DFT study of catalytic styrene oxidation using a bis-semicarbazide hexaazamacrocyclic Cu complex I. Preliminary calculations.

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Supplementary Information

Table S1. DFT energies, E_{DFT}, and Gibbs energies at 298 K, G_{298}, of the compounds under study with charges q, spin multiplicities M_s, and spin squares $\langle S^2 \rangle$. The most stable systems are in bold.

Table S2. Selected bond lengths (in Å) between relevant atoms in the the compounds under study with charges q and spin multiplicities M_s (see Fig. 1 and Table 2 for atom notation).

Table S3 Selected bond angles (in degrees) in the compounds under study with charges q and spin multiplicities M_s (see Fig. 1 and Table 2 for atom notation).

Figure S1. *X*-ray structure of H_2L with atom-labelling scheme and thermal ellipsoids drawn at 20% probability level [13].

Figure S2. DFT optimized structure of $(OOH)^q$ in various spin states M_s (O – red, H – gray).

Figure S3. DFT optimized structures of $[Ph\text{-}C_\alpha H(O)\text{-}C_\beta H_2OH]^q$ in various spin states (C – black, O – red, H – gray).

Figure S4. DFT optimized structure of $[(Ph\text{-}C_\alpha H\text{-}C_\beta H_2)(OH)]^q$ in various spin states (C – black, O – red, H – gray).

Figure S5. DFT optimized structure of $[CuL]^q$ in various spin states (Cu – green, C – black, N – blue, O – red, H – gray).

Figure S6. DFT optimized structure of $[CuL(O\text{-}O_H\text{-}H_O)]^0$ in singlet and triplet spin states (Cu – green, C – black, N – blue, O – red, H – gray).

Figure S7. DFT optimized structure of $\{[CuL(O_H\text{-}H_O)](Ph\text{-}C_\alpha H_2\text{-}C_\beta HO)\}^0$ in singlet and triplet spin states (Cu – green, C – black, N – blue, O – red, H – gray).

Figure S8. DFT optimized structure of $[CuL(Ph\text{-}C_\alpha H{=}C_\beta H_2)]^q$ in various spin states (Cu – green, C – black, N – blue, O – red, H – gray).

Figure S9. DFT optimized structure of $\{CuL[Ph\text{-}C_\alpha H(O\text{-}O_H\text{-}H_O)\text{-}C_\beta H_2]\}^0$ in singlet and triplet spin states (Cu – green, C – black, N – blue, O – red, H – gray).

Table S1. DFT energies, E_{DFT}, and Gibbs energies at 298 K, G_{298}, of the compounds under study with charges q, spin multiplicities M_s, and spin squares $<S^2>$. The most stable systems are in bold.

	q	M_s	$<S^2>$	E_{DFT} [hartree]	G_{298} [hartree]
H_2L	0	1	0.000	-1876.93425	-1876.26433
Reaction path A					
Ph-CH=CH_2	0	1	0.000	-309.71674	-309.61529
$(OOH)^q$	0	2	0.754	-150.95195	-150.96003
	-1	1	0.000	**-150.98813**	**-150.99705**
	-1	3	2.014	-150.96260	-150.97652
$[Ph\text{-}CH(O)\text{-}CH_2OH]^q$	0	2	0.755	-460.75049	-460.63349
	-1	1	0.000	**-460.84634**	**-460.72959**
	-1	3	2.006	-460.72388	-460.61229
$[Ph - CH - CH_2(OH)]^q$ \ / O	0	2	0.752	-460.70181	-460.59024
	-1	1	0.000	-460.79335	-460.68054
	-1	3	2.004	-460.74058	-460.63601
Reaction path B:					
$[CuL]^q$	0	2	0.754	-3516.26778	-3515.61885
	-1	1	0.000	**-3516.31625**	**-3515.67541**
	-1	3	2.007	-3516.28161	-3515.63809
	+1	1	0.000	-3516.03126	-3515.37966
	+1	3	2.011	-3516.01984	-3515.37085
$[CuL(OOH)]^q$	0	1	1.008	-3667.23105	-3666.56946
				-3667.23104[a)]	-3666.56843 [a)]
	0	3	2.008	-3667.23106	-3666.57048
	-1	2	0.754	**-3667.31654**	**-3666.65691**
$\{[CuL(OH)](Ph\text{-}CH_2\text{-}CHO)\}^q$	0	1	0.554	-3977.02647	-3976.24456
				-3977.02660 [a)]	-3976.24371 [a)]
	0	3	2.011	-3977.02613	-3976.24679
	-1	2	0.753	**-3977.14931**	**-3976.37377**
Reaction path C:					
$[CuL(Ph\text{-}CH=CH_2)]^q$	-1	1	0.000	**-3826.02113**	**-3825.25568**
	-1	3	2.006	-3826.00673	-3825.24806
	0	2	0.754	-3825.98858	-3825.22719
$\{CuL[Ph\text{-}CH(OOH)\text{-}CH_2]\}^q$	0	1	1.008	-3976.93793	-3976.15870
				-3976.94032 [a)]	-3976.15974 [a)]
	0	3	2.008	-3976.93556	-3976.15767
	-1	2	0.754	**-3977.01077**	**-3976.22939**

