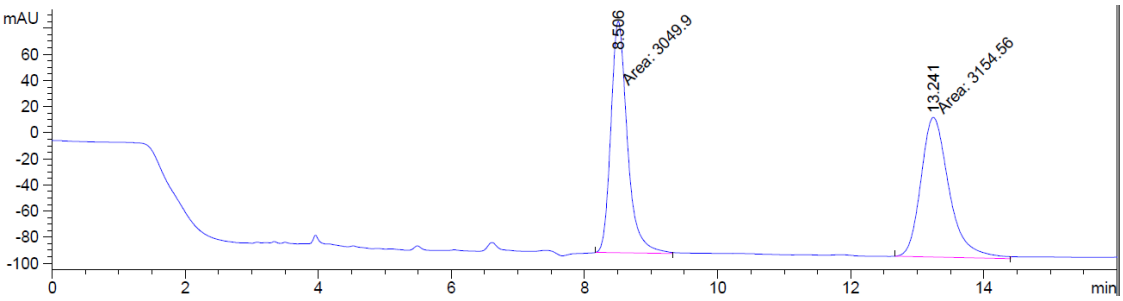


Figure S83: HPLC chromatogram of *rac*-**4e**

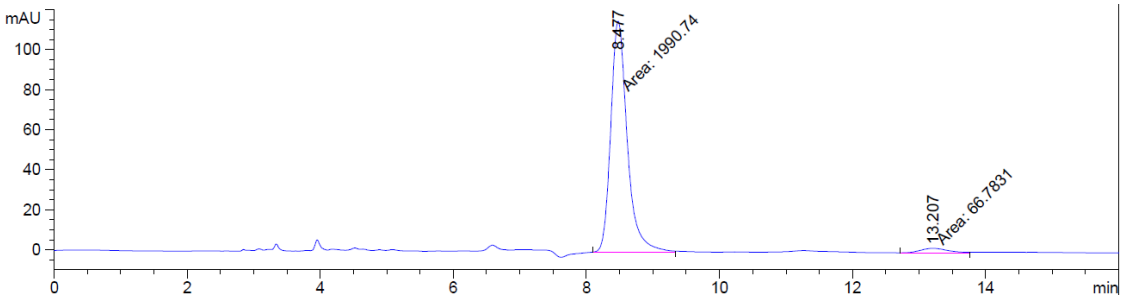


Figure S84: HPLC chromatogram of (*R*,*S*)-**4e**

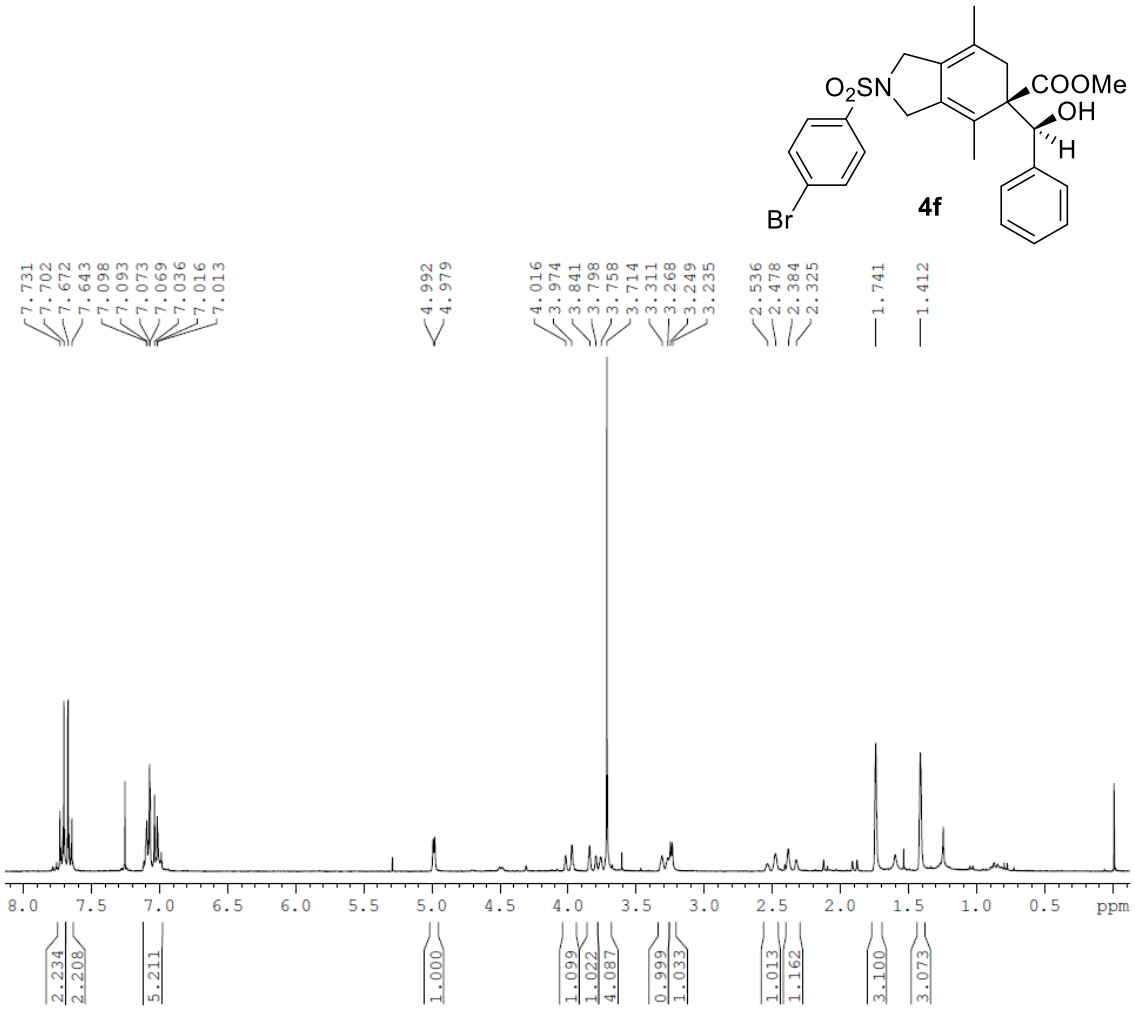


Figure S85: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **4f**

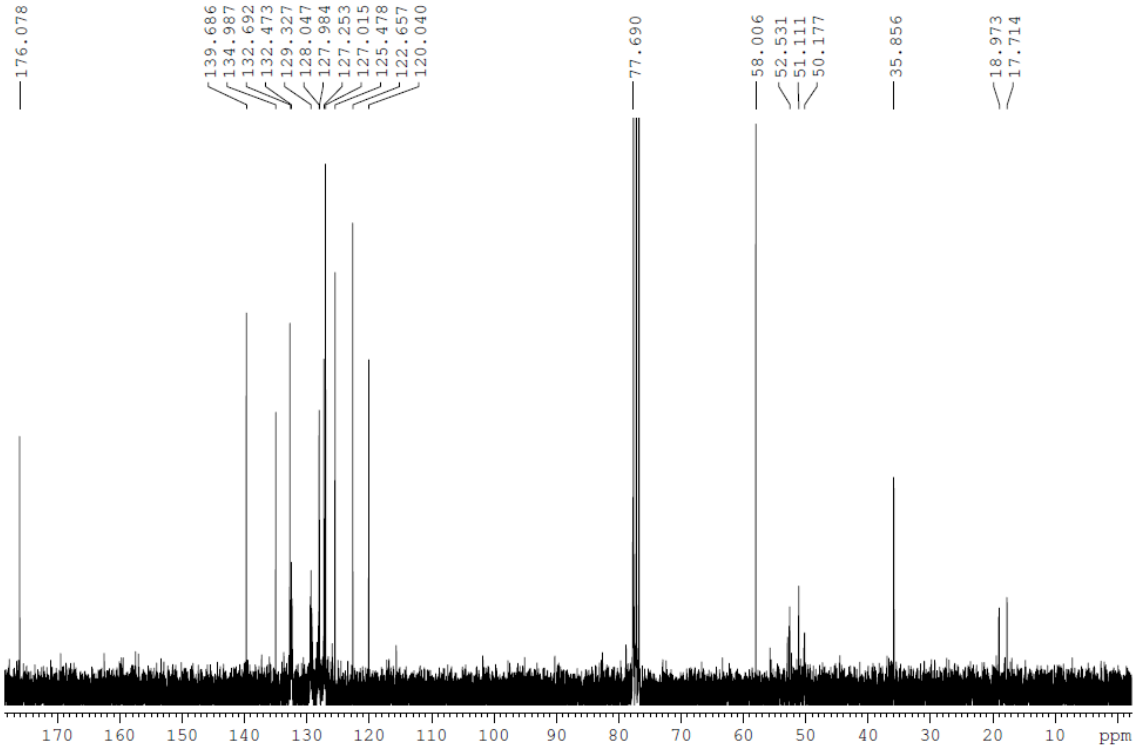


Figure S86: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **4f**

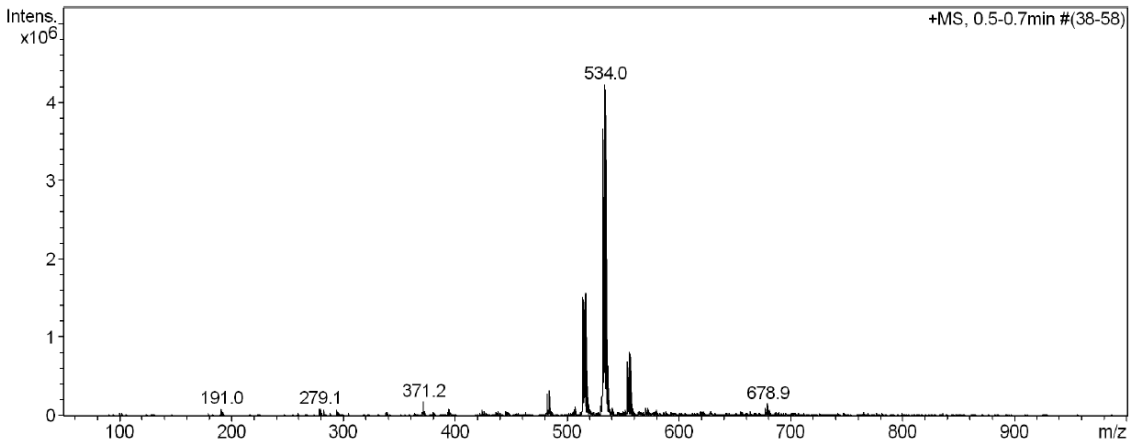


Figure S87: ESI-MS (*m/z*) spectrum of **4f**

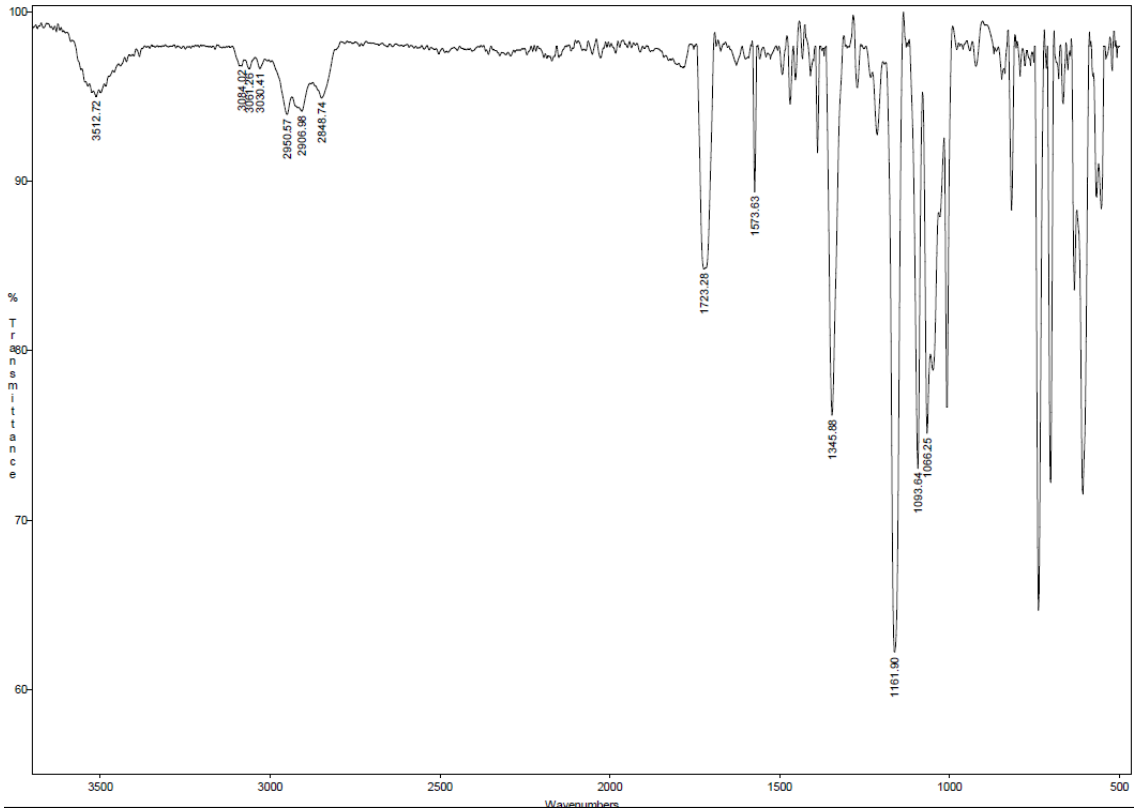


Figure S88: IR (ATR) spectrum of **4f**

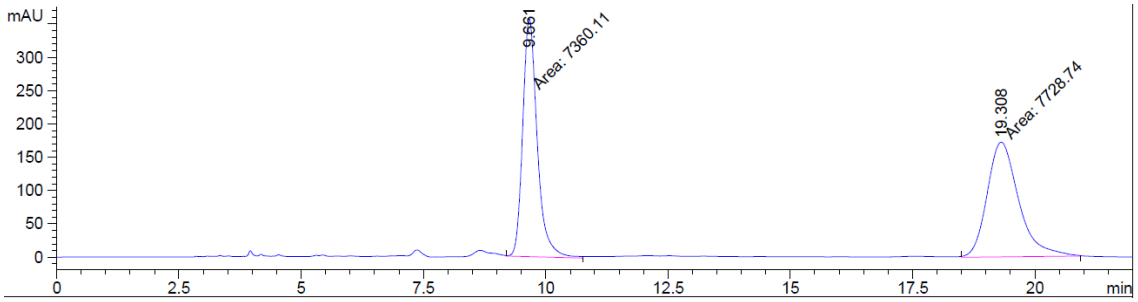


Figure S89: HPLC chromatogram of *rac*-**4f**

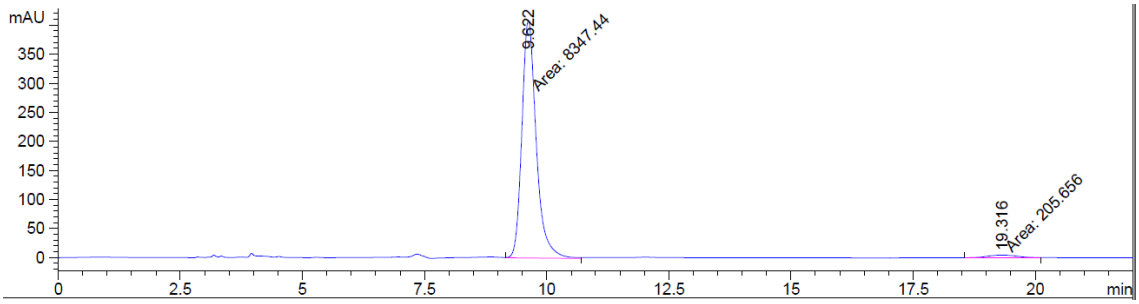


Figure S90: HPLC chromatogram of (*R*,*S*)-**4f**

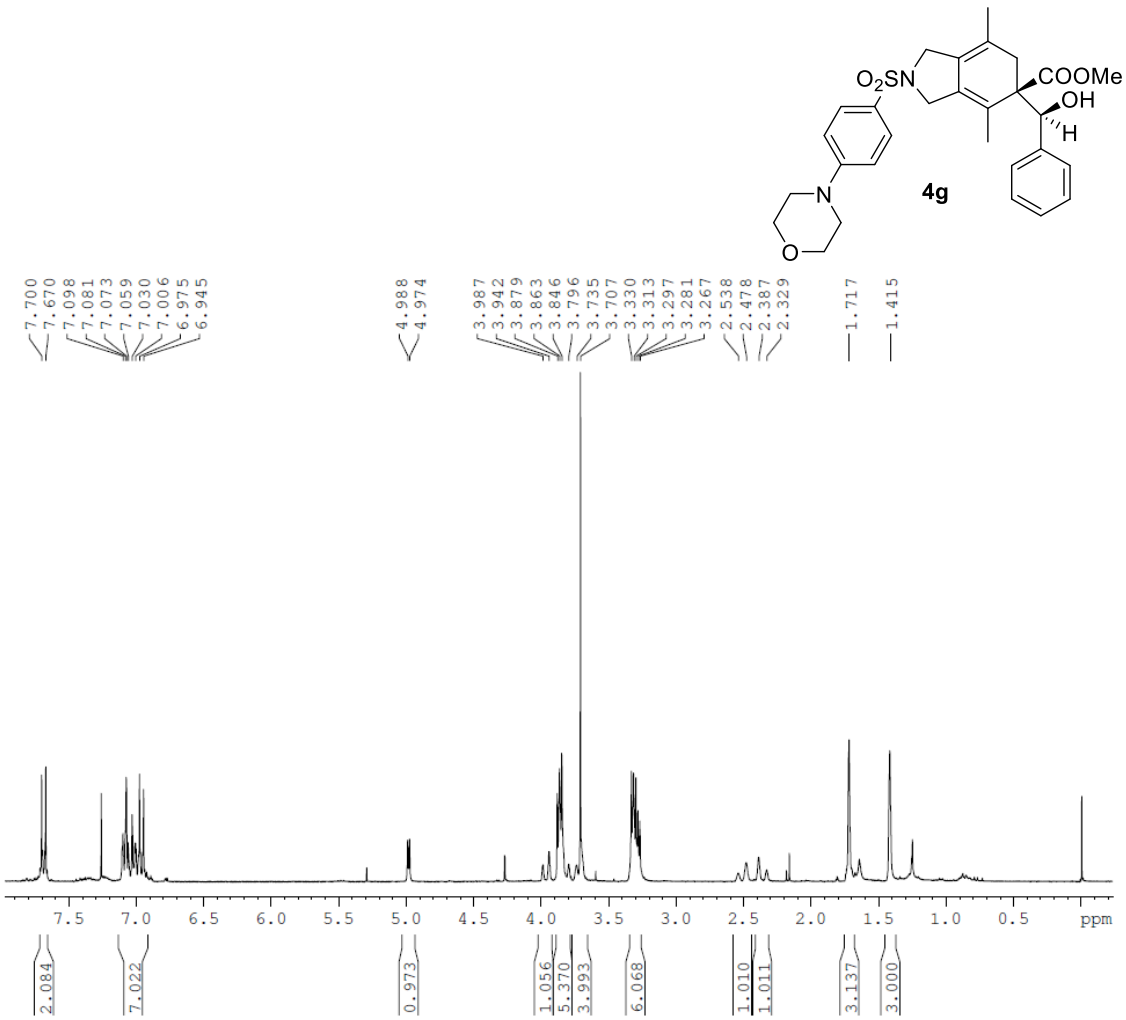


Figure S91: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **4g**

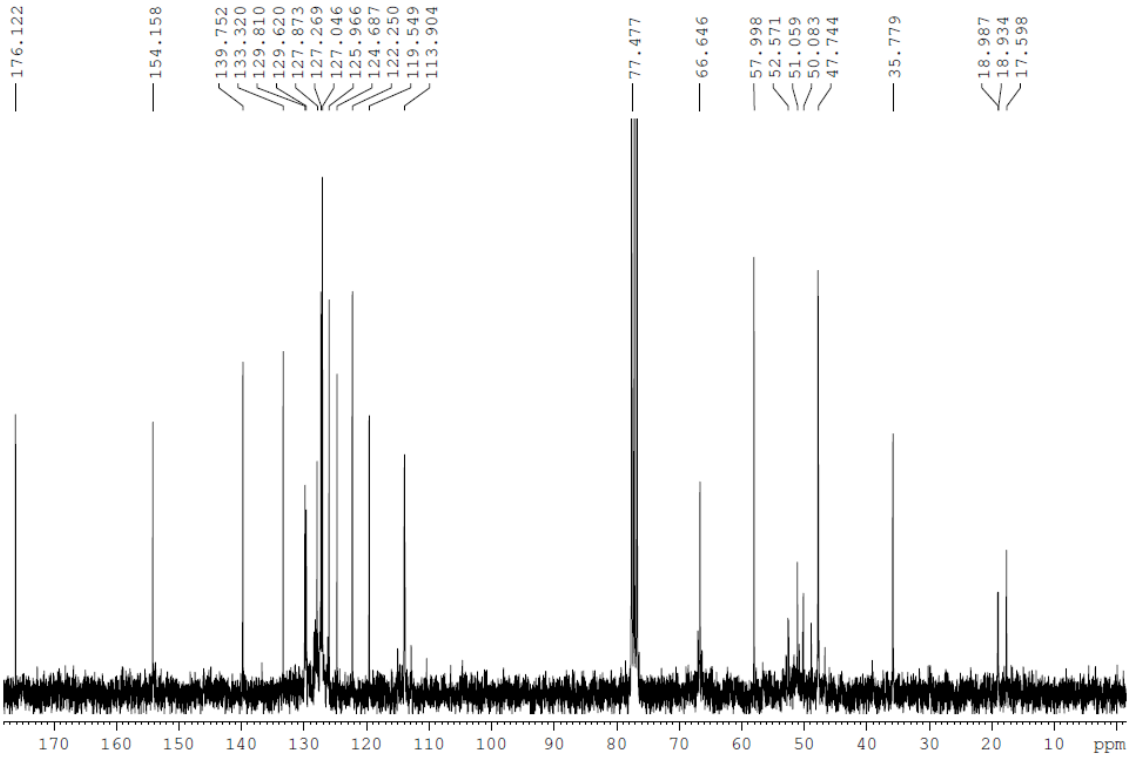


Figure S92: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **4g**

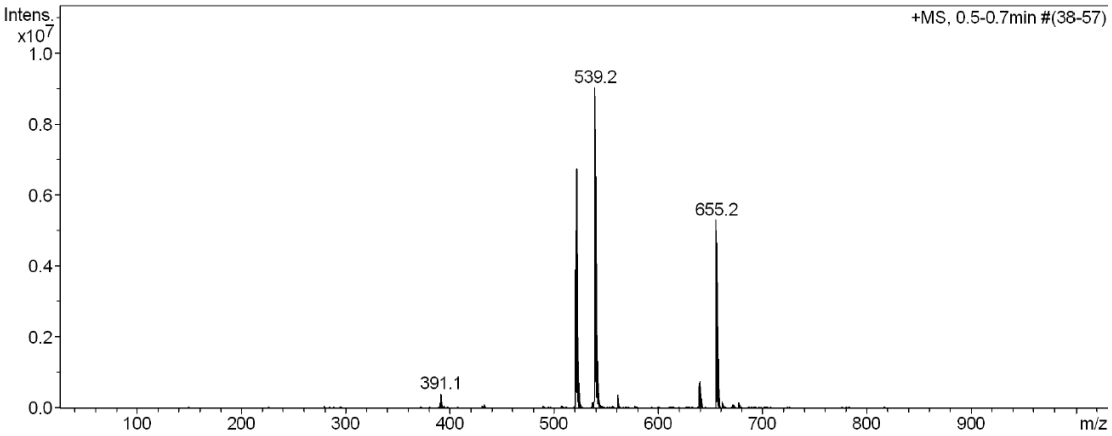


Figure S93: ESI-MS (*m/z*) spectrum of **4g**

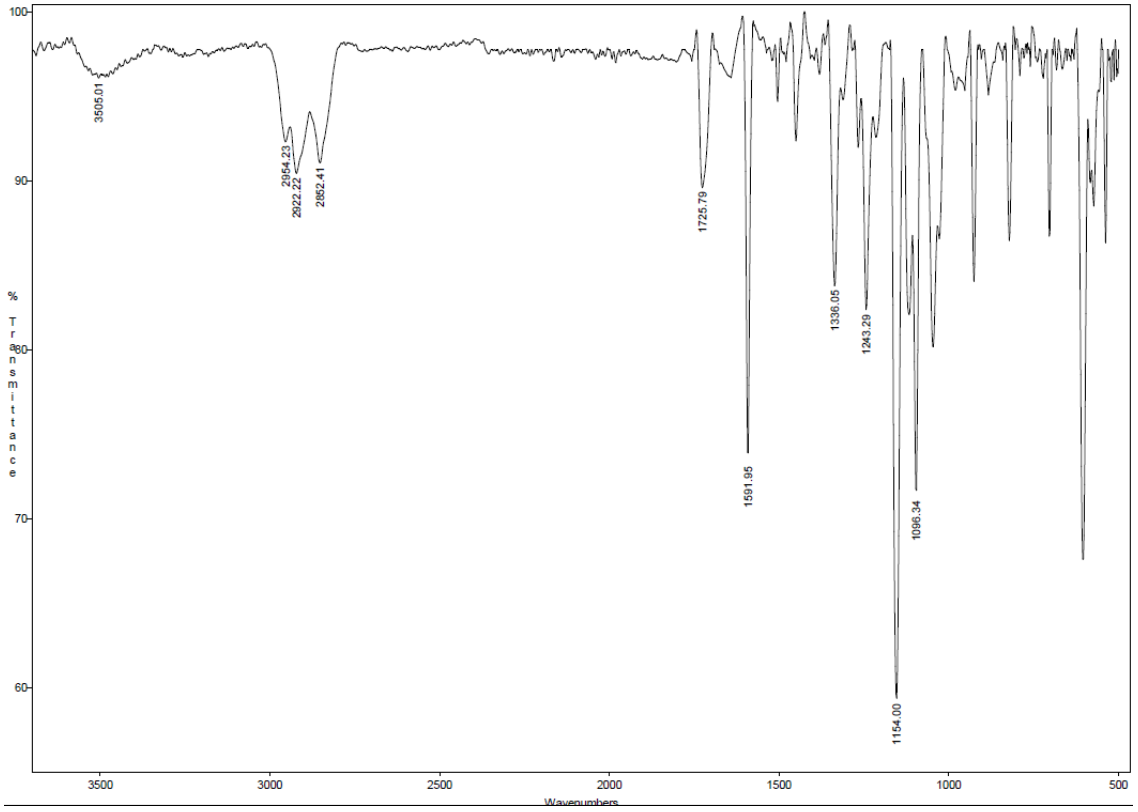


Figure S94: IR (ATR) spectrum of **4g**

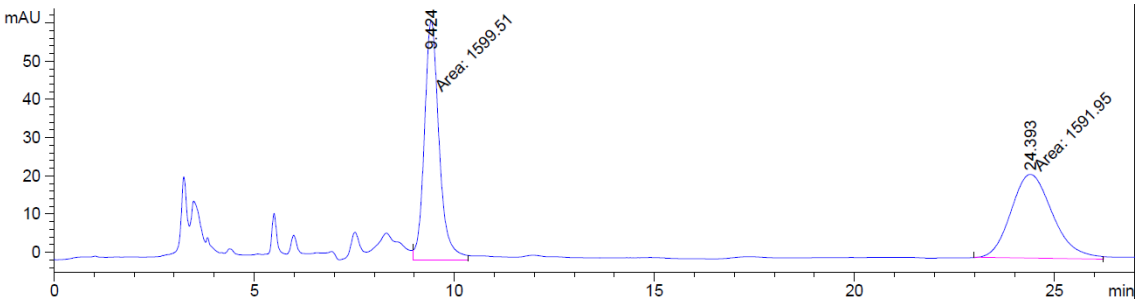


Figure S95: HPLC chromatogram of *rac*-**4g**

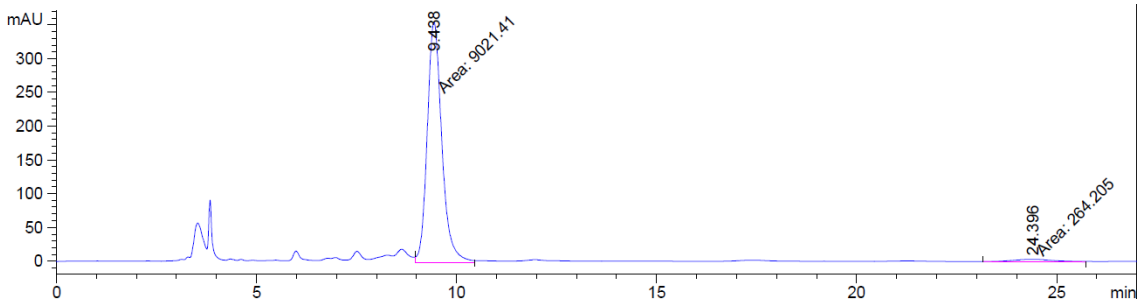


Figure S96: HPLC chromatogram of (*R*,*S*)-**4g**

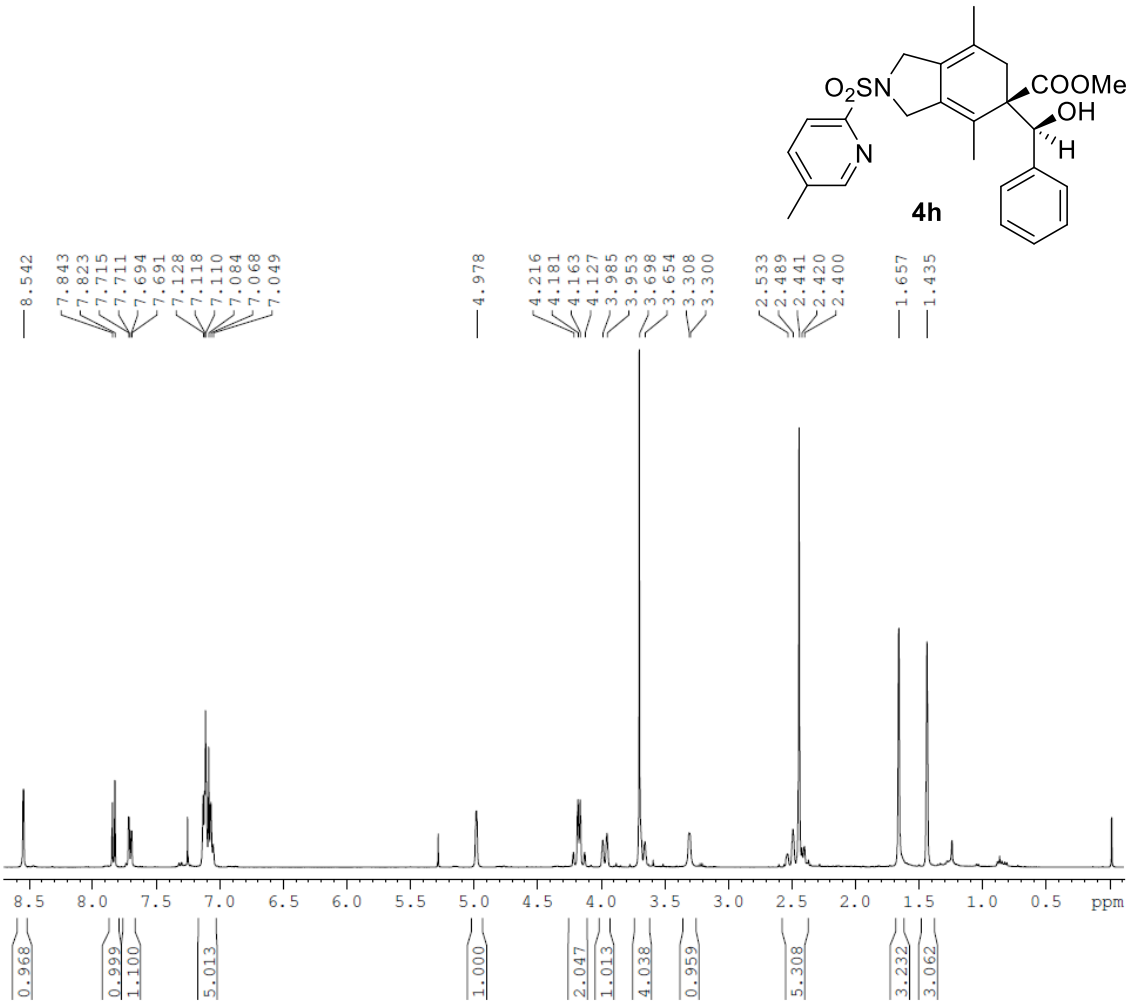


Figure S97: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4h**

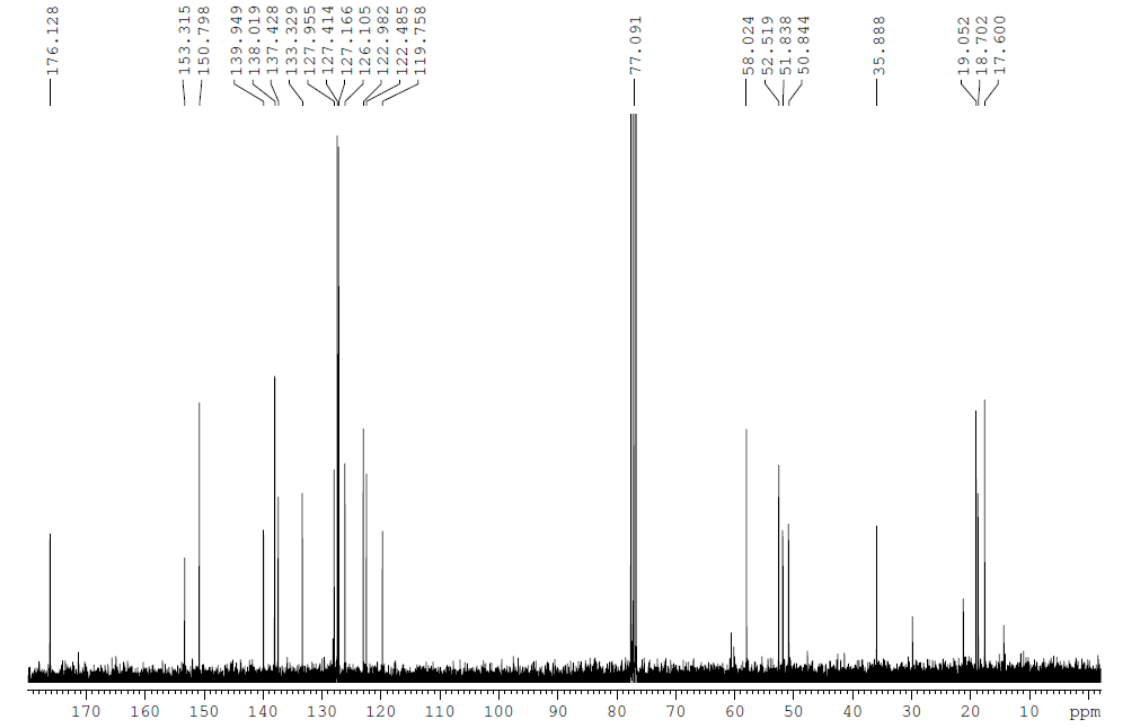


Figure S98: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **4h**

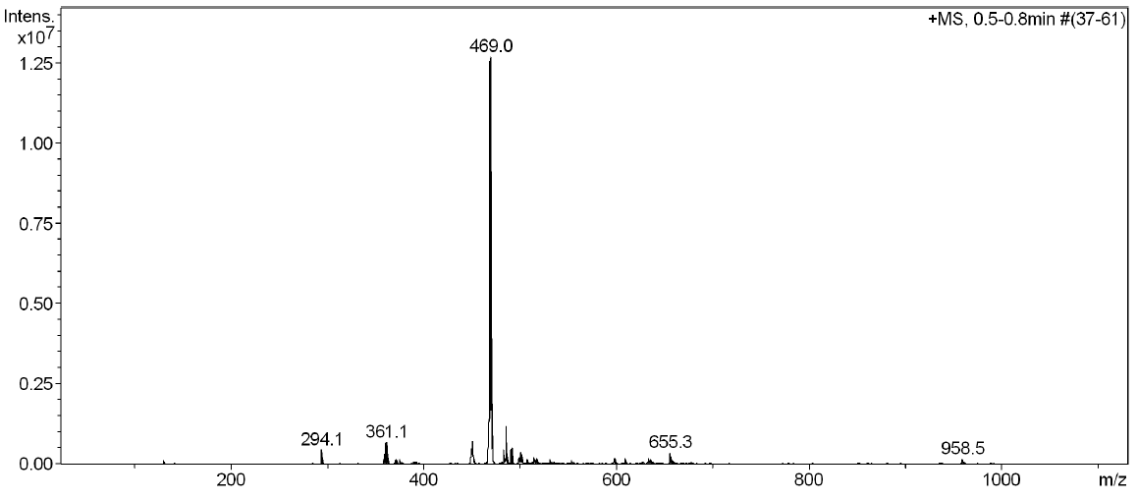


Figure S99: ESI-MS (*m/z*) spectrum of **4h**

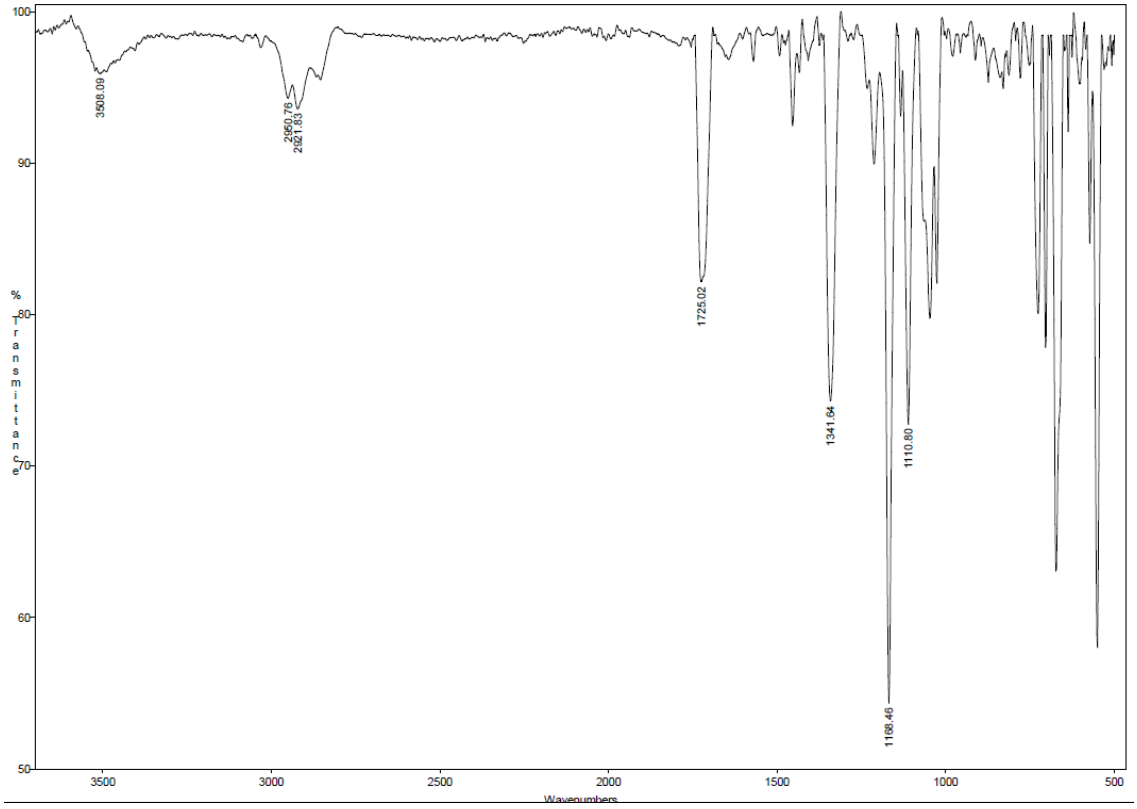


Figure S100: IR (ATR) spectrum of **4h**

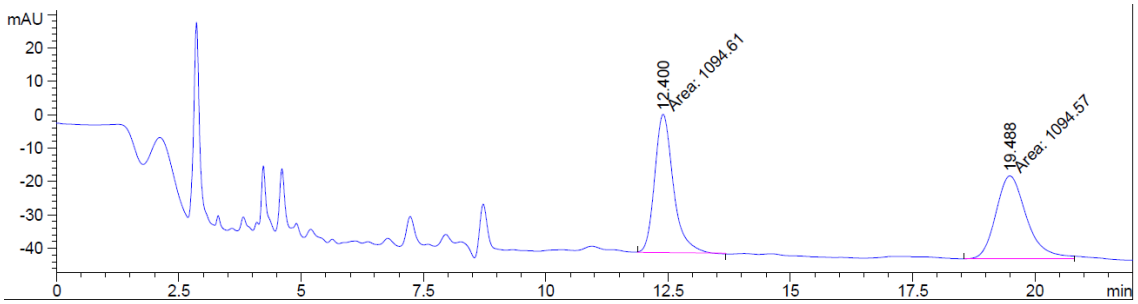


Figure S101: HPLC chromatogram of *rac*-**4h**

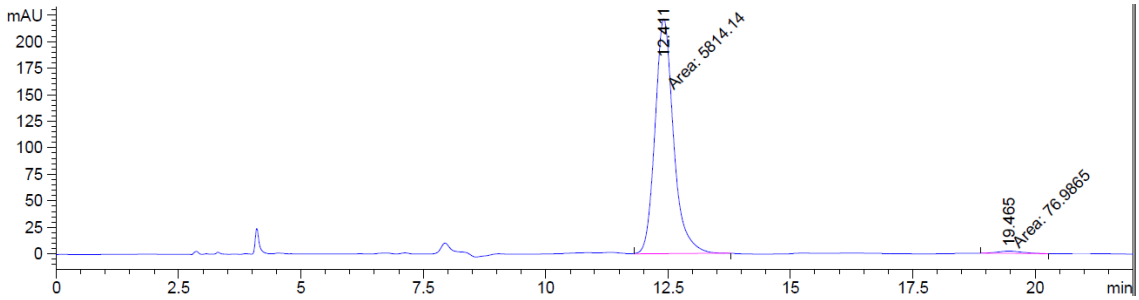


Figure S102: HPLC chromatogram of (*R*,*S*)-**4h**

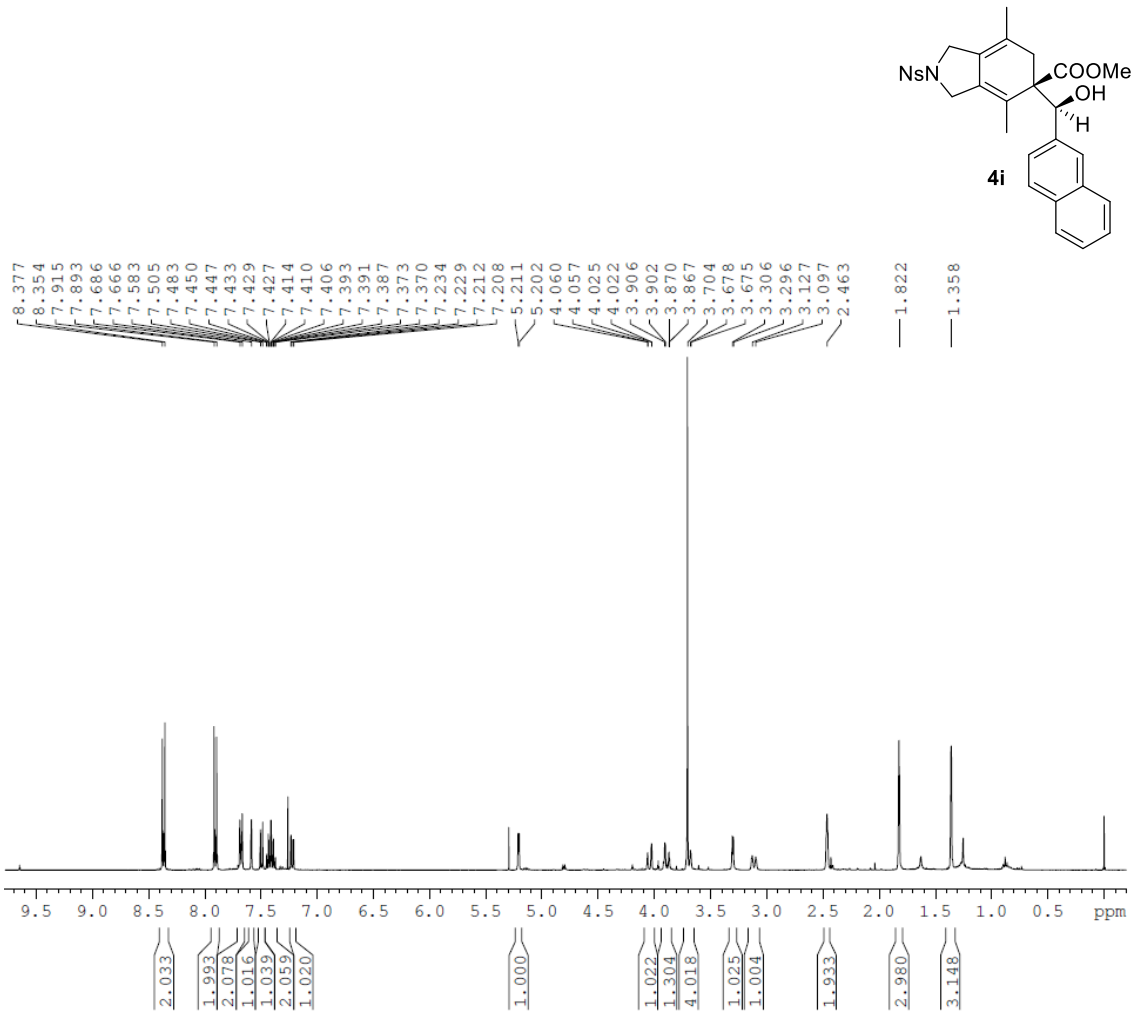


Figure S103: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4i**

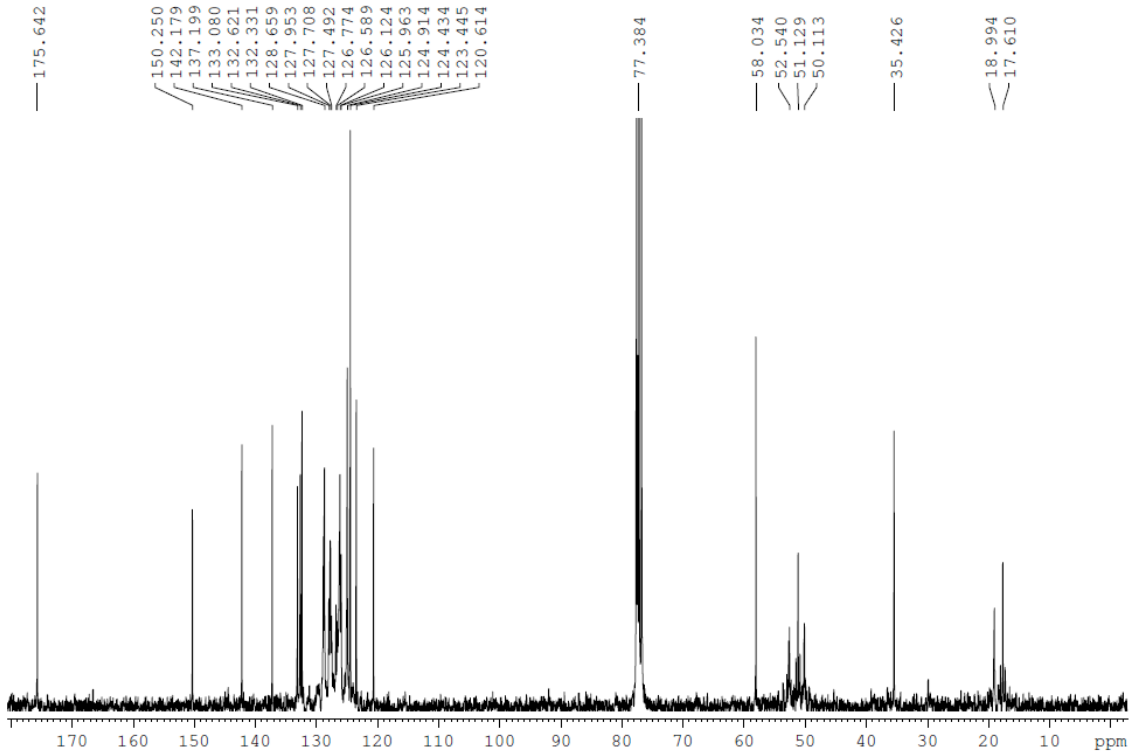


Figure S104: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **4i**

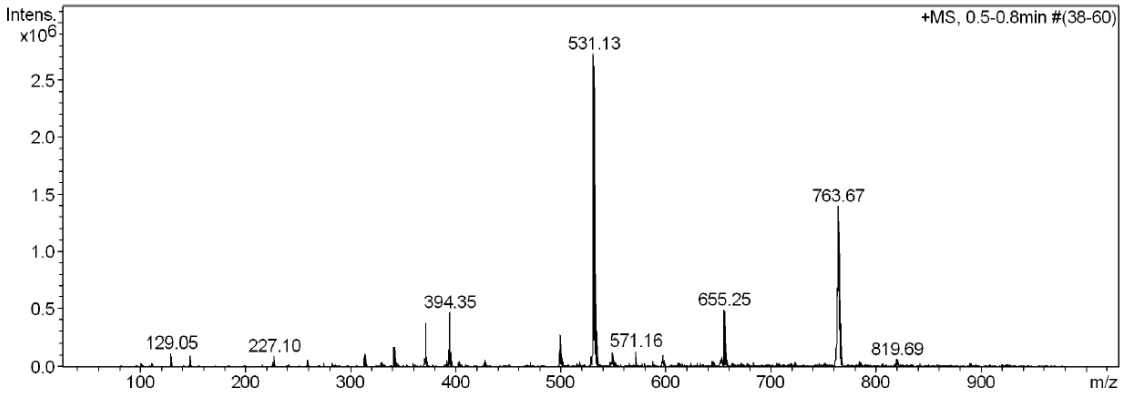


Figure S105: ESI-MS (*m/z*) spectrum of **4i**

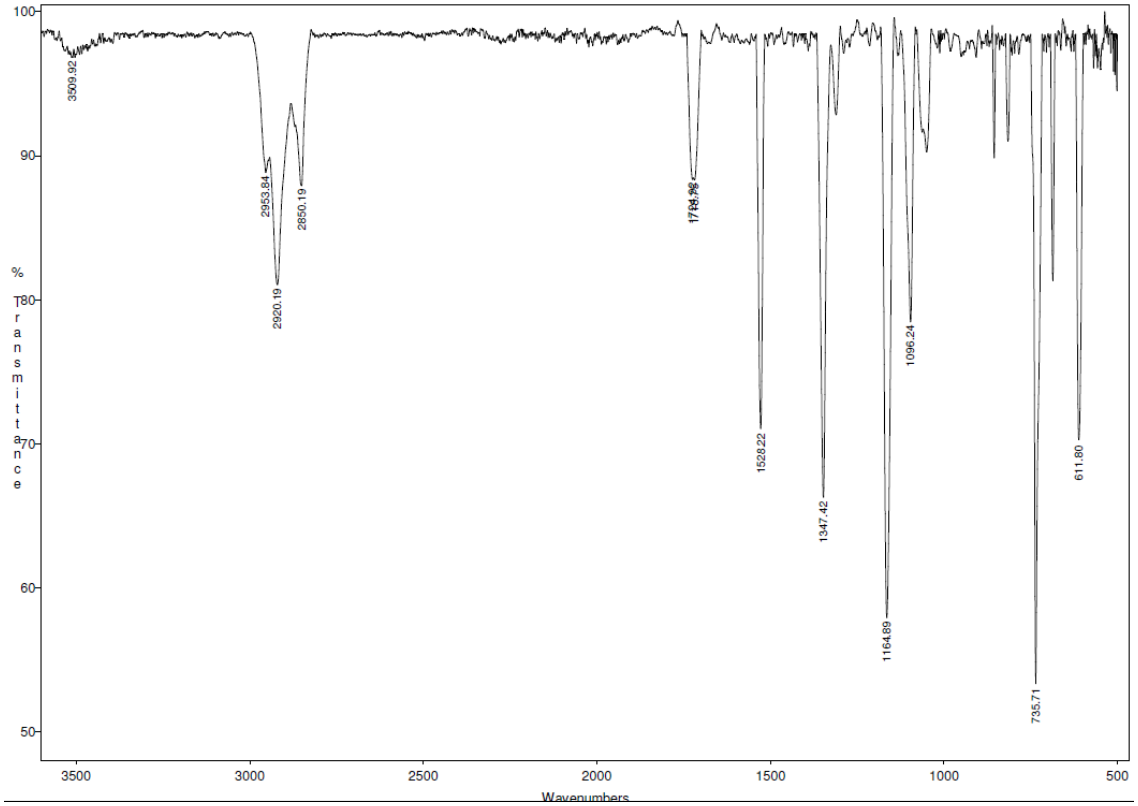


Figure S106: IR (ATR) spectrum of **4i**

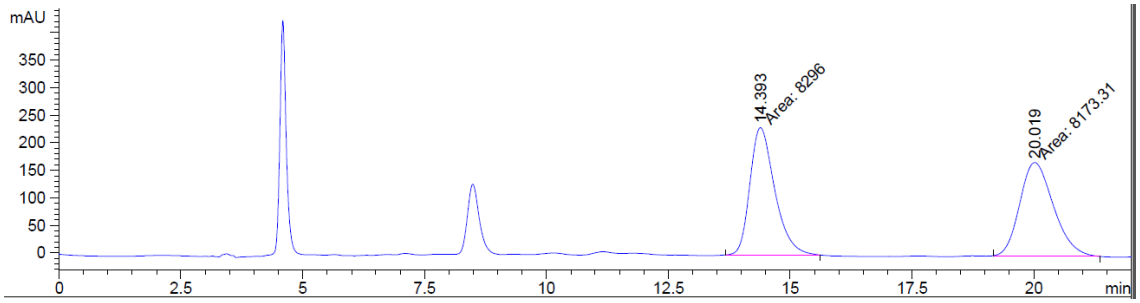


Figure S107: HPLC chromatogram of *rac*-**4i**

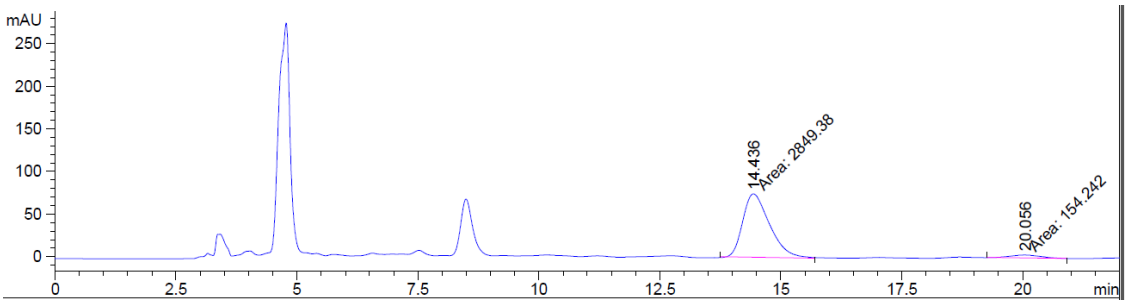


Figure S108: HPLC chromatogram of (*R*,*S*)-**4i**

Figure S109: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5a**

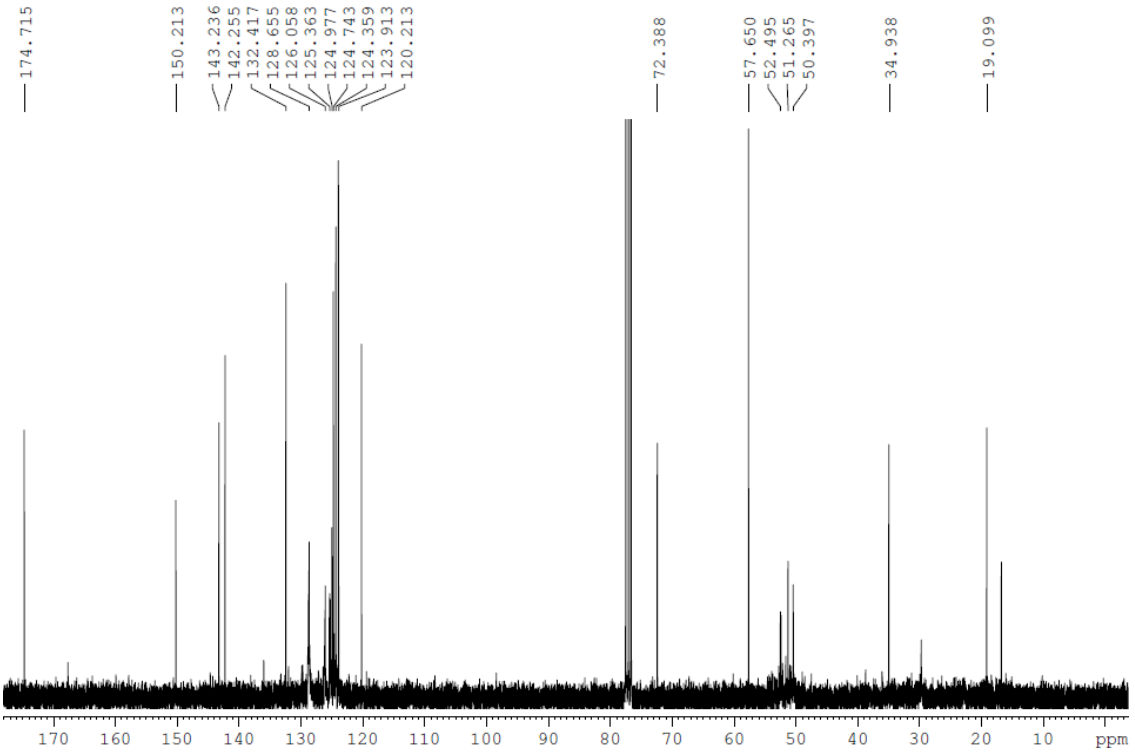


Figure S110: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **5a**

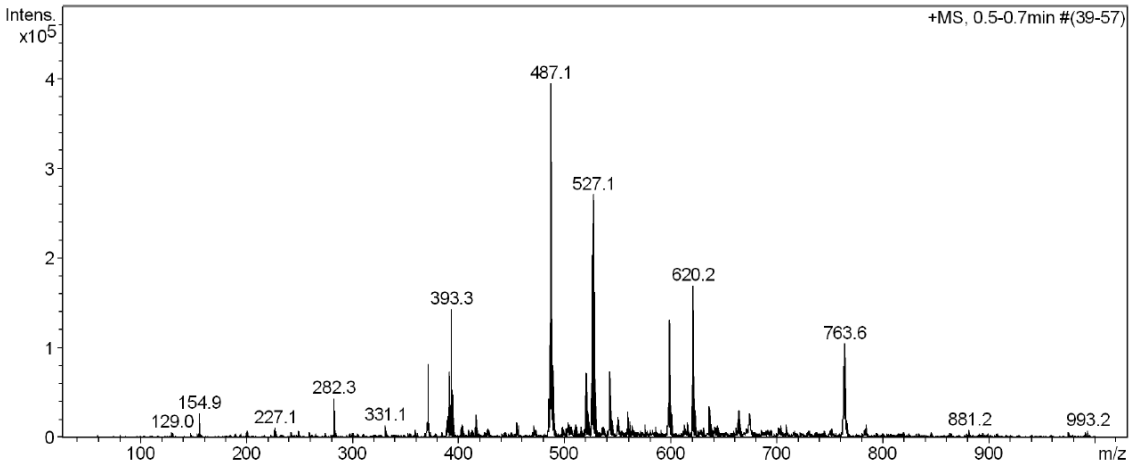


Figure S111: ESI-MS (*m/z*) spectrum of **5a**

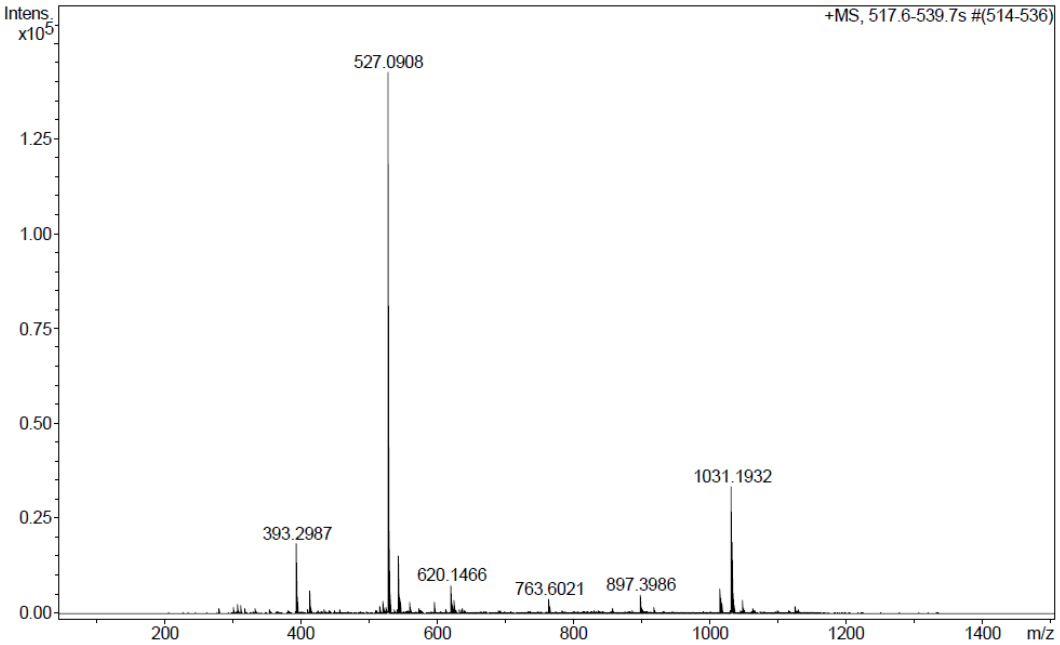


Figure S112: ESI-HRMS (*m/z*) spectrum of **5a**

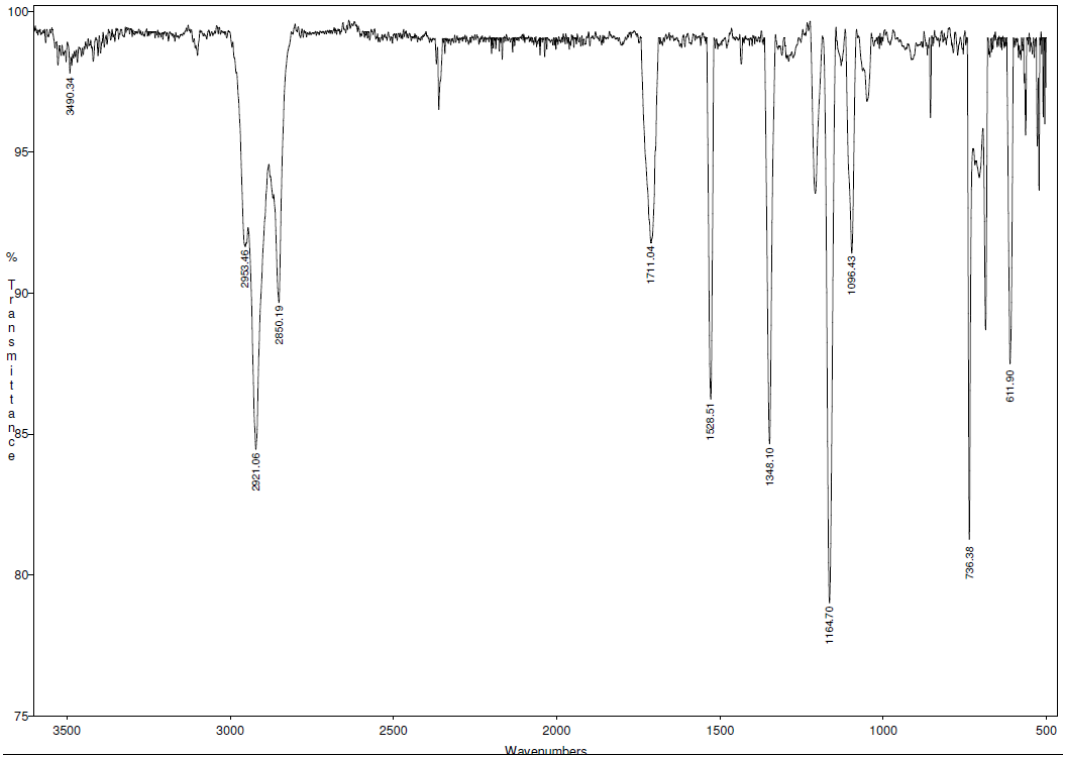


Figure S113: IR (ATR) spectrum of **5a**

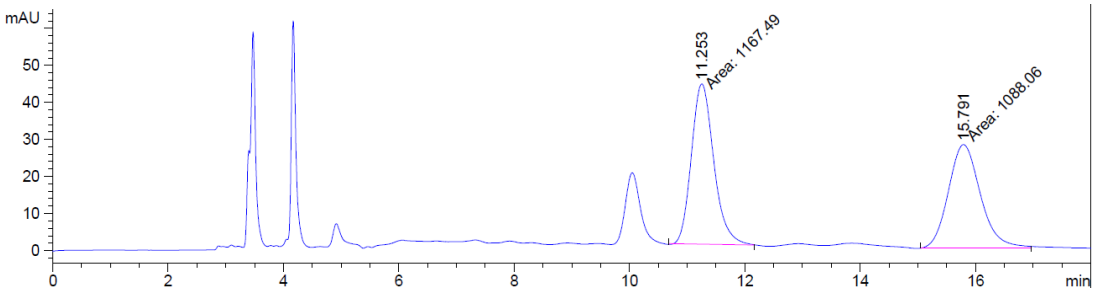


Figure S114: HPLC chromatogram of r*ac*-**5a**

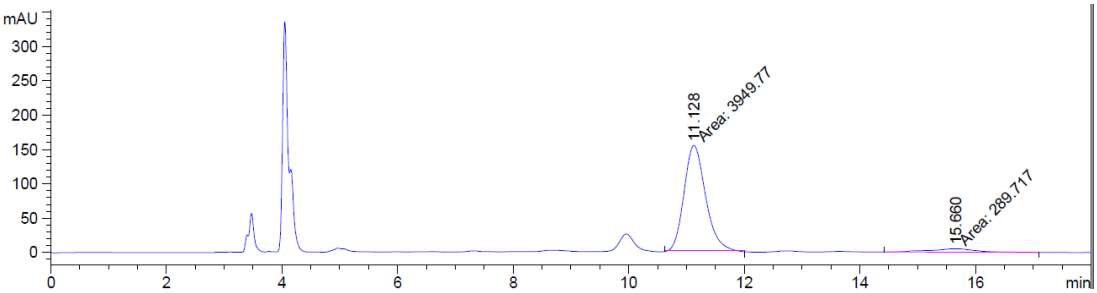
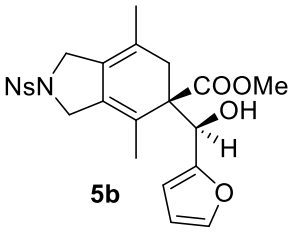


