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Theoretical study of the hydroxylation of phenols mediated by an end-on bound superoxo copper(II) complex

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Abstract

Peptidylglycine α-amidating monooxygenase (PAM) and dopamine β-monooxygenase (DβM) are copper containing proteins which catalyse essential hydroxylation reactions in biological systems. There are several possible mechanisms for the reductive O_2-activation at their mononuclear copper active site. Recently, Karlin *et al.* reported on the reactivity of a copper(II)-superoxo complex which is capable of inducing the hydroxylation of phenols with incorporated oxygen atoms derived from the Cu(II)–O_2·$^-$ moiety. In the present work the reaction mechanism for the abovementioned superoxo complex with phenols has been studied. The pathways found are analysed with the aim of providing some insight into the nature of the chemical and biological copper-promoted oxidative processes with 1:1 Cu(I)/O_2-derived species.

Keywords

Copper enzymes, mononuclear copper complexes, hydroxylation of phenols, density functional theory (DFT), B3LYP functional.

Introduction

Reductive activation of molecular oxygen is a common strategy for the generation of active-oxygen species in metalloenzymes. Peptidylglycine α-amidating monooxygenase (PAM) and dopamine β-monooxygenase (DβM) are copper containing proteins which catalyse essential hydroxylation reactions in biological systems.[1-3] These enzymes possess a similar active site consisting of a mononuclear copper ion supported by two histidine imidazoles and one methionine sulphur. The peptidylglycine α-hydroxylating monooxygenase (PHM) component of PAM catalyzes the first step of the C-terminal amidation of glycine-extended peptides and DβM catalyzes the conversion of dopamine to norepinephrine, the neurotransmitter in the central nervous system. Two of the electrons required for the O_2-activation process are stepwise supplied from an external reductant through another mononuclear copper site ligated by three histidine imidazoles, which is largely separated in space from the O_2-reaction center.[4]

There are several possible mechanisms for the reductive O_2-activation at a mononuclear copper active site (Scheme 1).[5] The reaction of copper(I) and O_2 could produce a copper(II)-superoxo species (**S**) or a copper(III)-peroxo species ($\mathbf{P_1}$). The subsequent transfer of another electron could afford a copper(II)-peroxo intermediate ($\mathbf{P_2}$), whose protonation would give a copper(II)-hydroperoxo complex (**H**). The donation of a hydrogen atom to **S** or $\mathbf{P_1}$ could also lead to a hydroperoxo intermediate **H**. Furthermore, O–O bond homolysis of **H** could take place to give a copper(III)-oxo species (**O**). The copper(II)-hydroperoxo species **H** has been suggested as the key reactive intermediate in PHM and DβM.[6] However, recent enzymatic studies [7, 8] as well as theoretical studies [9-13] have indicated that the copper(II)-superoxo species **S** is more likely to be the reactive species for the C–H bond activation of the substrates. Moreover, the X-ray structure of PHM at 1.85 Å resolution,[2] clearly shows the existence of dioxygen bound in an end-on fashion compatible with a copper(II)-superoxo formulation. In addition to **S** and **H**, the possibility of the mononuclear copper(III)-oxo species (**O**) as the key reactive intermediate in DβM has been examined by theoretical calculations using the QM/MM method.[11] Recent structural and spectroscopical studies on a series of biomimetic model compounds have provided new valuable insights into the key reactive intermediates involved in the dioxygen

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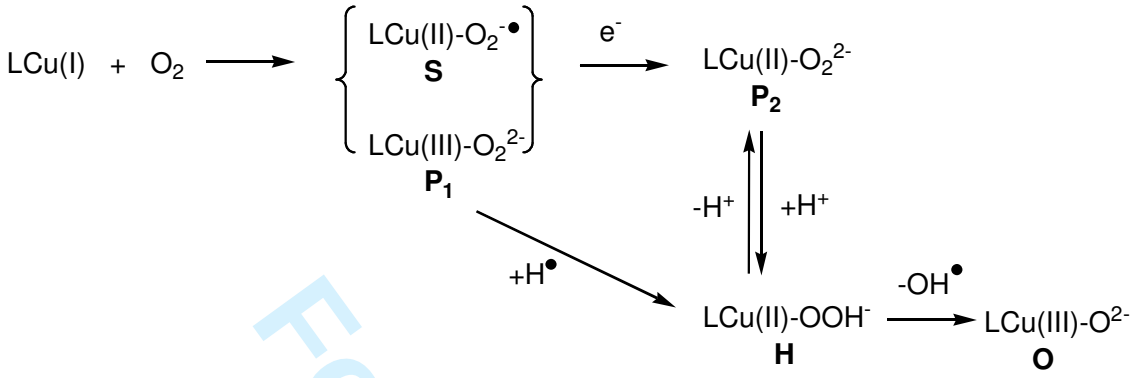
processing at the mononuclear copper reaction centers in biological systems.[5, 14-21] The mononuclear copper(II)-hydroperoxo (**H**) and copper(II)-superoxo species (**S**) have been widely investigated using several model compounds[5, 16-19, 22-27]



Scheme 1: A possible mechanism for reductive O_2-activation at a mononuclear copper active site.[5]

The reactivity of the **S** complex appears to be similar to that known for other M-superoxo species.[28-31] When these complexes intervene in reactions with phenols, initial H-abstraction (i.e., $M–O_2^{\cdot-}$ + ArOH → M–OOH + ArO•) is implicated but it may not be the rate-limiting step.[28] The quinone and the hydroperoxide products observed could be explained from reactions of initially formed ArO• and its further interactions with a $M–O_2^{\cdot-}$ complex. However, a number of different mechanisms have been suggested, including those that do not derive from initial $M–O_2^{\cdot-}$/ArOH H-atom abstraction chemistry.[29, 30, 32-34]

Recently, Karlin *et al.* reported on the reactivity of a copper(II)-superoxo complex with the NMe_2-TMPA (NMe_2-TMPA = tris(4-dimethylamino-2-pyridylmethyl)amine) ligand towards phenol derivative substrates.[19] This is the first report of a reaction of a well-characterized copper(II)-superoxo species with exogenous organic substrates. The reaction of $[Cu(II)(NMe_2\text{-TMPA})\text{-}(O_2^{\cdot-})]^+$ (**A**) with 2,6-di-*tert*-butylphenol (2,6-DTBP) and 2,4,6-tri-*tert*-butylphenol (2,4,6-TTBP) produces only 2,6-di-*tert*-butyl-1,4-benzoquinone (see Scheme 2). The superoxo complex **A** is able to induce hydroxylation and also hydroperoxylation of phenols,[19] with incorporated oxygen atoms derived from the $Cu(II)–O_2^{\cdot-}$ moiety.

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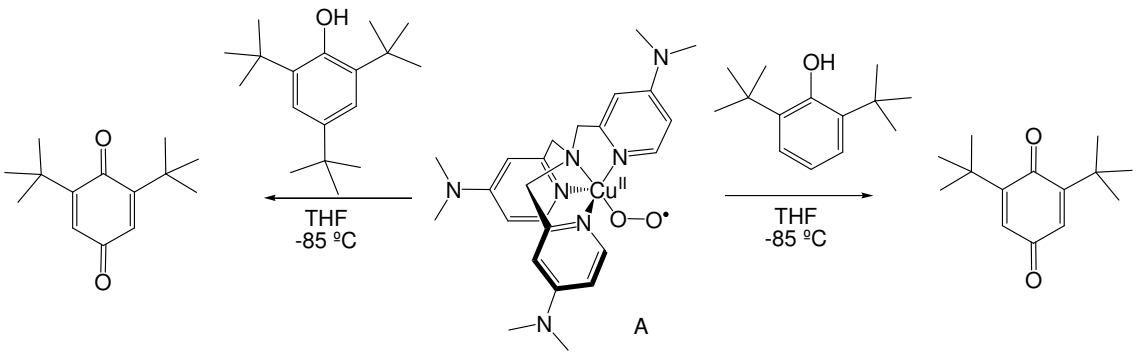

Scheme 2: Experimental results obtained by Karlin and coworkers.[19]

For another mononuclear Cu(II)–O_2·$^-$ complex, the [Cu(II)(TMG_3-tren)-(O_2·$^-$)]$^+$ (TMG_3-tren = 1,1,1-tris([2-*N*^{2}-(1,1,3,3-tetramethylguanidino)]ethyl}amine),[16] Karlin et al. were able to detect the hydroxylation of a methyl group of the coordinated ligand. This superoxo complex also reacts with a number of mono- and diphenolic substrates to the corresponding oxygenated and oxidized products, respectively, including phenoxyl radicals and the C–C coupled products that are typical for copper-dioxygen systems. This chemistry, however, had already been known for the complex **A**.[19] The authors concluded from their observations that the initial step of all hydroxylation reactions is abstraction of a hydrogen atom from a phenol. The decisive question is now whether the hydroxoperoxo intermediate itself is capable to mediate the hydroxylation, or whether OO cleavage has to occur first. In the latter case, a [Cu=O]$^{2-}$ species ([Cu(III)–O·$^-$] or [L·$^+$Cu(II)–O·$^-$]) would form which subsequently attacks the substrate.

In the present work the mechanism for the reaction between superoxo complex **A** and 2,6-DTBP has been studied.[19] The pathways found are analysed with the aim of providing some insight into the nature of the chemical and biological copper-promoted oxidative processes with 1:1 Cu(I)/O_2-derived species.

Methodology

All the calculations were done using the B3LYP[35, 36] hybrid density functional. Open shell systems were treated using broken-symmetry unrestricted formalism. For all the open-shell structures, both the open-shell singlet and the triplet states were considered. Geometry optimizations were performed using a standard valence LACVP basis set as implemented in the Jaguar 5.5 program.[37] For the first-

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and second-row elements, LACVP implies a 6-31G double-ξ basis set. For the copper atoms, LACVP uses a nonrelativistic effective core potential (ECP),[38] where the valence part is described by a double-ξ quality basis set. Local minima were optimized using the Jaguar 5.5 program.[37] Transition states and analytical Hessians (second derivatives of the energy with respect to the nuclear coordinates) for all the stationary points were obtained using the Gaussian 03 program[39] with the same functional and basis set. The Hessians were used to determine the nature of each stationary point and to calculate zero-point energies, thermal corrections, and entropy effects. These two latter terms were computed at -85ºC. Accurate single-point energies were obtained using the cc-pVTZ(-f) basis set[40, 41] for all the atoms but the copper atoms, for which the lacv3p+ effective core potential was used. The self-consistent reaction field method implemented in Jaguar was used to evaluate electrostatic solvation effects using the lacvp* basis set.[42, 43] For the solvent tetrahydrofuran, THF, a dielectric constant of 7.4 was used and the probe radius was set to 2.53 Å. In summary, final free energies given in this work include energies computed at B3LYP/cc-pvTZ(-f)&lacv3p+//B3LYP/lacvp level of theory together with solvent effects obtained with the B3LYP/lacvp* method and zero-point energies, thermal corrections, and entropy effects calculated with B3LYP/lacvp method at -85ºC.

In the literature, several benchmark tests on the accuracy of the B3LYP functional have been performed.[44] On the basis of those results, an average error of 3-5 kcal/mol is expected for the computed relative energies for transition-metal-containing systems.[45]

In the reaction mechanism studied here, we have analyzed three different spin states, namely, the closed and open-shell singlet and the triplet states. It is well-known that the B3LYP functional does not provide the correct spin-ground state of some iron complexes.[46-48] On the other hand, recent validation studies of several density functional theory (DFT) methods[49] have shown the good performance of the OPBE functional for spin-state splittings.[50-54] Consequently, to check whether B3LYP yields the same trends for the spin-state splittings as OPBE, single point calculations at OPBE/cc-pvTZ(-f)&lacv3p+//B3LYP/lacvp level of theory have been carried out for several structures that intervene in the studied reaction mechanism. In particular, we have analyzed the open-shell singlet and triplet of Structures 1, 2, TS12, and 3 of the

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reaction mechanism (*vide infra*). In all the studied cases, B3LYP and OPBE afford the same ground-state, thus providing confidence on the use of B3LYP for the systems analyzed in this work (see Table S32 in the Supporting Information).

The variations of the aromaticity of the substrate in the first step of the reaction have been measured using two aromaticity indexes. As a structure-based measure of aromaticity, we employed the harmonic oscillator model of aromaticity (HOMA) index, defined by Kruszewski and Krygowski as:[55, 56]

$$HOMA = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}\left(R_{opt} - R_i\right)^2 \qquad (1)$$

where *n* is the number of bonds considered, and α is an empirical constant fixed to give HOMA=0 for a model nonaromatic system, and HOMA=1 for a system with all bonds equal to an optimal R_{opt} value assumed to be achieved for fully aromatic systems. For C–C bonds the α value is 257.7 and R_{opt} corresponds to 1.388 Å. R_i stands for a running bond length. This index has been found to be one of the most effective structural indicators of aromaticity.[57, 58] As a magnetic index of aromaticity, we used the NICS, proposed by Schleyer et al.[59] This is one of the most widely employed indicators of aromaticity. It is defined as the negative value of the absolute shielding computed at a ring center or at some other point of interest in the system. Rings with large negative NICS values are considered aromatic. The more negative the NICS value, the more aromatic is the ring. The GIAO method[60] has been used to perform calculations of NICS at ring centers (NICS(0)) determined by the nonweighted mean of the heavy-atom coordinates. As shown by Lazzeretti and Aihara,[61-63] the NICS(0) values contain important spurious contributions from the in-plane tensor components that are not related to aromaticity. So, to complement the NICS analysis, we also calculated the NICS(1) values, that is, NICS measured 1 Å above the centre of the ring. NICS(1) reflects better the aromaticity patterns, because at 1 Å the effects of the π-electron ring current are dominant and local σ-bonding contributions are diminished.[61, 64, 65] Furthermore, we also calculated the out-of-plane component of the NICS(1) value, $NICS_{zz}(1)$, which is considered to describe the π-electron effects even more accurately and is judged to be a better descriptor of aromaticity.[65]

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Results and Discussion

The resonance Raman (rR) spectrum of complex **A**, in THF[19] upon $^{18}O_2$ isotopic substitution shows an O–O stretching frequency consistent with a bound superoxo species.[5, 66, 67] Furthermore, the rR spectrum upon a 1:2:1 stoichiometric mixture of $^{16}O_2/^{16/18}O_2/^{18}O_2$ ($^{16/18}O_2$) shows a Cu–O splitting pattern only consistent with an end-on, η^1 superoxo-Cu binding mode.[68] Still, we decided to study both the η^1 and η^2 superoxo-Cu complexes and take into account the lowest-lying closed-shell and open-shell singlet and triplet spin states.

From the geometrical parameters (see Table 1 and Figure 1), it can be seen that going from the end-on to the side-on structure, the Cu–O_A and the Cu–N_C distances increase by about 0.2 Å while the Cu–O_B distance is reduced by 0.6 Å. Cu(II) usually forms planar four-coordinated complexes, but pentacoordination (square-pyramidal or trigonal-bypiramidal) is also quite frequent. Cu(II) hexacoordinate complexes are less common. In line with this, coordination of a second oxygen atom to form the side-on structure, results in an increase of the distance between the copper and the nitrogen atom N_C of the complex *trans*- to the O_2 moiety, which is pushed out of the coordination sphere of the metal. Since the ligand is not symmetric the distance between the copper atom and each one of the oxygen atoms is not exactly the same. The values of the O_A–O_B bond length in Table 1 as compared to that of molecular oxygen (1.207 Å)[69] are consistent with a superoxide Cu(II)-$O_2^{\cdot -}$ electronic structure.

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Structures	Multiplicity[a]	Distances (Å)							Angle (º)
		$Cu–N_A$	$Cu–N_B$	$Cu–N_C$	$Cu–N_D$	$Cu–O_A$	$O_A–O_B$	$Cu–O_B$	$Cu-O_A-O_B$
End-on	*so*	2.10	2.09	2.13	2.11	1.96	1.35	2.78	112.7
	s	2.06	2.09	2.12	2.08	1.91	1.34	2.74	113.0
	t	2.10	2.09	2.15	2.11	1.98	1.33	2.80	113.7
Side-on[b]	*so*	2.18	2.06	2.36	2.12	2.18	1.35	2.12	69.2
	t	2.19	2.08	2.34	2.12	2.21	1.33	2.16	70.0

[a] *so* refers to the open-shell singlet spin state, *s* to the closed-shell singlet spin state and *t* to the triplet spin state.

[b] The side-on closed-shell singlet state converts to the end-on isomer during the geometry optimization process.

Table 1: Comparison of geometrical parameters for the η^1 and η^2 superoxo structures of the synthetic complex used in this study.

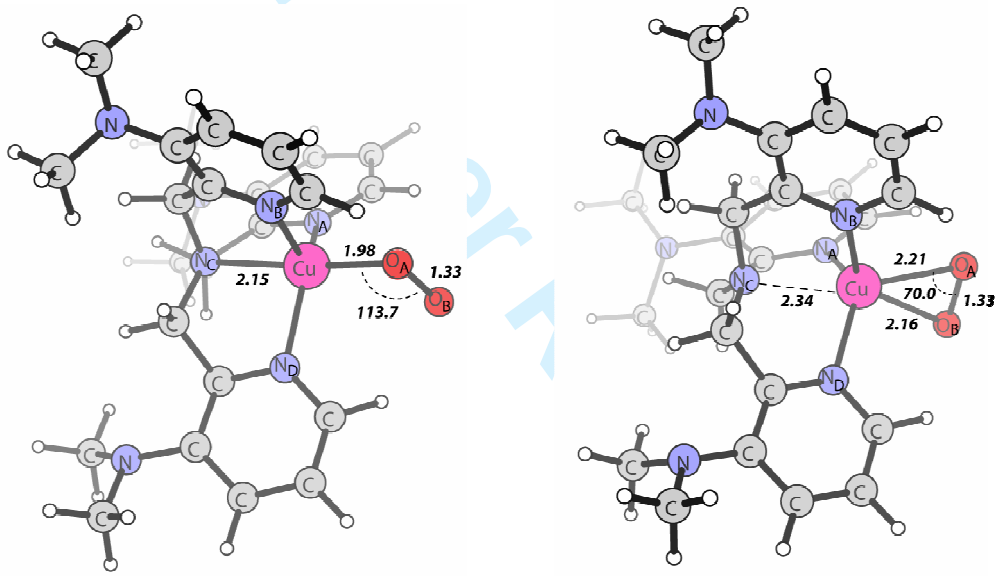

Fig. 1: End-on (left) and side-on triplet spin state structures for the synthetic complex studied by Karlin and coworkers.

When comparing the free energies of the different spin states studied for the end-on and the side-on structures, the triplets are always the most stable ones (see Table 2). DFT calculations are not fully reliable in computing energies for singlet open-shell species.[70, 71] Nevertheless, the energy difference between singlet open-shell and the triplet states in our system is large enough to be fairly confident that the order of the spin-state energies will not be changed by the use of a more sophisticated level of

theory. The singlet-triplet energy gap is larger for the side-on than for the end-on structure in this kind of species as reported in previous studies.[27, 72] The closed-shell singlet has only been found for the end-on structure and in this case it is 23.1 kcal/mol higher in energy than the corresponding triplet. For this reason, only the open-shell singlet and triplet spin states are going to be taken into consideration in our study. Furthermore, for both the open-shell singlet and triplet spin states, the end-on structure is always around 8 kcal/mol more stable than side-on structure. It should be mentioned that frequency calculations show that, for the two spin-states, the end-on structures correspond to minima while side-on structures are transition states connecting two end-on structures.

In the open-shell singlet and triplet spin state structures for **A** most of the spin density is found in the copper atom and in the superoxide moiety. As can be seen in Table 2, for the end-one structures, the singlet state has the two unpaired electrons localized in the Cu and O_2 moieties, thus in accordance with an end-on superoxide Cu(II)-O_2·$^-$ electronic structure, while for the most stable triplet state one of the electrons is clearly localized on the O_2 moiety, and the other is almost equally shared between Cu and O_2.

Structures	Multiplicity [a]	Spin density							ΔG (kcal/mol)
		Cu	N_A	N_B	N_C	N_D	O_A	O_B	
End-on	*so*	0.46	0.02	0.04	0.08	0.02	-0.13	-0.49	3.7
	s	-	-	-	-	-	-	-	23.1
	t	0.40	0.02	0.04	0.06	0.03	0.68	0.78	0.0
Side-on	*so*	0.47	0.01	0.06	0.00	0.03	-0.30	-0.26	14.2
	t	0.37	0.00	0.05	0.00	0.03	0.77	0.79	8.6

[a] *so* refers to the open-shell singlet spin state, *s* to the closed-shell singlet spin state and *t* to the triplet spin state.