Remarks:

[a)]Corrected according to Eq. (6)

Table S2. Selected bond lengths (in Å) between relevant atoms in the the compounds under study with charges q and spin multiplicities M_s (see Fig. 1 and Table 2 for atom notation).

	q	M_s	C_α-C_β	C_α-O	C_α-O_H	C_β-O	C_β-O_H	O-O_H	N3…H_O
Reaction path A									
$(OOH)^q$	0	2	-	-	-	-	-	1.326	-
	-1	1	-	-	-	-	-	1.519	-
	-1	3	-	-	-	-	-	2.222	-
Ph-CH=CH_2	0	1	1.337	-	-	-	-	-	-
$[Ph\text{-}CH(O)\text{-}CH_2OH]^q$	0	2	1.616	1.342	2.533	2.371	1.392	2.970	-
	-1	1	1.590	1.349	2.421	1.413	1.413	2.538	-
	-1	3	1.526	1.371	1.427	2.428	1.422	3.016	-
Ph - CH – $CH_2(OH)]^q$ \ / O	0	2	1.474	1.447	4.008	1.436	3.801	2.869	-
	-1	1	1.471	1.463	2.924	1.429	3.947	4.159	-
	-1	3	1.526	1.371	2.427	2.428	1.422	3.016	-
Reaction path B									
$[CuL(OOH)]^q$	0	1	-	-	-	-	-	1.326	1.795
	0	3	-	-	-	-	-	1.326	1.794
	-1	2	-	-	-	-	-	1.473	2.298
$\{[CuL(OH)](Ph\text{-}CH_2\text{-}CHO)\}^q$	0	1	1.519	2.411	4.376	1.212	3.236	3.750	5.123
	0	3	1.519	2.412	4.418	1.211	3.271	3.770	2.568
	-1	2	1.527	2.406	3.943	1.216	3.127	3.944	2.998
Reaction path C									
$[CuL(Ph\text{-}CH=CH_2)]^q$	-1	1	1.373	-	-	-	-	-	-
	-1	3	1.359	-	-	-	-	-	-
	0	2	1.338	-	-	-	-	-	-
$\{CuL[Ph\text{-}CH(OOH)\text{-}CH_2]\}^q$	0	1	1.486	1.457	2.375	2.435	2.849	1.449	8.104
	0	3	1.484	1.474	2.384	2.443	2.884	1.447	8.733
	-1	2	1.496	1.491	2.410	2.513	2.985	1.450	6.490

Table S2 (cont.)