Figure S115: HPLC chromatogram of (*R*,*R*)-**5a**



5b

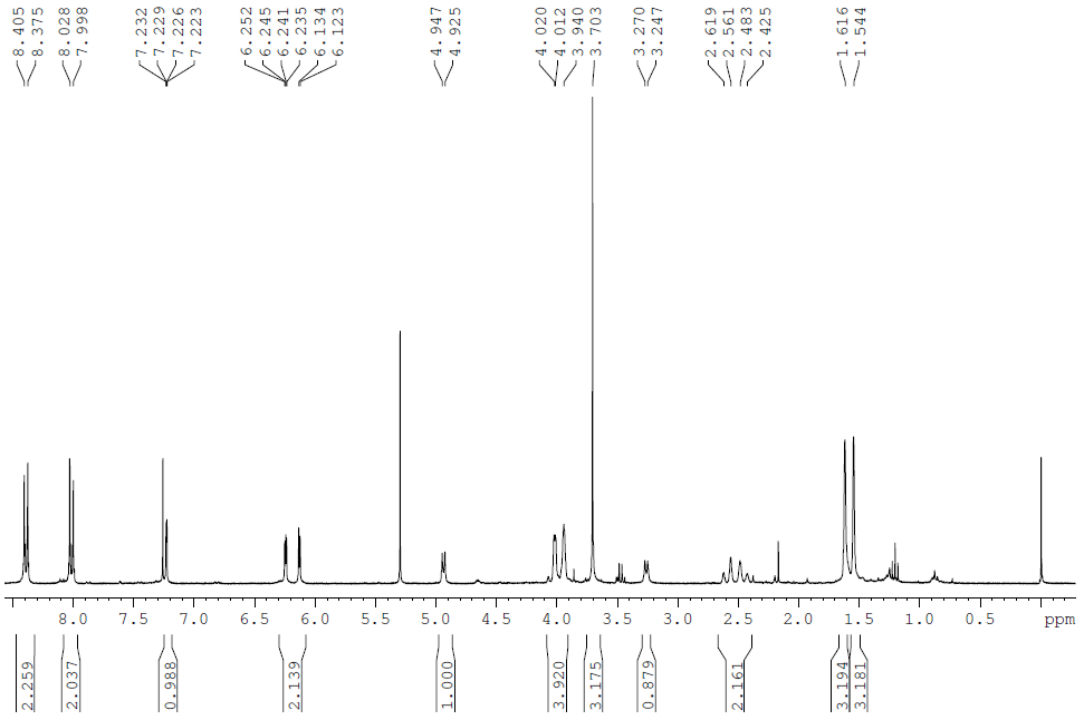


Figure S116: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **5b**

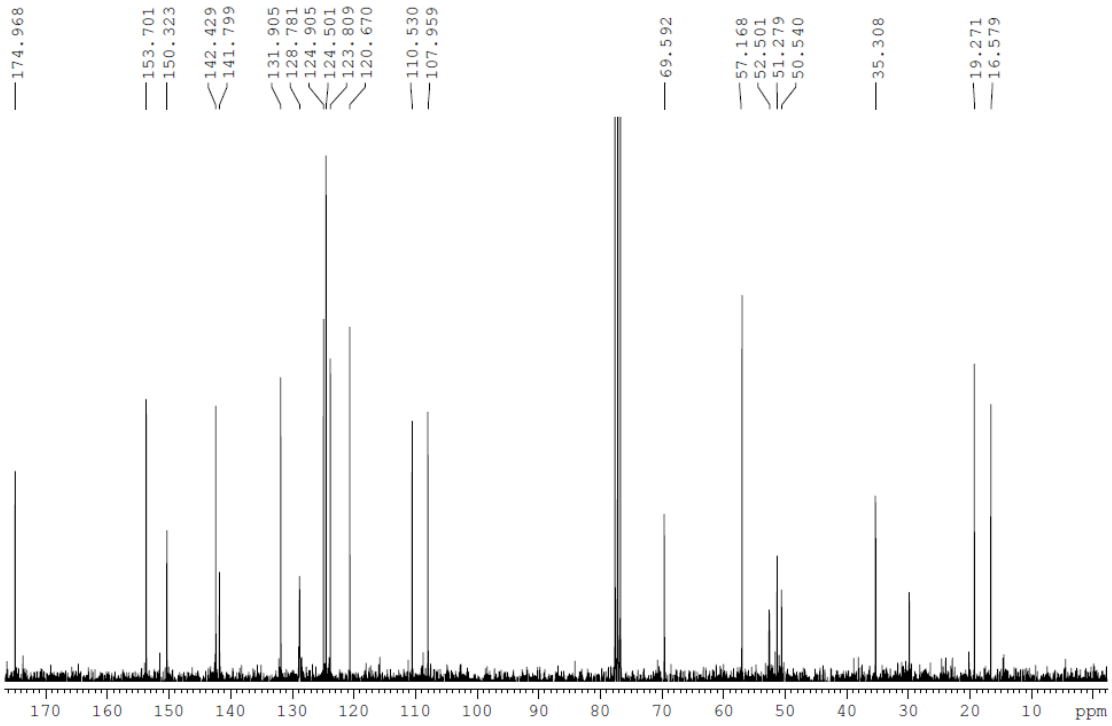


Figure S117: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **5b**

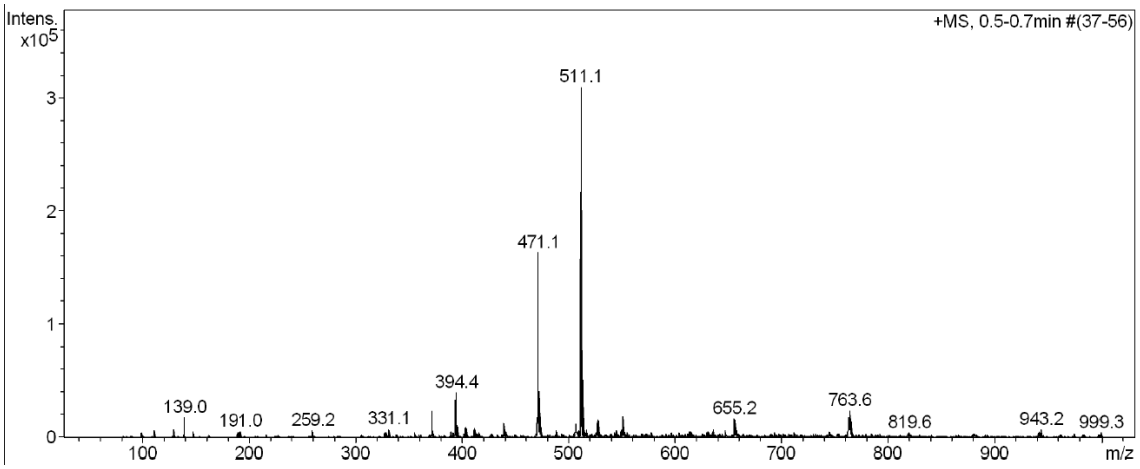


Figure S118: ESI-MS (*m/z*) spectrum of **5b**

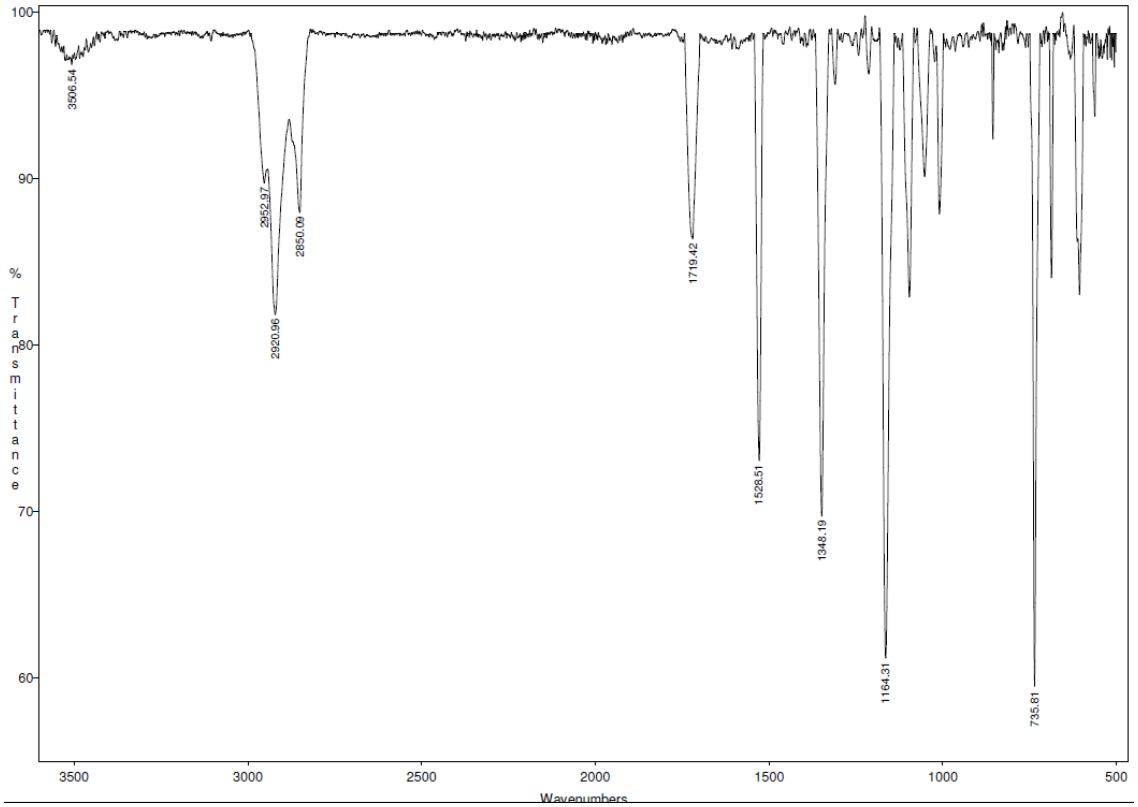


Figure S119: IR (ATR) spectrum of **5b**

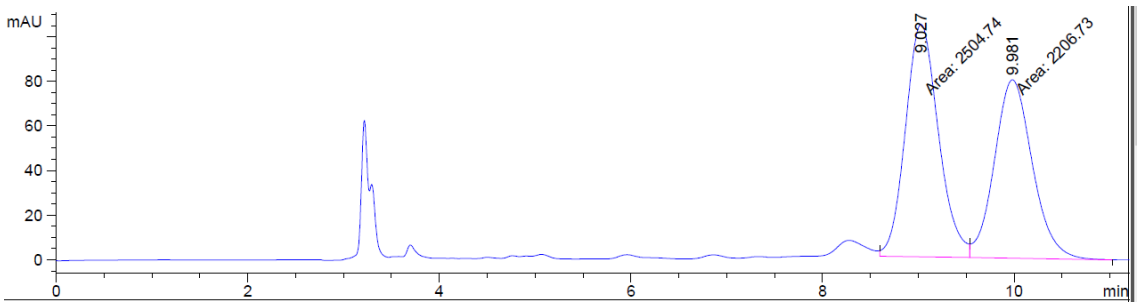


Figure S120: HPLC chromatogram of *rac*-**5b**

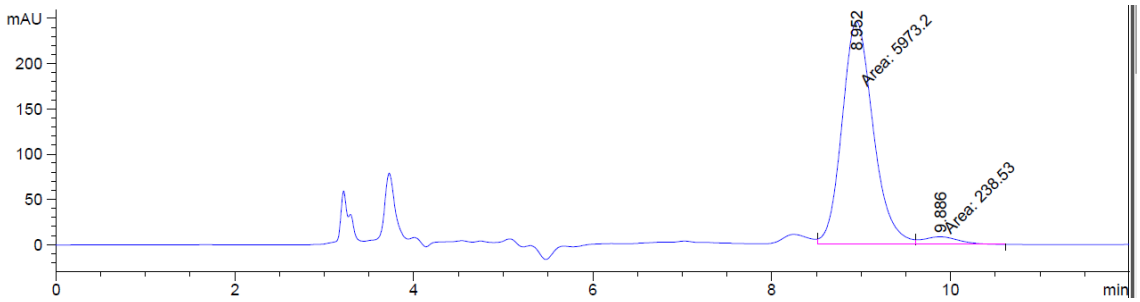


Figure S121: HPLC chromatogram of (*R*,*R*)-**5b**

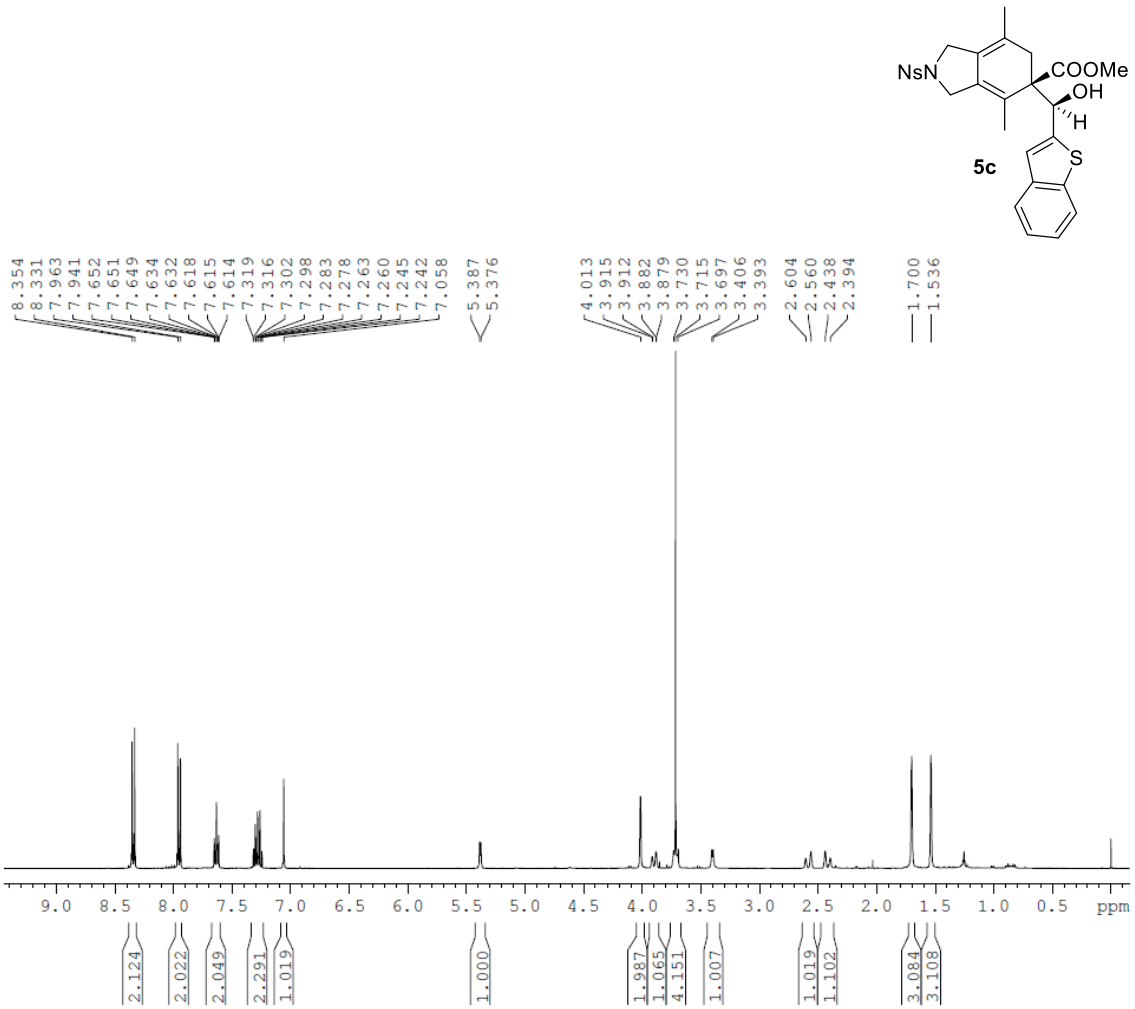


Figure S122: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5c**

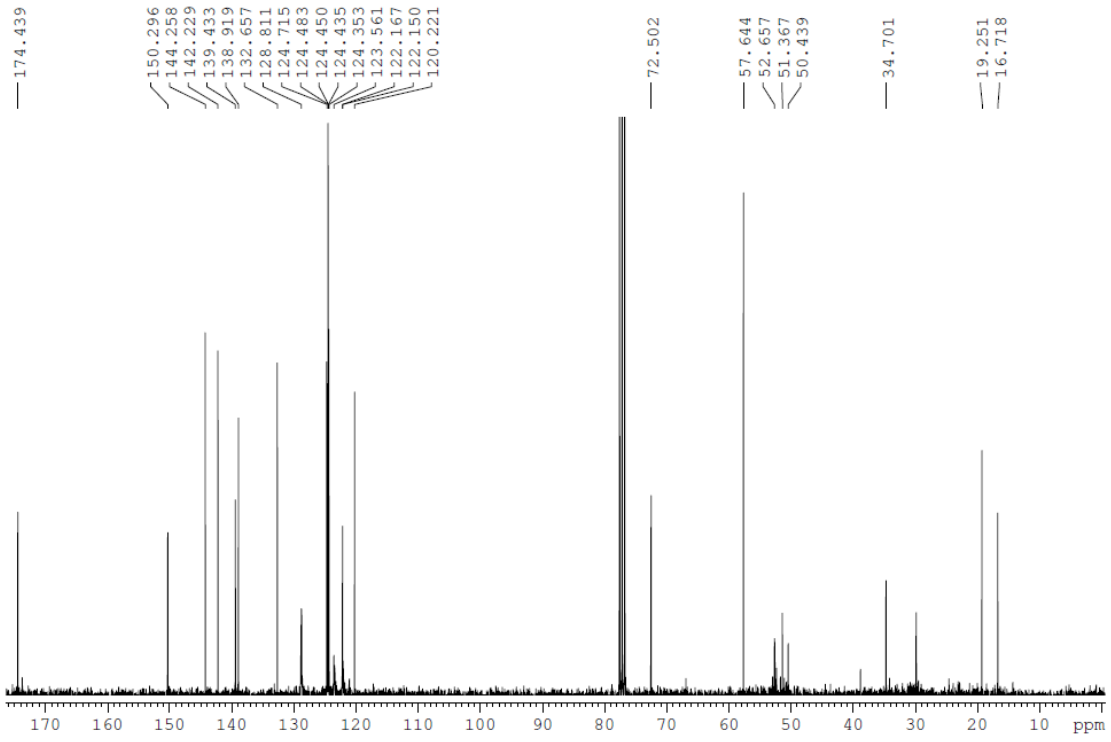


Figure S123: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **5c**

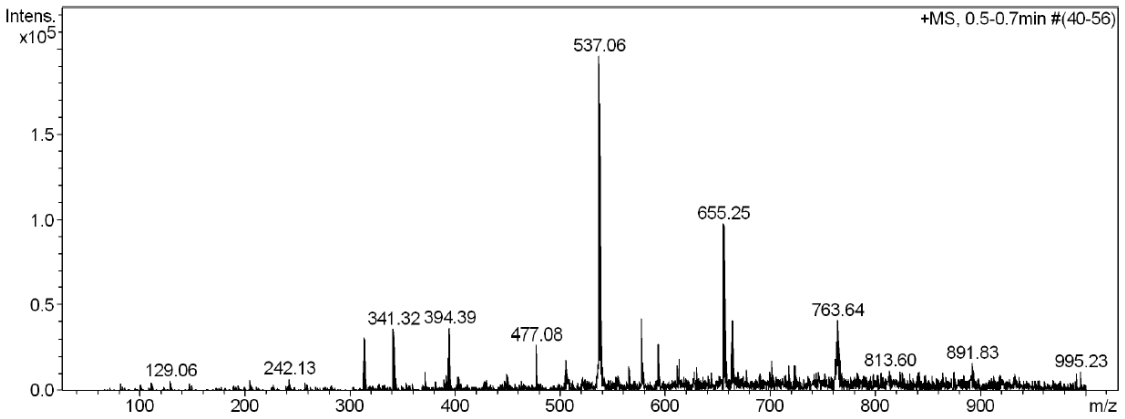


Figure S124: ESI-MS (*m/z*) spectrum of **5c**

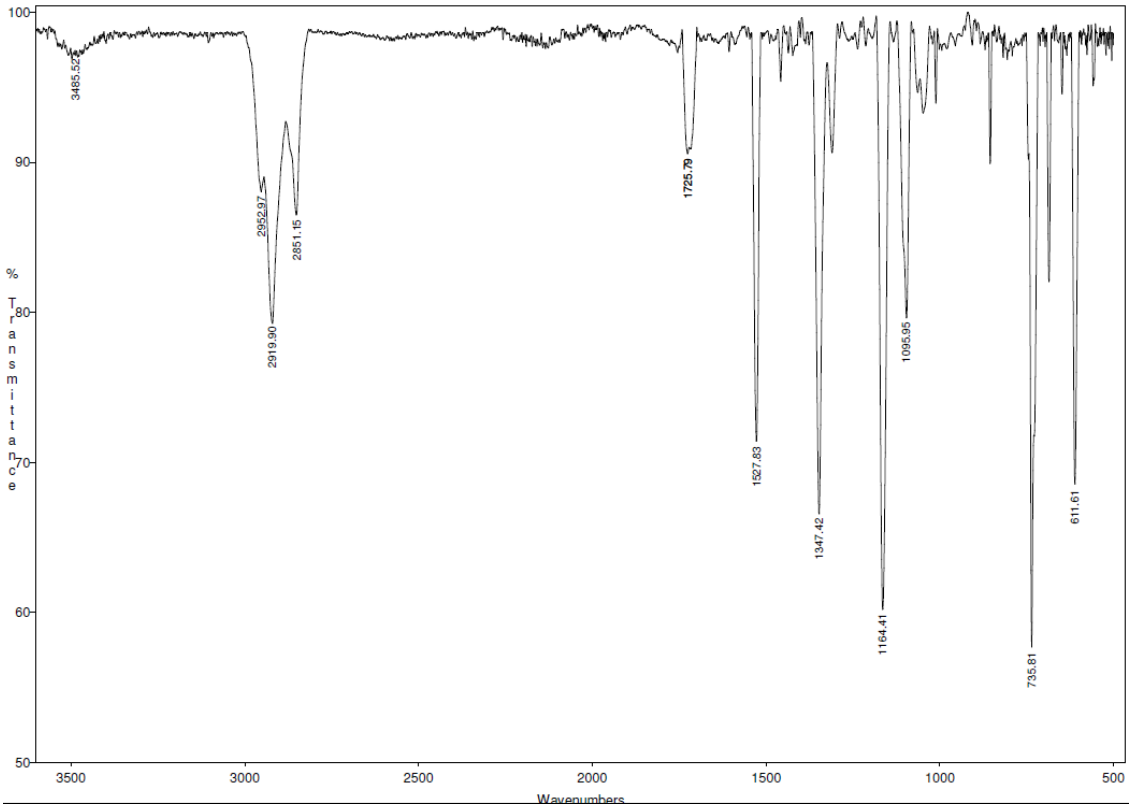


Figure S125: IR (ATR) spectrum of **5c**

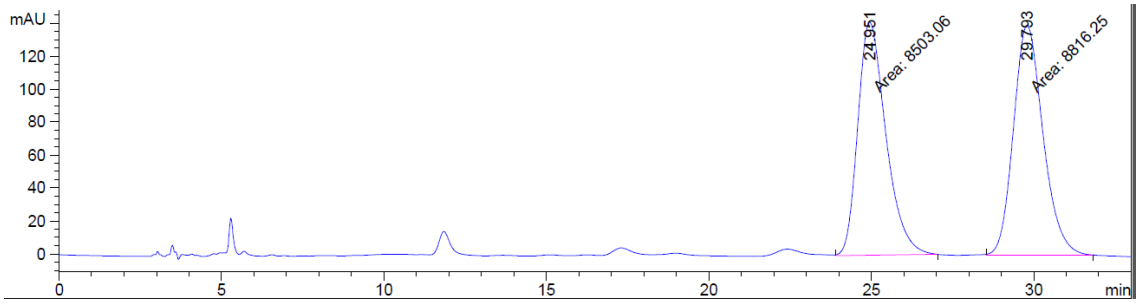


Figure S126: HPLC chromatogram of *rac*-**5c**

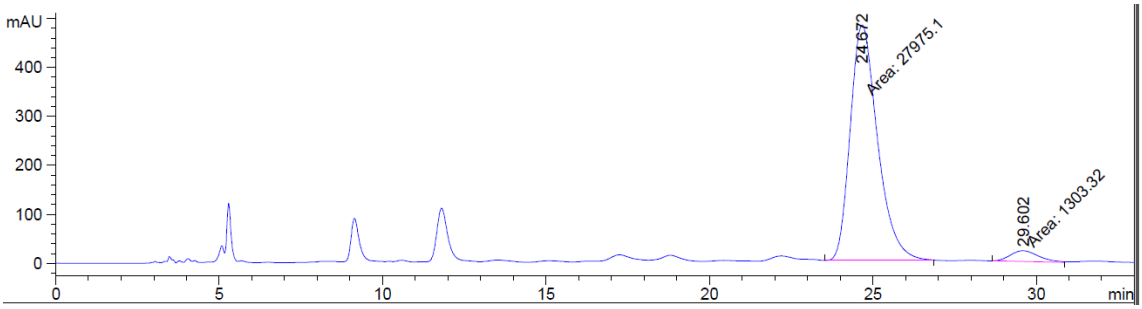


Figure S127: HPLC chromatogram of (*R*,*R*)-**5c**

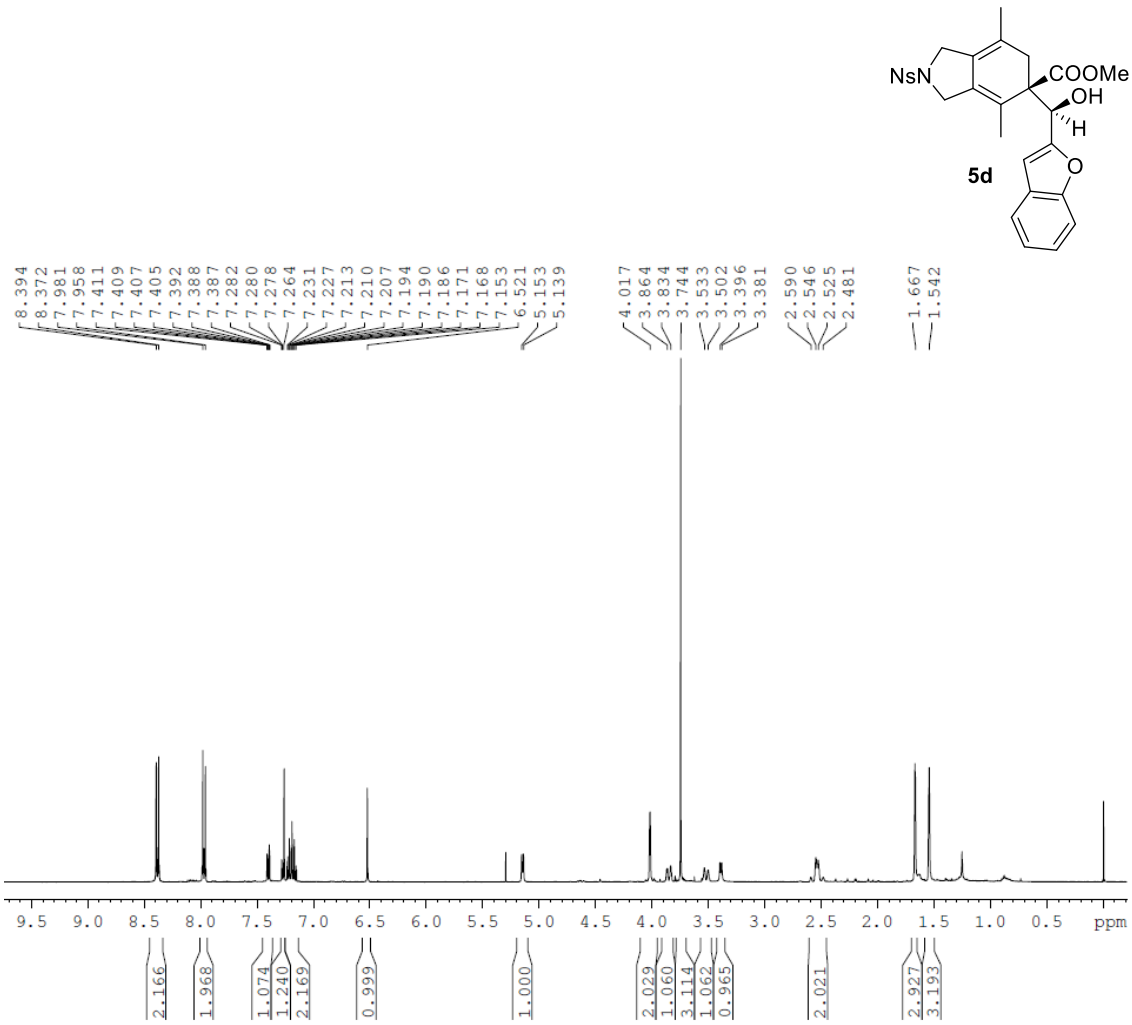


Figure S128: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **5d**

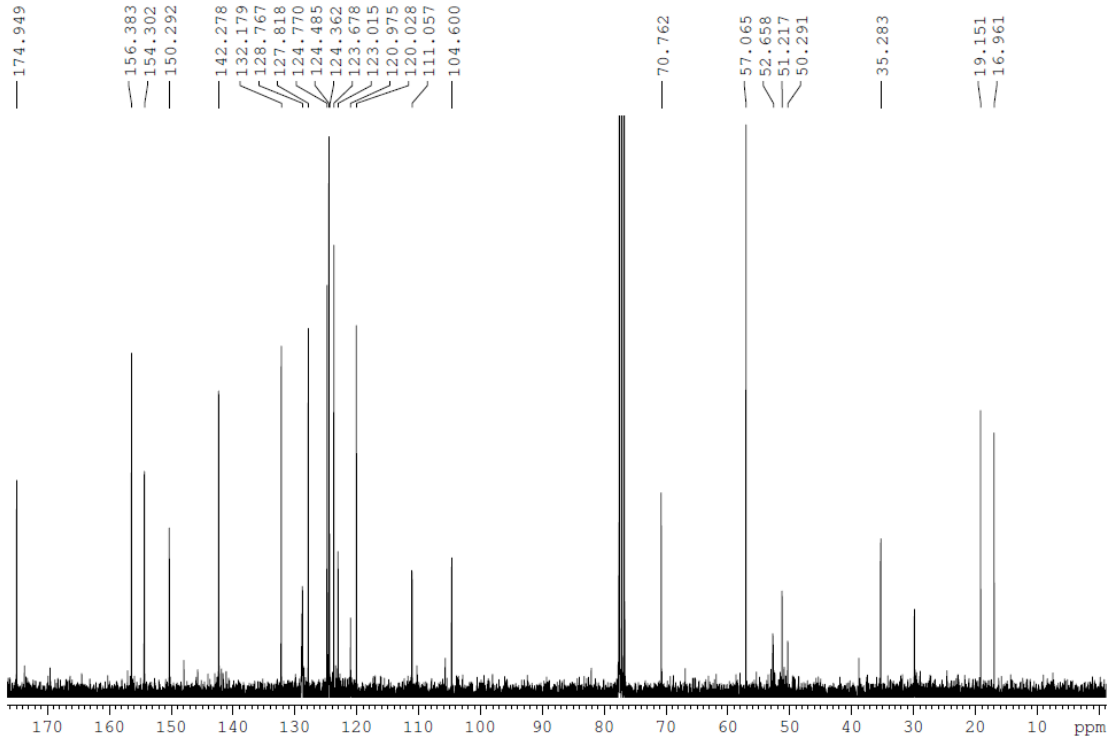


Figure S129: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **5d**

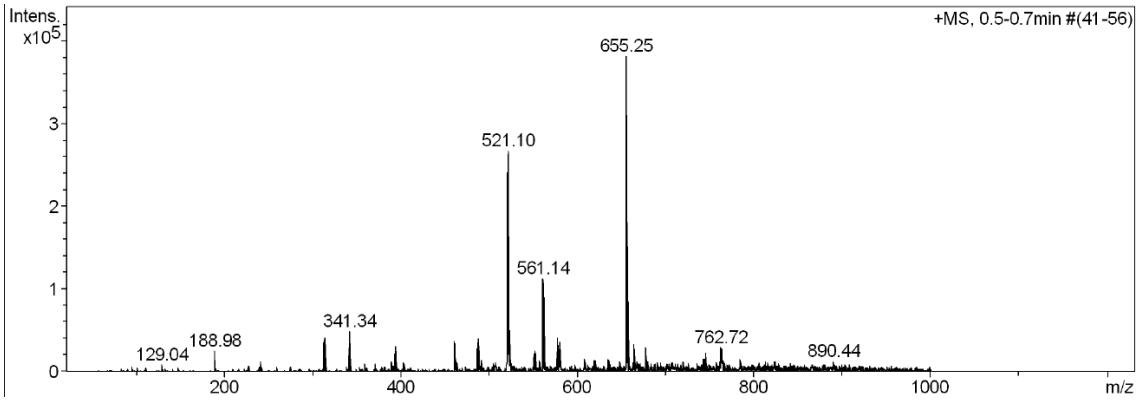


Figure S130: ESI-MS (*m/z*) spectrum of **5d**

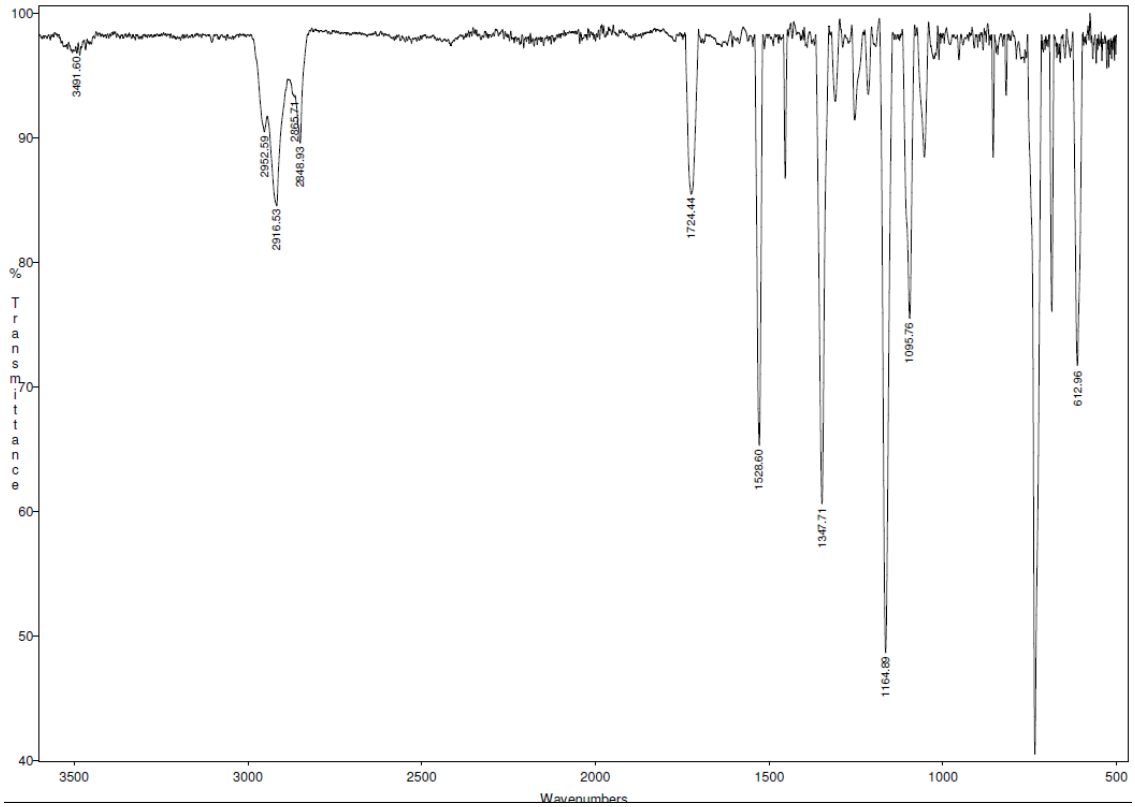


Figure S131: IR (ATR) spectrum of **5d**

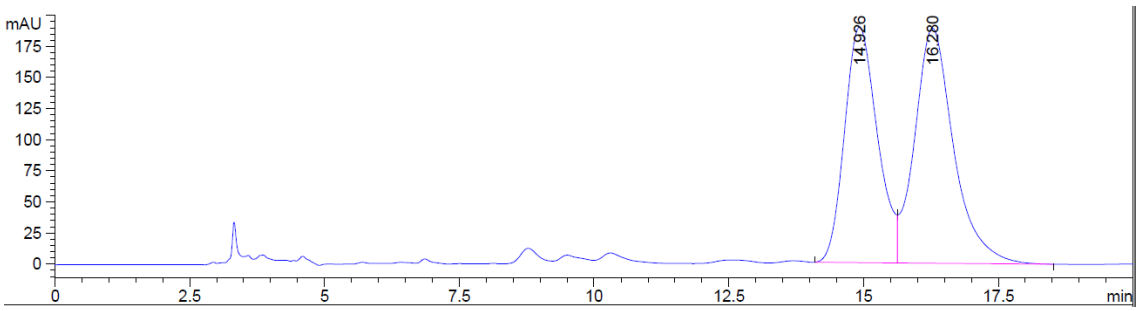


Figure S132: HPLC chromatogram of *rac*-**5d**

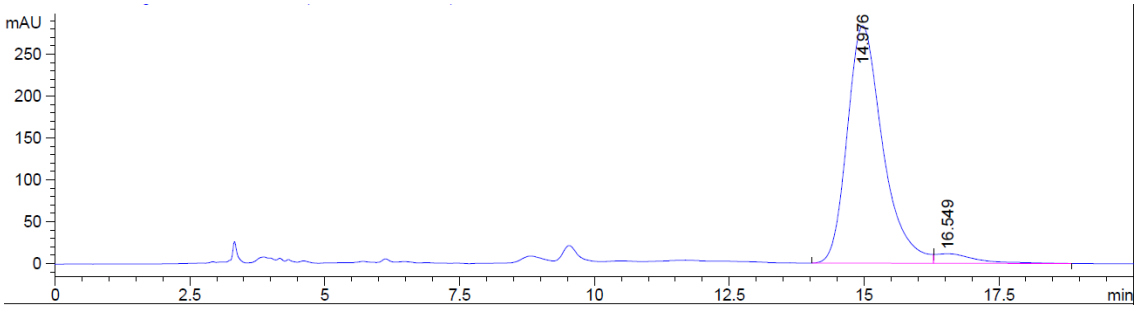
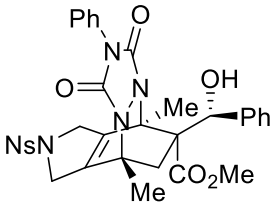


Figure S133: HPLC chromatogram of (*R*,*R*)-**5d**



9b

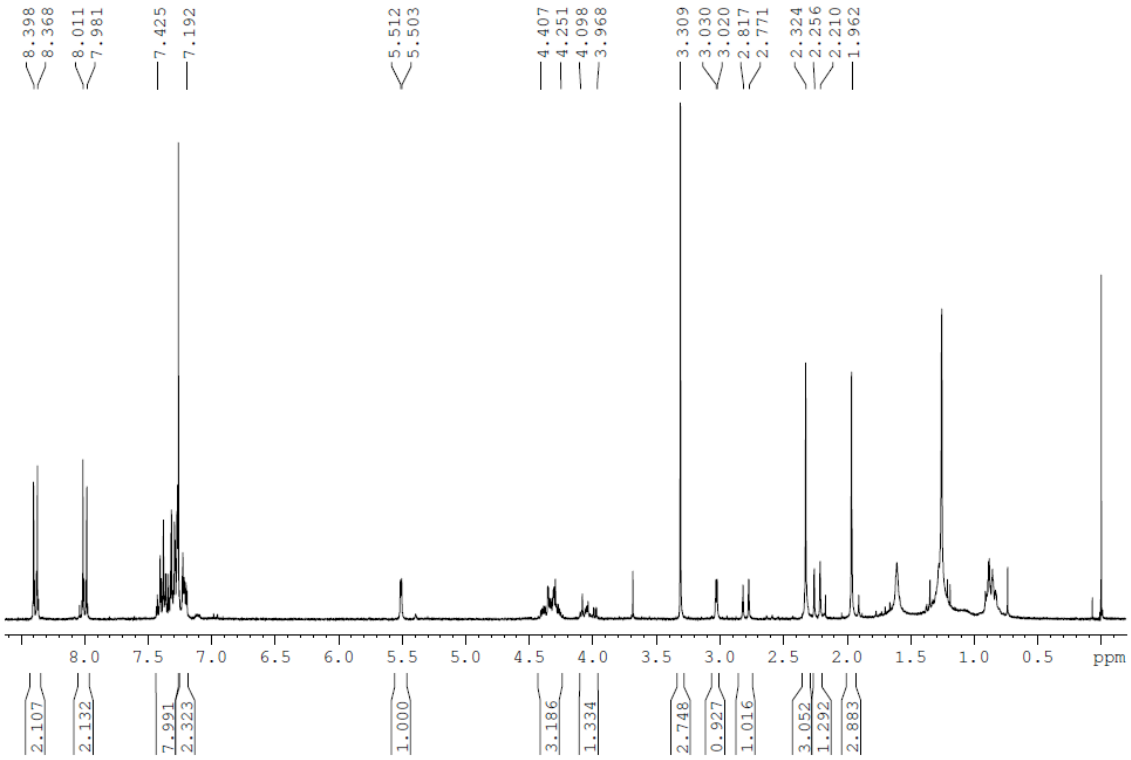


Figure S134: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **9b**

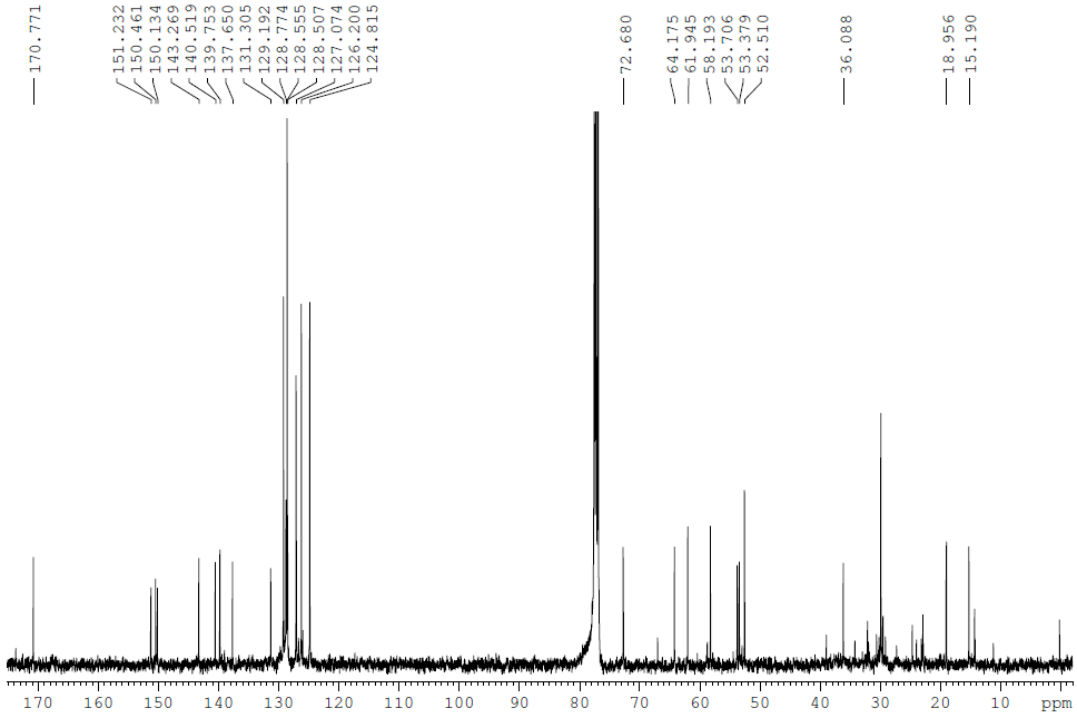


Figure S135: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **9b**

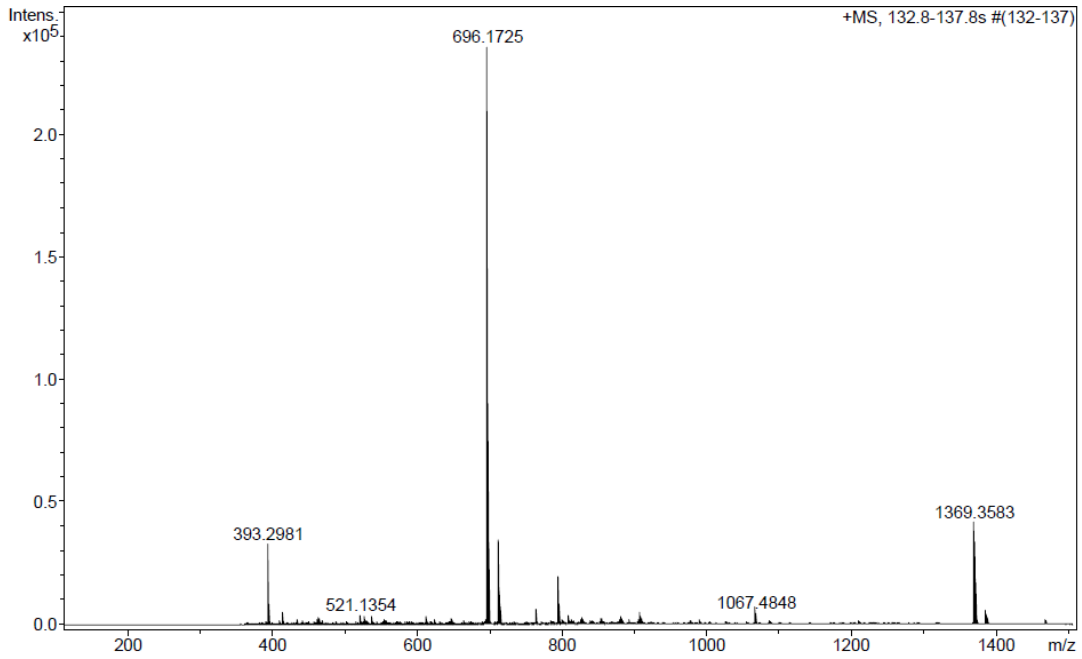


Figure S136: ESI-HRMS (*m/z*) spectrum of **9b**

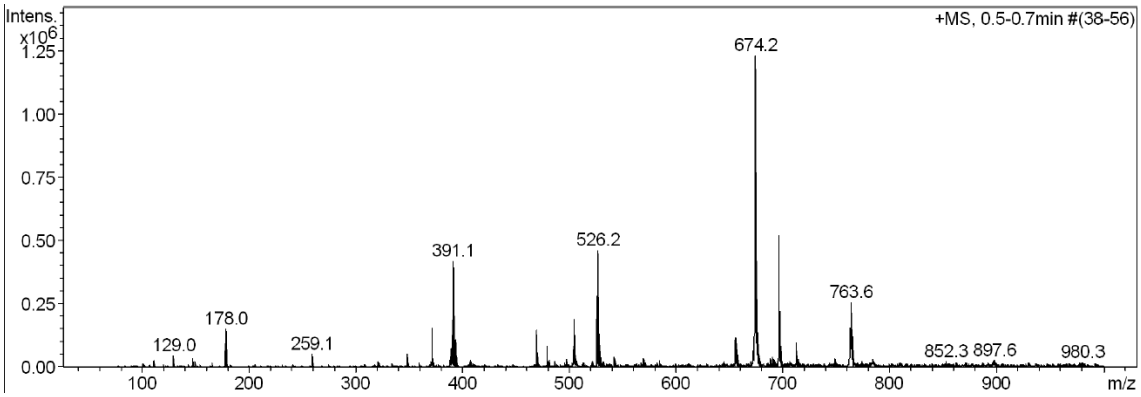


Figure S137: ESI-MS (*m/z*) spectrum of **9b**

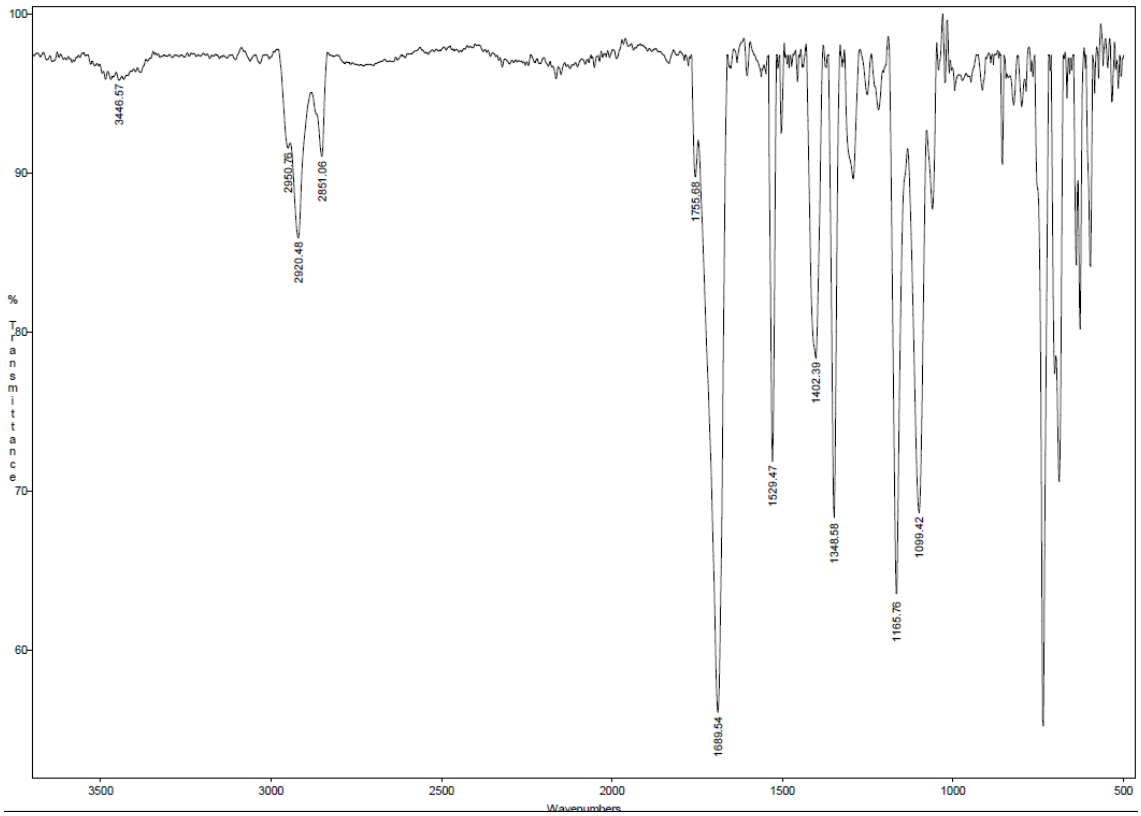
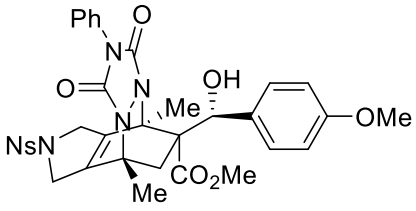


Figure S138: IR (ATR) spectrum of **9b**



9c

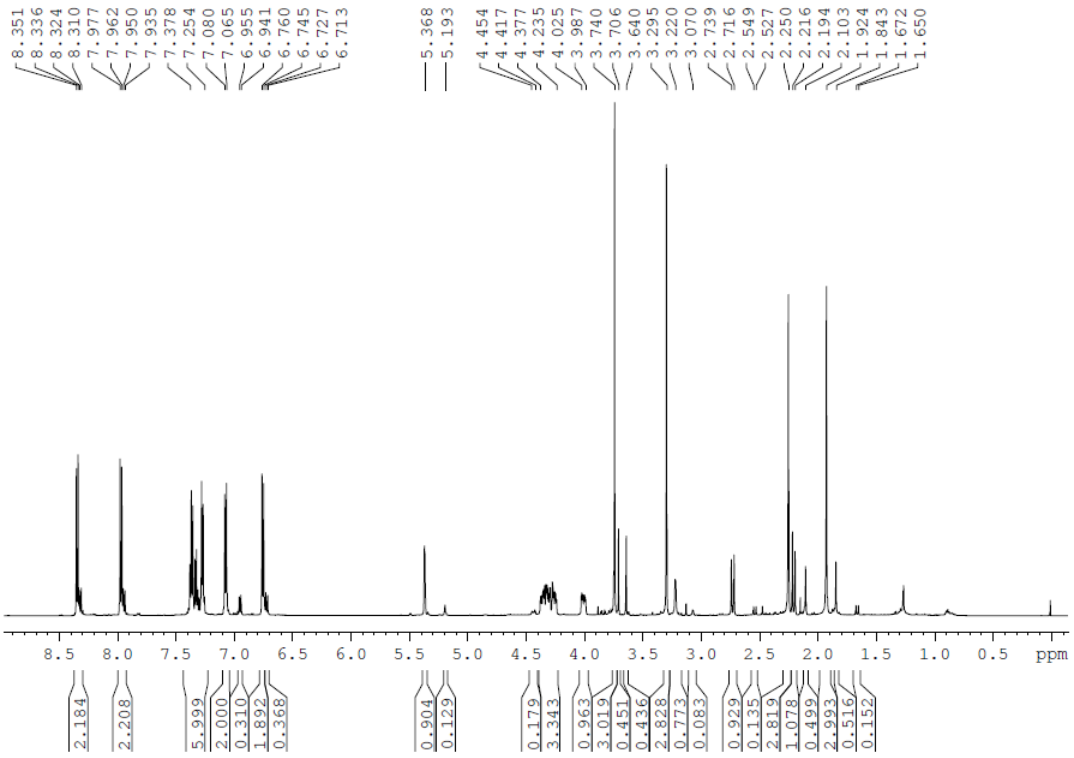


Figure S139: ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **9c**

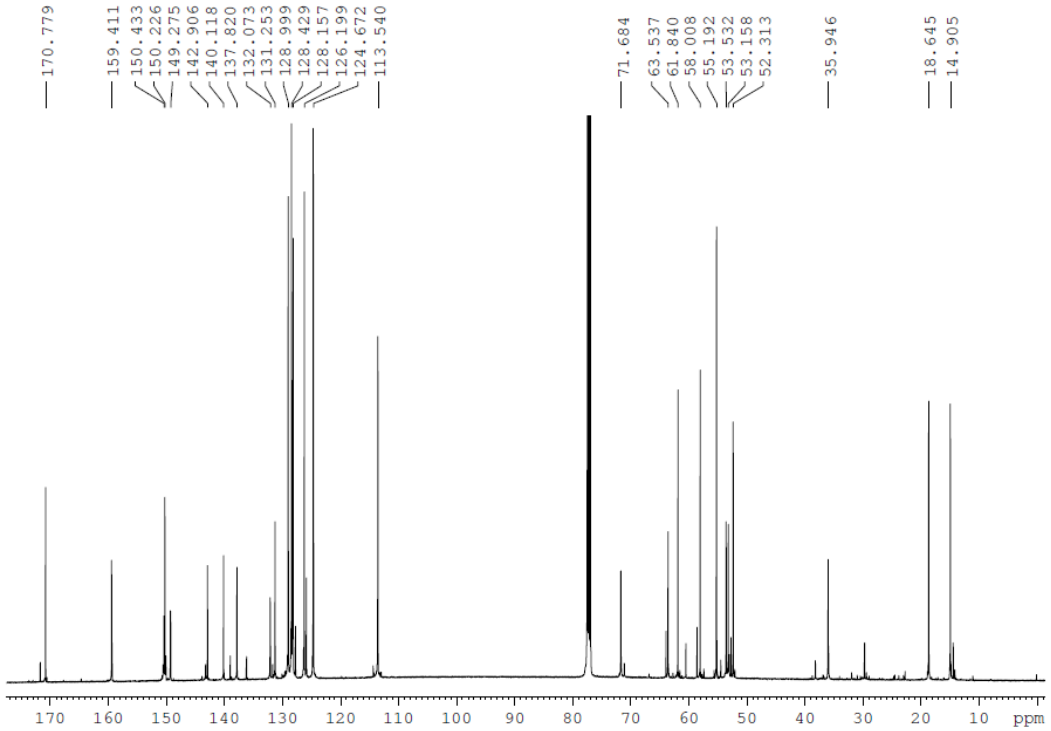


Figure S140: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **9c**

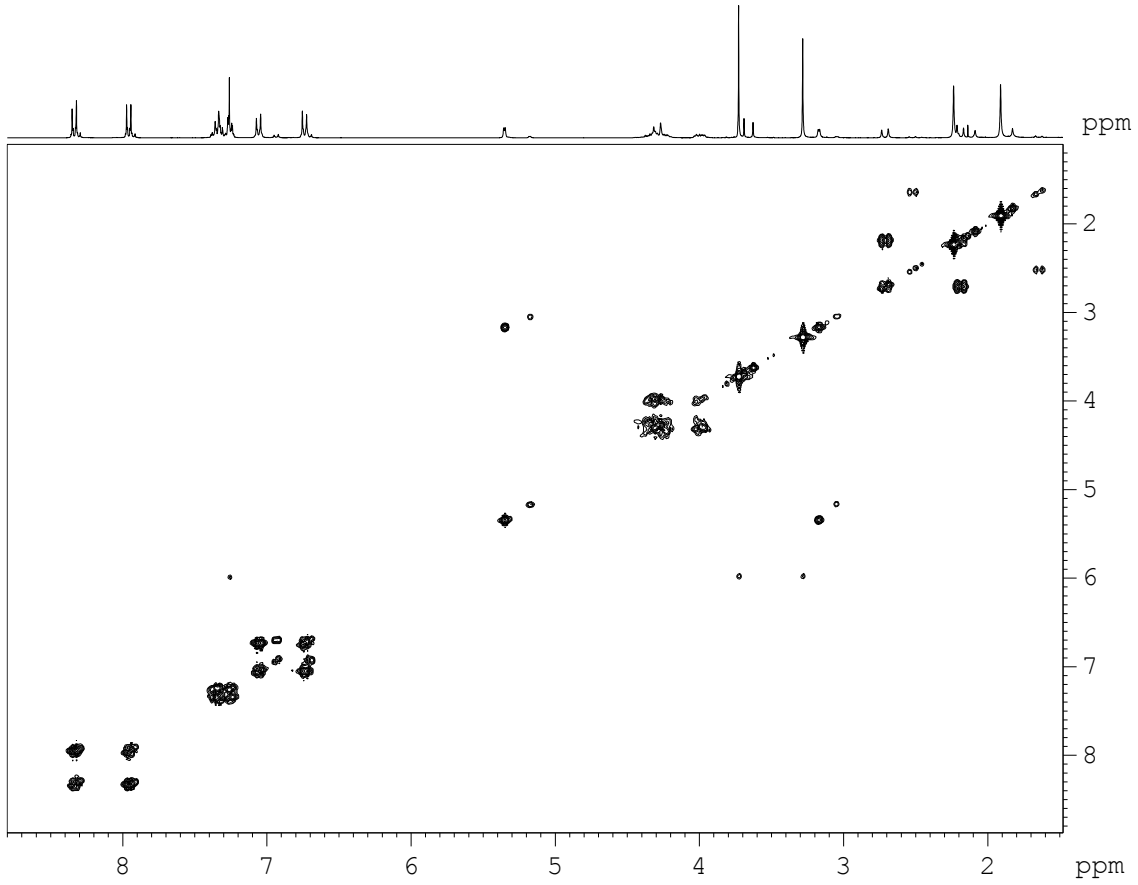


Figure S141: 2D ^{1}H-^{1}H COSY spectrum of **9c**

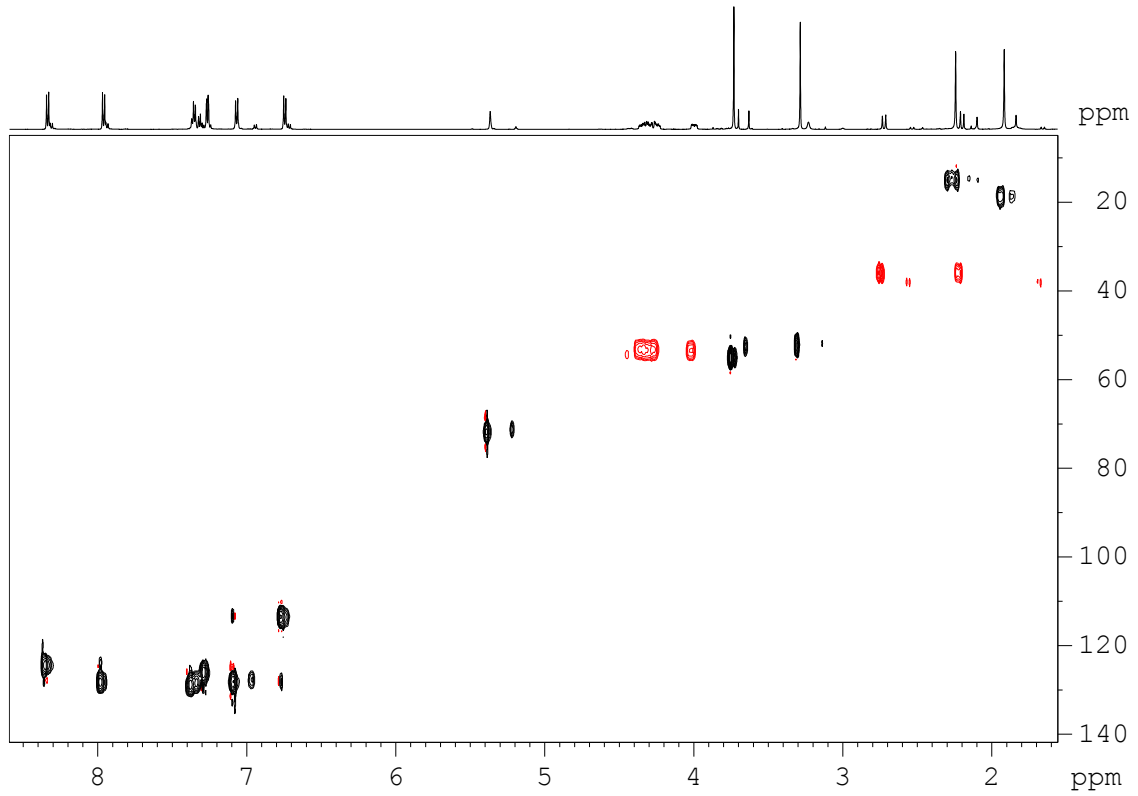
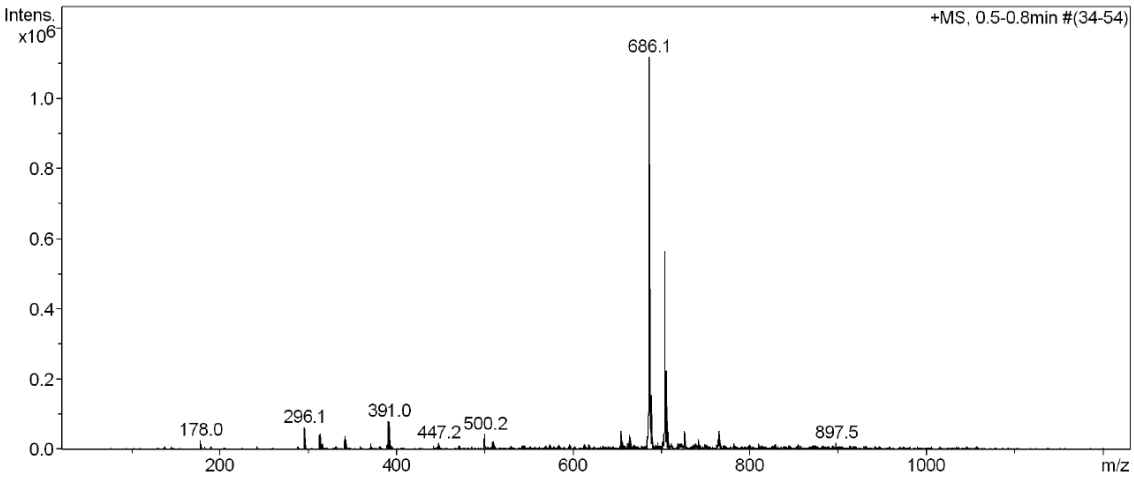


Figure S142: 2D ^{1}H-^{13}C HSQCed of **9c**



Figue S143: ESI-MS (*m/z*) spectrum of **9c**

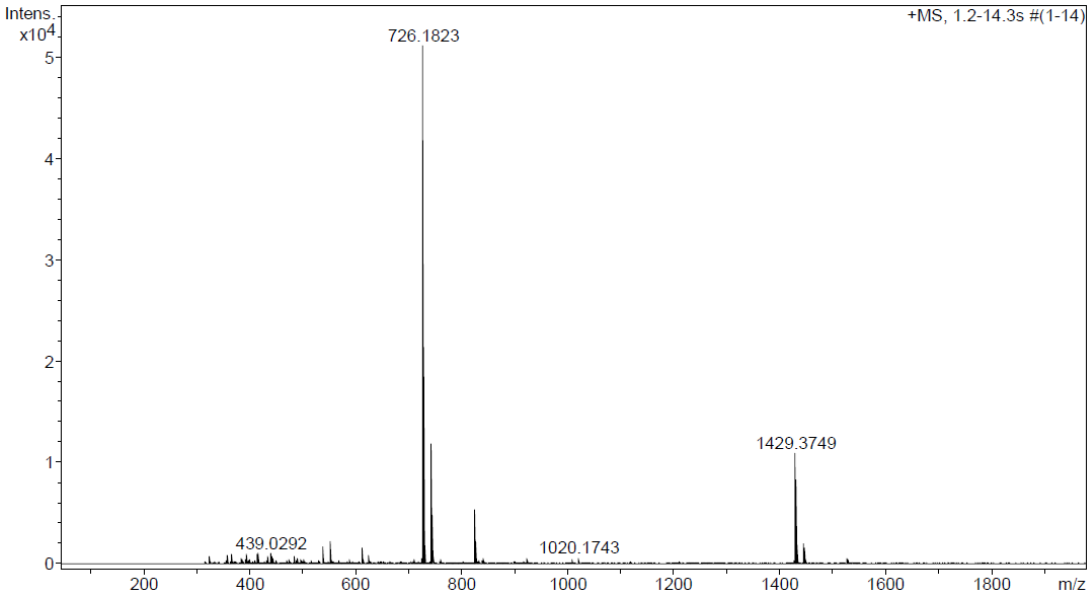


Figure S144: ESI-HRMS (*m/z*) of **9c**

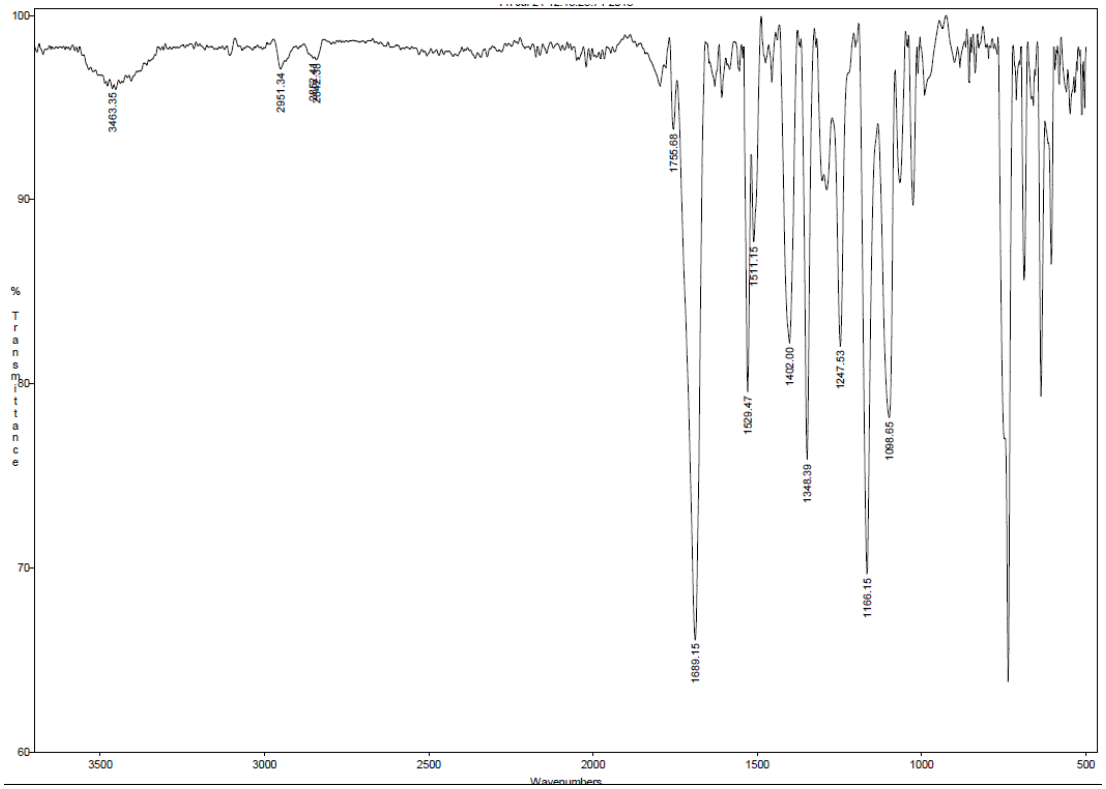
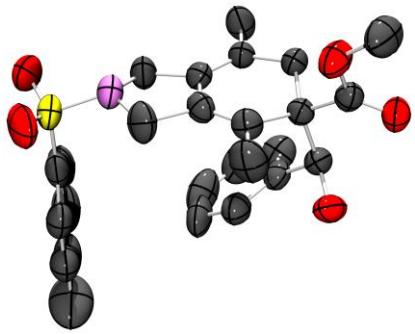


Figure S145: IR (ATR) spectrum of **9c**

Crystal parameters of 4a



Colorless crystals of $C_{26}H_{28}NO_5S$, were grown from slow diffusion of penthane in a CH_2Cl_2 solution of the compound, and used for room temperature (298(2) K) X-ray structure determination. The measurement was carried out on a BRUKER SMART APEX CCD diffractometer using graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) from an x-Ray Tube. The measurements were made in the range 2.085 to 28.325° for θ. Full-sphere data collection was carried out with ω and ϕ scans. A total of 39027 reflections were collected of which 11957 [R(int) = 0.0414] were unique. Programs used: data collection, Smart; data reduction, Saint+; absorption correction, SADABS. Structure solution and refinement was done using SHELXTL.

The structure was solved by direct methods and refined by full-matrix least-squares methods on F2. The non-hydrogen atoms were refined anisotropically. The H-atoms were placed in geometrically optimized positions and forced to ride on the atom to which they are attached.