Table 2: Spin density and free energies at different spin states for the η^1 and η^2 superoxo structures of the synthetic complex used in this study.

Experimentally the complex is EPR silent. At this point, it is interesting to remark that the ground state for a similar complex, [Cu(η^1-O_2)TMG_3tren]$^+$, did not exhibit an X-band EPR spectrum, which is consistent with the compound having either a triplet or singlet structure. However, the paramagnetic NMR spectrum, together with

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the solution magnetic susceptibility, provided evidence for the ground triplet spin state at least under experimental conditions.[27, 72, 73] Our results also point out that the ground state for the studied complex is a triplet.

To date few copper compounds have been reported to exhibit ground-state triplet electronic structures. Another recent example is a copper(II) compound containing an arylnitroxyl ligand,[27, 72] which exists predominantly in the triplet state at temperatures between 100 and 300K. The preference for the triplet spin state has been suggested to arise from the high-spin density on the nitroxyl, geometrically orthogonal to the orbital containing the unpaired electron on copper.

The analysis of the two singly occupied molecular orbitals (SOMOs) in the triplet state of the $[Cu(II)(NMe_2\text{-}TMPA)(O_2{\cdot}^-)]^+$ complex (Figure 2) is fully consistent with the spin density values given in Table 2. Thus, one of the unpaired electrons is mainly located in the out-of-plane π* molecular orbital (MO) of dioxygen (SOMO1 in Fig. 2), while the other corresponds mainly to the antibonding combination between the filled d_z^2 orbital on copper and the in-plane singly occupied π* MO on dioxygen with which it overlaps. As discussed by Cramer, splitting of the O_2 π* levels due to hybridization of one of these orbitals with the d_z^2 is apparently too weak to overcome the exchange energy required to pair the electrons in the lower-energy noninteracting out-of-plane O_2 π* MO.[74] Interestingly, as discussed by Cramer et al. stronger electron-donating ligands in *trans*- position with respect to the O_2 moiety should stabilize the singlet relative to the triplet state because of the higher mixing between the d_z^2 and the in-plane π* SOMO. Finally, like in the case of the copper(II) compound containing an arylnitroxyl ligand,[27, 72] the two SOMO orbitals are almost orthogonal to each other.

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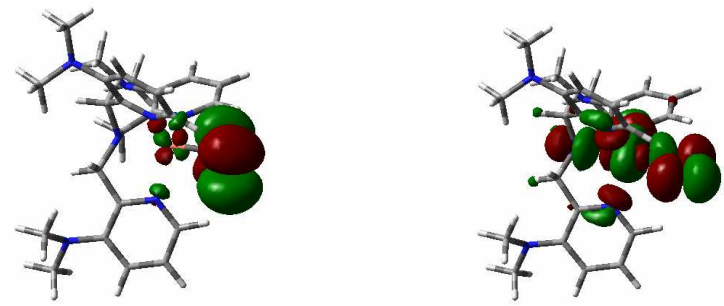

SOMO1 SOMO2

Fig. 2: Single occupied molecular orbitals (SOMOs) for the calculated triplet ground state of $[Cu(II)(NMe_2\text{-}TMPA)(O_2^{\cdot-})]^+$. See text for a detailed description.

In order to reduce the size of the studied system, we decided to replace the NMe_2 substituents of the ring by hydrogen atoms (see Fig. 3). In the new model, the geometry of the core (Table 3) and the spin density values as well as the relative energies of the different electronic states studied (see Table 4), are almost identical to the ones of the complete system (Tables 1 and 2).

Structures	Multiplicity [a]	Distances (Å)							Angle (º)
		Cu–N_A	Cu–N_B	Cu–N_C	Cu–N_D	Cu–O_A	O_A–O_B	Cu–O_B	Cu-O_A-O_B
End-on	*so*	2.10	2.09	2.17	2.11	1.97	1.34	2.78	112.9
	t	2.10	2.09	2.19	2.10	1.99	1.33	2.80	113.7
Side-on	*so*	2.06	2.11	2.43	2.18	2.14	1.35	2.17	73.2
	t	2.08	2.11	2.41	2.18	2.18	1.33	2.21	73.6

[a] *so* refers to the open-shell singlet spin state and *t* to the triplet spin state.

Table 3: Comparison of geometrical parameters for the model used in this study.

Structures	Multiplicity [a]	Spin density							ΔG (kcal/mol)
		Cu	N_A	N_B	N_C	N_D	O_A	O_B	
End-on	*so*	0.44	0.02	0.04	0.07	0.02	-0.12	-0.46	5.3
	t	0.37	0.02	0.03	0.05	0.03	0.71	0.80	0.0
Side-on	*so*	0.45	0.06	0.04	0.00	0.00	-0.26	-0.28	12.8
	t	0.35	0.04	0.03	0.00	0.00	0.80	0.79	9.6

[a] *so* refers to the open-shell singlet spin state and *t* to the triplet spin state.

Table 4: Spin density and free energies at different spin states for the model used in this study.

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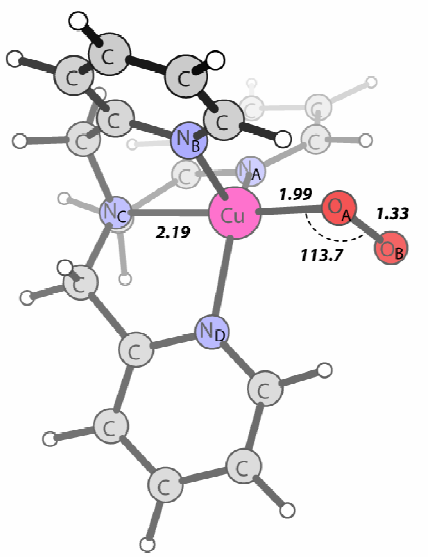
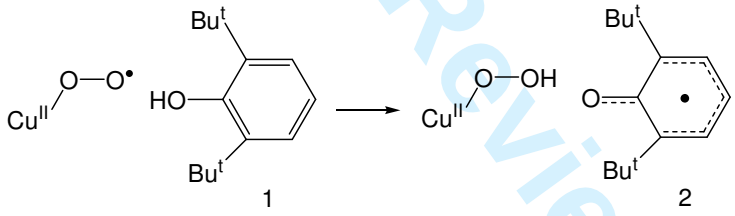


Fig. 3: End-on triplet spin structure of the model of the synthetic complex studied by Karlin and coworkers used in the present study.

The reaction starts with the end-on form of the complex. First of all, a hydrogen atom transfer takes place, which means that one proton and one electron are transferred at the same time (see Scheme 3 and Fig. 4).



Scheme 3: First hydrogen transfer in the studied system (1→2).

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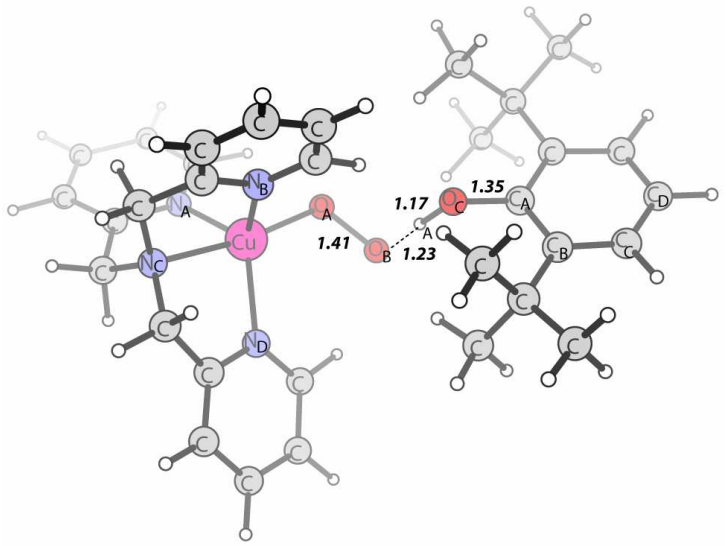


Fig. 4: Fully optimized transition state for the triplet state for the first hydrogen transfer (TS12). Distances are in angstroms.

For the triplet spin state of the product, the distance between the oxygen atom O_B of the complex and the proton from the hydroxyl group of the substrate is reduced from 2.07 (1.97 for the open-shell singlet) to 1.0 Å, while the O–O distance increases from 1.34 (1.35 for the open–shell singlet) to 1.48 Å, which would correspond to a peroxide O–O bond distance (see Table 5). In the substrate, there are also important changes in the bond distances. The O_C–C_A and C_B–C_C distances decrease, while the C_A–C_B and C_C–C_D increase (see Figure 4).

Structures	Multiplicity [a]	Distances (Å)							
		Cu–O_A	O_A–O_B	O_B–H_A	H_A–O_C	O_C–C_A	C_A –C_B	C_B –C_C	C_C –C_D
1	*so*	1.96	1.35	1.97	0.98	1.43	1.42	1.41	1.39
	t	1.98	1.34	2.07	0.98	1.43	1.42	1.41	1.39
TS12	*so*	1.94	1.41	1.27	1.14	1.35	1.45	1.40	1.40
	t	1.95	1.41	1.23	1.17	1.35	1.45	1.40	1.40
2	*so*	1.93	1.48	1.00	1.72	1.30	1.47	1.39	1.41
	t	1.93	1.48	1.00	1.72	1.30	1.47	1.39	1.40

[a] *so* refers to the open-shell singlet spin state and *t* to the triplet spin state.

Table 5: Comparison of geometrical parameters for the structures that intervene in the hydrogen transfer.

Before the hydrogen transfer, no spin density is observed in the substrate. However, once the reaction has taken place, the oxygen B has lost almost all the spin

density, while there is one electron delocalized in the ring (Table 6), which partially loses its aromaticity (*vide infra*).

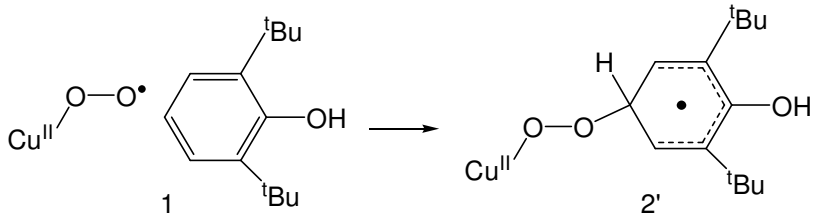
The triplet spin state of Structure 1 is 4.6 kcal/mol more stable than the open-shell singlet. The barrier for the hydrogen transfer is 9.40 kcal/mol for the triplet spin state, whereas TS12 for the open-shell singlet is placed at 13.07 kcal/mol respect to the triplet spin state of Structure 1 (see Table 6).

Structures	Multiplicity [a]	Spin density								ΔG (kcal/mol)
		Cu	N_A	N_B	N_C	N_D	O_A	O_B	Substrate	
1	*so*	0.49	0.03	0.09	0.03	0.04	-0.17	-0.49	0.00	4.6
	t	0.42	0.03	0.03	0.07	0.03	0.69	0.73	0.01	0.0
TS12	*so*	0.46	0.02	0.06	0.03	0.03	0.07	-0.17	-0.68	13.1
	t	0.43	0.03	0.03	0.06	0.02	0.52	0.37	0.54	9.4
2	*so*	0.45	0.03	0.03	0.05	0.02	0.35	0.07	-0.92	5.4
	t	0.45	0.03	0.03	0.05	0.02	0.35	0.08	0.99	4.7

[a] *so* refers to the open-shell singlet spin state and *t* to the triplet spin state.

Table 6: Spin density at different spin states for the structures that intervene in the hydrogen transfer.

We also took into account the possibility of a direct attack of the copper superoxo at the *para*-carbon of the substrate (Scheme 4). The energy barrier found for this step is 30.3 kcal/mol for the triplet spin state and 30.5 kcal/mol for the open-shell singlet spin state. The product of the direct attack (Structure 2') is 29.7 kcal/mol high in energy with respect to the initial Structure 1 for the triplet spin state and 29.4 kcal/mol for the open-shell singlet spin state. As we will see in the next paragraphs, the transition state with the highest energy in our proposed reaction mechanism is about 7 kcal/mol more stable than the most stable transition state found for this step. Consequently, the possibility of a direct attack of the copper superoxo at the *para*-carbon of the substrate has to be discarded.



Scheme 4: Direct attack of the copper superoxo at the *para*-carbon of the substrate (1→2').

Scheme 3 indicates that in the first step of the reaction there is a reduction of the aromaticity of the substrate. To obtain more information of how the aromaticity changes we decided to compute the HOMA, a structural index, and a series of NICS indexes as magnetic descriptors (see Computational Details). Since the two faces of the ring are not completely equivalent, we decided to compute the NICS(1) and NICS(1)$_{zz}$ in both sides of the ring (see Fig. 5).

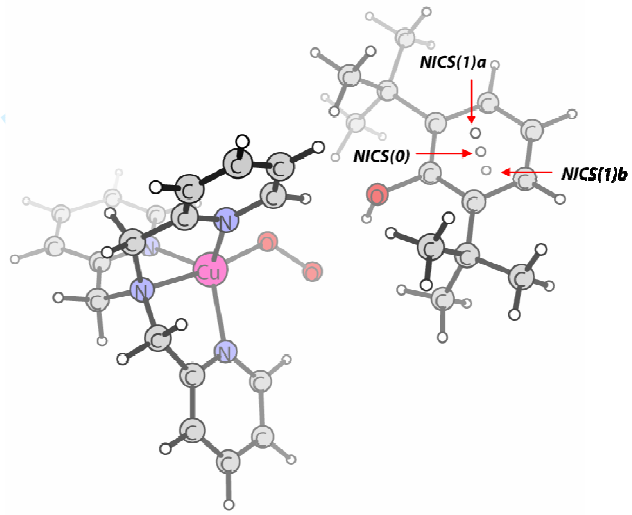


Fig. 5: Fully optimized Structure 1 for the triplet state with the positions used to compute NICS(0), NICS(1)a and NICS(1)b.

Results listed in Table 7 show that the HOMA value for the ring of the free substrate and of the same ring when the substrate interacts with the complex is almost the same. In the TS12, a small decrease is observed for this index, but the reduction of the HOMA value is much more important in Structure 2. This means that the main decrease of the aromaticity occurs once the TS structure has been reached.

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Structure	Multiplicity [a]	
	so	*t*
Phenolate	0.897	-
1	0.892	0.894
TS12	0.704	0.679
2	0.367	0.363

[a] *so* refers to the open-shell singlet spin state and *t* to the triplet spin state.

Table 7: HOMA values for the open-shell and triplet spin state structures that intervene in the first step of the mechanism.

Using the NICS indexes, NICS(0), NICS(1) and NICS(1)$_{zz}$, we can also conclude that the aromaticity of the ring decreases when this first step of the mechanism takes place (see Table 8). The NICS values computed at positions *a* and *b* are almost equivalent, since the variations they reflect are nearly the same. For this reason, only the values for the position *a* are reported in Table 8.

Structure	NICS(0)		NICS(1)a		NICS(1)$_{zz}$a	
	so	*t*	*so*	*t*	*so*	*t*
Phenolate	-8.27	-	-10.28	-	-22.14	-
1	-7.44	-8.27	-9.66	-10.37	-20.98	-22.47
TS12	-2.08	-1.61	-5.98	-5.78	-10.19	-9.48
2	2.84	2.82	-2.94	-2.90	-2.81	-2.69

[a] *so* refers to the open-shell singlet spin state and *t* to the triplet spin state.

Table 8: NICS values for the open-shell and triplet spin state structures that intervene in the first step of the mechanism.

The isomerisation of hydroperoxo species has been discussed in several theoretical studies on iron-based hydroxylation reactions.[75, 76] For this reason we decided to investigate the proton transfer from one of the oxygen atoms of the hydroperoxide moiety to the other (Scheme 5). The energy of the transition state for the isomerisation of the hydroperoxo species relative to Structure 1 is 39.3 kcal/mol for the triplet spin state and 39.7 kcal/mol for the open-shell spin state. The intermediate 2" that it is formed subsequently has a relative energy of 28.6 kcal/mol and 29.4 for the triplet and open-shell spin state, respectively. The high energy values we obtained for the structures that intervene in the isomerisation of the hydroperoxo species lead us to

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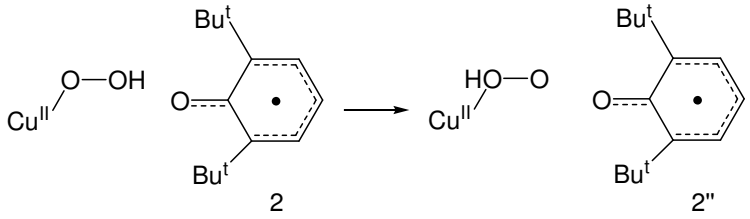
conclude that species 2" does not participate in the mechanism of the hydroxylation of phenols mediated by the complex that we have studied.



Scheme 5: Isomerization of the hydroperoxo species (2→2'').

After the hydrogen transfer, a change in the disposition of the substrate is needed. This is due to the fact that the carbon atom that has to be attacked by the hydroperoxide moiety is in a *para* position with respect to the oxygen of the ring from which the hydrogen has been abstracted. This reorganization of the system is endothermic for the open-shell singlet and the triplet structures by 4.4 and 0.2 kcal/mol, respectively. On the other hand, it could also be possible that the Cu(II) complex got the hydrogen atom from one molecule of substrate and subsequently the superoxide moiety formed attacks another different molecule of substrate. This alternative pathway would avoid the need of substrate reorientation. To study this possibility at least two molecules of substrate should be included in the model, which would increase considerably the size of the studied system. The analysis of such reaction pathway is out of our present available computational capabilities and will not be discussed here. This notwithstanding, the rate-limiting step for the studied mechanism is not the step that transforms Structure 2 into 3, and, consequently, the conclusions reached using the present model will not be modified substantially by using the enlarged model.

Once the substrate is in the right position, depending on the spin state, there are two different pathways. For the open-shell singlet spin state, first the attack on the ring by oxygen atom O_A takes place and then there is the OO bond cleavage (Scheme 6). On the other hand, for the triplet spin state we have a step where the CO bond formation and the OO bond cleavage occur in a concerted manner. Consequently, depending on the spin state there are different pathways. This is not surprising, as in the literature there are other examples of mechanisms for metal complexes that present differences depending on the spin state.[12, 77]

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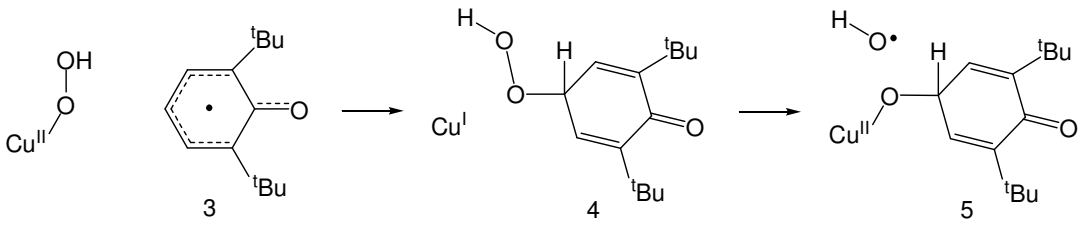

Scheme 6: CO bond formation and OO bond cleavage for the singlet state in the studied system (3→4→5). For the triplet spin state the CO bond formation and the OO bond cleavage take place in a single step (3→5).

One could think that structure 3 could generate oxidative coupling side reactions.[16] However, such side reactions have been not observed experimentally.[19] Then, it is unlikely that this possible side reactions could have a significant influence in the reaction mechanism and, for this reason, they have not been analyzed in the present work.

Starting from the open-shell singlet of Structure 3 (Scheme 6), the oxygen atom O_A of the complex attacks the carbon atom C_D of the substrate. Apart from the CO bond formation, it can be noticed that the O_A–C_D distance decreases from 3.60 to 1.53 Å, there is an increase of the C_A–C_B, C_C–C_D and Cu–O_A distances and a decrease of the C_B–C_C and O_C–C_A bonds (Table 9 and Fig. 6). These geometrical changes are consistent with the formation of a quinone ring. In this step, there is an electron transfer from the substrate to the copper atom. The copper is reduced form Cu(II) to Cu(I) and there is no spin density in Structure 4 with a closed-shell singlet ground state (Table 10).