	q	M_s	Cu-N1	Cu-N3	Cu-O/O_H	Cu-$C_{\alpha/\beta}$
Reaction path B						
[CuL] (exp.)	0	-	1.962(2) (2×)	1.867(2) (2×)	-	-
$[CuL]^q$	0	2	2.002(2×)	1.892(2×)	-	-
	-1	1	2.135(2×)	1.905(2×)	-	-
	-1	3	2.021	1.921	-	-
			1.934	1.908		
$[CuL(OOH)]^q$	0	1	2.018	1.912	3.285	-
			2.016	1.886	3.506	
	0	3	2.017(2×)	1.913	3.277	-
				1.886	3.503	
	-1	2	2.095	1.948	2.049	-
			2.140	1.941	2.914	
$\{[CuL(OH)](Ph\text{-}CH_2\text{-}CHO)\}^q$	0	1	2.046	1.872	5.064	5.881
			2.023	1.885	2.039	4.755
	0	3	2.051	1.928	4.946	5.745
			2.031	1.907	1.992	4.633
	-1	2	2.106	1.957	5.118	4.964
			2.090	1.961	2.064	4.398
Reaction path C						
$[CuL(Ph\text{-}CH{=}CH_2)]^q$	-1	1	2.282	2.164	-	2.212
			2.448	2.035		2.114
	-1	3	1.980	1.905	-	6.715
			1.969	1.908		6.200
	0	2	2.002	1.891		6.513
			2.001	1.893		7.013
$\{CuL[Ph\text{-}CH(OOH)\text{-}CH_2]\}^q$	0	1	2.000	1.891	8.398	8.642
			2.001	1.894	7.060	8.561
	0	3	2.006	1.891(2×)	7.748	6.808
			2.003		7.253	5.843
	-1	2	2.106	1.957	5.118	4.964
			2.090	1.961	2.064	4.398

Table S3. Selected bond angles (in degrees) in the compounds under study with charges q and spin multiplicities M_s (see Fig. 1 and Table 2 for atom notation).

	q	M_s	N1-Cu-N1′	N3-Cu-N3′	N1-Cu-N3	N3-Cu-N1′ N1-Cu-N3′
Reaction path B						
$[CuL]^q$ (exp.)			180.	180.	82.83(7) (2×)	97.17(7) (2×)
$[CuL]^q$	0	2	180.	180.	82.2(2×)	97.8(2×)
	-1	1	180.0	180.0	81.4(2×)	98.6(2×)
	-1	3	176.8	177.0	81.3	95.8
					83.2	99.7
$[CuL(OOH)]^q$	0	1	169.3	177.0	82.7	97.3
					82.4	98.2
	0	3	169.3	177.0	82.8	98.1
					82.3	97.3
	-1	2	139.7	159.4	79.4	94.5
					79.1	92.7
$\{[CuL(OH)](Ph\text{-}CH_2\text{-}CHO)\}^q$	0	1	156.1	165.7	81.2	95.6
					95.7	95.7
	0	3	158.9	158.6	79.8	95.7
					81.5	95.1
	-1	2	142.1	155.6	78.3	92.8
					79.6	93.4
Reaction path C						
$[CuL(Ph\text{-}CH{=}CH_2)]^q$	-1	1	124.9	123.7	70.8	79.6
					71.0	88.2
	-1	3	179.9	179.6	82.4(2×)	97.7
						97.5
	0	2	179.4	179.9	82.2(2×)	97.7(2×)
$\{CuL[Ph\text{-}CH(OOH)\text{-}CH_2]\}^q$	0	1	179.5	179.9	82.3	97.8(2×)
					82.1	
	0	3	178.3	179.8	82.3(2×)	97.5
						97.9
	-1	2	142.1	155.6	78.3	92.8
					79.6	93.4

Table S3. (cont.)