Table S1. Crystal data and structure refinement for 4a

Identification code	**4a**
Empirical formula	$C_{26}H_{28}NO_5S$
Formula weight	466.55
Temperature/K	298(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	9.9593(7)
b/Å	19.5349(14)
c/Å	13.4860(10)
α/°	90
β/°	111.4120(10)
γ/°	90
Volume/Å^3	2442.7(3)
Z	4
ρ_{calc}/g·cm^{-3}	1.269
μ/mm^{-1}	0.169
F(000)	988
Crystal size/mm	0.25 x 0.20 x 0.15
Θ range for data collection/°	2.085 to 28.325
Limiting indexes	$-13 \le h \le 13$, $-25 \le k \le 25$, $-17 \le l \le 17$
Reflections collected	39027
Independent reflections	11957 [R(int) = 0.0414]
Data/restraints/parameters	11957 / 1 / 597
Goodness-of-fit on F^2	1.012
Final R indexes [I>2σ (I)]	R1 = 0.0582, wR2 = 0.1331
Final R indexes (all data)	R1 = 0.1029, wR2 = 0.1581
Largest diff. peak and hole/e·Å^3	0.415 and -0.240
Completeness to theta	25.242 99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.0 and 0.842467
Absolute structure parameter	-0.08(3)
Extinction coefficient	n/a

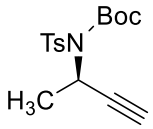
Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^4 x 10^3) for 4a.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	439(2)	2676(1)	9712(1)	69(1)
N(1)	1192(4)	3428(2)	9891(3)	64(1)
C(1)	-1221(5)	2751(2)	8631(4)	60(1)
O(1)	1357(5)	2233(2)	9418(4)	97(1)
O(2)	102(4)	2540(2)	10637(3)	82(1)
C(2)	-2441(6)	2886(3)	8838(4)	67(1)

O(3)	1476(5)	6018(2)	7320(3)	90(1)
C(3)	-3736(6)	3006(3)	7996(5)	75(1)
C(4)	-3797(7)	2990(3)	6964(4)	79(2)
O(4)	4960(5)	5785(3)	9488(4)	122(2)
O(5)	3691(5)	6691(3)	9372(5)	115(2)
C(5)	-2565(8)	2836(3)	6767(5)	84(2)
C(6)	-1290(6)	2708(3)	7584(4)	72(1)
C(7)	-5233(8)	3147(4)	6053(6)	125(3)
C(8)	515(5)	3990(3)	10285(4)	63(1)
C(9)	1281(4)	4614(3)	10117(3)	57(1)
C(10)	1339(5)	5227(3)	10542(4)	62(1)
C(11)	2246(6)	5759(3)	10266(4)	79(2)
C(12)	2419(6)	5659(3)	9161(5)	74(1)
C(13)	2563(5)	4913(3)	8917(4)	63(1)
C(14)	1975(4)	4445(3)	9358(4)	57(1)
C(15)	1798(5)	3697(3)	9115(4)	66(1)
C(16)	671(7)	5425(3)	11323(5)	86(2)
C(17)	1121(5)	5995(3)	8259(4)	67(1)
C(18)	-297(5)	5625(2)	8050(4)	57(1)
C(19)	-678(6)	5057(3)	7398(4)	67(1)
C(20)	-1927(7)	4694(3)	7282(5)	81(2)
C(21)	-2803(6)	4893(4)	7803(5)	87(2)
C(22)	-2444(6)	5470(3)	8439(5)	82(2)
C(23)	-1212(5)	5833(3)	8549(4)	67(1)
C(24)	3871(6)	6028(3)	9348(5)	74(1)
C(25)	5130(9)	7035(5)	9704(8)	141(4)
C(26)	3188(6)	4715(3)	8100(4)	79(2)

