Supporting Information

Oxygenolysis of a series of copper(II)-flavonolate adducts varying the electronic factors on supporting ligands as a mimic of quercetin 2,4-dioxygenase-like activity

Nirmalya Podder,[a] Subhasis Dey,[a] Anakuthil Anoop,[a]* and Sukanta Mandal[a]*

[a]Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, India.

E-mail: sukanta.mandal@chem.iitkgp.ac.in

anoop@chem.iitkgp.ac.in

Table S1. Data collection and structure refinement parameters for **I·2H₂O, II·MeOH**, **III·2H₂O** and **IV·MeOH**

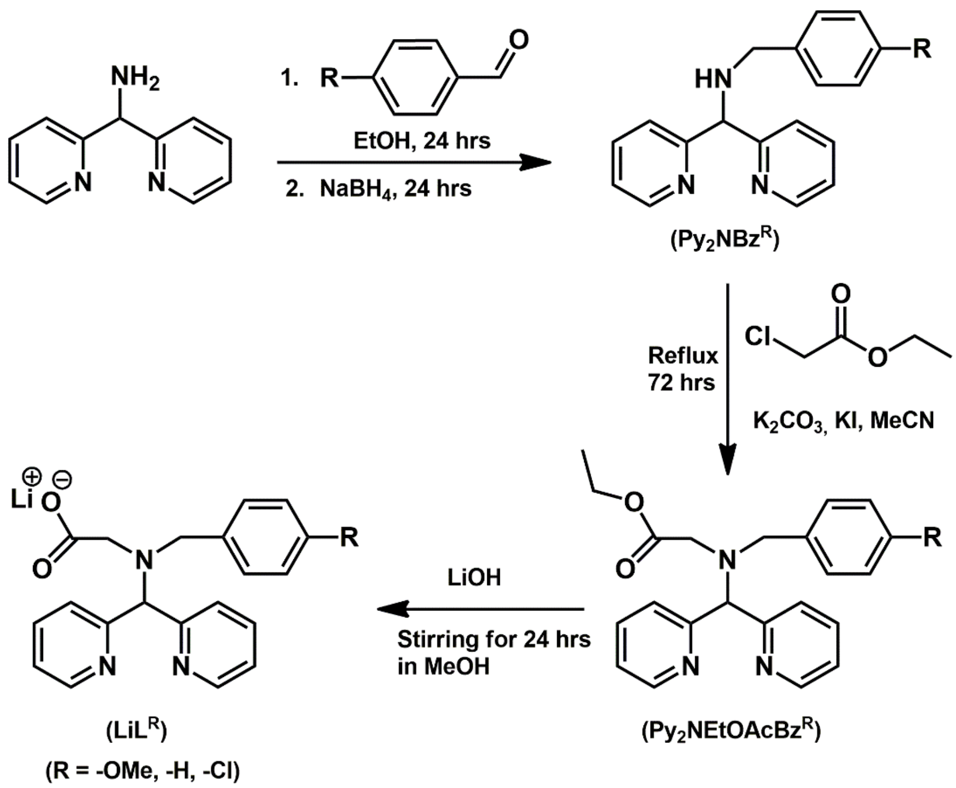
	I·2H$_2$O	**II·MeOH**	**III·2H$_2$O**	**IV·MeOH**
CCDC	2112719	2112720	2112721	2112723
Chemical formula	$C_{23}H_{27}CuN_3O_7$	$C_{23}H_{25}CuN_3O_5$	$C_{22}H_{24}ClCuN_3O_6$	$C_{23}H_{24}CuN_4O_7$
Formula weight	521.02	487.01	525.44	532.01
Temperature (K)	296(2)	296(2)	296(2)	296(2)
λ (Å)	*Mo*-$K\alpha$ (0.71073)	*Mo*-$K\alpha$ (0.71073)	*Mo*-$K\alpha$ (0.71073)	*Mo*-$K\alpha$ (0.71073)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ *(no. 2)*	$P2_1/n$ *(no. 14)*	$P\bar{1}$ *(no. 2)*	$P\bar{1}$ *(no. 2)*
a (Å)	8.7650(10)	17.329(5)	8.735(4)	8.813(7)
b (Å)	10.2565(12)	11.650(3)	10.000(4)	10.131(5)
c (Å)	13.7578(15)	24.282(6)	13.704(6)	14.050(12)
α (º)	85.880(3)	90	85.767(14)	87.22(4)
β (º)	74.947(3)	109.405(13)	76.846(12)	77.53(5)
γ (º)	75.207(3)	90	73.237(12)	72.62(4)
V/(Å^3)	1154.8(2)	4624(2)	1116.0(8)	1168.8(15)
Z	2	8	2	2
D_c (g cm^{-3})	1.493	1.396	1.552	1.509
μ (mm^{-1})	0.995	0.983	1.143	0.986
Reflections measured	15646	135862	12242	13441
Unique reflections [R_{int}]	5310 [0.0341]	11412 [0.0564]	3635 [0.0669]	5953 [0.0271]
Number of reflections used [$I > 2\sigma(I)$]	4636	7707	2808	4860
Number of parameters	324	579	307	317
Final R indices	$^aR_1$ = 0.0387; $^bwR_2$ = 0.1057	$^aR_1$ = 0.0426; $^bwR_2$ = 0.1103	$^aR_1$ = 0.0729; $^bwR_2$ = 0.2063	$^aR_1$ = 0.0514; $^bwR_2$ = 0.1528
R indices (all data)	$^aR_1$ = 0.0452; $^bwR_2$ = 0.1132	$^aR_1$ = 0.0787; $^bwR_2$ = 0.1380	$^aR_1$ = 0.0947; $^bwR_2$ = 0.2506	$^aR_1$ = 0.0642; $^bwR_2$ = 0.1616
Goodness-of-fit on F^2	1.070	1.079	1.192	1.062
Largest residual peak and hole (e.Å^{-3})	0.667 and -0.627	0.566 and -0.589	0.955 and -2.278	0.675 and -0.421

$^aR_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$.

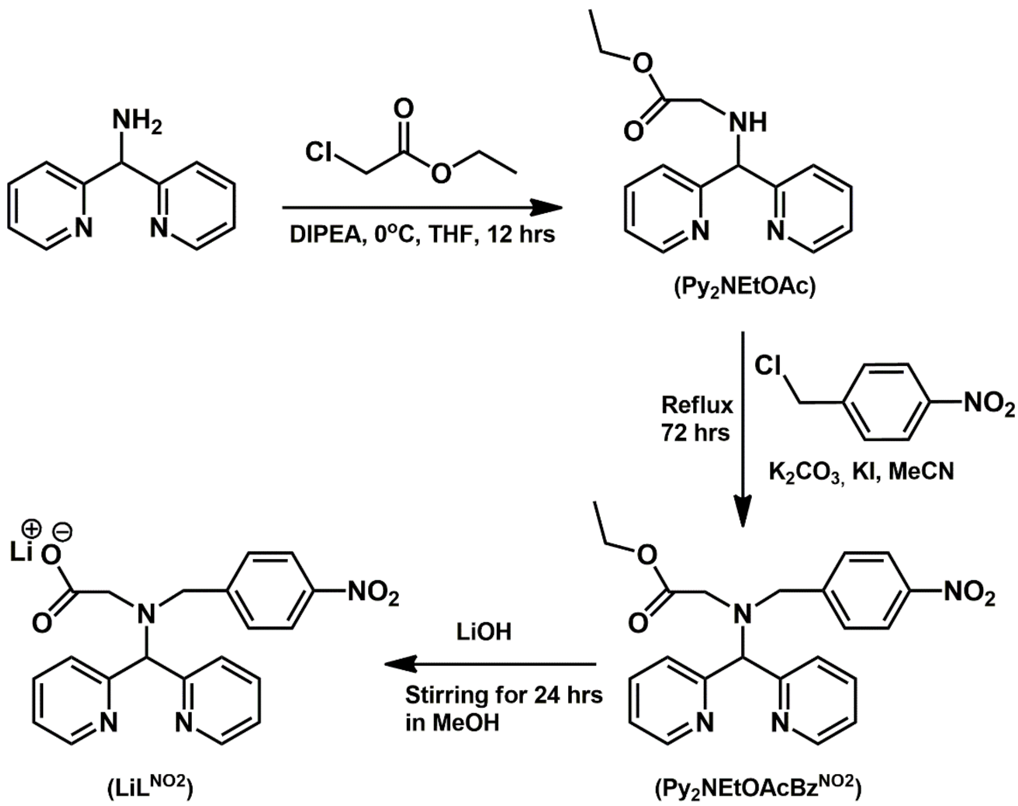
Table S2. Data collection and structure refinement parameters for **1·CH_2Cl_2·1.5H_2O**, **2·CH_2Cl_2·H_2O** and **5·2H_2O**.

	1·CH_2Cl_2·1.5H_2O	**2·CH_2Cl_2·H_2O**	**5·2H_2O**
CCDC	2112724	2112725	2112726
Chemical formula	2($C_{37}H_{34}Cl_2CuN_3O_{7.5}$)	$C_{36}H_{31}Cl_2CuN_3O_6$	$C_{36}H_{33}N_3O_8Zn$
Formula weight	2*(775.13)	736.10	701.04
Temperature (K)	296(2)	296(2)	296(2)
λ (Å)	*Mo-Kα* (0.71073)	*Mo-Kα* (0.71073)	*Mo-Kα* (0.71073)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c (no. 15)*	*$P2_1/c$ (no. 14)*	*$P2_1/c$ (no. 14)*
a (Å)	38.679(14)	16.4553(11)	17.50(2)
b (Å)	12.824(4)	9.4294(6)	21.47(3)
c (Å)	15.166(5)	20.5153(14)	8.797(17)
α (º)	90	90	90
β (º)	108.650(9)	90.578(2)	91.34(5)
γ (º)	90	90	90
V/(Å^3)	7127(4)	3183.1(4)	3304(9)
Z	4	4	4
D_c (g cm^{-3})	1.439	1.532	1.401
μ (mm^{-1})	0.818	0.908	0.800
Reflections measured	131686	36525	27282
Unique reflections [R_{int}]	7263 [0.0610]	5586 [0.0928]	8099 [0.0997]
Number of reflections used [$I > 2\sigma(I)$]	5879	3853	3071
Number of parameters	456	427	433
Final R indices	$^aR_1$ = 0.0502; $^bwR_2$ = 0.1454	$^aR_1$ = 0.0570; $^bwR_2$ = 0.1511	$^aR_1$ = 0.0791; $^bwR_2$ = 0.1942
R indices (all data)	$^aR_1$ = 0.0651; $^bwR_2$ = 0.1666	$^aR_1$ = 0.0869; $^bwR_2$ = 0.1733	$^aR_1$ = 0.2111; $^bwR_2$ = 0.2674
Goodness-of-fit on F^2	1.021	1.058	1.011
Largest residual peak and hole (e.Å^{-3})	1.157 and -0.667	0.630 and -0.865	0.699 and -0.408

$^aR_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$.



Scheme S1. General synthetic route of ligands LiL^R (R = -OMe, -H, -Cl).



Scheme S2. Synthetic route of ligand LiL^{NO2}.

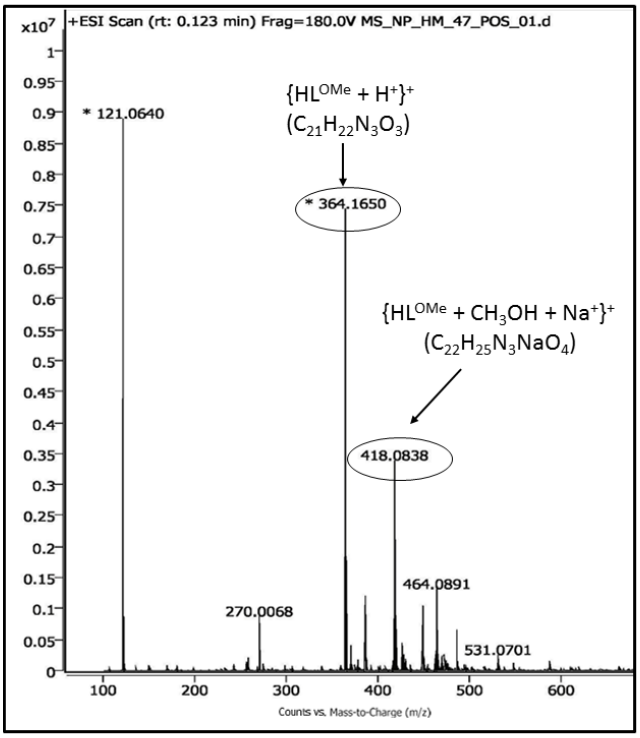


Figure S1. HRMS-ESI(+) spectrum of ligand LiL^{OMe} in methanol with a trace quantity of HCOOH.

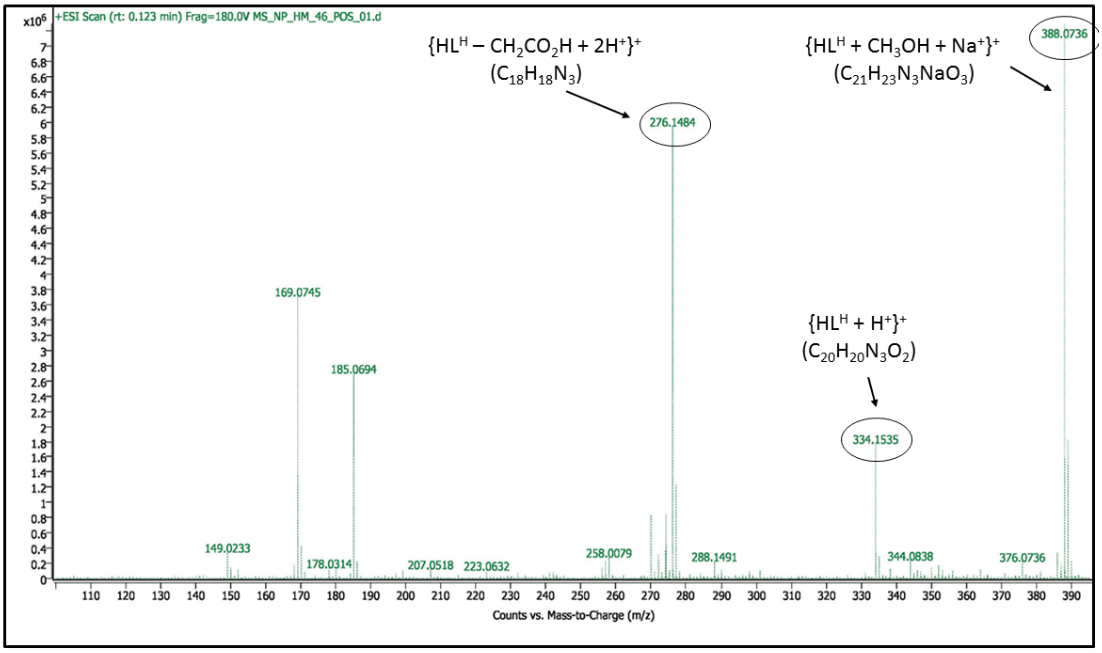


Figure S2. HRMS-ESI(+) spectrum of ligand LiL^{H} in methanol with a trace quantity of HCOOH.