	q	M_s	N1-Cu-O	N3-Cu-O	N1-Cu-$C_{\alpha/\beta}$	N3-Cu- $C_{\alpha/\beta}$
Reaction path B						
$[CuL]^q$ (exp.)			-	-	-	-
$[CuL]^q$	0	2	-	-	-	-
	-1	1	-	-	-	-
	-1	3	-	-	-	-
$[CuL(OOH)]^q$	0	1	106.0	74.2	-	-
			95.4	52.8		
	0	3	106.1	74.4	-	-
			95.6	52.8		
	-1	2	128.3	96.4	-	-
			105.3	79.0		
$\{[CuL(OH)](Ph\text{-}CH_2\text{-}CHO)\}^q$	0	1	145.9	93.0	133.1	113.6
			105.8	90.6	137.2	102.9
	0	3	145.2	96.0	132.3	117.6
			101.5	90.4	101.5	106.4
	-1	2	162.7	104.3	145.2	131.8
			117.6	100.7	154.1	114.7
Reaction path C						
$[CuL(Ph\text{-}CH{=}CH_2)]^q$	-1	1	-	-	143.0	119.3
					110.7	96.7
	-1	3	-	-	118.9	49.9
					110.9	51.8
	0	2	-	-	116.3	144.6
					111.2	137.5
$\{CuL[Ph\text{-}CH(OOH)\text{-}CH_2]\}^q$	0	1	101.1	134.1	109.1	138.8
			100.1	130.1	117.6	131.9
	0	3	107.3	110.5	115.0	106.1
			99.9	117.5	108.6	97.7
	-1	2	162.7	104.3	145.2	131.8
			117.6	100.7	117.6	114.7

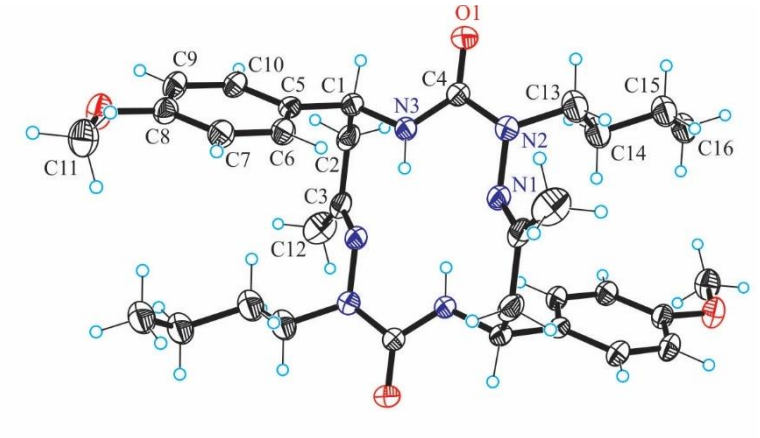

Figure S1. X-ray structure of **H_2L** with atom-labelling scheme. [13]

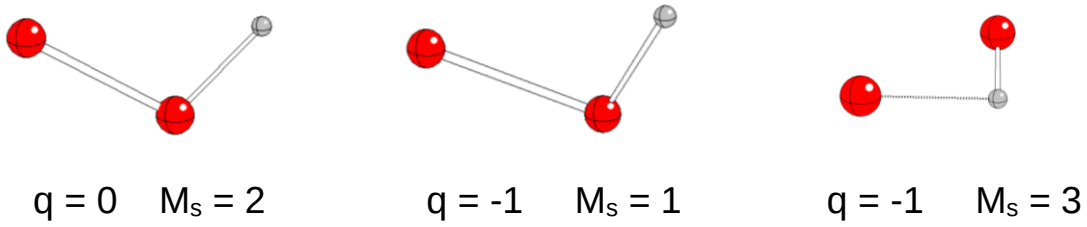

Figure S2. DFT optimized structure of $(OOH)^q$ in various spin states M_s (O – red, H – gray).