SUPPLEMENTARY DATA – CHAPTER 4



(*R*)-**19**

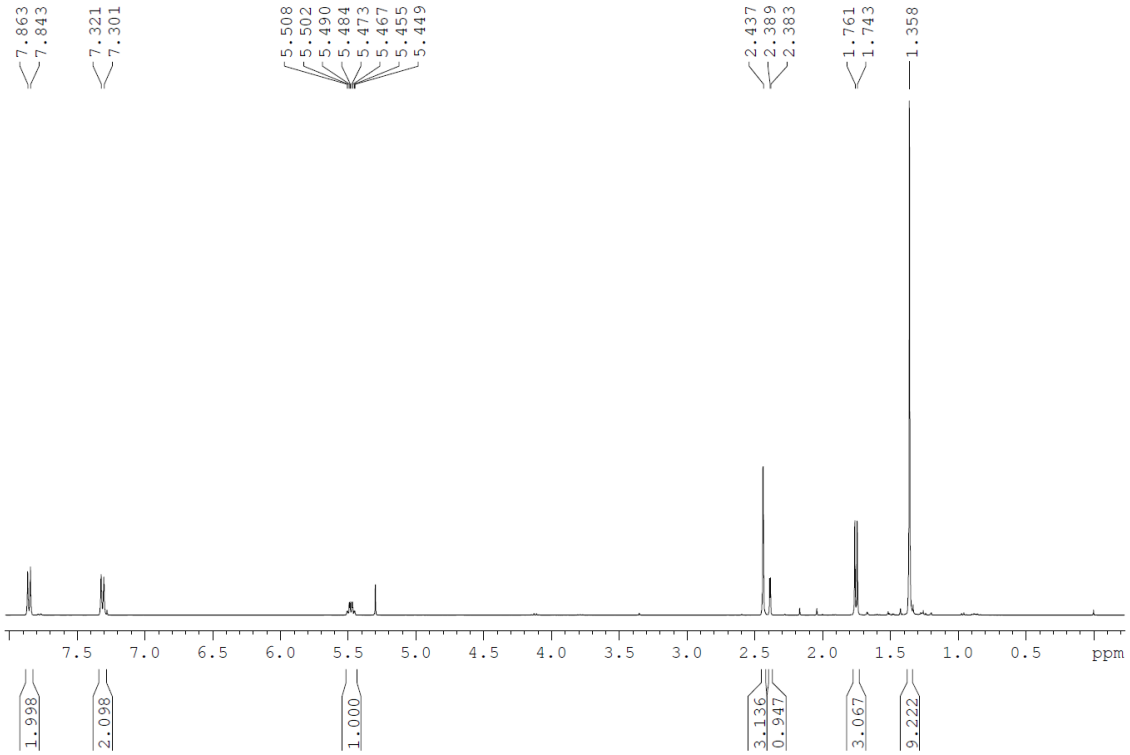


Figure S1: ^{1}H-NMR ($CDCl_3$, 400 MHz) of **(*R*)-19**

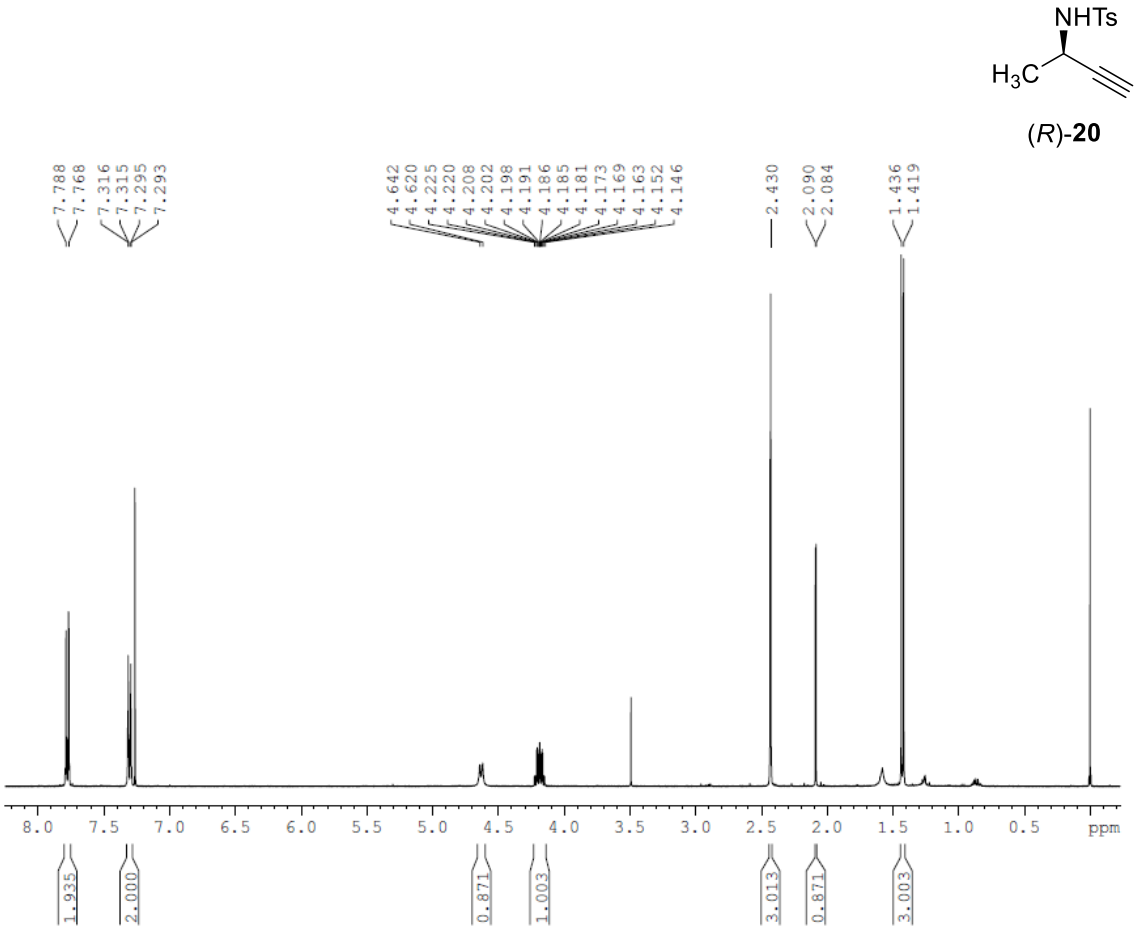


Figure S2: ^{1}H-NMR ($CDCl_3$, 400 MHz) of **(*R*)-20**

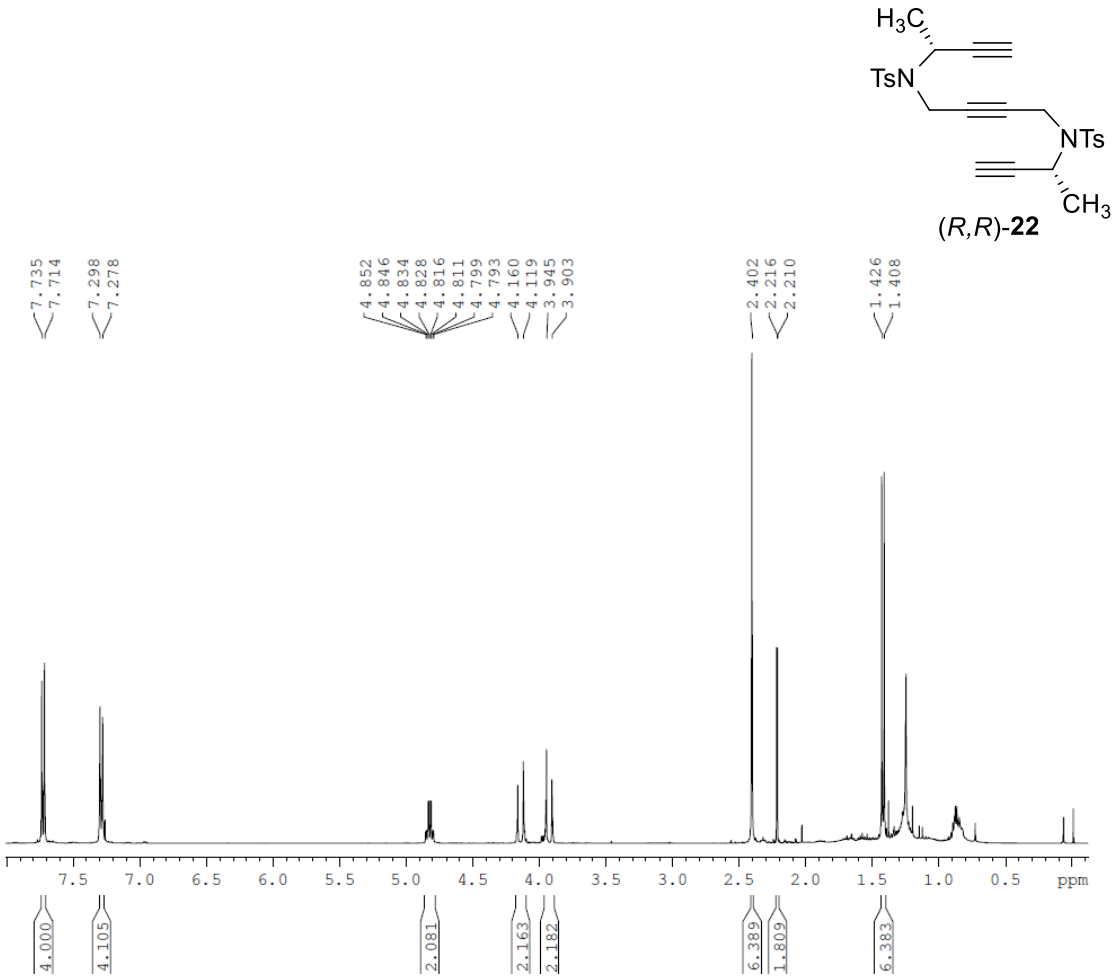


Figure S3: ^{1}H-NMR ($CDCl_3$, 400 MHz) of **(*R,R*)-22**

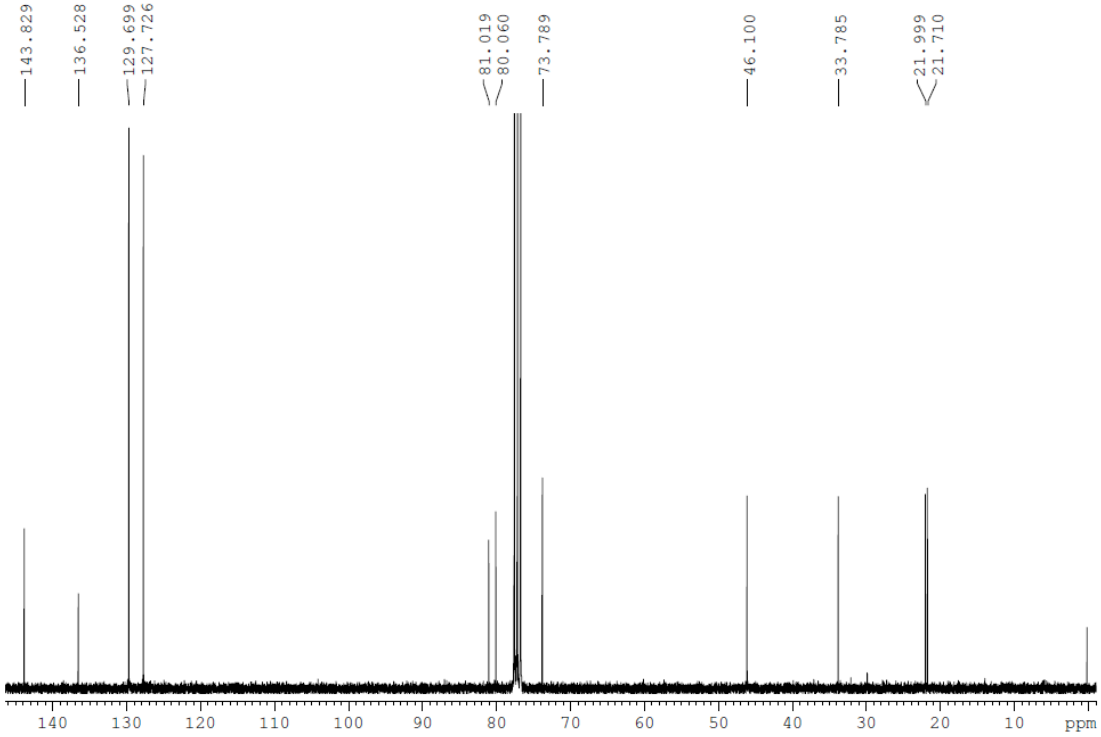


Figure S4: ^{13}C-NMR (75 MHz, $CDCl_3$) of **(*R,R*)-22**

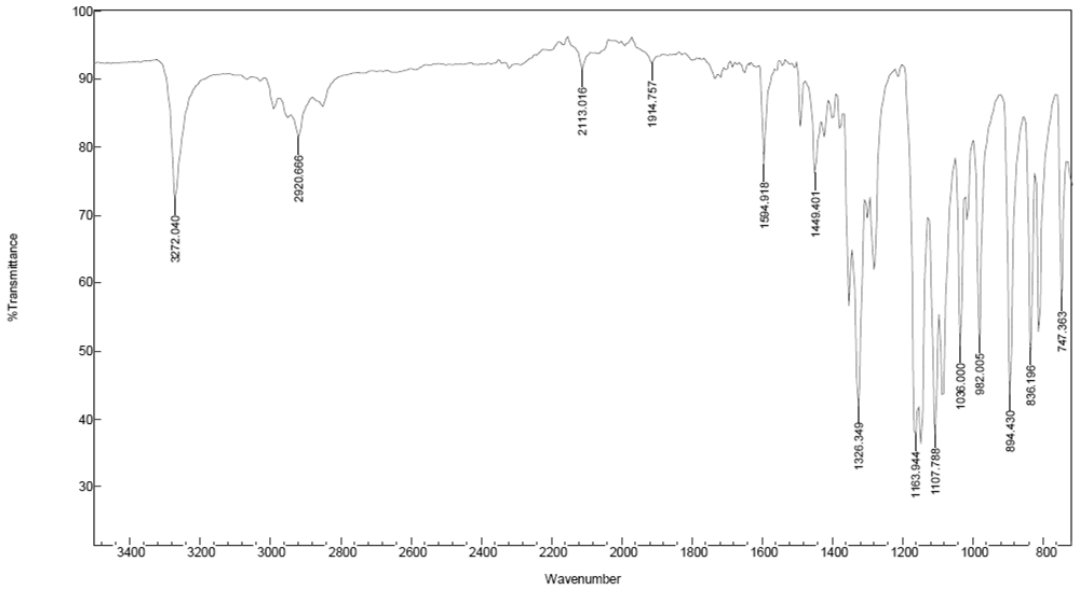


Figure S5: IR (ATR) of ***(R,R)*-22**

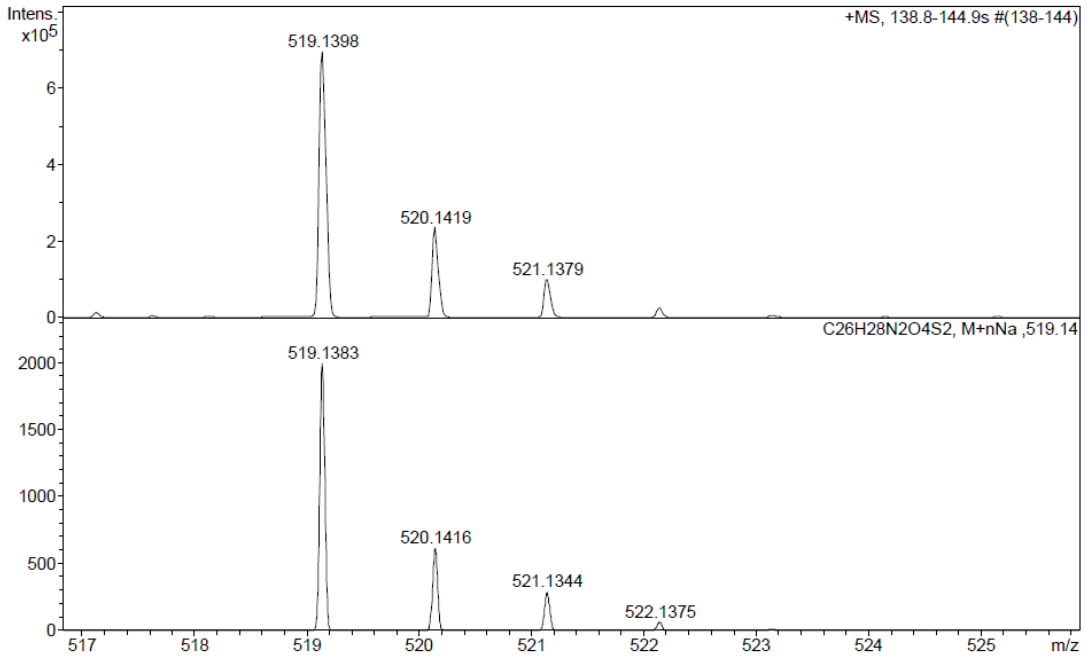


Figure S6: ESI-HRMS (+) of ***(R,R)*-22**

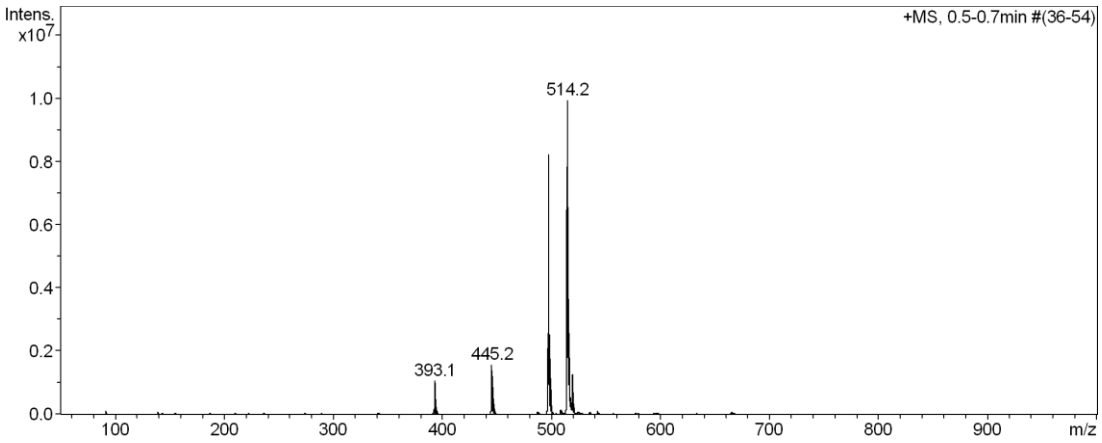


Figure S7: ESI-MS (+) of ***(R,R)*-22**

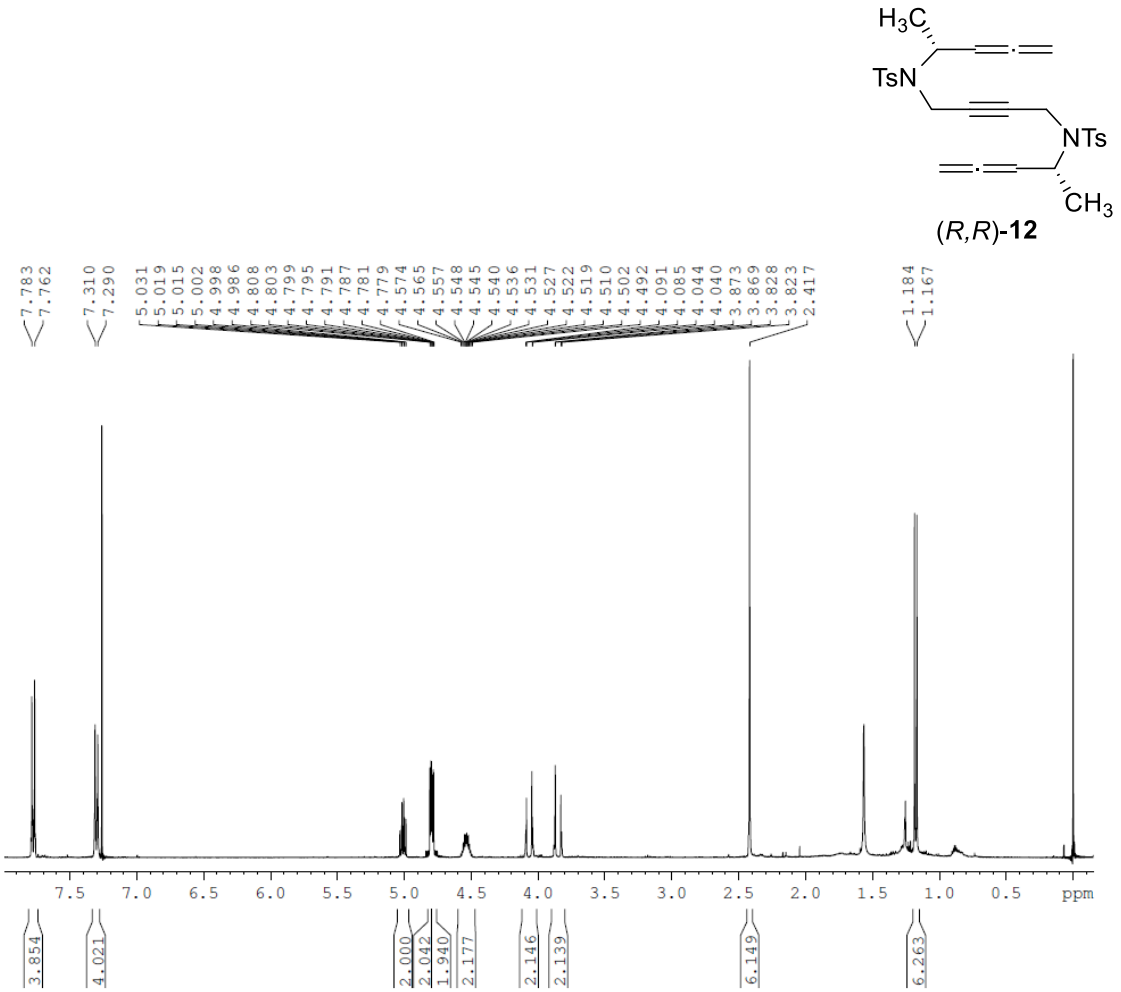


Figure S8: ^{1}H-NMR ($CDCl_3$, 400 MHz) of **(*R,R*)-12**

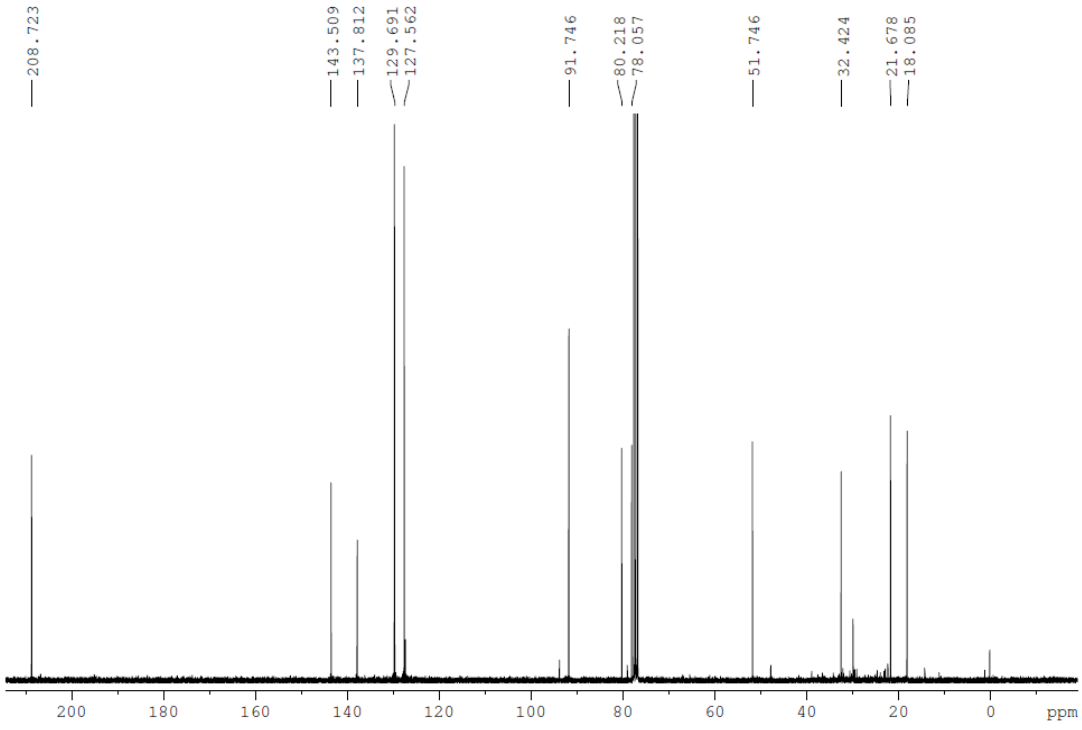


Figure S9: ^{13}C-NMR ($CDCl_3$, 75 MHz) of **(*R,R*)-12**

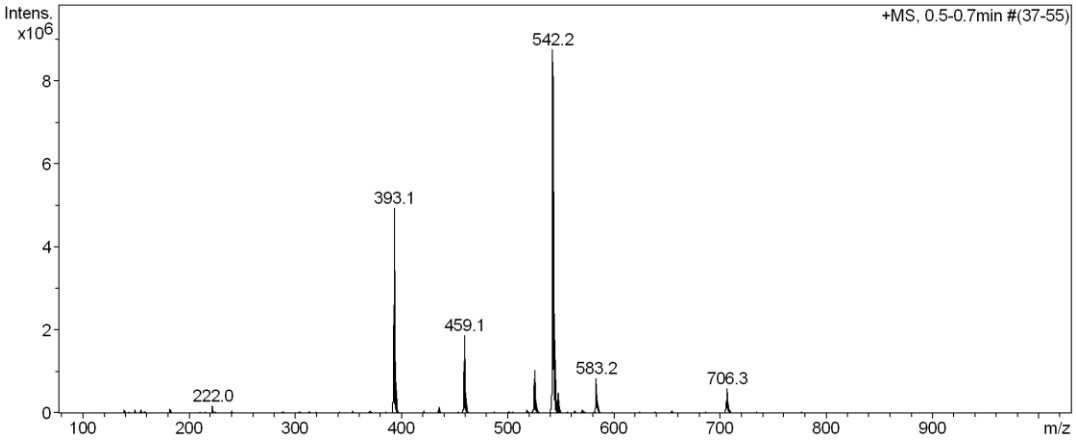


Figure S10: ESI-MS (+) of **(*R,R*)-12**

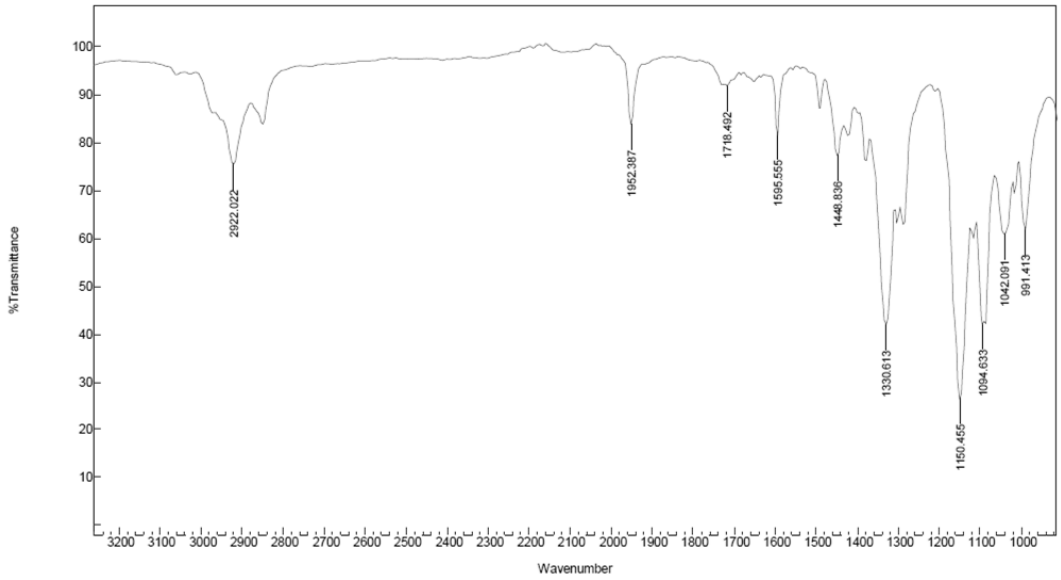


Figure S11: IR (ATR) of **(*R,R*)-12**

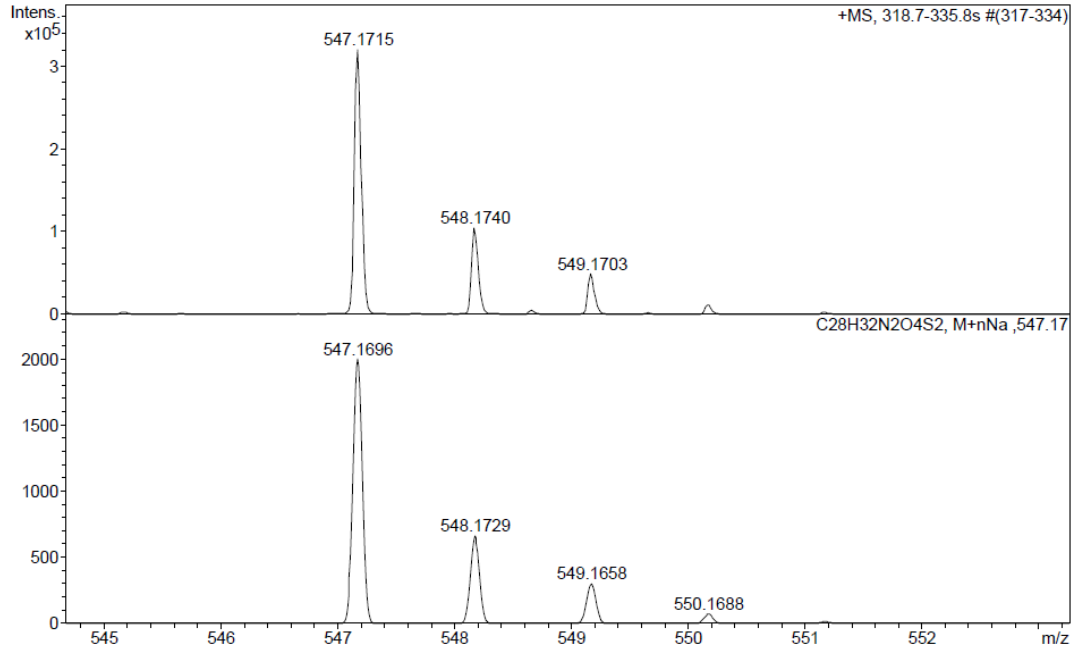


Figure S12: ESI-HRMS (+) of **(*R,R*)-12**

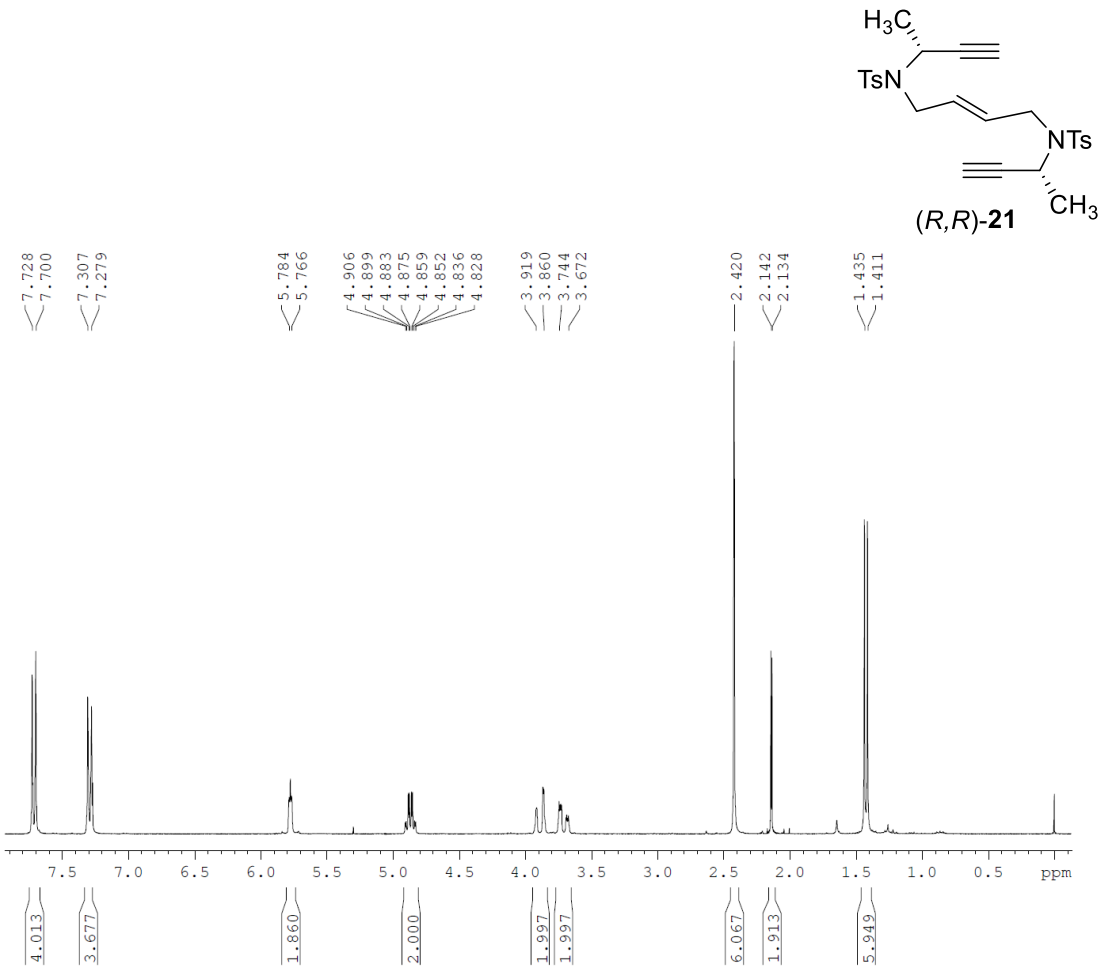


Figure S13: ^{1}H-NMR ($CDCl_3$, 300 MHz) of **(*R,R*)-21**

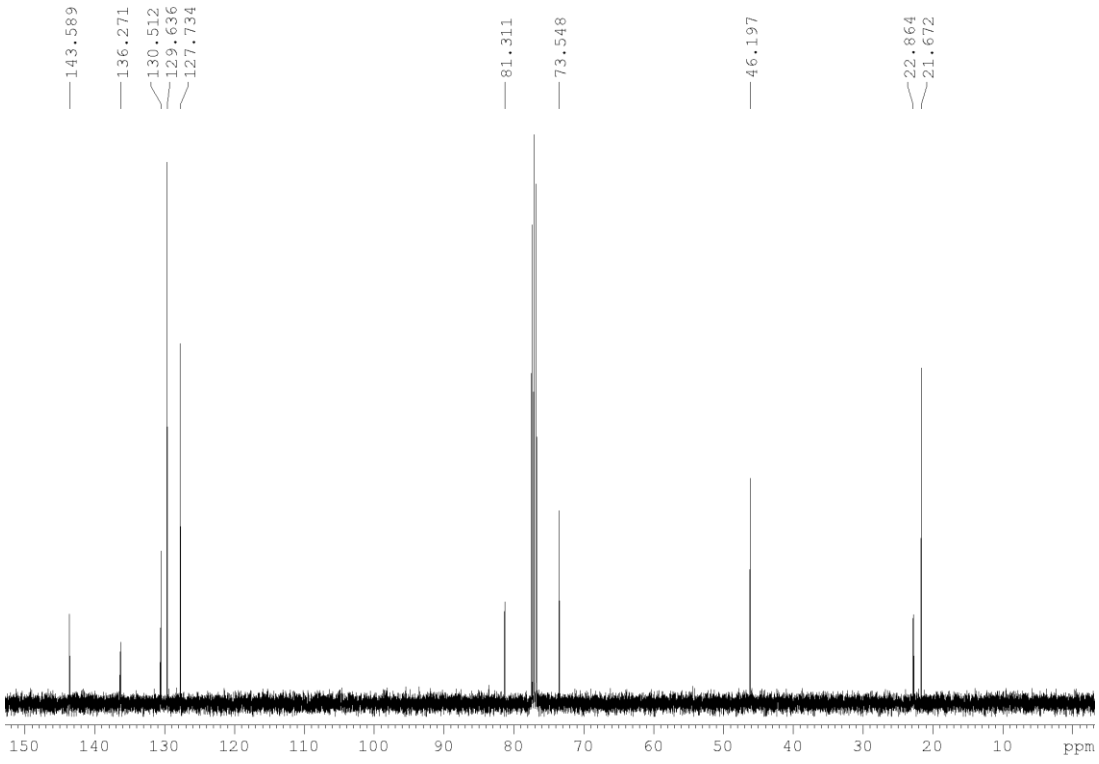


Figure S14: ^{13}C-NMR ($CDCl_3$, 100 MHz) of **(*R,R*)-21**

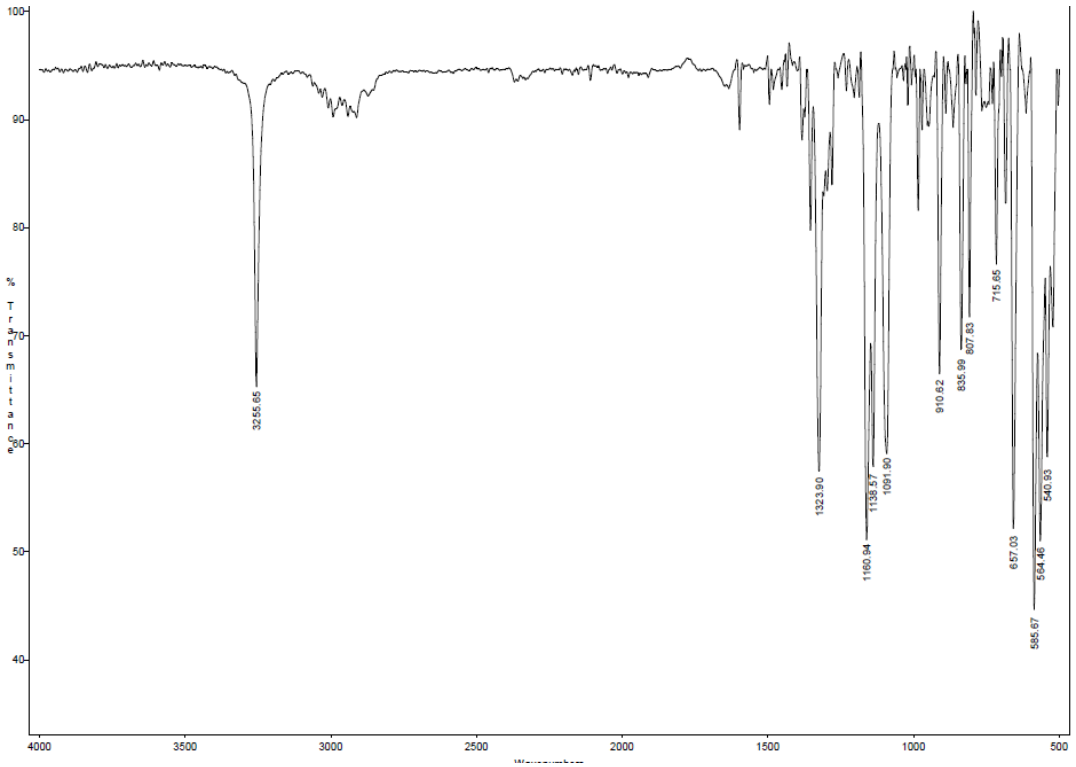


Figure S15: IR (ATR) of **(*R,R*)-21**

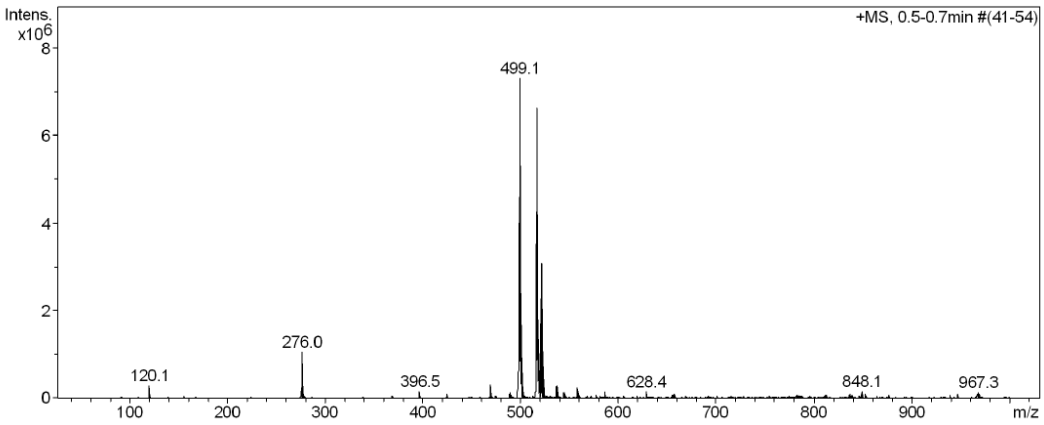


Figure S16: ESI-MS (+) of **(*R,R*)-21**

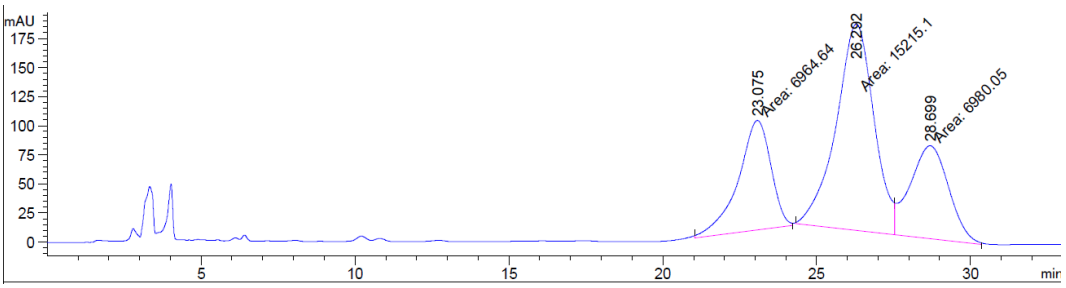


Figure S17: HPLC analysis of **(*rac*)-21**

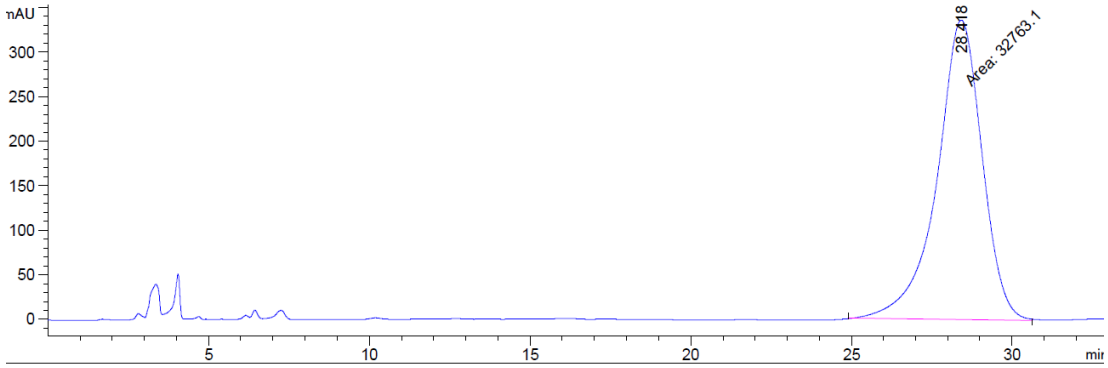


Figure S18: HPLC analysis of **(*R,R*)-21**

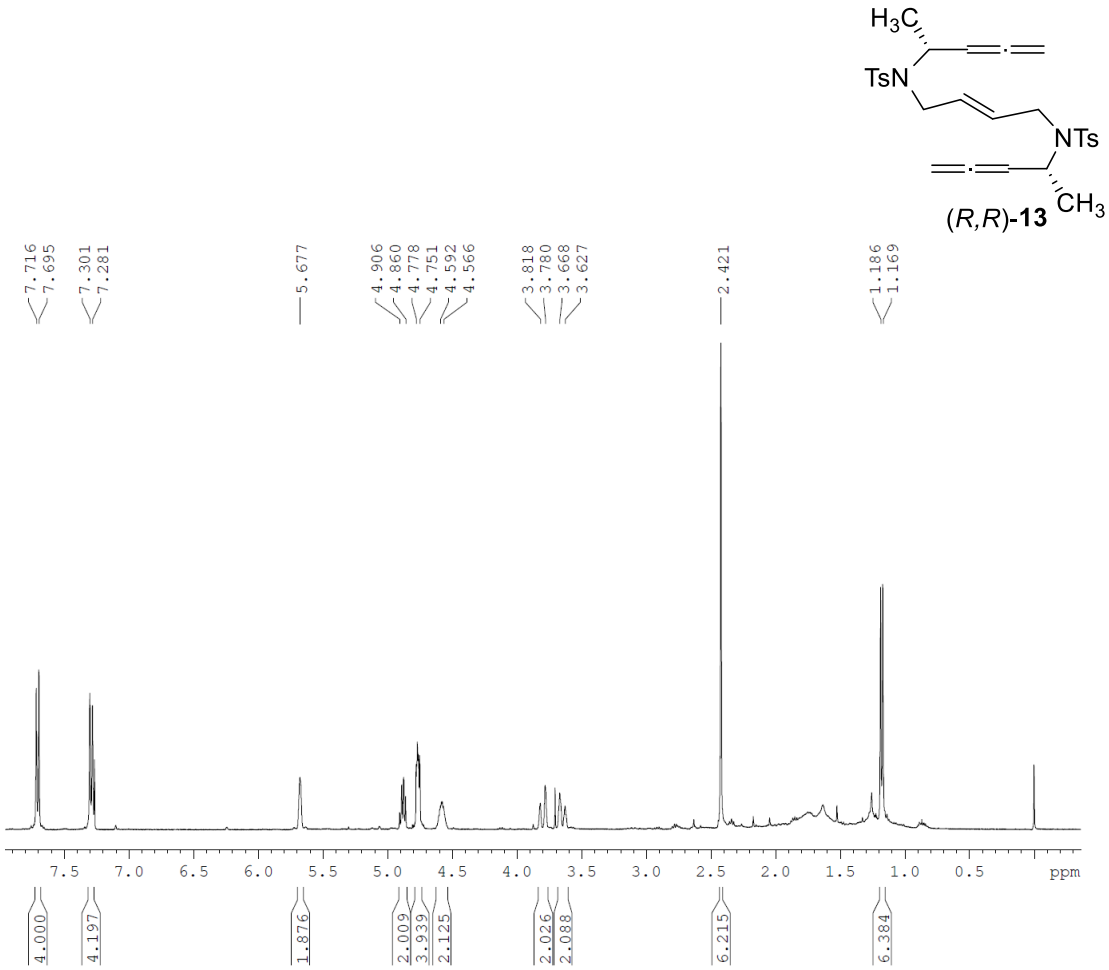


Figure S19: ^{1}H-NMR ($CDCl_3$, 400 MHz) of **(*R,R*)-13**

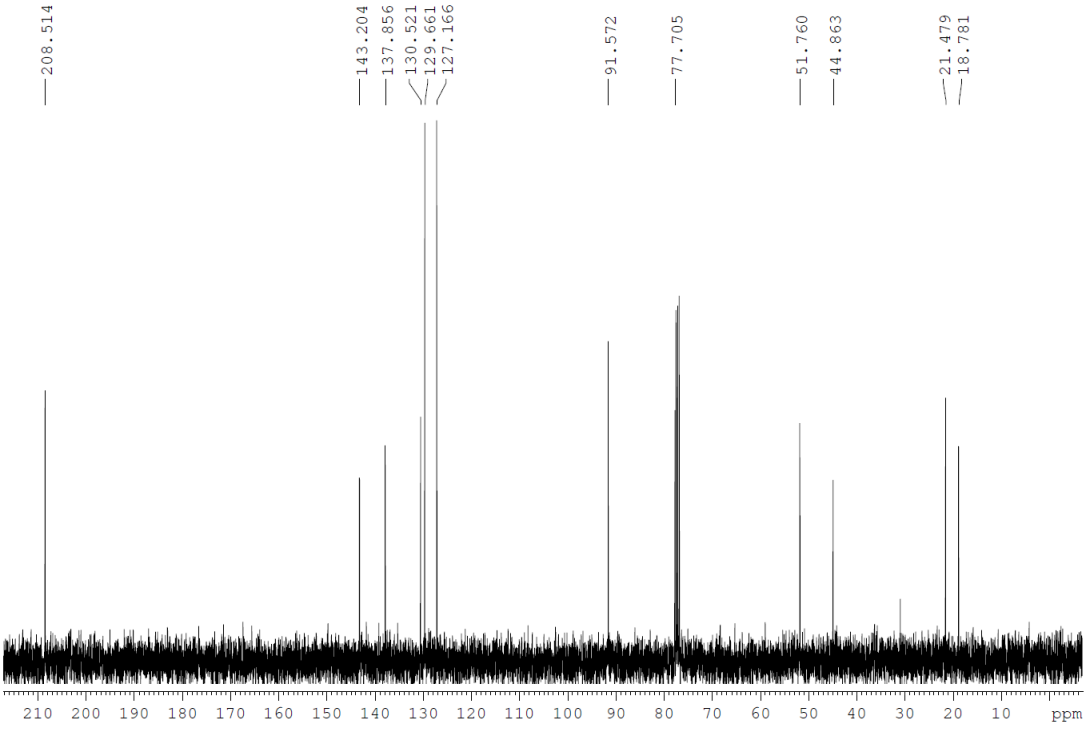


Figure S20: ^{13}C-NMR ($CDCl_3$, 100 MHz) of **(*R,R*)-13**

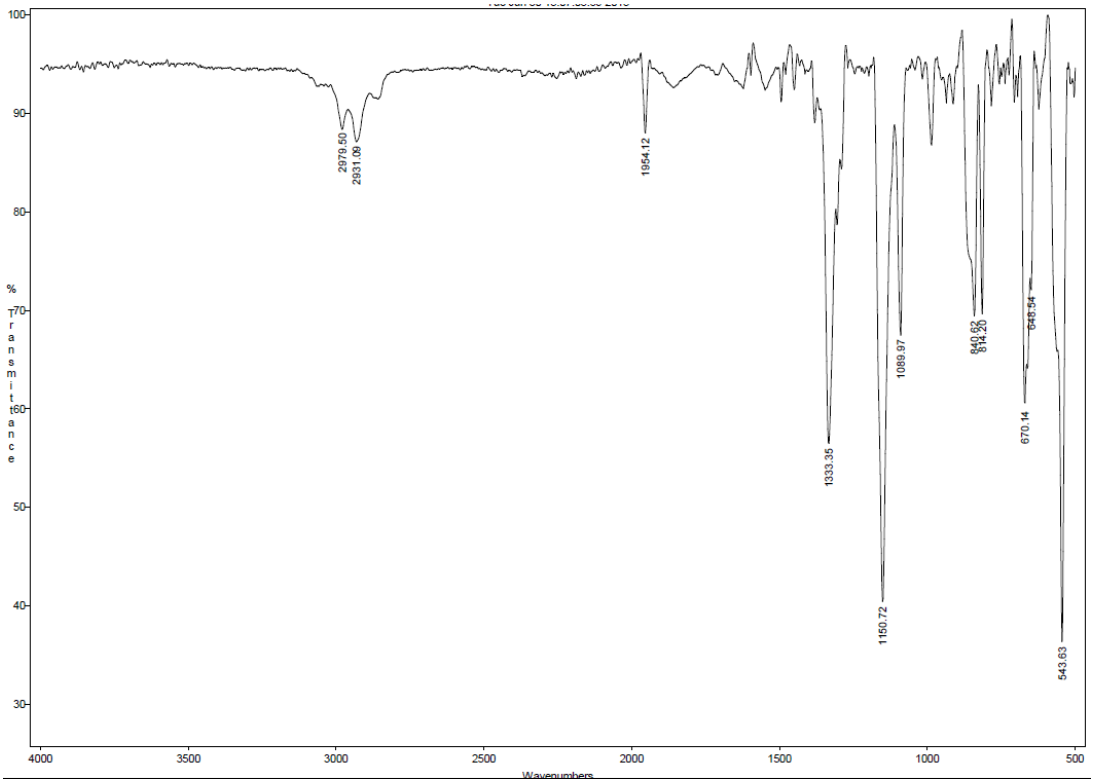


Figure S21: IR (ATR) of **(*R,R*)-13**

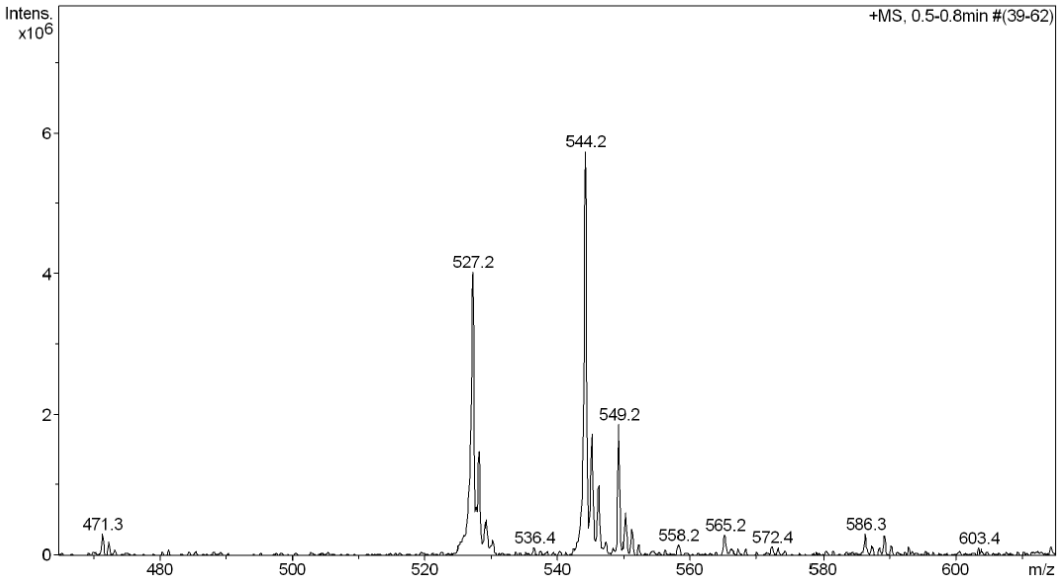


Figure S22: ESI-MS (+) of **(*R,R*)-13**

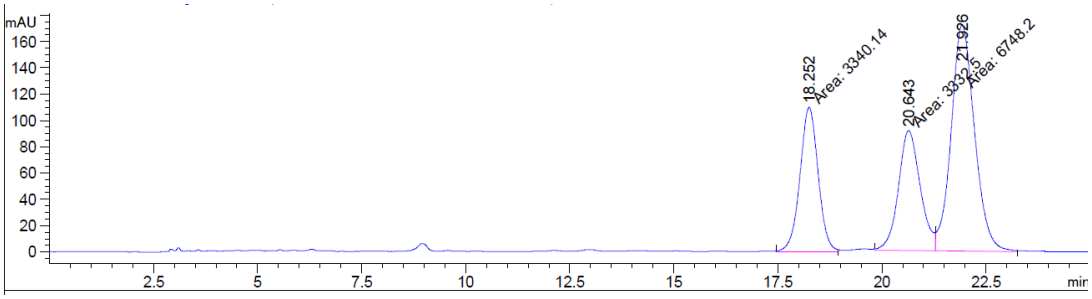


Figure S23:HPLC analysis of **(*rac*)-13**

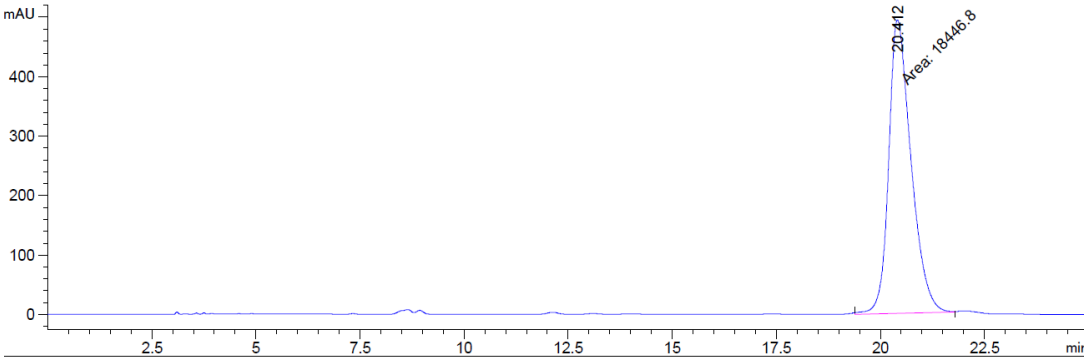


Figure S24: HPLC analysis of **(*R,R*)-13**

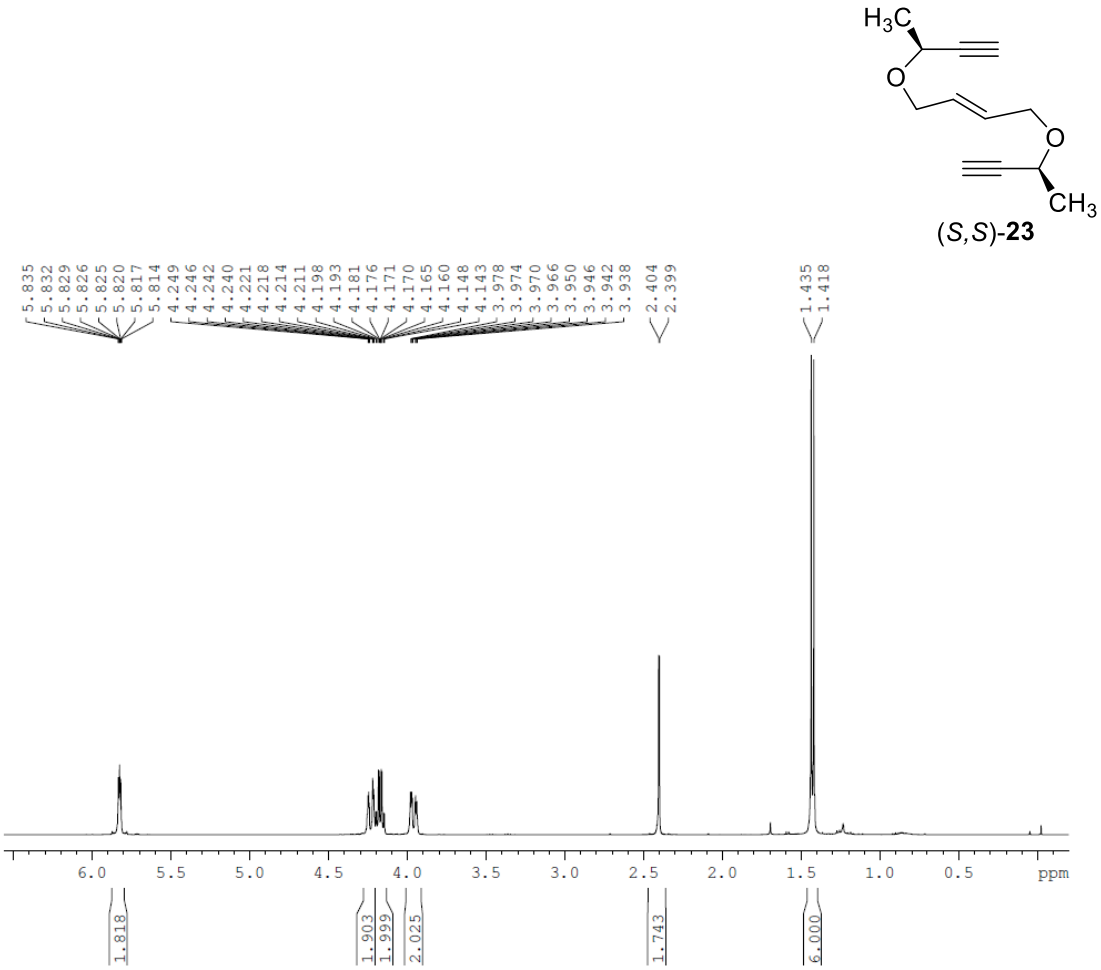


Figure S25: ^{1}H-NMR ($CDCl_3$, 400 MHz) of **(*S,S*)-23**

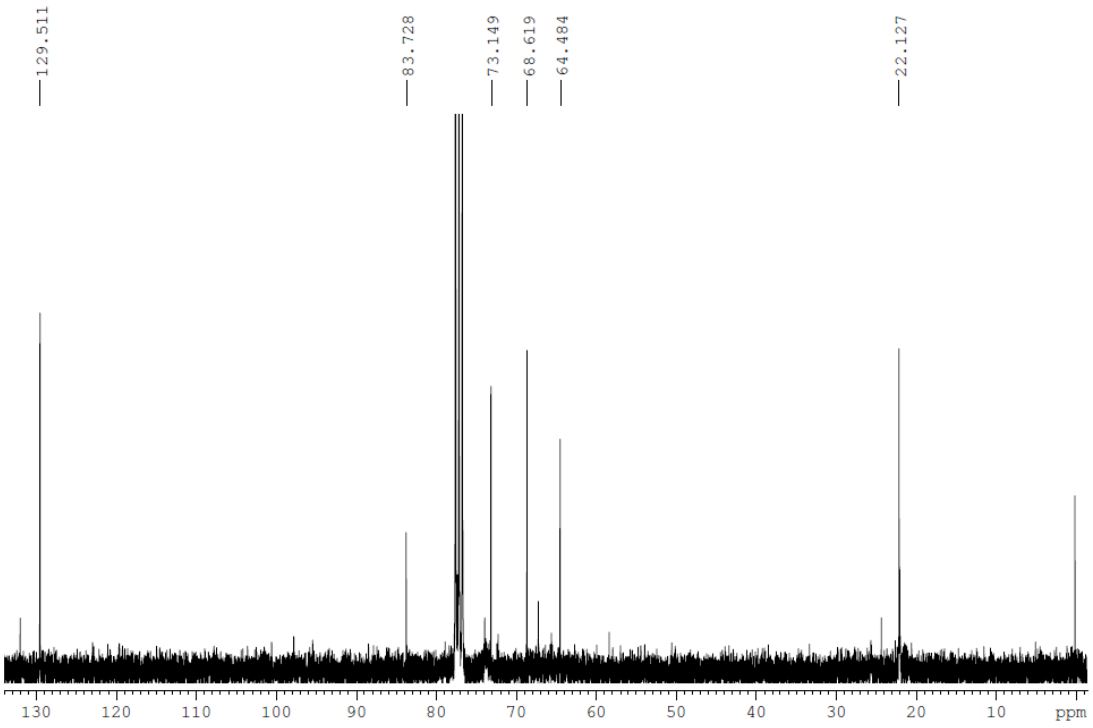


Figure S26: ^{13}C-NMR ($CDCl_3$, 75 MHz) of **(*S,S*)-23**

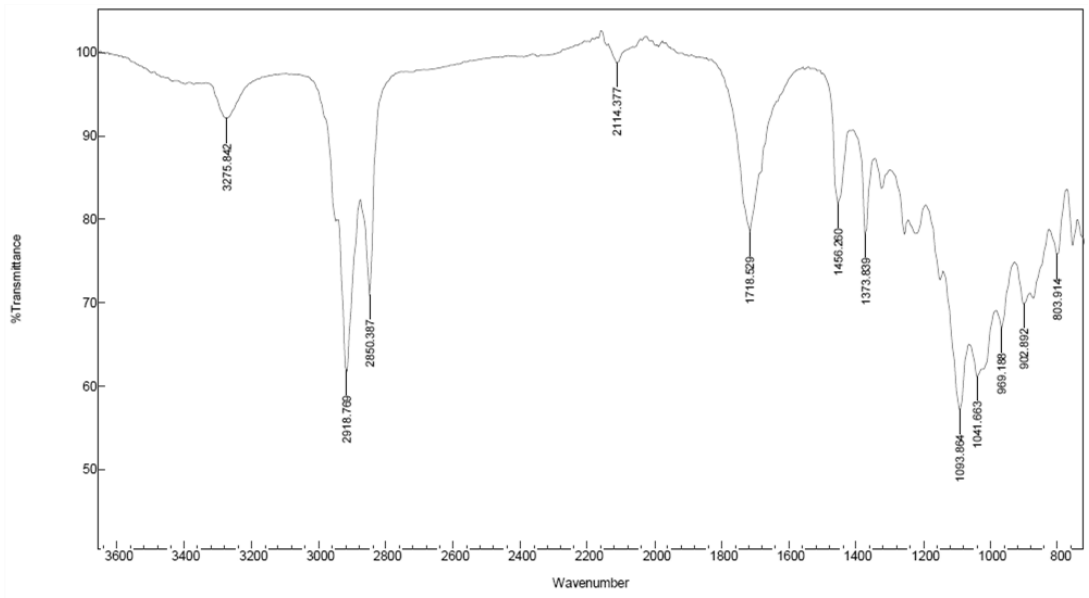


Figure S27: IR (ATR) of **(*S,S*)-23**

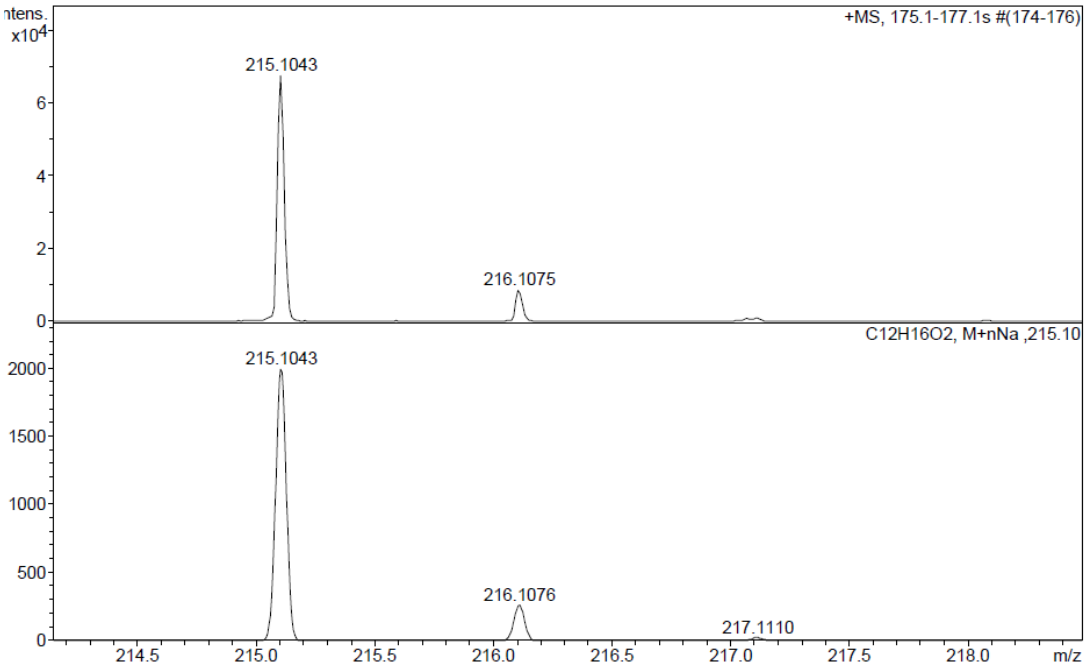


Figure S28: ESI-HRMS (+) of **(*S,S*)-23**

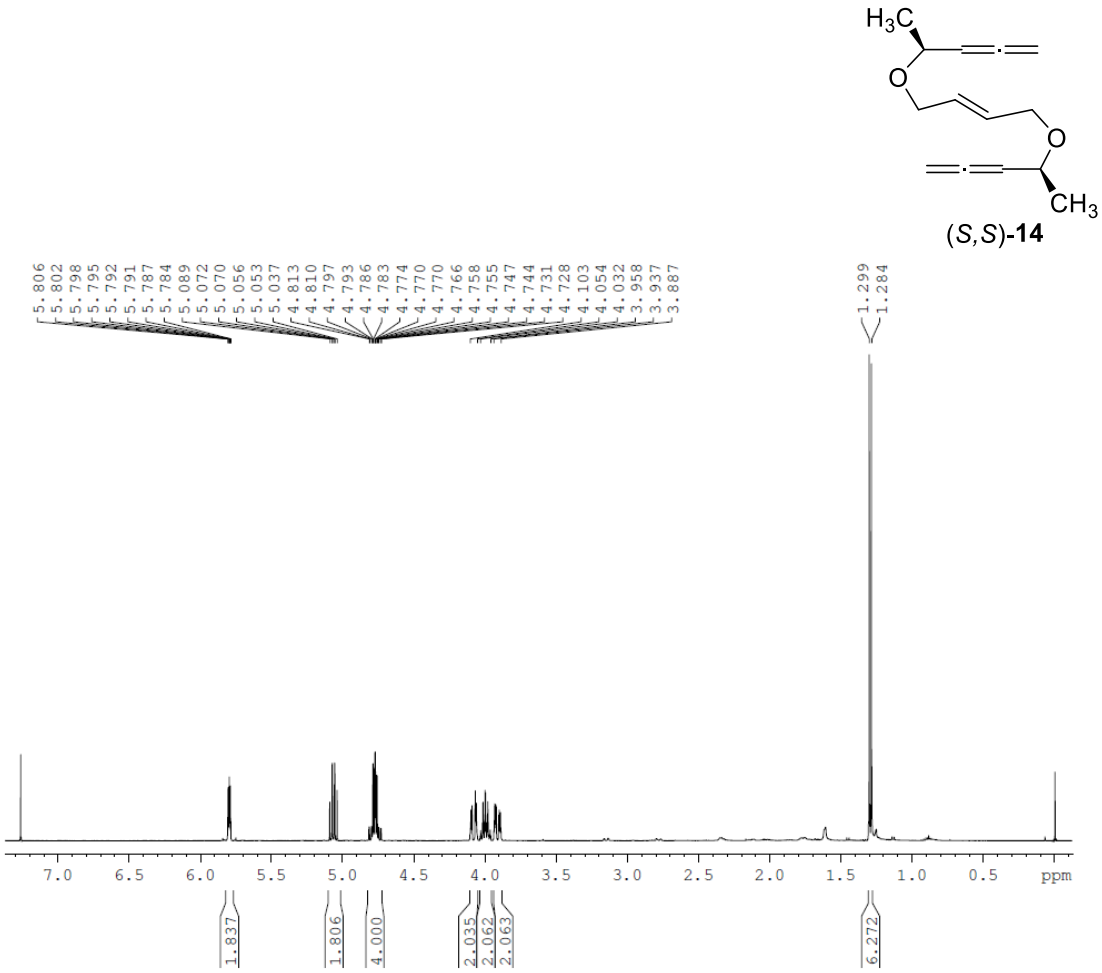


Figure S29: ^{1}H-NMR ($CDCl_3$, 400 MHz) of **(*S,S*)-14**

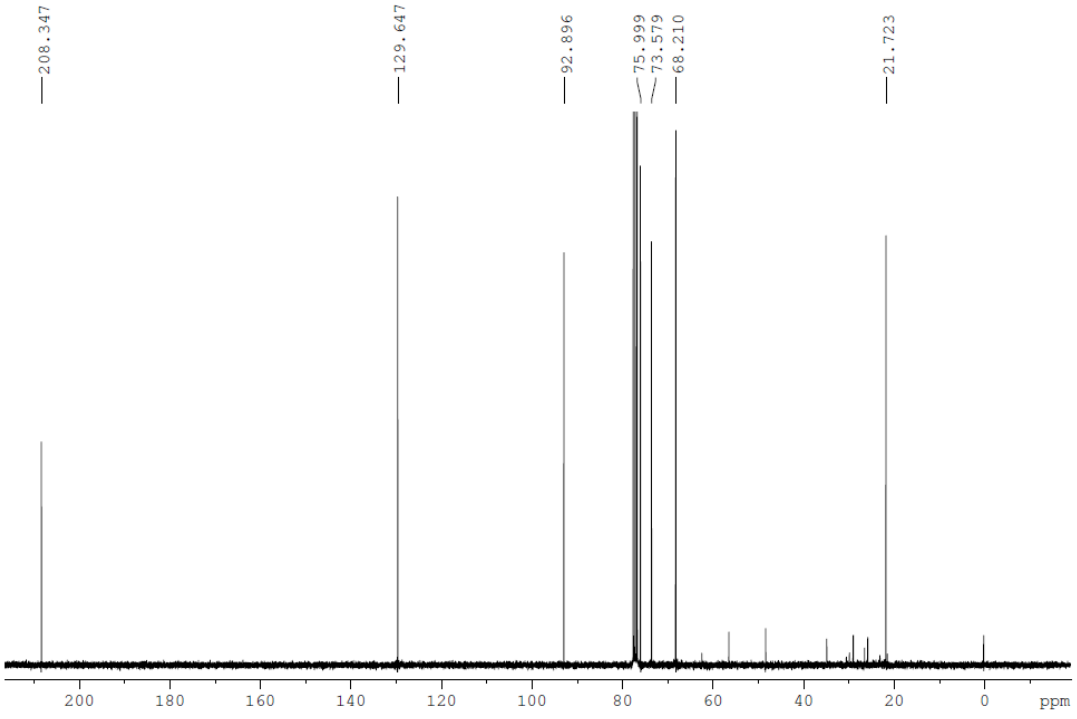


Figure S30: ^{13}C-NMR ($CDCl_3$, 75 MHz) of **(*S,S*)-14**

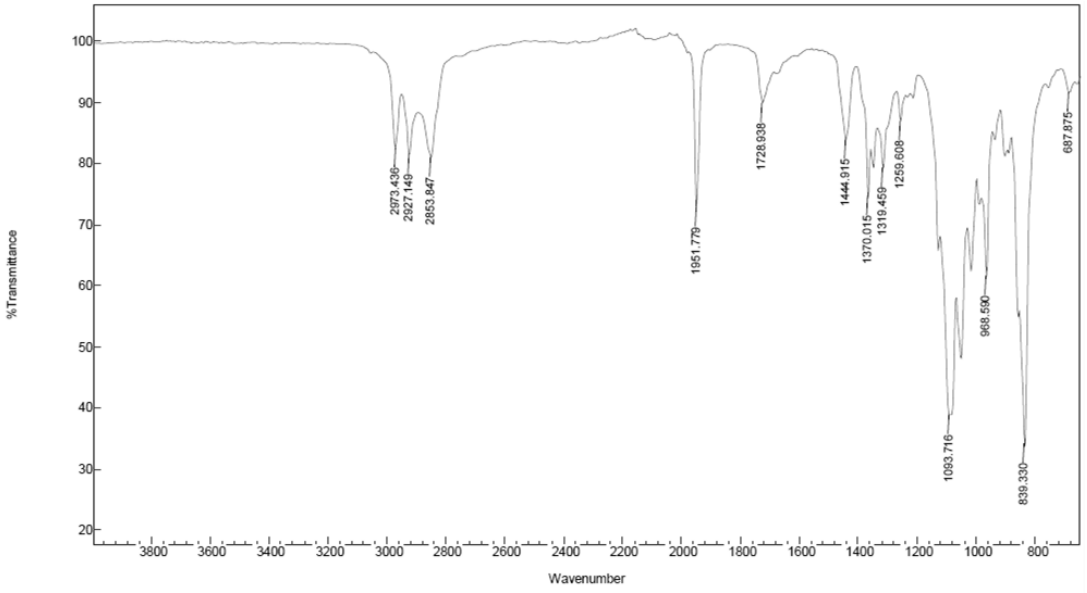


Figure S31: IR (ATR) of ***(S,S)*-14**

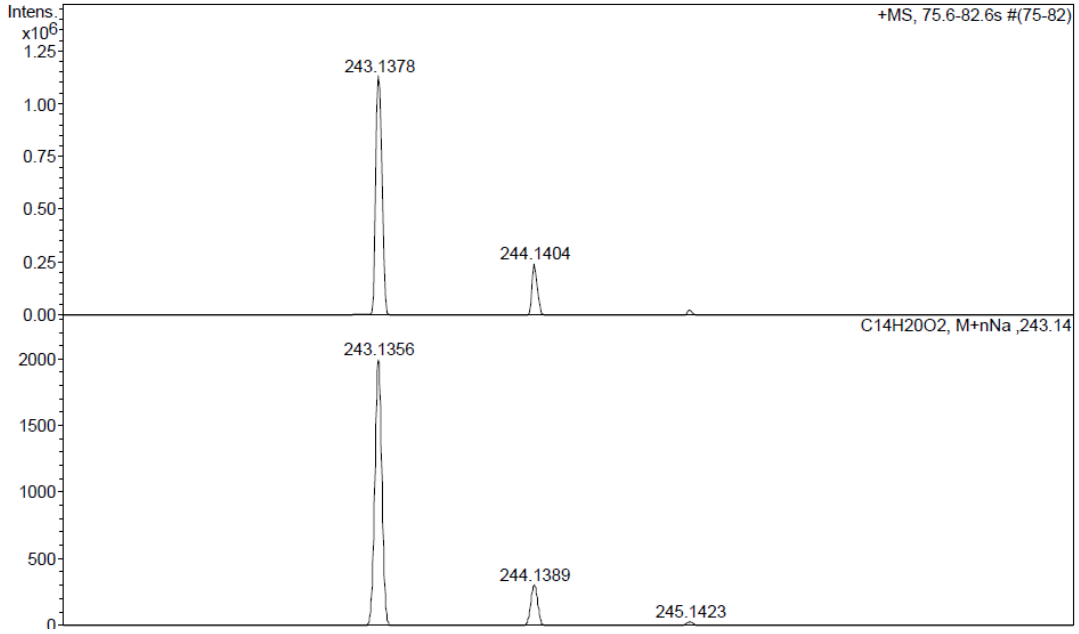
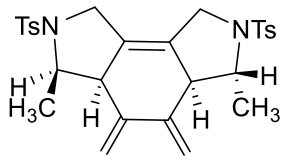


Figure S32: ESI-HRMS (+) of ***(S,S)*-14**



(3*R*, 4*R*, 9*R*, 10*S*)-**26**

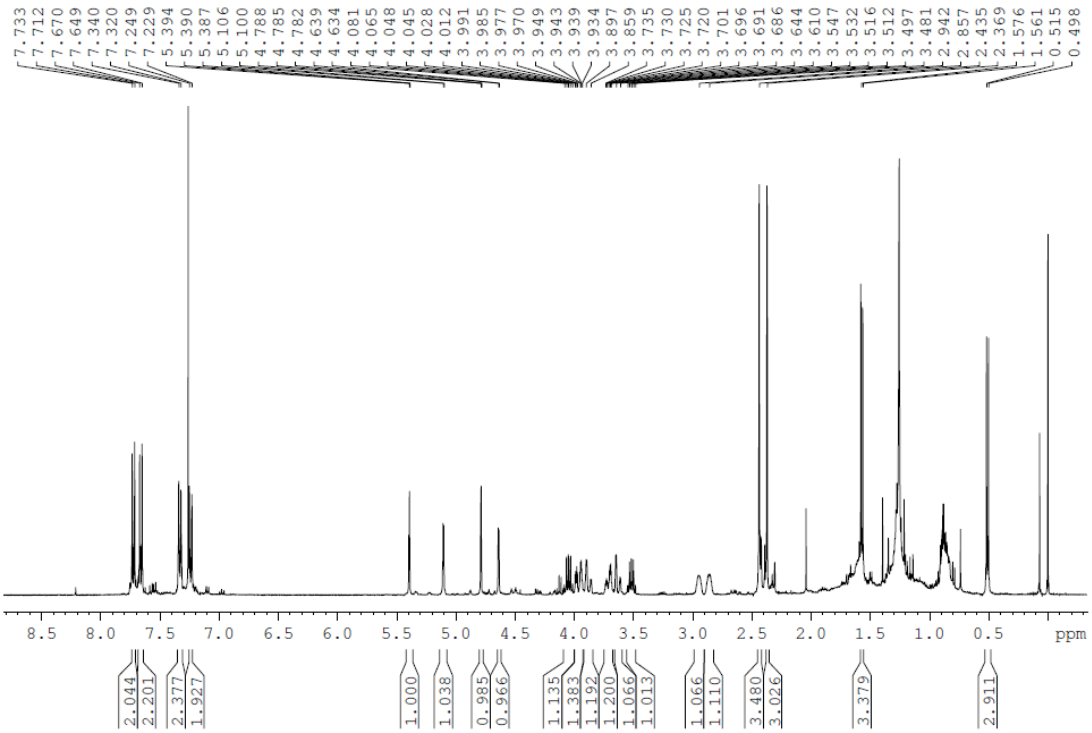


Figure S33: ^{1}H-NMR ($CDCl_3$, 400MHz) of (3*R*, 4*R*, 9*R*, 10*S*)-**26**

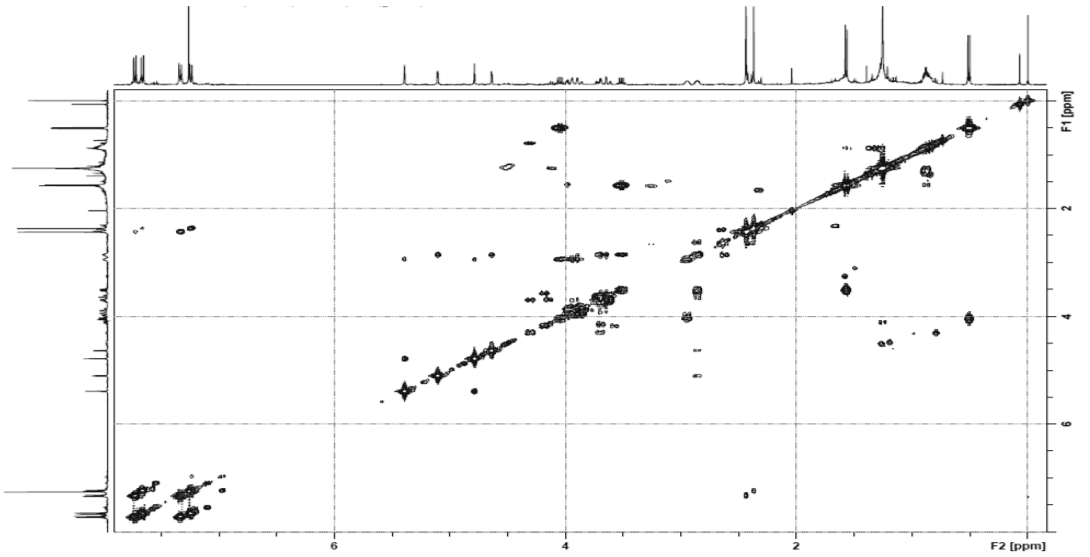


Figure S34: ^{1}H-^{1}H COSY of (3*R*, 4*R*, 9*R*, 10*S*)-**26**

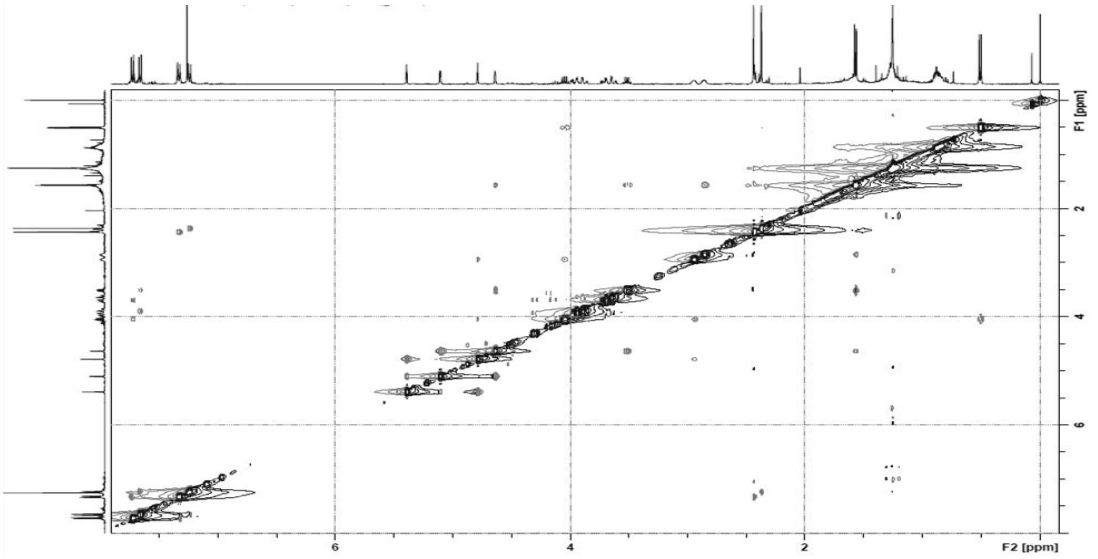


Figure S35: ^{1}H-^{1}H NOESY of (3*R*, 4*R*, 9*R*, 10*S*)-**26**

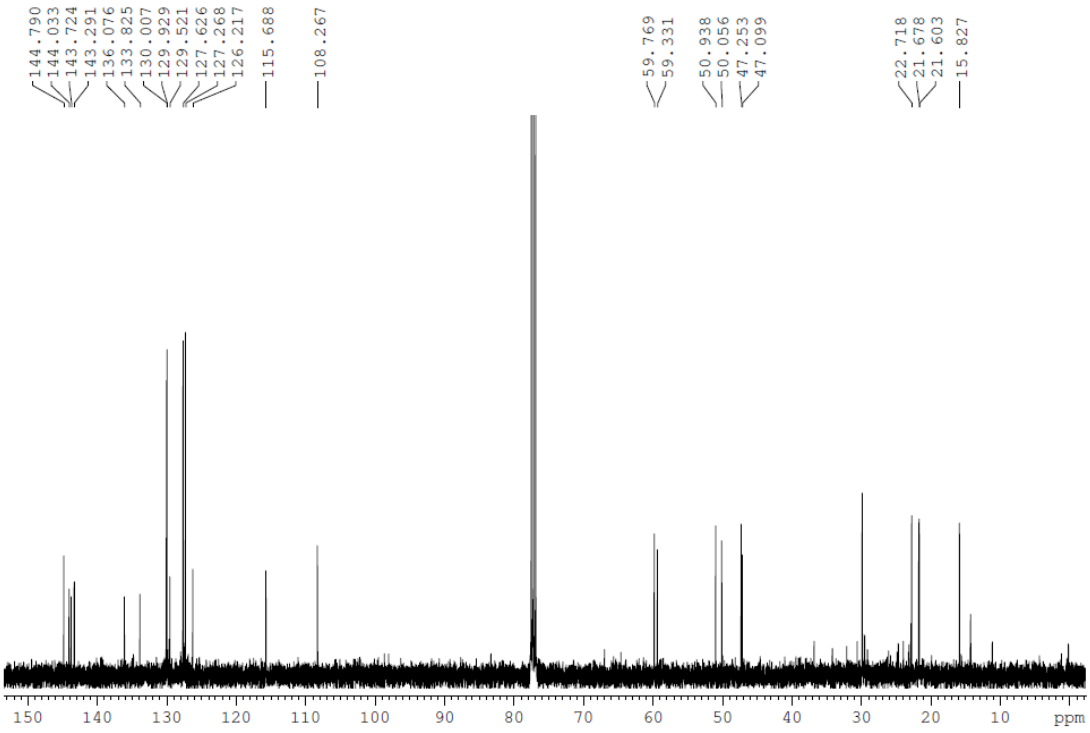


Figure S36: ^{13}C-NMR ($CDCl_3$, 100MHz) of (3*R*, 4*R*, 9*R*, 10*S*)-**26**

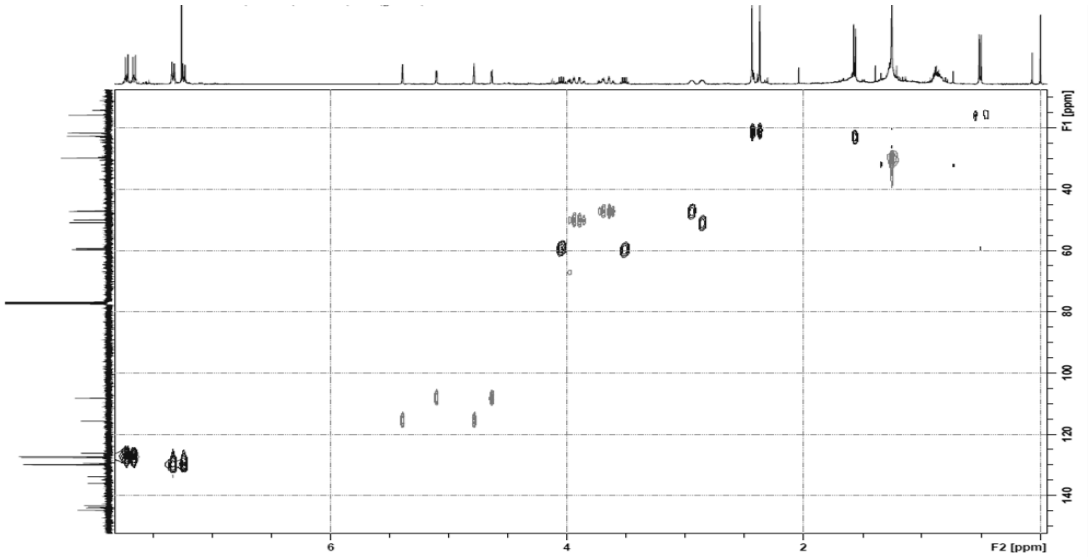


Figure S37: ^{1}H-^{13}C HSQC of (3*R*, 4*R*, 9*R*, 10*S*)-**26**

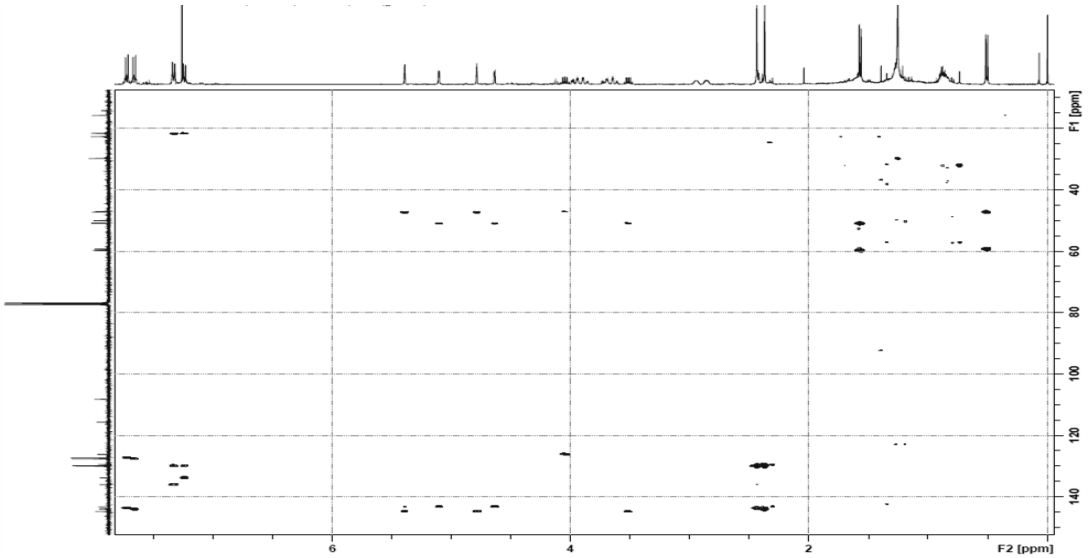


Figure S38: ^{1}H-^{13}C HMBC of (3*R*, 4*R*, 9*R*, 10*S*)-**26**

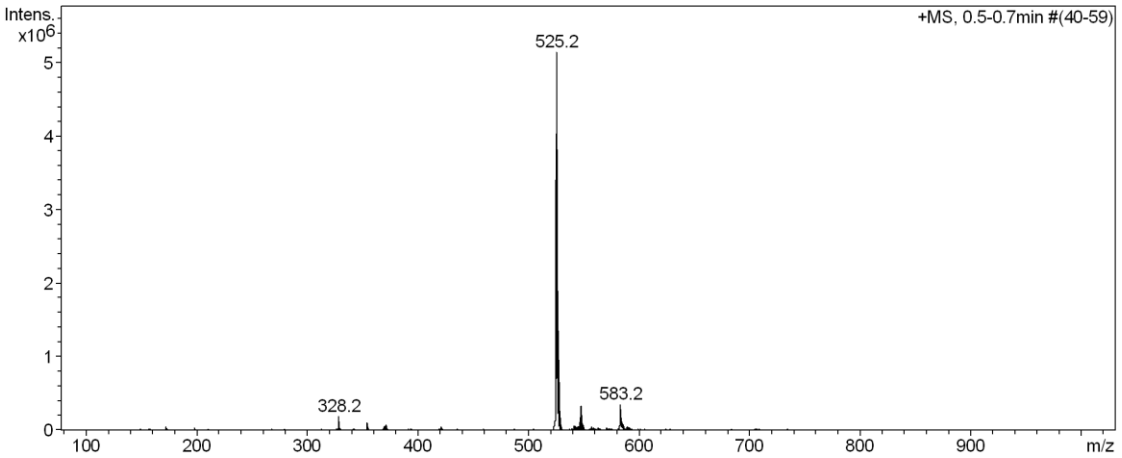


Figure S39: ESI-MS (+) of (3*R*, 4*R*, 9*R*, 10*S*)-**26**

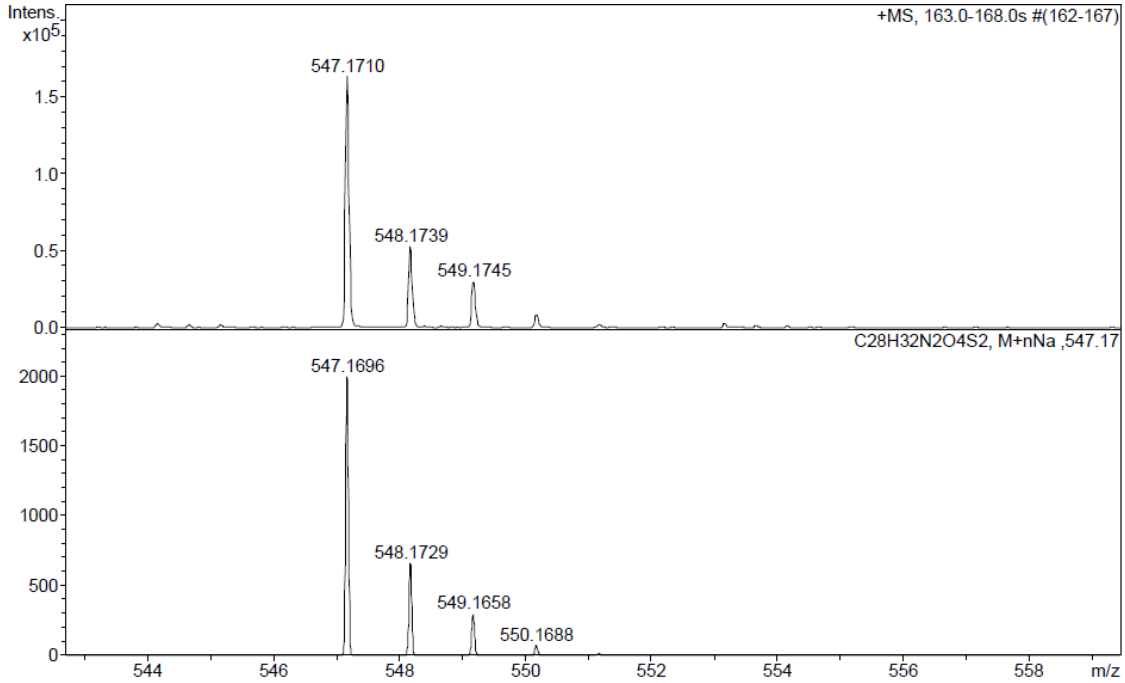


Figure S40: ESI-HRMS (+) of (3*R*, 4*R*, 9*R*, 10*S*)-**26**

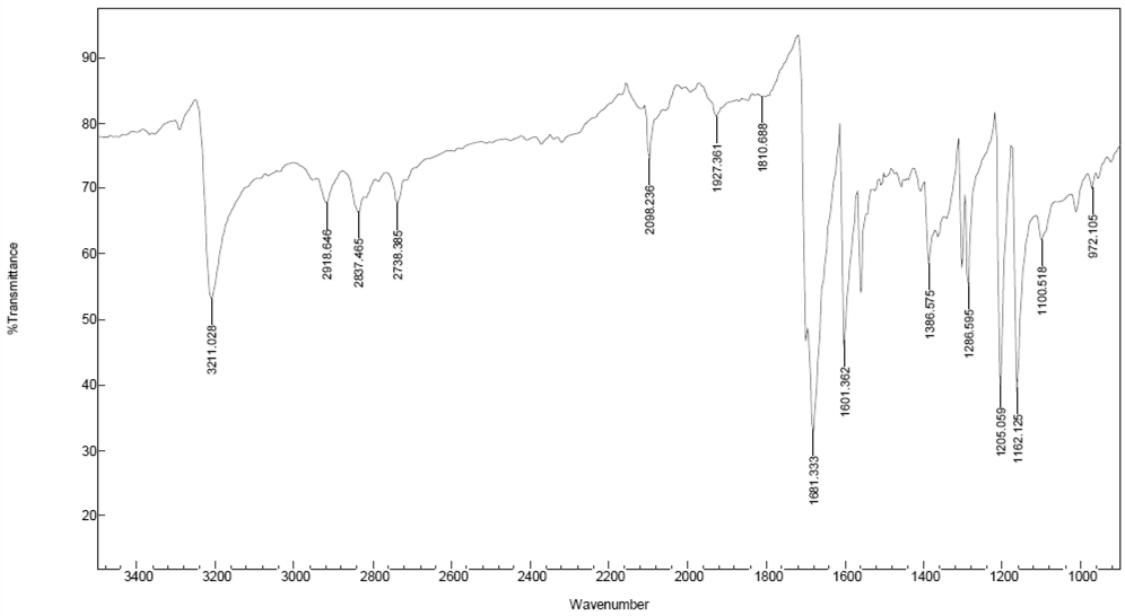


Figure S41: IR (ATR) of (3*R*, 4*R*, 9*R*, 10*S*)-**26**

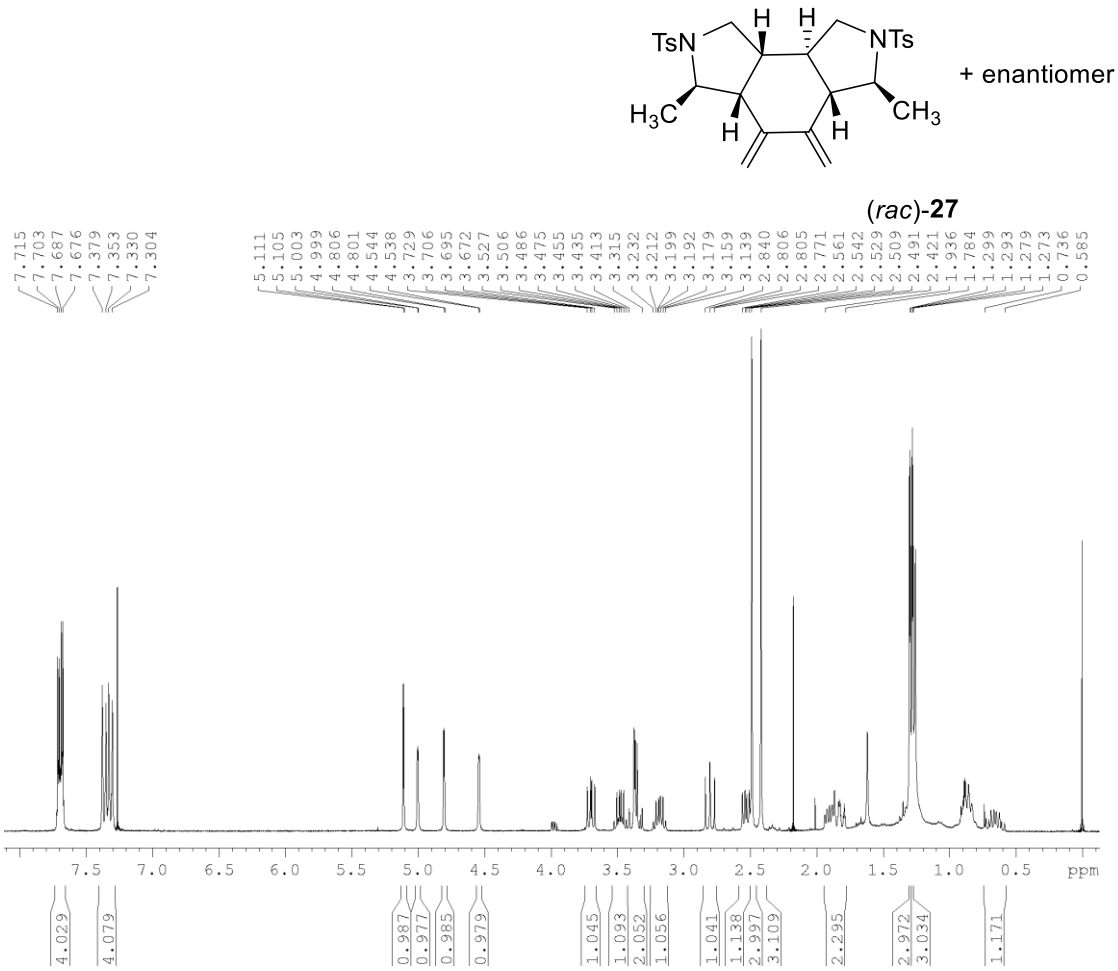


Figure S42: ^{1}H-NMR ($CDCl_3$, 300MHz) of (*rac*)-**27**

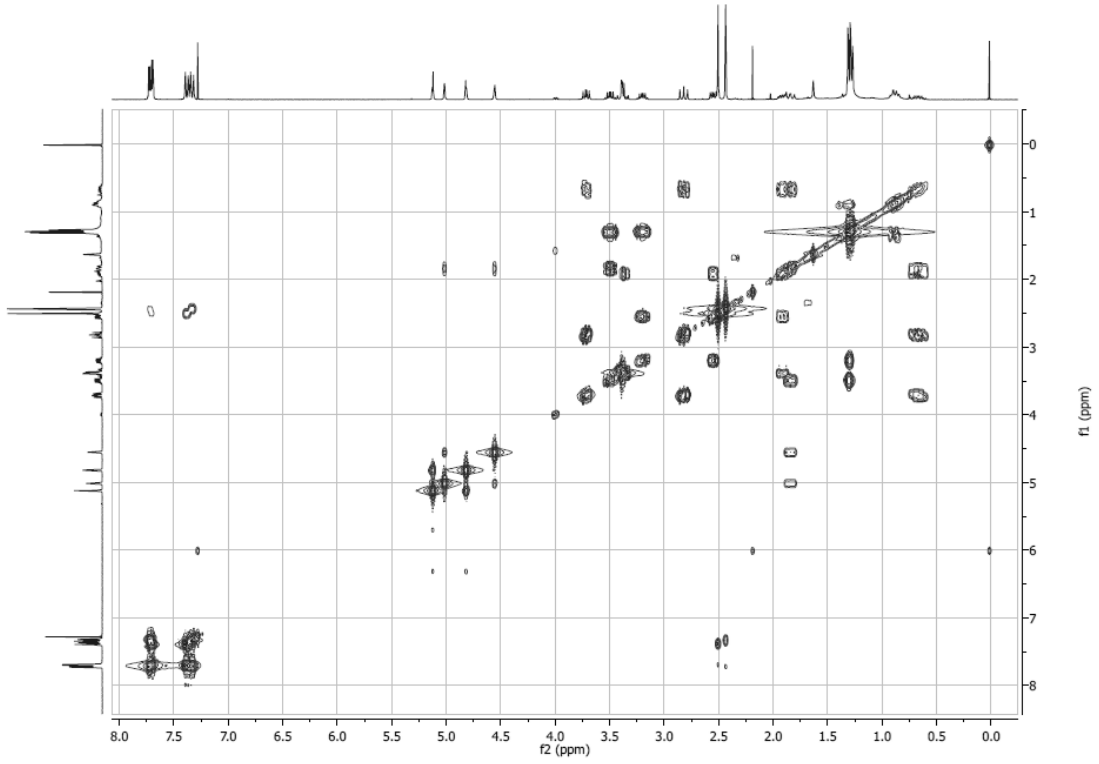


Figure S43: ^{1}H-^{1}H COSY of (*rac*)-**27**

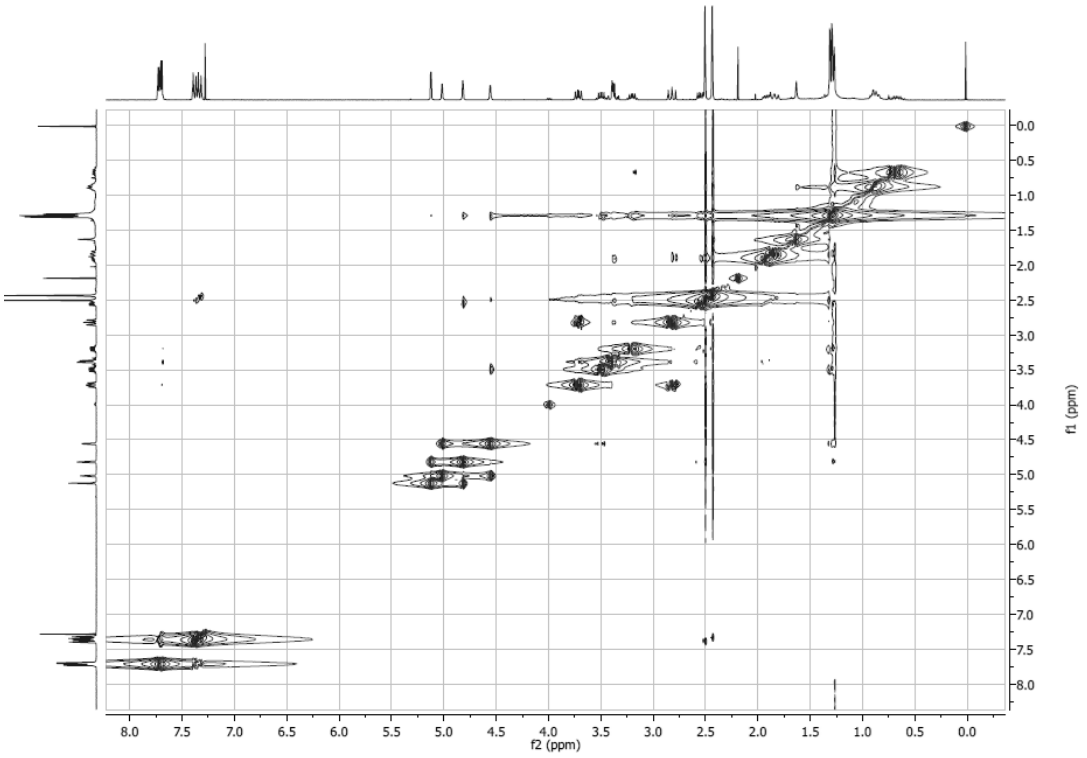


Figure S44: ^{1}H-^{1}H NOESY of (*rac*)-**27**

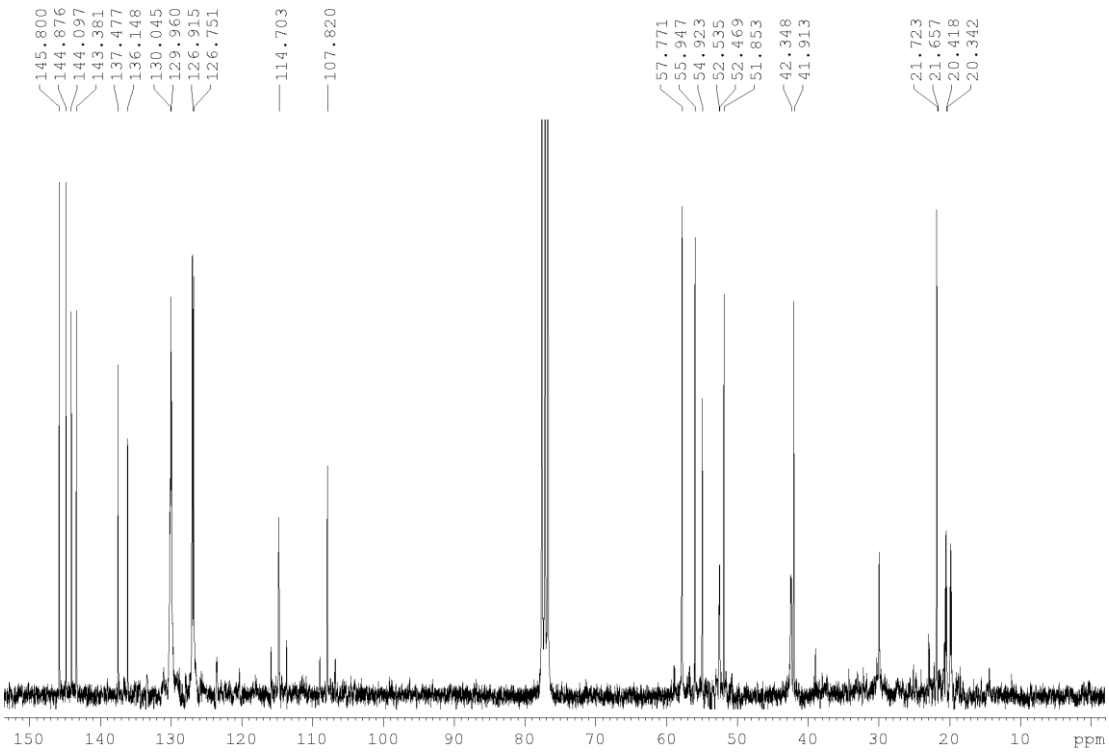


Figure S45: ^{13}C-NMR ($CDCl_3$, 75MHz) of (*rac*)-**27**

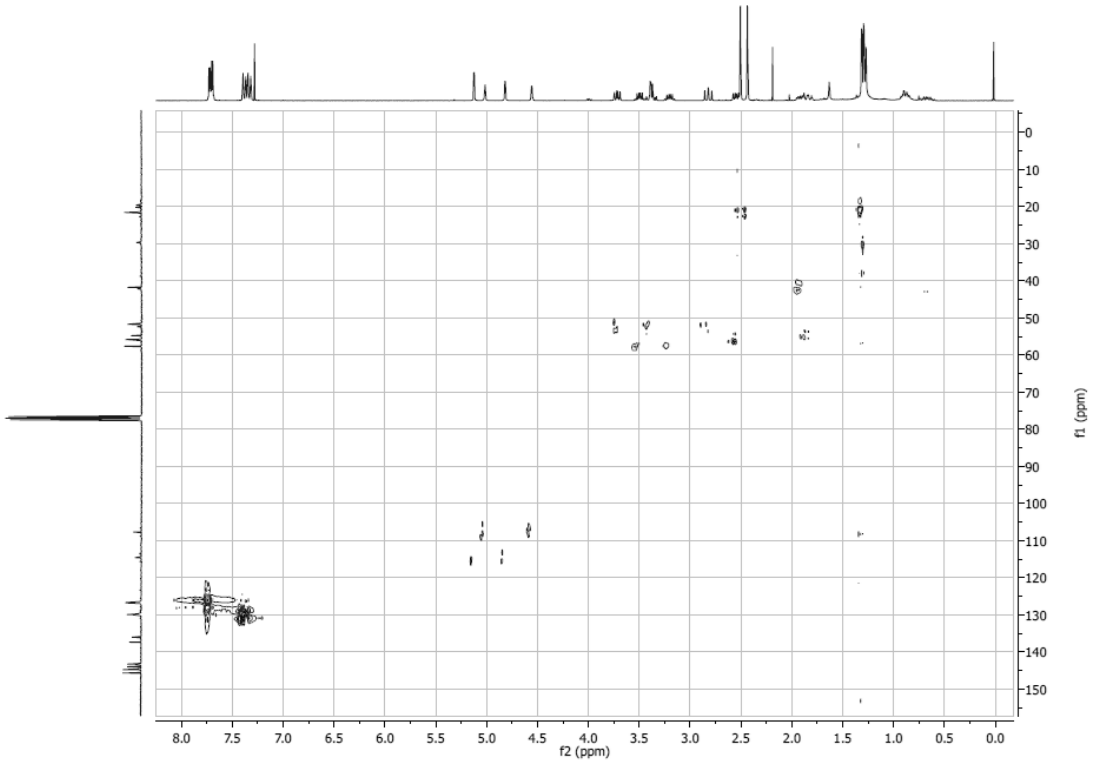


Figure S46: ^{1}H-^{13}C HSQCed of (*rac*)-**27**

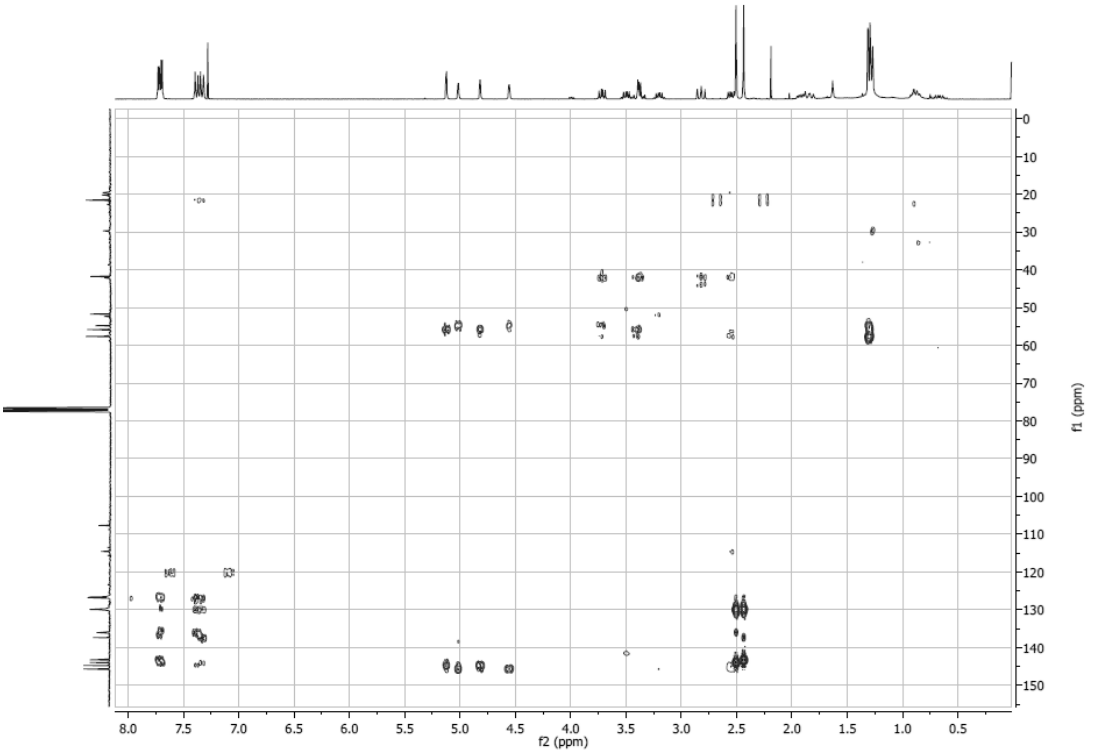


Figure S47: ^{1}H-^{13}C HMBC of (*rac*)-**27**

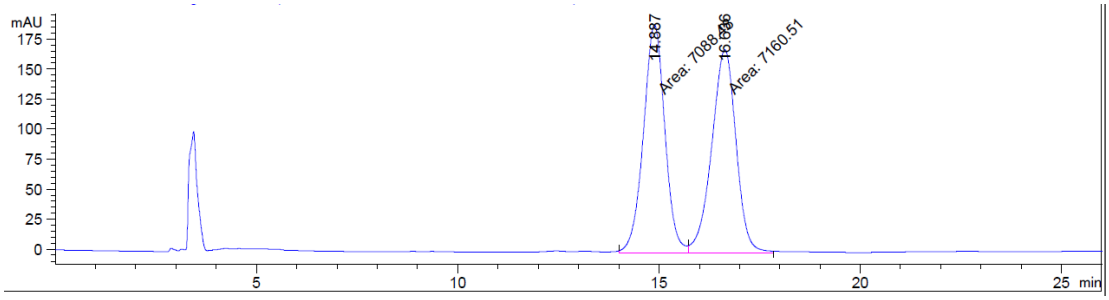


Figure S48: HPLC analysis of (*rac*)-**27**

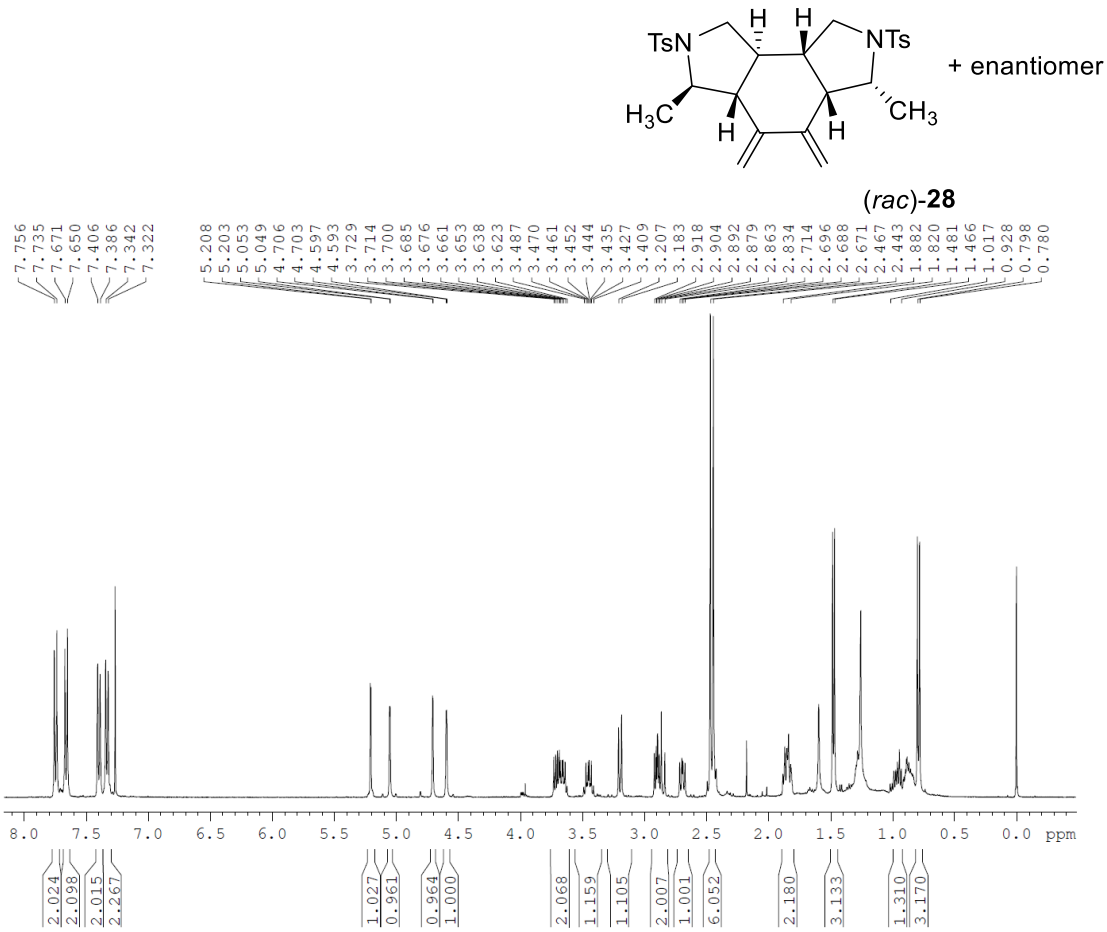


Figure S49: ^{1}H-NMR ($CDCl_3$, 400MHz) of (*rac*)-**28**

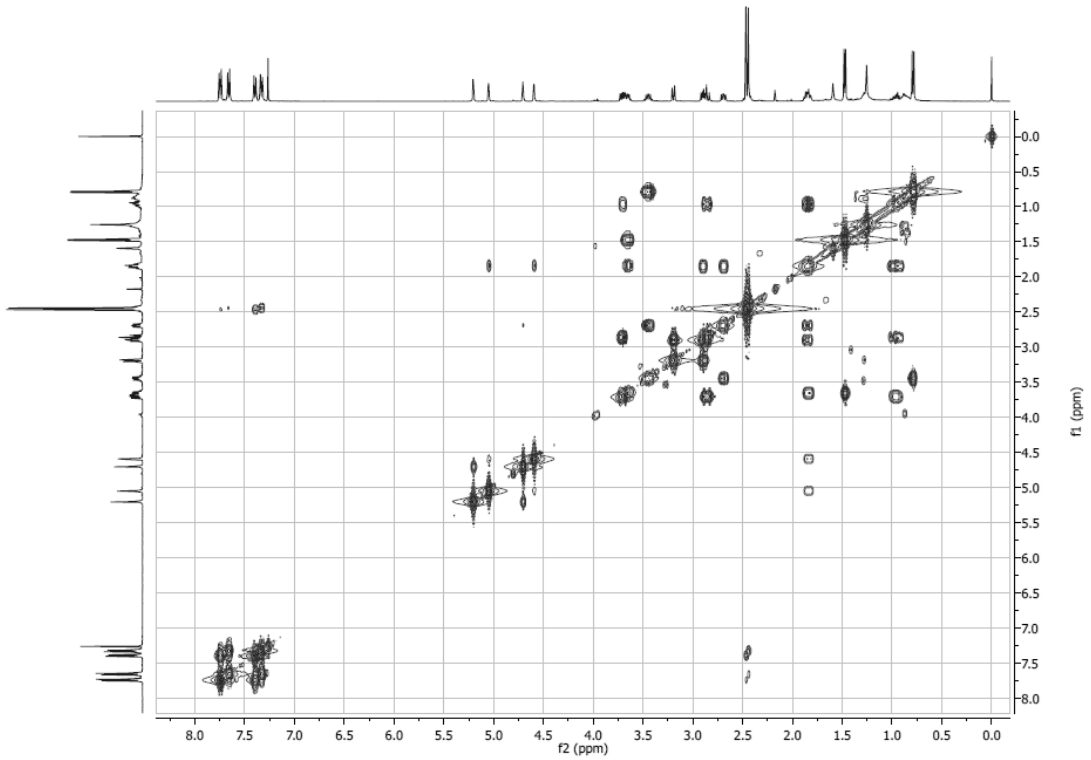


Figure S50: ^{1}H-^{1}H COSY of (*rac*)-**28**

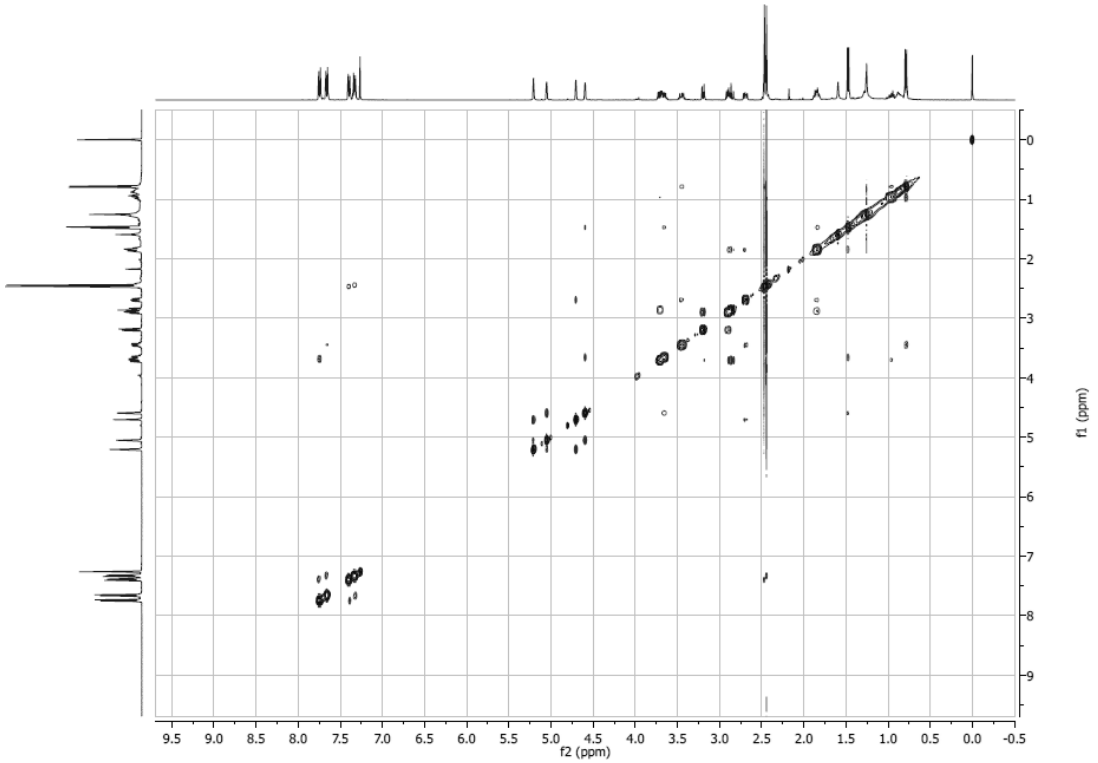


Figure S51: ^{1}H-^{1}H NOESY of (*rac*)-**28**

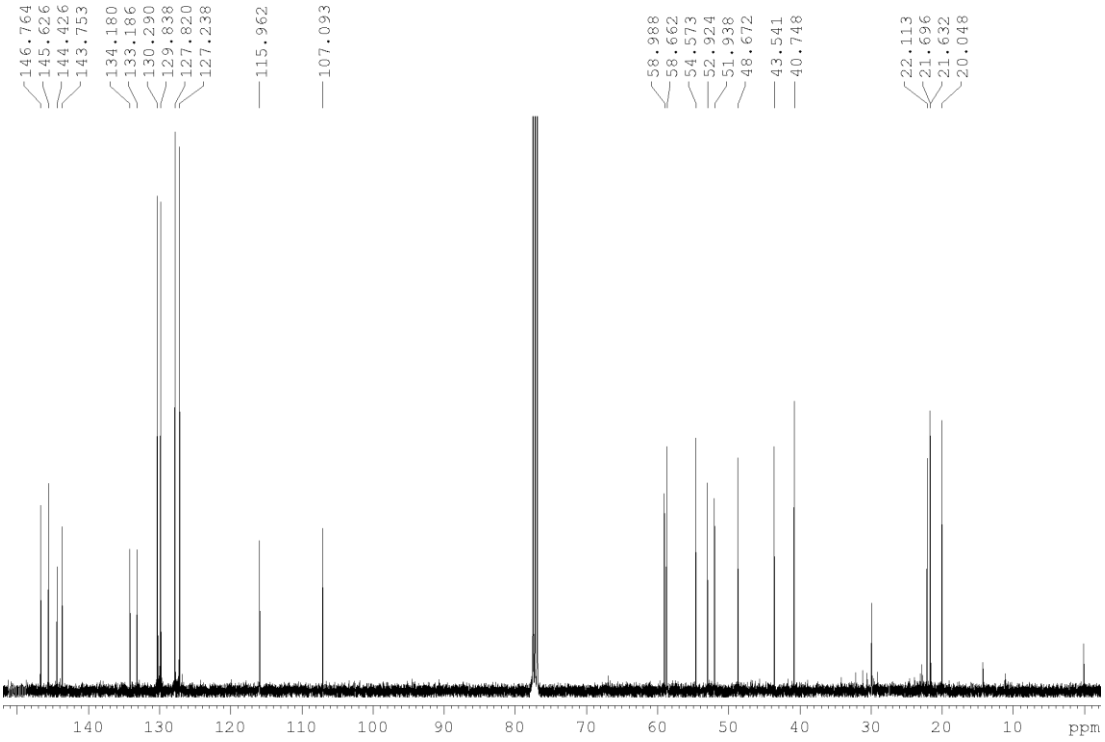


Figure S52: ^{13}C-NMR ($CDCl_3$, 100MHz) of (*rac*)-**28**

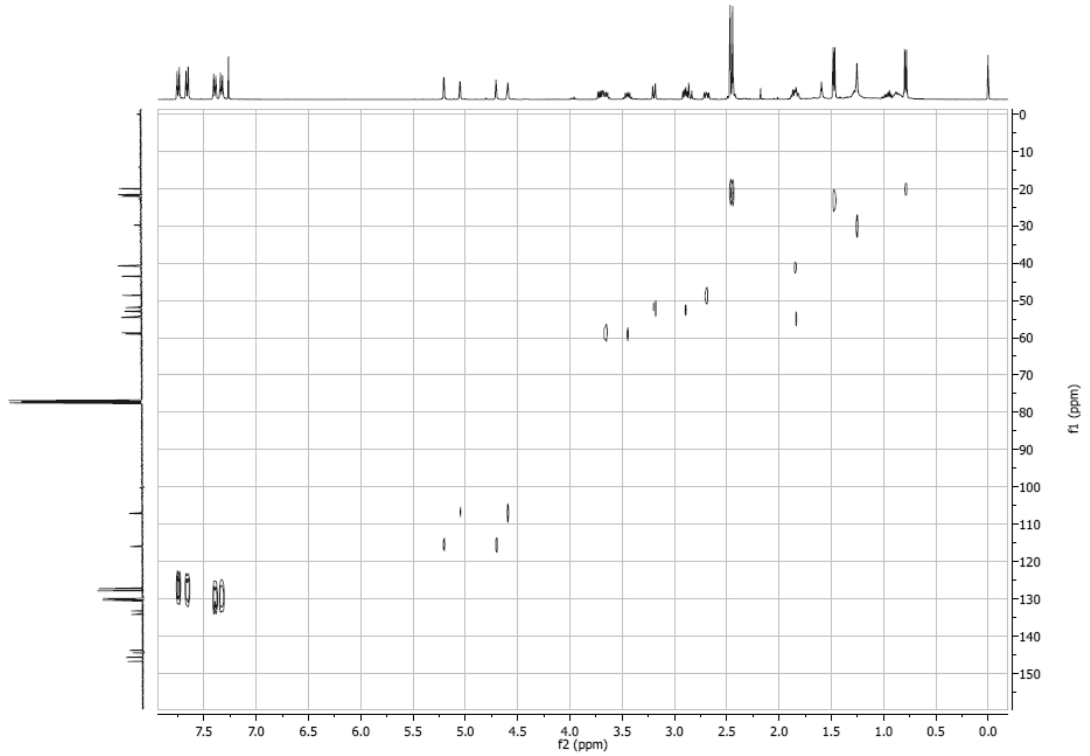


Figure S53: ^{1}H-^{13}C HSQCed of (*rac*)-**28**

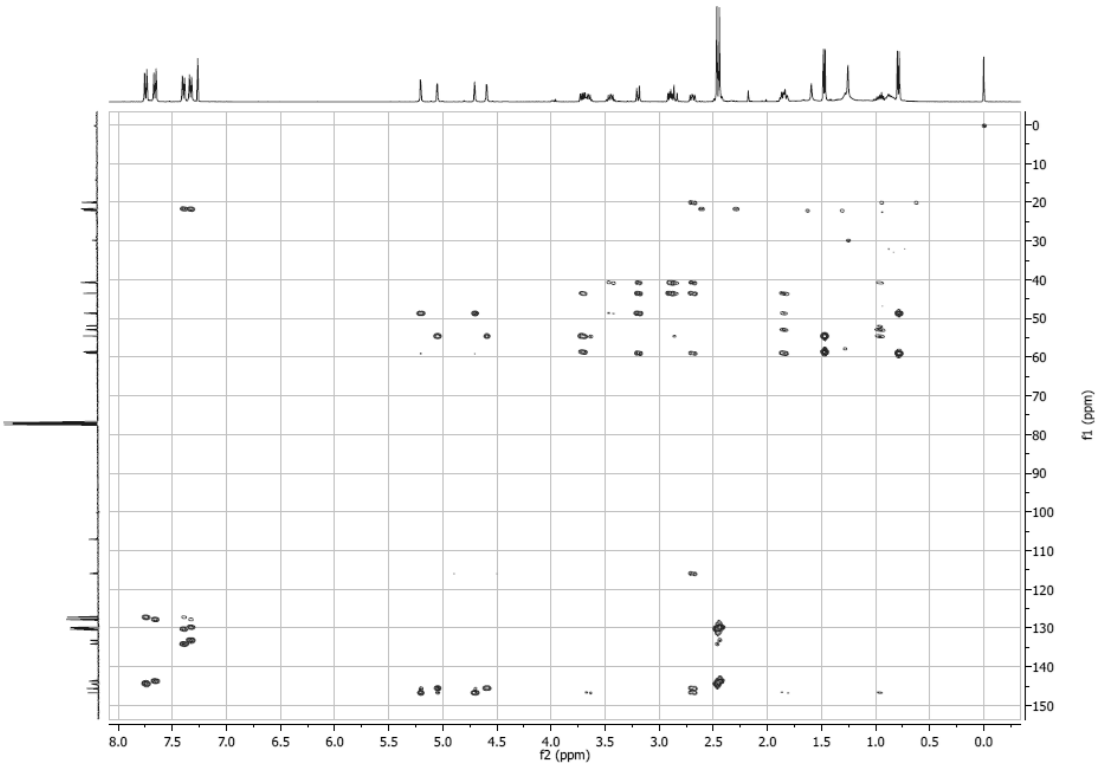


Figure S54: ^{1}H-^{13}C HMBC of (*rac*)-**28**

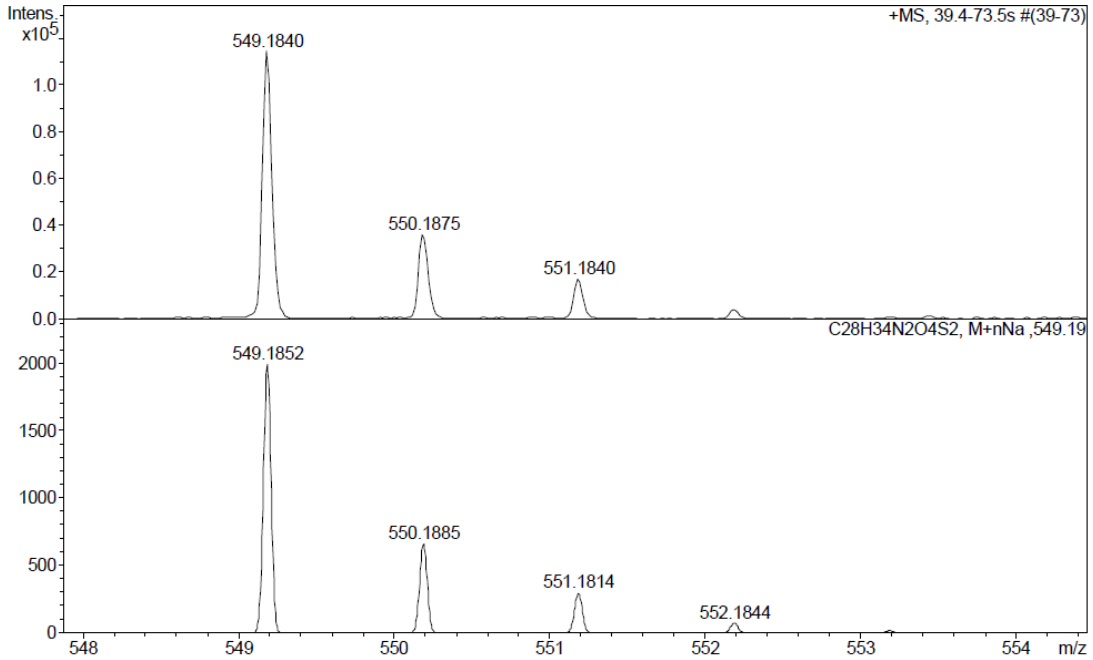


Figure S55: ESI-HRMS (+) of (*rac*)-**28**

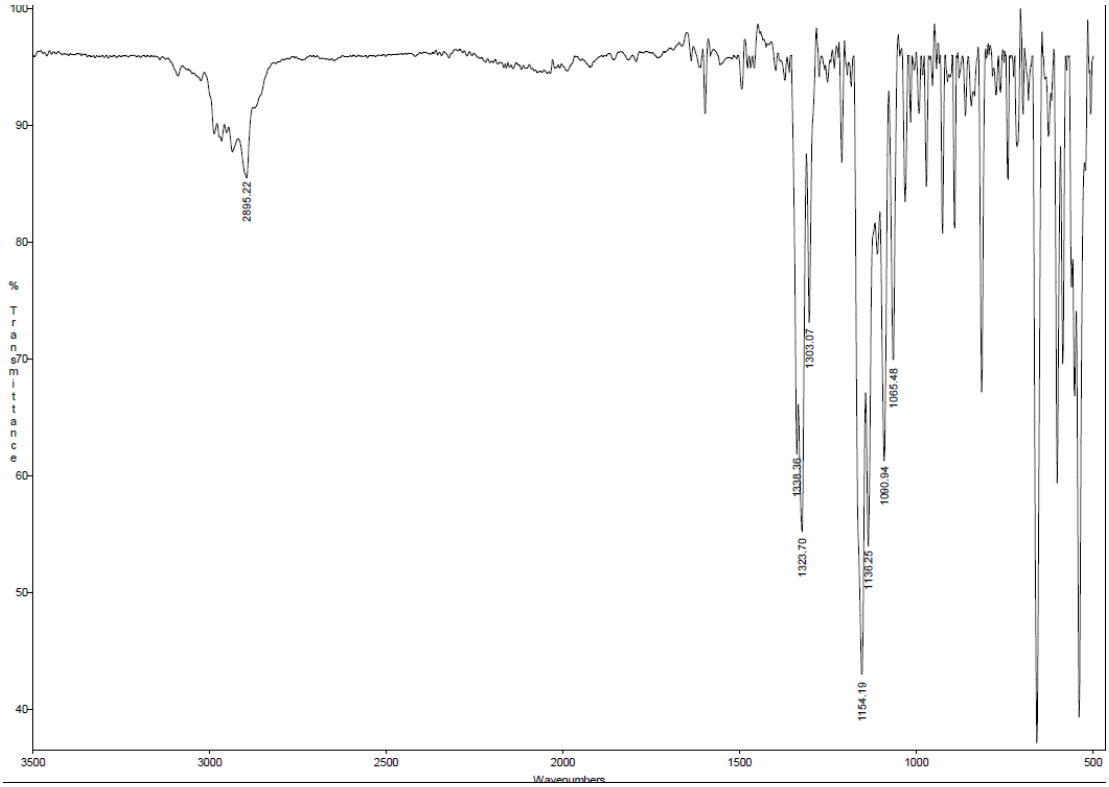


Figure S56: IR (ATR) of (*rac*)-**28**

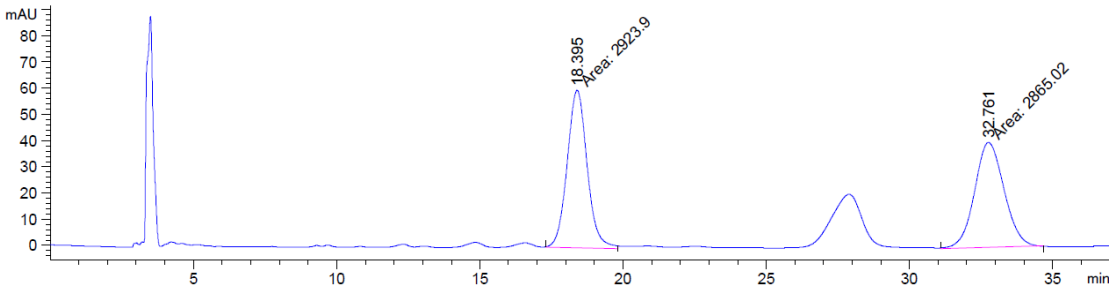
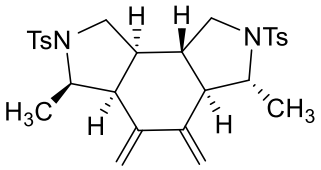