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Structures	Multiplicity [a]	Distances (Å)							
		$Cu–O_A$	$O_A–O_B$	$O_C–C_A$	$C_A–C_B$	$C_B–C_C$	$C_C–C_D$	$C_D–O_A$	$O_B–H_B$
3	*so*	1.93	1.50	1.29	1.47	1.39	1.40	3.60	3.94
	t	1.92	1.50	1.29	1.47	1.39	1.41	3.60	3.31
TS34	*so*	2.06	1.51	1.27	1.49	1.37	1.44	2.00	2.58
4	*s*	2.49	1.53	1.25	1.50	1.35	1.50	1.53	2.47
TS45	*so*	2.05	1.76	1.26	1.50	1.35	1.49	1.49	2.82
TS35	*t*	1.96	1.78	1.28	1.48	1.37	1.44	1.94	3.00
5	*so*	1.92	2.22	1.26	1.50	1.35	1.50	1.46	2.28
	t	1.93	2.22	1.26	1.50	1.35	1.50	1.46	2.48

[a] *so* refers to the open-shell singlet spin stet, *s* to the closed-shell singlet spin state and *t* to the triplet spin state.

Table 9: Comparison of geometrical parameters for the structures that intervene in the C–O bond formation and the O–O bond cleavage.

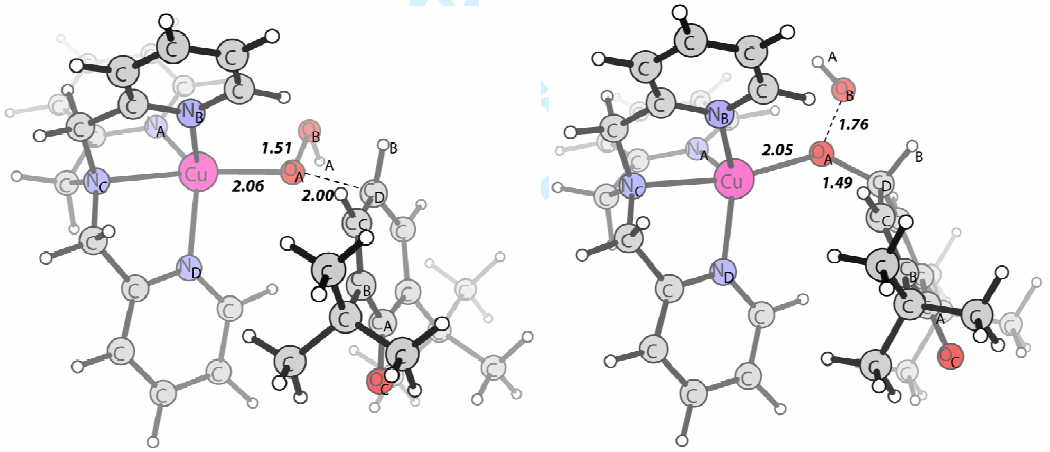


Fig. 6: Fully optimized transition states for the singlet state for the CO bond formation (TS34, left) and the OO bond cleavage (TS45, right). Distances are in angstroms.

After the CO bond formation, the OO cleavage occurs in the open-shell singlet potential energy surface. The OO distance increases from 1.53 to 2.22 Å going from Structure 4 to the open-shell singlet of Structure 5 (Table 9). In this reaction, a hydroxyl radical is obtained and the Cu(I) is oxidised to Cu(II) (Table 10). Consequently, the OO cleavage starts from a closed-shell singlet structure and ends in an open-shell singlet with one unpaired electron on the Cu(II) and the other in the hydroxyl radical.

Structures	Multiplicity [a]	Spin density								ΔG (kcal/mol)
		Cu	N_A	N_B	N_C	N_D	O_A	O_B	Substrate	
3	so	0.49	0.04	0.07	0.03	0.03	0.31	0.04	-1.00	9.8
	t	0.51	0.03	0.03	0.07	0.04	0.30	0.03	1.00	4.9
TS34	so	0.26	0.01	0.02	0.03	0.02	0.16	0.00	-0.49	22.7
4	s	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.3
TS45	so	0.26	0.00	-0.02	0.03	0.02	0.05	-0.39	0.00	19.1
TS35	t	0.61	0.05	0.04	0.10	0.02	0.22	0.36	0.61	38.2
5	so	0.61	0.04	0.02	0.09	0.04	-0.05	-0.79	0.01	6.5
	t	0.58	0.05	0.03	0.10	0.04	0.45	0.77	-0.01	5.0

[a] *so* refers to the open-shell singlet spin state, *s* to the closed-shell singlet spin state and t to the triplet spin state.

Table 10: Spin density at different spin states for the structures that intervene in the C–O bond formation and the O–O bond cleavage.

For the triplet spin state, the structure equivalent to Structure 4 found for the singlet state does not exist because TS35 connects Structures 3 and 5 directly. In this TS the CO bond formation and the OO bond cleavage take place in a concerted manner (Figure 7). In this structure (TS35), some spin density on the substrate can still be found. It should be mentioned that it was not possible to find this transition state for the open-shell singlet state and that all the attempts lead to TS34 or TS45 structures.

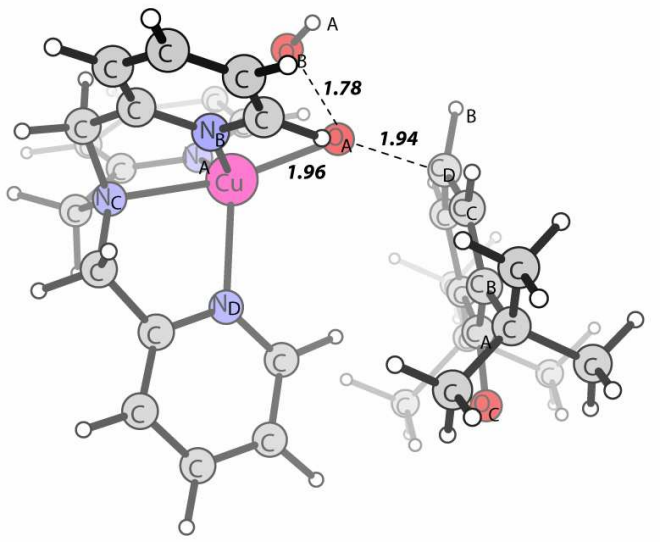
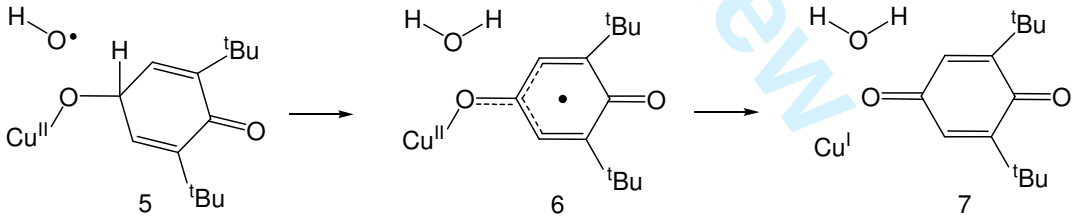


Fig. 7: Fully optimized transition state for the triplet state for the concerted CO bond formation and the OO bond cleavage (TS35). Distances are in angstroms.

For structures 1, TS12, 2, and 3, the triplet spin state is always slightly more stable than the open-shell singlet. However, the relative free energy of TS35, 38.2 kcal/mol, is much higher than that of TS34, 22.7 kcal/mol, which is the rate-determining step of the reaction. Consequently, there is a spin-state crossing while the CO bond cleavage is taking place, when moving from 3 to TS34. Since the triplet spin state for Structure 5 is again lower in energy than the corresponding open-shell singlet, when the OO bond cleavage occurs, there should be another spin state crossing in the path from TS45 to 5.

It should be mentioned, that we also tried to find a pathway where the OO bond cleavage took place before the CO bond formation occurred. However, all the attempts to find a transition state with the weakening of the OO bond and without forming the new CO bond lead to Structure 3.

Once the new CO bond is formed and the OO bond is cleaved, another hydrogen atom, one proton and one electron, is transferred from the substrate. This leads to the formation of one water molecule (Scheme 7).



Scheme 7: Second hydrogen transfer in the studied system (5→6) and the formation of the quinone (6→7).

Although the hydroxyl radical is not bound to the copper complex and is relatively far away from the substrate, it abstracts the hydrogen atom from the ring (Table 11 and Figure 8).

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Structures	Multiplicity [a]	Distances (Å)							
		$Cu–O_A$	$O_A–O_B$	$O_C–C_A$	$C_A–C_B$	$C_B–C_C$	$C_C–C_D$	$C_D–O_A$	$O_B–H_B$
TS56	*so*	1.91	2.57	1.26	1.50	1.35	1.50	1.44	1.88
	t	1.91	2.53	1.26	1.50	1.35	1.50	1.44	1.84
6	*so*	2.01	4.60	1.27	1.49	1.37	1.44	1.30	0.98
	t	1.91	4.13	1.29	1.47	1.38	1.42	1.35	0.98

[a] *so* refers to the open-shell singlet spin state and *t* to the triplet spin state.

Table 11: Comparison of geometrical parameters for the structures that intervene in the second proton transfer.

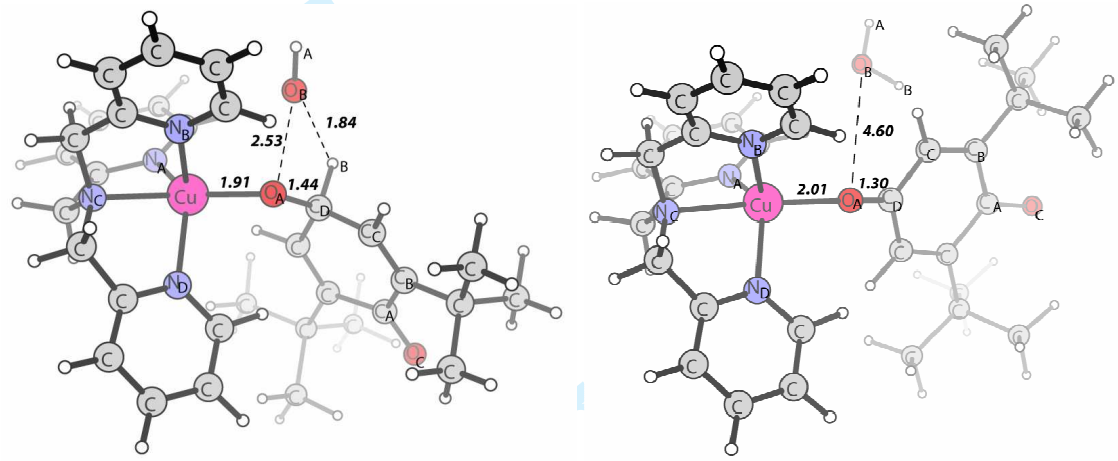

Figure 8: Fully optimized transition states for the triplet state for the second proton transfer (TS56, left) and the intermediate previous to the release of the quinone (6, right) for the open-shell singlet state. Distances are in angstroms.

In this step, spin density appears again on the substrate, which means that there is one delocalized electron again (Table 12). This electron is going to be transferred to the copper ion in the final step of the reaction, leading to the formation of Cu(I) and the quinone molecule.

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Structures	Multiplicity [a]	Spin density								ΔG (kcal/mol)
		Cu	N_A	N_B	N_C	N_D	O_A	O_B	Substrate	
TS56	*so*	0.59	0.04	0.03	0.10	0.04	-0.04	-0.77	0.02	8.2
	t	0.56	0.04	0.03	0.10	0.05	0.48	0.74	0.03	7.5
6	*so*	0.30	0.03	0.01	0.04	0.01	0.06	0.00	-0.44	-67.0
	t	0.59	0.05	0.02	0.11	0.05	0.30	0.00	0.89	-63.1

[a] *so* refers to the open-shell singlet spin state and *t* to the triplet spin state.

Table 12: Spin density at different spin states for the structures that intervene in the second hydrogen transfer (5→6).

The relative free energies for the suggested reaction mechanism for the hydroxylation of phenols with an end-on bound superoxo copper(II) complex are shown in Fig. 9. The reaction starts with the end-on triplet spin state of the complex. In the first step the first hydrogen atom transfer takes place with a barrier of 9.4 kcal/mol (TS12). Then, a rearrangement of the substrate occurs, placing its carbon atom in *para* position with respect to the oxo group of the ring close to the peroxide moiety of the complex (Structure 2 → Structure 3). Afterwards, a new CO bond between the oxygen atom closer to the copper atom and the ring is formed (Structure 3 → Structure 4). In this step, a transition from the triplet to the singlet surface occurs. Subsequently, the OO bond cleavage takes place (Structure 4 → Structure 5) forming a hydroxyl radical. During this transformation, the system returns to the triplet state. Then, another hydrogen atom is transferred from the ring of the substrate to the hydroxyl radical leading to the formation of a water molecule (Structure 5 → Structure 6) and recovering the open-shell singlet structure. Finally, one electron from the substrate is transferred to the copper(II) atom, which is reduced to copper(I) and the quinone molecule is formed (Structure 6 → Structure 7).

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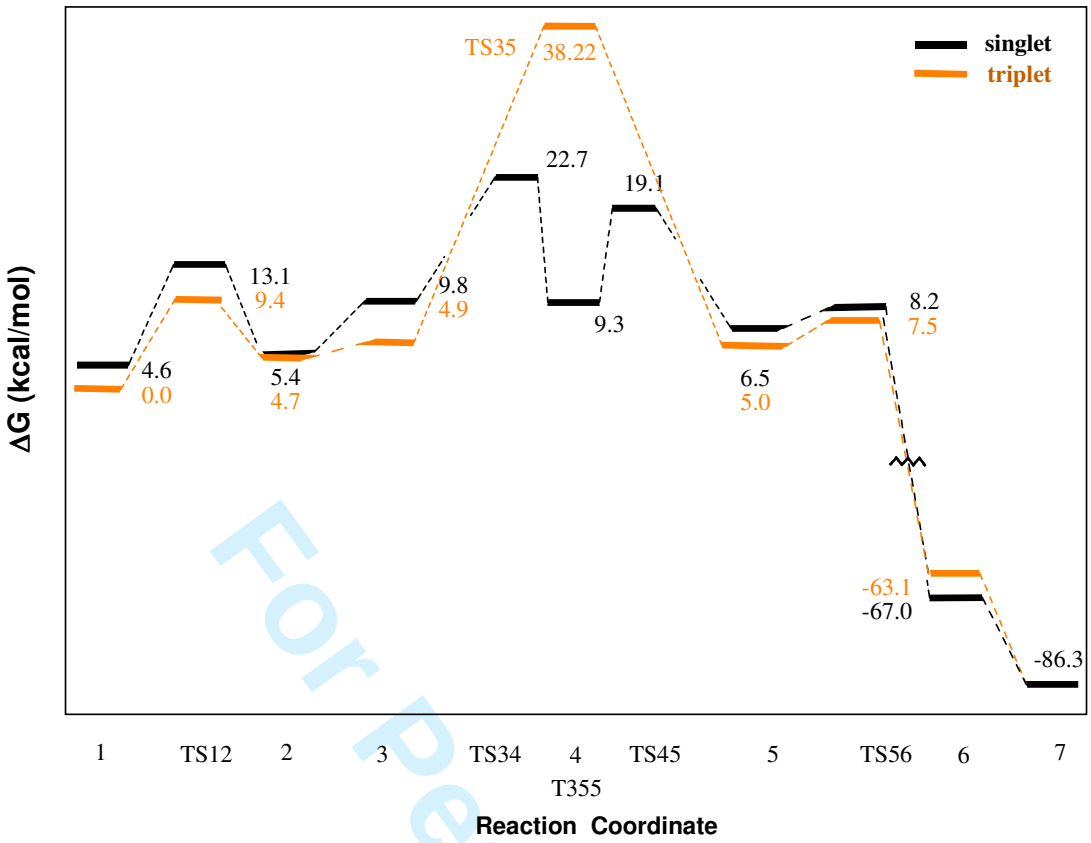

Figure 9: Free energy profile obtained for the mechanism of the complex at the B3LYP level of theory.

Conclusions

The mechanisms for enzymatic hydroxylations of substrates by dopamine β-monooxygenase (DβM) and peptidylglycine α-hydroxylating monooxygenase (PHM) are not completely known. For this reason, model studies addressing Cu(II)-superoxide reactivity patterns and the OO cleavage reaction of the Cu(II)OOH species are of considerable interest. In this article, the mechanism of the hydroxylation of phenols mediated by an end-on bound superoxo copper(II) complex is described. The triplet spin state is the ground state for the studied complex. The rate-determining step for the mechanism is the CO bond formation, which occurs in the open-shell singlet state. For the studied system, the OO bond cleavage cannot take place before the CO bond formation. Consequently, the corresponding $[Cu=O]^{2-}$ species does not exist as an intermediate. Finally, the hydroxoperoxo intermediate itself is capable of mediating the hydroxylation of the substrate.

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Acknowledgements

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Supporting Information Available: Molecular orbitals of the uB3LYP/lacvp optimized triplet electronic state for the studied complex, optimized cartesian xyz coordinates and spin density populations for the atoms of all stationary points located on the PES for the reaction mechanism studied at the B3LYP/lacvp level of theory, together with the OPBE energies for structures 1, TS12, 2, and 3 obtained at the OPBE/cc-pvTZ(-f)&lacv3p+//B3LYP/lacvp level of theory

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SUPPORTING INFORMATION

Theoretical study of the hydroxylation of phenols mediated by an end-on bound superoxo copper(II) complex

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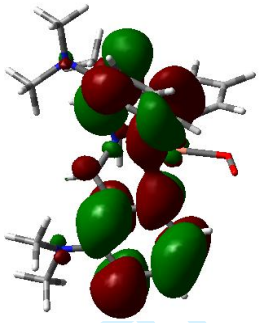
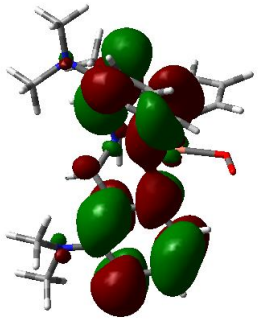
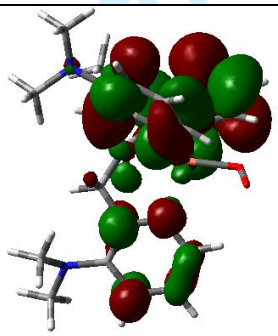
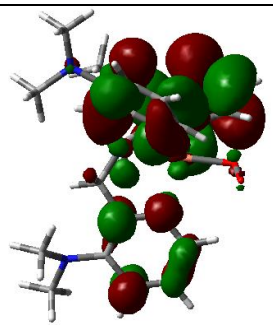
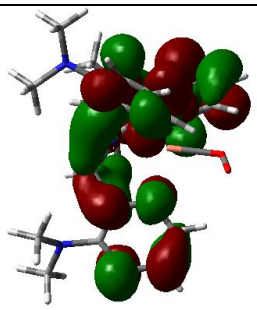
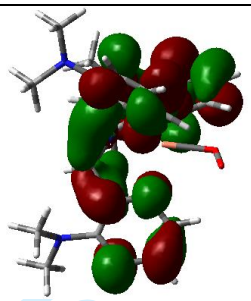
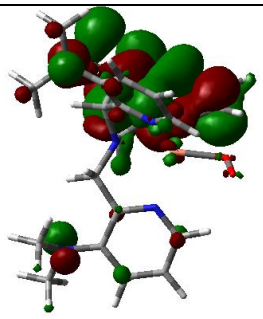
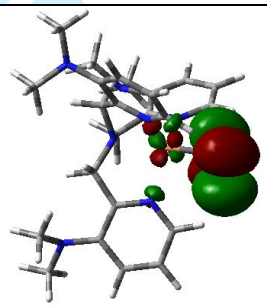
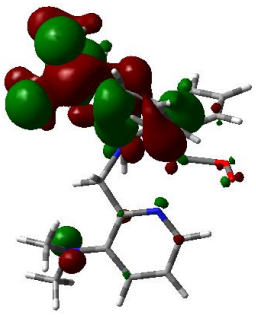
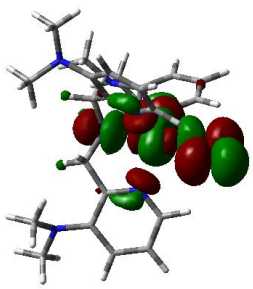
Table S1. Molecular orbitals of the uB3LYP/lacvp optimized triplet electronic state for the studied complex.