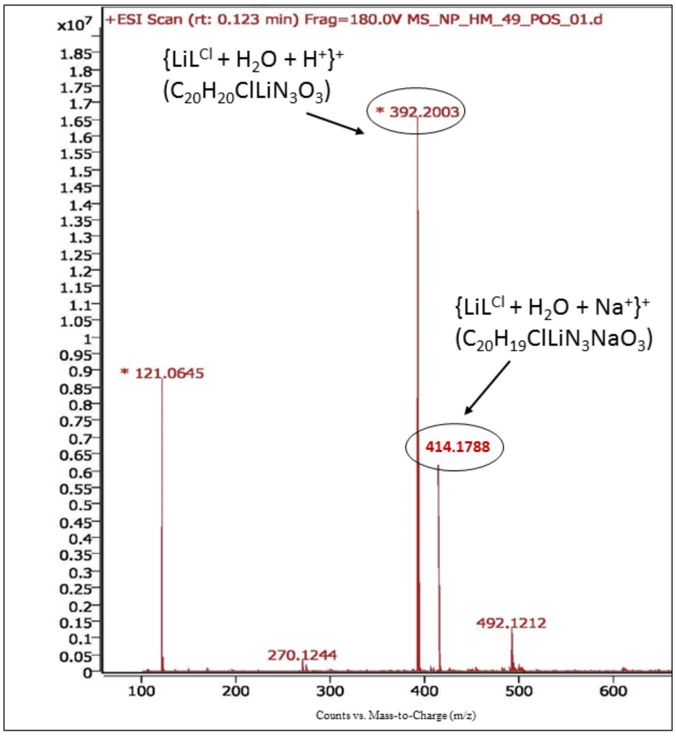


Figure S3. HRMS-ESI(+) spectrum of ligand LiL^{Cl} in methanol with a trace quantity of HCOOH.

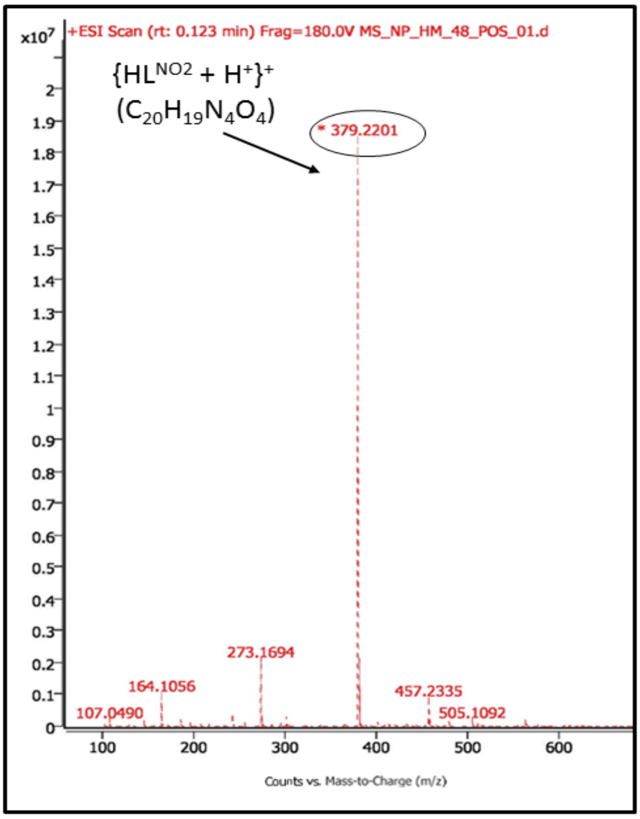


Figure S4. HRMS-ESI(+) spectrum of ligand LiL^{NO2} in methanol with a trace quantity of HCOOH.

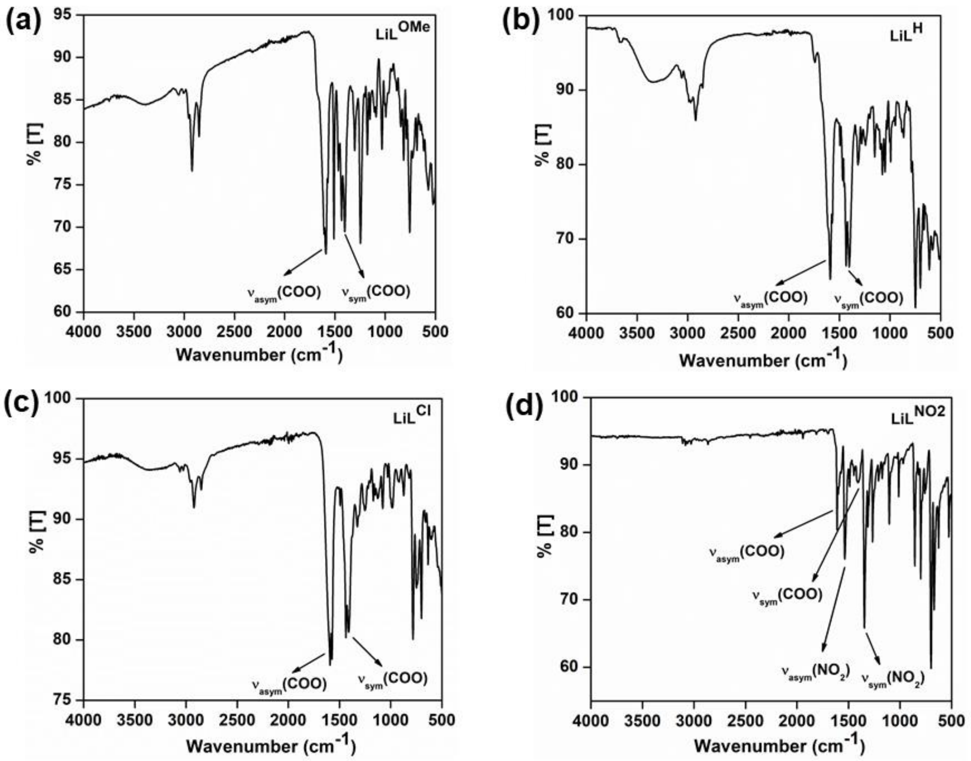


Figure S5. ATR-FTIR spectra (solid samples) of the lithium salts of ligands: (a) LiL^{OMe}; (b) LiL^{H}; (c) LiL^{Cl} and (d) LiL^{NO2}.

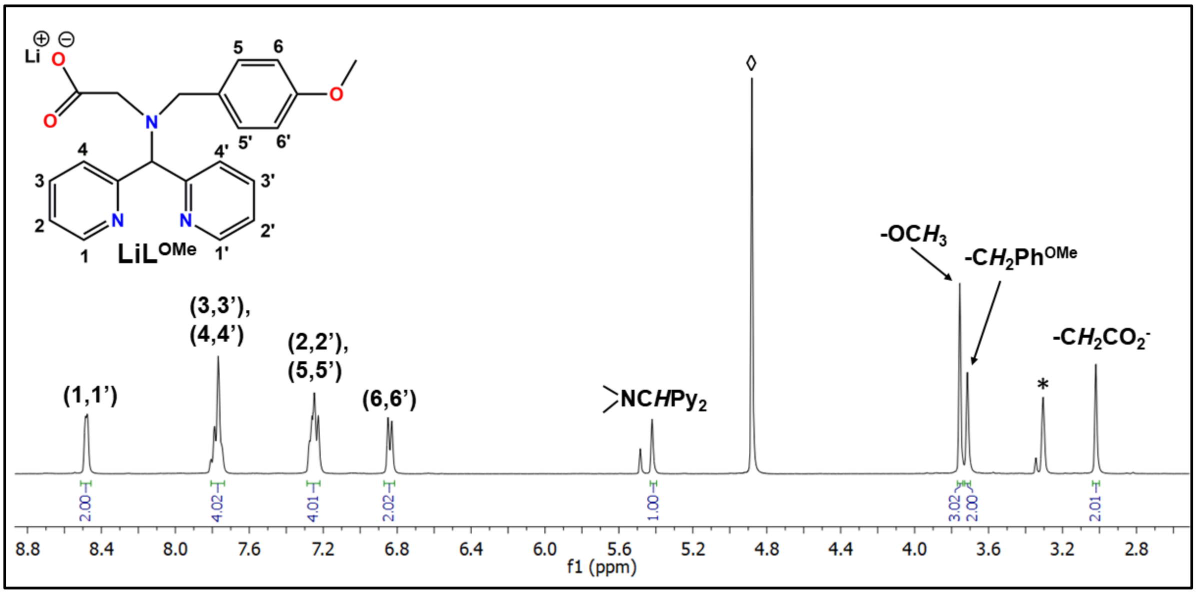


Figure S6. ^{1}H NMR (400 MHz, CD_3OD, 300 K) spectrum of ligand LiL^{OMe}. Symbols (◊) and (*) denote water and solvent residual peaks, respectively.

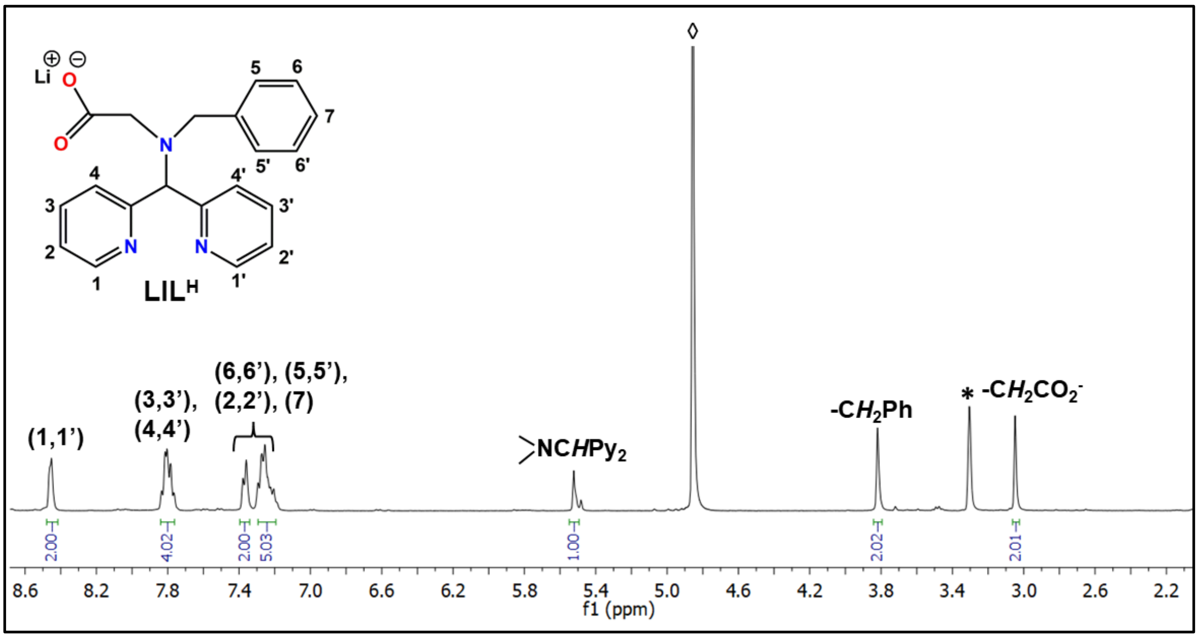


Figure S7. ^{1}H NMR (400 MHz, CD_3OD, 300 K) spectrum of ligand LiL^H. Symbols (◊) and (*) denote water and solvent residual peaks, respectively.

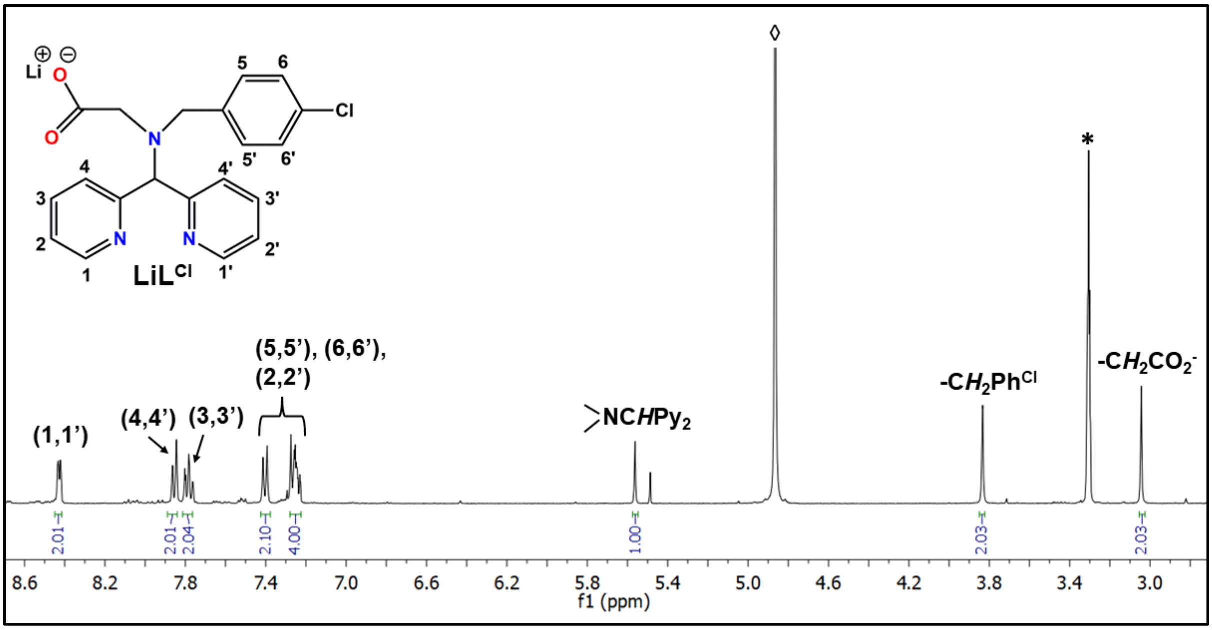


Figure S8. ^{1}H NMR (400 MHz, CD_3OD, 300 K) spectrum of ligand LiL^{Cl}. Symbols (◊) and (*) denote water and solvent residual peaks, respectively.