Figure S57: HPLC analysis of (*rac*)-**28**



(3*S*, 4*R*, 6*S*, 7*S*, 9*R*, 10*R*)-**28**

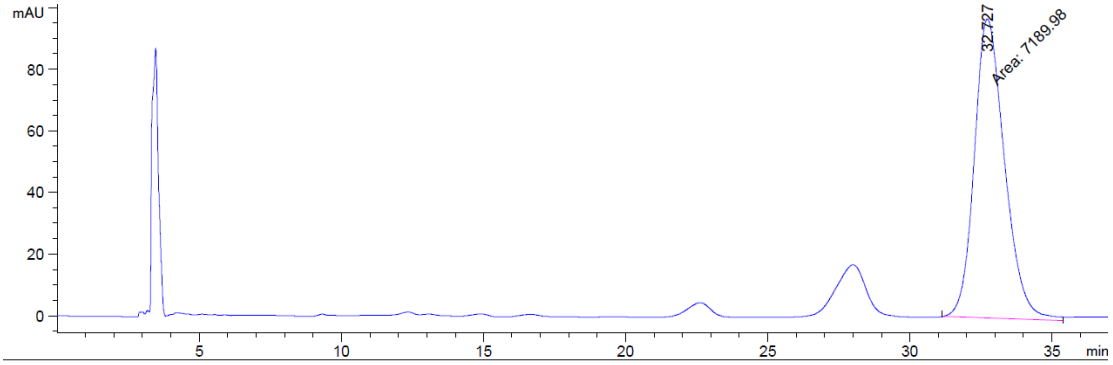
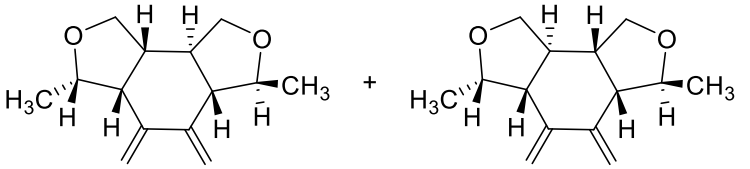


Figure S58: HPLC analysis of (3*S,* 4*R*, 6*S*, 7*S*, 9*R*, 10*R*)-**28**



(3*R*, 4*S*, 6*R*, 7*R*, 9*S*, 10*S*)-**30** (3*R*, 4*S*, 6*S*, 7*S*, 9*S*, 10*S*)-**31**

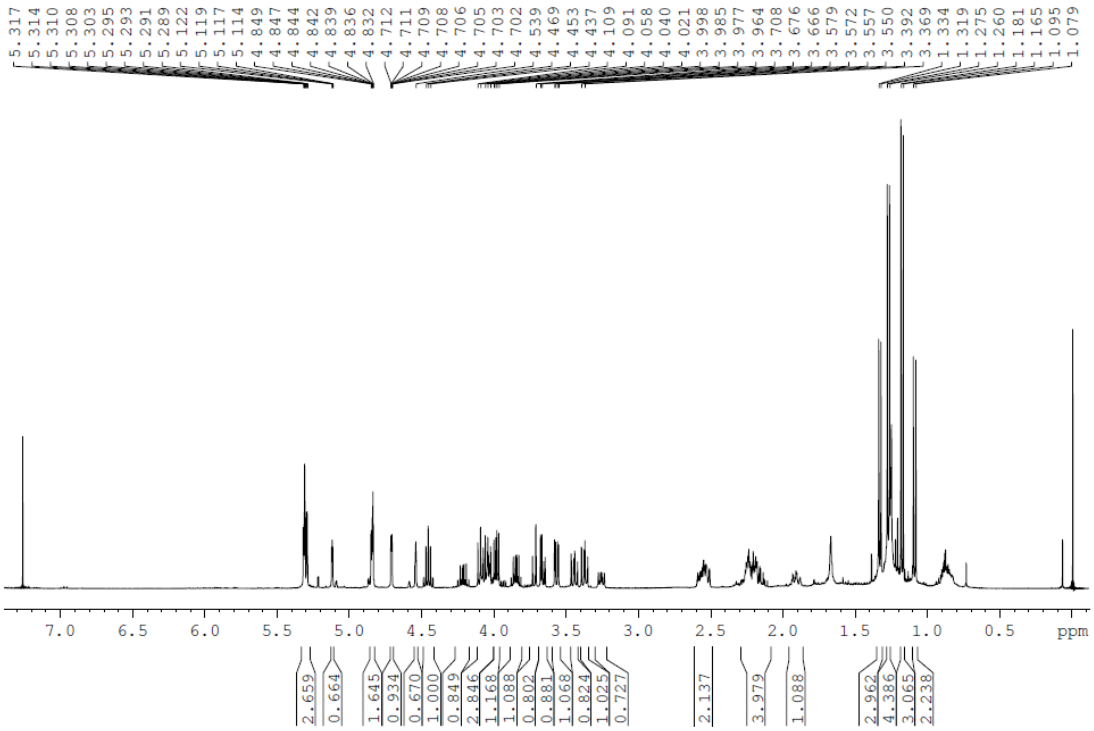


Figure S59: ^{1}H-NMR ($CDCl_3$, 400MHz) of **30** + **31**

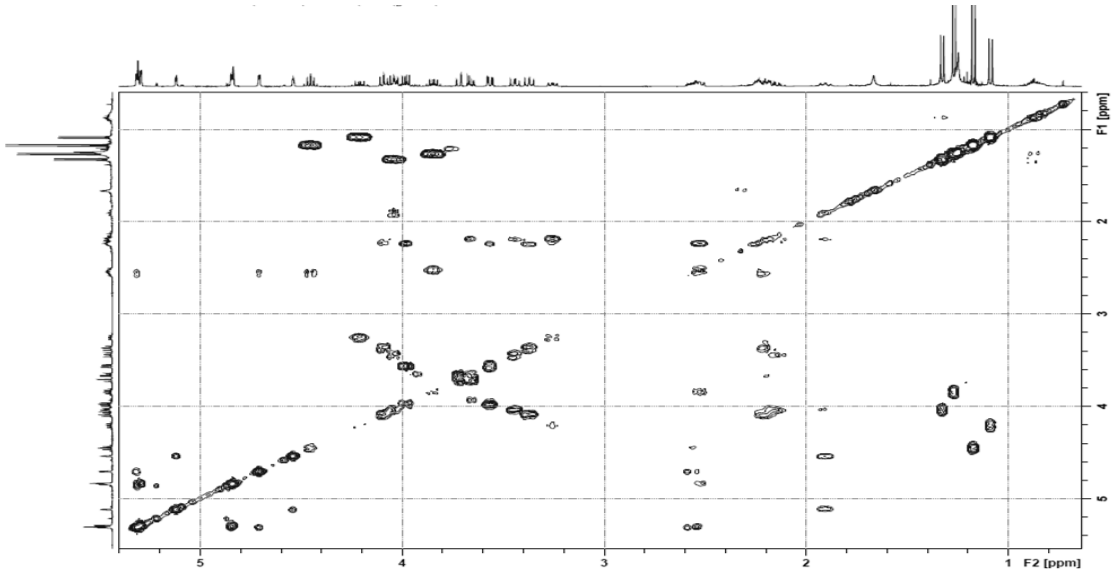


Figure S60: ^{1}H-^{1}H COSY of **30** + **31**

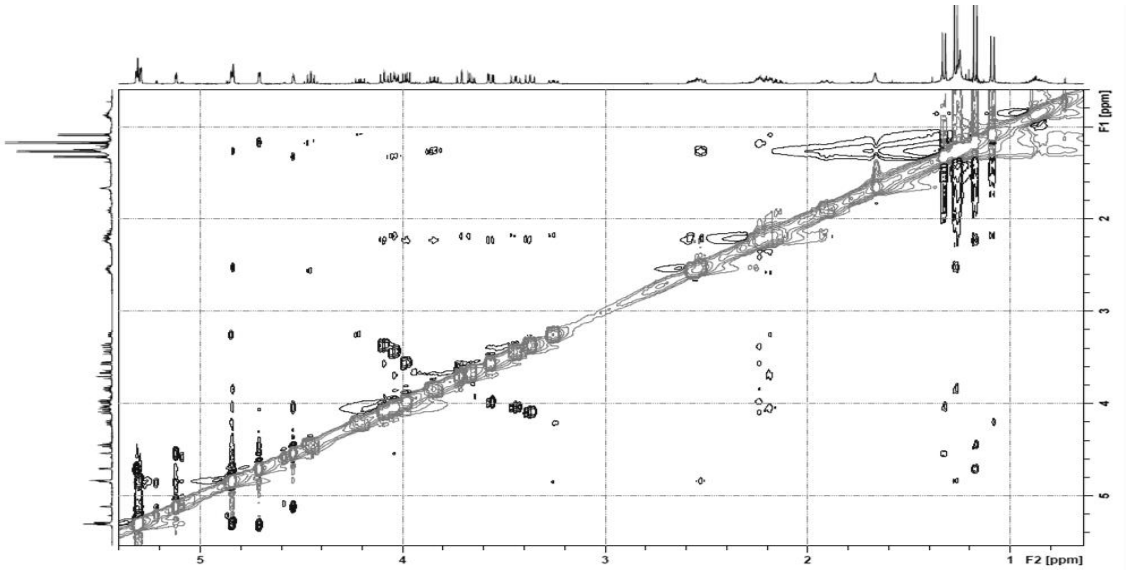


Figure S61: ^{1}H-^{1}H NOESY of **30** + **31**

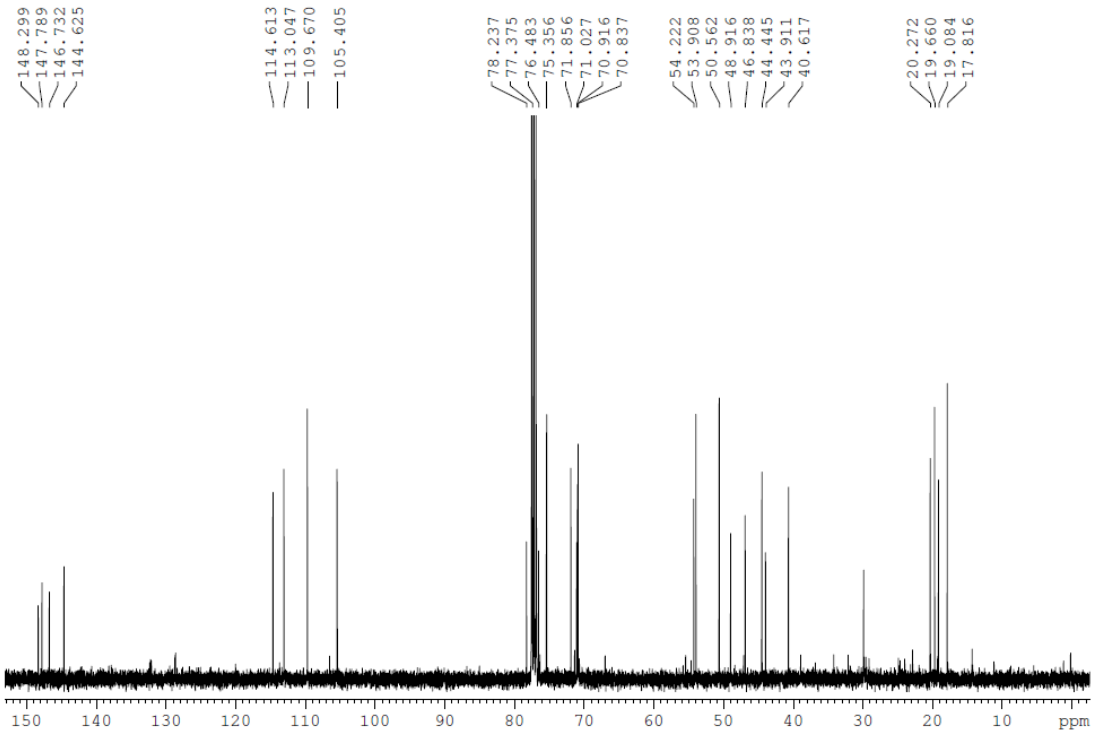


Figure S62: ^{13}C-NMR ($CDCl_3$, 100MHz) of **30** + **31**

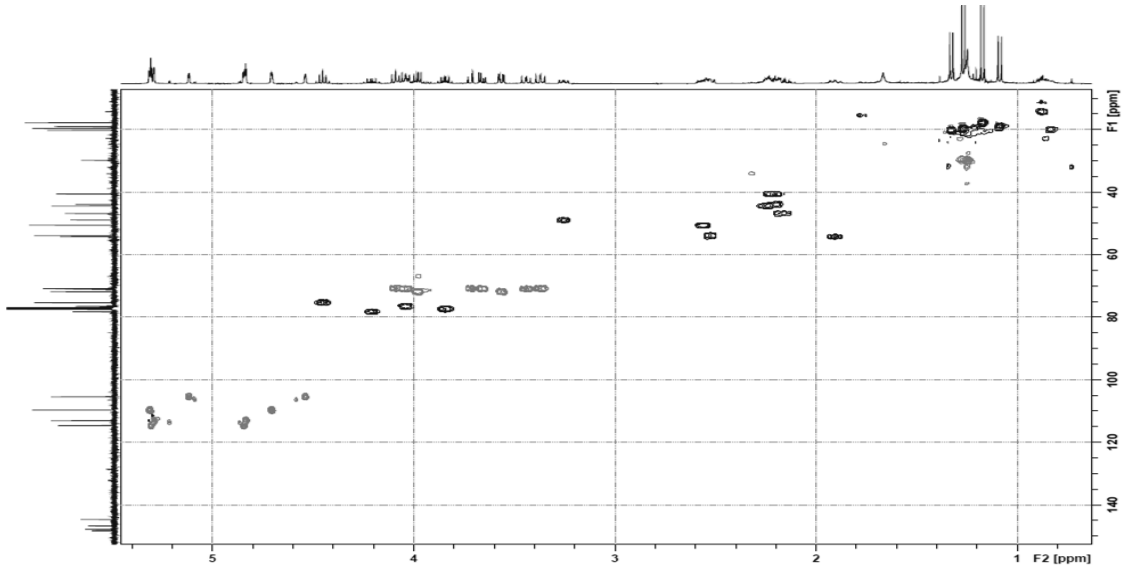


Figure S63: ^{1}H-^{13}C HSQC of **30** + **31**

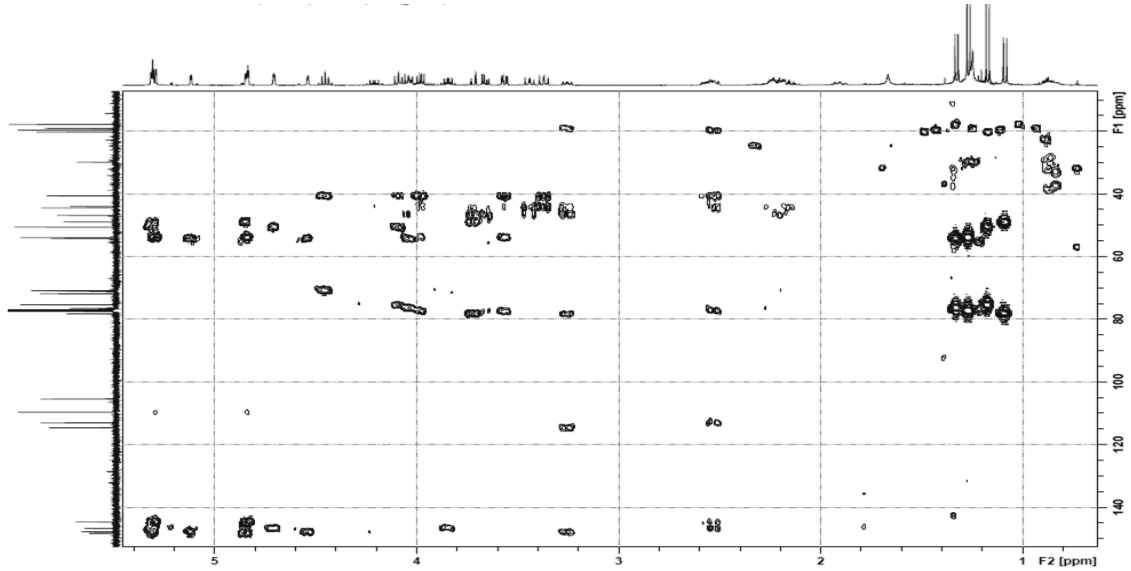


Figure S64: ^{1}H-^{13}C HMBC of **30** + **31**

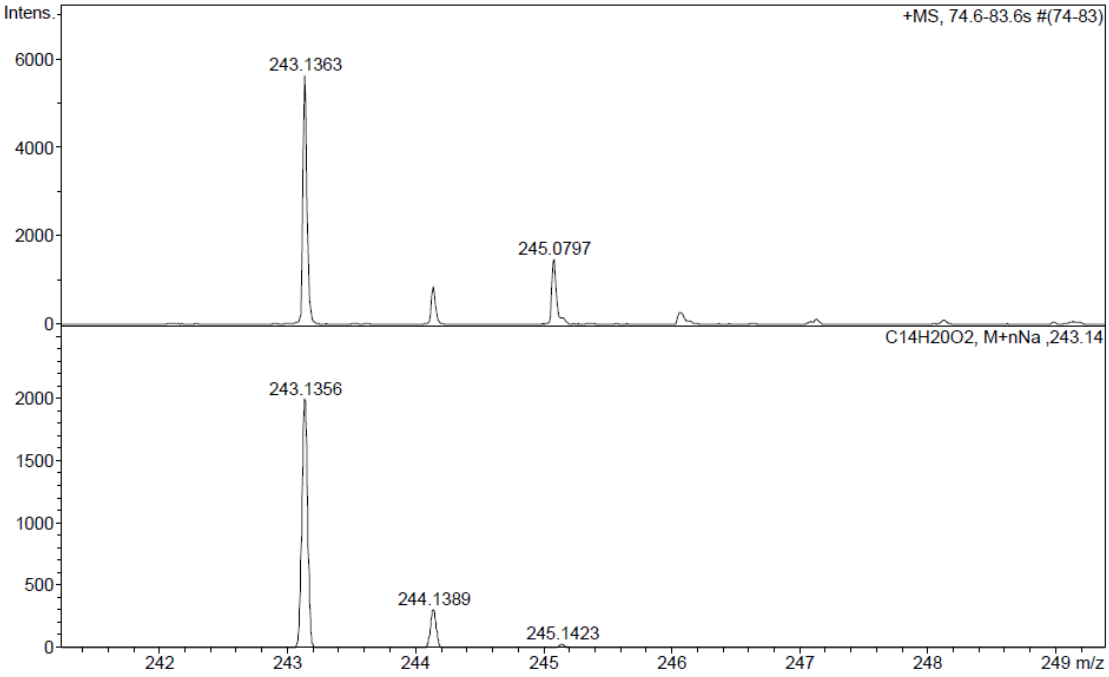


Figure S65: ESI-HRMS (+) of **30** + **31**

SUPPLEMENTARY DATA – CHAPTER 5

$MeO-PEG_{17}-OMs$

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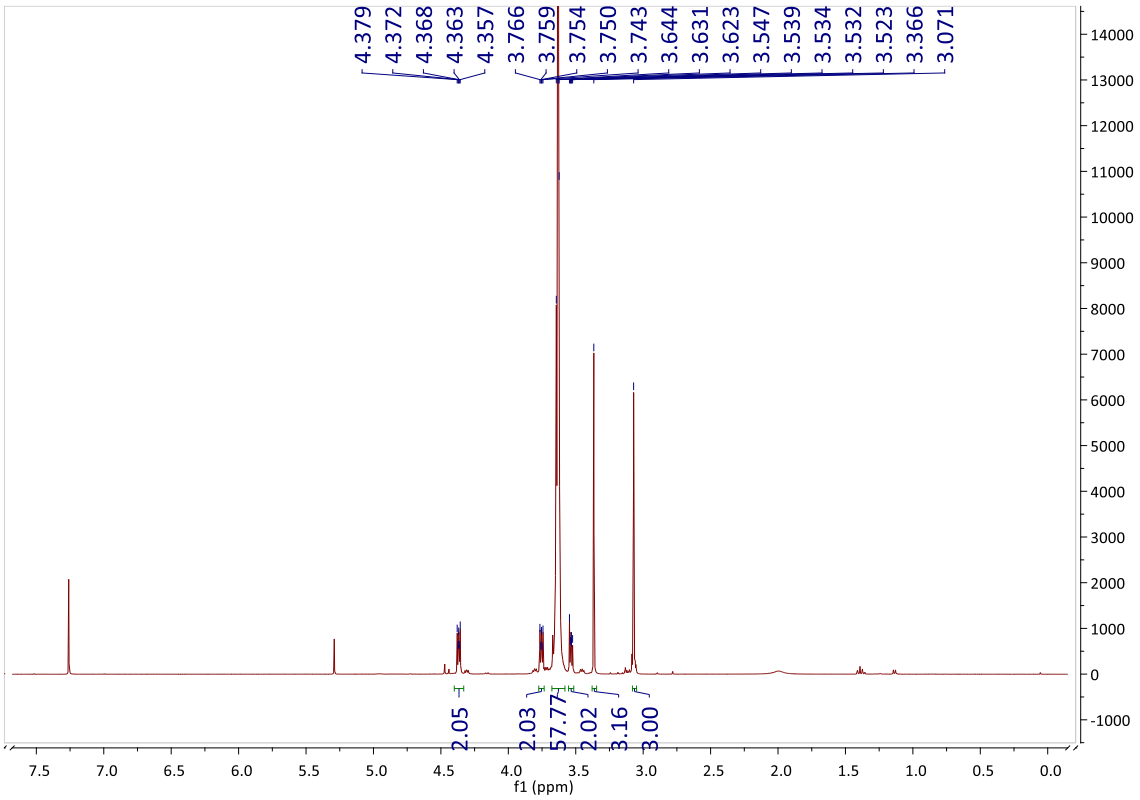


Figure S1: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **33**

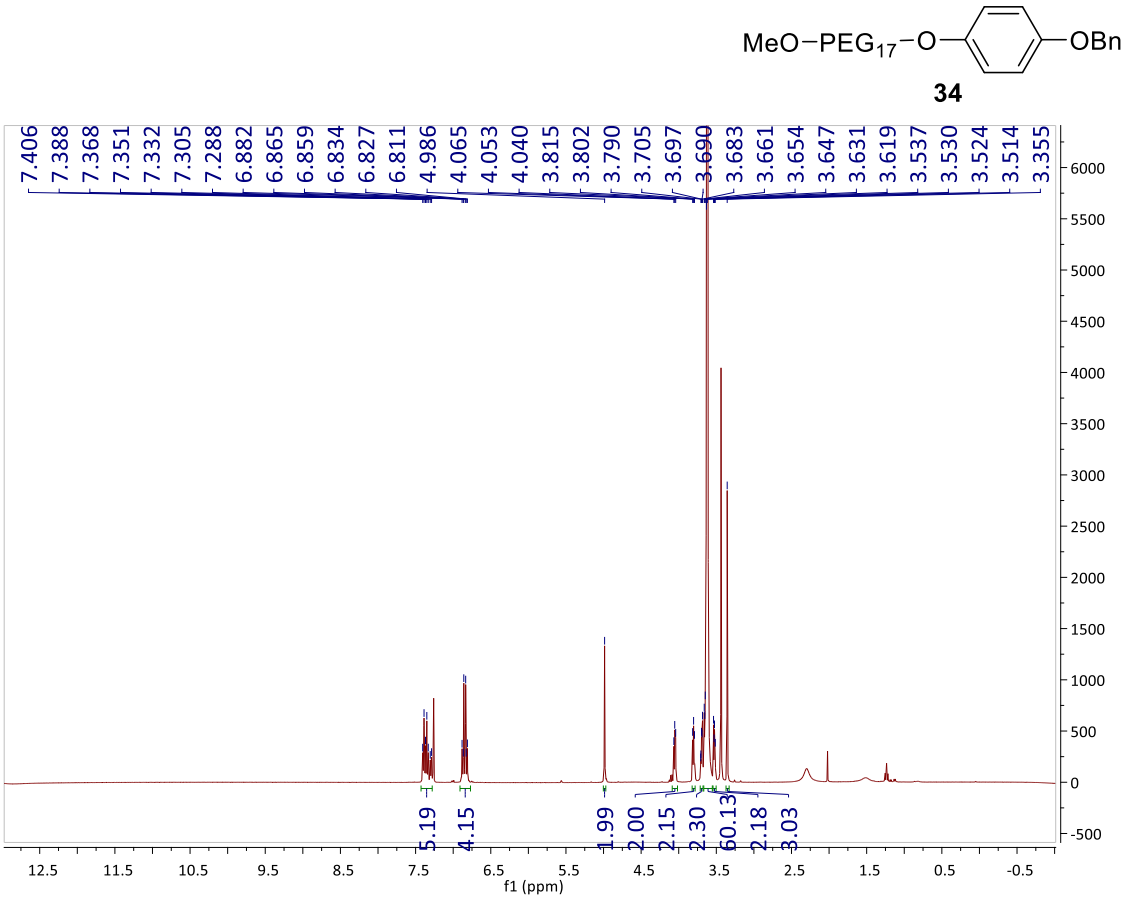


Figure S2: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **34**

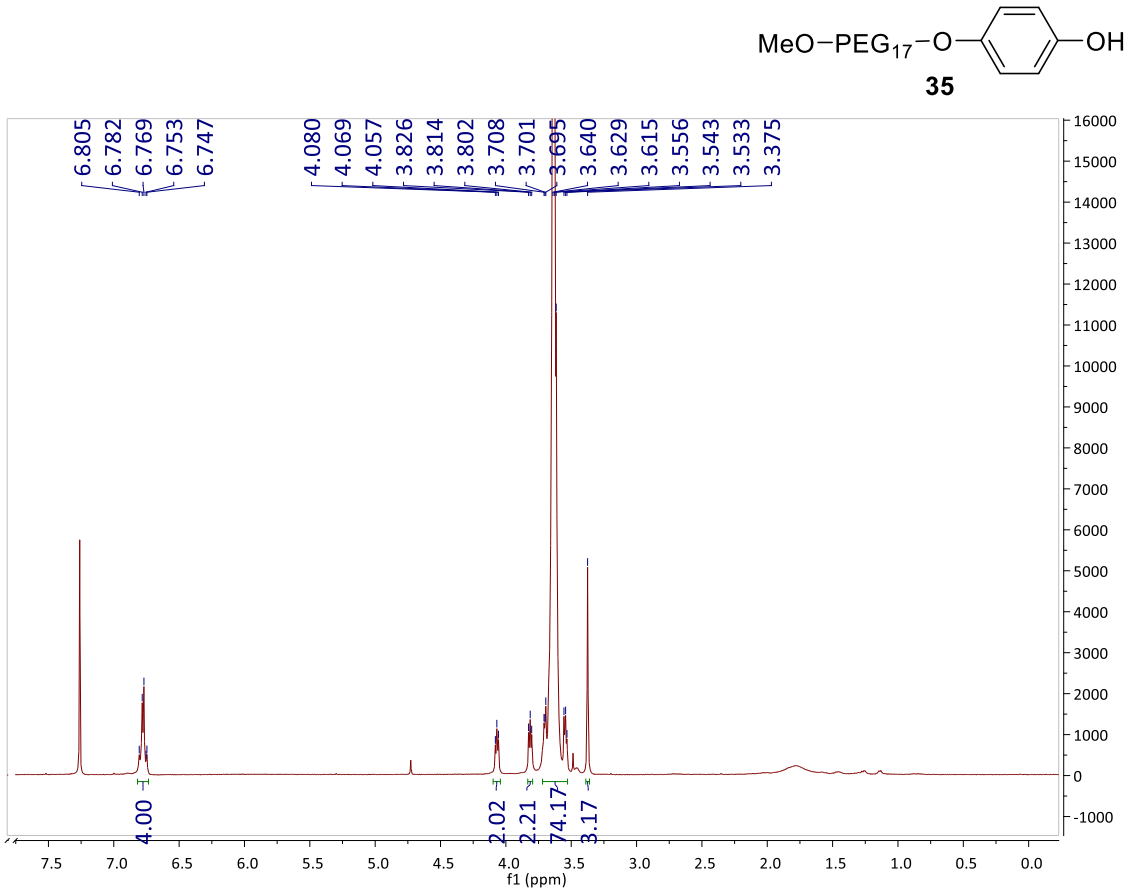


Figure S3: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **35**

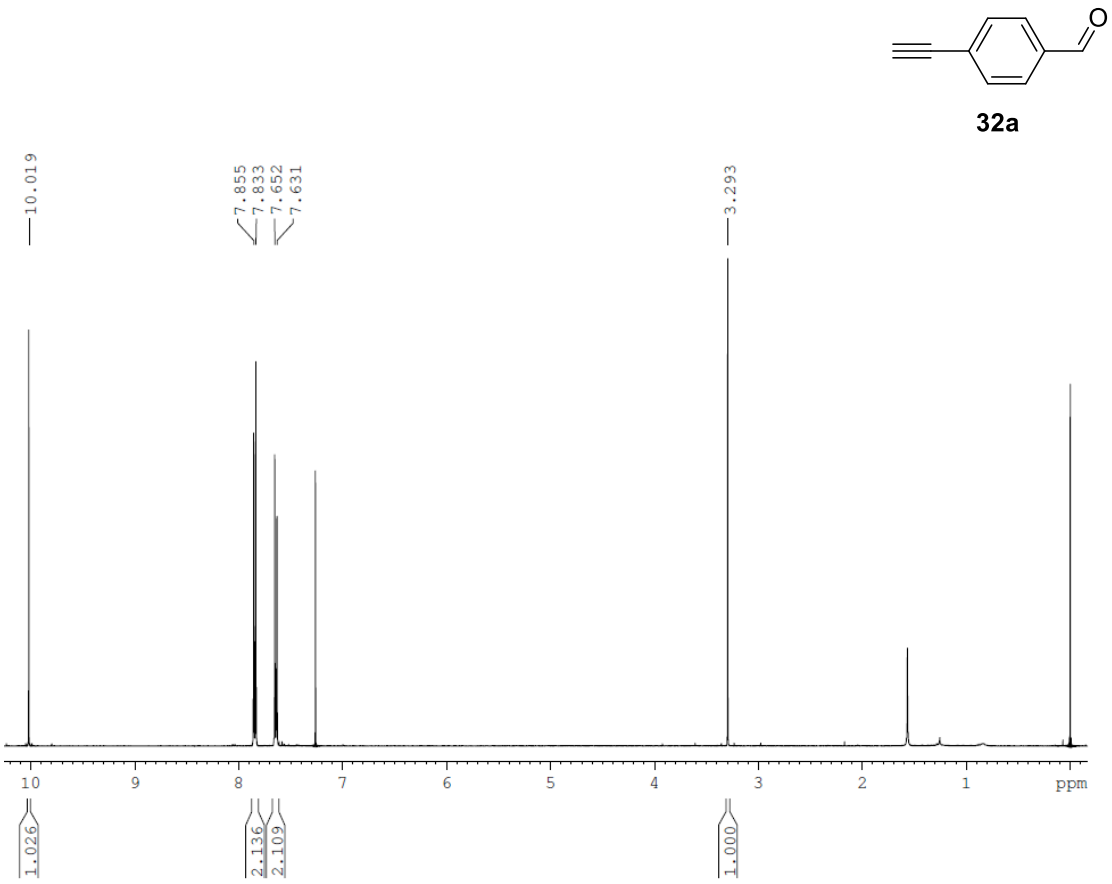
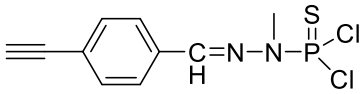


Figure S4: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **32a**



36a

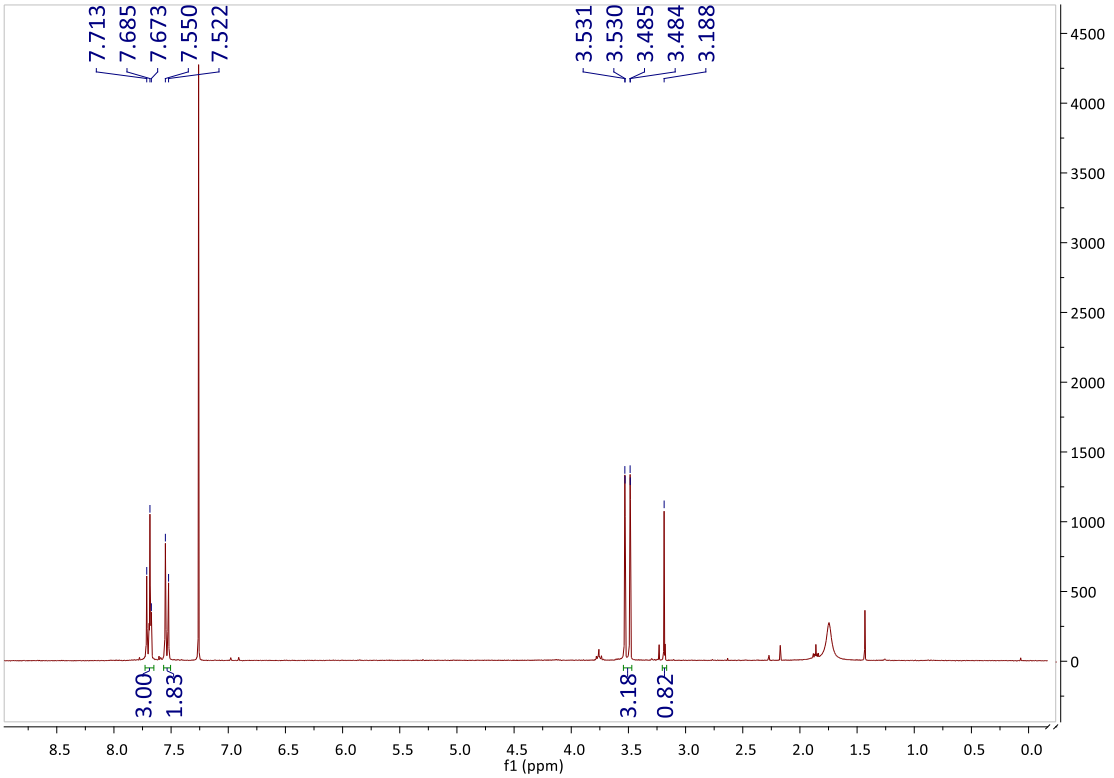


Figure S5: ^{1}H-NMR spectrum ($CDCl_3$, 300 MHz) of **36a**

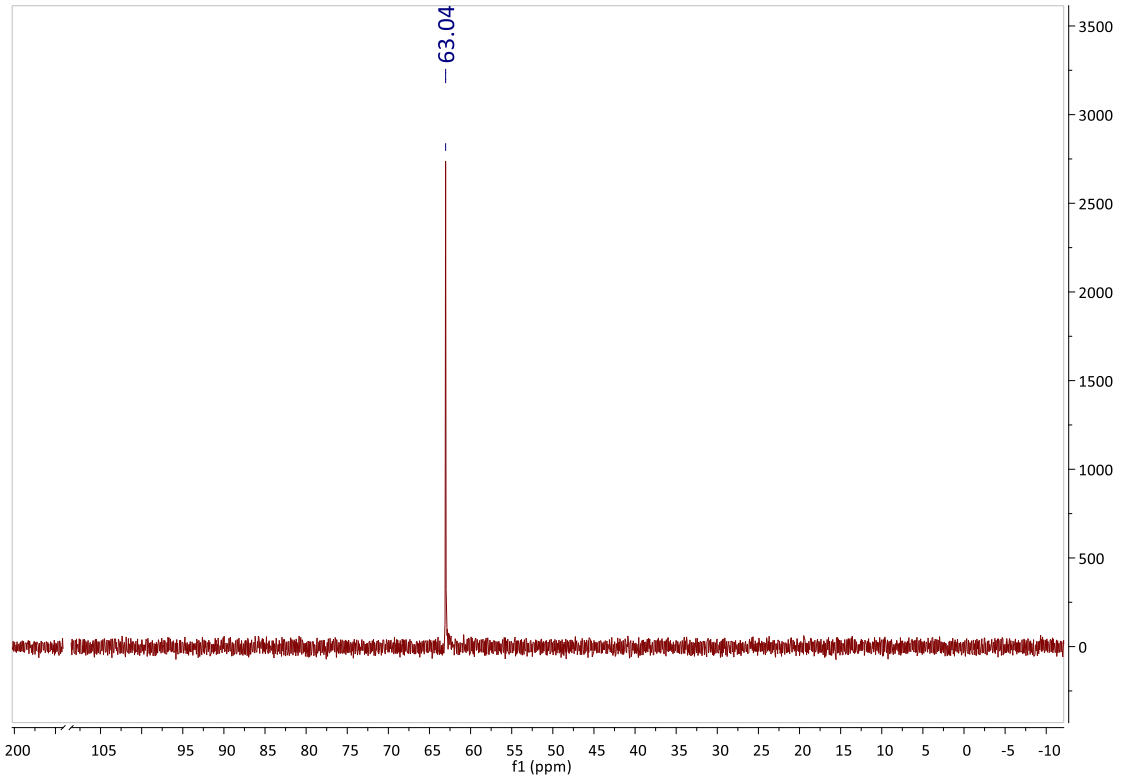
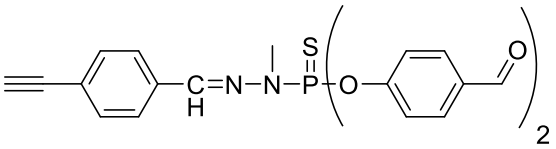


Figure S6: $^{31}P\{^{1}H\}$-NMR spectrum ($CDCl_3$, 121.5 MHz) of **35**



37

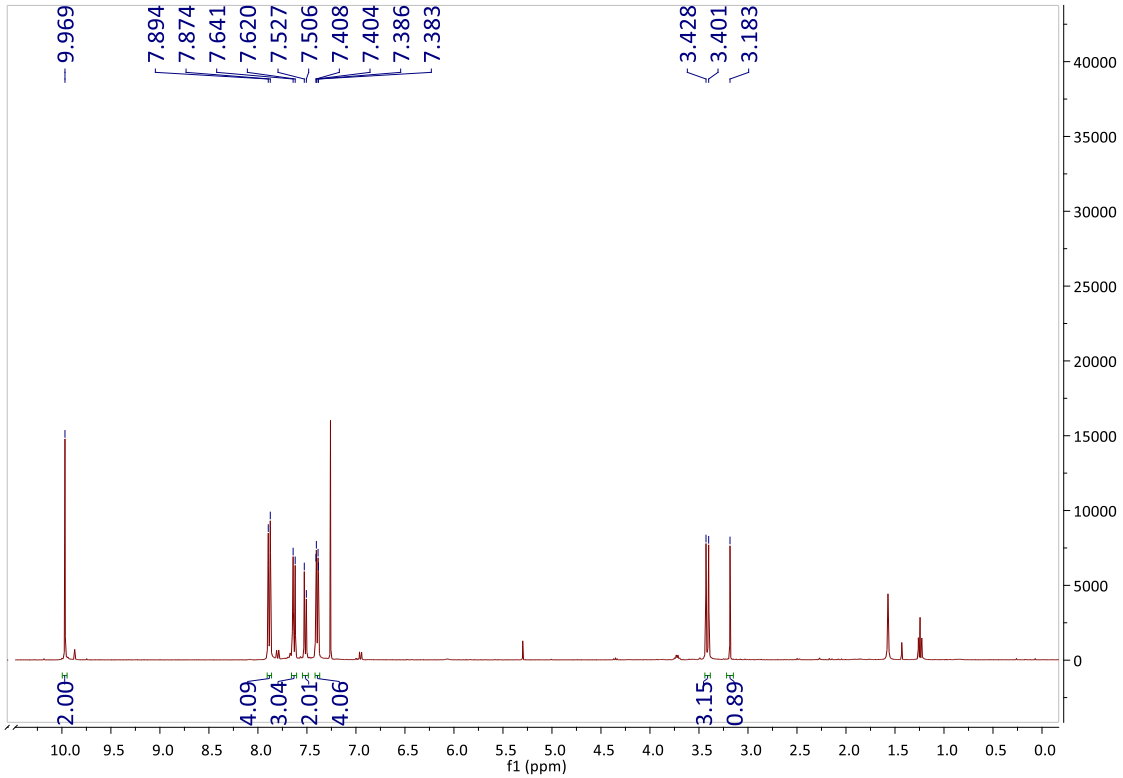


Figure S7: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **37**

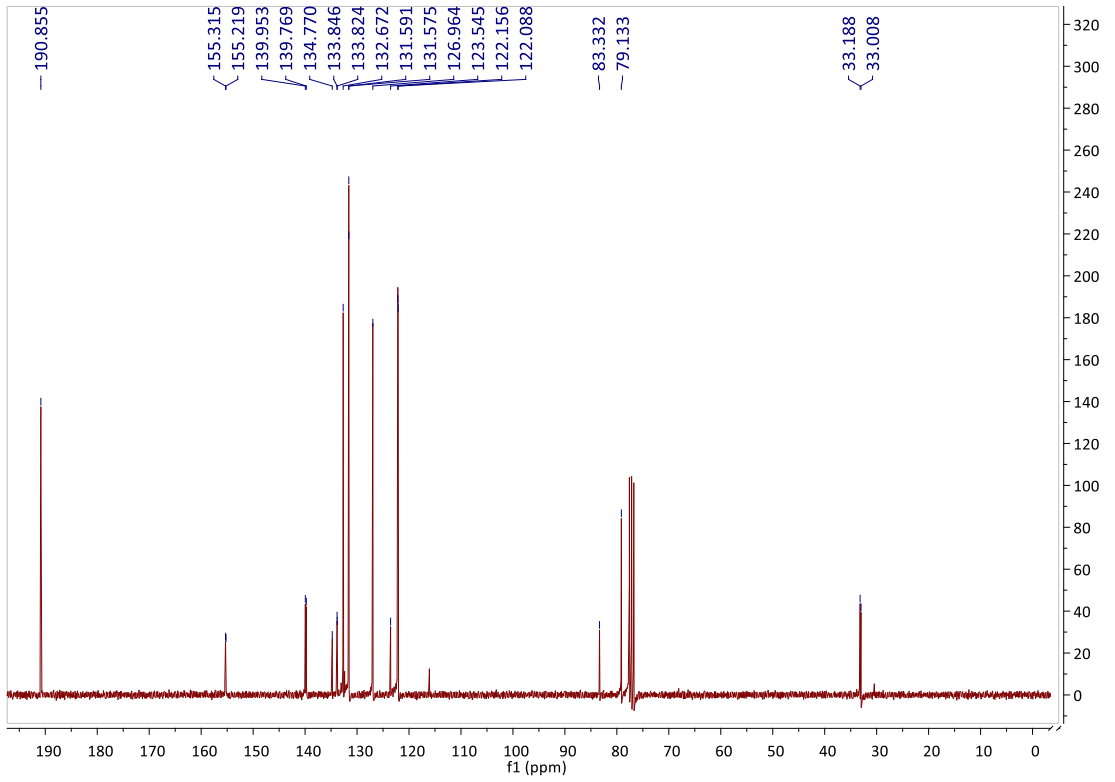


Figure S8: ^{13}C-NMR spectrum ($CDCl_3$, 75 MHz) of **37**

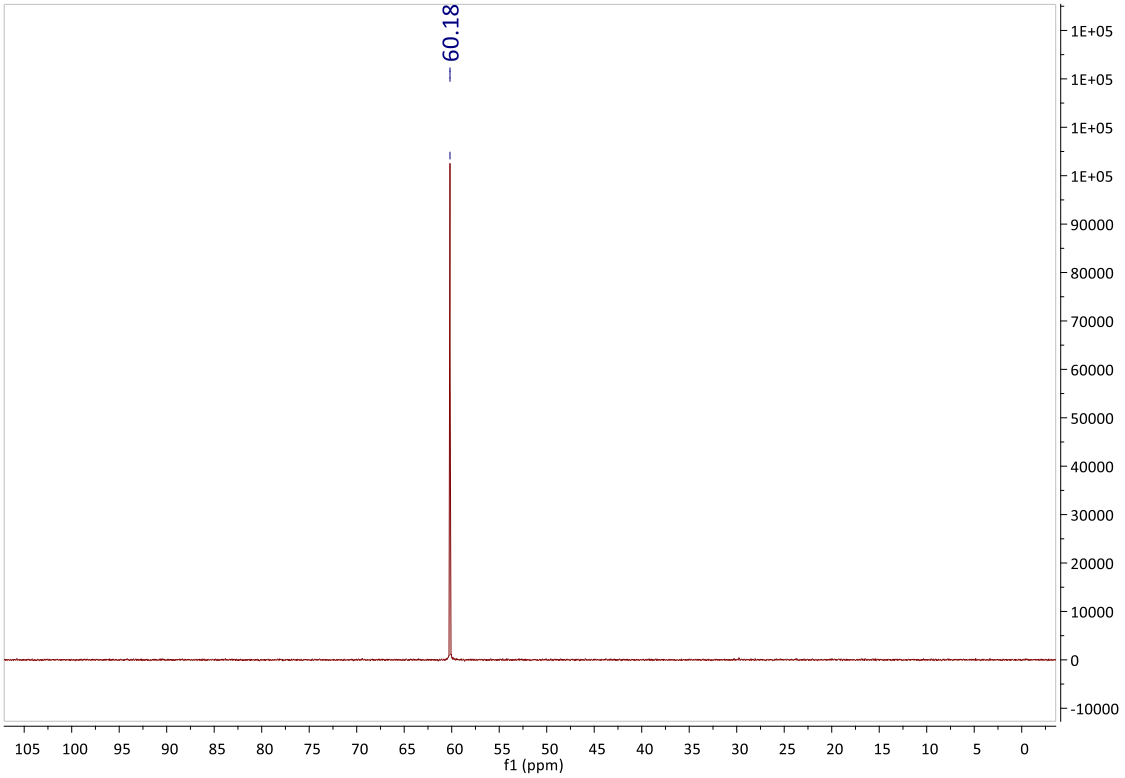
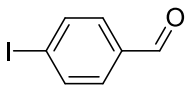


Figure S9: $^{31}P\{^{1}H\}$-NMR spectrum ($CDCl_3$, 162 MHz) of **37**



32b

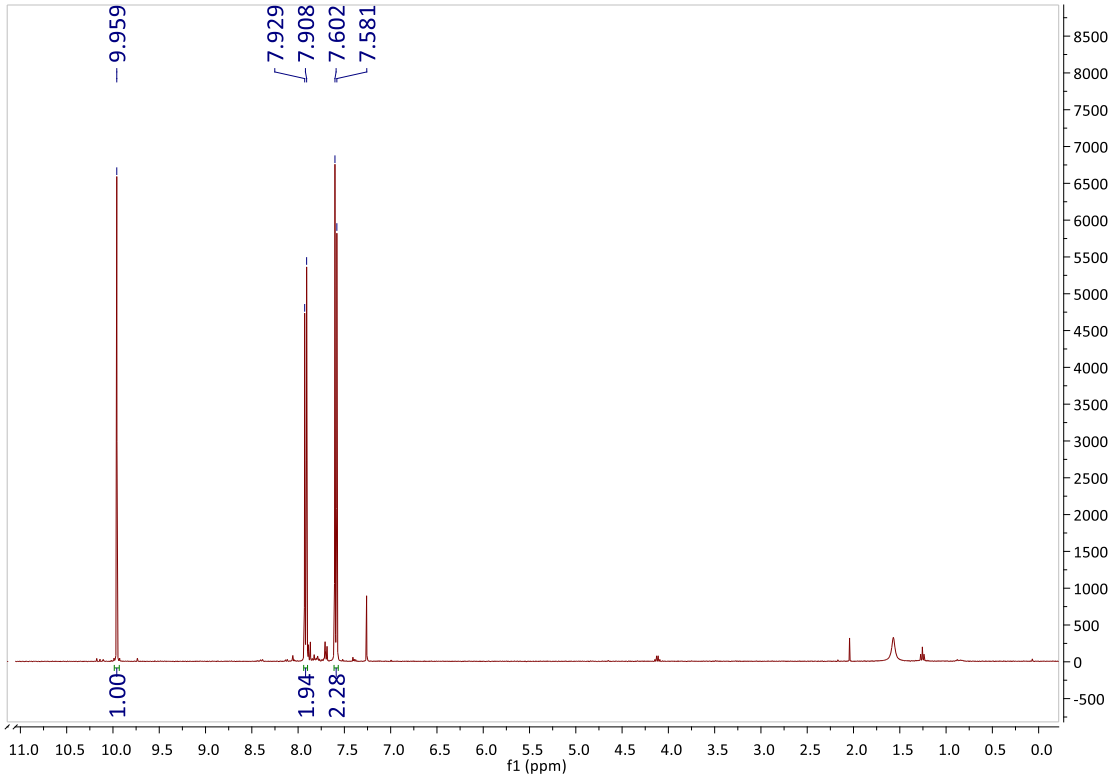
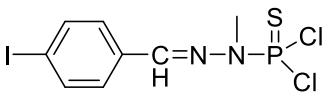


Figure S10: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **32b**



36b

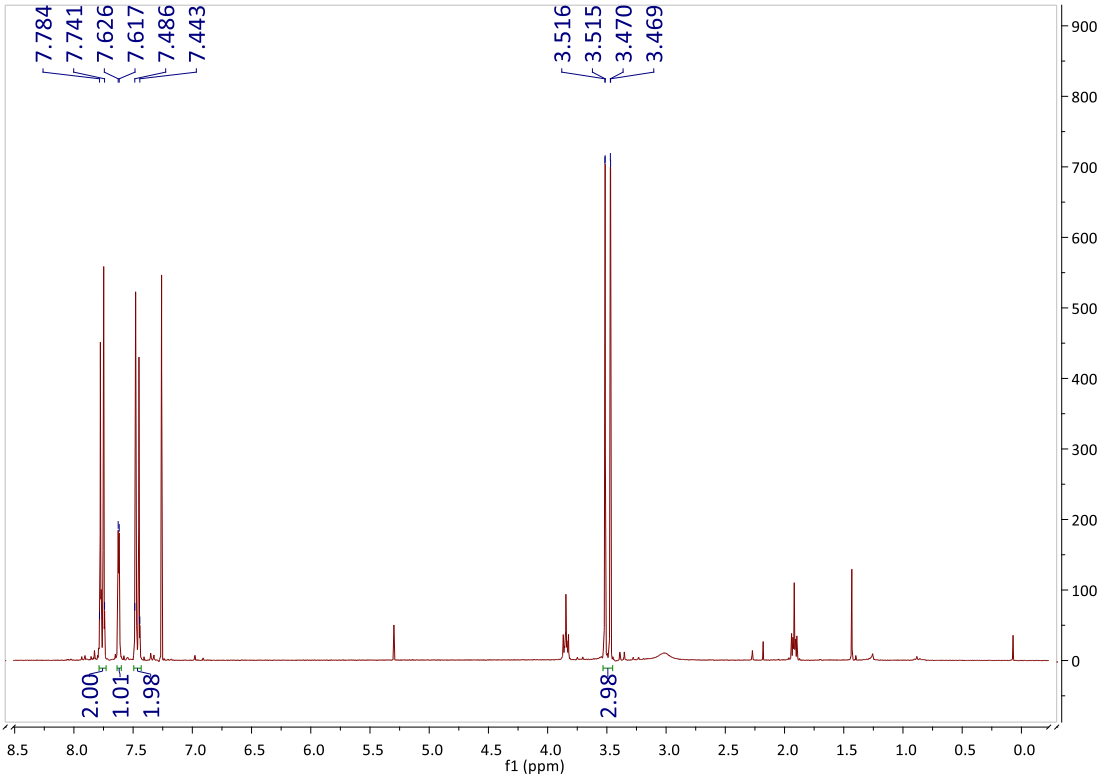


Figure S11: ^{1}H-NMR spectrum ($CDCl_3$, 300 MHz) of **36b**

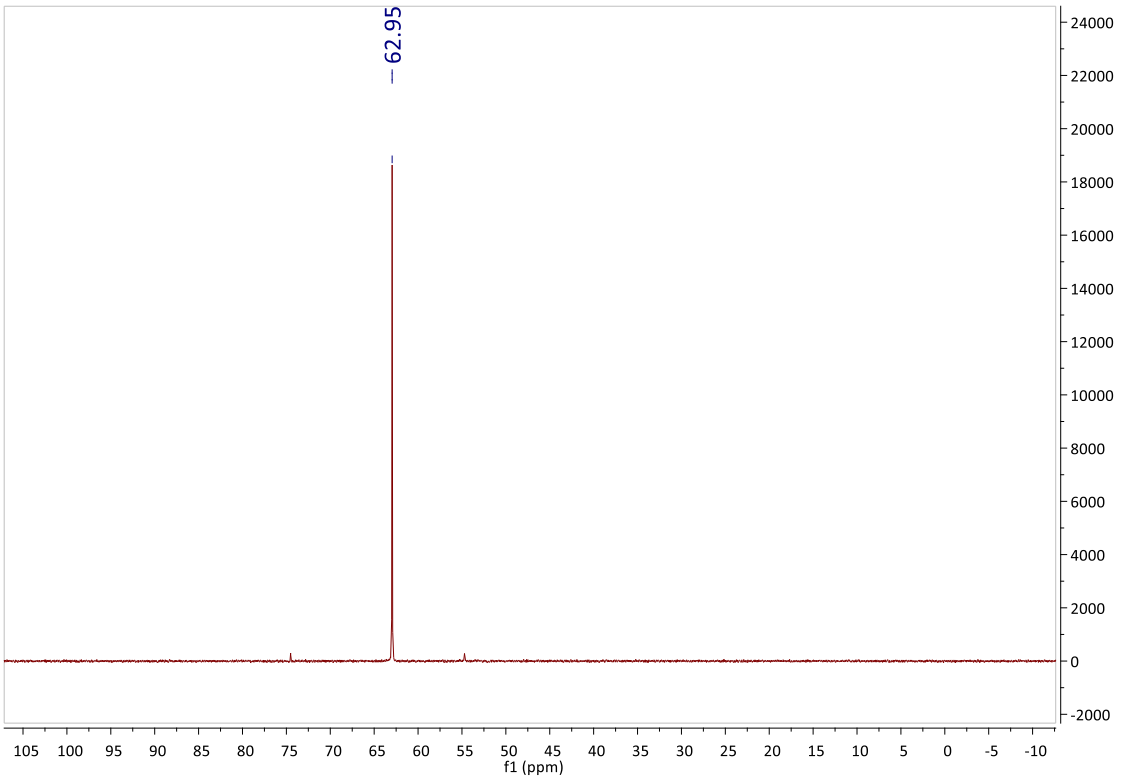
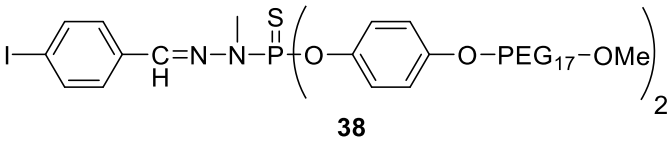


Figure S12: $^{31}P\{^{1}H\}$-NMR spectrum ($CDCl_3$, 121.5 MHz) of **36b**



38

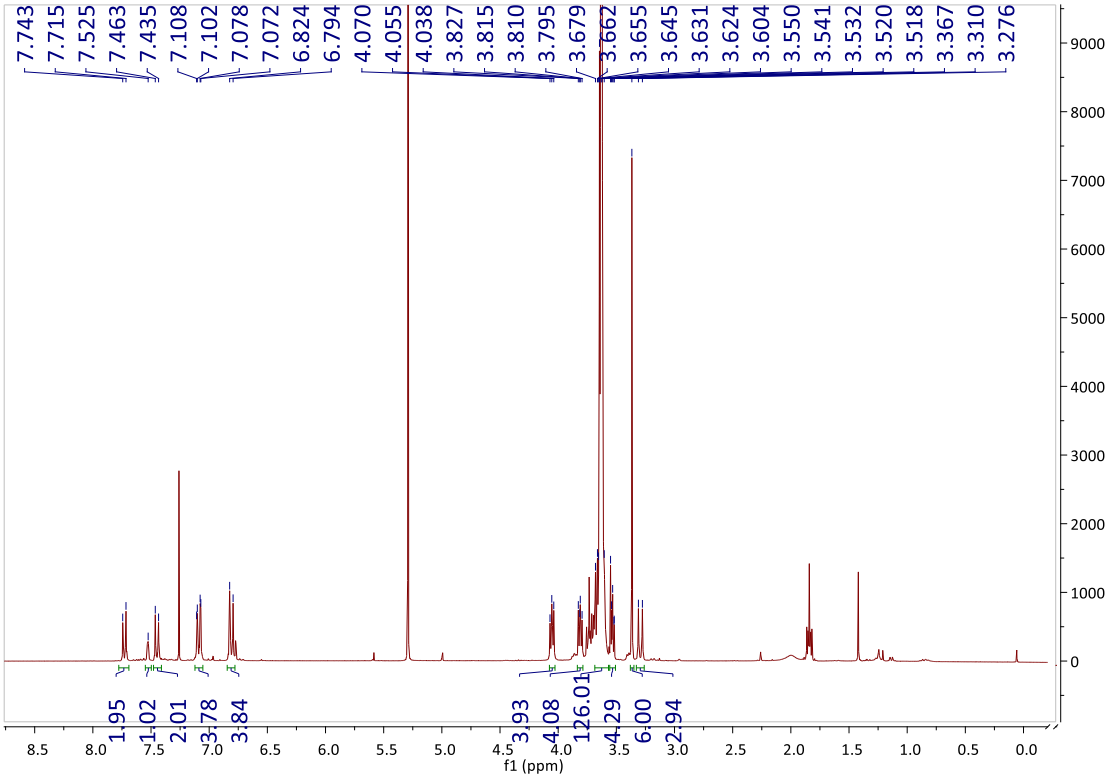


Figure S13: ^{1}H-NMR spectrum ($CDCl_3$, 300 MHz) of **38**

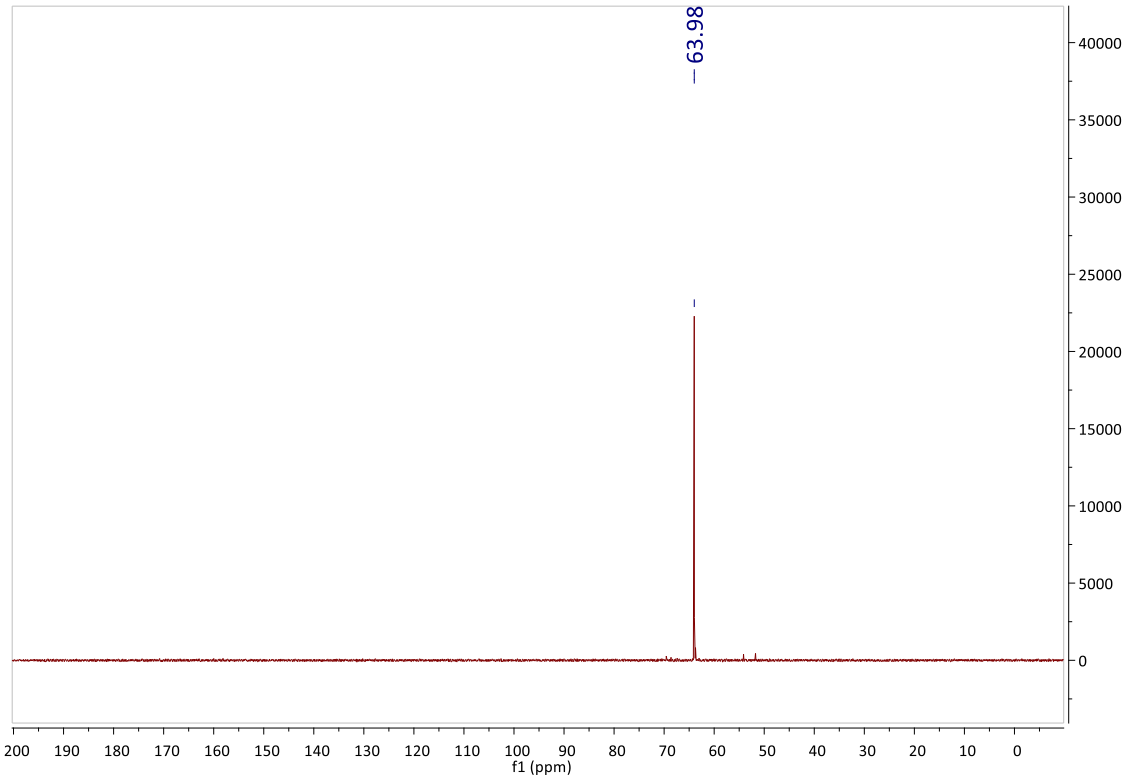
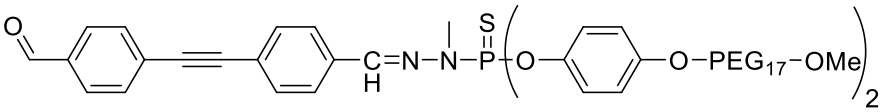