Tables S2-S30. Optimized cartesian xyz coordinates of all stationary points located on the PES for the reaction mechanism studied at the B3LYP/lacvp level of theory.

Table S31. Spin density populations for the atoms of the substrate of all stationary points located on the PES for the reaction mechanism studied at the B3LYP/lacvp level of theory.

Table S32: Electronic energies for structures 1, TS12, 2, and 3 of the mechanism for the hydroxylation of phenols mediated by $[Cu(II)(NMe_2\text{-}TMPA)\text{-}(O_2\cdot^-)]^+$ complex computed at the B3LYP/cc-pvTZ(-f)&lacv3p+//B3LYP/lacvp and OPBE/cc-pvTZ(-f)&lacv3p+//B3LYP/lacvp level of theory.

Table S1. Molecular orbitals of the uB3LYP/lacvp optimized triplet electronic state for the studied complex.

alpha	beta
 134 (-)	 134 (-)
 133 (-)	 133 (-)
 132 (-)	 132 (-)
 131 (↑)	 131 (-)
 130(↑)	 130 (-)

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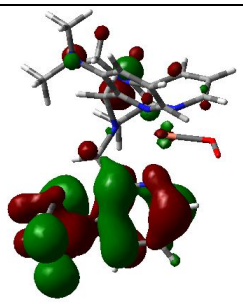
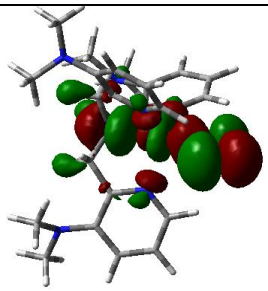
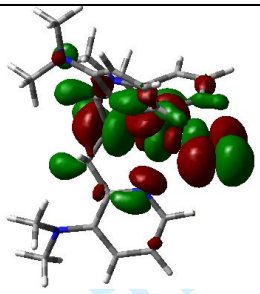
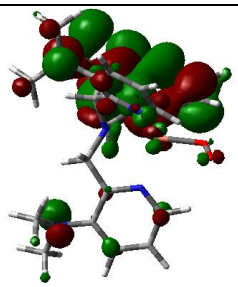
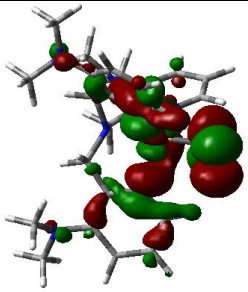
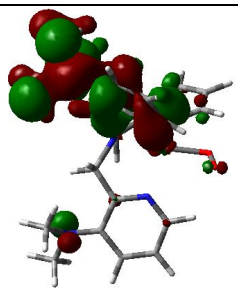
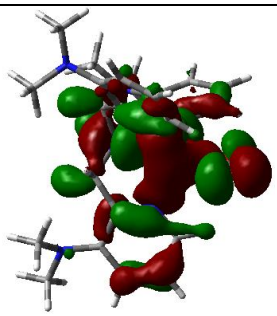
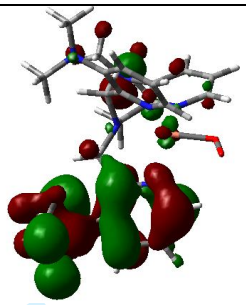
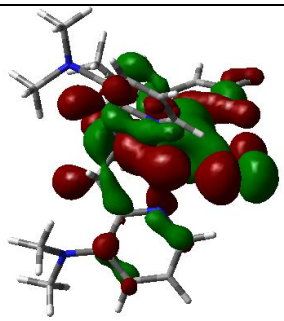
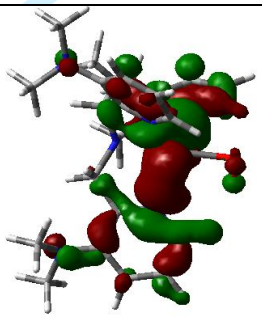
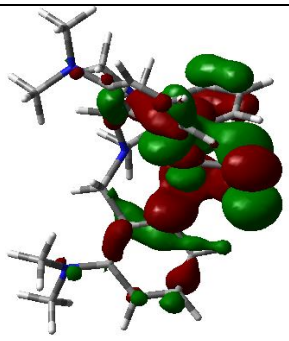
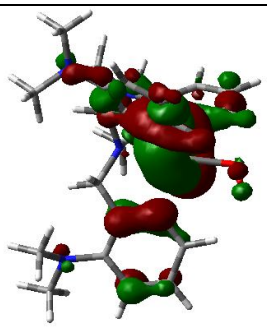
129 (↑) 	129 (↓) 
128 (↑) 	128 (↓) 
127 (↑) 	127 (↓) 
126 (↑) 	126 (↓) 
125 (↑) 	125 (↓) 
124 (↑) 	124 (↓) 

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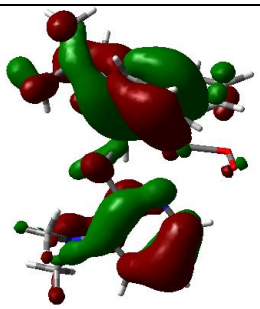
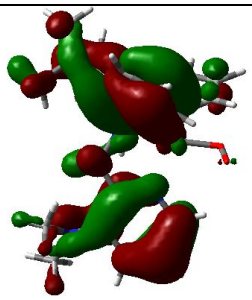
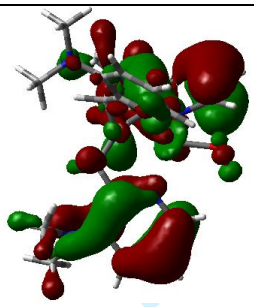
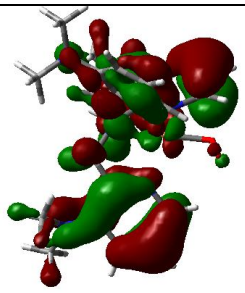
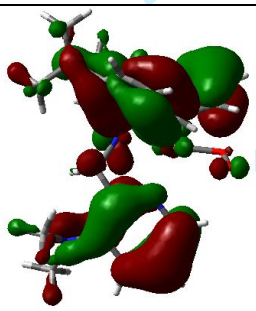
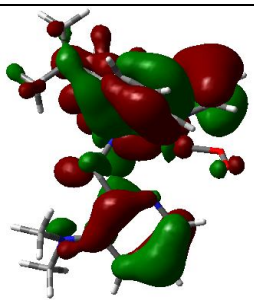
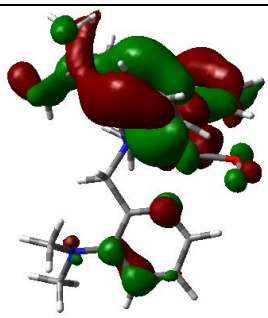
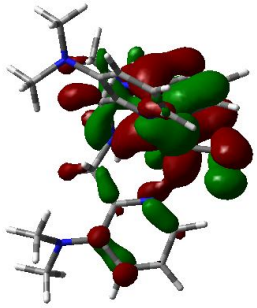
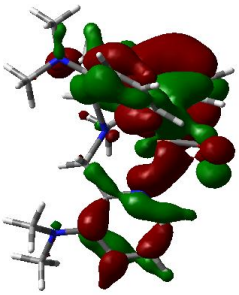
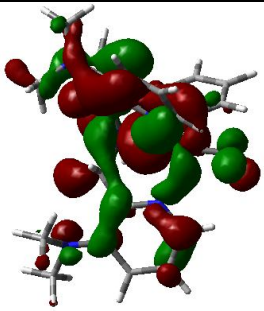
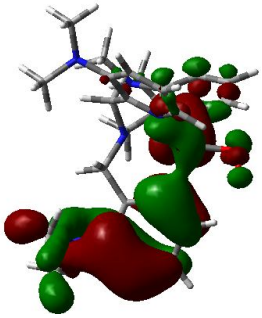
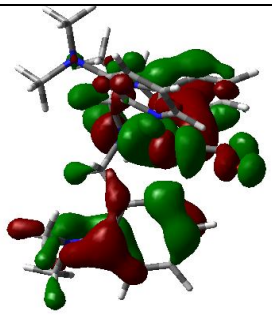
123 (↑) 	123 (↓) 
122 (↑) 	122 (↓) 
121 (↑) 	121 (↓) 
120 (↑) 	120 (↓) 
119 (↑) 	119 (↓) 
118 (↑) 	118 (↓) 

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Table S2. Optimized cartesian xyz coordinates of the open-shell singlet end-on structure of the synthetic complex used in this study at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.706564	-0.284581	-0.626726
C	1.215325	2.098553	-1.071817
C	0.290601	1.873540	1.086279
C	1.849820	3.285716	-0.709870
H	1.289729	1.665352	-2.061320
C	0.937482	3.048338	1.535602
C	1.710466	3.759634	0.596605
H	2.448760	3.824316	-1.434296
H	2.205469	4.676566	0.893992
C	-3.248583	-0.404367	0.809662
C	-3.620175	0.089057	-1.470323
C	-4.633914	-0.340534	1.097126
C	-4.999150	0.120585	-1.269732
H	-3.156477	0.243231	-2.436324
C	-5.503605	-0.088298	0.015472
H	-5.665707	0.317056	-2.100909
H	-6.572641	-0.048727	0.186841
C	0.535327	-2.327909	1.043722
C	0.397403	-3.102087	-1.179258
C	1.069913	-3.561818	1.490898
C	0.872018	-4.358354	-0.803310
H	0.139686	-2.853723	-2.200043
C	1.204001	-4.588998	0.532072
H	0.991706	-5.138424	-1.545520
H	1.587285	-5.557018	0.830763
N	0.444551	1.428880	-0.183844
N	-0.855545	-0.305840	1.498820
N	-2.783656	-0.175362	-0.441485
N	0.226822	-2.127171	-0.259131
C	-2.203113	-0.874053	1.808220
C	0.264872	-1.168379	1.983513
C	-0.721180	1.117705	1.931727
H	-0.493147	1.182725	3.000147
H	-1.698930	1.595320	1.789840
H	-2.123011	-1.965031	1.723276
H	-2.489773	-0.660275	2.842257
H	1.149983	-0.524044	2.046037
H	0.066554	-1.554708	2.993205
N	1.406211	-3.748527	2.851257
N	-5.113031	-0.580571	2.409368
N	0.750125	3.504933	2.869753
C	-6.444411	-1.190079	2.551812
H	-6.525142	-1.618001	3.555658
H	-7.269102	-0.468416	2.427401
H	-6.566462	-1.997452	1.826187
C	-4.835711	0.431459	3.449205
H	-5.581664	1.243060	3.435442
H	-4.859940	-0.040074	4.436602
H	-3.852753	0.881976	3.301786
C	1.352638	-5.116862	3.389481
H	2.233090	-5.723031	3.119839
H	1.308227	-5.059463	4.480950

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H	0.451077	-5.623332	3.037300
C	2.521613	-2.958668	3.414364
H	2.417299	-2.908450	4.502269
H	3.497918	-3.412453	3.179760
H	2.523202	-1.941862	3.020207
C	0.744031	4.960754	3.090177
H	0.274491	5.164057	4.057461
H	1.753328	5.405445	3.107478
H	0.153833	5.452730	2.313621
C	1.450125	2.769644	3.943747
H	2.508952	3.067154	4.023330
H	0.962728	2.974808	4.901750
H	1.418434	1.693052	3.762024
O	-0.781135	-0.262662	-2.585271
O	0.442901	-0.218643	-3.152687

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Table S3. Optimized cartesian xyz coordinates of the triplet end-on structure of the synthetic complex used in this study at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.693064	-0.283130	-0.636397
C	1.187876	2.131903	-1.073627
C	0.278416	1.879829	1.086839
C	1.816147	3.320195	-0.706967
H	1.261912	1.710615	-2.068253
C	0.920973	3.055800	1.541344
C	1.682560	3.781356	0.604297
H	2.406269	3.868934	-1.431104
H	2.173690	4.698648	0.906690
C	-3.237479	-0.413980	0.801330
C	-3.621852	0.074885	-1.475672
C	-4.621309	-0.343235	1.095854
C	-4.999637	0.110252	-1.268734
H	-3.166801	0.228567	-2.445755
C	-5.497659	-0.092832	0.019936
H	-5.670016	0.306157	-2.097031
H	-6.565494	-0.049402	0.197937
C	0.539509	-2.329836	1.046576
C	0.401837	-3.113968	-1.171570
C	1.062531	-3.567289	1.499920
C	0.864164	-4.372702	-0.790279
H	0.147288	-2.871567	-2.194694
C	1.191220	-4.600130	0.546477
H	0.977567	-5.156785	-1.529292
H	1.565851	-5.569840	0.850272
N	0.427697	1.446939	-0.188151
N	-0.849157	-0.308998	1.506956
N	-2.777287	-0.189234	-0.452675
N	0.236838	-2.131158	-0.258360
C	-2.193567	-0.885043	1.801554
C	0.273683	-1.167085	1.984787
C	-0.724133	1.113488	1.934946
H	-0.495064	1.186932	3.002771
H	-1.705651	1.583886	1.793144
H	-2.107640	-1.974913	1.706974
H	-2.492073	-0.683712	2.834849
H	1.159644	-0.522528	2.037819
H	0.085089	-1.552791	2.996954
N	1.392721	-3.753503	2.861791
N	-5.091704	-0.574123	2.413483
N	0.741958	3.500094	2.880549
C	-6.422341	-1.182749	2.568352
H	-6.497468	-1.601866	3.576393
H	-7.249164	-0.463513	2.441962
H	-6.547445	-1.996692	1.850595
C	-4.811110	0.450019	3.440923
H	-5.552421	1.265729	3.415429
H	-4.840814	-0.009562	4.433799
H	-3.824637	0.892846	3.291719
C	1.328580	-5.120529	3.402306
H	2.205218	-5.734065	3.136189

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H	1.281883	-5.060715	4.493518
H	0.424281	-5.621327	3.048895
C	2.508607	-2.968044	3.429668
H	2.399662	-2.917224	4.517087
H	3.484093	-3.425978	3.199256
H	2.515722	-1.951427	3.035061
C	0.733541	4.953766	3.113739
H	0.271275	5.147248	4.086508
H	1.741732	5.401266	3.126741
H	0.135683	5.450853	2.346308
C	1.452098	2.757332	3.942707
H	2.510433	3.058037	4.017155
H	0.970921	2.951882	4.906049
H	1.422757	1.682471	3.751065
O	-0.760705	-0.265859	-2.617575
O	0.440686	-0.211836	-3.194602

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Table S4. Optimized cartesian xyz coordinates of the open-shell singlet end-on structure of the synthetic complex used in this study at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.585254	-0.251827	-0.445931
C	1.284558	2.176265	-0.968032
C	0.439592	1.942479	1.210149
C	2.017309	3.308007	-0.600147
H	1.299443	1.77189	-1.972363
C	1.160355	3.058610	1.645563
C	1.957040	3.750992	0.726353
H	2.624723	3.823094	-1.333905
H	2.522883	4.619634	1.043022
C	-3.021279	-0.461678	1.134401
C	-3.583011	0.044811	-1.090545
C	-4.35974	-0.369012	1.524354
C	-4.937205	0.131650	-0.769522
H	-3.209137	0.191184	-2.096599
C	-5.329215	-0.069779	0.559678
H	-5.662304	0.356676	-1.541248
H	-6.372959	0.005573	0.842368
C	0.826173	-2.225259	1.191012
C	0.812079	-2.954288	-1.04122
C	1.436785	-3.412241	1.607482
C	1.439308	-4.151191	-0.693258
H	0.553821	-2.712771	-2.063702
C	1.744399	-4.387247	0.652117
H	1.676341	-4.880789	-1.457024
H	2.216835	-5.315426	0.952882
N	0.512091	1.515783	-0.076773
N	-0.620165	-0.259327	1.721712
N	-2.652135	-0.238246	-0.152104
N	0.505359	-2.020286	-0.111344
C	-1.920435	-0.872593	2.090246
C	0.563166	-1.070395	2.138058
C	-0.497532	1.175262	2.121302
H	-0.171918	1.25022	3.169327
H	-1.495709	1.62730	2.059899
H	-1.795364	-1.961438	2.037835
H	-2.198234	-0.629566	3.126631
H	1.434765	-0.404881	2.118784
H	0.457360	-1.433493	3.170824
O	-0.764706	-0.192829	-2.403324
O	0.419117	-0.224037	-3.03693
H	1.098394	3.381205	2.67953
H	-4.639379	-0.535625	2.558919
H	1.673763	-3.566134	2.654371

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Table S5. Optimized cartesian xyz coordinates of the open-shell triplet end-on structure of the synthetic complex used in this study at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.555986	-0.237645	-0.454156
C	1.279932	2.207312	-0.966018
C	0.434696	1.951825	1.210580
C	1.997118	3.346056	-0.595098
H	1.308203	1.807769	-1.972577
C	1.141690	3.075071	1.647623
C	1.927346	3.784904	0.731624
H	2.598499	3.868993	-1.328432
H	2.478760	4.662006	1.051089
C	-2.999660	-0.478670	1.135080
C	-3.556947	0.041386	-1.087048
C	-4.341085	-0.403106	1.519413
C	-4.914243	0.118312	-0.769275
H	-3.185802	0.206390	-2.091214
C	-5.310319	-0.103250	0.554496
H	-5.639038	0.350990	-1.539644
H	-6.356233	-0.041772	0.833535
C	0.825184	-2.227751	1.188468
C	0.761903	-2.984184	-1.033464
C	1.410551	-3.424993	1.608951
C	1.358198	-4.195752	-0.679895
H	0.487404	-2.756344	-2.055514
C	1.682148	-4.420511	0.662583
H	1.557155	-4.942973	-1.438190
H	2.137518	-5.355230	0.969694
N	0.512492	1.531576	-0.079148
N	-0.595617	-0.255072	1.739656
N	-2.624793	-0.249152	-0.150040
N	0.499658	-2.025149	-0.114886
C	-1.897190	-0.882402	2.096431
C	0.587081	-1.065965	2.136958
C	-0.500215	1.179534	2.124021
H	-0.193317	1.297715	3.173907
H	-1.508064	1.603514	2.034990
H	-1.759322	-1.968853	2.033673
H	-2.187277	-0.654118	3.132780
H	1.459708	-0.402511	2.100284
H	0.500455	-1.427209	3.172384
O	-0.714256	-0.223456	-2.439356
O	0.452326	-0.148591	-3.067232
H	1.075879	3.390274	2.683198
H	-4.622272	-0.578757	2.551916
H	1.653409	-3.573743	2.655326

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Table S6. Optimized cartesian xyz coordinates of the open-shell singlet side-on structure of the model of the synthetic complex used in this study at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.613264	-0.207532	-0.741752
C	0.985506	2.370159	-1.046747
C	0.252585	1.971637	1.156295
C	1.580125	3.571516	-0.674071
H	1.018564	1.998915	-2.062110
C	0.878947	3.157383	1.616125
C	1.529209	3.964582	0.664872
H	2.086394	4.179568	-1.414136
H	2.001302	4.889154	0.975175
C	-3.126150	-0.373396	0.819759
C	-3.473163	0.179067	-1.450396
C	-4.521974	-0.354225	1.072666
C	-4.853684	0.167201	-1.281350
H	-3.008088	0.376045	-2.406986
C	-5.378509	-0.096626	-0.014852
H	-5.505263	0.371277	-2.122390
H	-6.451412	-0.094998	0.135244
C	0.484464	-2.347555	1.117831
C	0.113161	-3.237730	-1.028638
C	0.951019	-3.598116	1.601718
C	0.500776	-4.508955	-0.608916
H	-0.200282	-3.034528	-2.044113
C	0.921269	-4.689312	0.708493
H	0.488618	-5.339207	-1.305021
H	1.244367	-5.668303	1.040777
N	0.325858	1.602274	-0.143369
N	-0.773434	-0.264394	1.609483
N	-2.641031	-0.095510	-0.414138
N	0.097551	-2.192485	-0.169804
C	-2.112325	-0.842630	1.850109
C	0.346150	-1.137226	2.023593
C	-0.646706	1.137367	2.056301
H	-0.329027	1.204181	3.102540
H	-1.645788	1.591536	2.014631
H	-2.029027	-1.932115	1.751956
H	-2.461627	-0.653680	2.870684
H	1.256979	-0.526092	1.976560
H	0.240064	-1.486474	3.062785
N	1.374805	-3.736297	2.941988
N	-5.019434	-0.650343	2.366259
N	0.791168	3.525688	2.986550
C	-6.320413	-1.331245	2.458349
H	-6.404987	-1.785839	3.449929
H	-7.179596	-0.652084	2.326446
H	-6.379364	-2.126811	1.712016
C	-4.821199	0.352662	3.433161
H	-5.609505	1.122794	3.415829
H	-4.842956	-0.140468	4.409741
H	-3.860189	0.857225	3.318867
C	1.254883	-5.059387	3.572102
H	2.063401	-5.752006	3.285115