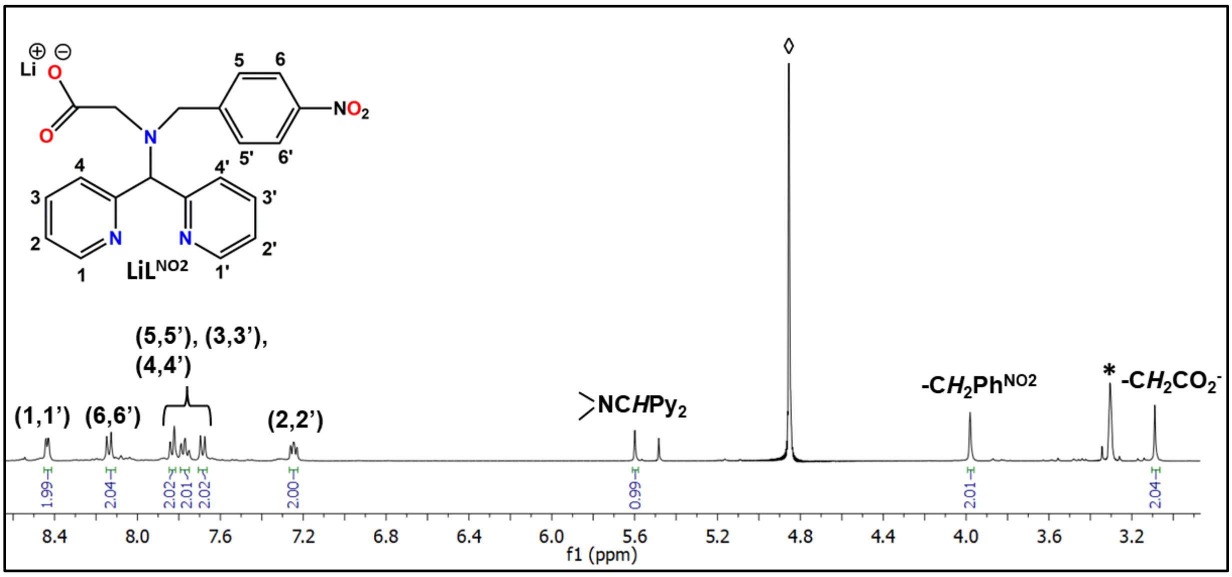


Figure S9. ^{1}H NMR (400 MHz, CD_3OD, 300 K) spectrum of ligand LiL^{NO2}. Symbols (◊) and (*) denote water and solvent residual peaks, respectively.

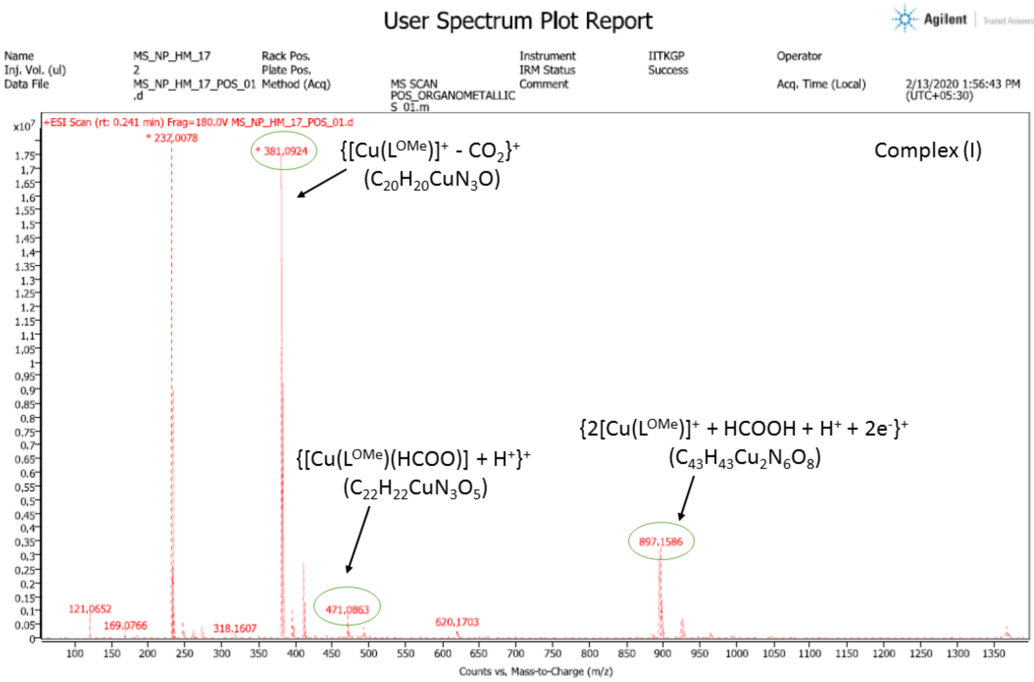


Figure S10. HRMS-ESI(+) spectrum of $[Cu(L^{OMe})(OAc)]$ (**I**) in methanol with a trace quantity of HCOOH.

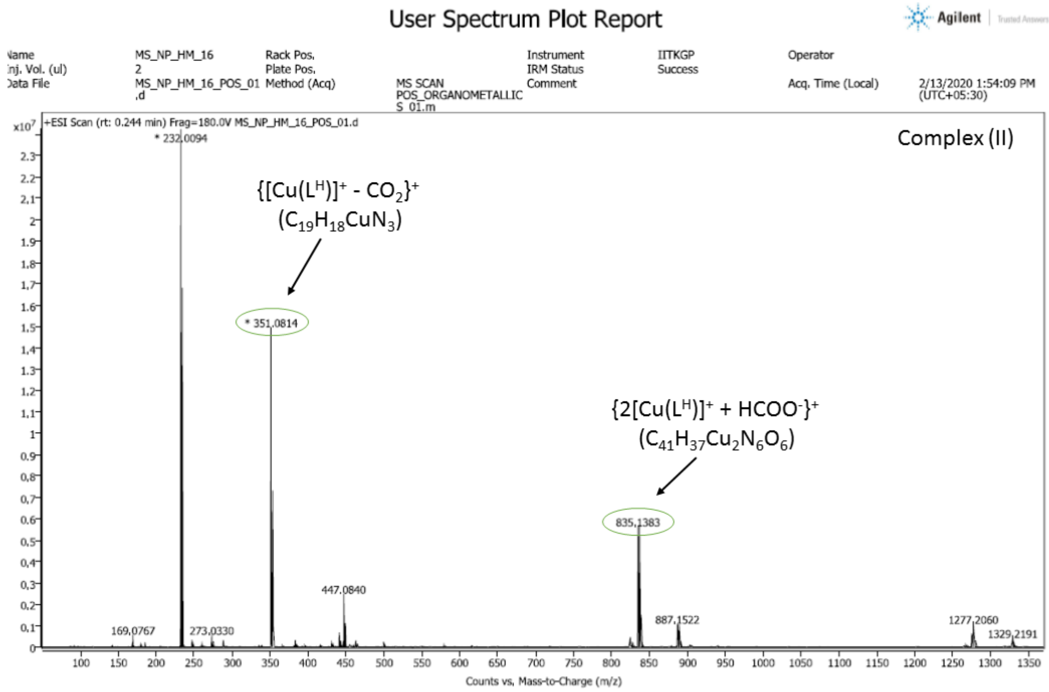


Figure S11. HRMS-ESI(+) spectrum of $[Cu(L^H)(OAc)]$ (**II**) in methanol with a trace quantity of HCOOH.

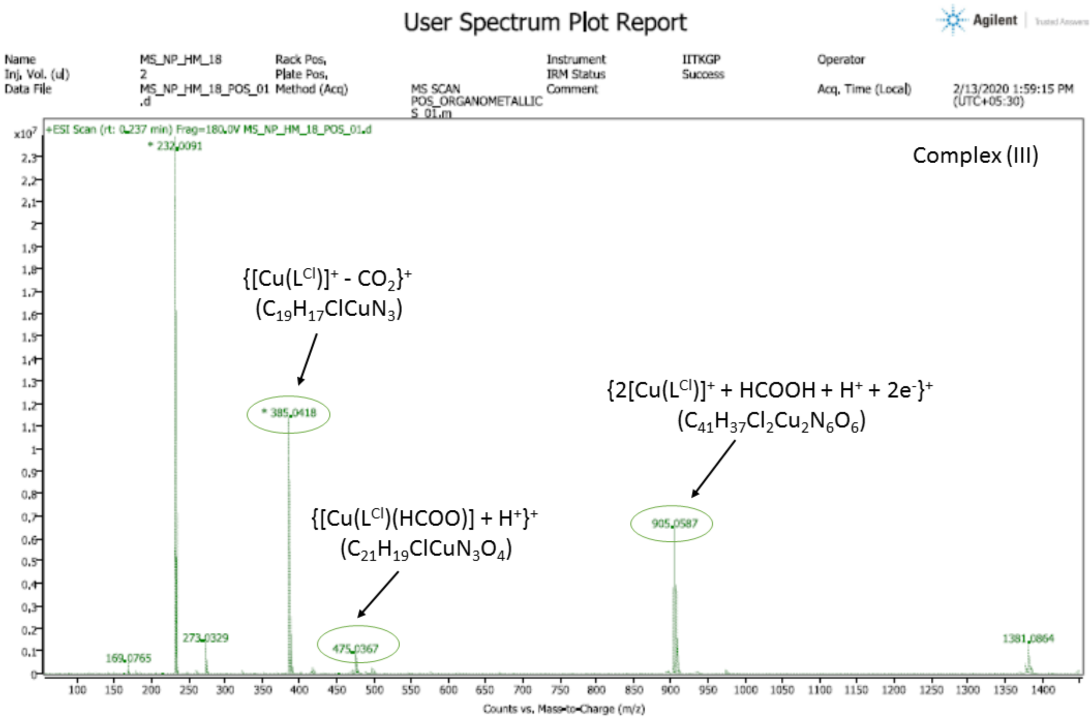


Figure S12. HRMS-ESI(+) spectrum of $[Cu(L^{Cl})(OAc)]$ (**III**) in methanol with a trace quantity of HCOOH.

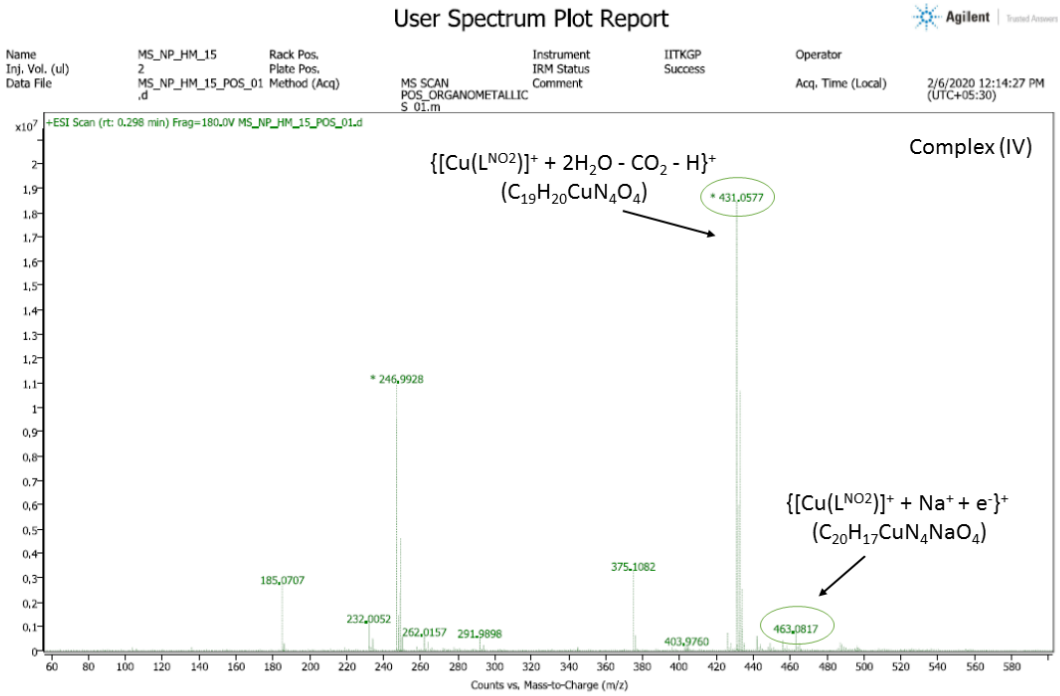


Figure S13. HRMS-ESI(+) spectrum of $[Cu(L^{NO2})(OAc)]$ (**IV**) in methanol with a trace quantity of HCOOH.

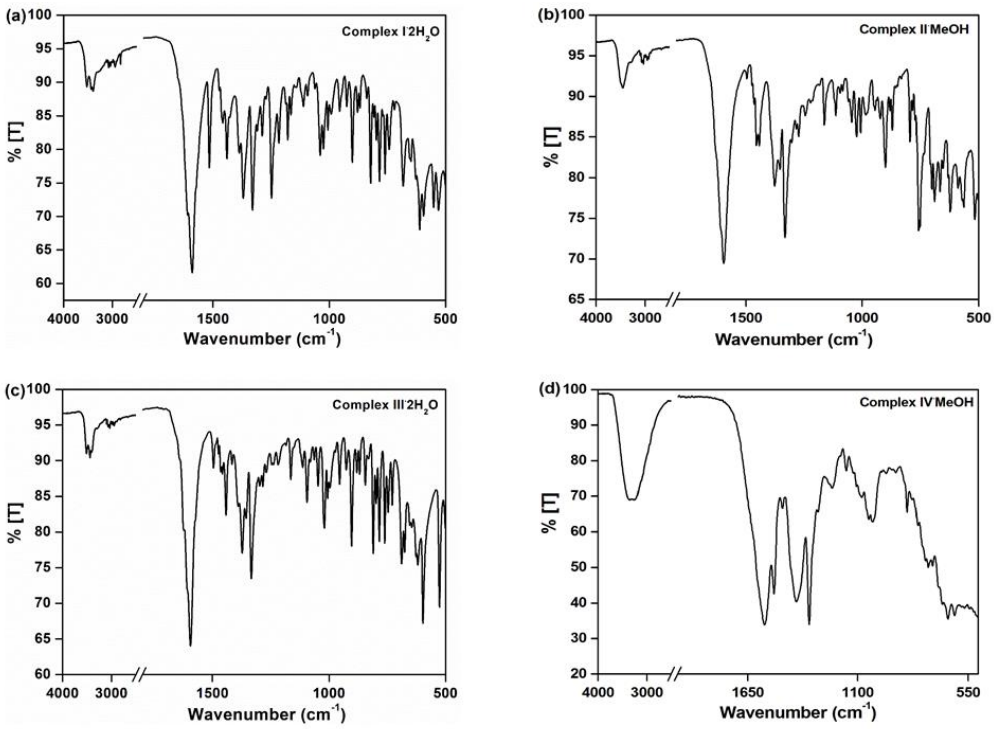


Figure S14. ATR-FTIR spectra (solid samples) of acetate-bound copper(II) complexes: (a) $[Cu(L^{OMe})(OAc)]\cdot 2H_2O$ (**I·2H₂O**); (b) $[Cu(L^{H})(OAc)]\cdot MeOH$ (**II·MeOH**); (c) $[Cu(L^{Cl})(OAc)]\cdot 2H_2O$ (**III·2H₂O**) and (d) $[Cu(L^{NO2})(OAc)]\cdot MeOH$ (**IV·MeOH**).