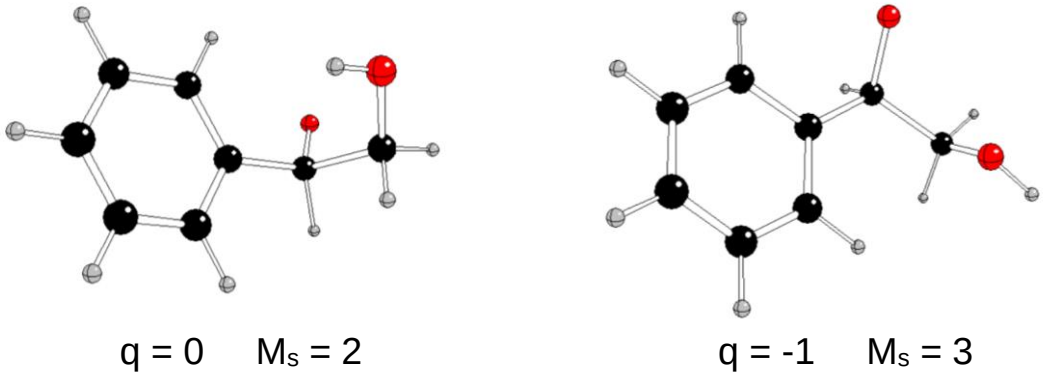

Figure S3. DFT optimized structures of $[Ph\text{-}C_\alpha H(O)\text{-}C_\beta H_2OH]^q$ in various spin states (C – black, O – red, H – gray).

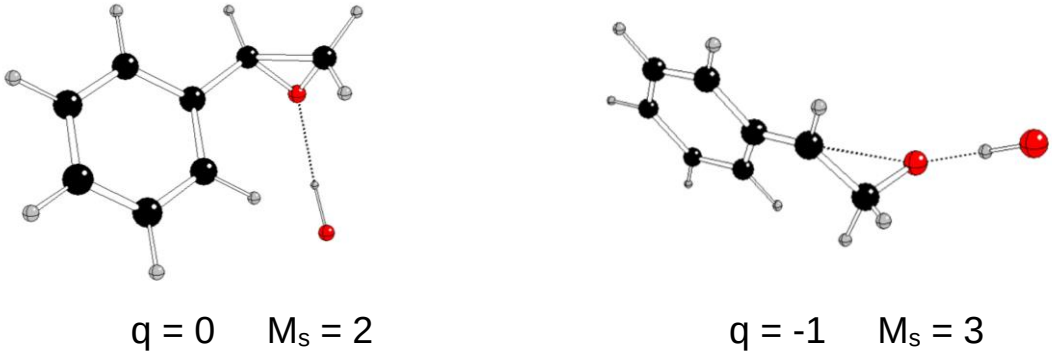

Figure S4. DFT optimized structure of [(Ph-C_{α}H-$C_{\beta}H_2$)(OH)]^q in various spin states (C – black, O – red, H – gray).

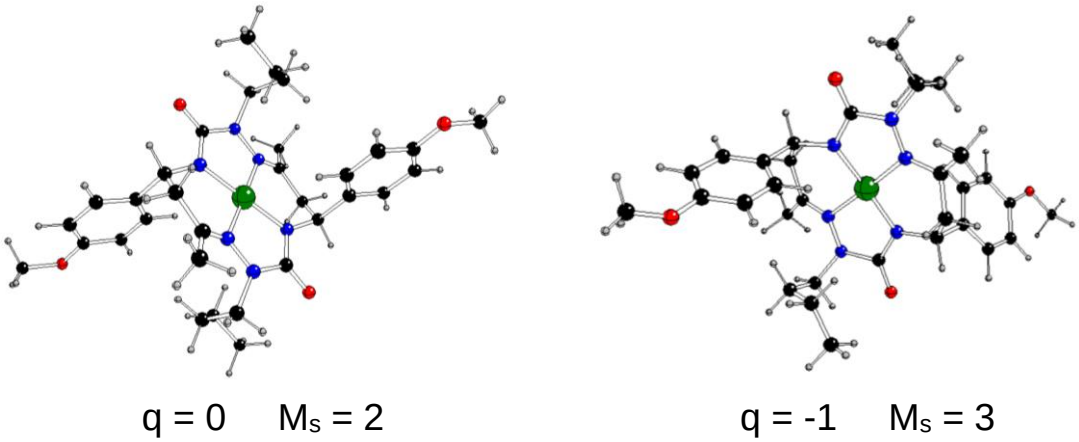

Figure S5. DFT optimized structure of [CuL]^q in various spin states (Cu – green, C – black, N – blue, O – red, H – gray).