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H	1.294647	-4.932028	4.657863
H	0.293448	-5.510629	3.316476
C	2.573641	-2.996701	3.387134
H	2.527302	-2.841778	4.469348
H	3.497452	-3.550615	3.155133
H	2.637671	-2.023732	2.899312
C	0.733573	4.963205	3.297531
H	0.346050	5.084011	4.313568
H	1.717083	5.461084	3.252870
H	0.051004	5.466270	2.608740
C	1.622063	2.767799	3.945838
H	2.665171	3.124735	3.954344
H	1.210656	2.881648	4.953287
H	1.633872	1.705551	3.693162
O	-0.637627	-0.618931	-2.886527
O	0.609548	-0.303786	-2.472255

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Table S7. Optimized cartesian xyz coordinates of the triplet side-on structure of the model of the synthetic complex used in this study at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.631201	-0.191762	-0.755087
C	1.040423	2.346396	-1.055223
C	0.258246	1.967244	1.133964
C	1.649760	3.537777	-0.674281
H	1.082225	1.976706	-2.070815
C	0.896455	3.143272	1.602609
C	1.580243	3.935589	0.662235
H	2.180505	4.134825	-1.406157
H	2.062801	4.852429	0.979259
C	-3.153381	-0.368893	0.799736
C	-3.524859	0.188557	-1.462885
C	-4.546533	-0.354878	1.066974
C	-4.903831	0.172298	-1.281041
H	-3.071981	0.391140	-2.424163
C	-5.415390	-0.096812	-0.010169
H	-5.564368	0.376947	-2.115010
H	-6.486690	-0.098954	0.151149
C	0.490377	-2.323720	1.093465
C	0.157574	-3.214832	-1.057724
C	0.959201	-3.571628	1.582706
C	0.548209	-4.483726	-0.634106
H	-0.146923	-3.016350	-2.076680
C	0.951359	-4.662381	0.688807
H	0.550843	-5.313400	-1.331051
H	1.276839	-5.639201	1.025120
N	0.350402	1.591498	-0.163687
N	-0.795042	-0.254223	1.581507
N	-2.679481	-0.086545	-0.437795
N	0.122697	-2.168528	-0.200314
C	-2.130975	-0.837258	1.823392
C	0.328972	-1.117976	2.001594
C	-0.673291	1.150999	2.017486
H	-0.385948	1.229244	3.071786
H	-1.668145	1.609847	1.940166
H	-2.042717	-1.926016	1.720328
H	-2.477877	-0.654446	2.846086
H	1.234202	-0.497920	1.965777
H	0.216696	-1.472453	3.038306
N	1.364756	-3.708126	2.929030
N	-5.029539	-0.654833	2.366306
N	0.788389	3.518989	2.969383
C	-6.324921	-1.344610	2.469834
H	-6.398463	-1.798421	3.462701
H	-7.190224	-0.671958	2.343857
H	-6.384167	-2.141519	1.724940
C	-4.832353	0.354861	3.427016
H	-5.622924	1.122800	3.407807
H	-4.850187	-0.133272	4.406206
H	-3.872810	0.861216	3.307643
C	1.244967	-5.032613	3.556143
H	2.062404	-5.719330	3.280269
H	1.268067	-4.906120	4.642491

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H	0.290560	-5.490283	3.286072
C	2.552862	-2.961583	3.390770
H	2.491572	-2.808721	4.472545
H	3.483250	-3.509097	3.169878
H	2.616687	-1.987359	2.905398
C	0.751976	4.958394	3.274085
H	0.345168	5.090575	4.281144
H	1.745686	5.437109	3.248815
H	0.094058	5.471812	2.569141
C	1.582052	2.748505	3.949691
H	2.631423	3.085372	3.980993
H	1.150101	2.873822	4.947158
H	1.578922	1.685284	3.700995
O	-0.719901	-0.660701	-2.917547
O	0.511190	-0.269167	-2.586372

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Table S8. Optimized cartesian xyz coordinates of the open-shell singlet side-on structure of the model of the synthetic complex used in this study at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.585254	-0.251827	-0.445931
C	1.284558	2.176265	-0.968032
C	0.439592	1.942479	1.210149
C	2.017309	3.308007	-0.600147
H	1.299443	1.771890	-1.972363
C	1.160355	3.058610	1.645563
C	1.957040	3.750992	0.726353
H	2.624723	3.823094	-1.333905
H	2.522883	4.619634	1.043022
C	-3.021279	-0.461678	1.134401
C	-3.583011	0.044811	-1.090545
C	-4.359740	-0.369012	1.524354
C	-4.937205	0.131650	-0.769522
H	-3.209137	0.191184	-2.096599
C	-5.329215	-0.069779	0.559678
H	-5.662304	0.356676	-1.541248
H	-6.372959	0.005573	0.842368
C	0.826173	-2.225259	1.191012
C	0.812079	-2.954288	-1.041220
C	1.436785	-3.412241	1.607482
C	1.439308	-4.151191	-0.693258
H	0.553821	-2.712771	-2.063702
C	1.744399	-4.387247	0.652117
H	1.676341	-4.880789	-1.457024
H	2.216835	-5.315426	0.952882
N	0.512091	1.515783	-0.076773
N	-0.620165	-0.259327	1.721712
N	-2.652135	-0.238246	-0.152104
N	0.505359	-2.020286	-0.111344
C	-1.920435	-0.872593	2.090246
C	0.563166	-1.070395	2.138058
C	-0.497532	1.175262	2.121302
H	-0.171918	1.250220	3.169327
H	-1.495709	1.627300	2.059899
H	-1.795364	-1.961438	2.037835
H	-2.198234	-0.629566	3.126631
H	1.434765	-0.404881	2.118784
H	0.457360	-1.433493	3.170824
O	-0.764706	-0.192829	-2.403324
O	0.419117	-0.224037	-3.036930
H	1.098394	3.381205	2.679530
H	-4.639379	-0.535625	2.558919
H	1.673763	-3.566134	2.654371

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Table S9. Optimized cartesian xyz coordinates of the open-shell triplet side-on structure of the model of the synthetic complex used in this study at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.557813	-0.269733	-0.556194
C	1.392557	2.179849	-0.861878
C	0.454499	1.941440	1.270983
C	2.133175	3.292547	-0.461972
H	1.447353	1.798404	-1.873117
C	1.179238	3.043237	1.737902
C	2.024599	3.731358	0.861566
H	2.779475	3.796023	-1.170411
H	2.590399	4.589199	1.207086
C	-2.986014	-0.537479	1.181986
C	-3.571022	-0.096178	-1.046521
C	-4.331048	-0.495972	1.564142
C	-4.928309	-0.057940	-0.729591
H	-3.219360	0.069867	-2.056340
C	-5.314976	-0.258927	0.599628
H	-5.658988	0.132344	-1.505985
H	-6.361372	-0.226223	0.881268
C	0.798446	-2.189428	1.269509
C	0.648697	-3.016688	-0.923199
C	1.416223	-3.370724	1.693488
C	1.270589	-4.211098	-0.562601
H	0.332219	-2.825716	-1.940653
C	1.658365	-4.391914	0.769568
H	1.441908	-4.977852	-1.307963
H	2.138331	-5.311766	1.083867
N	0.567923	1.516769	-0.014584
N	-0.608004	-0.231153	1.852929
N	-2.617756	-0.333383	-0.109840
N	0.415219	-2.027619	-0.023993
C	-1.893722	-0.869615	2.182442
C	0.582083	-1.020568	2.213417
C	-0.527290	1.206975	2.166776
H	-0.271009	1.390797	3.223117
H	-1.527255	1.629617	2.006303
H	-1.734591	-1.955275	2.167355
H	-2.236703	-0.617040	3.198718
H	1.452088	-0.355959	2.143959
H	0.545987	-1.385987	3.252447
O	-0.932034	0.513711	-2.555707
O	0.126444	-0.283816	-2.656817
H	1.079159	3.356241	2.771389
H	-4.599497	-0.648493	2.603667
H	1.704781	-3.483621	2.732581

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Table S10. Optimized cartesian xyz coordinates of Structure1 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	0.371600	-0.532163	-0.188062
C	1.708481	1.885768	1.222764
C	-0.339310	1.135665	2.097324
C	1.848648	2.815710	2.255338
H	2.428496	1.787840	0.419794
C	-0.251047	2.036231	3.160827
C	0.858958	2.886903	3.241080
H	2.715673	3.463982	2.283196
H	0.946326	3.592799	4.059319
C	-2.420980	-0.922744	-0.927476
C	-1.306126	0.139230	-2.707364
C	-3.643012	-0.839132	-1.596531
C	-2.498399	0.237207	-3.431823
H	-0.368063	0.507366	-3.110773
C	-3.680582	-0.251912	-2.868507
H	-2.488175	0.693471	-4.413663
H	-4.619052	-0.179349	-3.406646
C	0.402689	-2.956389	1.450392
C	1.965874	-3.174300	-0.291072
C	0.661126	-4.257606	1.887934
C	2.279190	-4.476254	0.104291
H	2.434560	-2.692228	-1.140301
C	1.614723	-5.025123	1.207012
H	3.020564	-5.044942	-0.443198
H	1.831645	-6.036641	1.531516
N	0.638211	1.059738	1.155614
N	-1.164676	-1.038929	1.220983
N	-1.280283	-0.428146	-1.477060
N	1.046341	-2.438005	0.373850
C	-2.268513	-1.630461	0.404703
C	-0.548275	-2.018360	2.166393
C	-1.546014	0.245605	1.878780
H	-2.077639	0.066262	2.823708
H	-2.244149	0.756290	1.205093
H	-2.004485	-2.678726	0.221133
H	-3.216501	-1.627587	0.961102
H	0.015269	-1.439770	2.908147
H	-1.318287	-2.582079	2.711946
O	1.748607	-0.336524	-1.573179
O	2.340364	0.874837	-1.691695
H	-1.035819	2.075631	3.908054
H	-4.544743	-1.229840	-1.137901
H	0.131907	-4.661942	2.743630
C	1.730528	1.876621	-5.503414
C	2.146402	0.996013	-6.533748
C	1.674064	3.284523	-5.662073
C	2.555774	1.583559	-7.744177
C	2.097228	3.801396	-6.899741
C	2.537545	2.965107	-7.923568
H	2.891505	0.960783	-8.561736
H	2.083530	4.868297	-7.074473
H	2.861573	3.391447	-8.867590

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O	1.280516	1.312420	-4.274225
H	1.988328	1.232176	-3.595478
C	1.157593	4.236101	-4.549303
C	2.135567	-0.548021	-6.375527
C	2.044301	4.138492	-3.275835
H	1.730511	4.897977	-2.548073
H	1.963377	3.163321	-2.791810
H	3.097163	4.321527	-3.520239
C	-0.316991	3.894258	-4.194904
H	-0.403481	2.868440	-3.834133
H	-0.682408	4.576281	-3.415951
H	-0.959877	4.011974	-5.075405
C	1.186034	5.718387	-5.002570
H	2.202657	6.059478	-5.227851
H	0.558072	5.888958	-5.883747
H	0.797839	6.346404	-4.192772
C	0.682755	-1.043532	-6.128743
H	0.672666	-2.136430	-6.024574
H	0.268430	-0.601009	-5.221501
H	0.038034	-0.778827	-6.975299
C	3.053813	-1.000728	-5.205218
H	2.660705	-0.692582	-4.235167
H	3.131518	-2.095632	-5.200787
H	4.064865	-0.593516	-5.323142
C	2.651493	-1.258808	-7.653227
H	2.033507	-1.029430	-8.528190
H	3.689876	-0.992391	-7.880435
H	2.613756	-2.342865	-7.497767

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Table S11. Optimized cartesian xyz coordinates of Structure 1 triplet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	0.393904	-0.541181	-0.151139
C	1.699208	1.876166	1.286004
C	-0.353170	1.112113	2.134200
C	1.824120	2.804312	2.321733
H	2.432484	1.786448	0.494185
C	-0.279729	2.010209	3.201539
C	0.823670	2.867083	3.297113
H	2.687267	3.457267	2.360327
H	0.897974	3.570982	4.118371
C	-2.402590	-0.915142	-0.920573
C	-1.272801	0.161550	-2.679621
C	-3.619629	-0.817256	-1.597997
C	-2.458457	0.274998	-3.411955
H	-0.332149	0.531659	-3.073017
C	-3.646748	-0.215760	-2.863039
H	-2.438958	0.743860	-4.387759
H	-4.581190	-0.132687	-3.406674
C	0.377844	-2.984269	1.458556
C	1.950728	-3.208739	-0.272078
C	0.610390	-4.295954	1.880189
C	2.237660	-4.521236	0.107581
H	2.436007	-2.727239	-1.112152
C	1.555146	-5.072375	1.197821
H	2.972392	-5.096018	-0.442548
H	1.750746	-6.091876	1.510671
N	0.635061	1.043532	1.202622
N	-1.182290	-1.059401	1.247991
N	-1.254809	-0.421666	-1.456306
N	1.039860	-2.462042	0.394185
C	-2.271073	-1.637154	0.407483
C	-0.569118	-2.046264	2.182297
C	-1.559421	0.222205	1.906092
H	-2.096737	0.047465	2.849454
H	-2.252416	0.738143	1.230854
H	-2.006894	-2.684004	0.215561
H	-3.230922	-1.640069	0.944220
H	-0.000492	-1.475772	2.927021
H	-1.336681	-2.614851	2.727323
O	1.801830	-0.325981	-1.531629
O	2.383640	0.871310	-1.652919
H	-1.073003	2.042521	3.940148
H	-4.526391	-1.208054	-1.149400
H	0.065700	-4.701479	2.725555
C	1.731038	1.898458	-5.553802
C	2.138576	1.007532	-6.578039
C	1.660878	3.303477	-5.727403
C	2.524953	1.583179	-7.801581
C	2.063216	3.808254	-6.976901
C	2.494360	2.962358	-7.996843
H	2.853212	0.952757	-8.616385
H	2.039886	4.872831	-7.163939
H	2.802007	3.379435	-8.950363

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O	1.305191	1.345716	-4.307768
H	2.029710	1.285331	-3.648689
C	1.148493	4.263501	-4.620086
C	2.149413	-0.533956	-6.397847
C	2.038576	4.179328	-3.347833
H	1.729217	4.949044	-2.629264
H	1.954658	3.211367	-2.849518
H	3.091396	4.355882	-3.597016
C	-0.324480	3.920735	-4.259822
H	-0.408230	2.896800	-3.892275
H	-0.689433	4.606334	-3.483939
H	-0.969560	4.031778	-5.139479
C	1.172631	5.741949	-5.086210
H	2.187609	6.082249	-5.319982
H	0.539539	5.904371	-5.965222
H	0.787795	6.376434	-4.279954
C	0.710604	-1.044550	-6.104421
H	0.717180	-2.136436	-5.990584
H	0.315928	-0.598715	-5.190217
H	0.039039	-0.795760	-6.934796
C	3.107995	-0.955864	-5.248330
H	2.751358	-0.620745	-4.272499
H	3.185656	-2.050191	-5.216177
H	4.114183	-0.552880	-5.413212
C	2.638932	-1.256817	-7.679021
H	1.994621	-1.046263	-8.539749
H	3.667721	-0.982106	-7.938302
H	2.617930	-2.338962	-7.507600

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Table S12. Optimized cartesian xyz coordinates of Structure TS12 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	0.291130	-0.632540	-0.436373
C	2.005949	1.747338	0.577747
C	0.004649	1.328413	1.735685
C	2.359601	2.750824	1.483327
H	2.614536	1.482134	-0.278918
C	0.307273	2.312592	2.679404
C	1.501251	3.033637	2.550412
H	3.288473	3.292157	1.352583
H	1.754628	3.801612	3.272659
C	-2.626288	-0.816530	-0.766230
C	-1.673228	-0.038970	-2.768332
C	-3.913923	-0.695306	-1.293744
C	-2.933953	0.089092	-3.357070
H	-0.762443	0.215324	-3.297704
C	-4.068606	-0.239847	-2.609023
H	-3.017065	0.445922	-4.376133
H	-5.059282	-0.141647	-3.038562
C	0.292429	-2.851511	1.503758
C	1.630765	-3.403733	-0.347792
C	0.494136	-4.114191	2.066749
C	1.882249	-4.676797	0.168043
H	2.043334	-3.051924	-1.285941
C	1.301197	-5.036948	1.389154
H	2.514267	-5.367152	-0.376856
H	1.472351	-6.021598	1.809546
N	0.852554	1.051343	0.710569
N	-1.123772	-0.825228	1.220846
N	-1.531203	-0.483512	-1.497447
N	0.848060	-2.520313	0.311727
C	-2.362489	-1.389058	0.612414
C	-0.482096	-1.749539	2.199629
C	-1.300387	0.557637	1.748426
H	-1.737944	0.550346	2.757217
H	-2.014581	1.064580	1.088564
H	-2.208341	-2.470883	0.518694
H	-3.233648	-1.241069	1.267268
H	0.220073	-1.152106	2.793803
H	-1.220504	-2.171362	2.896822
O	1.529604	-0.769868	-1.923922
O	2.261489	0.403220	-2.214815
H	-0.377376	2.513690	3.495983
H	-4.777110	-0.956112	-0.691291
H	0.035987	-4.369534	3.015899
C	1.738227	1.859700	-5.229101
C	2.403544	1.103768	-6.265587
C	1.595802	3.295379	-5.305904
C	2.915058	1.826693	-7.347712
C	2.138489	3.936693	-6.420696
C	2.792075	3.217320	-7.427677
H	3.417556	1.311013	-8.153227
H	2.059875	5.009631	-6.523744
H	3.204931	3.743931	-8.282036

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O	1.160459	1.218090	-4.185866
H	1.757827	0.823567	-3.301816
C	0.859941	4.106214	-4.212746
C	2.582899	-0.433474	-6.206669
C	1.545297	3.916587	-2.830042
H	1.045173	4.549984	-2.086598
H	1.492618	2.882071	-2.489499
H	2.598326	4.218634	-2.876077
C	-0.628794	3.662845	-4.132783
H	-0.708809	2.607780	-3.868958
H	-1.150325	4.259468	-3.373866
H	-1.131691	3.824825	-5.093501
C	0.869854	5.625120	-4.520824
H	1.887740	6.028381	-4.567105
H	0.358805	5.859004	-5.461294
H	0.341254	6.152915	-3.719802
C	1.240446	-1.162324	-5.913448
H	1.393610	-2.244665	-5.998797
H	0.871794	-0.942598	-4.912722
H	0.474475	-0.872277	-6.642720
C	3.634523	-0.789654	-5.114918
H	3.334725	-0.458706	-4.119180
H	3.772877	-1.877580	-5.083607
H	4.602402	-0.333601	-5.353944
C	3.112153	-0.995384	-7.552390
H	2.441446	-0.759751	-8.386474
H	4.114508	-0.624979	-7.792273
H	3.180104	-2.085568	-7.476228