Figure S14: $^{31}P\{^{1}H\}$-NMR spectrum ($CDCl_3$, 121.5 MHz) of **38**



40

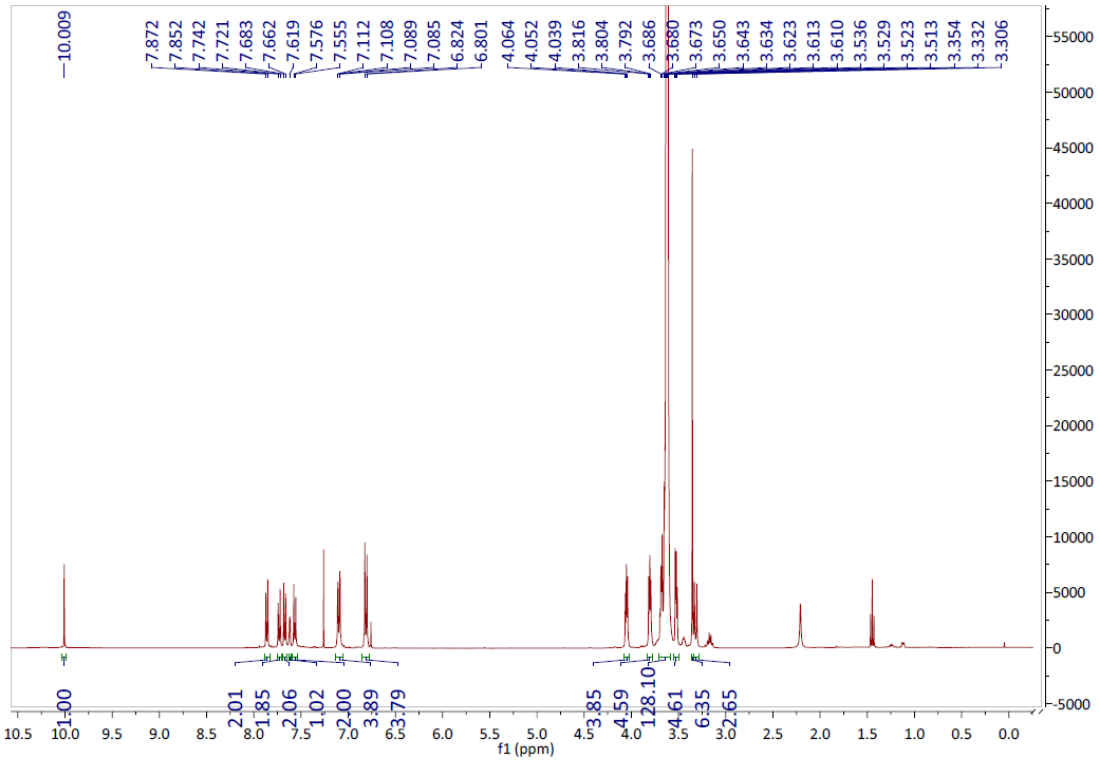


Figure S15: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **40**

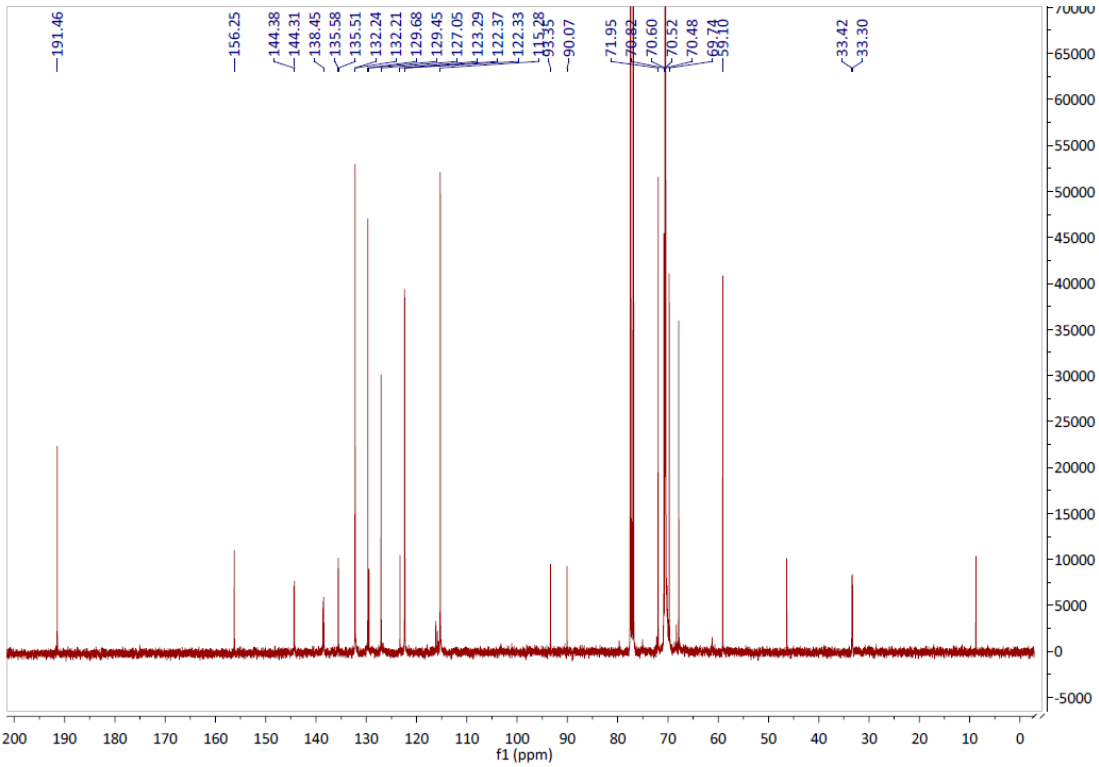


Figure S16: ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **40**

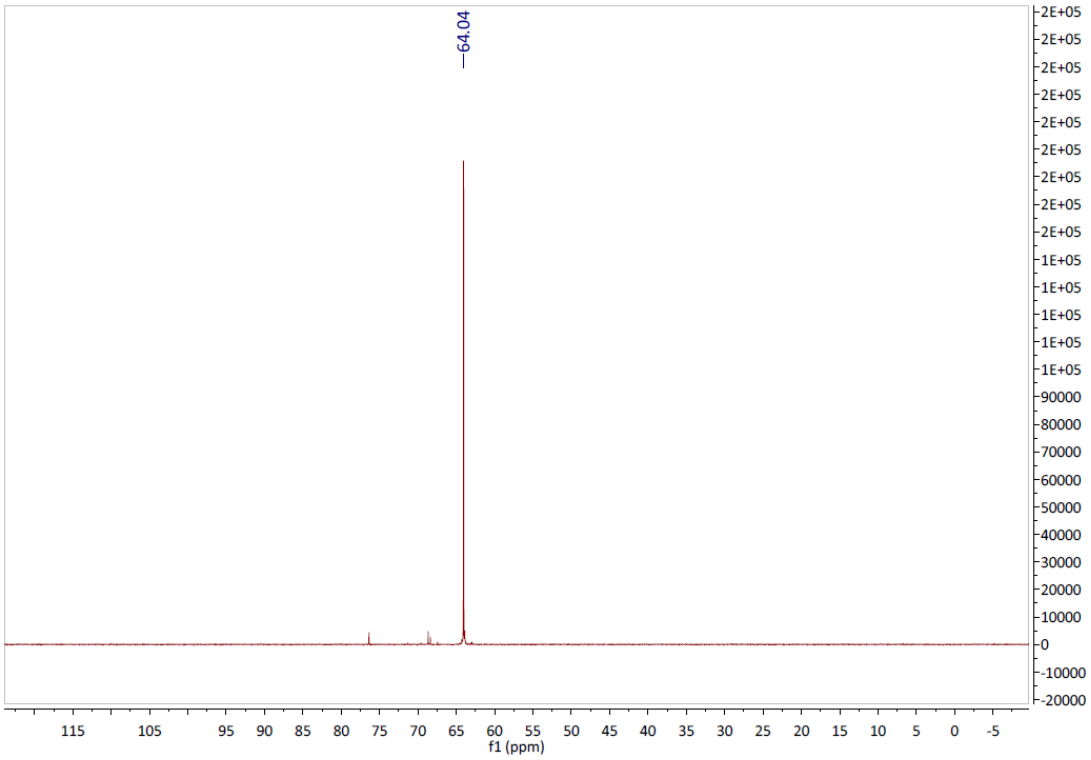
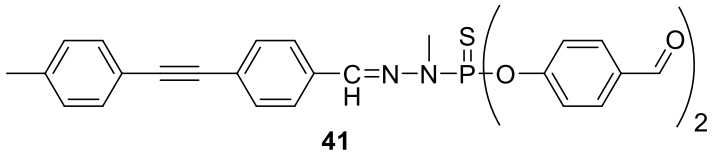


Figure S17: $^{31}P\{^{1}H\}$-NMR spectrum ($CDCl_3$, 162 MHz) of **40**



41

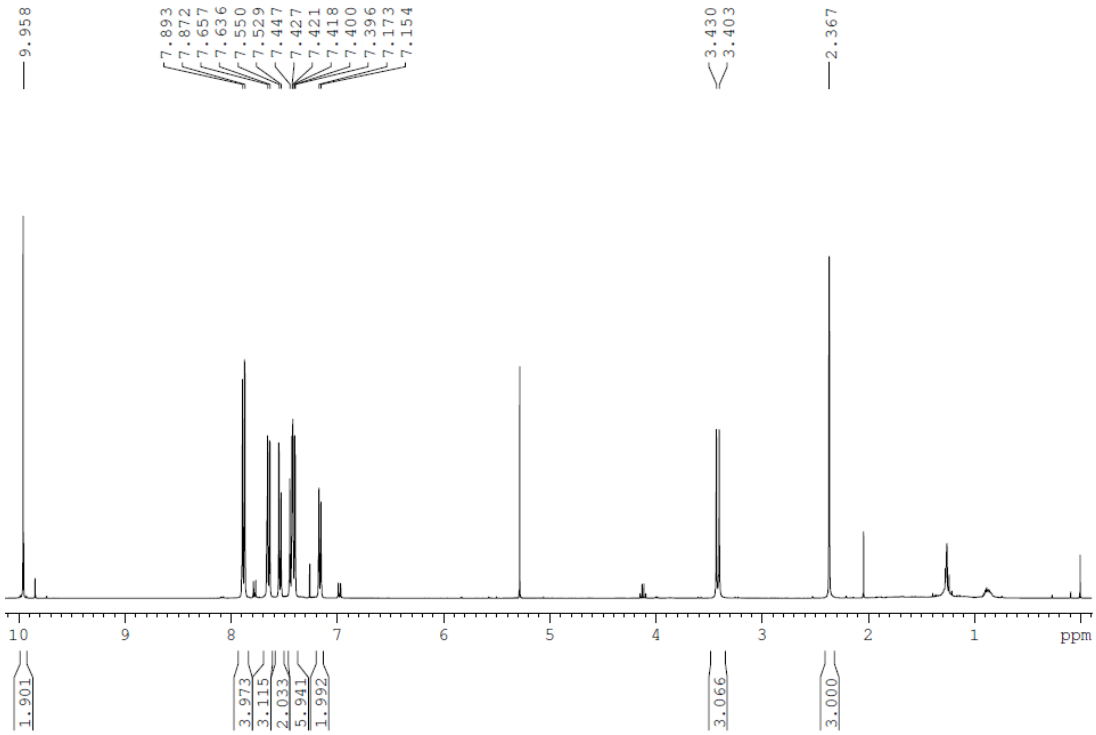


Figure S18: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **41**

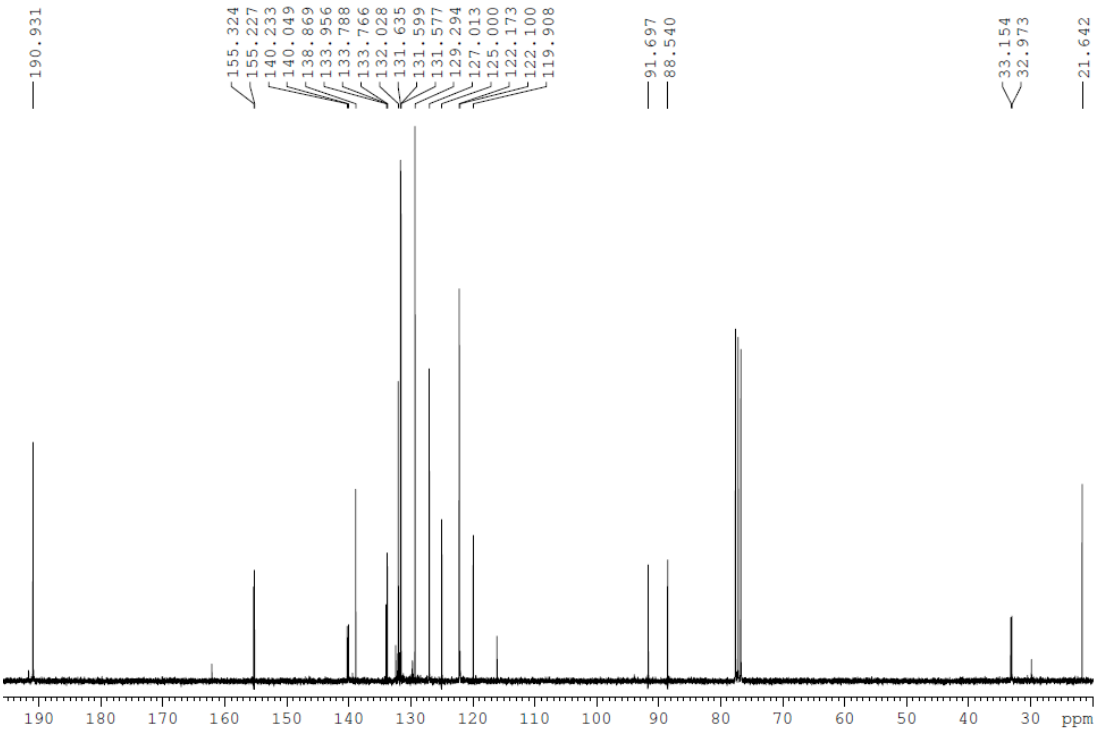


Figure S19: ^{13}C-NMR spectrum ($CDCl_3$, 75 MHz) of **41**

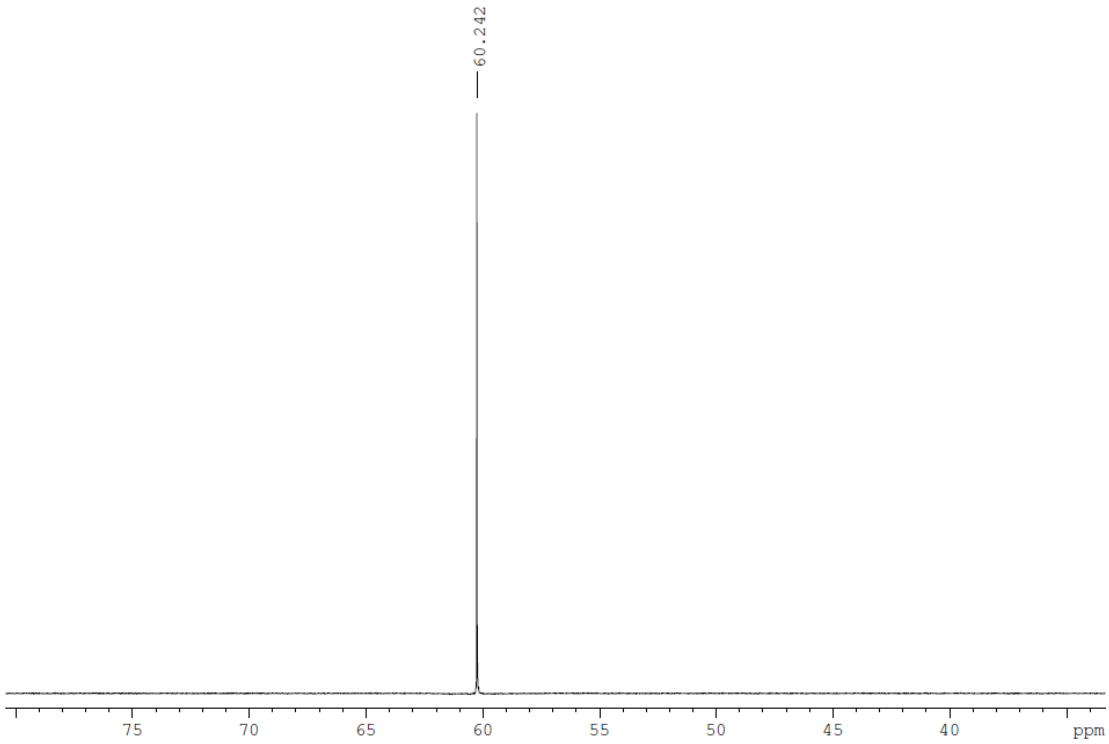
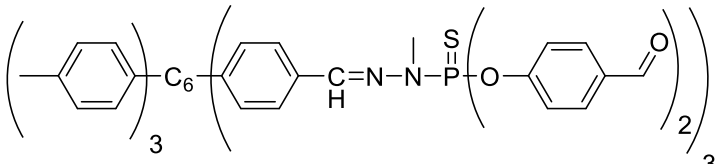


Figure S20: $^{31}P\{^{1}H\}$-NMR spectrum ($CDCl_3$, 162 MHz) of **41**



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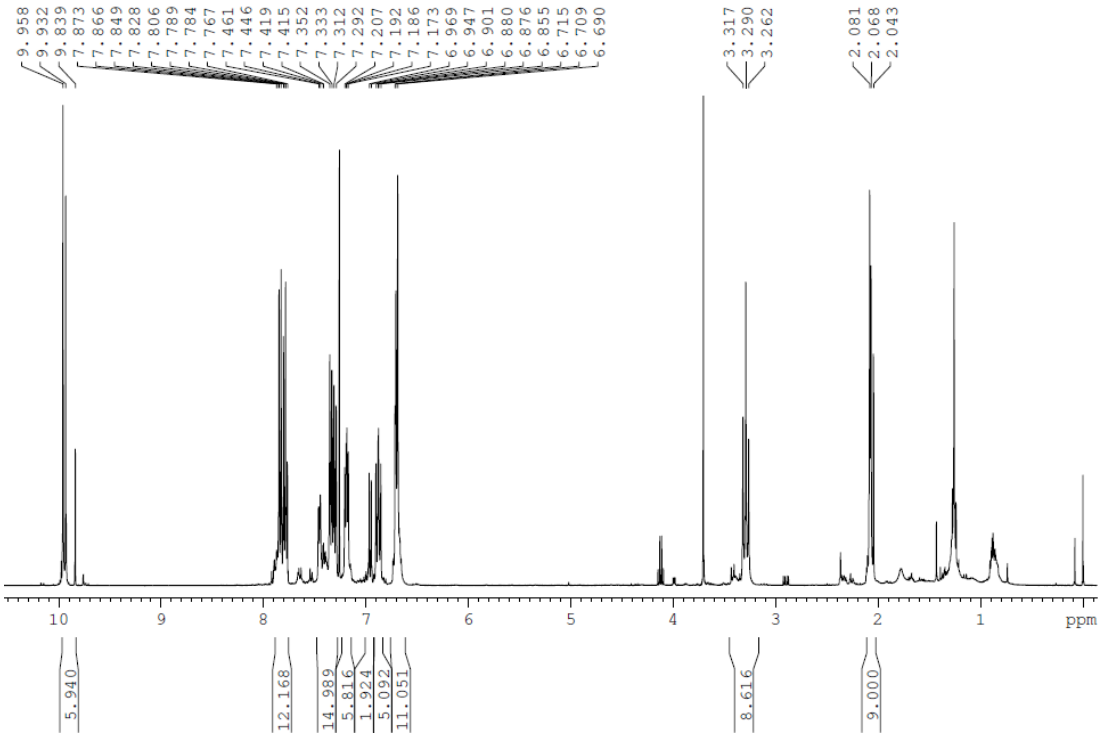


Figure S21: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **42**

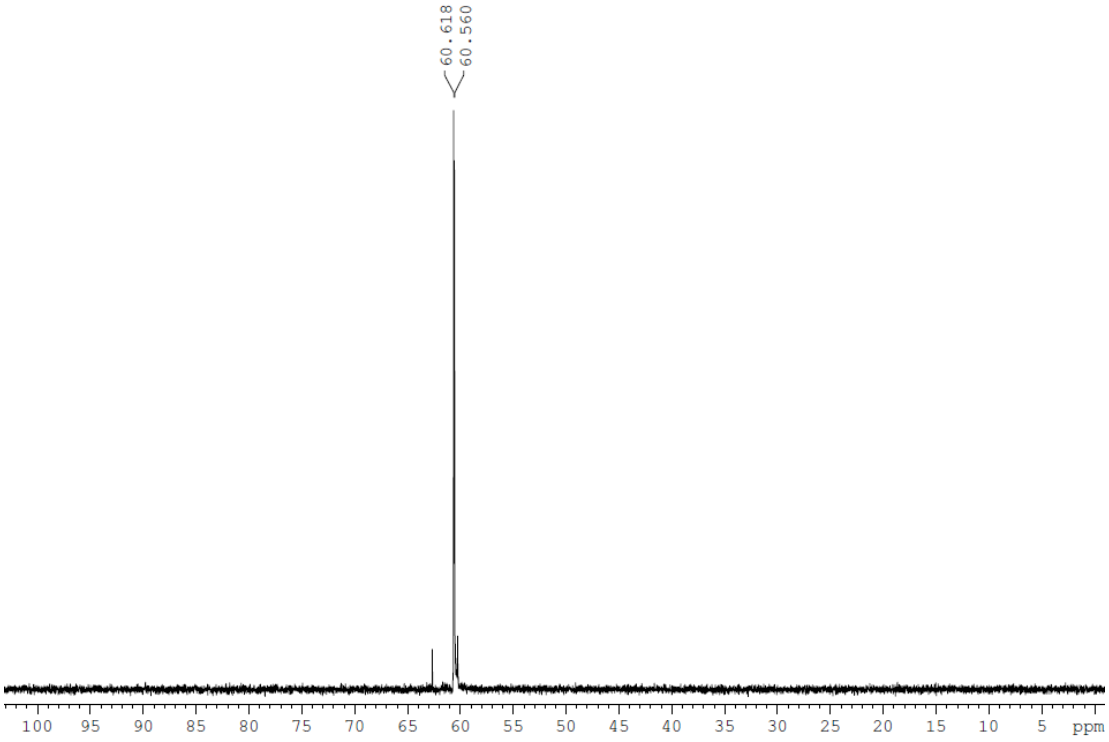


Figure S22: ^{31}P{^{1}H}-NMR spectrum ($CDCl_3$, 162 MHz) of **42**

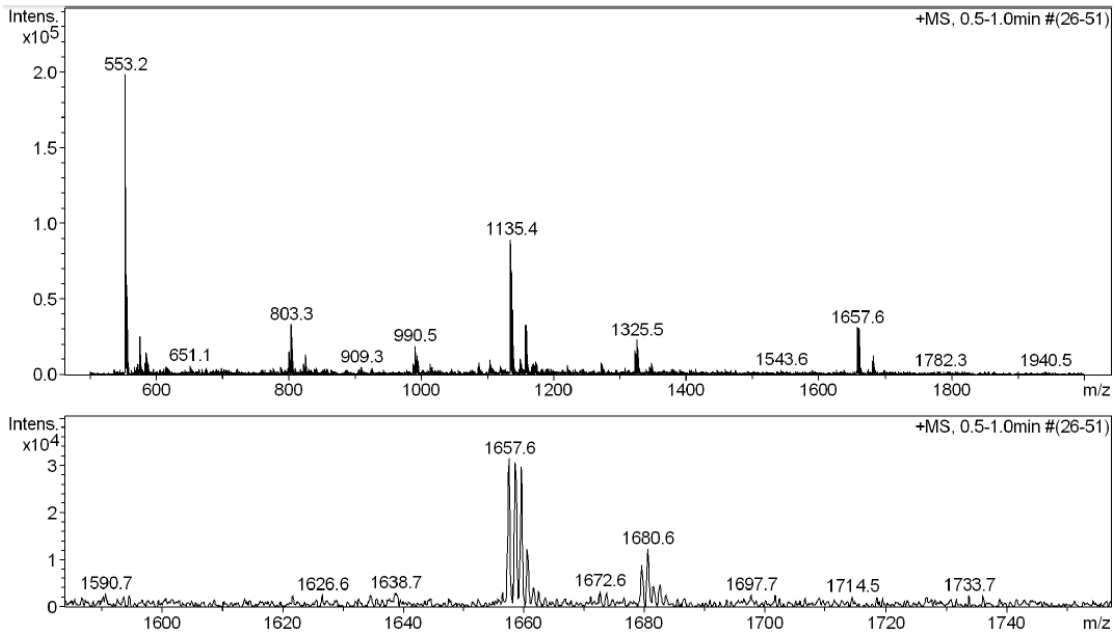
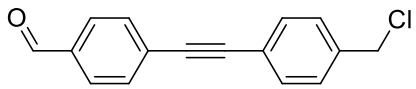


Figure S23: ESI-MS (+) of **42**



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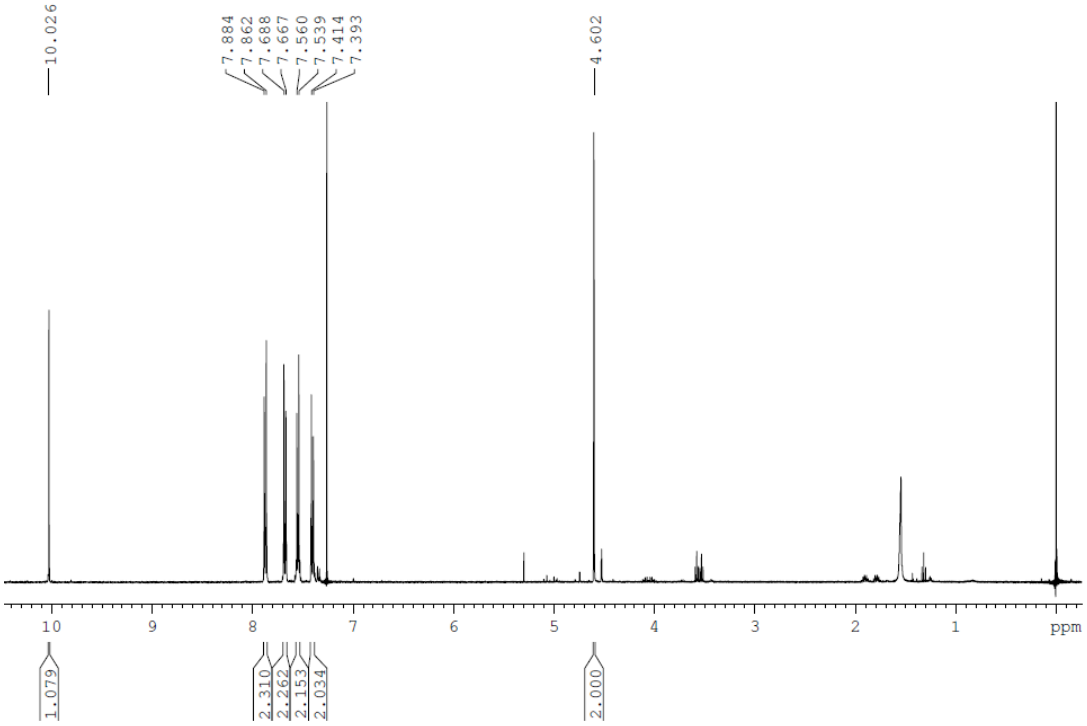


Figure S24: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **50**

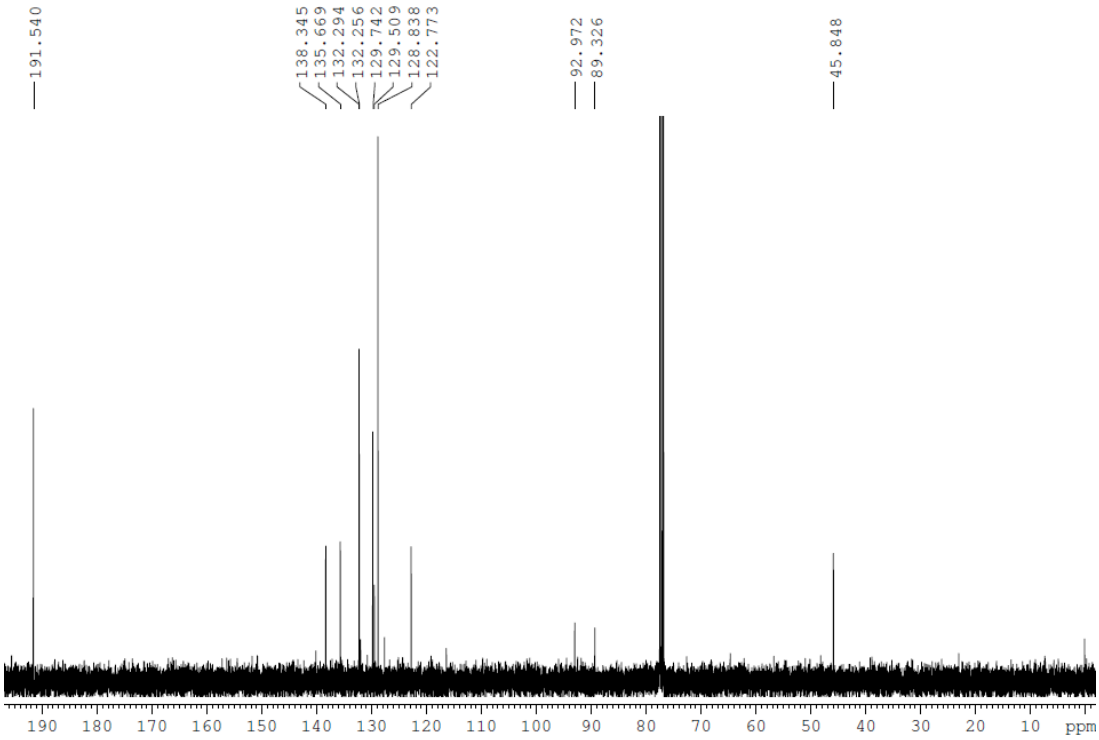


Figure S25: ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **50**

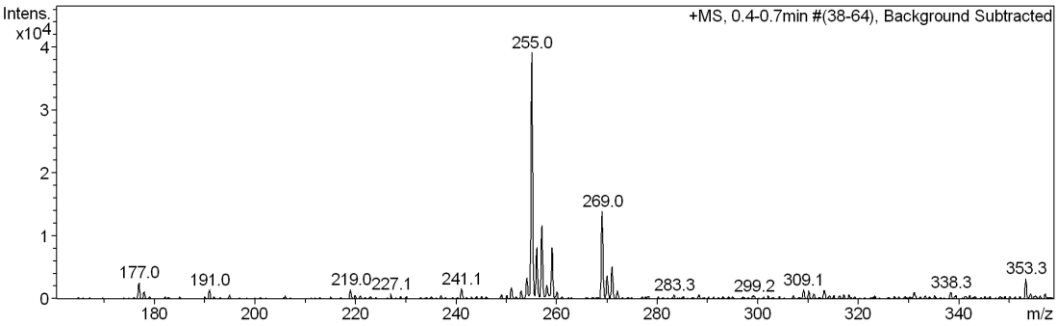
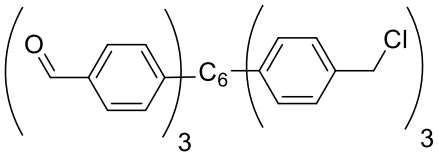


Figure S26: ESI-MS (+) of **50**



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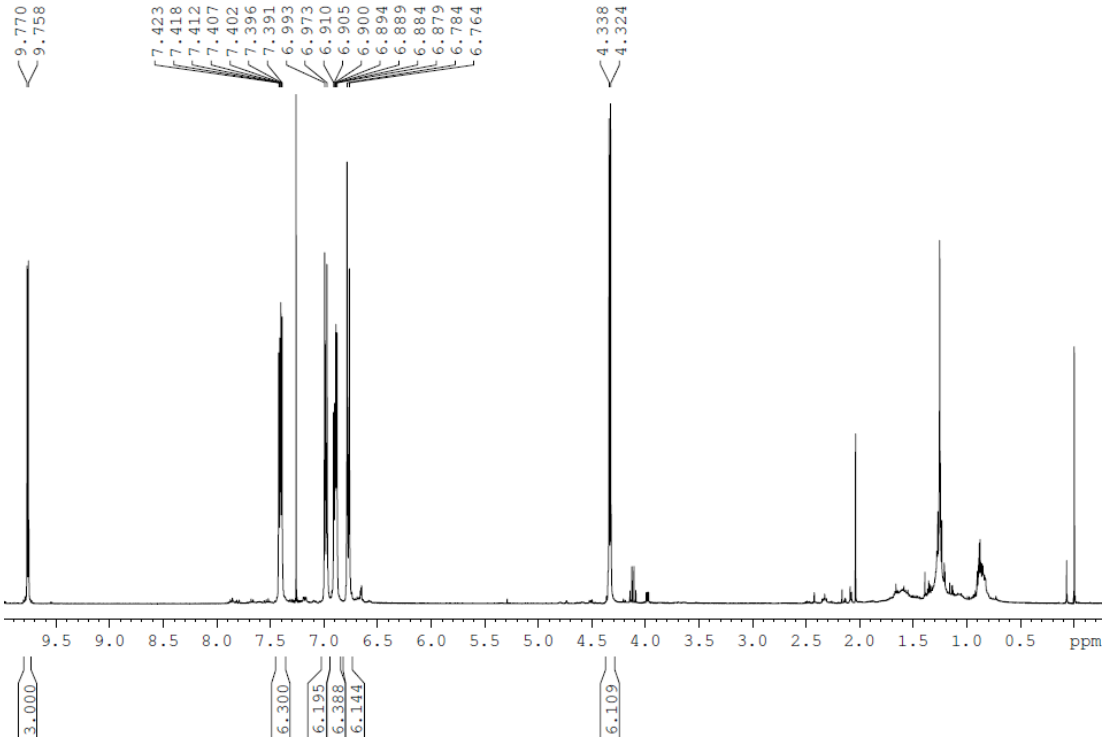


Figure S27: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **51**

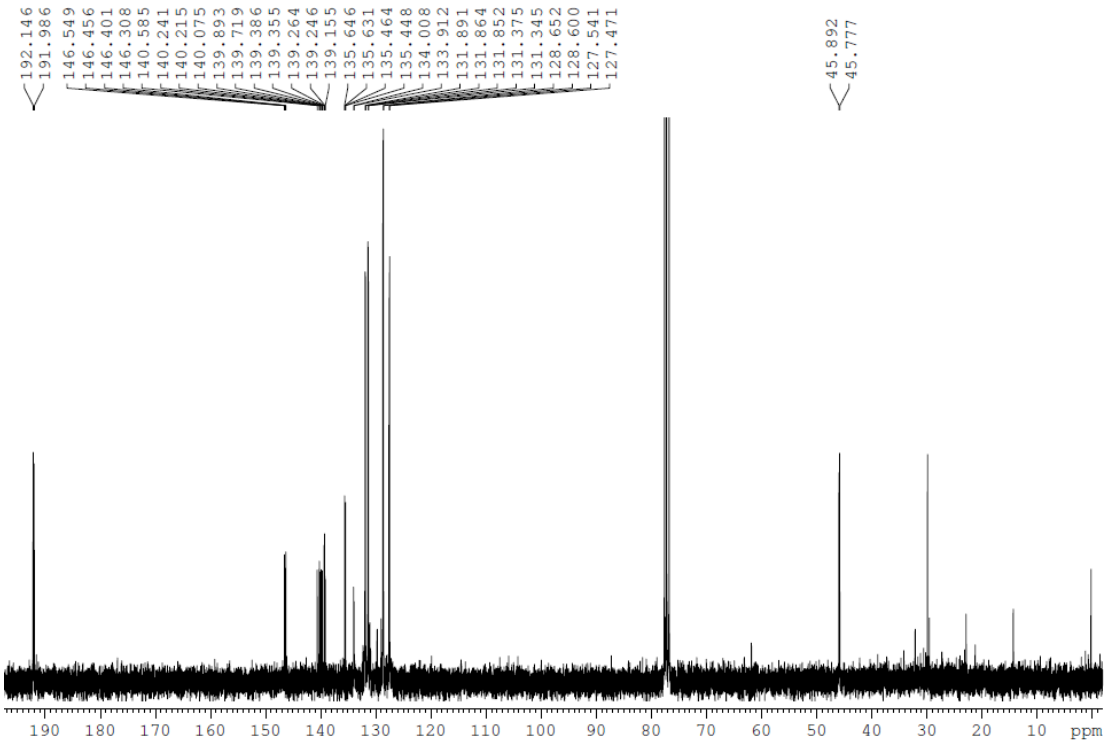


Figure S28: ^{13}C-NMR spectrum ($CDCl_3$, 75 MHz) of **51**

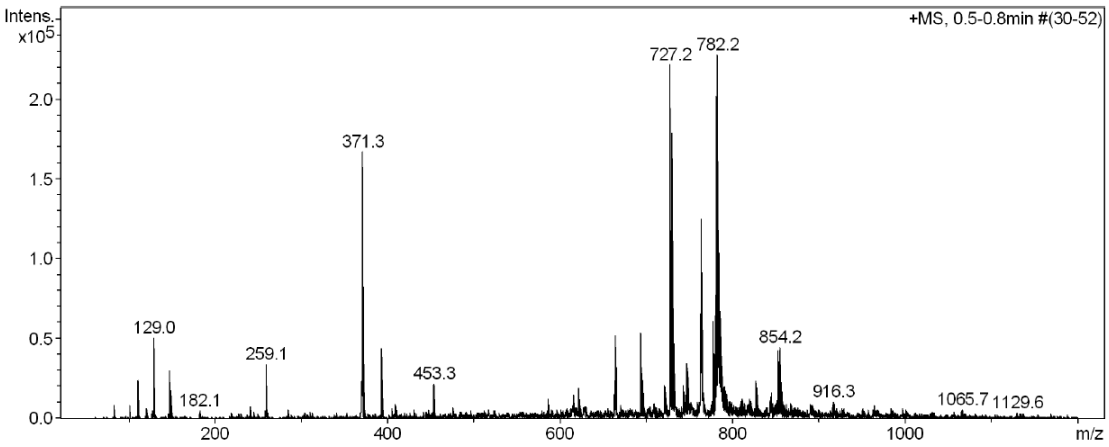
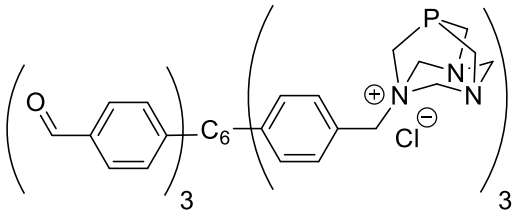


Figure S29: ESI-MS (+) of **51**



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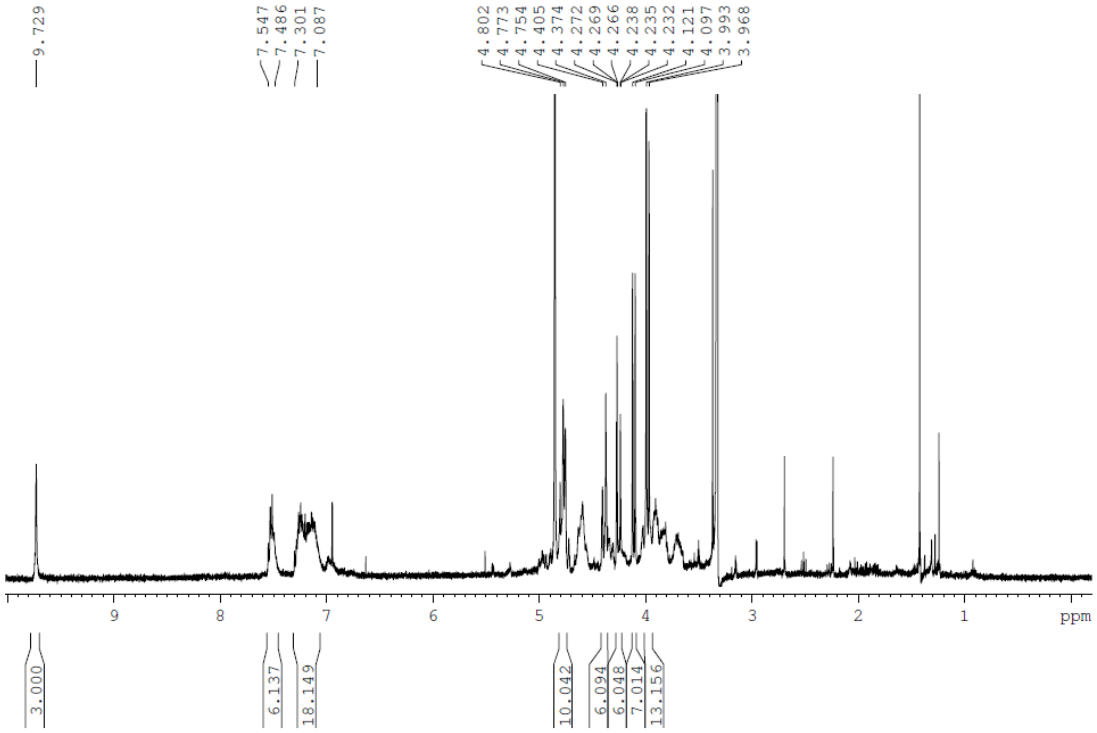

Figure S30: ^{1}H-NMR spectrum (CD_3OD, 400 MHz) of **52**

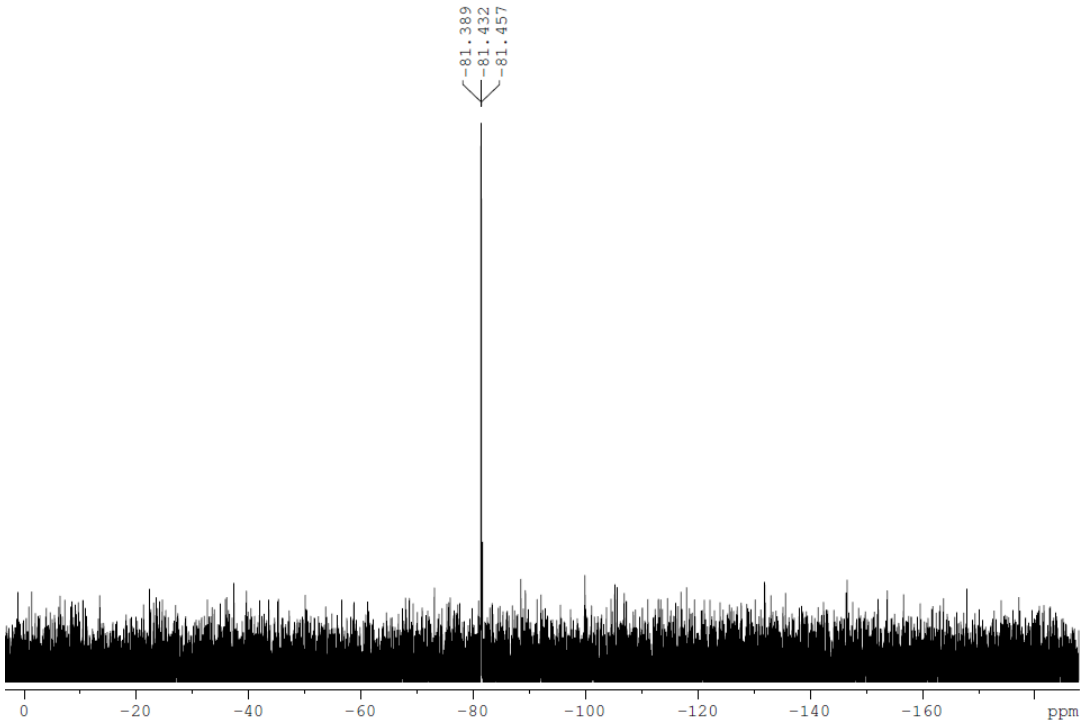

Figure S31: ^{31}P{^{1}H}-NMR spectrum (CD_3OD, 162 MHz) of **52**

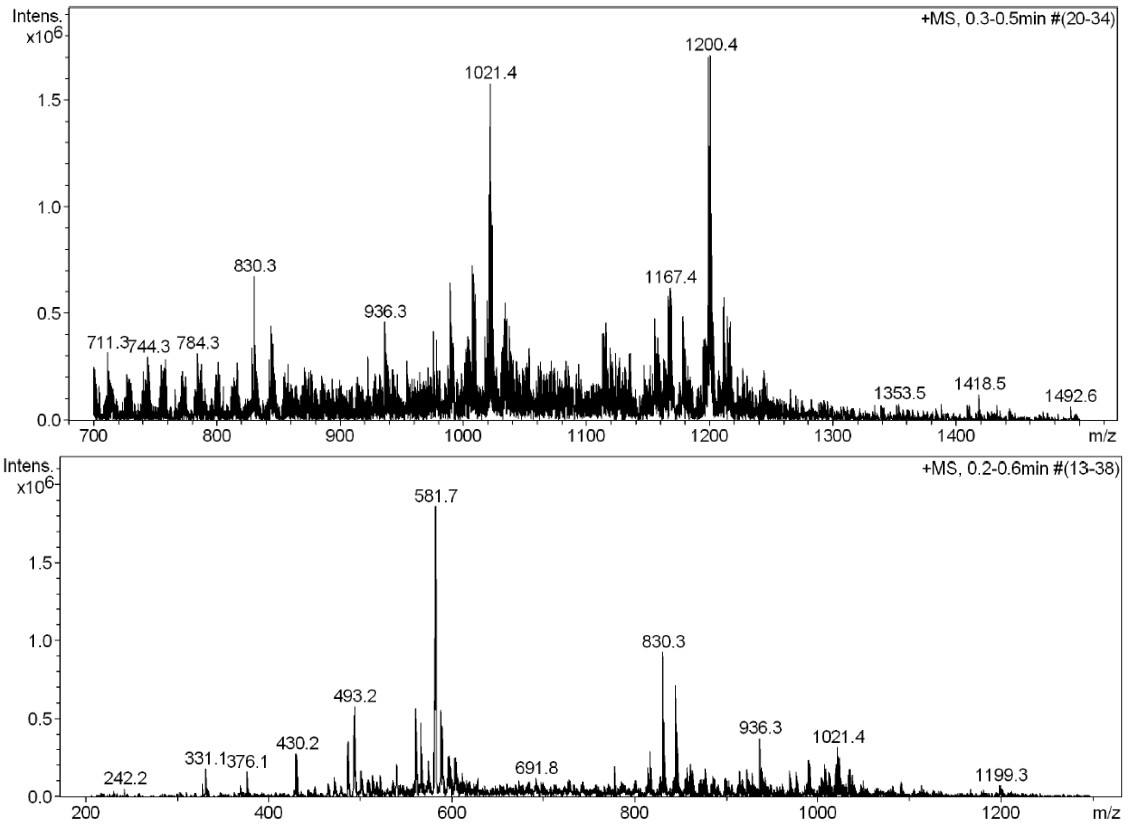

Figure S32: ESI-MS (+) of **52**

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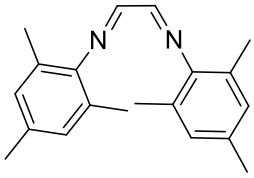

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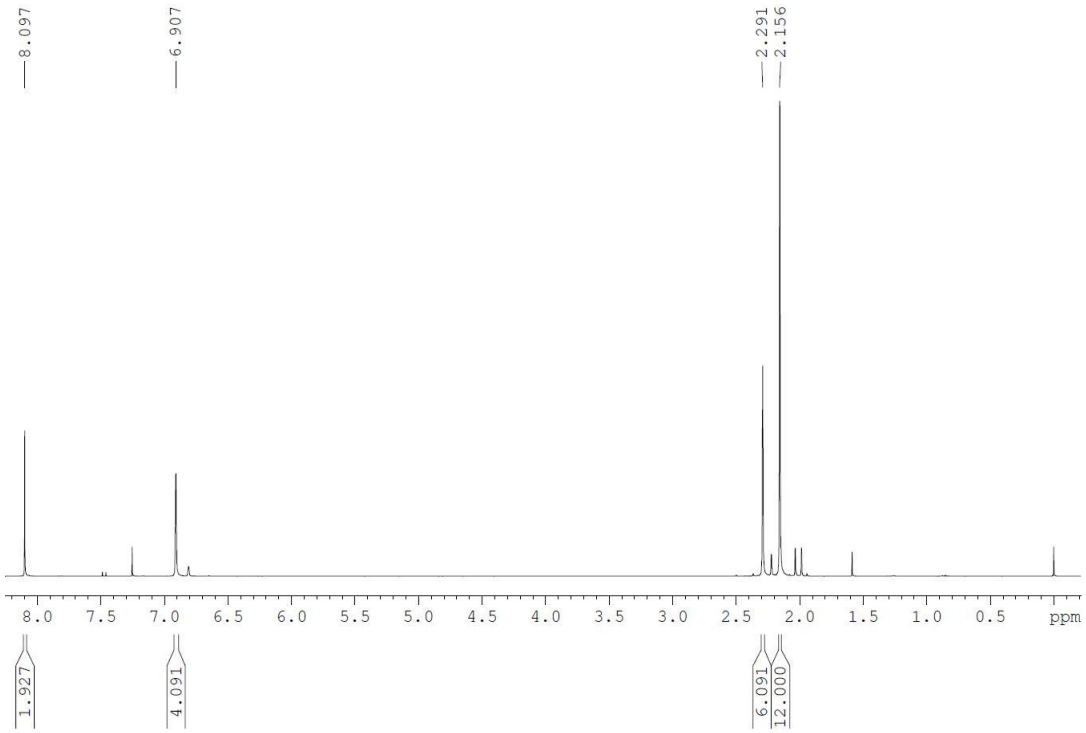
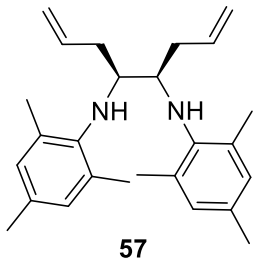


Figure S1: ^{1}H-NMR ($CDCl_3$, 300MHz) of **56**



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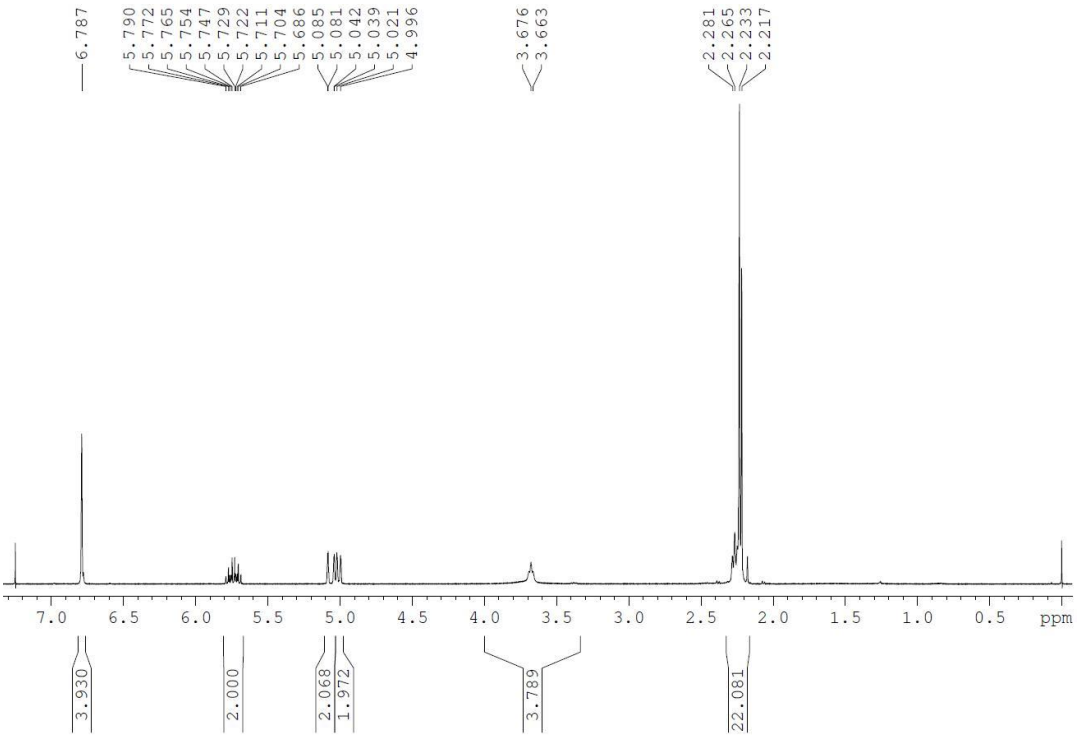
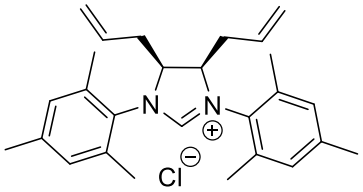


Figure S2: ^{1}H-NMR ($CDCl_3$, 400MHz) of **57**



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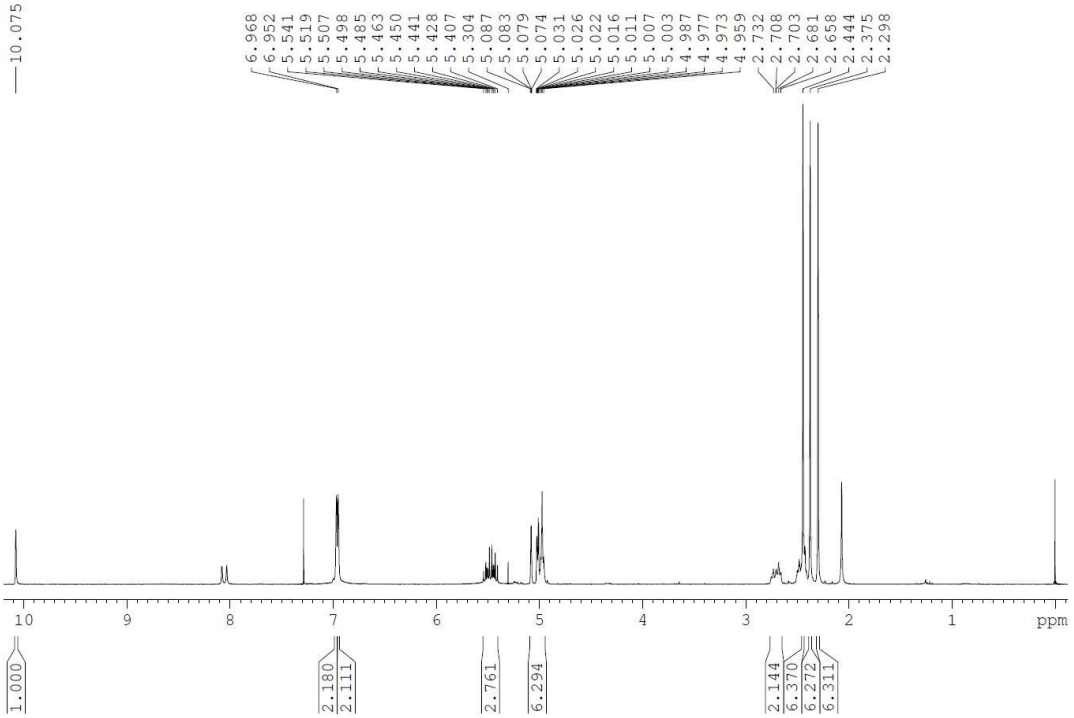
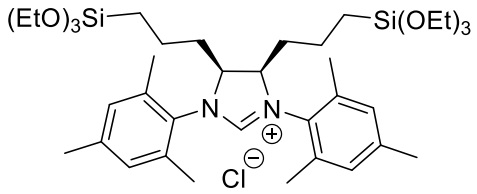


Figure S3: ^{1}H-NMR ($CDCl_3$, 300MHz) of **58**



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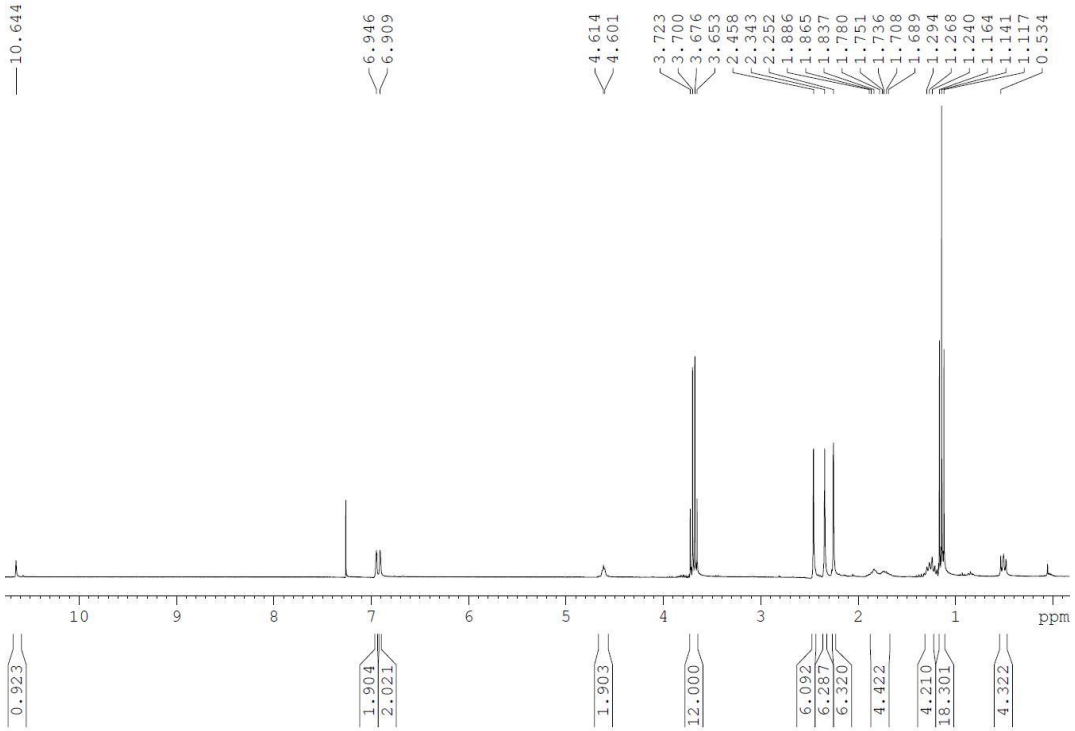
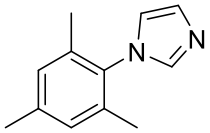


Figure S4: ^{1}H-NMR ($CDCl_3$, 300MHz) of **54**



59

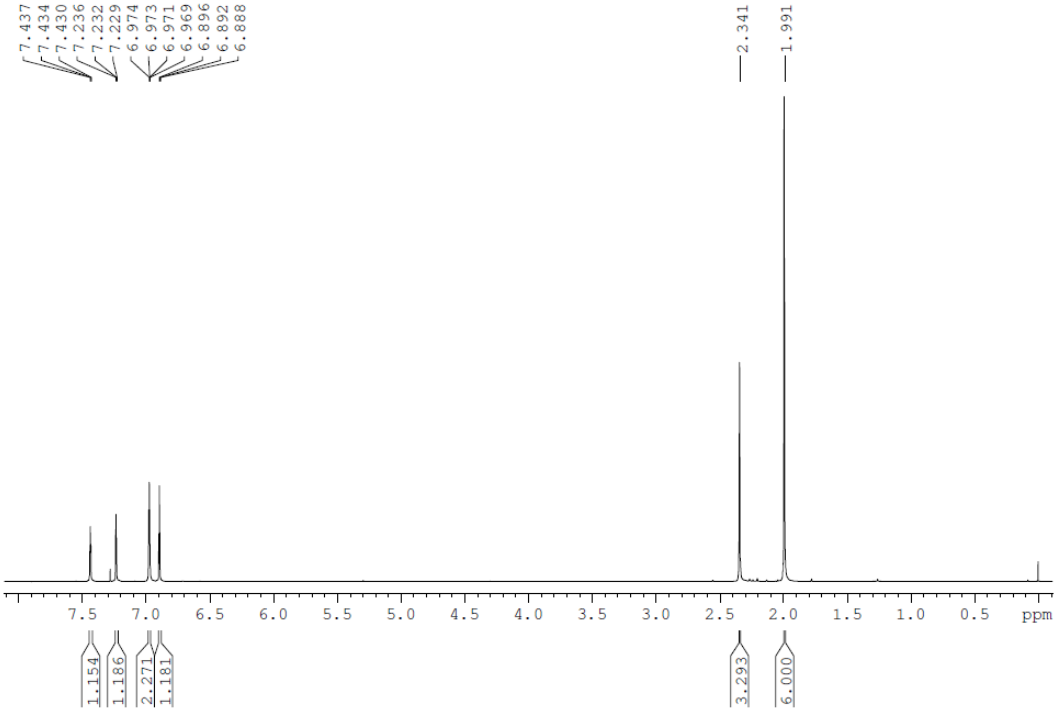


Figure S5: ^{1}H-NMR ($CDCl_3$, 300MHz) of **59**

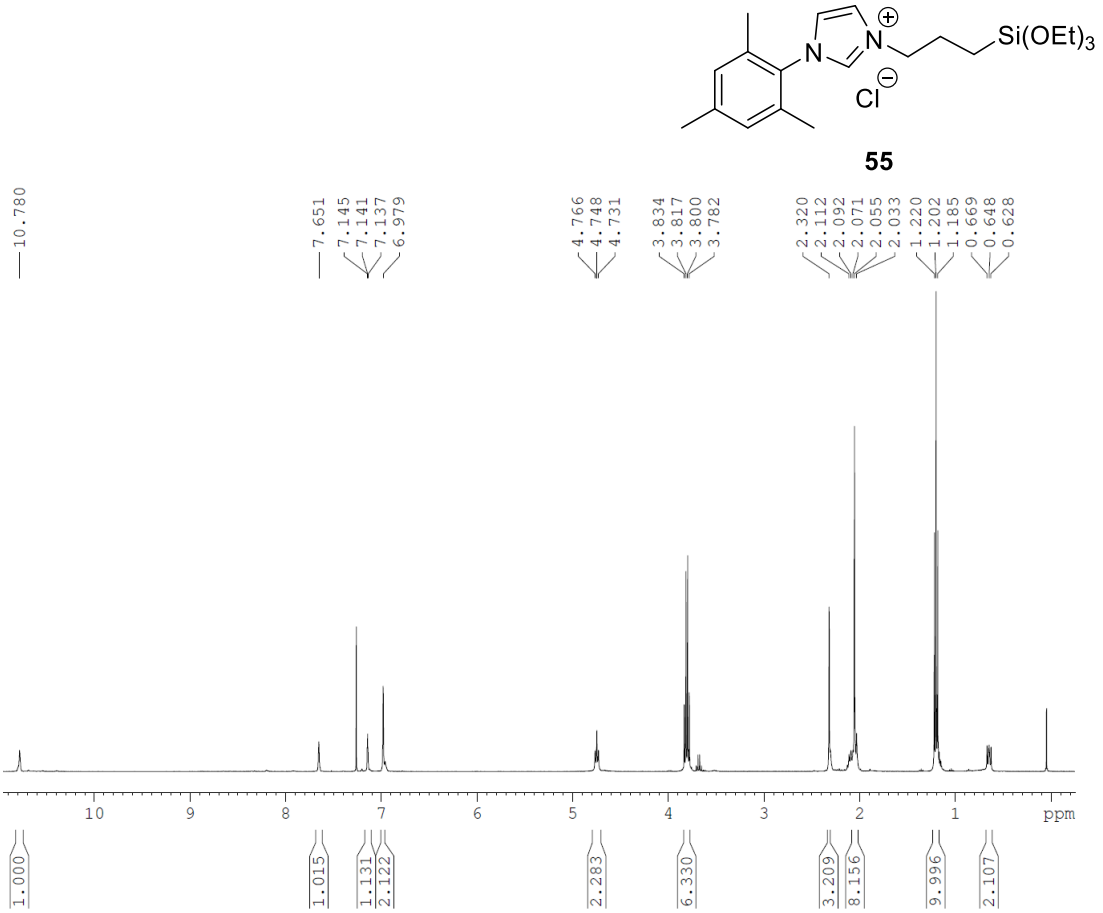
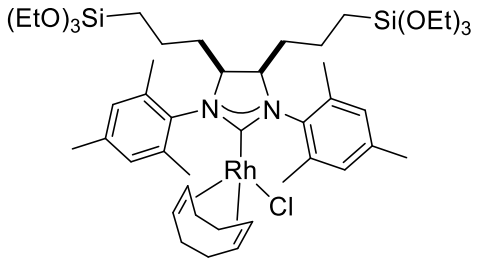


Figure S6: ^{1}H-NMR ($CDCl_3$, 400MHz) of **55**



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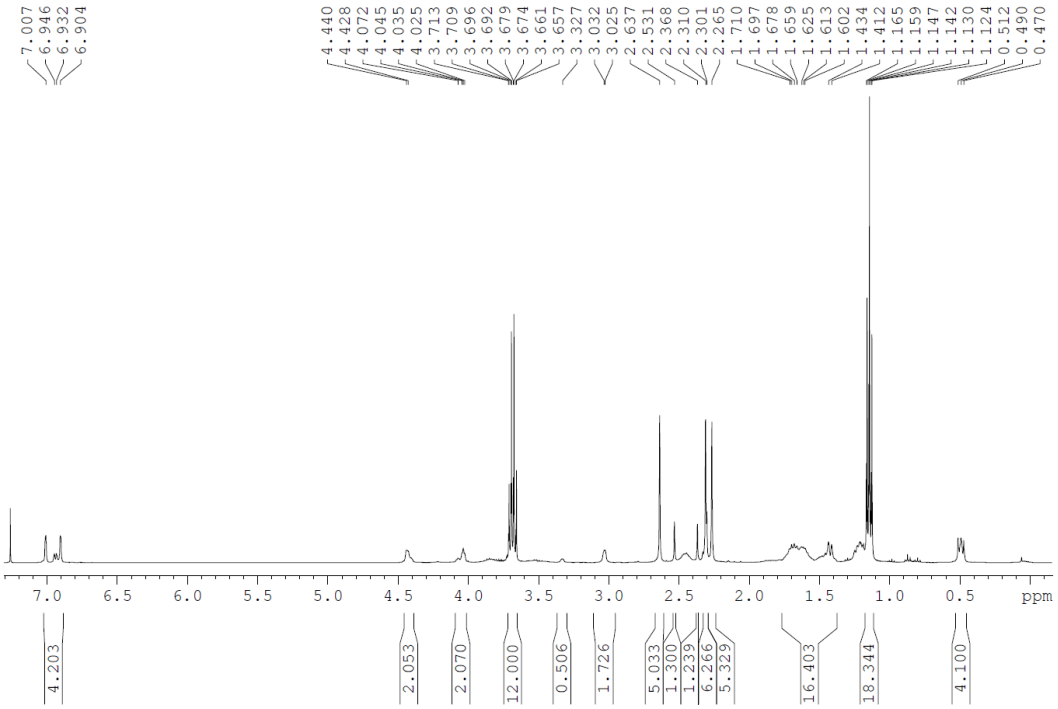


Figure S7: ^{1}H-NMR ($CDCl_3$, 400MHz) of **60**

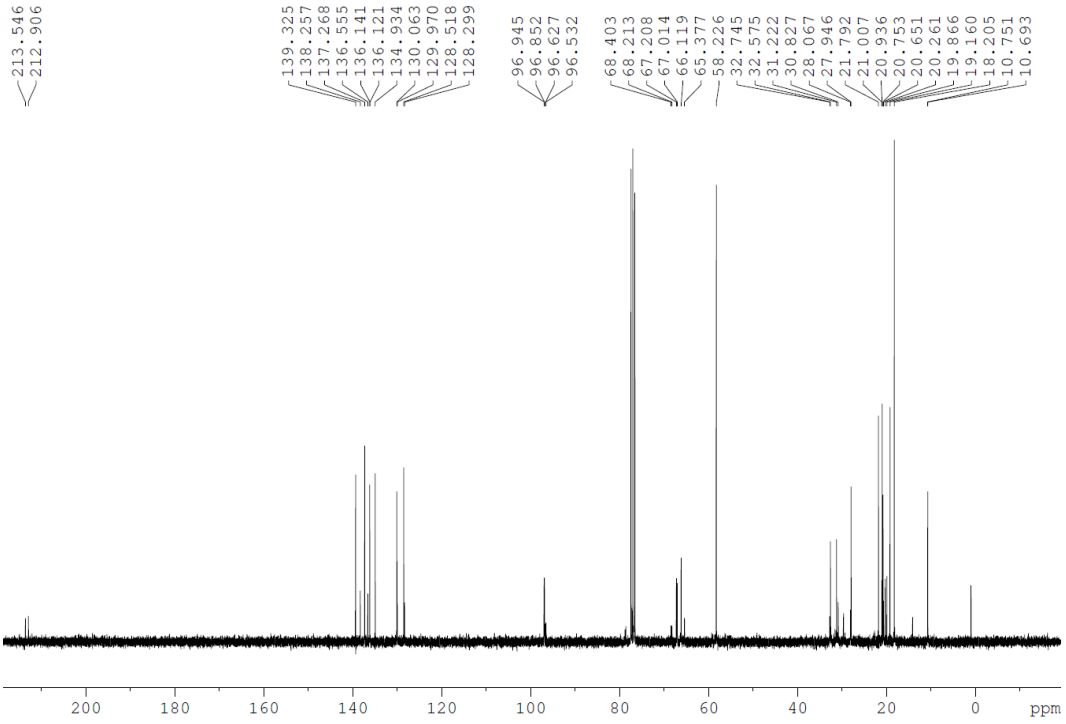


Figure S8: ^{13}C-NMR ($CDCl_3$, 75MHz) of **60**

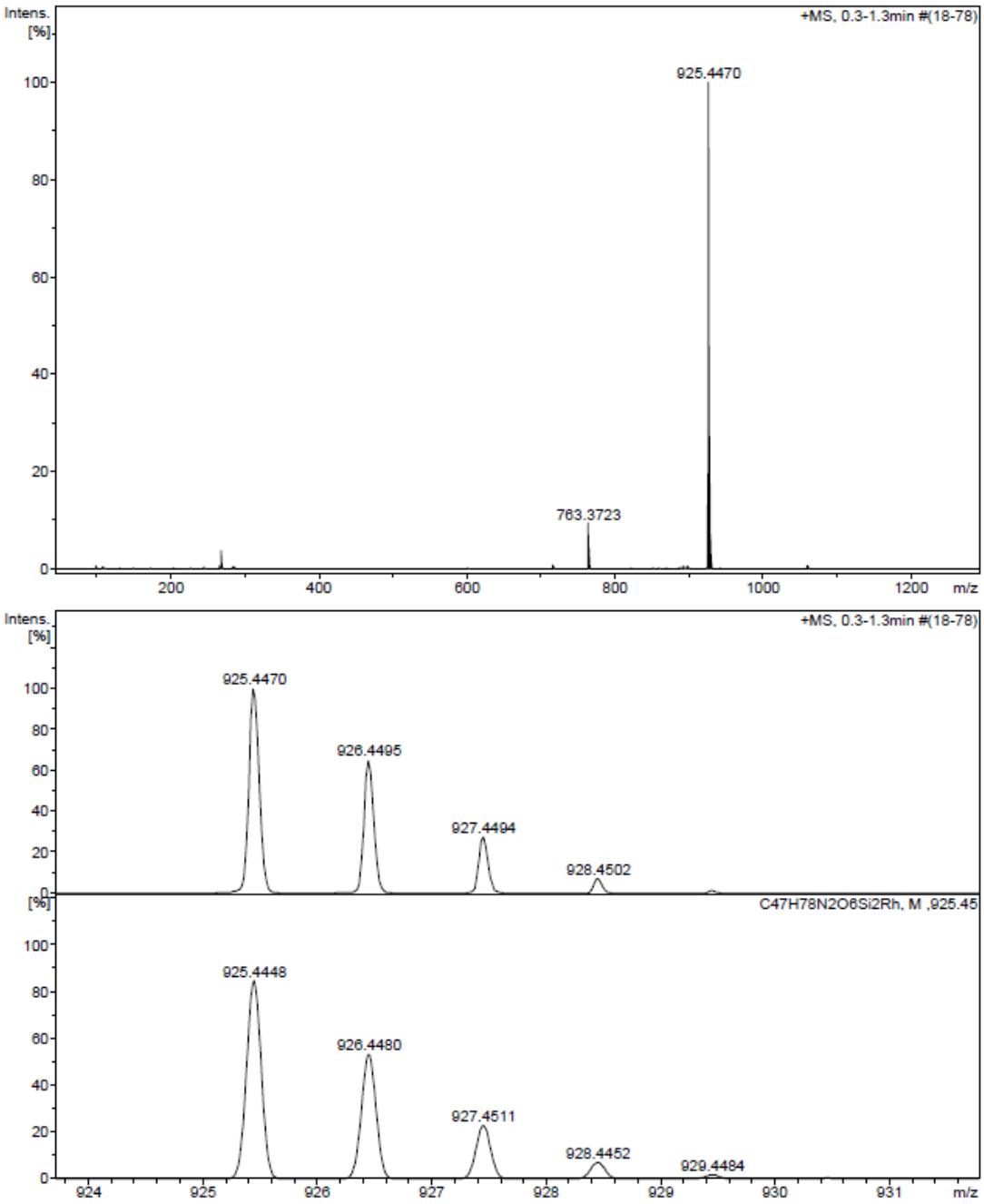
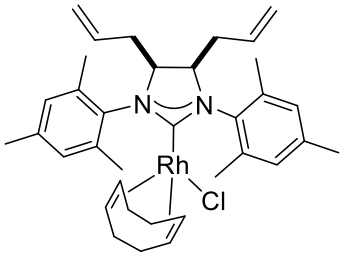