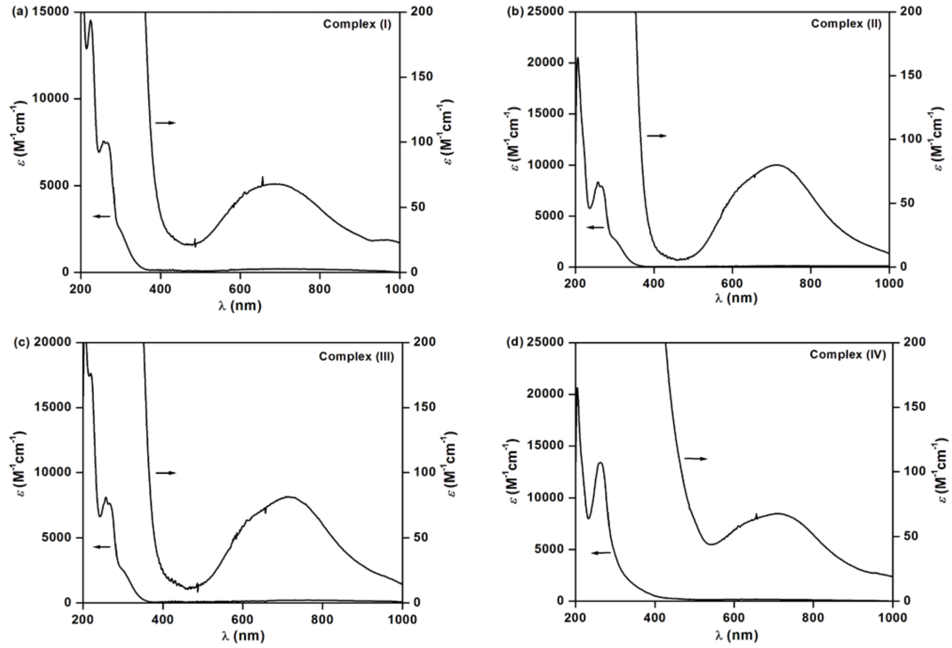


Figure S15. UV-vis spectra of the acetate-bound copper(II) complexes in methanol: (a) [Cu(L^{OMe})(OAc)]·2H_2O (**I·2H$_2$O**); (b) [Cu(L^{H})(OAc)]·MeOH (**II·MeOH**); (c) [Cu(L^{Cl})(OAc)]·2H_2O (**III·2H$_2$O**) and (d) [Cu(L^{NO2})(OAc)]·MeOH (**IV·MeOH**).

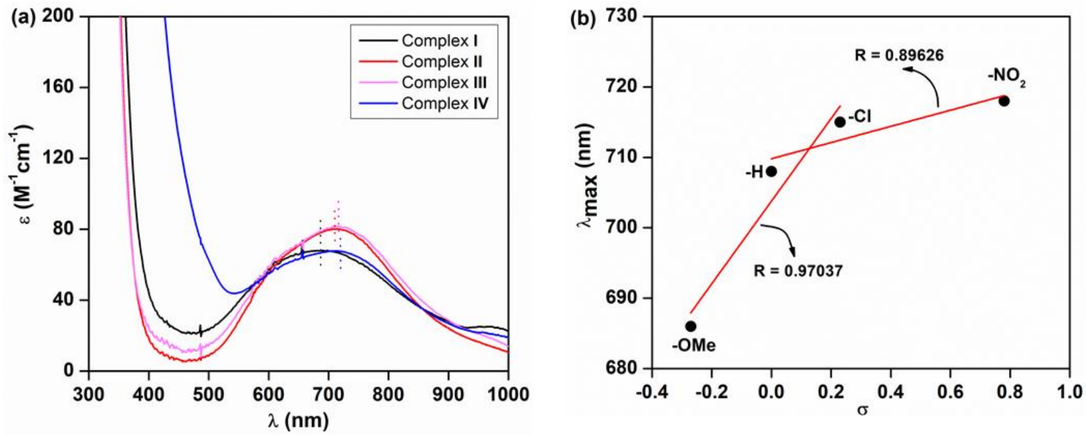


Figure S16. (a) Electronic absorption spectra of the complexes [Cu(L^{R})(OAc)] (**I-IV**) in MeOH (only *d-d* bands are shown). (b) Plot of λ_{max} values of the *d-d* bands of [Cu(L^{R})(OAc)] (**I-IV**) versus Hammett constants σ.

Table S3. Selected bond lengths (Å) and bond angles (°) of **I·2H$_2$O**			
Cu(1)–N(1)	2.0442(19)	N(1)–Cu(1)–N(2)	81.33(8)
Cu(1)–N(2)	2.0124(18)	N(1)–Cu(1)–N(3)	77.91(7)
Cu(1)–N(3)	2.3571(19)	N(2)–Cu(1)–N(3)	83.58(7)
Cu(1)–O(1)	1.9464(16)	N(1)–Cu(1)–O(1)	84.30(7)
Cu(1)–O(3)	1.9418(17)	N(1)–Cu(1)–O(3)	178.54(7)
		N(2)–Cu(1)–O(1)	163.42(8)
		N(2)–Cu(1)–O(3)	100.10(8)
		N(3)–Cu(1)–O(1)	101.47(7)
		N(3)–Cu(1)–O(3)	102.50(7)
		O(1)–Cu(1)–O(3)	94.24(7)

Table S4. Selected bond lengths (Å) and bond angles (°) of **II·MeOH**			
Cu(1)–N(1a)	2.056(2)	Cu(2)–N(1b)	2.049(2)
Cu(1)–N(2a)	2.014(2)	Cu(2)–N(2b)	2.026(2)
Cu(1)–N(3a)	2.402(3)	Cu(2)–N(3b)	2.508(2)
Cu(1)–O(1a)	1.937(2)	Cu(2)–O(1b)	1.9347(19)
Cu(1)–O(3a)	1.948(2)	Cu(2)–O(3b)	1.966(2)
N(1a)–Cu(1)–N(2a)	81.67(10)	N(1b)–Cu(2)–N(2b)	82.39(9)
N(1a)–Cu(1)–N(3a)	77.06(9)	N(1b)–Cu(2)–N(3b)	74.60(8)
N(2a)–Cu(1)–N(3a)	83.37(9)	N(2b)–Cu(2)–N(3b)	84.12(8)
N(1a)–Cu(1)–O(1a)	83.98(9)	N(1b)–Cu(2)–O(1b)	85.41(8)
N(1a)–Cu(1)–O(3a)	177.09(10)	N(1b)–Cu(2)–O(3b)	175.98(8)
N(2a)–Cu(1)–O(1a)	165.22(10)	N(2b)–Cu(2)–O(1b)	167.51(8)
N(2a)–Cu(1)–O(3a)	99.10(10)	N(2b)–Cu(2)–O(3b)	95.09(9)
N(3a)–Cu(1)–O(1a)	96.86(10)	N(3b)–Cu(2)–O(1b)	90.07(8)
N(3a)–Cu(1)–O(3a)	105.81(10)	N(3b)–Cu(2)–O(3b)	108.33(8)
O(1a)–Cu(1)–O(3a)	95.06(10)	O(1b)–Cu(2)–O(3b)	97.24(8)

Table S5. Selected bond lengths (Å) and bond angles (°) of **III·2H$_2$O**			
Cu(1)–N(1)	2.032(5)	N(1)–Cu(1)–N(2)	82.0(2)
Cu(1)–N(2)	2.023(6)	N(1)–Cu(1)–N(3)	77.44(19)
Cu(1)–N(3)	2.340(5)	N(2)–Cu(1)–N(3)	83.9(2)
Cu(1)–O(1)	1.925(5)	N(1)–Cu(1)–O(1)	83.5(2)
Cu(1)–O(3)	1.931(4)	N(1)–Cu(1)–O(3)	178.7(2)
		N(2)–Cu(1)–O(1)	163.3(2)
		N(2)–Cu(1)–O(3)	99.1(2)
		N(3)–Cu(1)–O(1)	100.92(19)
		N(3)–Cu(1)–O(3)	103.32(18)
		O(1)–Cu(1)–O(3)	95.3(2)

Table S6. Selected bond lengths (Å) and bond angles (°) of **IV·MeOH**			
Cu(1)–N(1)	2.050(3)	N(1)–Cu(1)–N(2)	81.18(12)
Cu(1)–N(2)	2.028(3)	N(1)–Cu(1)–N(3)	76.94(11)
Cu(1)–N(3)	2.392(3)	N(2)–Cu(1)–N(3)	84.03(12)
Cu(1)–O(1)	1.936(3)	N(1)–Cu(1)–O(1)	83.79(12)
Cu(1)–O(3)	1.933(3)	N(1)–Cu(1)–O(3)	178.81(11)
		N(2)–Cu(1)–O(1)	162.98(12)
		N(2)–Cu(1)–O(3)	99.55(13)
		N(3)–Cu(1)–O(1)	100.33(12)
		N(3)–Cu(1)–O(3)	104.05(12)
		O(1)–Cu(1)–O(3)	95.35(13)

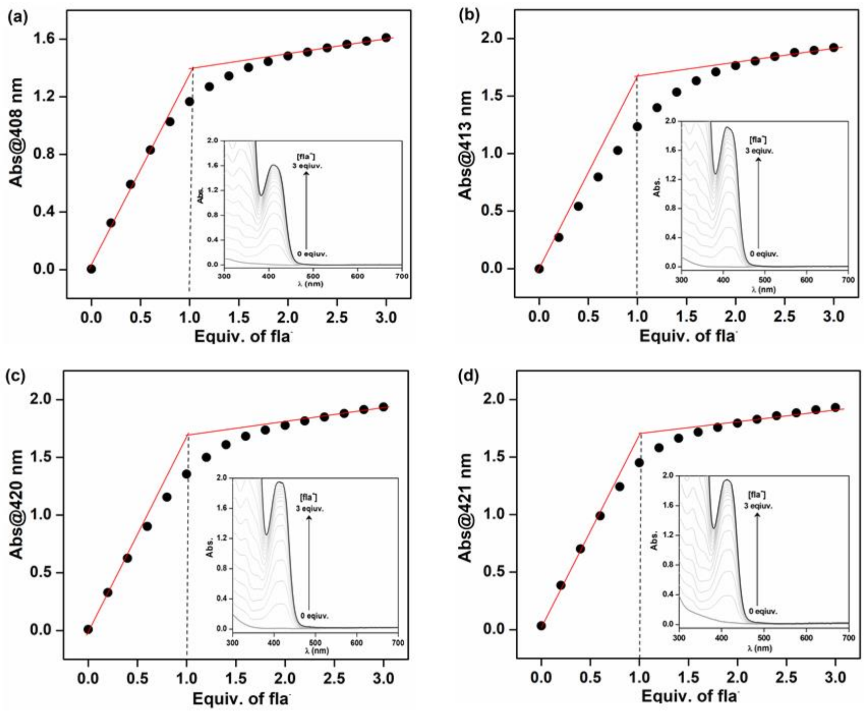


Figure S17. Spectrophotometric titration curves for the formation of Cu(II)-flavonolate adducts upon addition of flavonolate into the methanol solution of complex (a) [Cu(L^{OMe})(OAc)] , (b) [Cu(L^{H})(OAc)], (c) [Cu(L^{Cl})(OAc)], (d) Cu(L^{NO2})(OAc)]} at room temperature under N_2. Inset shows the growth of $\pi \rightarrow \pi^*$ bands due to coordinated flavonolate.

Determination of equilibrium constant (K_{eq}) from spectrophotometric titration

$$[L^RCu\text{-}OAc]_t \; + \; [fla^-]_t \; \underset{}{\overset{K_{eq}}{\rightleftharpoons}} \; [L^RCu\text{-}fla]_t \; + \; [OAc^-]_t$$

The equilibrium constant can be expressed as: $$K_{eq} = \frac{[L^RCu\text{-}fla]_t * [OAc^-]_t}{[L^RCu\text{-}OAc]_t * [fla^-]_t} \quad \cdots\cdots\cdots\cdots \text{(S1)}$$

The concentration of $[L^RCu\text{-}fla]_t$, $[L^RCu\text{-}OAc]_t$, $[fla^-]_t$ and $[OAc^-]_t$ species are determined considering the mass balance. A known concentration of [L^RCu-OAc] was taken in a UV-vis cuvette (pathlength = 1 cm) and its absorption spectrum was recorded. Then, a known concentration of fla^- was added portion-wise and the absorbance at 408-421 nm due to $\pi \rightarrow \pi^*$ band of Cu-bound flavonolate was measured. Each addition of fla^- makes the solution diluted; therefore, the volume correction due to dilution was performed for the observed absorbance at each titration.

At the beginning of the titration, when the solution is purely [L^RCu-OAc] the initial absorbance at any wavelength can be expressed as:

$A_i = \varepsilon_{LRCu\text{-}OAc}$ [L^RCu-OAc] …………. (S2)

Then fla^- was added gradually to the solution of [L^RCu-OAc] to form complex [L^RCu-fla]. $[fla^-]_a$ is the amount of fla^- added to the solution at any given point of titration. At the end of the titration when all [L^RCu-OAc] are converted to [L^RCu-fla] by adding excess fla^-, the final absorbance at any wavelength can be given as:

$A_f = \varepsilon_{LRCu\text{-}fla}$ [L^RCu-fla] …………. (S3)

Following mass balance, at any point of titration the total concentration of Cu^{II} ion can be expressed as:

$[L^RCu\text{-}OAc]_i = [L^RCu\text{-}fla]_f = [L^RCu\text{-}OAc]_t + [L^RCu\text{-}fla]_t$ …………. (S4)

Since fla^- is substituting the bound OAc^-, we can write:

$[fla^-]_a = [fla^-]_t + [OAc^-]_t$ …………… (S5)

Assuming the mass balance as described above, the ratio of $[L^RCu\text{-}fla]_t/[L^RCu\text{-}OAc]_t$ at any point of titration can be expressed as:

$$\frac{A_t - A_i}{A_f - A_t} = \frac{\varepsilon_{LRCuOAc}[L^RCuOAc]_t + \varepsilon_{LRCufla}[L^RCufla]_t - \varepsilon_{LRCuOAc}[L^RCuOAc]_i}{\varepsilon_{LRCufla}[L^RCufla]_f - \varepsilon_{LRCuOAc}[L^RCuOAc]_t - \varepsilon_{LRCufla}[L^RCufla]_t}$$

$$= \frac{\varepsilon_{LRCuOAc}\{[L^RCuOAc]_t - [L^RCuOAc]_i\} + \varepsilon_{LRCufla}[L^RCufla]_t}{\varepsilon_{LRCufla}\{[L^RCufla]_f - [L^RCufla]_t\} - \varepsilon_{LRCuOAc}[L^RCuOAc]_t}$$

$$= \frac{\varepsilon_{LRCufla}[L^RCufla]_t - \varepsilon_{LRCuOAc}[L^RCufla]_t}{\varepsilon_{LRCufla}[L^RCuOAc]_t - \varepsilon_{LRCuOAc}[L^RCuOAc]_t}$$

$$= \frac{[L^RCufla]_t\{\varepsilon_{LRCufla} - \varepsilon_{LRCuOAc}\}}{[L^RCuOAc]_t\{\varepsilon_{LRCufla} - \varepsilon_{LRCuOAc}\}} = \frac{[L^RCufla]_t}{[L^RCuOAc]_t} \quad \text{……….. (S6)}$$

Therefore, $[L^RCufla]_t = \frac{A_t - A_i}{A_f - A_t}\ [L^RCuOAc]_t$

So, $[L^RCufla]_t = \frac{A_t - A_i}{A_f - A_t}\ \{[L^RCuOAc]_i - [L^RCufla]_t\}$ ………. (S7)

Rearranging eq. (S7), the concentration of $[L^RCufla]_t$ can be expressed in terms of initial concentration of $[L^RCuOAc]_i$ as:

$$[L^RCufla]_t = \frac{\frac{A_t - A_i}{A_f - A_t}}{1 + \frac{A_t - A_i}{A_f - A_t}}\ [L^RCuOAc]_i \quad \text{…………. (S8)}$$

At equilibrium, the concentration of $[L^RCufla]_t$ is equal to the concentration of $[OAc^-]_t$.