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Table S13. Optimized cartesian xyz coordinates of Structure TS12 triplet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	0.272912	-0.634240	-0.424539
C	2.020495	1.728147	0.571914
C	0.030606	1.325762	1.754411
C	2.395654	2.726475	1.474399
H	2.616684	1.459054	-0.292125
C	0.355179	2.305356	2.695847
C	1.553978	3.015498	2.553008
H	3.328032	3.258976	1.332607
H	1.823907	3.779588	3.273384
C	-2.647022	-0.798380	-0.719074
C	-1.704582	-0.049531	-2.737191
C	-3.938146	-0.664057	-1.235312
C	-2.968891	0.090595	-3.314810
H	-0.794986	0.186347	-3.276530
C	-4.100182	-0.216962	-2.552466
H	-3.057705	0.439976	-4.335982
H	-5.093778	-0.108898	-2.972797
C	0.273638	-2.855610	1.517490
C	1.585748	-3.423937	-0.346824
C	0.464921	-4.121516	2.077372
C	1.826460	-4.700563	0.165142
H	1.993107	-3.079408	-1.289866
C	1.253284	-5.054233	1.391816
H	2.443798	-5.398527	-0.386891
H	1.415872	-6.041303	1.809934
N	0.862297	1.042462	0.717608
N	-1.129658	-0.816175	1.258444
N	-1.555382	-0.485156	-1.463940
N	0.821679	-2.529803	0.320287
C	-2.378782	-1.366005	0.661361
C	-0.482091	-1.747263	2.224762
C	-1.282422	0.568448	1.785307
H	-1.706467	0.569722	2.800127
H	-1.999444	1.082824	1.134166
H	-2.239654	-2.450236	0.571330
H	-3.244506	-1.204635	1.320577
H	0.233707	-1.157011	2.809902
H	-1.212588	-2.165340	2.932822
O	1.477410	-0.769595	-1.951658
O	2.235738	0.384629	-2.236007
H	-0.317011	2.511000	3.521618
H	-4.798618	-0.908764	-0.622300
H	0.012425	-4.371631	3.030648
C	1.754363	1.861072	-5.249131
C	2.446911	1.120288	-6.282131
C	1.592137	3.297240	-5.323982
C	2.967216	1.856363	-7.350181
C	2.145980	3.951385	-6.424800
C	2.827947	3.246290	-7.423718
H	3.489626	1.352527	-8.150519
H	2.054607	5.023705	-6.523945
H	3.249205	3.783350	-8.267395

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O	1.179435	1.209638	-4.217890
H	1.775061	0.793431	-3.304928
C	0.824728	4.090951	-4.240633
C	2.637423	-0.415561	-6.232822
C	1.490884	3.908670	-2.847570
H	0.967740	4.530363	-2.110186
H	1.450657	2.872000	-2.512067
H	2.539027	4.229357	-2.875641
C	-0.656701	3.619845	-4.186525
H	-0.720919	2.562160	-3.928898
H	-1.201031	4.202997	-3.433194
H	-1.147212	3.777293	-5.154363
C	0.811896	5.610793	-4.543741
H	1.822577	6.033639	-4.569144
H	0.314509	5.838248	-5.493086
H	0.258153	6.125579	-3.751296
C	1.294163	-1.155080	-5.972146
H	1.458150	-2.236257	-6.051548
H	0.898274	-0.935433	-4.981698
H	0.544895	-0.872486	-6.721366
C	3.670802	-0.775846	-5.125130
H	3.345521	-0.465782	-4.130905
H	3.822720	-1.862235	-5.108458
H	4.637500	-0.303582	-5.335588
C	3.196731	-0.961727	-7.573043
H	2.540695	-0.723355	-8.417899
H	4.200931	-0.582200	-7.790181
H	3.270723	-2.052085	-7.505284

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Table S14. Optimized cartesian xyz coordinates of Structure 2 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	0.303297	-0.670596	-0.303221
C	1.955249	1.635497	0.925460
C	-0.121540	1.190918	1.932097
C	2.270974	2.572086	1.913677
H	2.608206	1.403109	0.091908
C	0.140267	2.107216	2.953176
C	1.354024	2.806944	2.943123
H	3.217125	3.097990	1.875390
H	1.577493	3.520961	3.727996
C	-2.579561	-0.838543	-0.849160
C	-1.446511	-0.046267	-2.749386
C	-3.815105	-0.694873	-1.486637
C	-2.647909	0.106368	-3.445399
H	-0.484940	0.190581	-3.186323
C	-3.847973	-0.218514	-2.803071
H	-2.639211	0.475526	-4.463517
H	-4.795973	-0.102673	-3.316563
C	0.155495	-2.957095	1.565390
C	1.664393	-3.411920	-0.178225
C	0.312760	-4.246030	2.082038
C	1.876155	-4.709048	0.294826
H	2.156588	-3.004284	-1.053940
C	1.185560	-5.131815	1.436580
H	2.561128	-5.370172	-0.221862
H	1.322933	-6.136510	1.820794
N	0.782755	0.959107	0.945455
N	-1.244963	-0.920260	1.256755
N	-1.424564	-0.506287	-1.477432
N	0.815975	-2.567421	0.448562
C	-2.440671	-1.440422	0.536784
C	-0.685794	-1.890246	2.241163
C	-1.437696	0.446067	1.818262
H	-1.951561	0.415379	2.790451
H	-2.090458	0.989274	1.124130
H	-2.305704	-2.524003	0.433076
H	-3.361177	-1.285482	1.119411
H	-0.042270	-1.321472	2.923432
H	-1.478637	-2.347334	2.851529
O	1.581802	-0.781363	-1.746351
O	2.424273	0.431911	-1.867954
H	-0.589518	2.271839	3.738289
H	-4.730753	-0.955718	-0.967331
H	-0.229599	-4.549960	2.970647
C	1.760045	1.959725	-5.389422
C	2.260566	1.122541	-6.491796
C	1.515237	3.396733	-5.592733
C	2.460062	1.736689	-7.722596
C	1.751943	3.918521	-6.857189
C	2.211467	3.107170	-7.910399
H	2.819121	1.163109	-8.565616
H	1.586634	4.968489	-7.055442
H	2.382901	3.549605	-8.886532

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O	1.519975	1.432726	-4.230104
H	2.108406	0.814326	-2.733028
C	1.017240	4.282344	-4.433668
C	2.574942	-0.371206	-6.280021
C	2.035440	4.250250	-3.255509
H	1.696009	4.928930	-2.463741
H	2.129694	3.247679	-2.836342
H	3.024637	4.586956	-3.586845
C	-0.374264	3.787550	-3.941545
H	-0.312721	2.771426	-3.549688
H	-0.737015	4.449756	-3.146108
H	-1.105709	3.810393	-4.758508
C	0.858212	5.759456	-4.872037
H	1.807658	6.192593	-5.206308
H	0.119714	5.873871	-5.673791
H	0.509775	6.348837	-4.017347
C	1.322896	-1.138167	-5.762415
H	1.542028	-2.212147	-5.741799
H	1.055651	-0.824291	-4.753420
H	0.466036	-0.983410	-6.429713
C	3.741287	-0.517980	-5.257813
H	3.477705	-0.121003	-4.276622
H	3.986940	-1.579853	-5.138975
H	4.639342	-0.002662	-5.617935
C	3.021016	-1.049545	-7.599925
H	2.240497	-1.006612	-8.368579
H	3.936873	-0.604546	-8.004858
H	3.231453	-2.105462	-7.401219

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Table S15. Optimized cartesian xyz coordinates of Structure 2 triplet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	0.308065	-0.672315	-0.314770
C	1.972536	1.620847	0.919376
C	-0.113376	1.195839	1.915528
C	2.289722	2.558667	1.906006
H	2.629392	1.378445	0.091527
C	0.149214	2.114318	2.934453
C	1.368064	2.805113	2.928642
H	3.240461	3.076495	1.871821
H	1.591974	3.520842	3.711866
C	-2.573610	-0.820077	-0.871379
C	-1.427583	-0.042655	-2.770395
C	-3.805762	-0.669178	-1.513910
C	-2.625188	0.113717	-3.472454
H	-0.462250	0.185602	-3.203919
C	-3.830127	-0.198761	-2.832876
H	-2.609824	0.476487	-4.492944
H	-4.775418	-0.078295	-3.350558
C	0.140134	-2.954826	1.556565
C	1.654019	-3.419418	-0.180436
C	0.289794	-4.243370	2.076318
C	1.859015	-4.716258	0.296486
H	2.150823	-3.015324	-1.055330
C	1.161790	-5.133837	1.436255
H	2.543763	-5.381250	-0.215727
H	1.293597	-6.138316	1.823084
N	0.794467	0.954363	0.934486
N	-1.247292	-0.909657	1.240118
N	-1.413934	-0.496893	-1.495947
N	0.806194	-2.570579	0.441216
C	-2.443826	-1.422003	0.515594
C	-0.698776	-1.882903	2.227699
C	-1.433492	0.458842	1.798254
H	-1.951358	0.433517	2.768461
H	-2.080208	1.004486	1.100297
H	-2.315711	-2.506479	0.412723
H	-3.365501	-1.260971	1.094778
H	-0.055591	-1.317856	2.913511
H	-1.497585	-2.335422	2.833983
O	1.586758	-0.791445	-1.756218
O	2.449011	0.407508	-1.866715
H	-0.583787	2.287285	3.714851
H	-4.725424	-0.920667	-0.996862
H	-0.257561	-4.543548	2.963207
C	1.752801	1.953242	-5.370403
C	2.249467	1.117231	-6.475951
C	1.489320	3.386799	-5.576759
C	2.429784	1.729033	-7.710604
C	1.707539	3.905903	-6.845165
C	2.165081	3.095738	-7.900211
H	2.785548	1.156128	-8.555661
H	1.529662	4.953144	-7.045415
H	2.322492	3.536324	-8.879214

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O	1.530746	1.427085	-4.206965
H	2.140164	0.802661	-2.727921
C	0.996939	4.274631	-4.417026
C	2.580921	-0.372934	-6.266737
C	2.030789	4.259576	-3.252948
H	1.696705	4.940717	-2.461178
H	2.138527	3.260615	-2.828619
H	3.012395	4.601947	-3.599847
C	-0.382414	3.769551	-3.902411
H	-0.304263	2.759664	-3.498205
H	-0.743535	4.437699	-3.111145
H	-1.123552	3.773208	-4.710751
C	0.816955	5.746986	-4.862424
H	1.755179	6.184693	-5.221794
H	0.058787	5.850439	-5.647453
H	0.484322	6.339616	-4.003740
C	1.343830	-1.153288	-5.734091
H	1.571039	-2.226454	-5.729096
H	1.093096	-0.852648	-4.715746
H	0.474161	-0.997032	-6.385092
C	3.762105	-0.509319	-5.260316
H	3.508359	-0.116383	-4.275054
H	4.019194	-1.568376	-5.145985
H	4.650097	0.014369	-5.631641
C	3.015980	-1.045519	-7.593249
H	2.224511	-1.009091	-8.350865
H	3.921133	-0.590822	-8.010362
H	3.239566	-2.099376	-7.398883

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Table S16. Optimized cartesian xyz coordinates of Structure 3 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.828215	-1.156959	-0.421168
C	0.870348	0.861275	-1.993458
C	0.841116	1.132935	0.340021
C	1.804043	1.889857	-2.140802
H	0.457089	0.320177	-2.834388
C	1.779969	2.164062	0.262826
C	2.267857	2.544804	-0.994134
H	2.150329	2.165999	-3.128873
H	2.997004	3.342962	-1.075921
C	-2.658427	-0.705531	1.847986
C	-3.835952	-0.596870	-0.185349
C	-3.803377	-0.357442	2.568887
C	-5.018746	-0.261505	0.477884
H	-3.759197	-0.708587	-1.260690
C	-4.998589	-0.135259	1.872192
H	-5.929836	-0.099401	-0.084955
H	-5.899827	0.133616	2.411790
C	0.778899	-2.993695	1.212920
C	-0.139720	-4.182074	-0.593629
C	1.326658	-4.163093	1.744814
C	0.390528	-5.383470	-0.117312
H	-0.725774	-4.108822	-1.502098
C	1.132432	-5.374065	1.068454
H	0.218319	-6.303042	-0.663100
H	1.550013	-6.292725	1.464987
N	0.414133	0.489773	-0.776121
N	-0.178929	-0.738721	1.620935
N	-2.688787	-0.807685	0.497093
N	0.053928	-3.013704	0.063699
C	-1.338123	-1.062527	2.505033
C	0.995810	-1.631520	1.840414
C	0.180005	0.710352	1.636676
H	0.815923	0.955607	2.499601
H	-0.755006	1.271718	1.753409
H	-1.317014	-2.144643	2.681538
H	-1.241715	-0.573035	3.484884
H	1.857323	-1.151543	1.360425
H	1.232075	-1.728029	2.910016
O	-1.571683	-1.202883	-2.204861
O	-1.410186	-2.538537	-2.862592
H	2.118666	2.662647	1.164249
H	-3.765147	-0.267065	3.648831
H	1.894403	-4.127304	2.667957
C	0.437229	1.742345	-5.752961
C	-0.664078	2.674226	-5.472871
C	0.177618	0.297352	-5.847701
C	-1.909822	2.132404	-5.173556
C	-1.101631	-0.149503	-5.538136
C	-2.127050	0.745675	-5.182145
H	-2.744332	2.780470	-4.939968
H	-1.345289	-1.203381	-5.586987
H	-3.107114	0.355817	-4.933721

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O	1.642338	2.191703	-5.903204
H	-0.815508	-2.316496	-3.615667
C	1.292910	-0.663451	-6.304411
C	-0.435265	4.194761	-5.546824
C	2.495495	-0.627834	-5.317831
H	3.261517	-1.338868	-5.649399
H	2.936375	0.368771	-5.279982
H	2.181740	-0.920822	-4.306854
C	1.778626	-0.251446	-7.726155
H	2.205109	0.752902	-7.716129
H	2.546611	-0.954267	-8.070119
H	0.949561	-0.277566	-8.442983
C	0.792588	-2.125372	-6.385714
H	0.454118	-2.499634	-5.409519
H	-0.026270	-2.243853	-7.103760
H	1.615564	-2.769775	-6.711834
C	0.045273	4.572888	-6.979933
H	0.174622	5.659529	-7.046573
H	0.997171	4.093476	-7.214521
H	-0.696435	4.274617	-7.730318
C	0.630142	4.647440	-4.506639
H	1.595670	4.183604	-4.713664
H	0.746470	5.736395	-4.557115
H	0.313854	4.389021	-3.488249
C	-1.737974	4.980024	-5.261105
H	-2.530277	4.731817	-5.976455
H	-2.114059	4.801234	-4.246496
H	-1.535264	6.052259	-5.352935

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Table S17. Optimized cartesian xyz coordinates of Structure 3 triplet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-1.191619	-0.932139	-0.289616
C	0.785288	0.586804	-2.089566
C	1.066425	0.860479	0.228950
C	1.911015	1.371154	-2.354813
H	0.184774	0.140446	-2.872176
C	2.210583	1.636156	0.031592
C	2.634979	1.896430	-1.278688
H	2.211441	1.556249	-3.378846
H	3.519225	2.498794	-1.454022
C	-2.554756	-0.084656	2.164726
C	-3.861997	0.495780	0.301501
C	-3.472527	0.513532	3.032906
C	-4.822642	1.100008	1.113780
H	-3.937562	0.470914	-0.778390
C	-4.623565	1.106968	2.499821
H	-5.698563	1.558869	0.671740
H	-5.349290	1.573781	3.156246
C	0.162428	-3.141644	1.131431
C	-1.211344	-4.052356	-0.540604
C	0.543440	-4.415540	1.559869
C	-0.853930	-5.351763	-0.172412
H	-1.902439	-3.833659	-1.344762
C	0.031315	-5.536251	0.894611
H	-1.267441	-6.196893	-0.708985
H	0.317915	-6.534130	1.207298
N	0.381902	0.342819	-0.822421
N	-0.213992	-0.736236	1.636499
N	-2.759473	-0.086479	0.823833
N	-0.708142	-2.971786	0.103348
C	-1.311257	-0.806819	2.646246
C	0.741965	-1.877288	1.732134
C	0.471362	0.590955	1.597657
H	1.238709	0.667304	2.381297
H	-0.287318	1.353441	1.811249
H	-1.549713	-1.868039	2.786722
H	-0.985929	-0.415032	3.620800
H	1.636791	-1.594569	1.164693
H	1.058036	-2.047734	2.771610
O	-1.975943	-0.912079	-2.045928
O	-2.881507	-2.108313	-2.155181
H	2.756129	2.032282	0.880951
H	-3.292285	0.514275	4.102177
H	1.230216	-4.528874	2.391499
C	0.737741	1.866482	-6.624862
C	-0.535389	2.322739	-6.050786
C	1.109540	0.445845	-6.569281
C	-1.350501	1.373739	-5.443082
C	0.232770	-0.430021	-5.936115
C	-0.978114	0.018891	-5.377443
H	-2.296180	1.666137	-5.006036
H	0.466491	-1.484706	-5.871829
H	-1.630268	-0.689976	-4.877267

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O	1.537010	2.720926	-7.178998
H	-3.754799	-1.693794	-2.334300
C	2.424245	-0.036670	-7.209139
C	-0.929081	3.808779	-6.129690
C	3.638952	0.674535	-6.543016
H	4.570434	0.298973	-6.983061
H	3.589015	1.753707	-6.694533
H	3.669579	0.463730	-5.465267
C	2.410418	0.275241	-8.735644
H	2.336632	1.349002	-8.914962
H	3.335680	-0.095303	-9.192846
H	1.566743	-0.224973	-9.225998
C	2.618563	-1.563199	-7.038750
H	2.672162	-1.856027	-5.982757
H	1.816076	-2.135068	-7.518898
H	3.561506	-1.858006	-7.511657
C	-1.021432	4.252557	-7.619628
H	-1.324871	5.304871	-7.670046
H	-0.058528	4.141260	-8.119544
H	-1.770887	3.658308	-8.155921
C	0.128525	4.679796	-5.389008
H	1.110426	4.578296	-5.853369
H	-0.172469	5.733387	-5.428861
H	0.200113	4.389028	-4.332763
C	-2.305011	4.074374	-5.471565
H	-3.109892	3.518246	-5.966029
H	-2.307129	3.818862	-4.404636
H	-2.540412	5.140560	-5.556463

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Table S18. Optimized cartesian xyz coordinates of Structure TS34 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.693047	-0.957802	-0.738161
C	1.683251	0.405387	-2.158146
C	1.267551	1.107164	0.039383
C	2.813911	1.218801	-2.250178
H	1.348722	-0.209100	-2.983439
C	2.394688	1.933340	0.016542
C	3.176945	1.991971	-1.143004
H	3.383954	1.247224	-3.169998
H	4.051966	2.630964	-1.180026
C	-2.730061	0.020064	1.195477
C	-3.674374	-0.167537	-0.941268
C	-3.910036	0.582364	1.694959
C	-4.885273	0.368354	-0.501929
H	-3.516103	-0.486209	-1.962986
C	-5.000871	0.758254	0.837232
H	-5.712911	0.479925	-1.191883
H	-5.923958	1.189377	1.208123
C	0.300770	-2.719111	1.454911
C	-0.605015	-4.066942	-0.234937
C	0.515386	-3.835536	2.268402
C	-0.409374	-5.221839	0.525739
H	-1.052036	-4.085699	-1.220872
C	0.161602	-5.104857	1.796563
H	-0.704974	-6.186052	0.130155
H	0.321902	-5.981898	2.413601
N	0.928468	0.348781	-1.036723
N	-0.257646	-0.302525	1.396955
N	-2.617790	-0.330769	-0.110615
N	-0.251547	-2.839635	0.217869
C	-1.559083	-0.309562	2.104310
C	0.701908	-1.322491	1.886576
C	0.331016	1.046891	1.229666
H	0.851457	1.384607	2.139842
H	-0.500760	1.741780	1.058895
H	-1.712031	-1.322999	2.495443
H	-1.553642	0.366214	2.973524
H	1.678697	-1.083592	1.449135
H	0.820503	-1.283444	2.980654
O	-1.090255	-1.228008	-2.745548
O	-1.210952	-2.716183	-2.999638
H	2.651770	2.523579	0.889263
H	-3.974305	0.870333	2.738686
H	0.950846	-3.712041	3.253976
C	0.339946	1.430677	-5.322563
C	-0.842206	1.913976	-4.554099
C	0.377025	0.021329	-5.809010
C	-1.771756	0.990132	-4.158085
C	-0.608767	-0.827811	-5.383861
C	-1.650522	-0.405549	-4.484174
H	-2.641590	1.295279	-3.591740
H	-0.636234	-1.856026	-5.721756
H	-2.539538	-1.021914	-4.430009