Figure S9: ESI-HRMS (+) of **60**



60-allyl

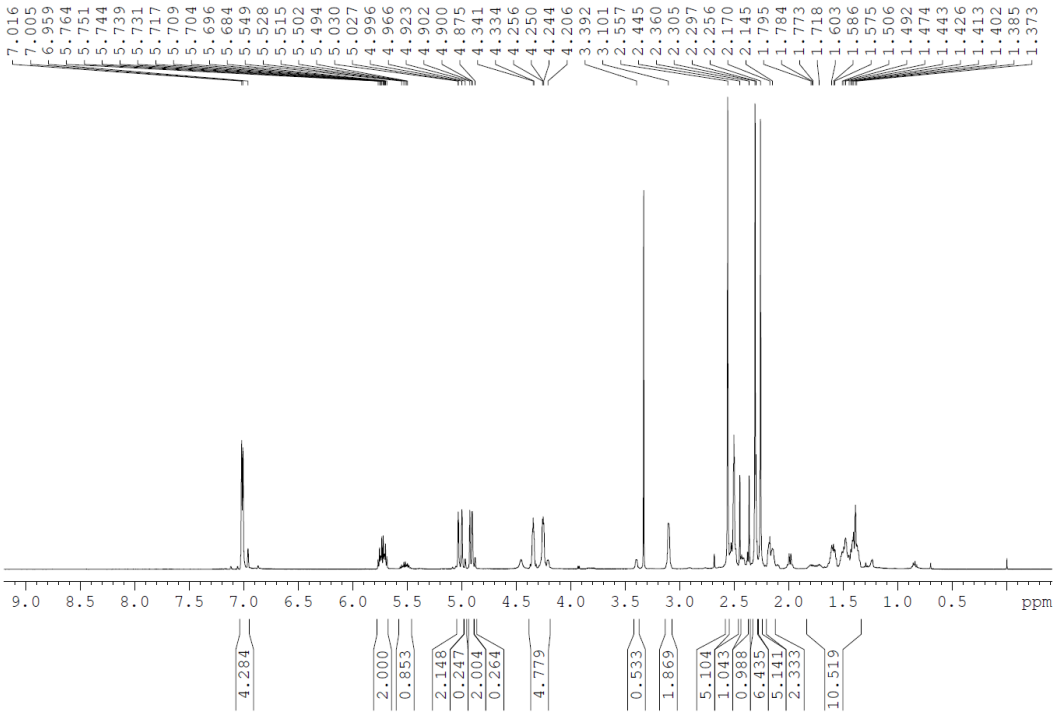


Figure S10: ^{1}H-NMR (DMSO-d_6, 500MHz) of **60**-allyl

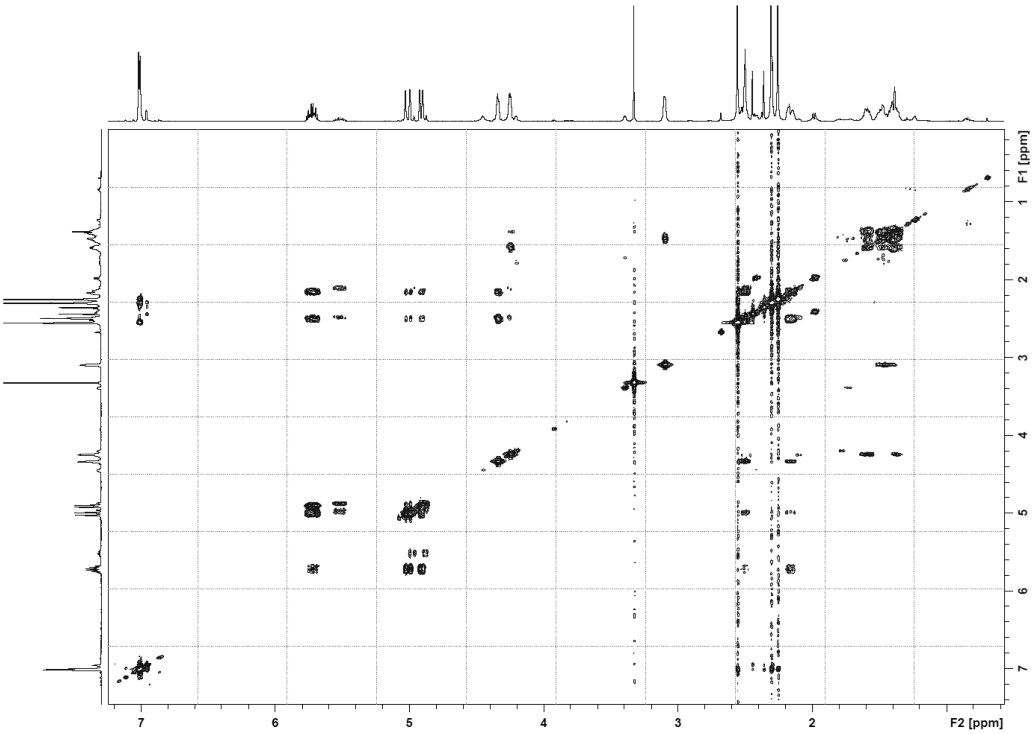


Figure S11: ^{1}H-^{1}H COSY of **60**-allyl

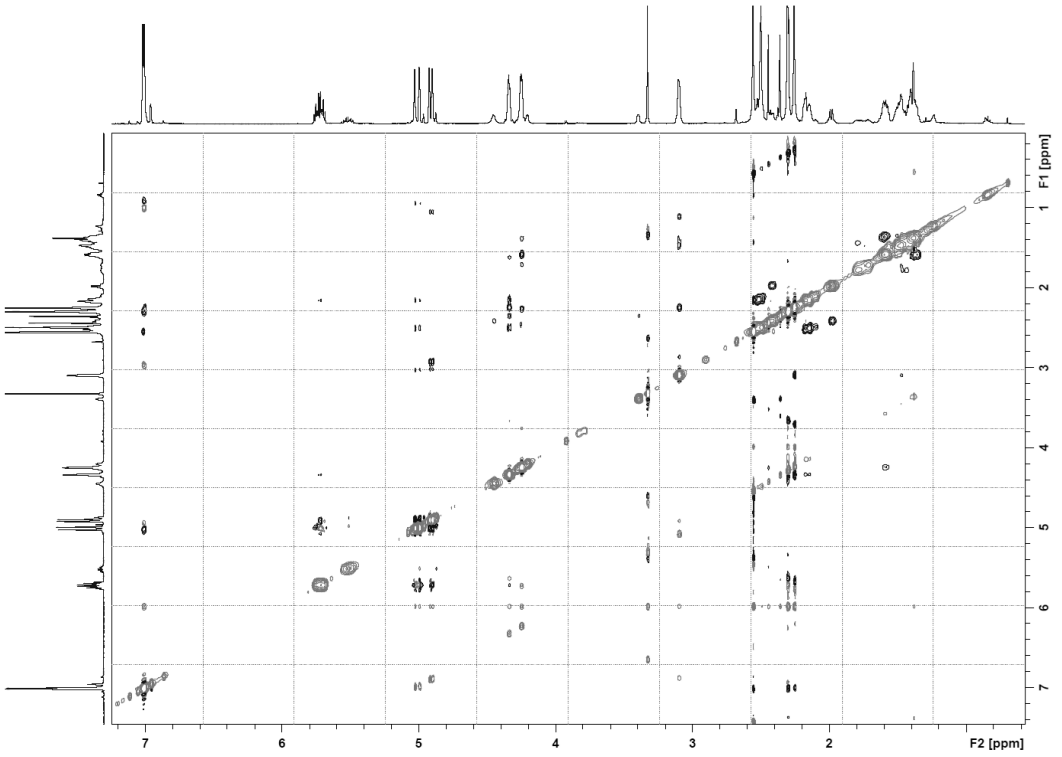


Figure S12: ^{1}H-^{1}H NOESY of **60**-allyl

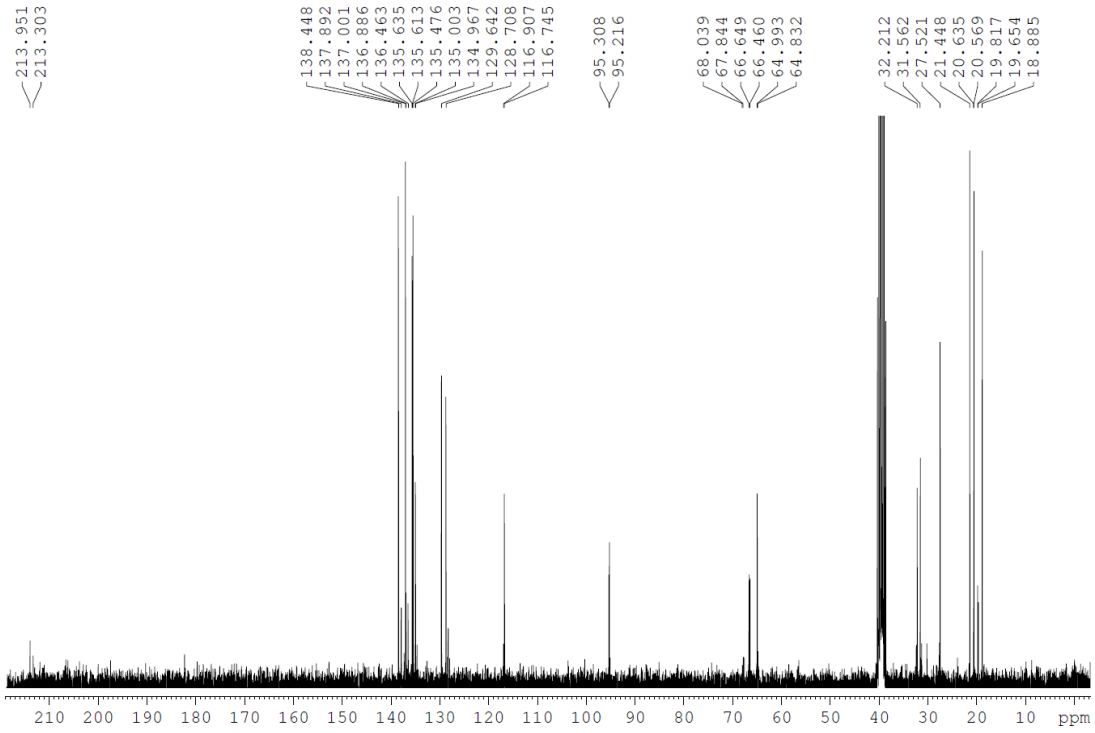


Figure S13: ^{13}C-NMR (DMSO-d_6, 75MHz) of **60**-allyl

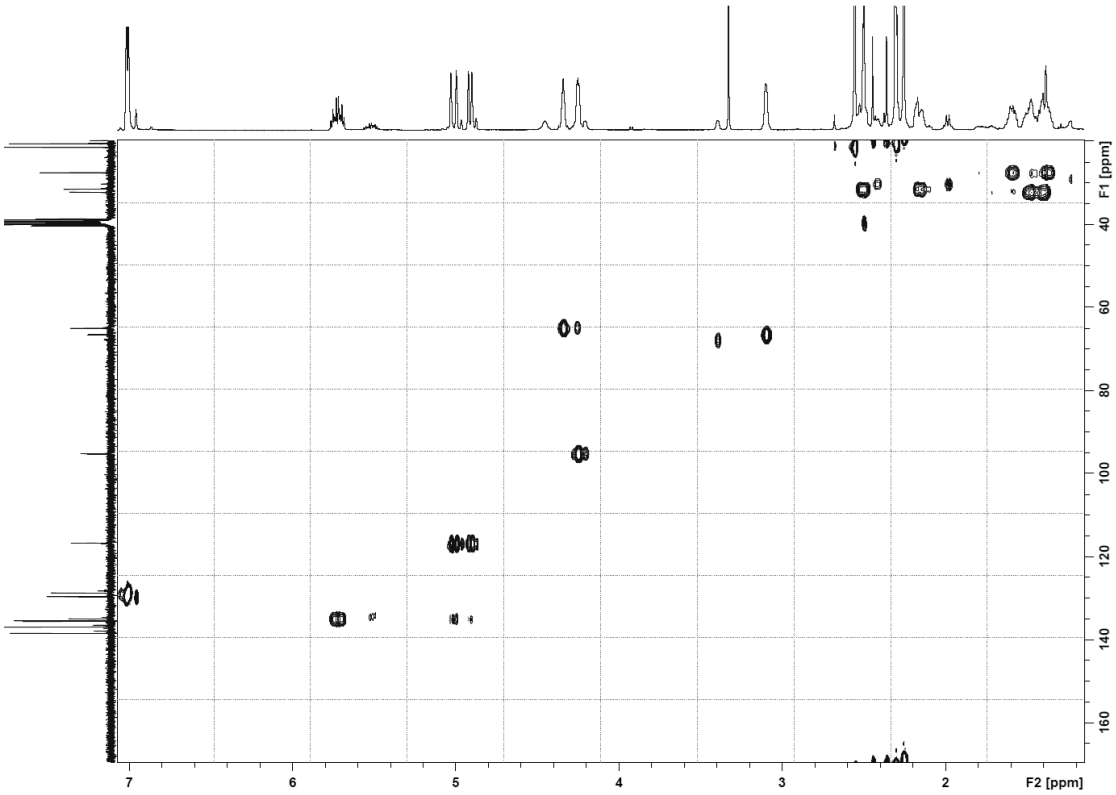


Figure S14: ^{1}H-^{13}C HSQC of **60**-allyl

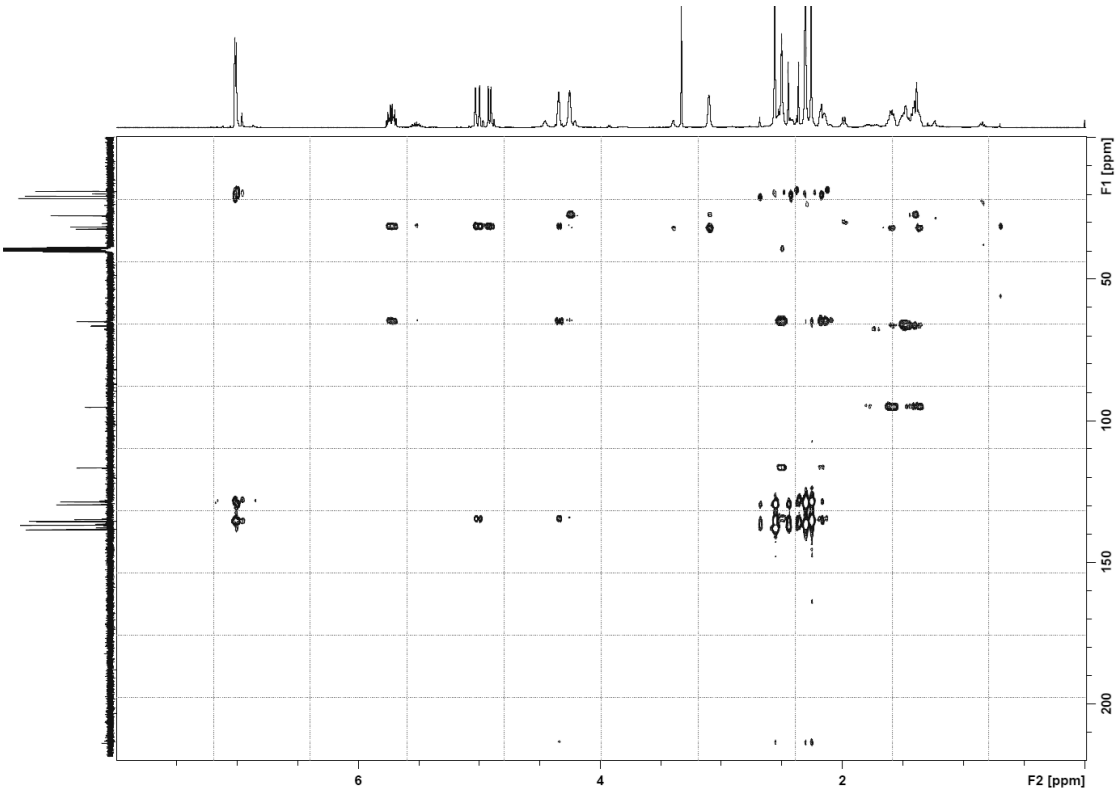


Figure S15: ^{1}H-^{13}C HMBC of **60**-allyl

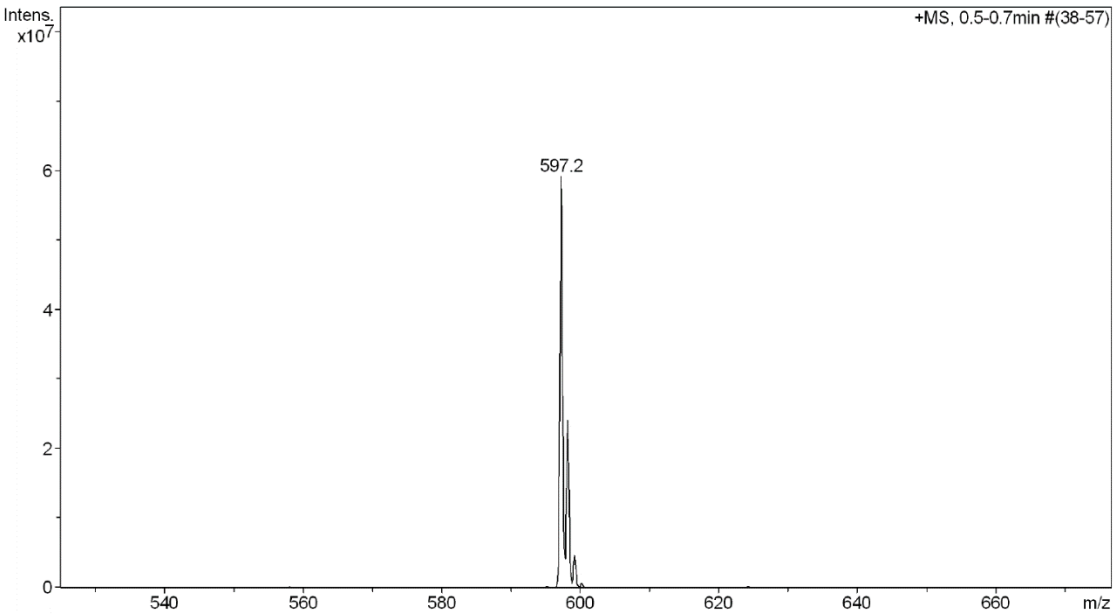
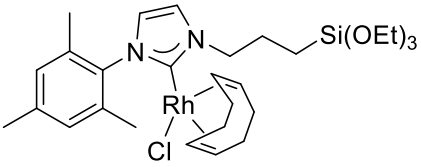


Figure S16: ESI-MS (+) of **60**-allyl



61

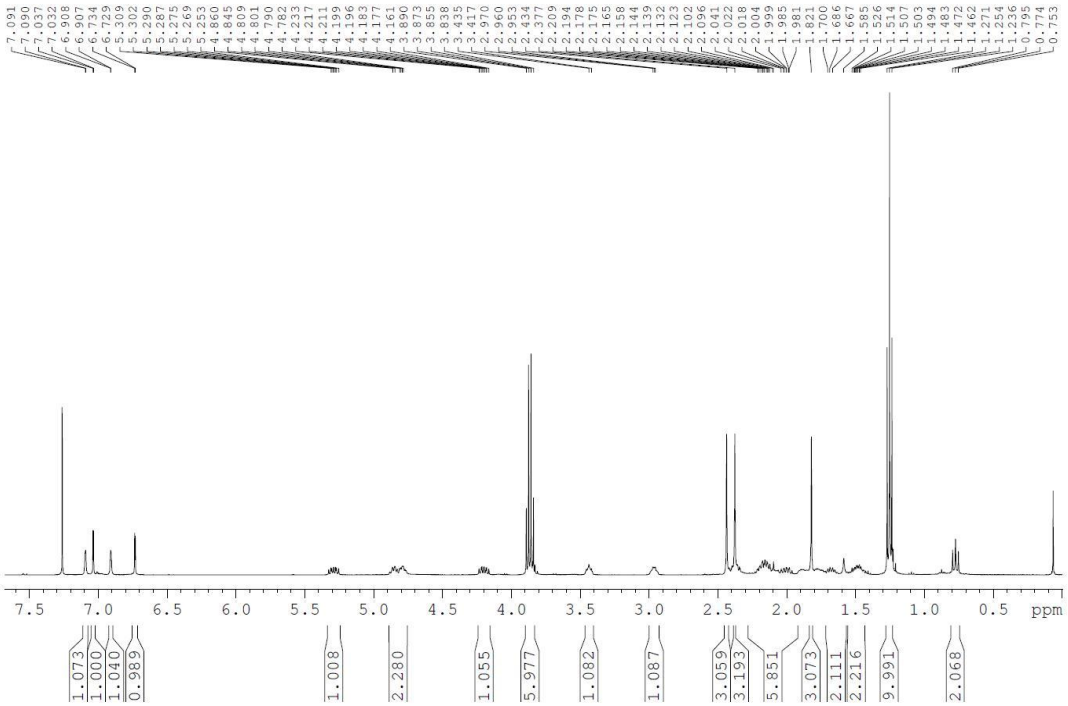


Figure S17: ^{1}H-NMR ($CDCl_3$, 400MHz) of **61**

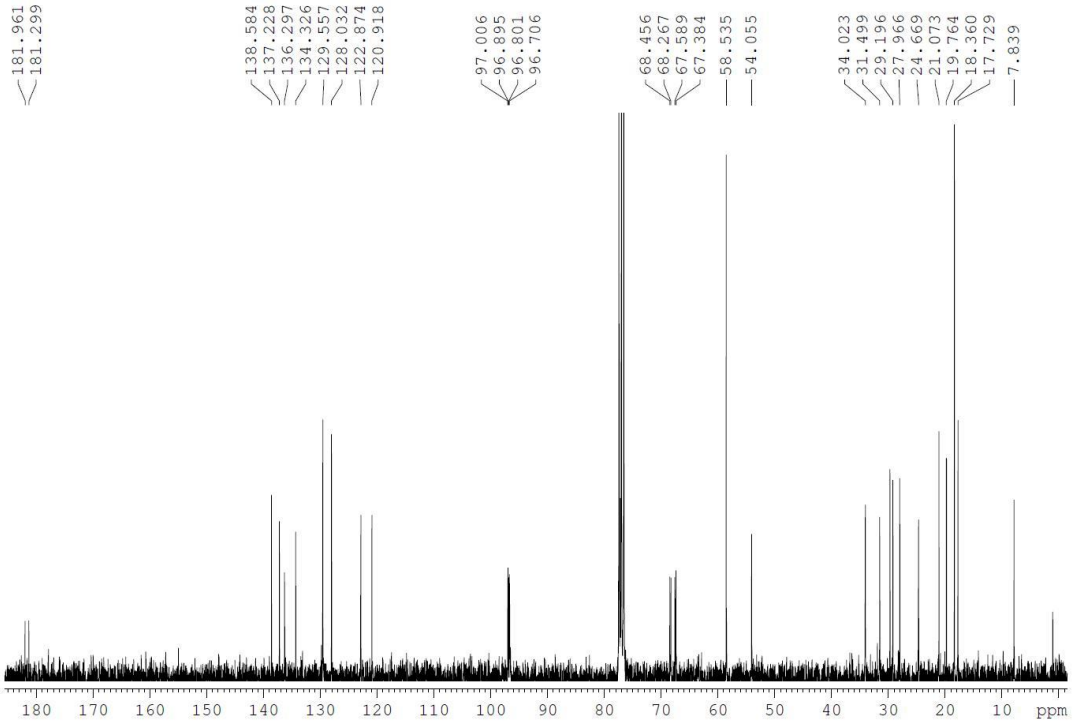


Figure S18: ^{13}C-NMR ($CDCl_3$, 75MHz) of **61**

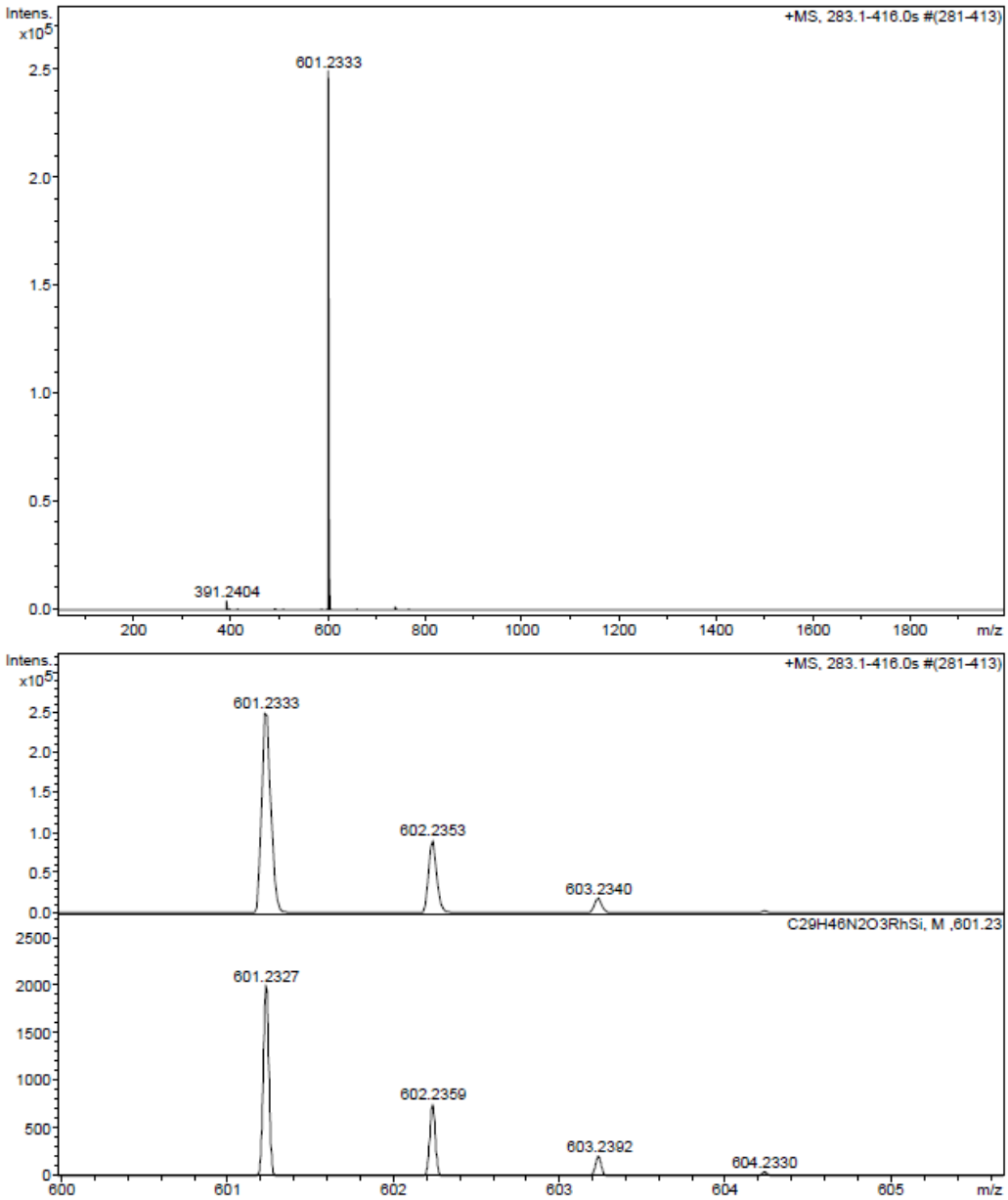
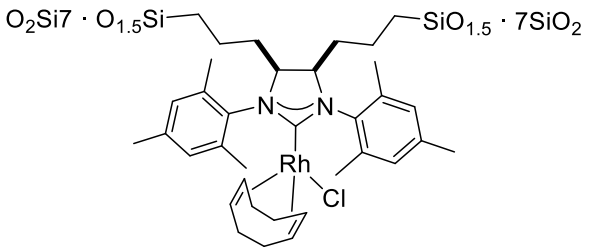


Figure S19: ESI-HRMS (+) of **4**



M1

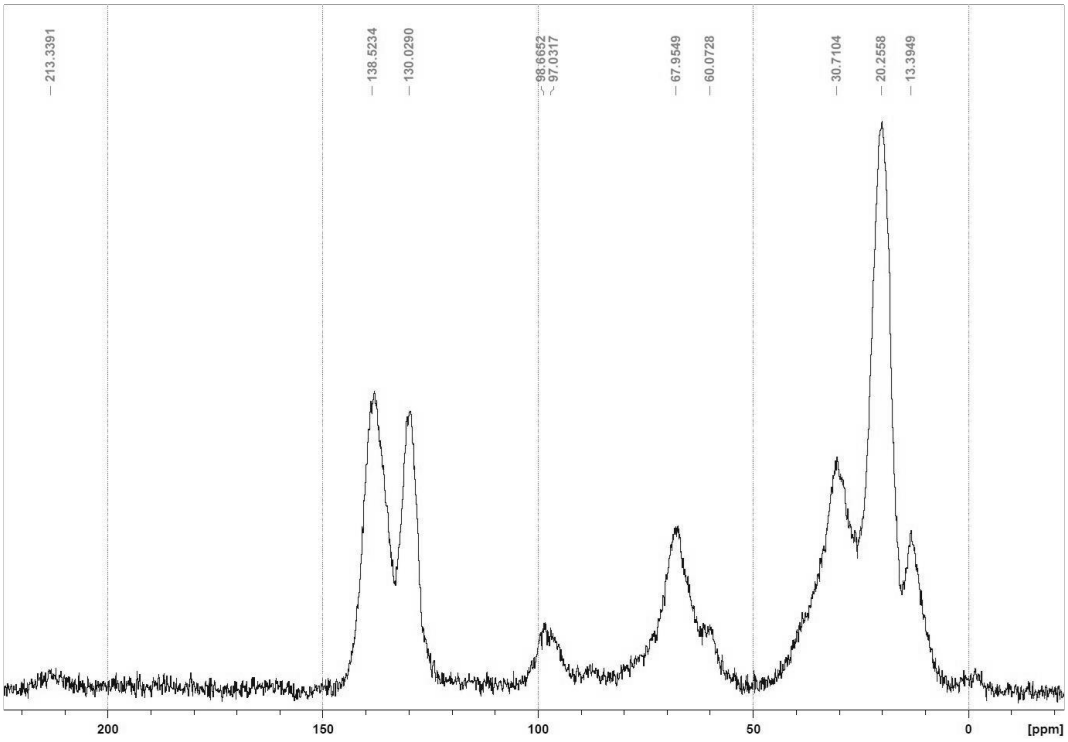


Figure S20: ^{13}C-SSNMR (100MHz) of **M1**

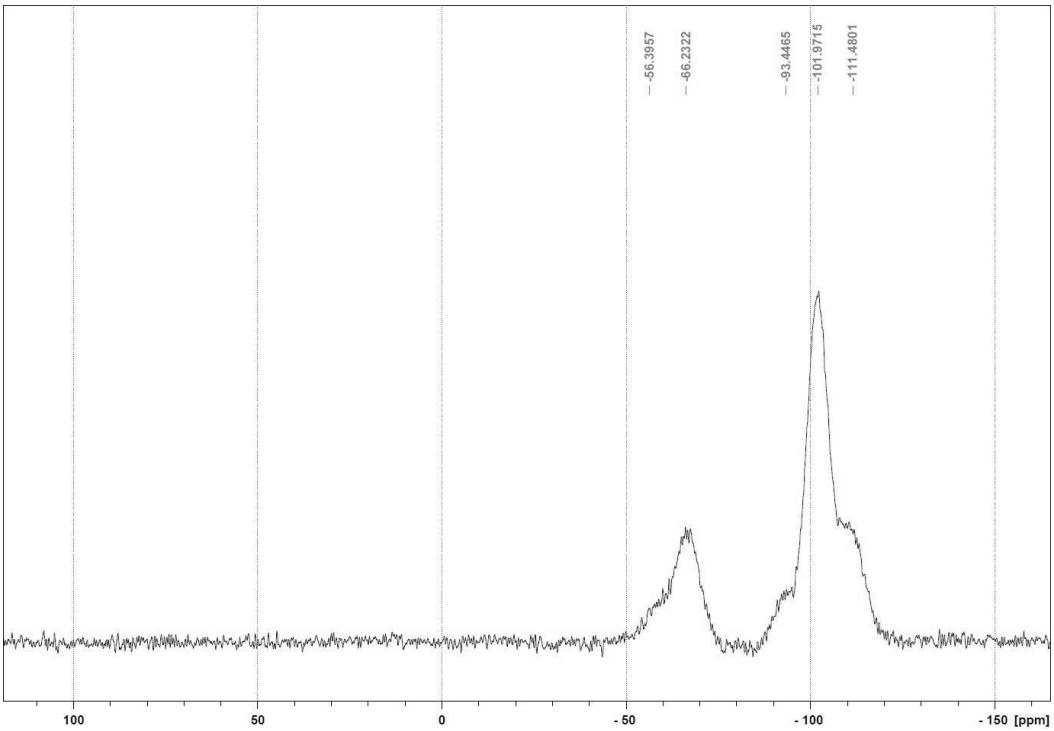


Figure S21: ^{29}Si-SSNMR (79.5MHz) of **M1**

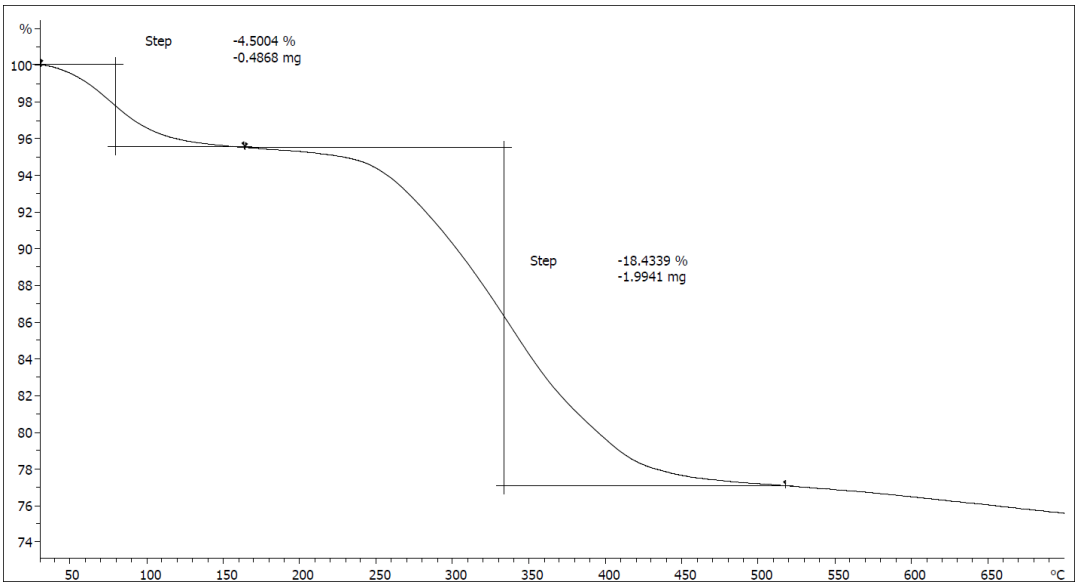


Figure S22: TGA of **M1**

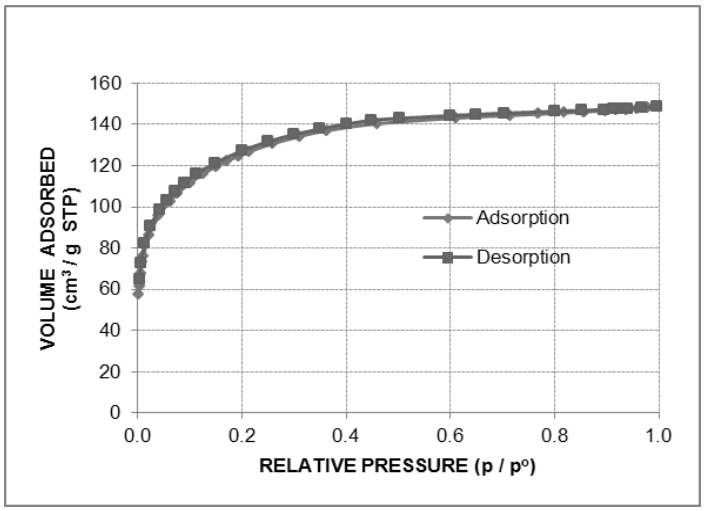


Figure S23: N_2 adsorption-desorption isotherm of **M1**

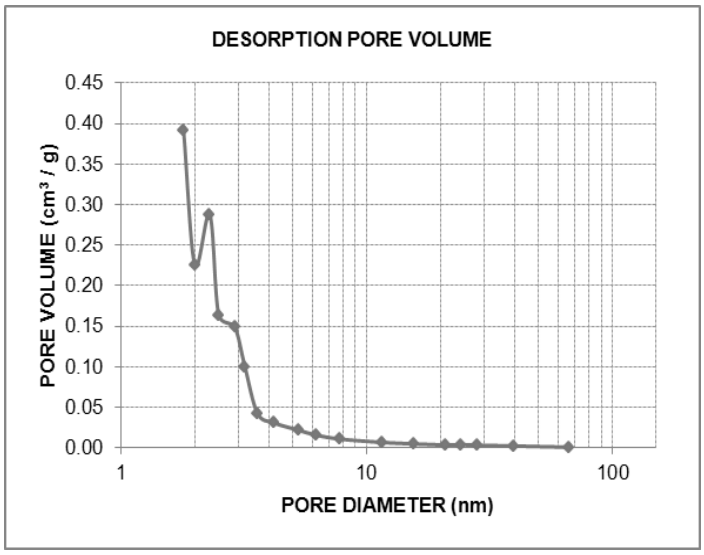
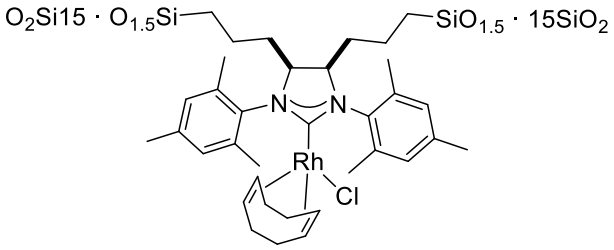


Figure S24: Pore size distribution of **M1**



M2

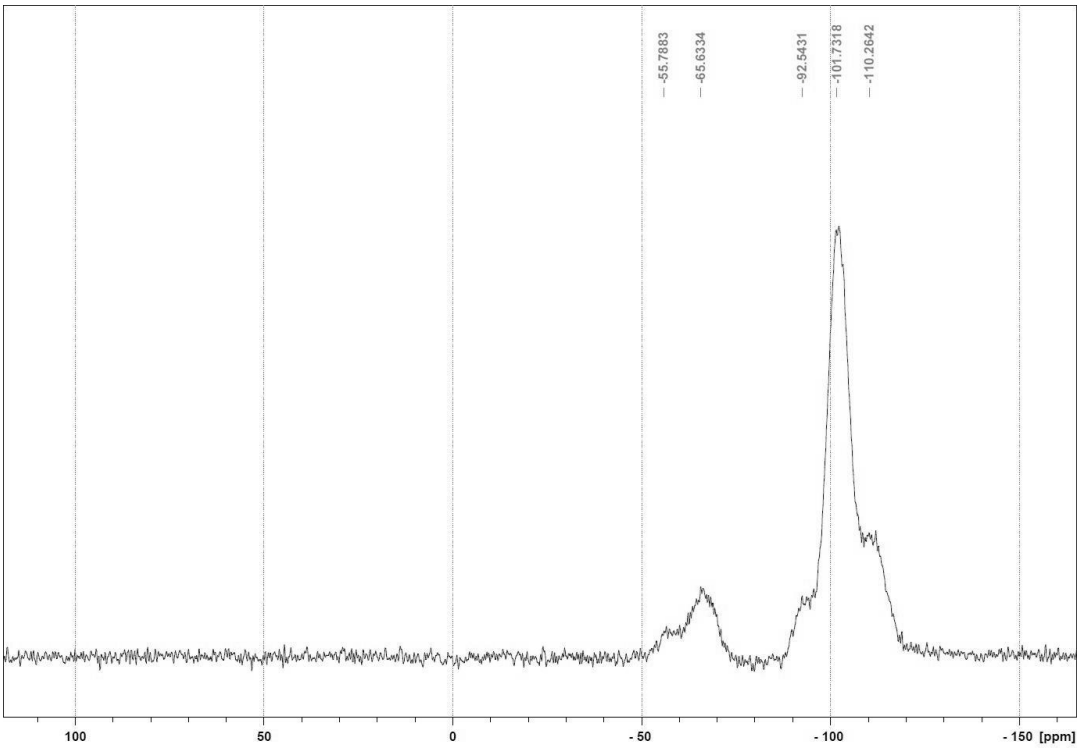


Figure S25: ^{29}Si-SSNMR (79.5MHz) of **M2**

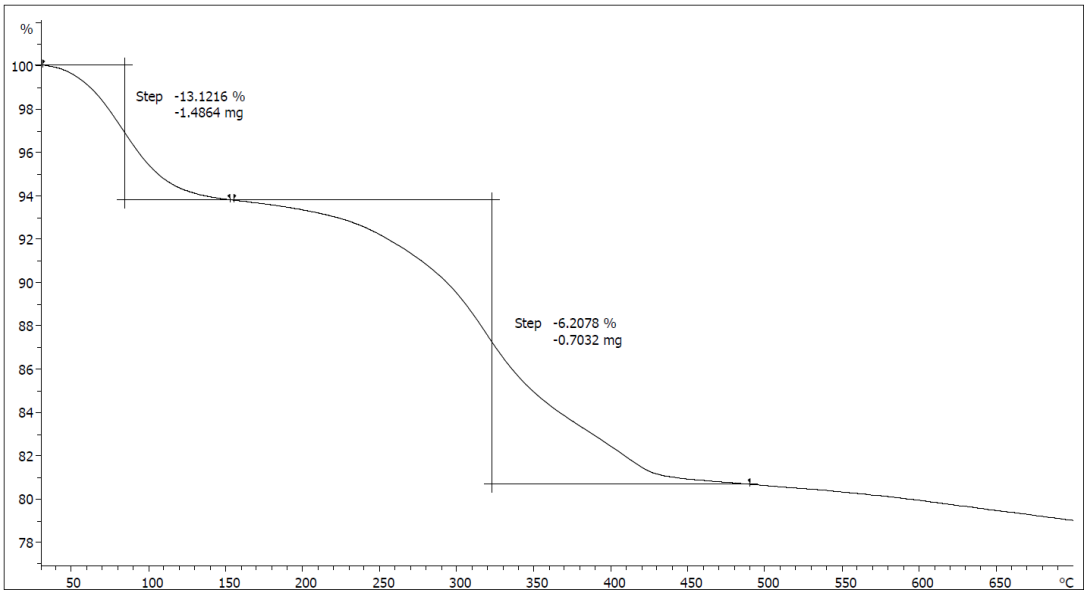


Figure S26: TGA of **M2**

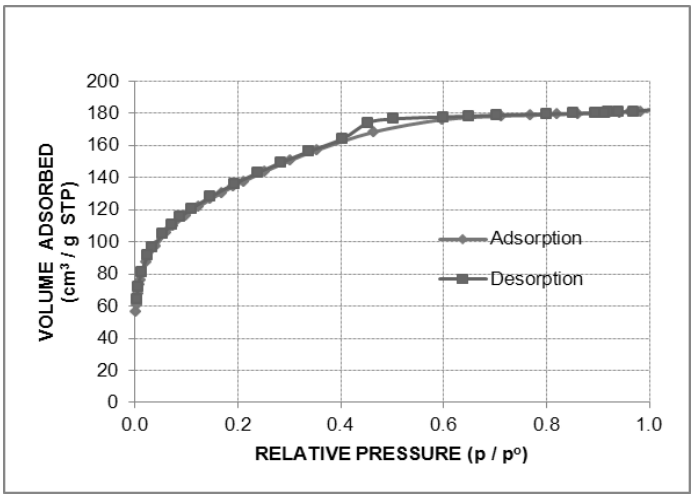


Figure S27: N_2 adsorption-desorption isotherm of **M2**

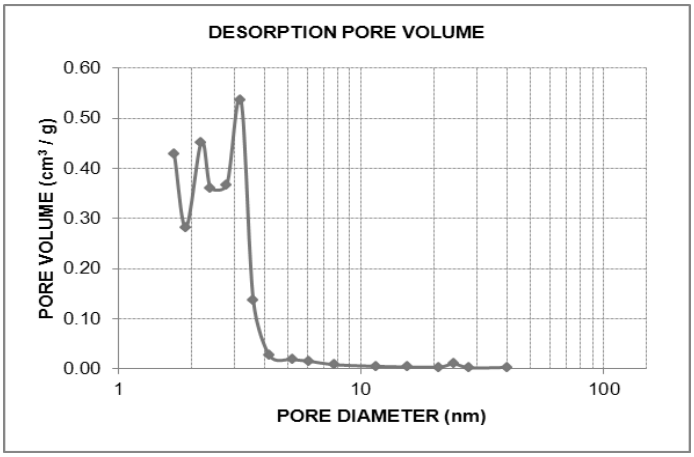
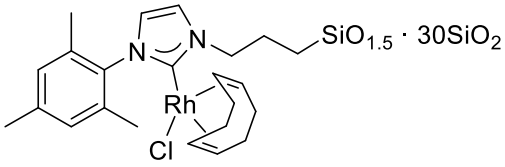


Figure S28: Pore size distribution of **M2**



M3

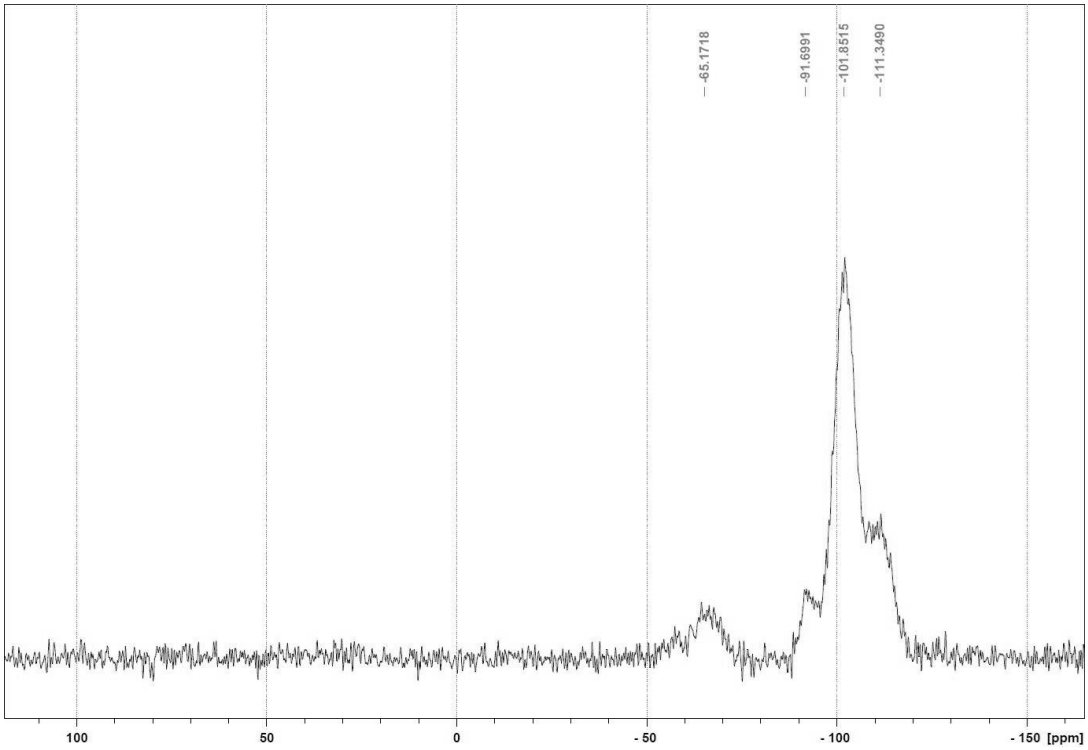


Figure S29: ^{29}Si-SSNMR (79.5MHz) of **M3**

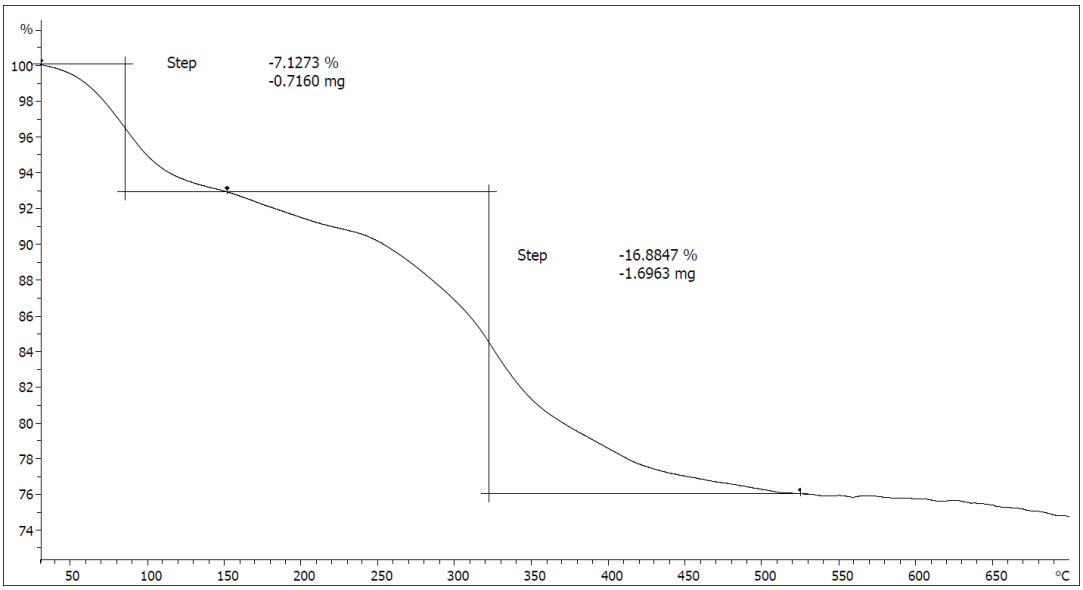


Figure S30: TGA of **M3**

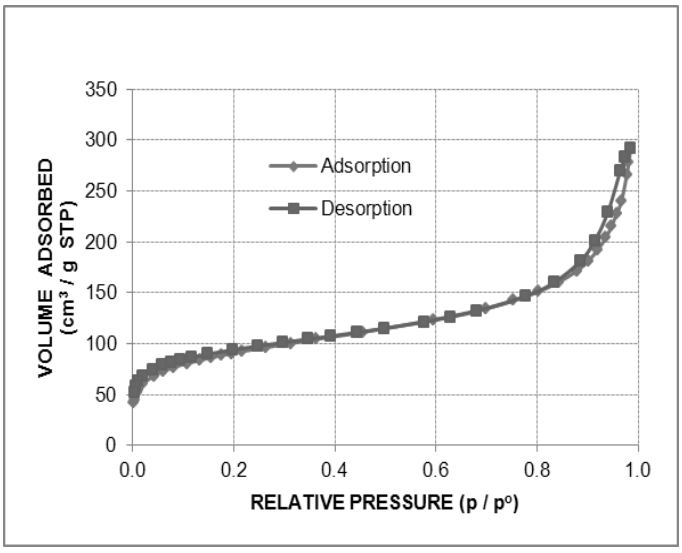


Figure S31: N_2 adsorption-desorption isotherm of **M3**

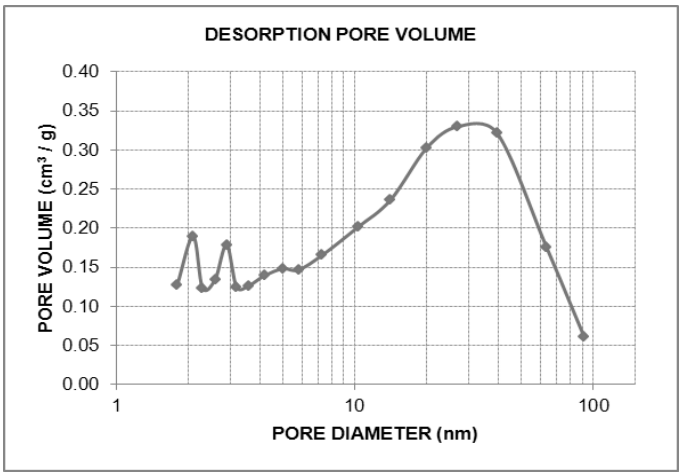
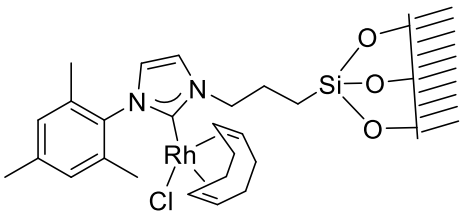


Figure S32: Pore size distribution of **M3**



M4

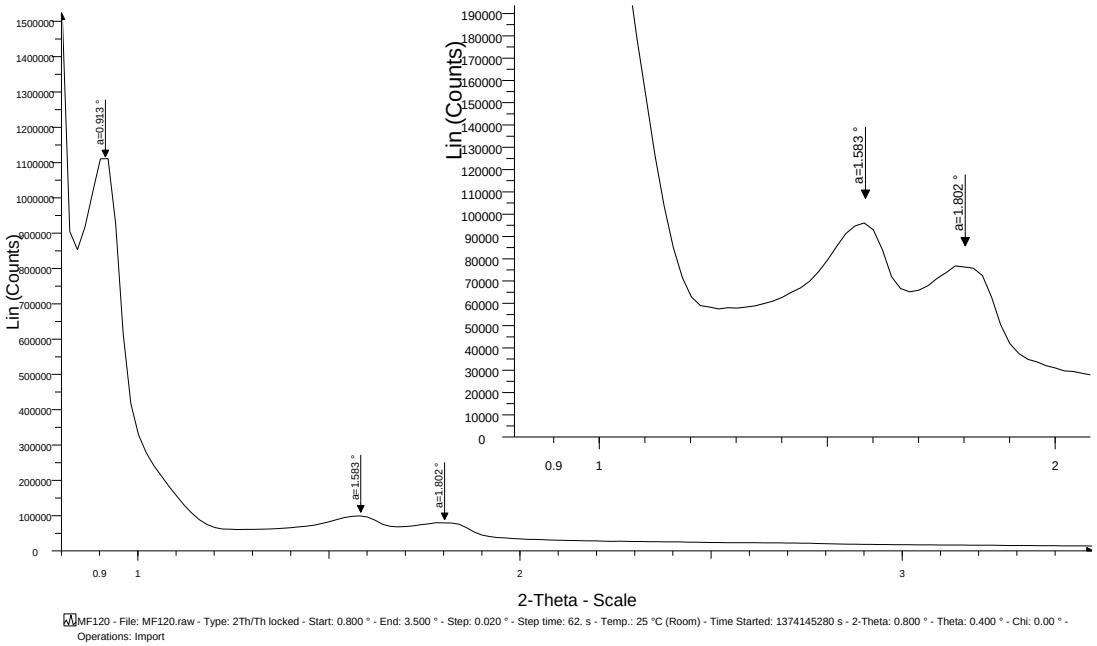


Figure S33: Powder XRD of **M4**

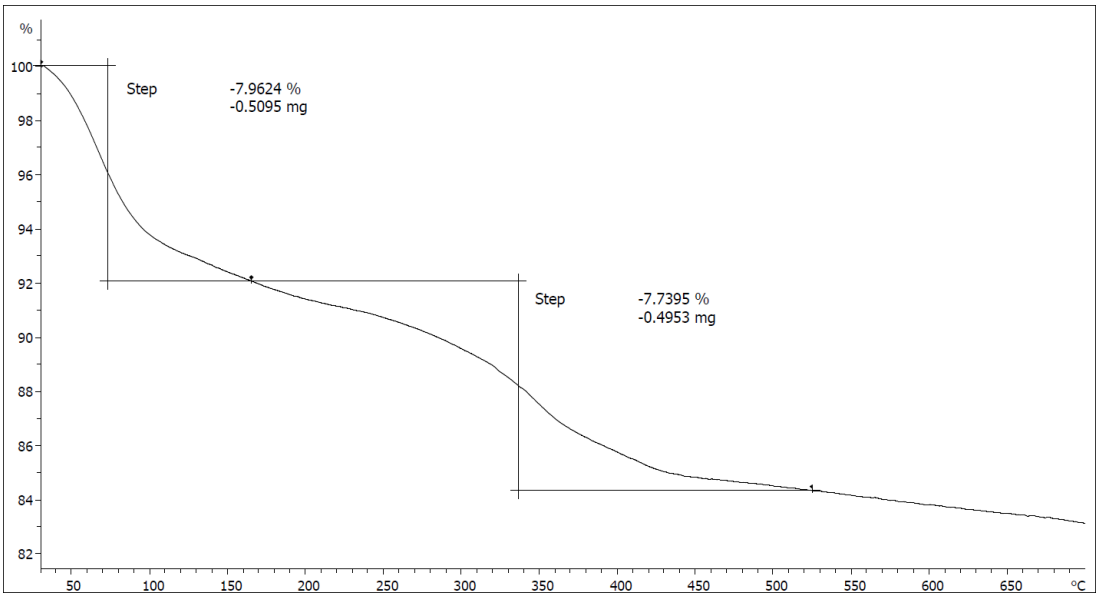


Figure S34: TGA of **M4**

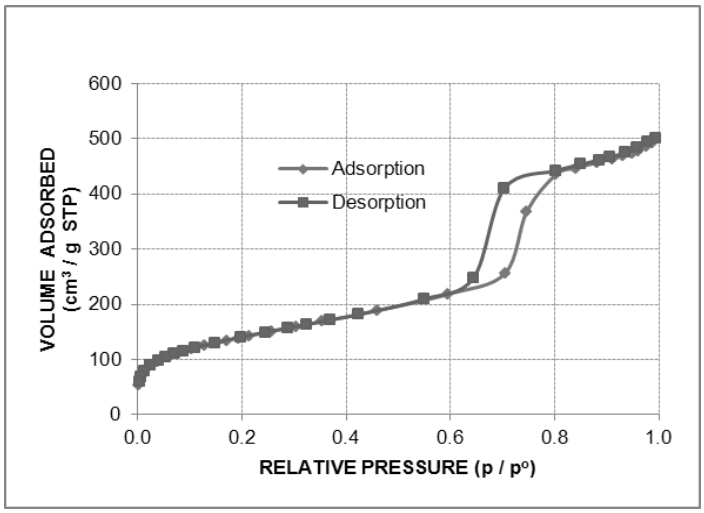


Figure S35: N_2 adsorption-desorption isotherm of **M4**

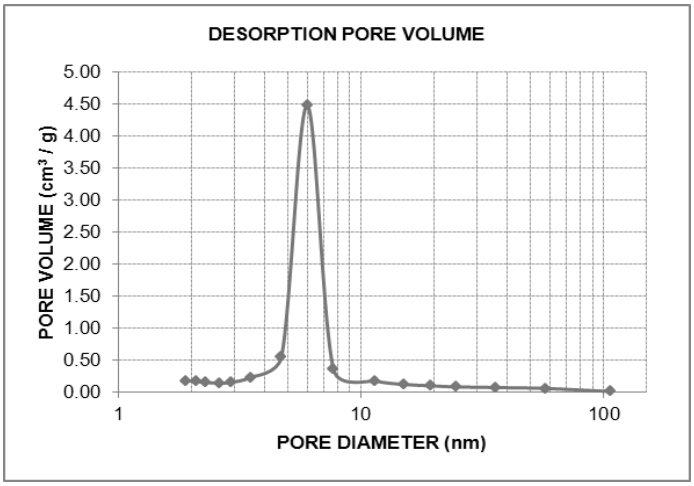
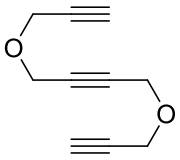


Figure S36: Pore size distribution of **M4**



62

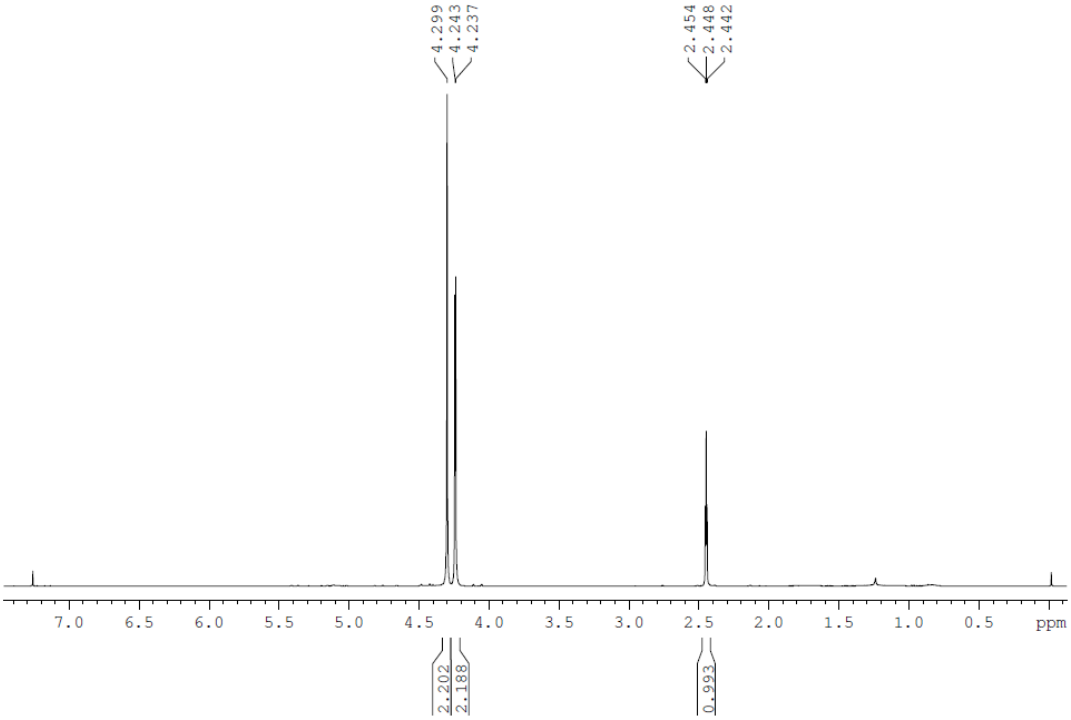
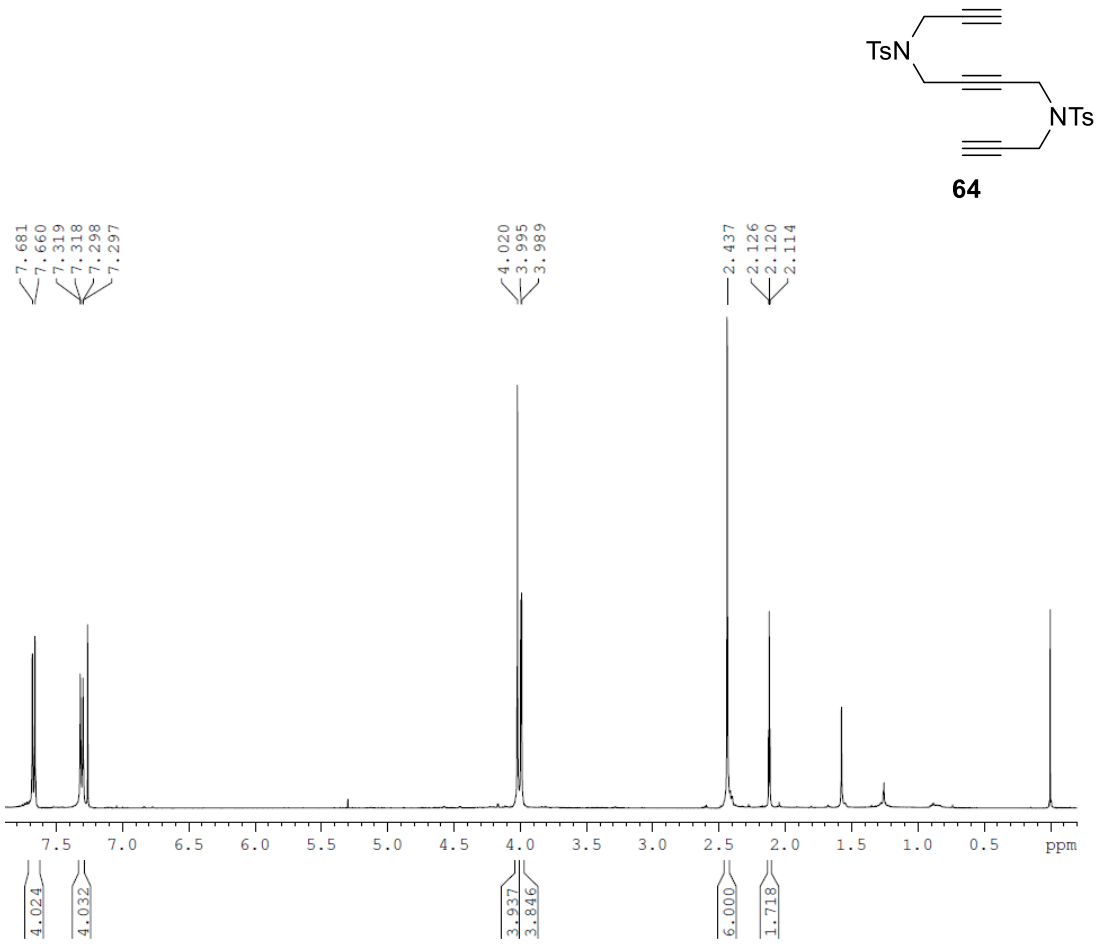