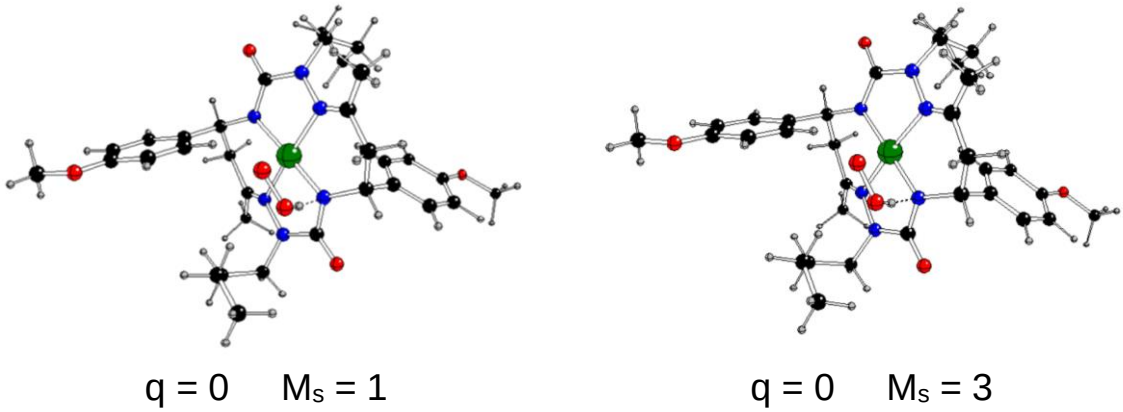

Figure S6. DFT optimized structure of $[CuL(O\text{-}O_H\text{-}H_O)]^0$ in singlet and triplet spin states (Cu – green, C – black, N – blue, O – red, H – gray).

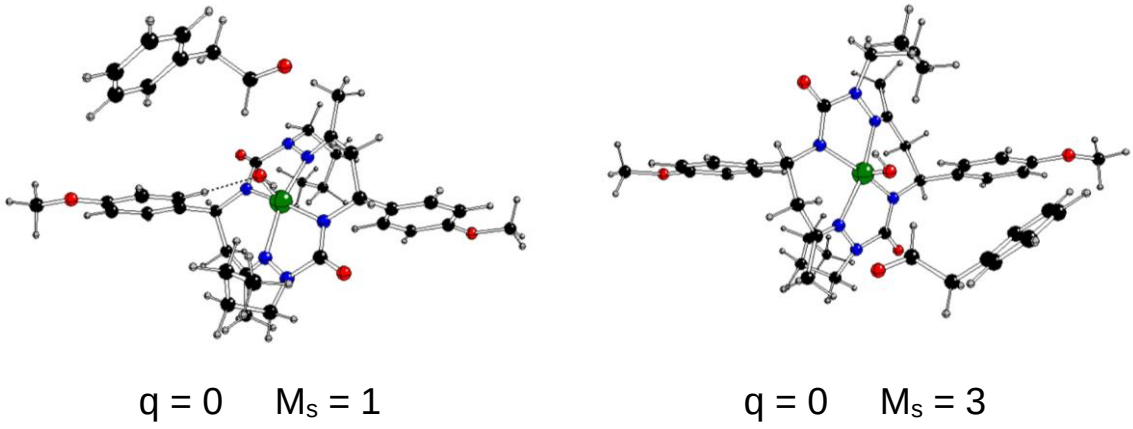

Figure S7. DFT optimized structure of $\{[CuL(O_H\text{-}H_O)](Ph\text{-}C_\alpha H_2\text{-}C_\beta HO)\}^0$ in singlet and triplet spin states (Cu – green, C – black, N – blue, O – red, H – gray).