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O	1.311849	2.212444	-5.556881
H	-0.351173	-2.913240	-3.441091
C	1.490848	-0.419825	-6.776904
C	-0.993938	3.418086	-4.261550
C	2.881959	-0.304367	-6.086923
H	3.661246	-0.643820	-6.778986
H	3.091322	0.729016	-5.806261
H	2.928842	-0.942007	-5.194017
C	1.467864	0.476799	-8.049182
H	1.656905	1.522096	-7.799627
H	2.244171	0.139901	-8.745596
H	0.500912	0.401963	-8.560270
C	1.305110	-1.888214	-7.227508
H	1.363778	-2.589663	-6.385806
H	0.350593	-2.040887	-7.744074
H	2.105005	-2.150567	-7.927335
C	-0.969611	4.215395	-5.598955
H	-1.113667	5.281688	-5.389811
H	-0.017278	4.090191	-6.116687
H	-1.779936	3.889793	-6.261970
C	0.159584	3.913906	-3.341999
H	1.129282	3.769955	-3.819468
H	0.023762	4.982188	-3.135485
H	0.148726	3.379798	-2.383505
C	-2.333229	3.726937	-3.551000
H	-3.196581	3.427308	-4.156446
H	-2.402649	3.234752	-2.572993
H	-2.406333	4.806294	-3.382842

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Table S19. Optimized cartesian xyz coordinates of Structure 4 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.777710	-0.878936	-0.724373
C	1.720545	0.139446	-2.160625
C	1.297521	1.070955	-0.053501
C	2.938921	0.812135	-2.265226
H	1.363222	-0.510561	-2.947524
C	2.509911	1.767016	-0.095158
C	3.341334	1.641636	-1.213817
H	3.550541	0.688279	-3.150446
H	4.283046	2.176766	-1.260351
C	-2.758579	0.183558	1.171508
C	-3.736107	-0.201113	-0.922787
C	-3.958921	0.725431	1.649001
C	-4.963957	0.303740	-0.498862
H	-3.594413	-0.589072	-1.923151
C	-5.074587	0.787338	0.810074
H	-5.808248	0.319595	-1.177477
H	-6.010447	1.198910	1.170928
C	0.208306	-2.538607	1.522107
C	-0.685810	-3.916481	-0.150440
C	0.406690	-3.646068	2.354800
C	-0.503636	-5.060019	0.628483
H	-1.130962	-3.961620	-1.137237
C	0.054021	-4.922383	1.903968
H	-0.799354	-6.029875	0.246559
H	0.204340	-5.788688	2.538534
N	0.911322	0.262884	-1.080321
N	-0.272016	-0.088475	1.476899
N	-2.648392	-0.252757	-0.111575
N	-0.332837	-2.680102	0.281405
C	-1.585721	-0.023654	2.125117
C	0.634977	-1.143138	1.958487
C	0.348296	1.198162	1.126403
H	0.882560	1.658473	1.974994
H	-0.464390	1.883356	0.852564
H	-1.747087	-0.983309	2.633337
H	-1.622638	0.749163	2.910676
H	1.626793	-0.939109	1.536594
H	0.751965	-1.128546	3.054847
O	-1.174087	-1.409228	-3.121823
O	-1.457477	-2.883479	-3.414903
H	2.796175	2.396907	0.739981
H	-4.015944	1.083725	2.671367
H	0.831882	-3.506812	3.342946
C	0.395767	1.415394	-5.314792
C	-0.759456	1.771682	-4.422882
C	0.514949	0.017382	-5.854207
C	-1.571899	0.779944	-3.995386
C	-0.347301	-0.919958	-5.401131
C	-1.430344	-0.642838	-4.416414
H	-2.399135	0.985247	-3.329054
H	-0.297060	-1.941466	-5.758598
H	-2.388495	-1.040928	-4.772608

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O	1.264819	2.276040	-5.594120
H	-0.539082	-3.234549	-3.510431
C	1.610125	-0.291676	-6.894986
C	-0.975469	3.246351	-4.028119
C	3.020286	-0.065270	-6.275349
H	3.787645	-0.307824	-7.019304
H	3.153840	0.972106	-5.965335
H	3.174410	-0.726328	-5.411967
C	1.427779	0.627253	-8.137293
H	1.539598	1.680657	-7.875769
H	2.185043	0.376462	-8.888540
H	0.441106	0.476880	-8.591417
C	1.534752	-1.760703	-7.373206
H	1.705096	-2.469272	-6.553285
H	0.571061	-1.991399	-7.841827
H	2.315221	-1.933735	-8.120849
C	-1.136978	4.113280	-5.309977
H	-1.331576	5.152879	-5.023131
H	-0.235483	4.089981	-5.924232
H	-1.985490	3.766041	-5.911758
C	0.231638	3.762390	-3.191774
H	1.159067	3.713708	-3.763167
H	0.052533	4.805267	-2.904781
H	0.346975	3.173295	-2.273687
C	-2.253730	3.420292	-3.173263
H	-3.152994	3.100360	-3.712837
H	-2.195700	2.866159	-2.228268
H	-2.376491	4.480053	-2.927070

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Table S20. Optimized cartesian xyz coordinates of Structure TS45 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.870112	-0.667974	-0.900922
C	1.582913	0.804405	-2.071349
C	1.129249	1.170199	0.198458
C	2.735631	1.589756	-2.010911
H	1.278743	0.318522	-2.987254
C	2.271549	1.964792	0.324369
C	3.082619	2.185310	-0.794852
H	3.340599	1.724355	-2.898974
H	3.971420	2.800756	-0.714337
C	-2.791250	-0.110798	1.330179
C	-3.848949	0.263526	-0.725175
C	-3.915044	0.355764	2.020880
C	-5.006632	0.724300	-0.097860
H	-3.764405	0.198611	-1.801890
C	-5.036876	0.777935	1.300110
H	-5.857868	1.037054	-0.690347
H	-5.916454	1.141070	1.819548
C	0.376193	-2.822635	0.821325
C	-0.499542	-3.820495	-1.111093
C	0.780862	-4.066380	1.316219
C	-0.104053	-5.089204	-0.680427
H	-1.034447	-3.659504	-2.041198
C	0.544011	-5.214579	0.552555
H	-0.308896	-5.956380	-1.296674
H	0.854605	-6.187347	0.917323
N	0.788397	0.603764	-0.992673
N	-0.328462	-0.484307	1.308145
N	-2.760127	-0.140324	-0.027359
N	-0.258950	-2.707679	-0.373208
C	-1.588463	-0.678555	2.057357
C	0.685129	-1.535302	1.562926
C	0.203424	0.898648	1.365727
H	0.721811	1.104695	2.315421
H	-0.655495	1.579085	1.312511
H	-1.734512	-1.760310	2.166460
H	-1.529523	-0.260048	3.074531
H	1.648951	-1.152097	1.207300
H	0.801111	-1.737016	2.639222
O	-1.710156	-1.025750	-2.733958
O	-2.554273	-2.521001	-3.130339
H	2.522825	2.399282	1.285509
H	-3.911140	0.382222	3.105052
H	1.275155	-4.133406	2.279477
C	0.271242	1.292676	-5.519406
C	-0.795521	1.905962	-4.656376
C	0.445795	-0.198172	-5.541511
C	-1.611126	1.084836	-3.957023
C	-0.419910	-0.957655	-4.831964
C	-1.584044	-0.402843	-4.083143
H	-2.393266	1.483466	-3.322568
H	-0.348944	-2.037975	-4.815566
H	-2.506843	-0.728334	-4.588835

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O	1.032142	2.028872	-6.195239
H	-3.179102	-2.459531	-2.367624
C	1.594290	-0.806255	-6.374938
C	-0.937997	3.442803	-4.619072
C	2.965498	-0.258774	-5.884929
H	3.770617	-0.710242	-6.475848
H	3.022962	0.825103	-5.997834
H	3.138066	-0.525181	-4.833307
C	1.397705	-0.455095	-7.878040
H	1.427241	0.623179	-8.040333
H	2.197605	-0.918109	-8.467513
H	0.440586	-0.843708	-8.245588
C	1.627306	-2.347530	-6.246436
H	1.782320	-2.670251	-5.209451
H	0.707342	-2.810422	-6.621792
H	2.458650	-2.737828	-6.842306
C	-1.289051	3.967620	-6.041749
H	-1.421890	5.055148	-6.005583
H	-0.495443	3.739116	-6.754402
H	-2.226207	3.525201	-6.400188
C	0.382329	4.103555	-4.130285
H	1.209082	3.880061	-4.805566
H	0.250672	5.191121	-4.091632
H	0.640455	3.760262	-3.120594
C	-2.068308	3.883562	-3.658763
H	-3.047086	3.501450	-3.972264
H	-1.878709	3.561483	-2.626854
H	-2.128527	4.976658	-3.657997

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Table S21. Optimized cartesian xyz coordinates of Structure TS35 triplet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.935917	-0.606900	-0.938915
C	1.316718	1.315217	-2.171860
C	1.194558	1.225758	0.161585
C	2.398440	2.197269	-2.125166
H	0.910063	0.965582	-3.106786
C	2.284482	2.091223	0.283549
C	2.889870	2.590243	-0.876828
H	2.834197	2.556012	-3.049159
H	3.732795	3.268173	-0.804241
C	-2.511723	-0.014957	1.469566
C	-3.494904	1.087943	-0.354595
C	-3.539337	0.402418	2.319582
C	-4.553474	1.534468	0.438357
H	-3.420613	1.304059	-1.413131
C	-4.573894	1.186042	1.794399
H	-5.339862	2.140095	0.004761
H	-5.381996	1.520834	2.434876
C	0.555436	-2.867562	0.206938
C	-0.418312	-3.477787	-1.840746
C	0.992840	-4.175518	0.428647
C	0.009162	-4.797922	-1.688437
H	-1.019381	-3.142961	-2.672839
C	0.722803	-5.151272	-0.538238
H	-0.226101	-5.532580	-2.448479
H	1.056080	-6.172206	-0.389530
N	0.721748	0.844278	-1.053028
N	-0.158591	-0.641501	1.078111
N	-2.498087	0.335019	0.159894
N	-0.134605	-2.536604	-0.911864
C	-1.370904	-0.908164	1.911556
C	0.866798	-1.729083	1.151454
C	0.435992	0.702257	1.359498
H	1.082298	0.663025	2.247591
H	-0.388179	1.385993	1.588077
H	-1.648210	-1.957944	1.756838
H	-1.155775	-0.774331	2.981549
H	1.825320	-1.283799	0.860396
H	0.978506	-2.092045	2.182629
O	-1.952644	-0.707486	-2.616160
O	-2.870402	-1.952965	-1.741084
H	2.650373	2.372893	1.264952
H	-3.533327	0.119448	3.366287
H	1.532874	-4.425406	1.335185
C	0.303102	1.252166	-5.467910
C	-1.017148	1.823669	-5.108169
C	0.497568	-0.222272	-5.451359
C	-1.991365	0.967464	-4.655177
C	-0.523962	-1.001848	-4.975560
C	-1.778048	-0.449059	-4.529319
H	-2.976475	1.338014	-4.404795
H	-0.430320	-2.079938	-4.961061
H	-2.646957	-1.093047	-4.601467

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O	1.277639	2.021648	-5.764863
H	-3.739778	-1.511280	-1.871796
C	1.807048	-0.825659	-5.998986
C	-1.266879	3.334934	-5.281781
C	3.027230	-0.355836	-5.155429
H	3.941965	-0.811283	-5.552967
H	3.132681	0.729144	-5.196826
H	2.924369	-0.671234	-4.108862
C	2.003813	-0.385678	-7.479136
H	2.092088	0.699061	-7.559654
H	2.918756	-0.839999	-7.877047
H	1.163635	-0.719963	-8.099199
C	1.779122	-2.372585	-5.964361
H	1.683018	-2.758870	-4.941831
H	0.962835	-2.781101	-6.571242
H	2.719095	-2.755822	-6.374714
C	-1.009369	3.743871	-6.761407
H	-1.218797	4.812637	-6.887091
H	0.027066	3.557451	-7.047069
H	-1.669263	3.188743	-7.438609
C	-0.327163	4.151480	-4.348046
H	0.719472	3.962386	-4.590393
H	-0.528313	5.222061	-4.473680
H	-0.505699	3.896454	-3.295362
C	-2.725605	3.716553	-4.934408
H	-3.448606	3.200672	-5.576800
H	-2.969595	3.498973	-3.886940
H	-2.857920	4.792728	-5.086064

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Table S22. Optimized cartesian xyz coordinates of Structure 5 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.933032	-0.536879	-0.847918
C	0.961962	1.744347	-1.856282
C	1.220286	1.098022	0.380847
C	2.020307	2.650093	-1.755836
H	0.401989	1.623910	-2.770772
C	2.300344	1.969562	0.541694
C	2.706929	2.756752	-0.542327
H	2.296887	3.249055	-2.614731
H	3.541769	3.440708	-0.438382
C	-2.340013	-0.492585	1.775070
C	-3.592262	0.731896	0.210549
C	-3.251603	-0.194948	2.791365
C	-4.546211	1.060120	1.176916
H	-3.651214	1.060048	-0.820777
C	-4.370982	0.589708	2.484460
H	-5.399920	1.672420	0.913190
H	-5.091894	0.833614	3.256694
C	0.366177	-3.077617	-0.117959
C	-1.184994	-3.480453	-1.838362
C	0.721925	-4.426256	-0.071692
C	-0.860372	-4.840195	-1.848131
H	-1.978929	-3.047987	-2.438787
C	0.109142	-5.318368	-0.961312
H	-1.372036	-5.507362	-2.530879
H	0.373525	-6.369934	-0.946657
N	0.576377	0.976709	-0.809476
N	-0.013116	-0.946656	1.064969
N	-2.517602	-0.029101	0.514335
N	-0.562103	-2.617614	-0.997872
C	-1.123299	-1.373079	1.974366
C	0.974317	-2.035041	0.790552
C	0.643917	0.308628	1.533085
H	1.413463	0.091136	2.287435
H	-0.125601	0.916438	2.023529
H	-1.377712	-2.407024	1.716395
H	-0.797562	-1.366616	3.024214
H	1.837556	-1.569892	0.299410
H	1.334340	-2.488744	1.725255
O	-1.985122	-0.065763	-2.382792
O	-3.461613	-1.713284	-2.556975
H	2.807325	2.036426	1.497996
H	-3.093038	-0.567197	3.797589
H	1.457709	-4.772655	0.645772
C	0.270326	1.173795	-5.629417
C	-0.905912	1.975974	-5.157883
C	0.537471	-0.170211	-5.014798
C	-1.769813	1.399641	-4.291340
C	-0.376952	-0.681566	-4.159999
C	-1.670486	-0.013458	-3.811012
H	-2.635592	1.935110	-3.920414
H	-0.231650	-1.655744	-3.710142
H	-2.482053	-0.593045	-4.284994

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O	1.043756	1.632283	-6.508618
H	-3.951036	-1.185555	-1.884745
C	1.834510	-0.918721	-5.389942
C	-1.089355	3.417711	-5.678158
C	3.075147	-0.037335	-5.066905
H	3.990488	-0.590982	-5.306130
H	3.066687	0.884677	-5.650045
H	3.106221	0.216469	-3.998749
C	1.820206	-1.270554	-6.905224
H	1.770733	-0.368573	-7.517098
H	2.733675	-1.819371	-7.163746
H	0.961687	-1.909130	-7.145878
C	1.977586	-2.239419	-4.595232
H	2.005043	-2.063061	-3.511802
H	1.164188	-2.941515	-4.813488
H	2.917080	-2.726532	-4.876866
C	-1.303533	3.398656	-7.218498
H	-1.468642	4.420956	-7.578939
H	-0.435192	2.983887	-7.731662
H	-2.186561	2.802700	-7.478080
C	0.161153	4.275509	-5.331308
H	1.060806	3.872569	-5.799424
H	0.014397	5.300814	-5.690432
H	0.308690	4.323407	-4.243552
C	-2.320537	4.098423	-5.033667
H	-3.251506	3.572684	-5.273374
H	-2.228552	4.165739	-3.942710
H	-2.410058	5.118021	-5.421581

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Table S23. Optimized cartesian xyz coordinates of Structure 5 triplet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.912028	-0.483226	-0.905082
C	0.993409	1.832622	-1.806870
C	1.213525	1.116183	0.414185
C	2.028169	2.756912	-1.650520
H	0.455846	1.726543	-2.737156
C	2.266982	2.007920	0.632370
C	2.679963	2.839548	-0.415250
H	2.314664	3.390181	-2.481066
H	3.494195	3.539918	-0.267397
C	-2.355256	-0.559240	1.681487
C	-3.556782	0.780036	0.178566
C	-3.330304	-0.390466	2.668500
C	-4.572088	0.985224	1.114339
H	-3.578889	1.201372	-0.818504
C	-4.455186	0.390565	2.376768
H	-5.430615	1.595312	0.861476
H	-5.227071	0.533822	3.124555
C	0.399834	-3.040479	-0.290879
C	-1.105541	-3.365780	-2.065485
C	0.760193	-4.388928	-0.301556
C	-0.776272	-4.721823	-2.134173
H	-1.873711	-2.909252	-2.677422
C	0.173533	-5.239091	-1.247626
H	-1.267528	-5.356347	-2.861521
H	0.442618	-6.288968	-1.278294
N	0.603297	1.023958	-0.794339
N	-0.013939	-0.970152	0.989462
N	-2.475545	0.025609	0.466990
N	-0.507376	-2.541514	-1.170805
C	-1.135994	-1.441649	1.859968
C	0.983796	-2.039529	0.679683
C	0.627891	0.268688	1.521091
H	1.389240	0.022088	2.274740
H	-0.152797	0.846762	2.028356
H	-1.382638	-2.463218	1.550207
H	-0.826245	-1.483068	2.913813
H	1.852515	-1.546039	0.227445
H	1.329813	-2.536814	1.597152
O	-1.814946	0.156780	-2.482596
O	-3.284355	-1.485155	-2.244506
H	2.748217	2.055981	1.602980
H	-3.217260	-0.861721	3.638630
H	1.479821	-4.767049	0.415942
C	0.373983	1.232320	-5.813070
C	-0.850038	1.994908	-5.407421
C	0.697298	-0.059705	-5.120725
C	-1.690742	1.432001	-4.510308
C	-0.186452	-0.553909	-4.224110
C	-1.512934	0.069703	-3.912274
H	-2.586046	1.945926	-4.181817
H	0.011490	-1.486289	-3.711268
H	-2.290033	-0.596010	-4.330652

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O	1.139210	1.682106	-6.703423
H	-3.867156	-0.728327	-2.483237
C	2.022635	-0.774845	-5.461612
C	-1.103639	3.387952	-6.022501
C	3.228002	0.164168	-5.168420
H	4.164850	-0.362904	-5.384187
H	3.187489	1.062484	-5.785833
H	3.243850	0.458853	-4.110629
C	2.030173	-1.187115	-6.962165
H	1.960688	-0.312744	-7.610372
H	2.961089	-1.719203	-7.191466
H	1.192667	-1.859611	-7.183886
C	2.209164	-2.058305	-4.617234
H	2.233649	-1.840084	-3.541587
H	1.417510	-2.793193	-4.806628
H	3.163211	-2.525728	-4.882940
C	-1.288701	3.262871	-7.562148
H	-1.497358	4.251948	-7.986802
H	-0.391866	2.862877	-8.036979
H	-2.136727	2.608829	-7.798337
C	0.093067	4.332266	-5.711912
H	1.019240	3.955798	-6.149055
H	-0.107018	5.326480	-6.127937
H	0.226344	4.445662	-4.627521
C	-2.381025	4.037704	-5.439623
H	-3.278597	3.447601	-5.659136
H	-2.310755	4.176662	-4.353696
H	-2.518576	5.025560	-5.891581