$[L^RCufla]_t = [OAc^-]_t$ ……….(S9)

So, from eq. (S5) & (S9): $[fla^-]_a = [fla^-]_t + [OAc^-]_t = [fla^-]_t + [L^RCufla]_t$

So, $[fla^-]_t = [fla^-]_a - [L^RCufla]_t = [fla^-]_a - \frac{\frac{A_t - A_i}{A_f - A_t}}{1 + \frac{A_t - A_i}{A_f - A_t}} [L^R CuOAc]_i$ …… (S10)

The equilibrium constant described in eq. (S1) can be rearranged as:

$$K_{eq}[fla^-]_t = \frac{[L^R Cufla]_t \, [OAc^-]_t}{[L^R CuOAc]_t}$$

The values of $[L^RCufla]_t/[L^RCuOAc]_t$, $[OAc^-]_t$ and $[fla^-]_t$ can be determined from equations (S6), (S9) and (S10), respectively.

Therefore, the plot of $[fla^-]_t$ vs $\frac{[L^R Cufla]_t \, [OAc^-]_t}{[L^R CuOAc]_t}$ gives a straight line and the slope of the line gives the value of equilibrium constant, K_{eq}.

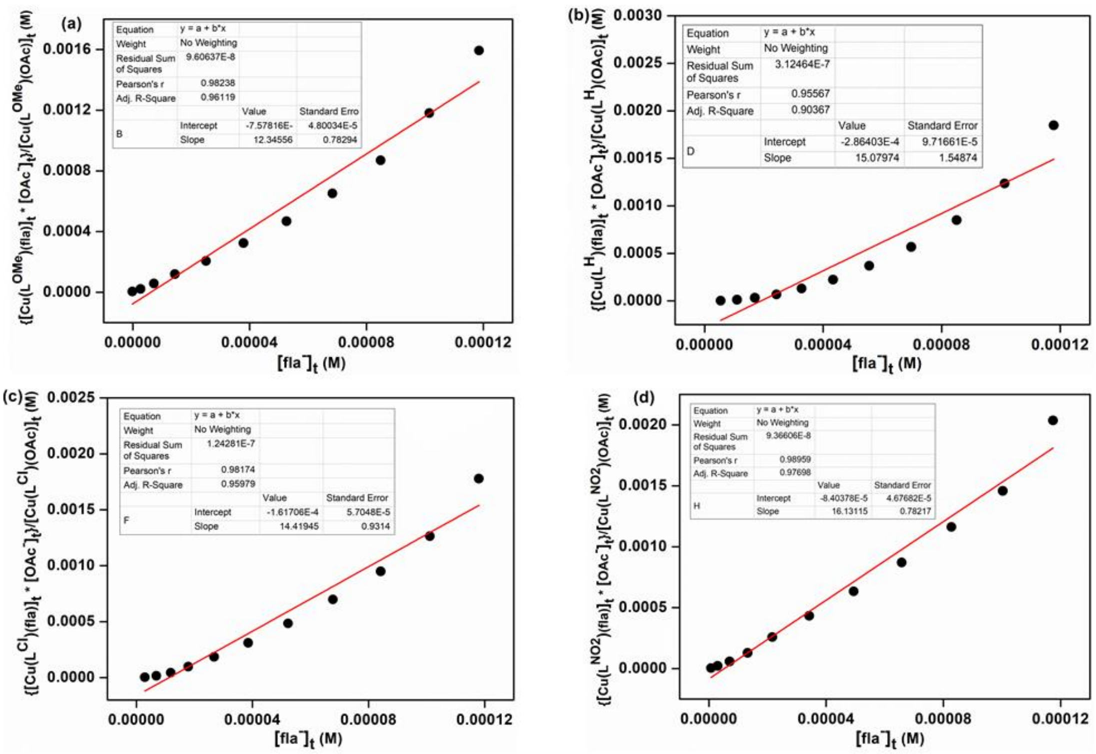


Figure S18. Plots of $\{[Cu(L^R)(fla)]_t * [OAc^-]_t\}/[Cu(L^R)(OAc)]_t$ *versus* $[fla^-]_t$ to determine the equilibrium constants (K_{eq}). The slope of the linear fit represents K_{eq} value.

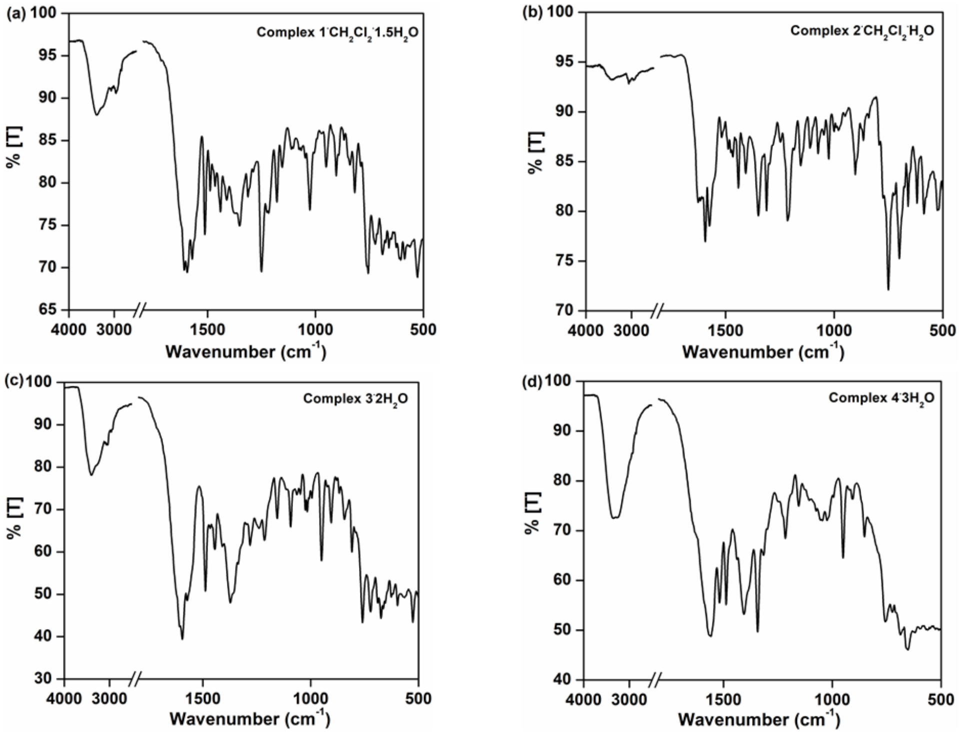


Figure S19. ATR-FTIR spectra (solid samples) of copper(II)-flavonolate complexes: (a) [Cu(L^{OMe})(fla)]·CH_2Cl_2·1.5H_2O (**1·CH_2Cl_2·1.5H_2O**); (b) [Cu(L^{H})(fla)]·CH_2Cl_2·H_2O (**2·CH_2Cl_2·H_2O**); (c) [Cu(L^{Cl})(fla)]·2H_2O (**3·2H_2O**) and (d) [Cu(L^{NO2})(fla)]·3H_2O (**4·3H_2O**).

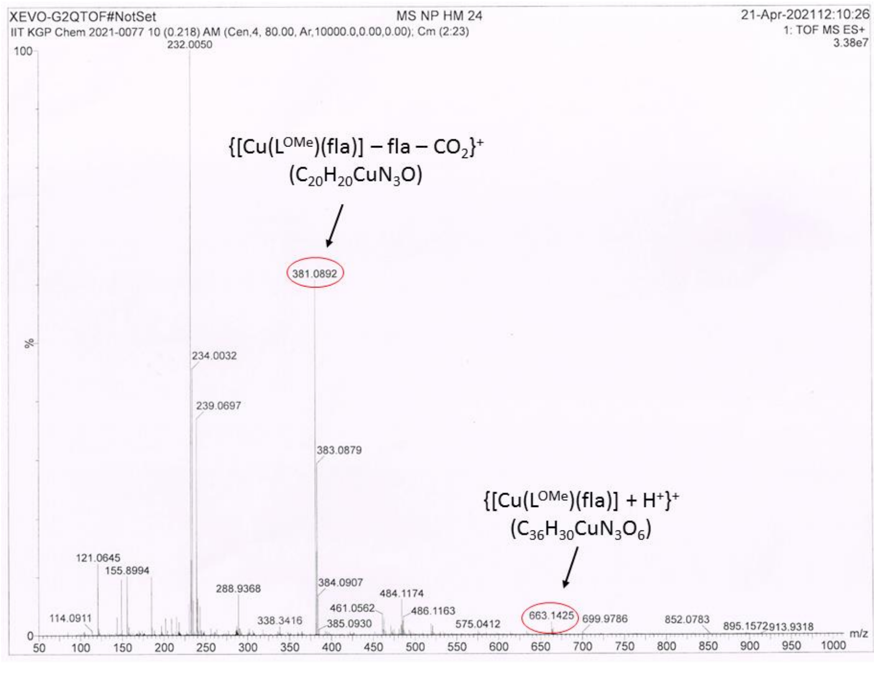


Figure S20. HRMS-ESI(+) spectrum of [Cu(L^{OMe})(fla)] (**1**) in methanol.

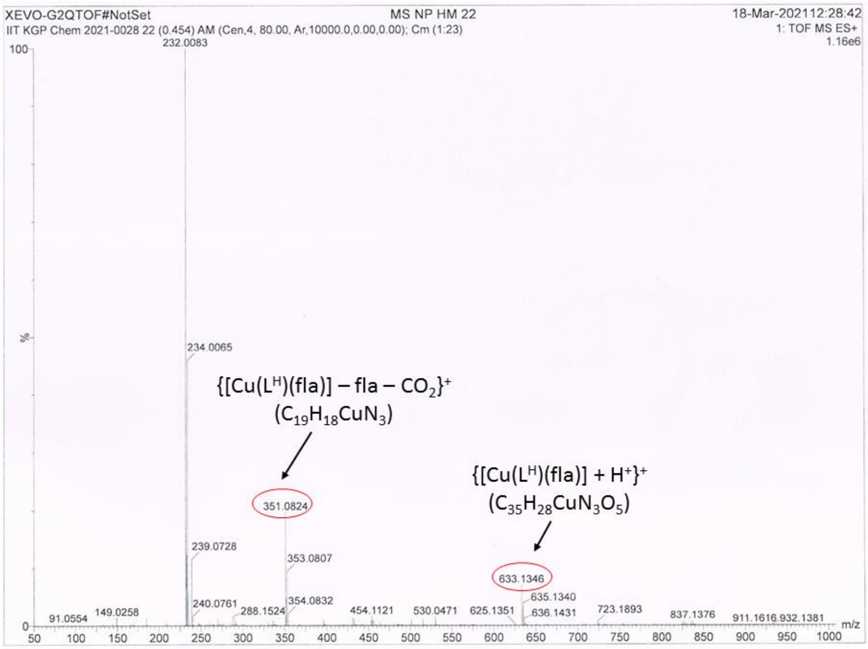


Figure S21. HRMS-ESI(+) spectrum of [Cu(L^{H})(fla)] (**2**) in methanol.

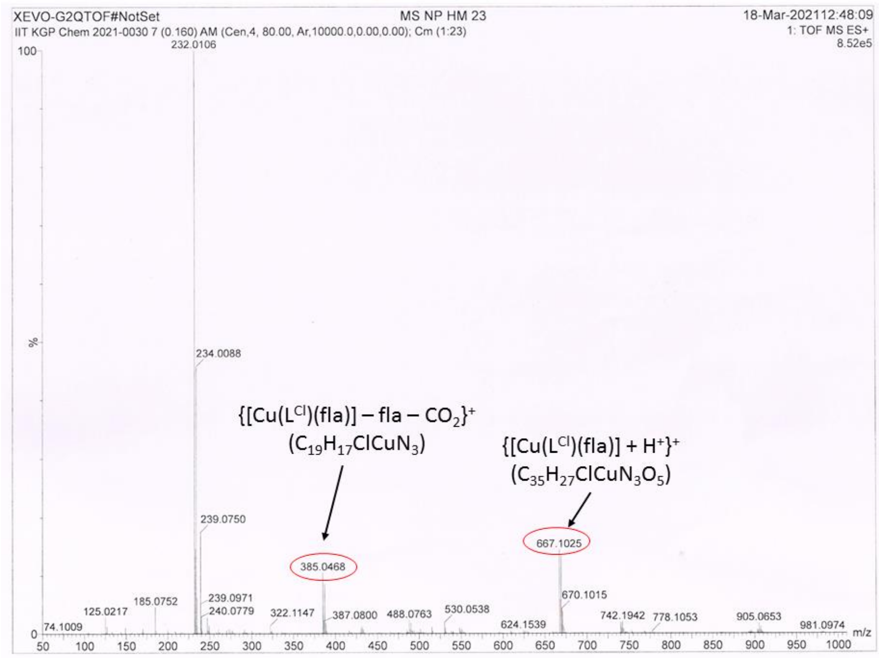


Figure S22. HRMS-ESI(+) spectrum of [Cu(L^{Cl})(fla)] (**3**) in methanol.

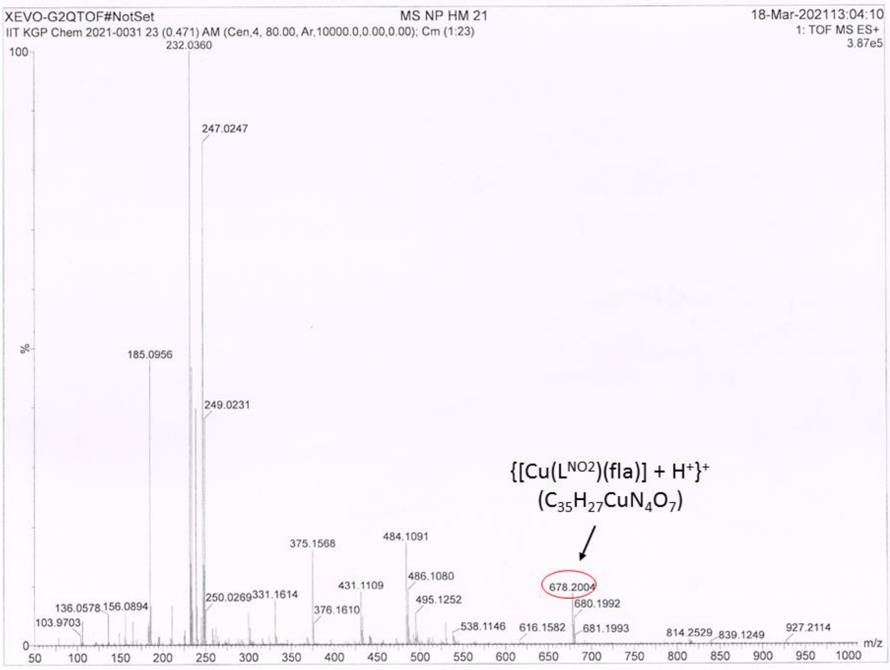


Figure S23. HRMS-ESI(+) spectrum of [Cu(L^{NO2})(fla)] (**4**) in methanol.