Figure S37: ^{1}H-NMR ($CDCl_3$, 400MHz) of **62**



64

Figure S38: ^{1}H-NMR ($CDCl_3$, 400MHz) of **64**

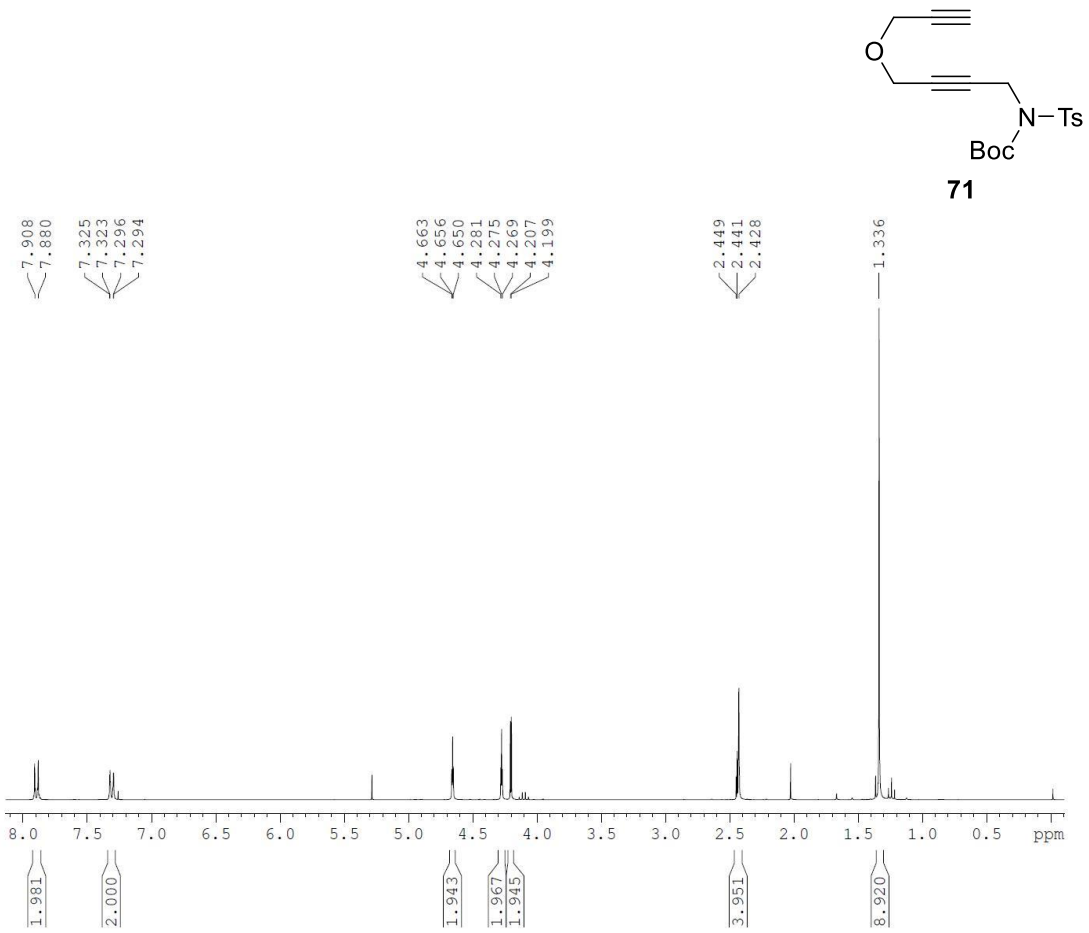


Figure S39: ^{1}H-NMR ($CDCl_3$, 300MHz) of **71**

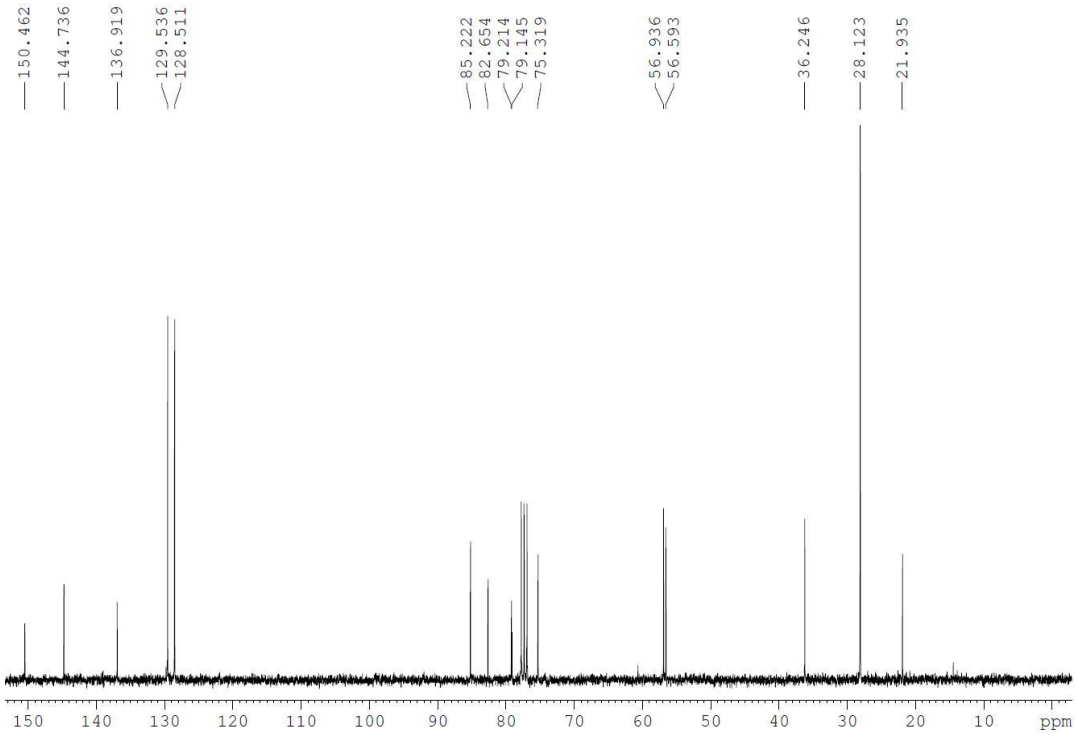


Figure S40: ^{13}C-NMR ($CDCl_3$, 75MHz) of **71**

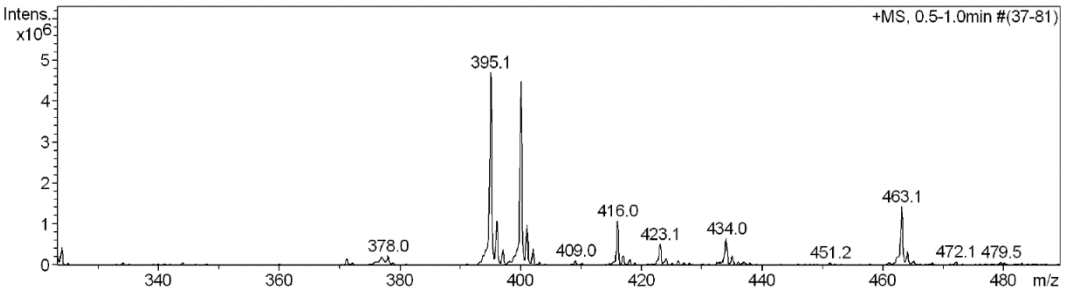


Figure S41: ESI-MS (+) of **71**

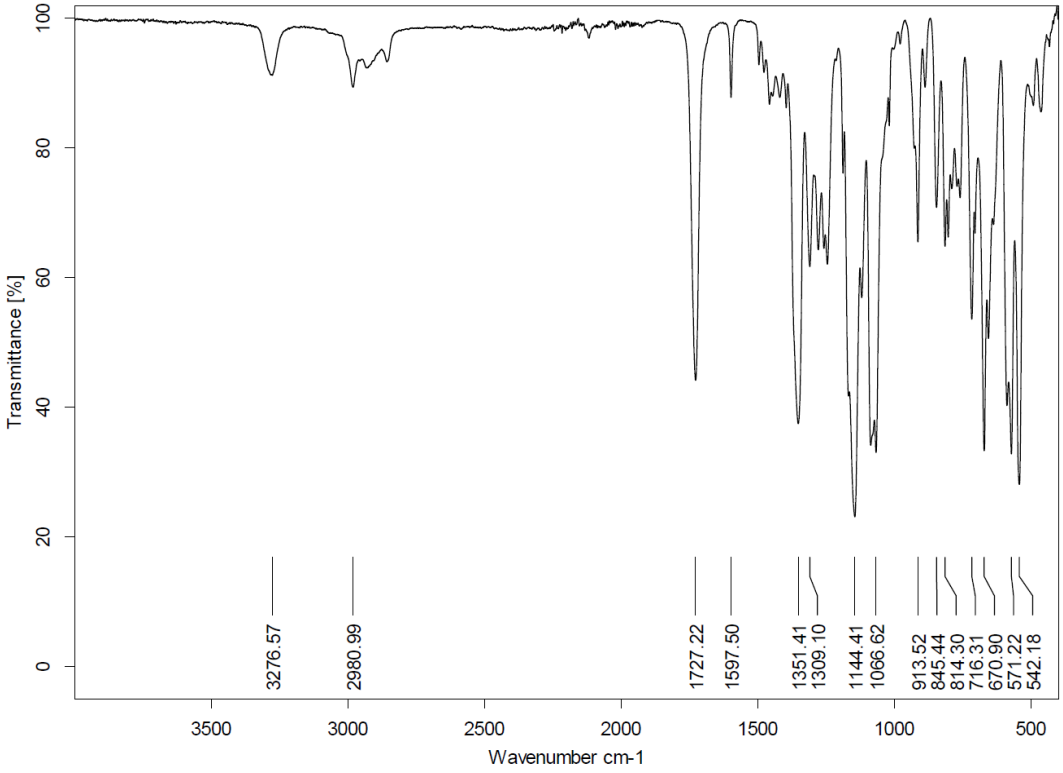


Figure S42: IR (ATR) of **71**

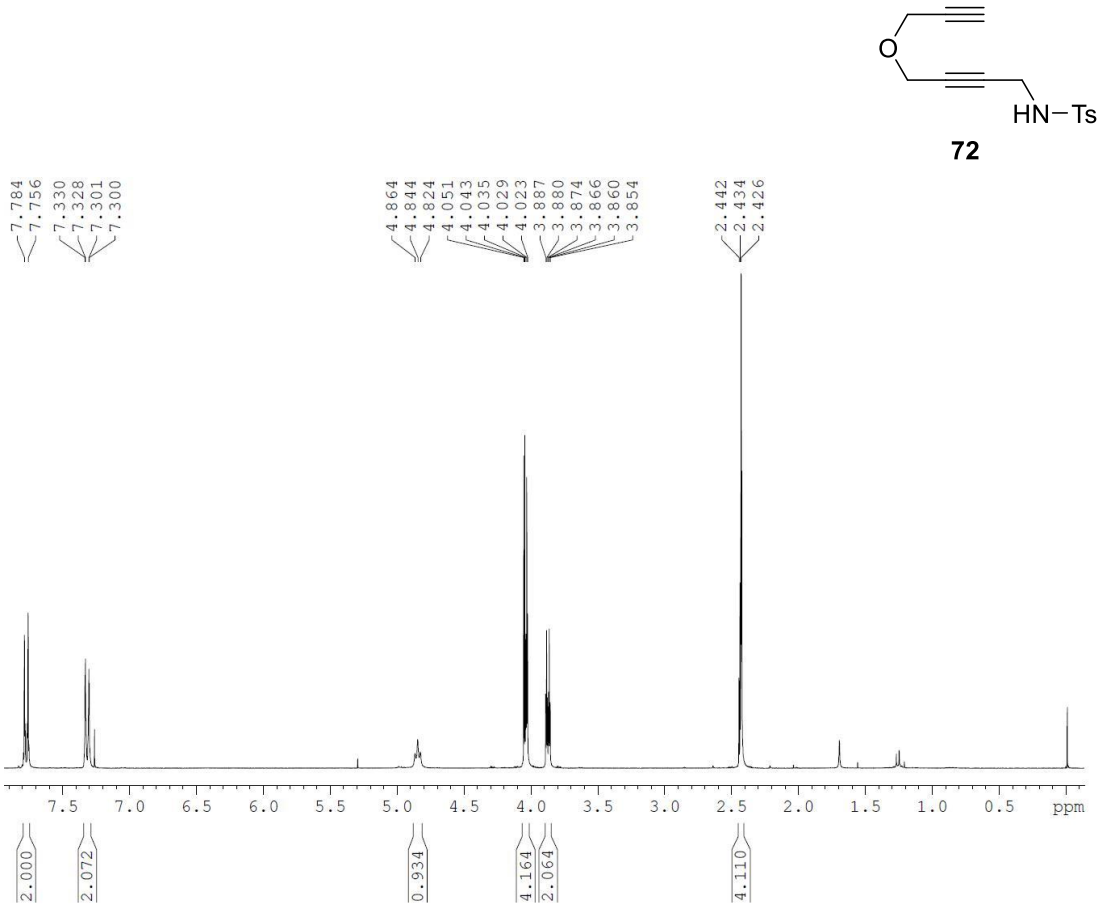


Figure S43: ^{1}H-NMR ($CDCl_3$, 300MHz) of **72**

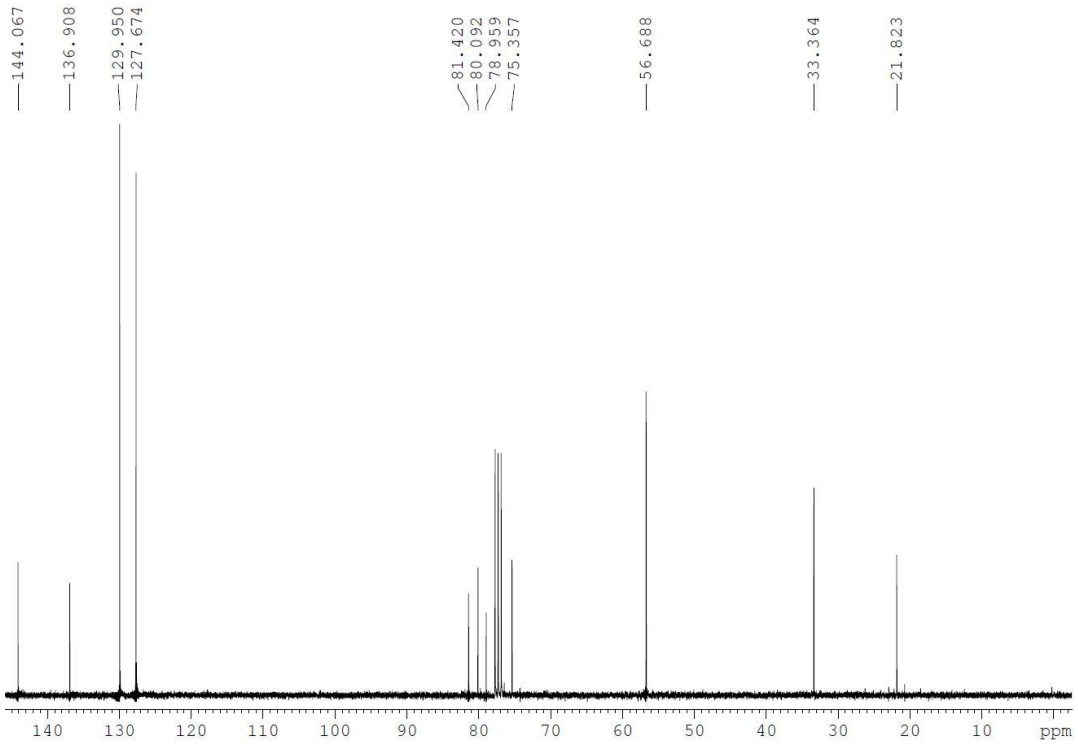


Figure S44: ^{13}C-NMR ($CDCl_3$, 75MHz) of **72**

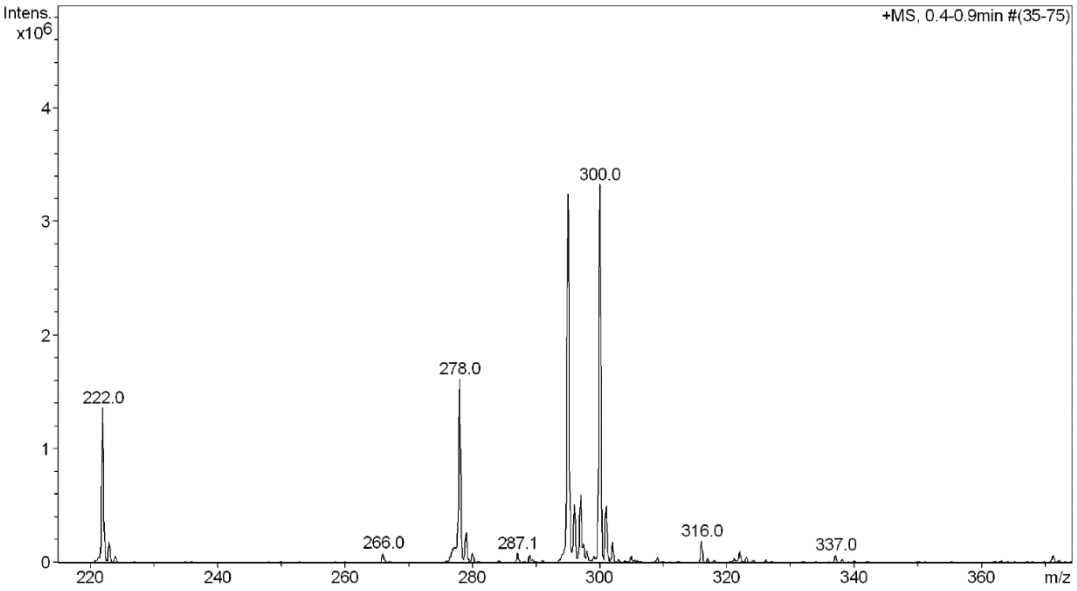


Figure S45: ESI-MS (+) of **72**

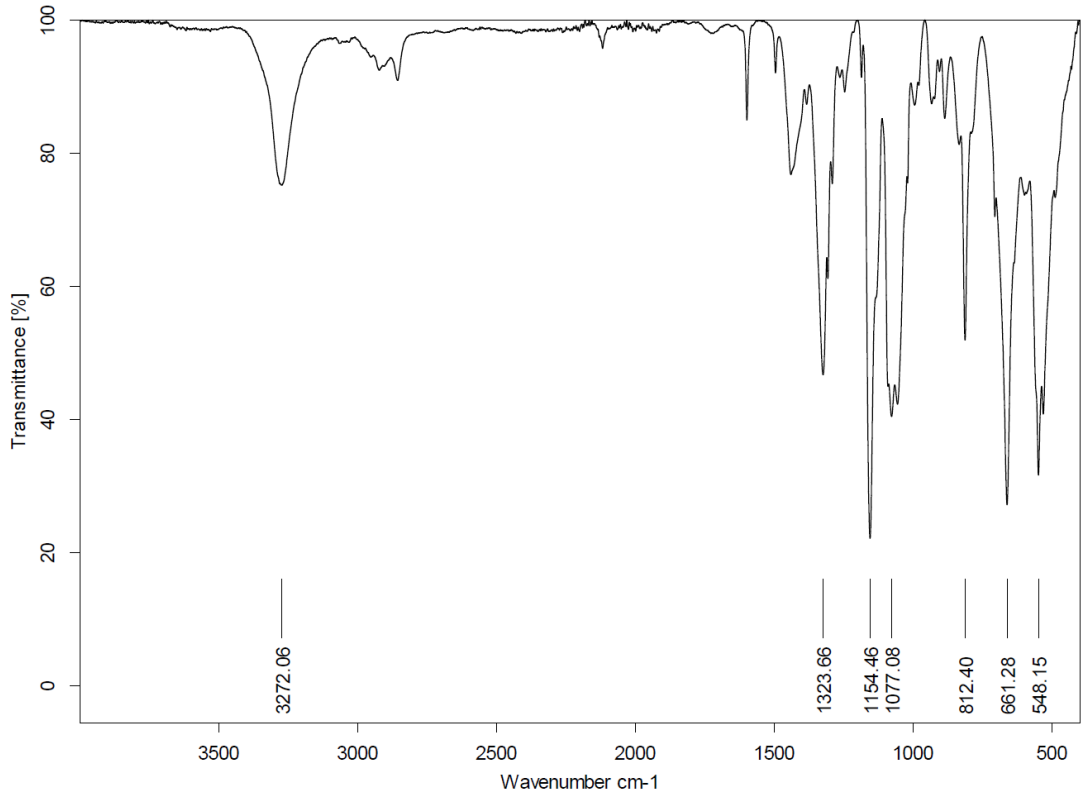
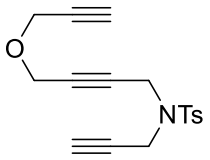


Figure S46: IR (ATR) of **72**



66

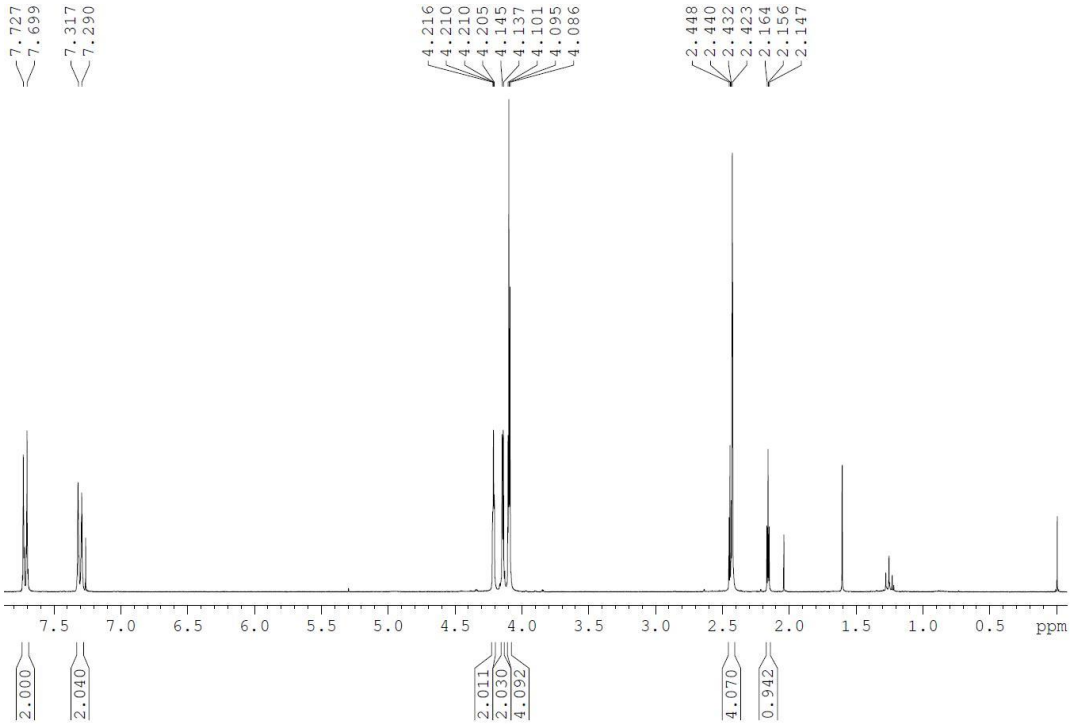


Figure S47: ^{1}H-NMR ($CDCl_3$, 300MHz) of **66**

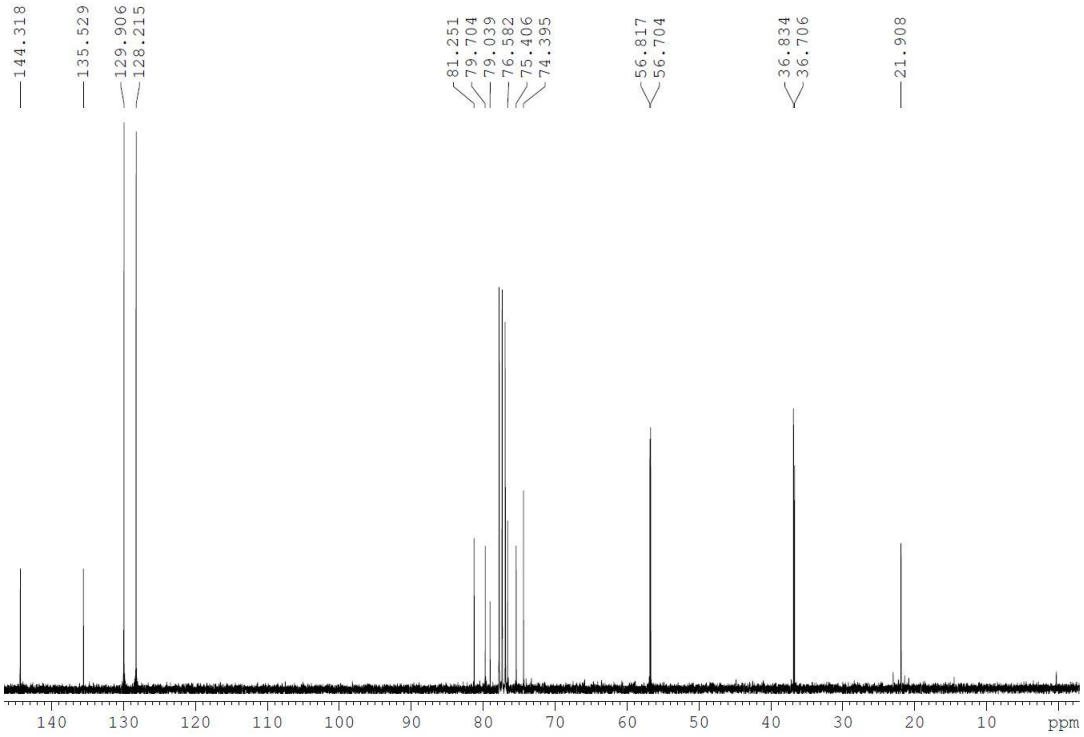


Figure S48: ^{13}C-NMR ($CDCl_3$, 75MHz) of **66**

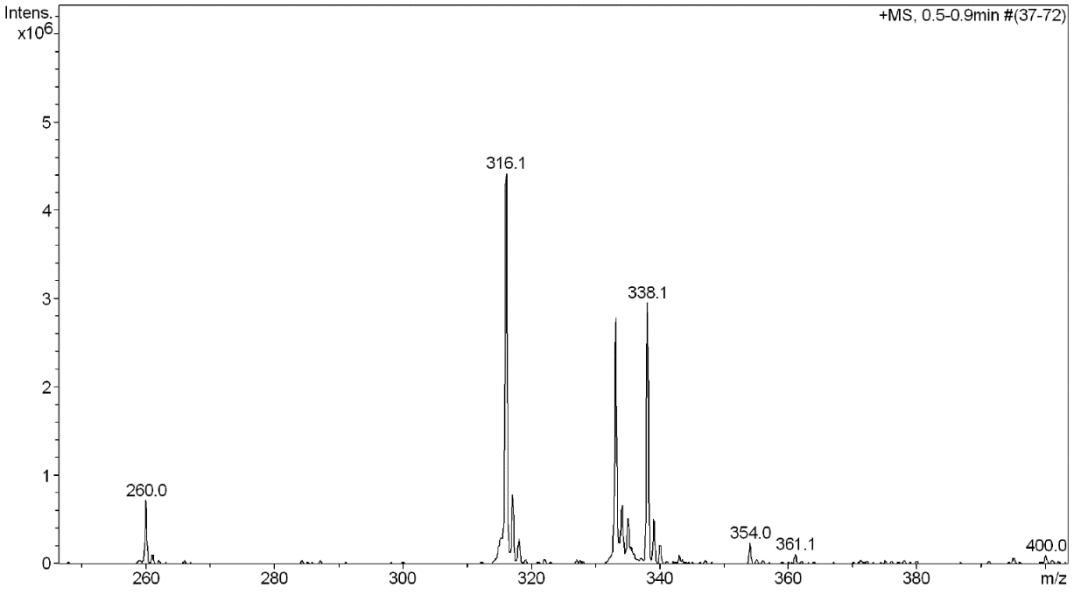


Figure S49: ESI-MS (+) of **66**

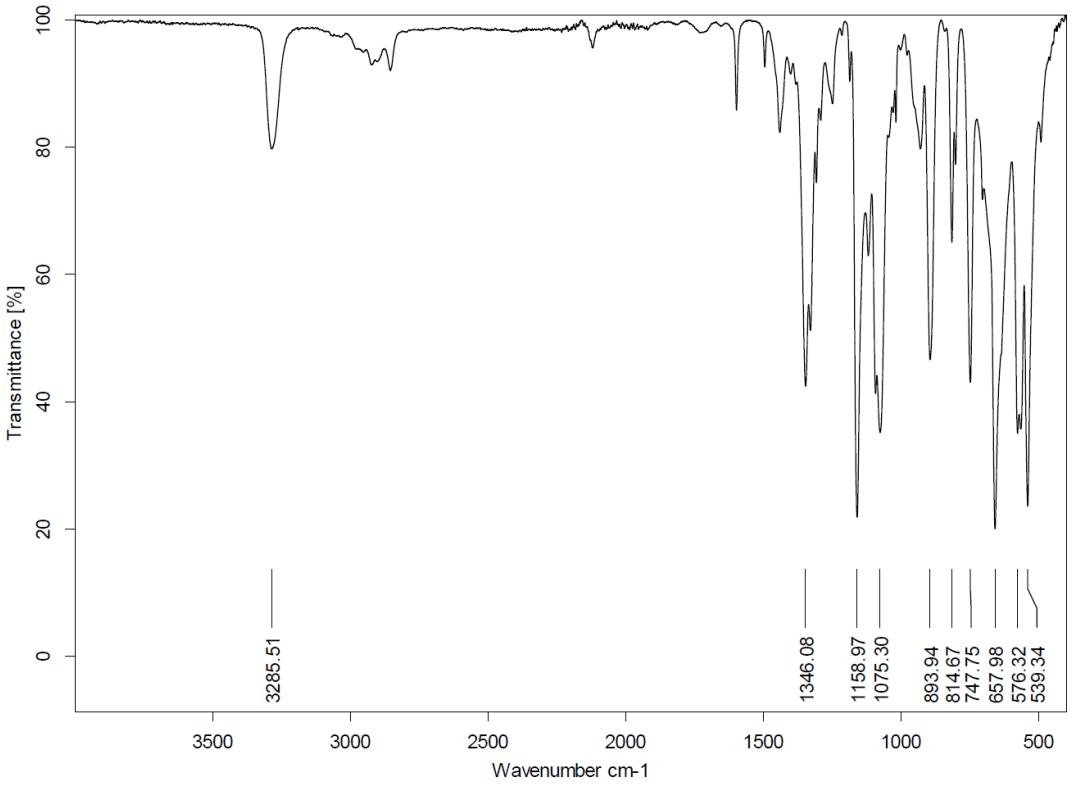
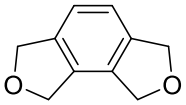


Figure S50: IR (ATR) of **66**



63

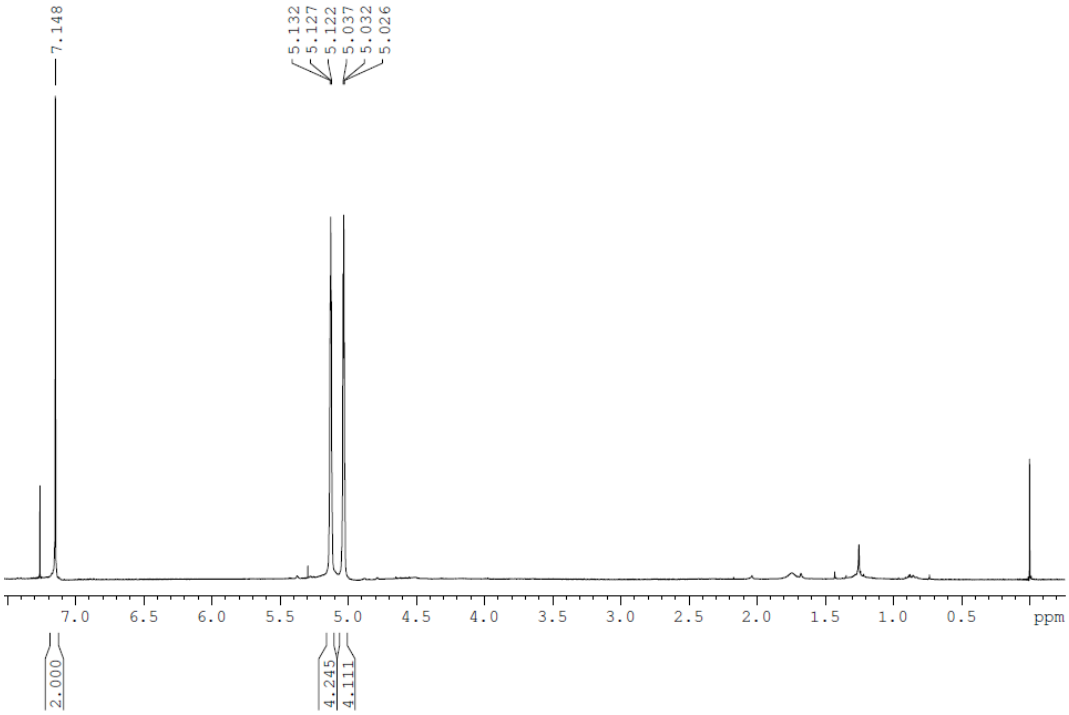


Figure S51: ^{1}H-NMR ($CDCl_3$, 400MHz) of **63**

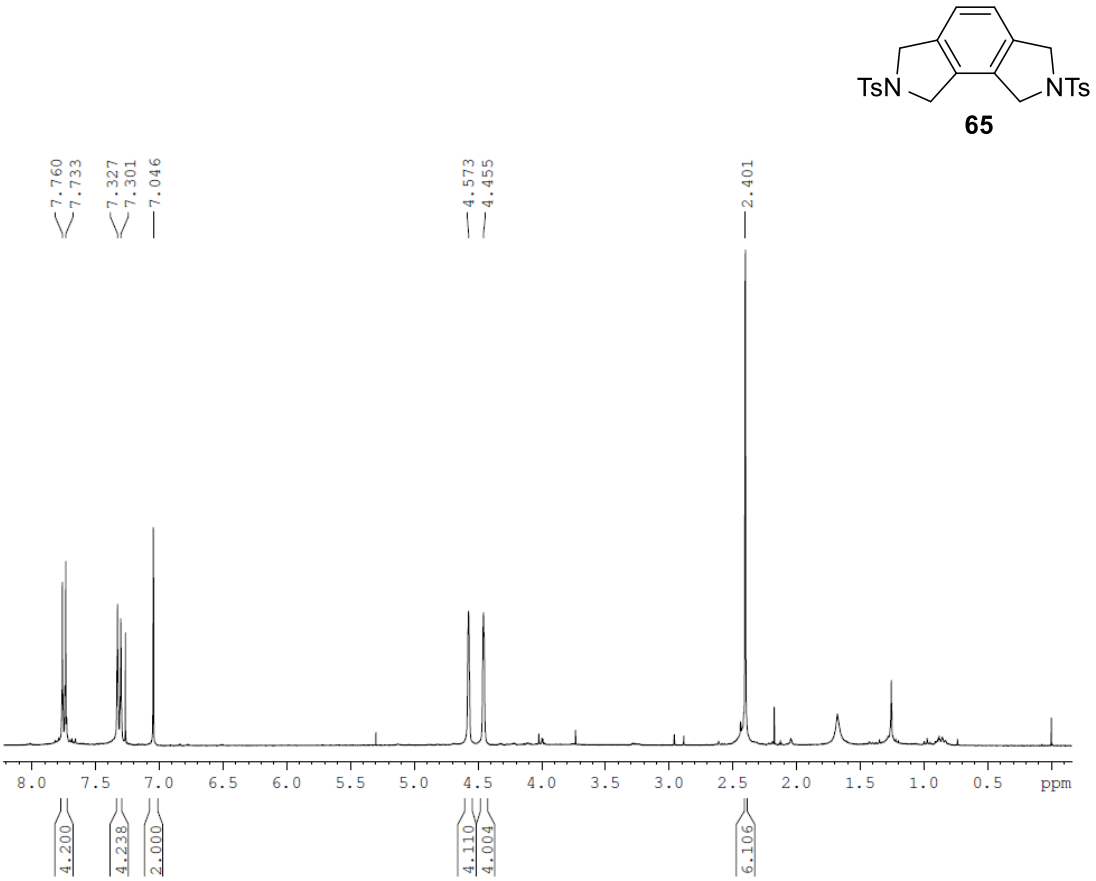
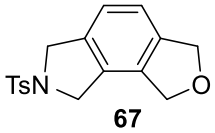


Figure S52: ^{1}H-NMR ($CDCl_3$, 300MHz) of **65**



67

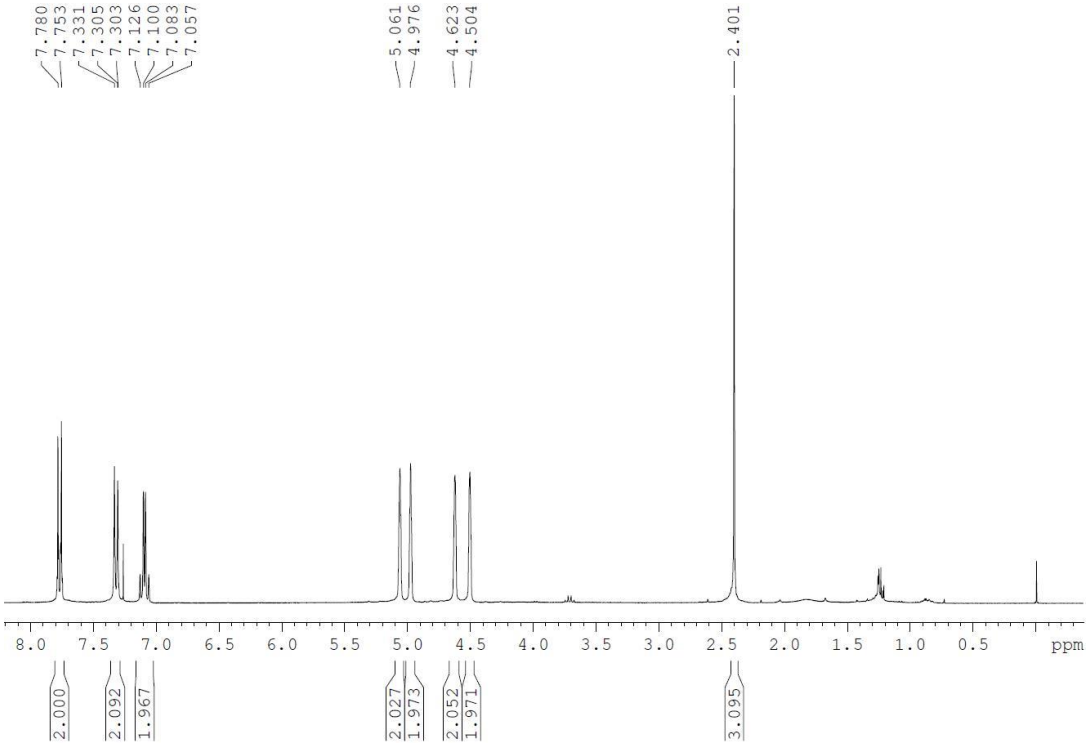


Figure S53: ^{1}H-NMR ($CDCl_3$, 300MHz) of **67**

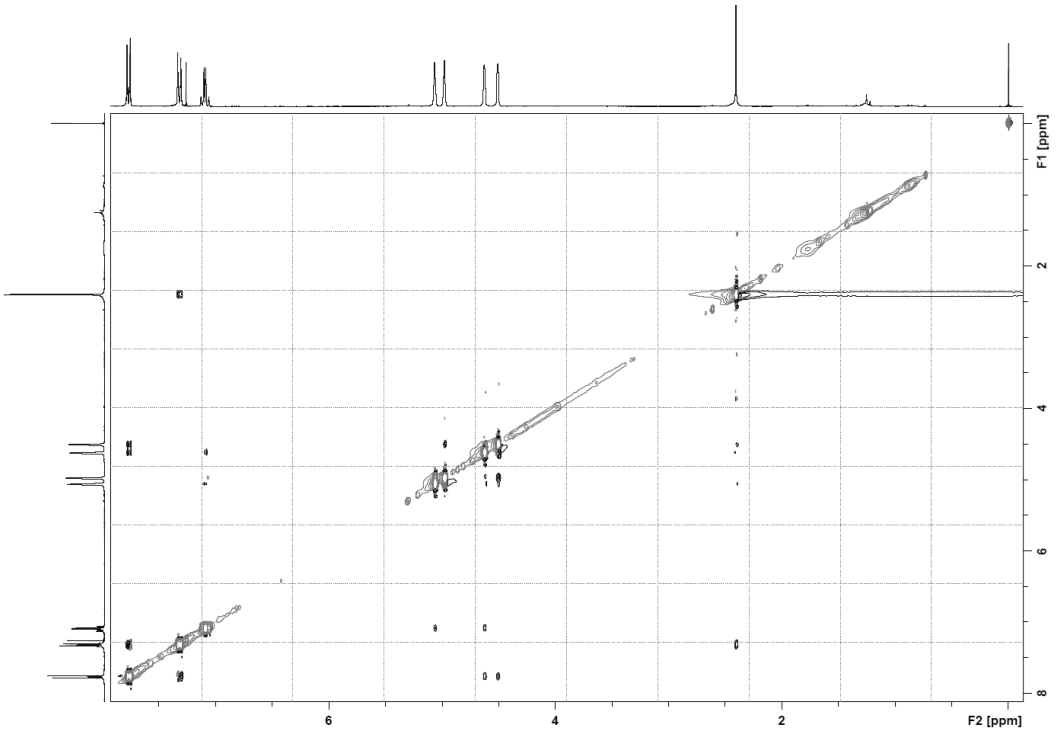


Figure S54: ^{1}H-^{1}H NOESY of **67**

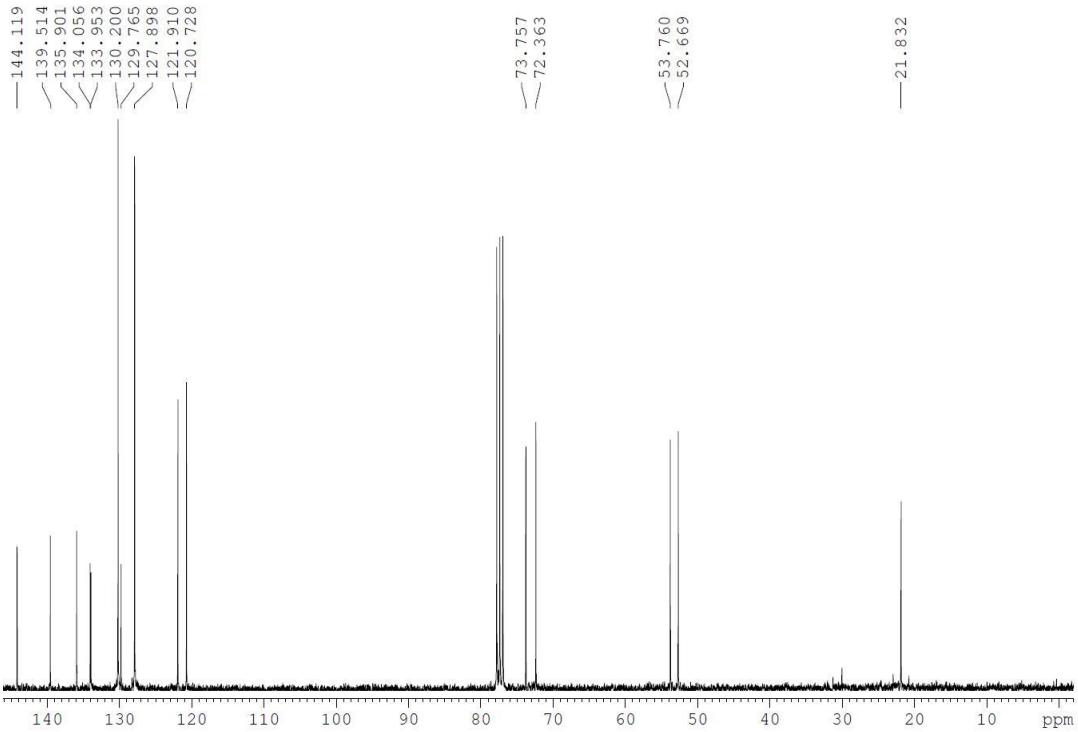


Figure S55: ^{13}C-NMR ($CDCl_3$, 75MHz) of **67**

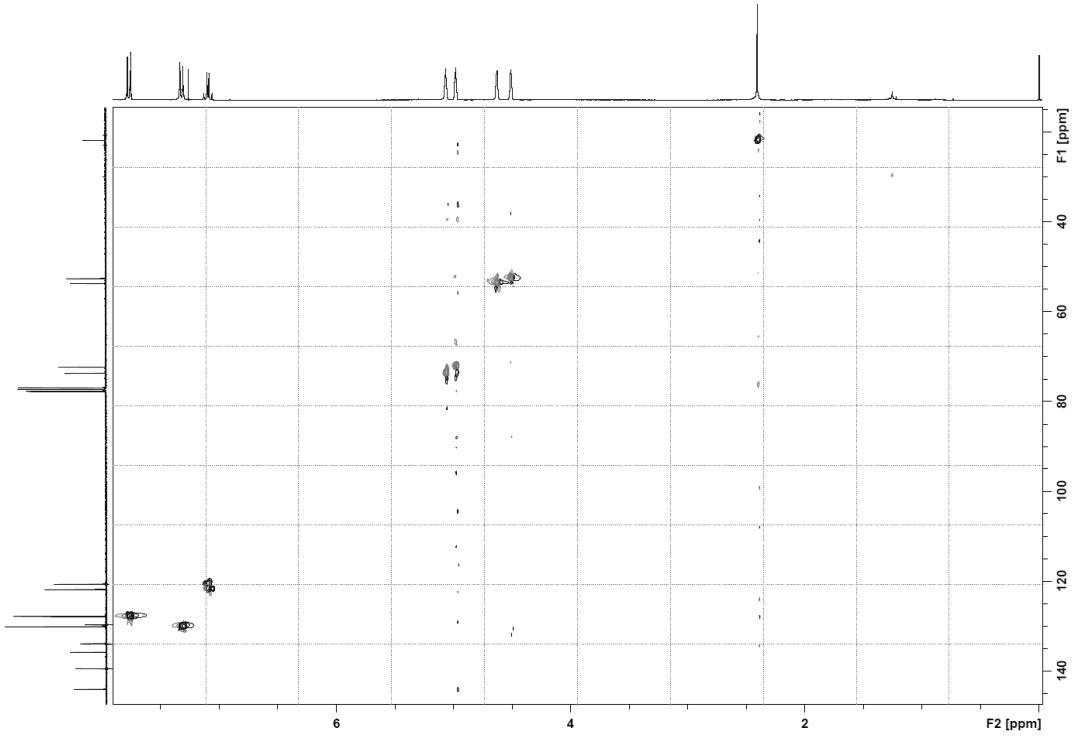


Figure S56: ^{1}H-^{13}C HSQC of **67**

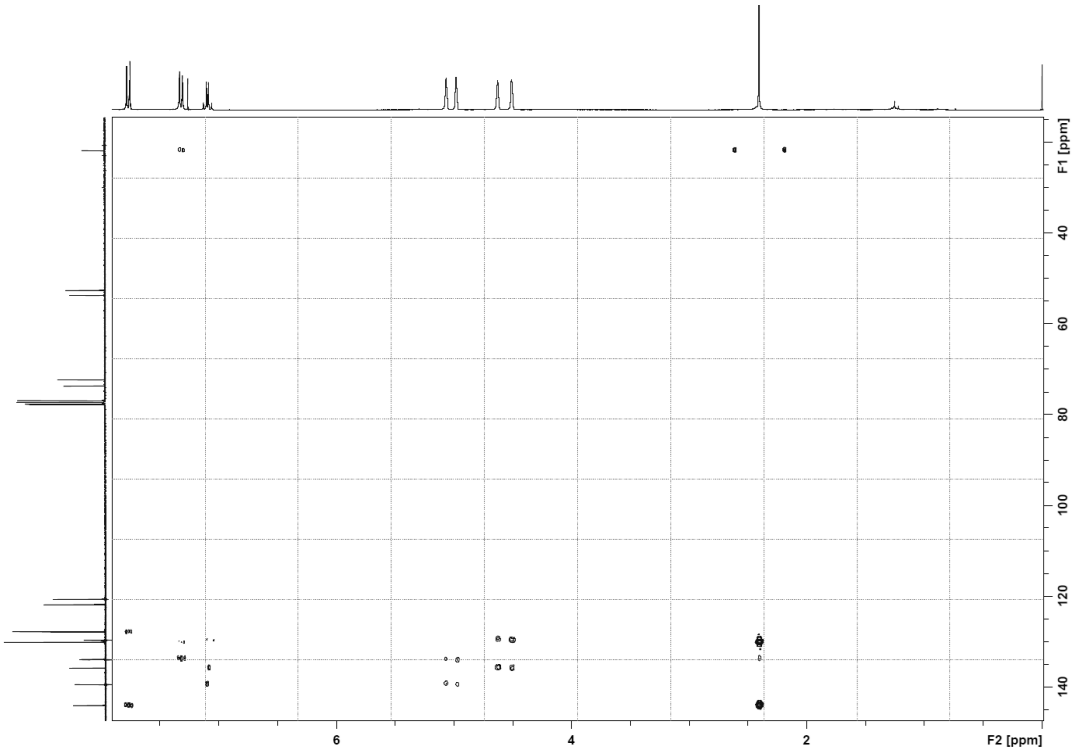


Figure S57: ^{1}H-^{13}C HMBC of **67**

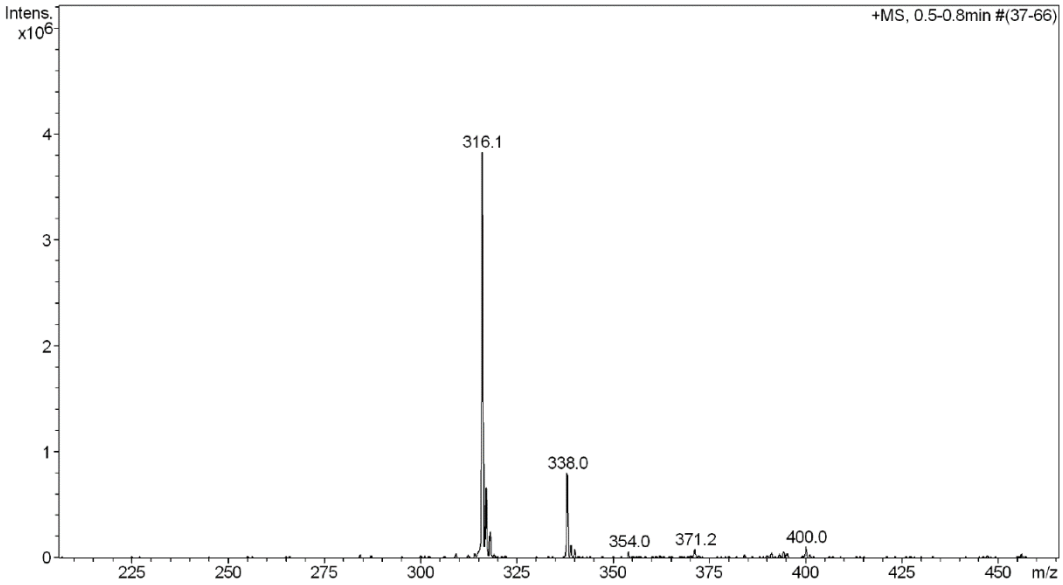


Figure S58: ESI-MS (+) of **67**

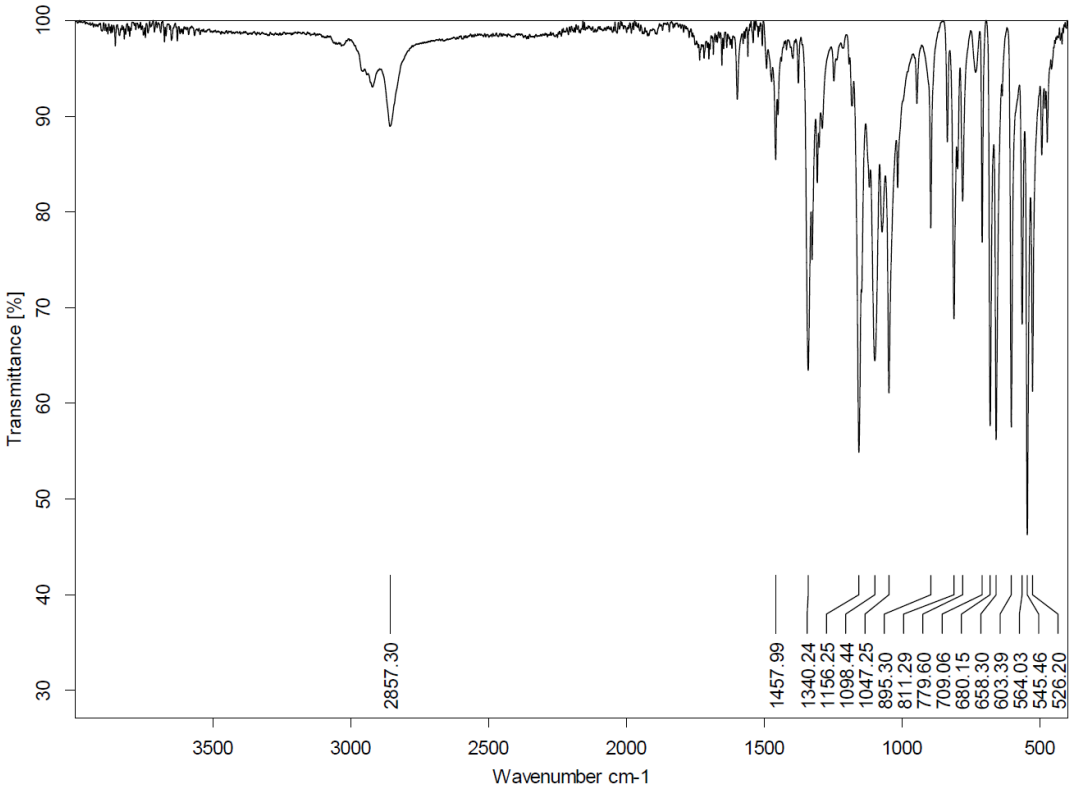


Figure S59: IR (ATR) of **67**

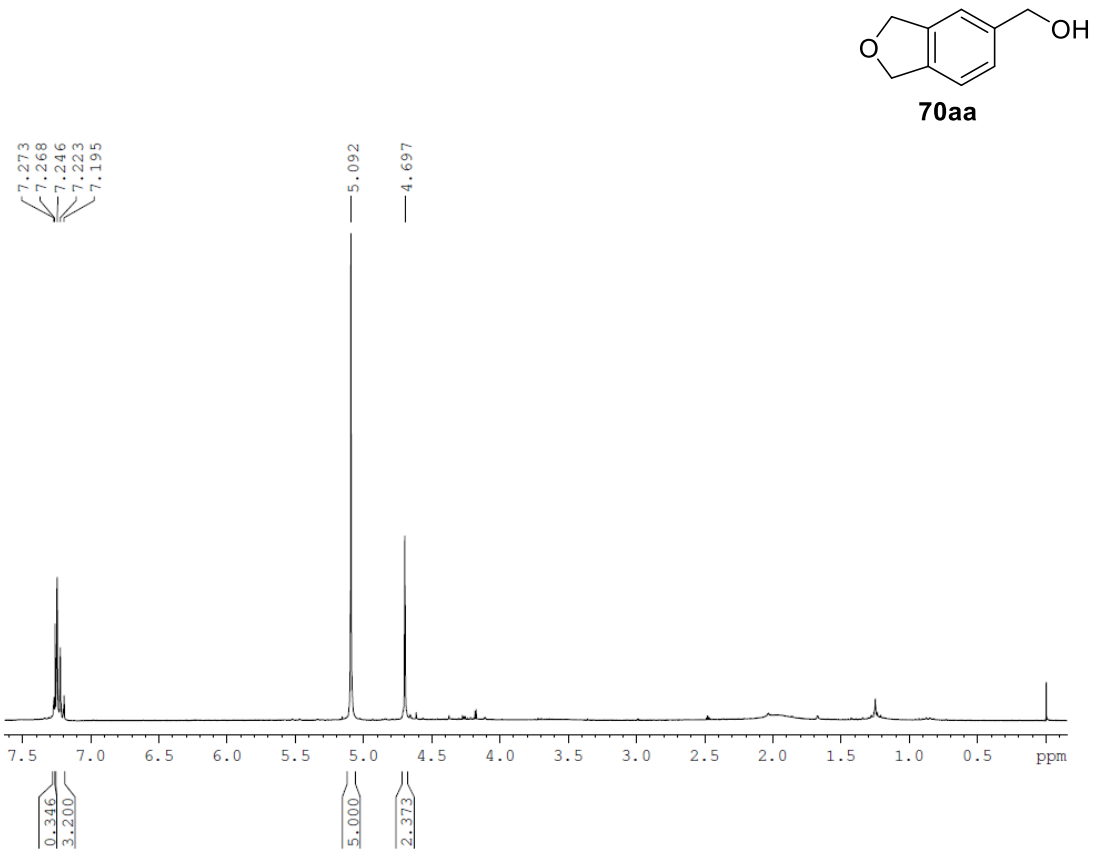
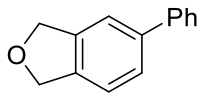


Figure S60: ^{1}H-NMR ($CDCl_3$, 300MHz) of **70aa**



70ab

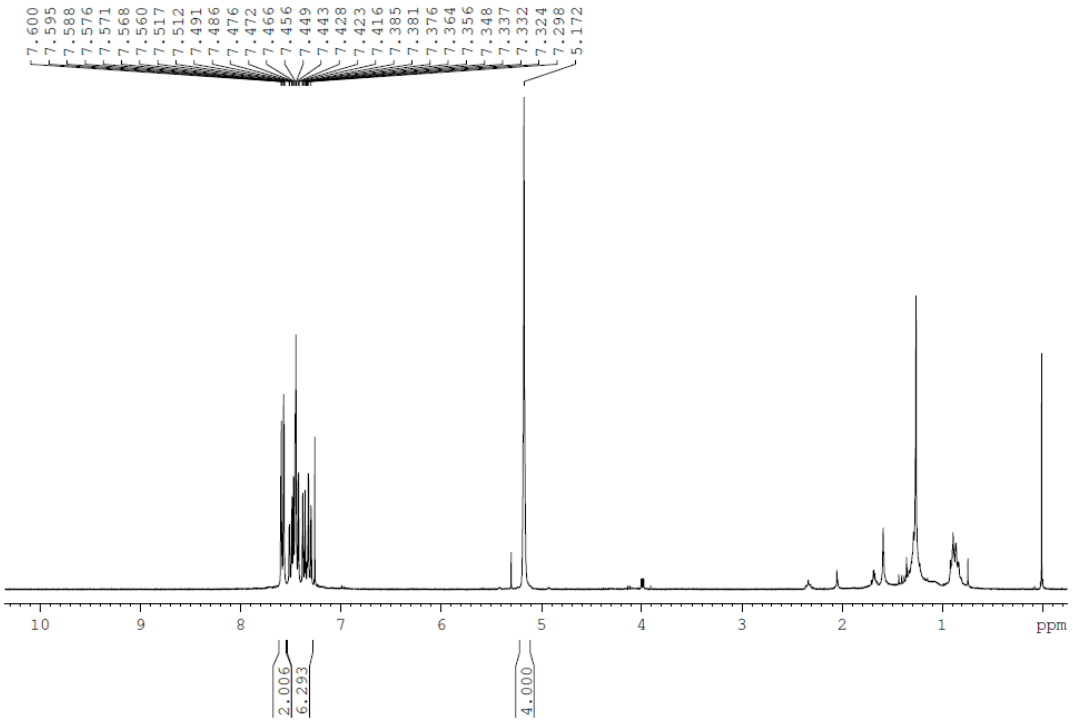


Figure S61: ^{1}H-NMR ($CDCl_3$, 300MHz) of **70ab**

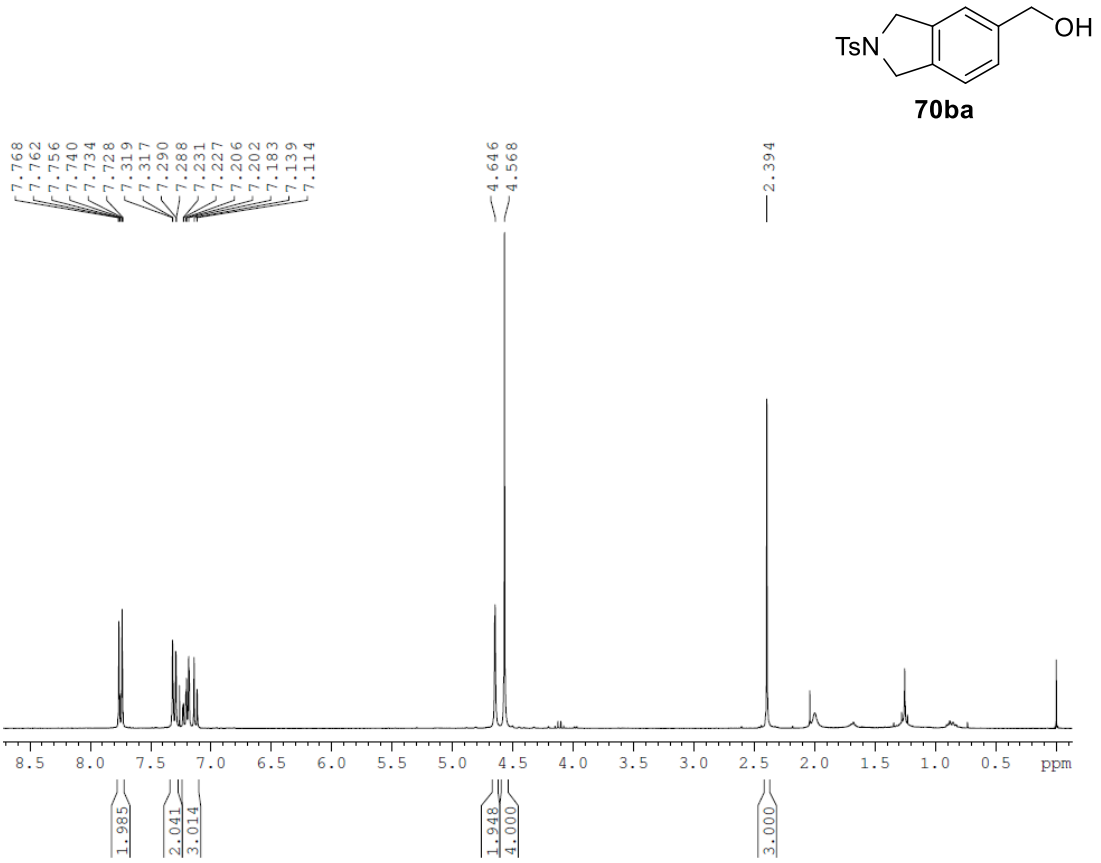


Figure S62: ^{1}H-NMR ($CDCl_3$, 300MHz) of **70ba**

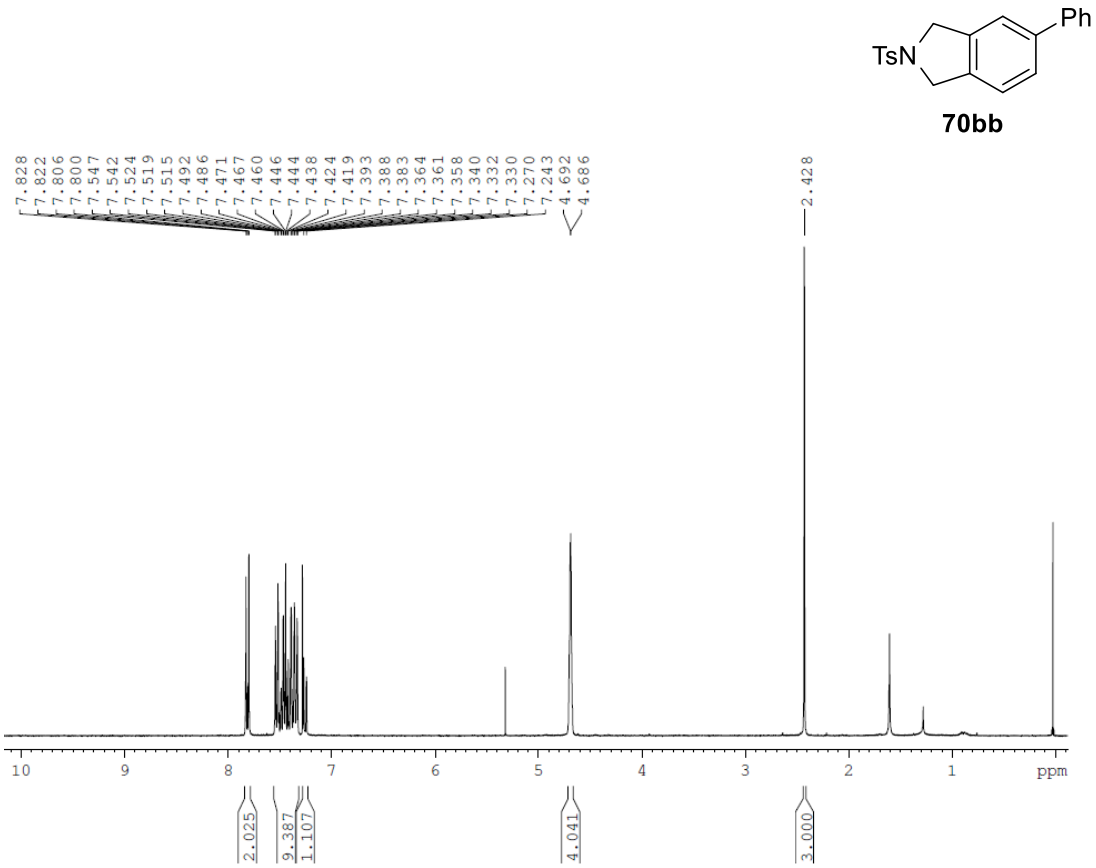


Figure S63: ^{1}H-NMR ($CDCl_3$, 300MHz) of **70bb**

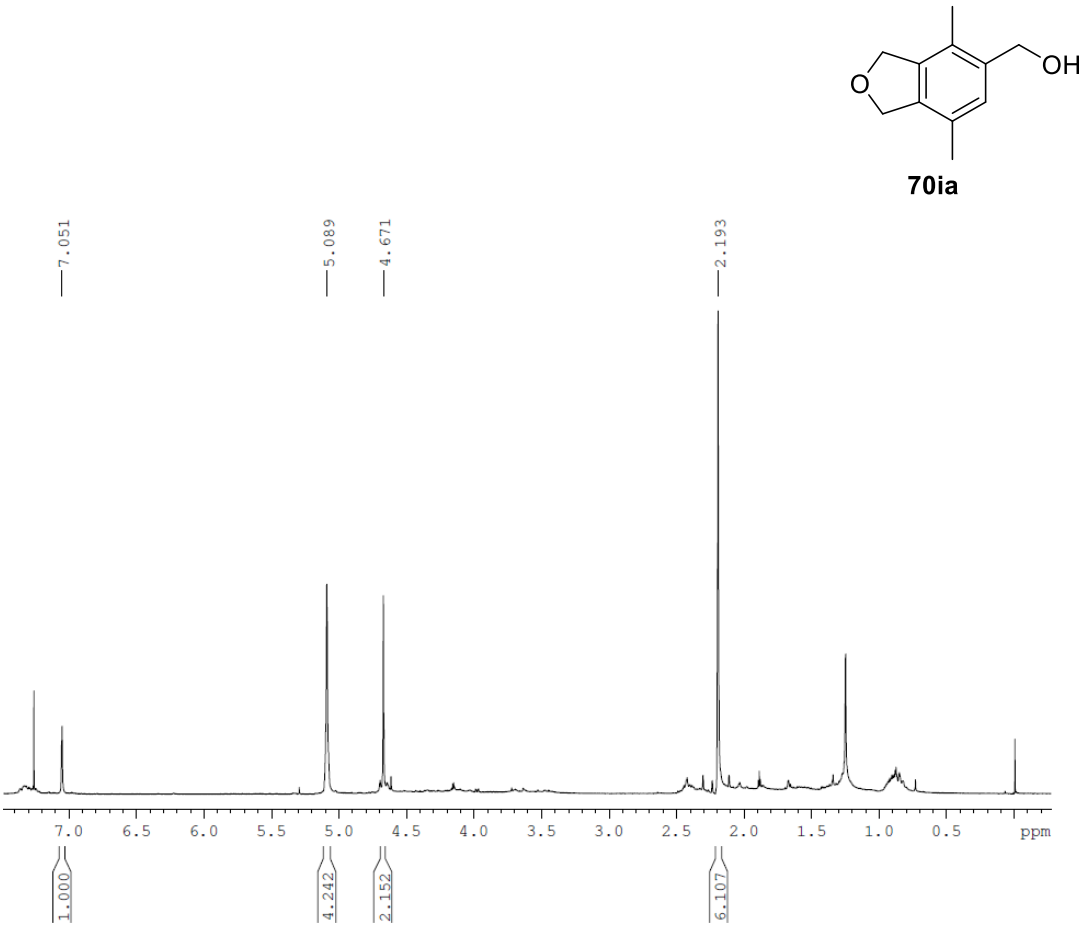


Figure S64: ^{1}H-NMR ($CDCl_3$, 300MHz) of **70ia**

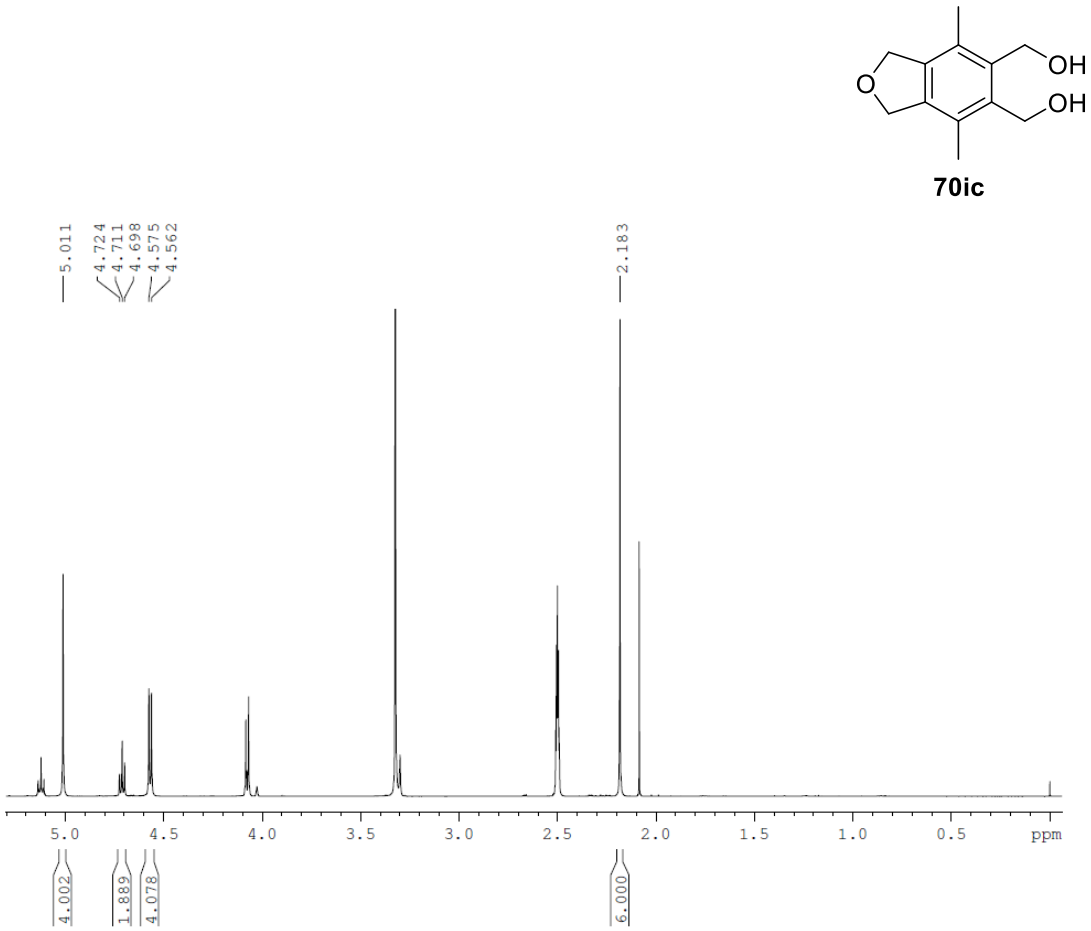


Figure S65: ^{1}H-NMR (DMSO-d_6, 400MHz) of **70ic**