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Table S24. Optimized cartesian xyz coordinates of Structure TS56 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.845461	-0.454652	-0.697259
C	1.277569	1.643583	-1.561572
C	1.385966	0.926362	0.670002
C	2.390517	2.468546	-1.387553
H	0.749838	1.576243	-2.502393
C	2.511755	1.718823	0.905475
C	3.020828	2.500073	-0.139077
H	2.752509	3.066396	-2.214777
H	3.892892	3.123790	0.021522
C	-2.395078	-0.571658	1.822794
C	-3.592384	0.626430	0.191227
C	-3.376493	-0.316104	2.783545
C	-4.615224	0.906829	1.100815
H	-3.597918	0.946202	-0.844097
C	-4.500817	0.434174	2.413606
H	-5.475855	1.485680	0.788651
H	-5.275380	0.646167	3.142164
C	0.244730	-3.123626	-0.100326
C	-1.258725	-3.317956	-1.898526
C	0.510566	-4.493996	-0.128348
C	-1.022630	-4.692853	-1.983969
H	-1.989655	-2.799139	-2.513453
C	-0.121022	-5.286662	-1.094975
H	-1.544824	-5.282765	-2.727339
H	0.077084	-6.351692	-1.140085
N	0.796386	0.882187	-0.551631
N	-0.029990	-1.044058	1.212086
N	-2.510330	-0.092340	0.561241
N	-0.614858	-2.551201	-0.983838
C	-1.185108	-1.449313	2.075099
C	0.889483	-2.180325	0.891393
C	0.695097	0.140374	1.761646
H	1.406647	-0.161232	2.543339
H	-0.055087	0.784399	2.235834
H	-1.438848	-2.482946	1.813952
H	-0.902626	-1.441136	3.136846
H	1.795797	-1.745865	0.453125
H	1.190580	-2.716323	1.802722
O	-1.651200	0.363138	-2.223810
O	-3.502697	-1.339662	-2.746350
H	2.975503	1.731293	1.885590
H	-3.270071	-0.695605	3.793851
H	1.194379	-4.932793	0.589755
C	0.202374	1.210316	-5.788053
C	-0.974854	2.008675	-5.324064
C	0.576394	-0.046623	-5.057882
C	-1.726226	1.521856	-4.310090
C	-0.217418	-0.467686	-4.047003
C	-1.492391	0.202875	-3.641810
H	-2.584132	2.062867	-3.930828
H	0.020729	-1.369453	-3.495489
H	-2.336979	-0.473439	-3.942867

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O	0.892980	1.598995	-6.765007
H	-4.408227	-1.669065	-2.506732
C	1.849778	-0.806704	-5.487806
C	-1.286971	3.353230	-6.016421
C	3.094167	0.117427	-5.359301
H	3.995635	-0.437488	-5.644746
H	3.004072	0.989423	-6.008241
H	3.221812	0.455414	-4.322121
C	1.706052	-1.291130	-6.959304
H	1.588286	-0.447026	-7.639651
H	2.601996	-1.852784	-7.249752
H	0.840193	-1.955746	-7.066310
C	2.094400	-2.052444	-4.602514
H	2.233437	-1.783960	-3.547075
H	1.272008	-2.774550	-4.673783
H	3.006481	-2.556020	-4.939525
C	-1.610448	3.113202	-7.518904
H	-1.858561	4.068492	-7.996605
H	-0.759066	2.674415	-8.040908
H	-2.475436	2.447687	-7.627301
C	-0.071537	4.315100	-5.888073
H	0.812165	3.903927	-6.378353
H	-0.313951	5.275486	-6.358044
H	0.161015	4.508120	-4.832640
C	-2.509726	4.049145	-5.373585
H	-3.420147	3.445265	-5.465924
H	-2.344154	4.272144	-4.312376
H	-2.691158	4.998978	-5.887389

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Table S25. Optimized cartesian xyz coordinates of Structure TS56 triplet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.842139	-0.453661	-0.688303
C	1.294760	1.638527	-1.542395
C	1.387357	0.919722	0.689252
C	2.409899	2.458980	-1.361750
H	0.773408	1.573704	-2.486983
C	2.514852	1.707845	0.931344
C	3.032981	2.487792	-0.109611
H	2.779155	3.055466	-2.186753
H	3.906457	3.108108	0.056368
C	-2.401433	-0.577337	1.824689
C	-3.595584	0.622410	0.192433
C	-3.386789	-0.326279	2.782616
C	-4.622191	0.898261	1.099100
H	-3.600557	0.943755	-0.842217
C	-4.511330	0.422738	2.411087
H	-5.483173	1.475575	0.785086
H	-5.288839	0.631151	3.137529
C	0.244394	-3.122464	-0.097222
C	-1.253318	-3.307825	-1.901632
C	0.507769	-4.493176	-0.129247
C	-1.019050	-4.682820	-1.991063
H	-1.982902	-2.783388	-2.514428
C	-0.121454	-5.281286	-1.101195
H	-1.540003	-5.269284	-2.738036
H	0.075025	-6.346496	-1.149325
N	0.804011	0.878681	-0.535685
N	-0.033496	-1.048822	1.223559
N	-2.512661	-0.094500	0.563933
N	-0.610679	-2.545438	-0.982335
C	-1.192214	-1.455214	2.080319
C	0.885993	-2.184502	0.901737
C	0.689569	0.134425	1.777063
H	1.396944	-0.167533	2.562474
H	-0.062483	0.779175	2.247332
H	-1.445077	-2.488299	1.816065
H	-0.914895	-1.449287	3.143488
H	1.794901	-1.749190	0.469734
H	1.182425	-2.725469	1.811690
O	-1.632750	0.385453	-2.217283
O	-3.452647	-1.299430	-2.725177
H	2.973135	1.717683	1.914048
H	-3.283092	-0.708656	3.792124
H	1.187716	-4.935827	0.590164
C	0.199369	1.212397	-5.797553
C	-0.975287	2.013586	-5.331544
C	0.578212	-0.039913	-5.061863
C	-1.719028	1.534647	-4.308159
C	-0.208066	-0.454057	-4.042220
C	-1.479461	0.220138	-3.635155
H	-2.574648	2.077867	-3.927004
H	0.032998	-1.352415	-3.486592
H	-2.330423	-0.459868	-3.919689

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O	0.883740	1.594936	-6.781146
H	-4.353736	-1.639630	-2.485778
C	1.847991	-0.803566	-5.495812
C	-1.294117	3.351963	-6.032575
C	3.093695	0.120550	-5.380319
H	3.992870	-0.436385	-5.668987
H	2.999731	0.989254	-6.033102
H	3.228459	0.463700	-4.345750
C	1.694456	-1.295966	-6.963689
H	1.574057	-0.455561	-7.648124
H	2.587757	-1.860702	-7.256215
H	0.826962	-1.959803	-7.061810
C	2.097176	-2.044629	-4.605242
H	2.243779	-1.770671	-3.552245
H	1.273528	-2.766178	-4.667053
H	3.006376	-2.551080	-4.945665
C	-1.628314	3.098696	-7.530535
H	-1.881540	4.049534	-8.014364
H	-0.780038	2.657029	-8.055176
H	-2.492972	2.430933	-7.626965
C	-0.078823	4.316180	-5.921297
H	0.801233	3.902624	-6.416082
H	-0.326545	5.272830	-6.396031
H	0.162481	4.516981	-4.869344
C	-2.512958	4.051759	-5.386527
H	-3.423351	3.446115	-5.466919
H	-2.339738	4.284226	-4.328567
H	-2.699385	4.996920	-5.907066

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Table S26. Optimized cartesian xyz coordinates of Structure 6 open-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.566109	-0.306694	-0.455601
C	2.276452	1.000430	-0.272402
C	1.599115	-0.159211	1.643642
C	3.531914	1.264476	0.276879
H	1.988369	1.356265	-1.252437
C	2.844577	0.051904	2.246118
C	3.823583	0.772549	1.554489
H	4.261406	1.836981	-0.283155
H	4.793432	0.949864	2.005836
C	-2.496535	0.005597	1.782898
C	-2.618792	1.876611	0.373333
C	-3.396522	0.586515	2.681418
C	-3.529607	2.508642	1.223163
H	-2.264333	2.328400	-0.545081
C	-3.921569	1.853084	2.395776
H	-3.914537	3.490458	0.975115
H	-4.620177	2.320816	3.080569
C	-0.775653	-3.204053	-0.264231
C	-1.594204	-2.467917	-2.338165
C	-1.124843	-4.522291	-0.565727
C	-1.960445	-3.765722	-2.700364
H	-1.808614	-1.638301	-2.995504
C	-1.715255	-4.809825	-1.803722
H	-2.434883	-3.923495	-3.659955
H	-1.989676	-5.828896	-2.052608
N	1.333396	0.294772	0.394734
N	-0.522439	-1.472553	1.497692
N	-2.117224	0.653080	0.652498
N	-1.003966	-2.196576	-1.150898
C	-1.923804	-1.386896	1.982255
C	-0.105753	-2.821812	1.041874
C	0.455194	-0.814438	2.394882
H	0.847004	-1.512744	3.150747
H	-0.081846	-0.029145	2.941330
H	-2.515249	-2.099296	1.395192
H	-2.011202	-1.687820	3.037557
H	0.980260	-2.783981	0.891133
H	-0.298607	-3.592283	1.805121
O	-0.512732	0.953854	-2.016815
O	-3.194473	-1.533020	-4.802391
H	3.039045	-0.333474	3.241272
H	-3.680475	0.059490	3.585792
H	-0.940741	-5.308859	0.157841
C	0.040464	1.093735	-6.121329
C	-1.289402	1.425614	-5.530699
C	1.137470	0.600728	-5.237420
C	-1.446671	1.302224	-4.176709
C	0.895675	0.515085	-3.895179
C	-0.364160	0.902290	-3.308732
H	-2.378678	1.547959	-3.685029
H	1.657834	0.169666	-3.208969
H	-2.675260	-0.947155	-5.384648

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O	0.236463	1.232703	-7.364388
H	-4.102231	-1.606470	-5.148686
C	2.498542	0.234576	-5.853432
C	-2.414341	1.947117	-6.445697
C	3.121168	1.487276	-6.540268
H	4.105270	1.225956	-6.946372
H	2.492029	1.844537	-7.356378
H	3.259560	2.299664	-5.816309
C	2.319142	-0.904991	-6.898579
H	1.671979	-0.589782	-7.718051
H	3.297860	-1.175096	-7.311418
H	1.892089	-1.800138	-6.429742
C	3.495076	-0.260165	-4.777334
H	3.706428	0.512506	-4.027994
H	3.132171	-1.158474	-4.263006
H	4.443776	-0.516130	-5.260234
C	-2.714784	0.936720	-7.591429
H	-3.518338	1.332250	-8.222829
H	-1.834492	0.764568	-8.210548
H	-3.058668	-0.028301	-7.193324
C	-1.979145	3.308834	-7.064079
H	-1.090539	3.190784	-7.686226
H	-2.790988	3.703252	-7.686054
H	-1.767690	4.042628	-6.277440
C	-3.725350	2.170347	-5.653960
H	-4.074710	1.245546	-5.178016
H	-3.612395	2.937731	-4.879918
H	-4.506521	2.510081	-6.341332

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Table S27. Optimized cartesian xyz coordinates of Structure 6 triplet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.588734	-0.194431	-0.451436
C	1.963112	1.542393	-0.562194
C	1.653717	0.255248	1.378388
C	3.197768	2.003507	-0.103109
H	1.549127	1.847461	-1.514150
C	2.889655	0.664715	1.884910
C	3.671349	1.550367	1.133522
H	3.773718	2.695518	-0.704904
H	4.632716	1.881572	1.509160
C	-2.436906	-0.377564	1.854825
C	-3.007486	1.489961	0.547947
C	-3.428156	-0.072331	2.790785
C	-4.022273	1.846580	1.439754
H	-2.784417	2.043984	-0.355641
C	-4.230778	1.056162	2.576529
H	-4.630273	2.722162	1.248945
H	-5.007063	1.313311	3.288530
C	-0.328940	-3.089889	-0.488973
C	-1.495651	-2.397798	-2.411470
C	-0.455506	-4.430486	-0.852032
C	-1.640319	-3.722165	-2.835735
H	-1.923281	-1.590044	-2.991241
C	-1.111995	-4.749846	-2.050232
H	-2.161235	-3.914780	-3.764556
H	-1.213957	-5.785857	-2.353974
N	1.215905	0.678666	0.165334
N	-0.231346	-1.376949	1.292861
N	-2.236826	0.402689	0.765678
N	-0.840127	-2.096581	-1.266291
C	-1.565291	-1.615231	1.933516
C	0.392273	-2.631712	0.760840
C	0.689351	-0.597599	2.175723
H	1.227765	-1.262328	2.865604
H	0.065172	0.065314	2.787211
H	-2.048244	-2.428460	1.380228
H	-1.446116	-1.952687	2.972336
H	1.435519	-2.394665	0.520952
H	0.402385	-3.422638	1.524063
O	-1.068490	0.969512	-1.891052
O	-2.991491	-1.263912	-4.788227
H	3.229889	0.304975	2.849631
H	-3.574591	-0.700613	3.662464
H	-0.050022	-5.209454	-0.215679
C	-0.008999	1.002315	-5.945254
C	-1.227718	1.677152	-5.472988
C	0.838055	0.292853	-4.977550
C	-1.523115	1.647641	-4.121010
C	0.463156	0.289708	-3.644032
C	-0.700963	0.961036	-3.186740
H	-2.400320	2.137990	-3.721731
H	1.055963	-0.240300	-2.908976
H	-2.495884	-0.506811	-5.155255

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O	0.310695	1.030038	-7.196704
H	-3.854090	-1.332283	-5.236657
C	2.110987	-0.430199	-5.460067
C	-2.142248	2.406230	-6.479003
C	3.082674	0.593766	-6.117453
H	3.990536	0.076709	-6.452043
H	2.613537	1.073248	-6.977653
H	3.378146	1.367726	-5.397870
C	1.731295	-1.529698	-6.495042
H	1.244101	-1.086947	-7.365137
H	2.636934	-2.053949	-6.825046
H	1.054680	-2.269009	-6.046577
C	2.865775	-1.117837	-4.295881
H	3.199463	-0.395201	-3.539715
H	2.251458	-1.883346	-3.803989
H	3.757890	-1.615523	-4.692235
C	-2.631669	1.412794	-7.572456
H	-3.301188	1.930174	-8.269528
H	-1.789259	1.001359	-8.129514
H	-3.197692	0.584499	-7.122916
C	-1.355286	3.568250	-7.150792
H	-0.488477	3.185726	-7.691227
H	-2.008061	4.094349	-7.857824
H	-1.016467	4.291431	-6.399556
C	-3.391918	3.005555	-5.790306
H	-4.003699	2.234212	-5.305484
H	-3.126238	3.759032	-5.039936
H	-4.015676	3.496832	-6.544643

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Table S28. Optimized cartesian xyz coordinates of Structure 7 closed-shell singlet at the B3LYP/lacvp level of theory.

atom	X	Y	Z
Cu	-0.633663	-0.168921	-0.365520
C	1.950053	1.469377	-0.599510
C	1.631606	0.219063	1.360074
C	3.220502	1.873181	-0.190597
H	1.535075	1.788049	-1.547258
C	2.905317	0.574796	1.815581
C	3.708752	1.414400	1.037380
H	3.811362	2.524323	-0.823113
H	4.696007	1.701222	1.381259
C	-2.458993	-0.354624	1.861266
C	-3.098191	1.460810	0.520863
C	-3.439397	-0.028602	2.803884
C	-4.103445	1.826829	1.416128
H	-2.921910	2.021930	-0.388027
C	-4.274761	1.070822	2.580423
H	-4.729414	2.685594	1.206461
H	-5.040466	1.332634	3.301843
C	-0.325656	-3.018442	-0.487588
C	-1.248521	-2.279170	-2.514300
C	-0.472622	-4.350980	-0.884368
C	-1.408161	-3.587849	-2.970833
H	-1.546702	-1.431251	-3.117657
C	-1.016287	-4.642567	-2.140195
H	-1.834954	-3.771708	-3.949269
H	-1.134747	-5.671552	-2.460238
N	1.167128	0.659495	0.157097
N	-0.242877	-1.443905	1.451686
N	-2.289421	0.392802	0.734349
N	-0.719535	-1.995038	-1.298166
C	-1.593093	-1.596950	2.027587
C	0.333300	-2.656535	0.836956
C	0.693345	-0.610187	2.229212
H	1.287242	-1.204096	2.942170
H	0.086983	0.082113	2.827358
H	-2.079071	-2.424383	1.495267
H	-1.563408	-1.881750	3.091385
H	1.393570	-2.446767	0.646342
H	0.298027	-3.526051	1.512687
H	3.258866	0.201186	2.770373
H	-3.547202	-0.631682	3.698851
H	-0.163454	-5.148270	-0.217379

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Table S29. Optimized cartesian xyz coordinates of quinone at the B3LYP/lacvp level of theory.

atom	X	Y	Z
O1	-0.991026	0.907073	-1.945005
C2	-0.019654	0.990475	-5.940712
C3	-1.271310	1.674195	-5.457903
C4	0.875992	0.273514	-4.965087
C5	-1.553820	1.623767	-4.134491
C6	0.519874	0.270076	-3.658726
C7	-0.694619	0.932059	-3.164782
H8	-2.432978	2.089942	-3.709340
H9	1.109943	-0.221819	-2.896580
O10	0.278132	1.018588	-7.159341
C11	2.148286	-0.419400	-5.484172
C12	-2.170846	2.398498	-6.475104
C13	3.090530	0.626626	-6.149002
H14	4.009117	0.127388	-6.479089
H15	2.618540	1.092882	-7.014897
H16	3.370221	1.408197	-5.432290
C17	1.770440	-1.522106	-6.516191
H18	1.273960	-1.096071	-7.389116
H19	2.681343	-2.033912	-6.848327
H20	1.110112	-2.270169	-6.061084
C21	2.926876	-1.094769	-4.330007
H22	3.254167	-0.368460	-3.577127
H23	2.331281	-1.868716	-3.832262
H24	3.822044	-1.576033	-4.737865
C25	-2.688261	1.389708	-7.541985
H26	-3.358751	1.909811	-8.236217
H27	-1.865061	0.957785	-8.112715
H28	-3.255925	0.579978	-7.067806
C29	-1.374415	3.541340	-7.170524
H30	-0.526791	3.148976	-7.734043
H31	-2.036872	4.074278	-7.862745
H32	-1.006906	4.263829	-6.431815
C33	-3.401675	3.030143	-5.781961
H34	-4.028490	2.275214	-5.293431
H35	-3.112098	3.778918	-5.035691
H36	-4.015844	3.533728	-6.535956

Table S30. Optimized cartesian xyz coordinates of water at the B3LYP/lacvp level of theory.

atom	X	Y	Z
O	-0.06	0.00	0.00
H	0.49	0.80	0.00
H	0.52	-0.78	0.00

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Table S31. Spin density populations for the atoms of the substrate of all stationary points located on the PES for the reaction mechanism studied at the B3LYP/lacvp level of theory.

Structures	Multiplicity[a]	Spin density				
		O_C	C_A	C_B	C_C	C_D
1	s	0.00	0.00	0.00	0.00	0.00
TS12		-0.21	0.02	-0.14	0.09	-0.21
2		-0.39	0.02	-0.29	0.17	-0.40
3		-0.44	0.09	-0.32	0.18	-0.39
TS34		-0.20	0.04	-0.15	0.10	-0.24
4		0.00	0.00	0.00	0.00	0.00
TS45		0.01	0.00	0.02	-0.01	0.01
5		0.00	0.00	0.00	0.00	0.01
TS56		0.00	0.00	-0.01	0.00	0.02
6		-0.19	0.05	-0.14	0.09	-0.19
1	t	0.01	0.00	0.00	0.00	0.00
TS12		0.22	0.02	0.15	-0.09	0.22
2		0.39	-0.02	0.29	-0.17	0.40
3		0.46	-0.11	0.32	-0.18	0.38
TS35		0.26	-0.06	0.23	-0.14	0.27
5		0.00	0.00	0.01	0.00	-0.02
TS56		0.00	0.00	0.01	0.01	0.01
6		0.40	-0.05	0.21	-0.07	0.25

[a] *so* refers to the open-shell singlet state and *t* to the triplet spin state.

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Table S32: Electronic energies for structures 1, TS12, 2, and 3 of the mechanism for the hydroxylation of phenols mediated by $[Cu(II)(NMe_2\text{-}TMPA)\text{-}(O_2\cdot^-)]^+$ complex computed at the B3LYP/cc-pvTZ(-f)&lacv3p+//B3LYP/lacvp and OPBE/cc-pvTZ(-f)&lacv3p+//B3LYP/lacvp level of theory.

Structures	Multiplicity[a]	DFT functional	
		B3LYP	OPBE
		ΔE(kcal/mol)	
1	*so*	4.2	8.8
TS12	*so*	15.4	14.0
2	*so*	2.1	9.6
3	*so*	10.0	18.0
1	*t*	0.0	0.0
TS12	*t*	12.3	9.8
2	*t*	2.2	9.1
3	*t*	9.7	15.9

[a] *so* refers to the open-shell singlet state and *t* to the triplet spin state.

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