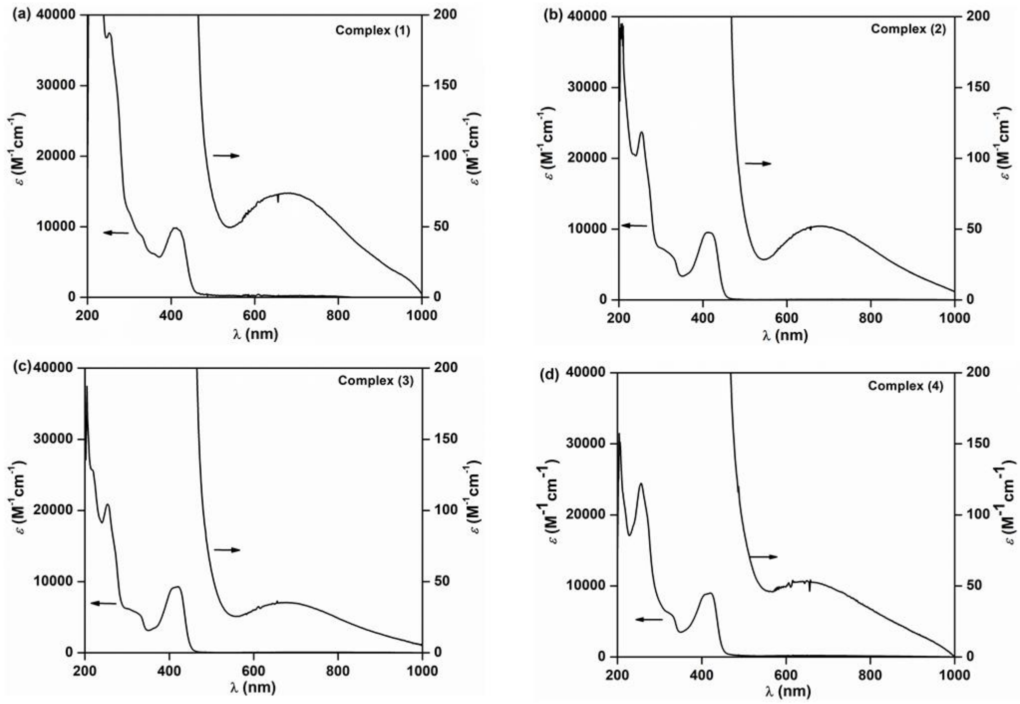


Figure S24. UV-vis spectra of copper(II)-flavonolate complexes in methanol: (a) [Cu(L^{OMe})(fla)]·CH_2Cl_2·1.5H_2O (**1·CH_2Cl_2·1.5H_2O**); (b) [Cu(L^{H})(fla)]·CH_2Cl_2·H_2O (**2·CH_2Cl_2·H_2O**); (c) [Cu(L^{Cl})(fla)]·2H_2O (**3·2H_2O**) and (d) [Cu(L^{NO2})(fla)]·3H_2O (**4·3H_2O**).

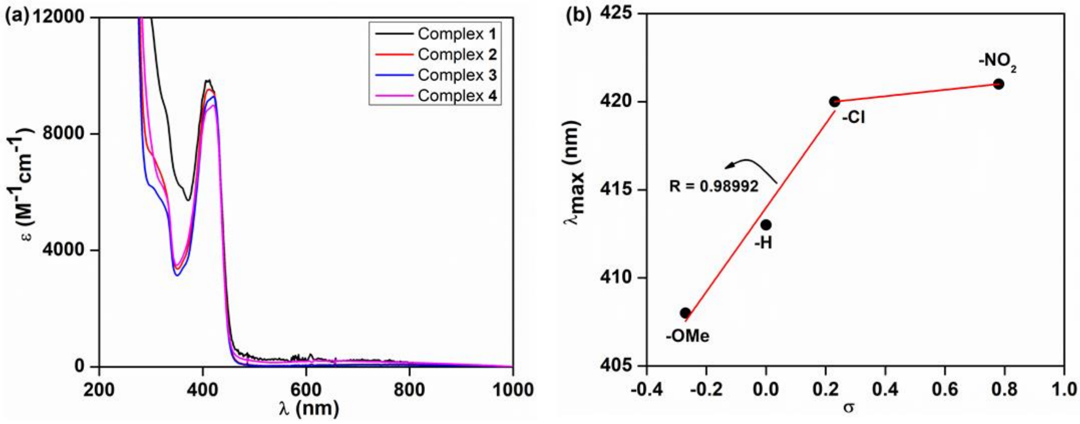


Figure S25. (a) Electronic absorption spectra of the complexes [Cu(L^R)(fla)] (**1-4**) in MeOH. (b) Plot of λ_{max} values of the $\pi \rightarrow \pi^*$ transition of the coordinated fla$^-$ in complexes [Cu(L^R)(fla)] (**1-4**) versus Hammett constants σ.

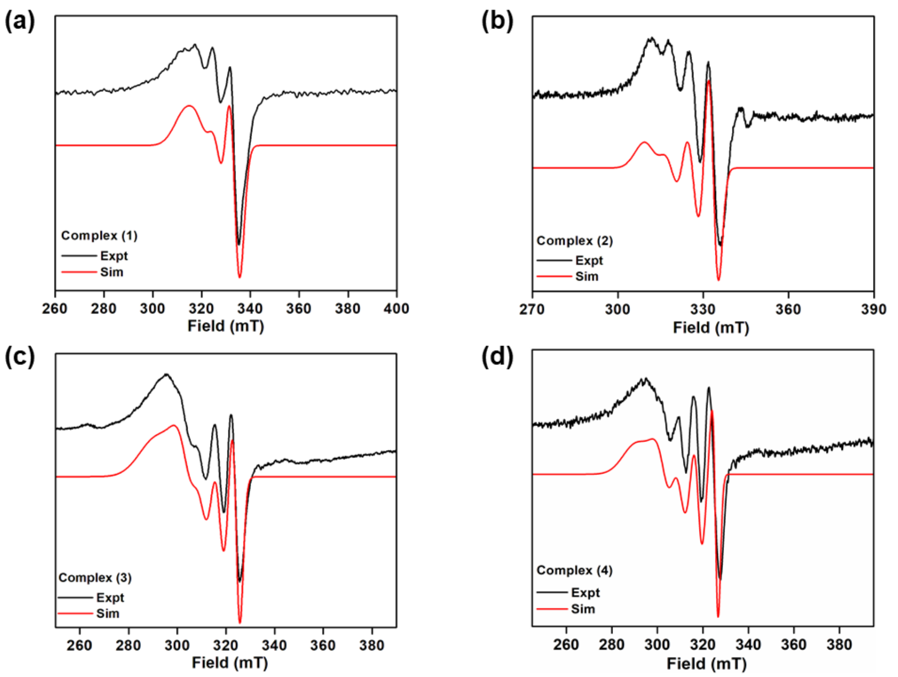


Figure S26. Experimental (black line) and simulated (red line) X-band EPR spectra of Cu(II)-flavonolate complexes in methanol at 298 K: (a) [Cu(L^{OMe})(fla)] (**1**); (b) [Cu(L^H)(fla)] (**2**); (c) [Cu(L^{Cl})(fla)] (**3**); (d) [Cu(L^{NO2})(fla)] (**4**). Microwave frequency ≈ 9.64 GHz (**1**), 9.65 GHz (**2**), 9.36 GHz (**3**), 9.36 (**4**); microwave power = 15 mW; modulation frequency = 5 kHz; modulation amplitude = 3 G.

Table S7. Parameters for the simulations of the EPR signals of complexes **1-4** as depicted in Figure S26

Complex 1	Complex 2	Complex 3	Complex 4
g_{iso} = 2.12 A_{iso} = 160.40 MHz g-strain = 0.055 A-strain = 58.40 MHz	g_{iso} = 2.13 A_{iso} = 200 MHz g-strain = 0.045 A-strain = 50 MHz	$g_{\perp}$ = 2.125 $g_{\parallel}$ = 2.30 $A_{\perp}$ = 192.43 MHz $A_{\parallel}$ = 23.43 MHz $g_{\perp}$-strain = 0.040 $g_{\parallel}$-strain = 0.125 $A_{\perp}$-strain = 48.30 MHz $A_{\parallel}$-strain = 5 MHz	$g_{\perp}$ = 2.123 $g_{\parallel}$ = 2.30 $A_{\perp}$ = 211.94 MHz $A_{\parallel}$ = 40 MHz $g_{\perp}$-strain = 0.035 $g_{\parallel}$-strain = 0.099 $A_{\perp}$-strain = 50 MHz $A_{\parallel}$-strain = 10 MHz

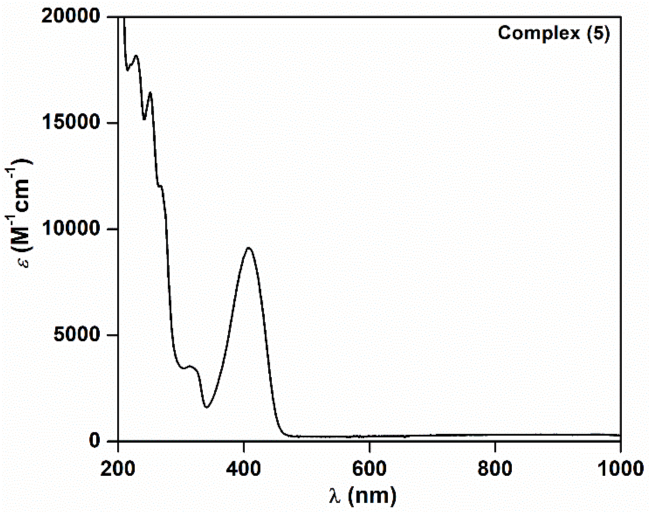


Figure S27. UV-vis spectrum of [Zn(L^{OMe})(fla)]·2H_2O (**5·2H_2O**) in methanol.

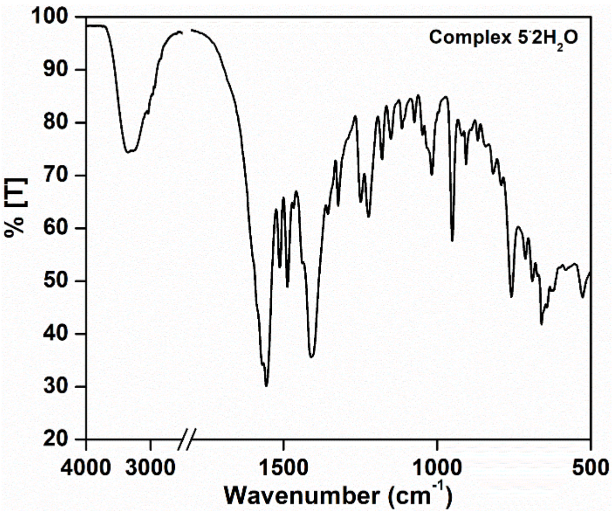


Figure S28. ATR-FTIR spectrum (solid sample) of [Zn(L^{OMe})(fla)]·2H_2O (**5·2H_2O**).

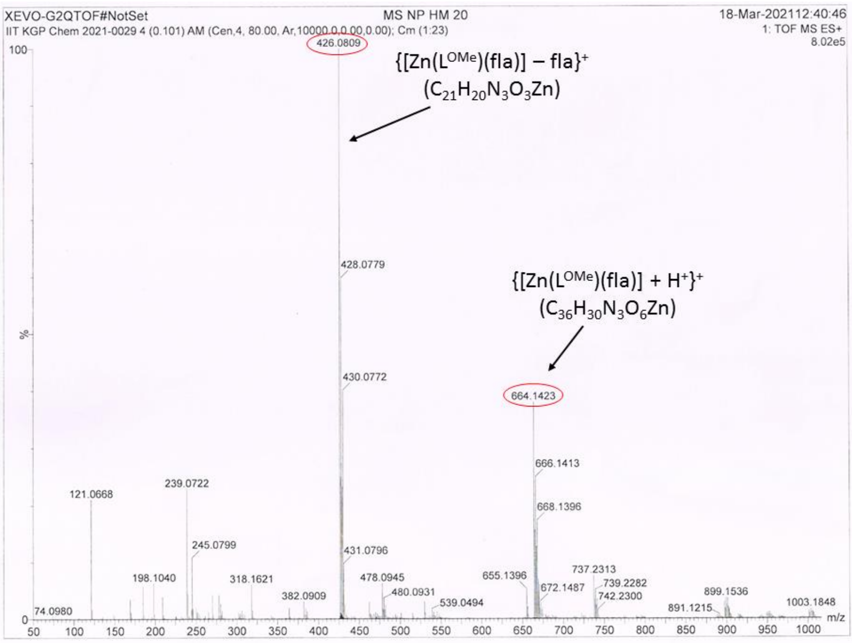


Figure S29. HRMS-ESI(+) spectrum of [Zn(L^{OMe})(fla)] (**5**) in methanol.

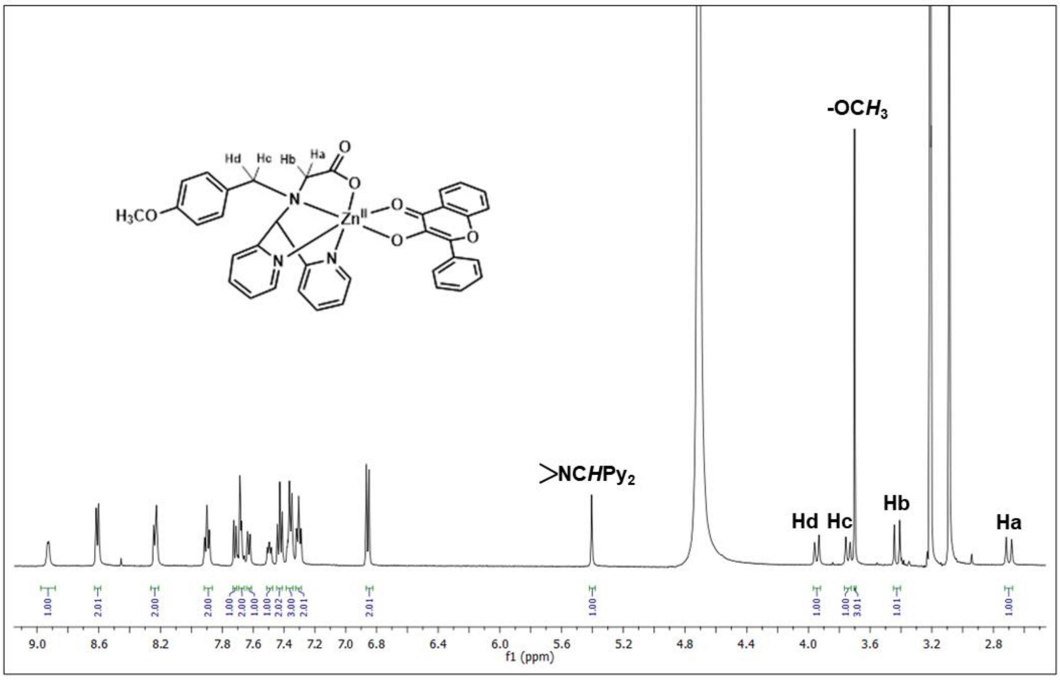


Figure S30. ^{1}H NMR spectrum (500 MHz, 300 K) of complex [Zn(L^{OMe})(fla)] (**5**) in CD_3OD.