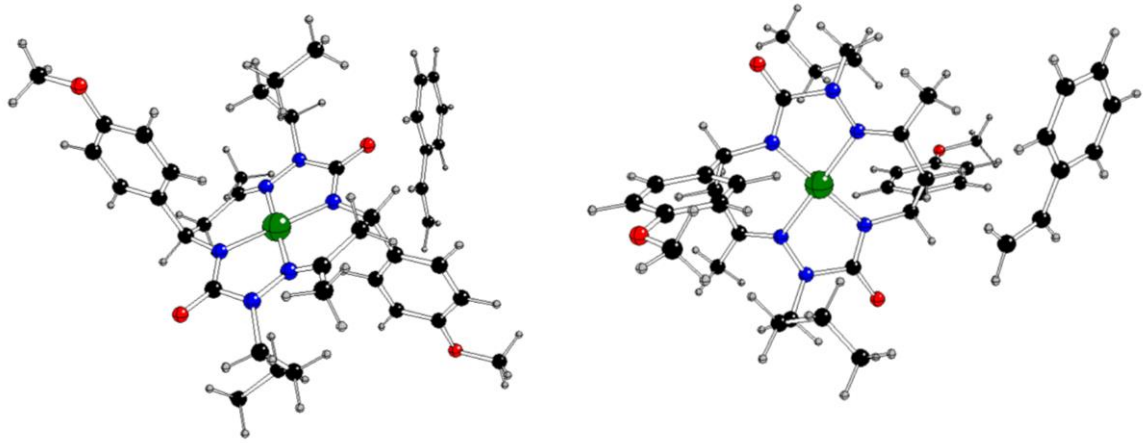

Figure S8. DFT optimized structure of $[CuL(Ph\text{-}C_{\alpha}H{=}C_{\beta}H_2)]^{q}$ in various spin states (Cu – green, C – black, N – blue, O – red, H – gray).

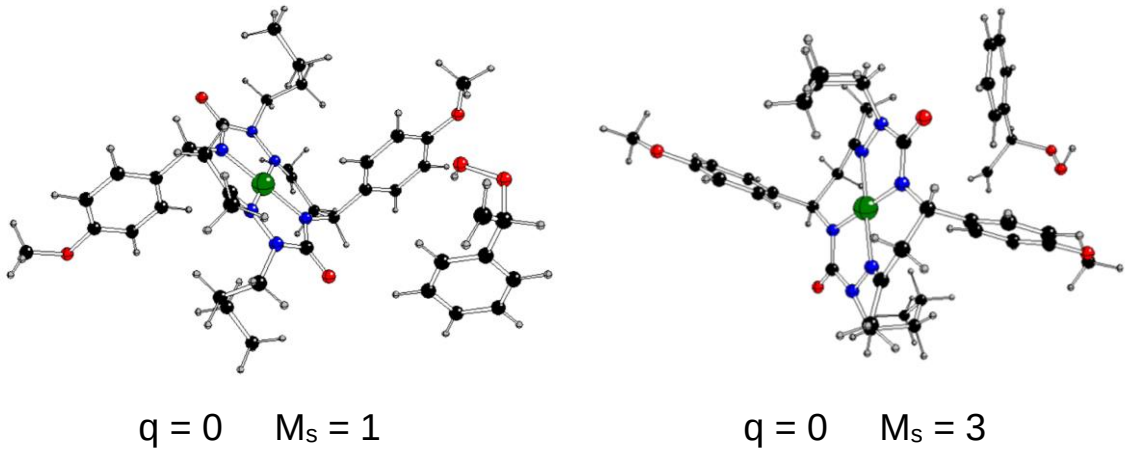

Figure S9. DFT optimized structure of $\{CuL[Ph\text{-}C_{\alpha}H(O\text{-}O_{H}\text{-}H_{O})\text{-}C_{\beta}H_2]\}^{0}$ in singlet and triplet spin states (Cu – green, C – black, N – blue, O – red, H – gray).