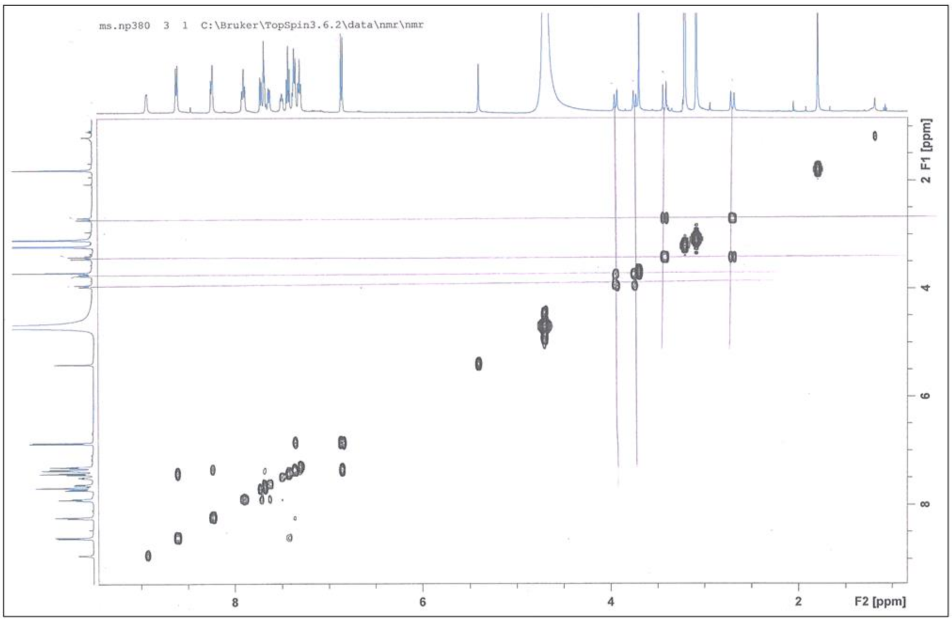


Figure S31. 2D ^{1}H ^{1}H COSY (500 MHz, 300 K) of complex [Zn(L^{OMe})(fla)] (**5**) in CD_3OD.

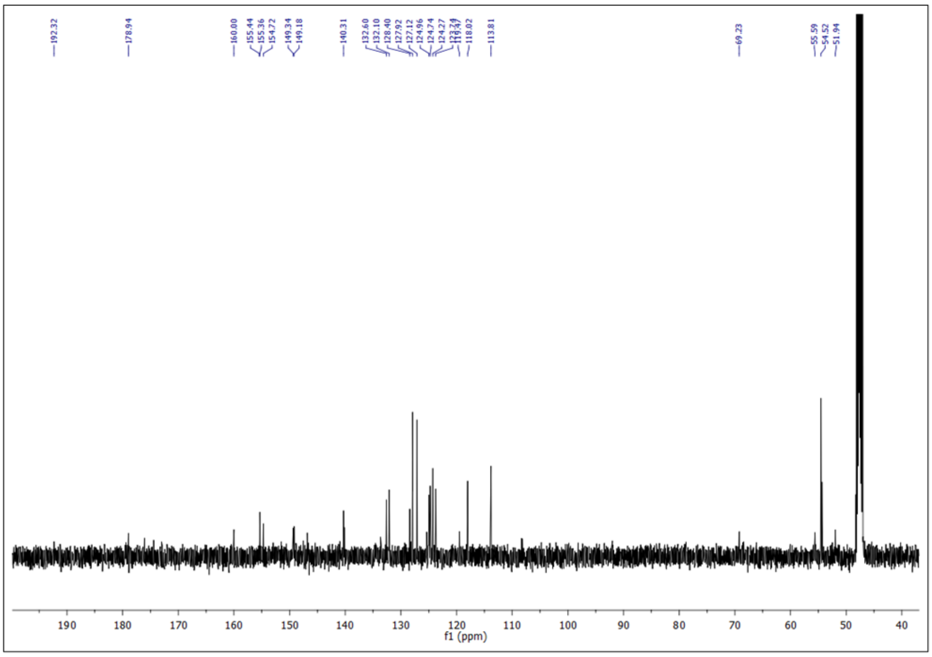


Figure S32. ^{13}C NMR spectrum (125 MHz, 300 K) of complex [Zn(L^{OMe})(fla)] (**5**) in CD_3OD.

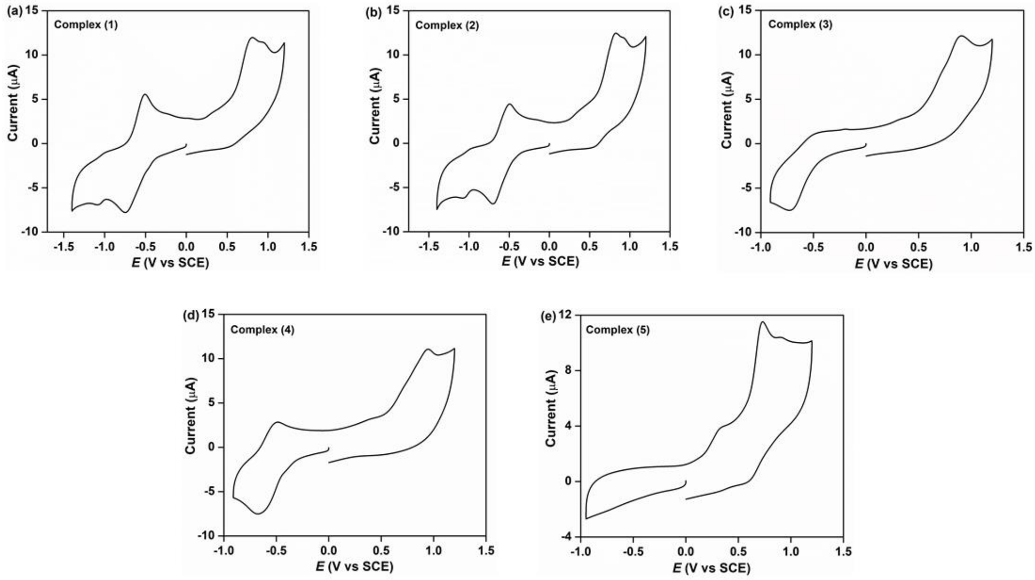


Figure S33. Cyclic voltammograms of the metal-flavonolate complexes **1-5** in DMF (scan rate: 100 mV/s; supporting electrolyte: KPF_6).

Table S8. Percentage of product distribution obtained from GC-MS analysis

	o-benzoyl -salicylic acid (RT: 21.73)	salicylic acid (RT: 13.29)	benzoic acid (RT: 17.37-17.43)	2-hydroxy-*N*,*N*-dimethyl -benzamide (RT: 15.30)	*N*,*N*-dimethyl -benzamide (RT: 11.25)
[Cu(L^{OMe})(fla)] (**1**)	22	-	67	-	11
[Cu(L^{H})(fla)] (**2**)	13	19	11	54	3
[Cu(L^{Cl})(fla)] (**3**)	72	-	27	-	1
[Cu(L^{NO2})(fla)] (**4**)	10	-	29	59	2
[Zn(L^{OMe})(fla)] (**5**)	42	-	-	57	1

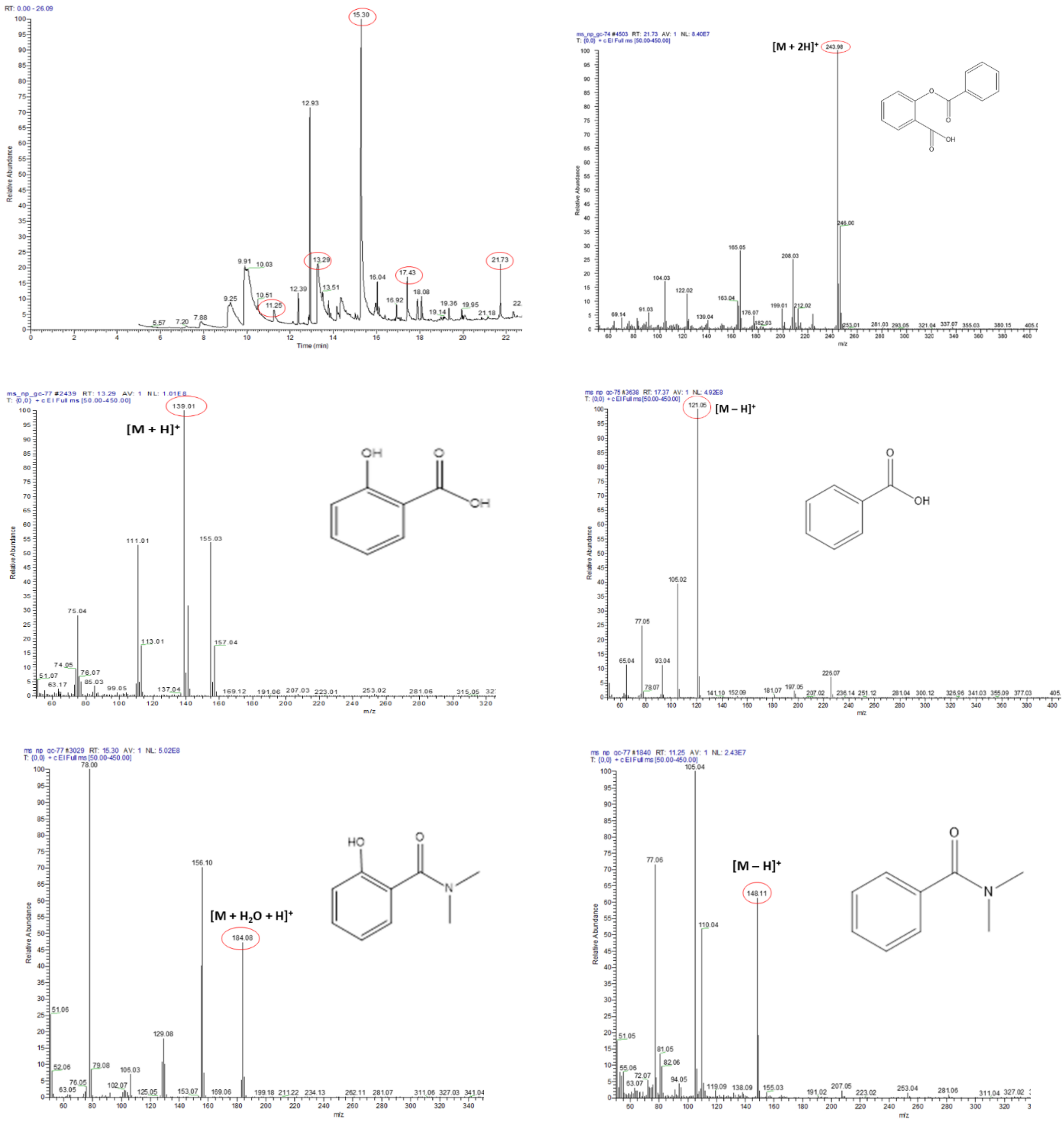


Figure S34. Reaction product analysis by GC-MS. (Top left) Representative GC-MS chromatogram for complex **2**. The illustrative mass spectra of products from few selected reaction solutions: (top right) *o*-benzoylsalicylic acid (from **3**), (middle left) salicylic acid (from **2**), (middle right) benzoic acid (from **4**), (bottom left) 2-hydroxy-*N*,*N*-dimethylbenzamide (from **2**) and (bottom right) *N*,*N*-dimethylbenzamide (from **2**).

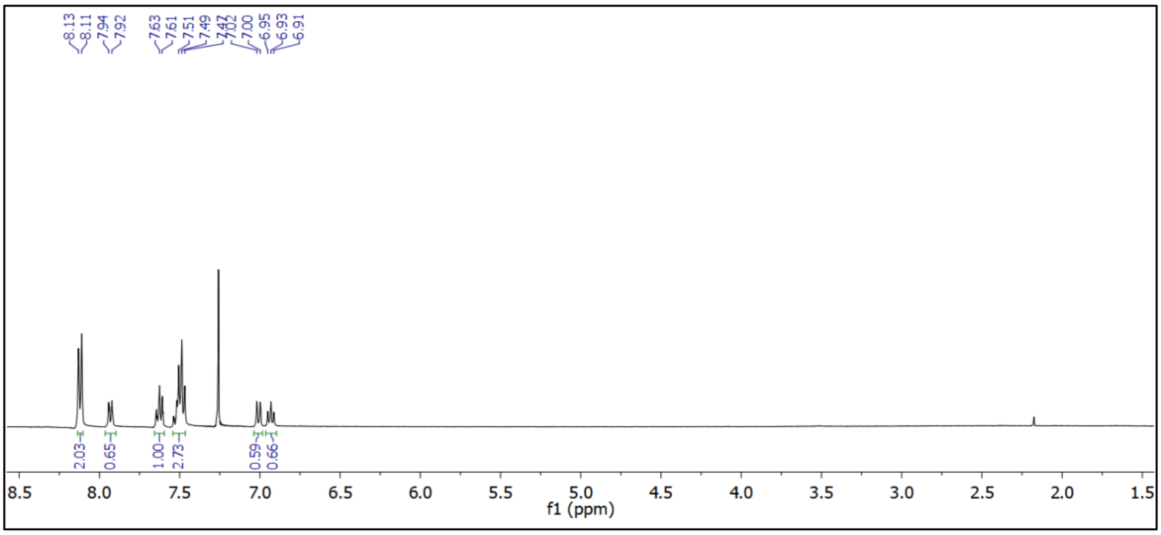
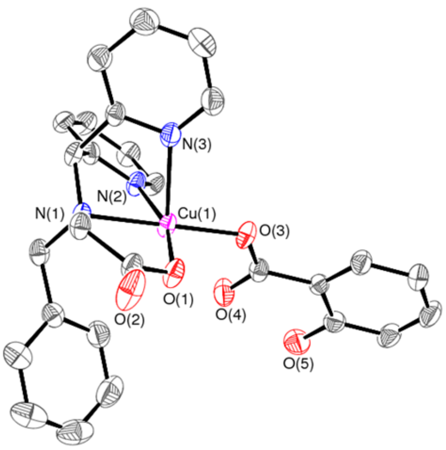


Figure S35. ^{1}H NMR spectrum (in $CDCl_3$) of the degraded products obtained from $[L^{H}Cu(fla)]$ (**2**). Signals correspond to mixture of benzoic acid [δ(ppm) = 8.12 (d, 2H), 7.62 (t, 1H), 7.48 (t, 2H))] and salicylic acid [δ(ppm) = 7.93 (d, 1H), 7.51 (t, 1H), 7.01 (d, 1H), 6.93 (t, 1H)] in 60:40 ratio.



Selected bond lengths (Å) and bond angles (°)

Cu(1)–N(1)	2.085(3)	O(3)–Cu(1)–O(1)	92.92(13)
Cu(1)–N(2)	2.070(4)	O(3)–Cu(1)–N(2)	102.90(13)
Cu(1)–N(3)	2.296(4)	O(1)–Cu(1)–N(2)	163.17(13)
Cu(1)–O(1)	1.977(3)	O(3)–Cu(1)–N(1)	176.32(13)
Cu(1)–O(3)	1.952(3)	O(1)–Cu(1)–N(1)	83.92(12)
		N(2)–Cu(1)–N(1)	80.45(13)
		O(3)–Cu(1)–N(3)	99.78(13)
		O(1)–Cu(1)–N(3)	98.37(14)
		N(2)–Cu(1)–N(3)	84.72(15)
		N(1)–Cu(1)–N(3)	78.88(14)

Figure S36. ORTEP (30% ellipsoid) diagram of the salicylate bound copper(II) complex, $[Cu(L^{H})(sal)]$. Hydrogen atoms are omitted for clarity. Carbon atoms are not labelled. {Crystal data: CCDC = 2112727, λ (Å): *Mo-Kα* (0.71073), Monoclinic, $P2_1/n$ (# 14), a = 18.135(4) Å, b = 9.278(2) Å, c = 15.307(3) Å, $\alpha = \gamma$ = 90°, β = 103.47(3)°, V = 2504.6(10) Å^{3}, Z = 4, D_c = 1.411 g cm^{-3}, Reflections measured = 15536, Unique reflections [R_{int}] = 5303 [0.1383], Number of reflections used [$I > 2\sigma(I)$] = 2890, Final R indices: R_1 = 0.0577 , wR_2 = 0.1402, R indices (all data): R_1 = 0.1173 , wR_2 = 0.1825 , Goodness-of-fit on F^2 = 0.960, T = 296(2) K}.

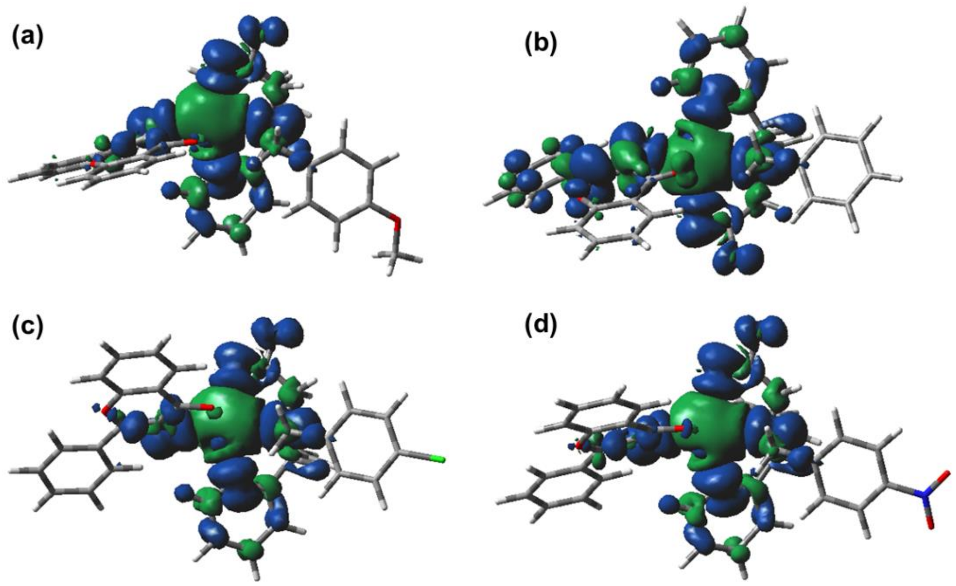


Figure S37. Mulliken atomic spin density plots of (a) [Cu(L^{OMe})(fla)] (**1**), (b) [Cu(L^{H})(fla)] (**2**), (c) [Cu(L^{Cl})(fla)] (**3**), and (d) [Cu(L^{NO2})(fla)] (**4**) in doublet ground state.

Table S9. Mulliken atomic spin density values of complexes **1-4**.

		Spin Density		
Complex	**Spin State**	**Cu**	**fla**	**L^{R}**
[Cu(L^{OMe})(fla)] (**1**)	doublet	0.698	0.089	0.276
[Cu(L^{H})(fla)] (**2**)	doublet	0.660	0.104	0.236
[Cu(L^{Cl})(fla)] (**3**)	doublet	0.689	0.079	0.278
[Cu(L^{NO2})(fla)] (**4**)	doublet	0.697	0.088	0.267

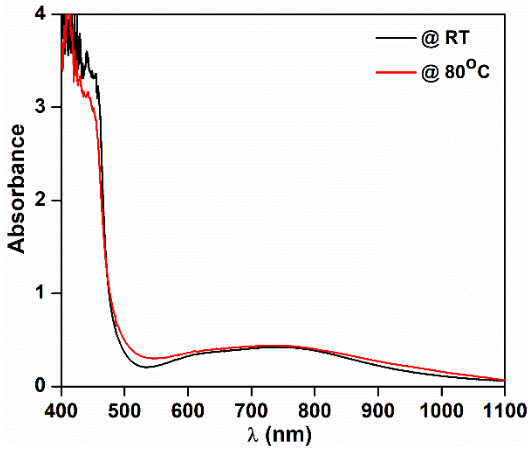


Figure S38. Electronic spectra of complex [Cu(L^{H})(fla)] (**2**) (~6.5 mM) in DMF at: (black line) room temperature, and (red line) 80 °C under N_2 atmosphere. The visible region bands correspond to the *d*-*d* transitions.

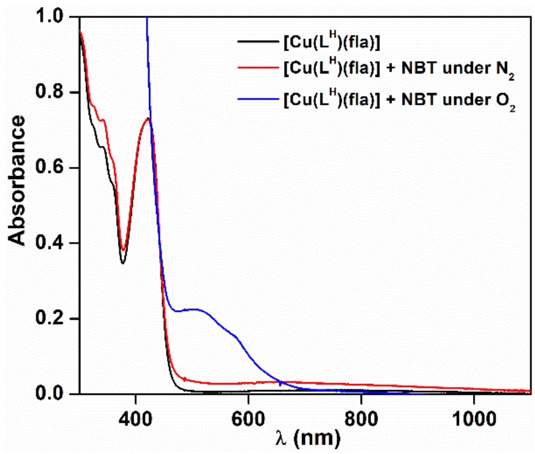


Figure S39. Spectral changes of reaction of [Cu(L^{H})(fla)] (**2**) with NBT under O_2 in DMF.

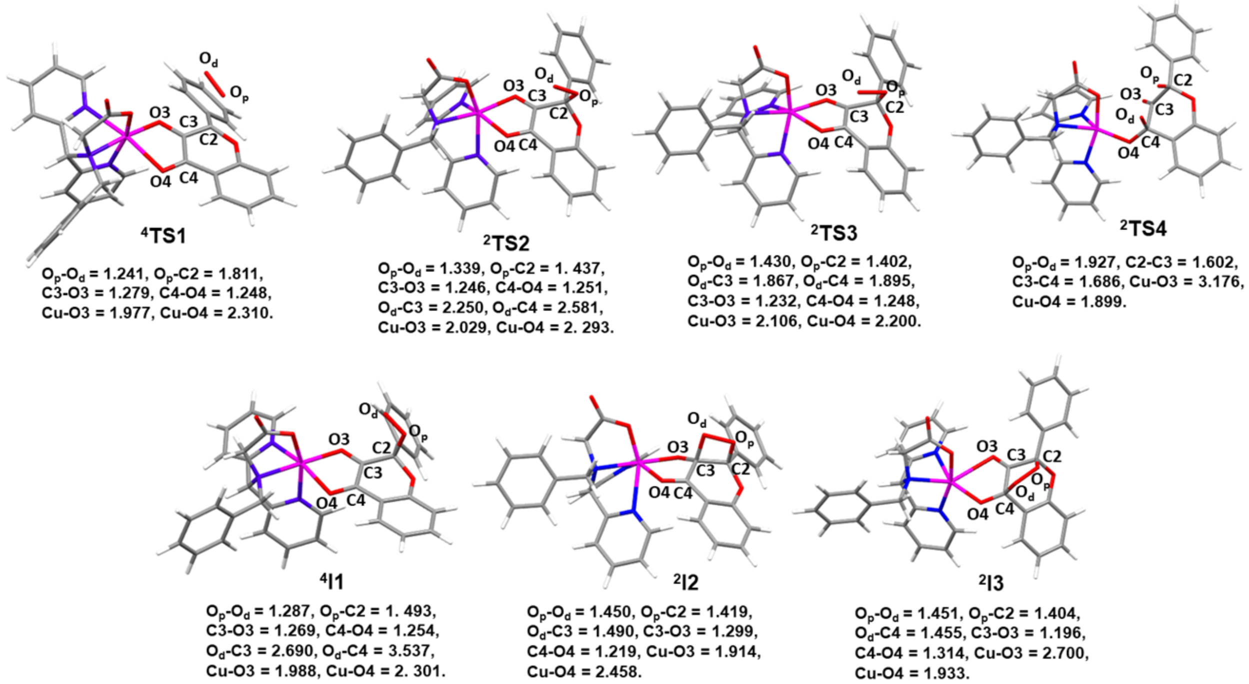


Figure S40. Optimized structures of various transition states (**TS**s) and intermediates (**I**s) of oxygenolysis reaction starting with complex [Cu(L^H)(fla)] (**2**). The bond lengths are shown in Å. Color code: Cu, magenta; C, gray; N, blue; O, red; H, white.

Table S10. Mulliken atomic spin density values of various states during oxygenolysis reaction with complex [Cu(L^H)(fla)] (**2**)

State	Cu	fla	O_p	O_d	L^H
^{4}R	0.670	0.101	1.022	0.976	0.231
^{4}TS1	0.686	0.690	0.611	0.760	0.253
^{4}I1	0.677	1.045	0.310	0.708	0.260
^{2}TS2	0.683	-0.692	0.144	0.601	0.264
^{2}I2	0.683	0.093	0	0	0.224
^{2}TS3	0.678	0.053	0	-0.002	0.271
^{2}I3	0.662	0.105	-0.001	0	0.234
^{2}TS4	0.650	0.053	0.056	0.004	0.237
^{2}P	0.669	0.083	0	-0.001	0.249

Table S11. Optimized coordinates of reactants **^{4}R**

Cu	-0.07252882939979	-0.32060697486603	-0.16859498155090
O	1.73831796591438	-0.68727535080118	0.39368386280761
O	0.66109070391988	1.74679847015307	0.76990425594567
N	-2.09121734123350	0.02497565961324	-0.58890274239032
O	0.19032853623221	0.43338066617237	-1.93605994043421
N	-0.92724357629547	-0.82860284935306	1.66253770869354
O	4.65456871770223	1.43053709378649	0.20660648027829
C	1.88024777310193	1.67087740397754	0.58697271985497
C	2.52020761925328	0.35623361084048	0.37488268950420
C	-0.30919282465011	-0.85131824740632	2.83739486770211
H	0.76704429183966	-0.65853153395306	2.80227778200688
C	2.75770989679278	2.83460642435582	0.57073177588948
O	-0.93852424182513	1.18171622165171	-3.72266689870582
C	-0.86324386447026	0.61538433699662	-2.65142829435322
C	4.12991620382537	2.64770748871546	0.37437180590546
C	-2.37741983317810	1.38576741628141	-0.06766611448248
H	-1.65865381059695	2.05937926399467	-0.55588208327102
H	-2.12257442158456	1.40742155065181	1.00087579839662
C	3.88605568693485	0.29914323457165	0.19477027106730
C	-2.24057949543765	-1.05665157919009	1.57050149602970
C	2.26097988202465	4.14135558720171	0.74554321104343
H	1.18477826568139	4.25628159875901	0.89120045278313
C	-2.75888666276079	-1.06445879073820	0.13671625071403
H	-3.85901666751409	-0.97527175052304	0.12292934631159
C	6.27383602456526	-3.20356766814234	-0.46200978660923
H	6.88621426733059	-4.09216321347597	-0.63592209793772
C	-2.37626433530883	-1.35020336701455	3.93798953191743
H	-2.95309040992119	-1.55301995272010	4.84368563432447
C	4.69278015762509	-0.91415862074596	-0.02087841378505
C	-3.01132021245786	-1.32584957337183	2.69503493029319
H	-4.08363640868331	-1.50988654161895	2.59982704828961
C	5.00761744971566	3.74571814849048	0.35281552679058
H	6.07267671750663	3.56559377442077	0.19638115481219
C	-3.79427917994956	1.86371056440503	-0.28327514141942
C	4.49692473366933	5.01723321800542	0.52634820091365
H	5.17524289726260	5.87407667621886	0.50717240877515
C	-1.00653173381707	-1.11279035652669	4.01514549163019
H	-0.48178277051184	-1.12545306979602	4.97172674545922
C	3.11665965501232	5.22329806819919	0.72394240054302
H	2.73048746817489	6.23647238799704	0.85469114179268
C	6.05389502513174	-0.79922111910349	-0.35398648498458
H	6.49903487265829	0.19190626618675	-0.44640687517214
C	4.13929764455155	-2.20214087698968	0.09285462849860
H	3.08455540943244	-2.29187547942124	0.34880024416584
C	4.92689628605073	-3.32909823227772	-0.12716545165855
H	4.47799757603017	-4.32190154931346	-0.03456235452889
C	-4.14267471874863	2.55700202200107	-1.44945538028453
H	-3.37225412236372	2.77224318582899	-2.19671418967207
C	6.83262218743502	-1.93064662872786	-0.57279427143468
H	7.88741767212336	-1.81583926470500	-0.83594575486664
C	-4.78534917520604	1.62046487808554	0.67506331396902
H	-4.51784212243415	1.11581617546125	1.60933424557826
C	-5.45562479438650	2.97323873714943	-1.66166740837883
H	-5.71124901697258	3.51236271974090	-2.57709116292634
C	-6.09963700221226	2.03553555301709	0.46549206821045
H	-6.86085877238366	1.84253502029098	1.22577084251368
C	-6.43764288830645	2.70908062314445	-0.70736457358154

H	-7.46632185072040	3.03878659307493	-0.87317436524359
C	-2.14760186698903	-0.01492115513562	-2.05714375387555
H	-3.04216185427526	0.48107447391304	-2.45857722880525
H	-2.17253205091250	-1.05751754990073	-2.39936844699340
N	-1.03828709545688	-2.54229108279200	-0.68554255021456
C	-2.34551049492811	-2.40899166881767	-0.45753593718640
C	-2.76622977438012	-4.63734182128968	-1.21396541468201
H	-3.45041602450751	-5.46240637922009	-1.42673097987617
C	-1.40262716541938	-4.76923997811834	-1.45476427164597
H	-0.98442566065283	-5.69280223472289	-1.85901880195848
C	-3.25425294631161	-3.43266793121282	-0.70582446129666
H	-4.32018309739420	-3.28711729692179	-0.51743283471344
C	-0.57073233190471	-3.68339423486920	-1.17567998143102
H	0.50770608813524	-3.72412228047285	-1.35645639183609
O	2.02325918102021	-1.88011004244141	-2.52118189997566
O	2.75403758980886	-0.95425886665732	-2.66513561124882

Table S12. Optimized coordinates of transition state ^{4}**TS1**

Cu	-0.20703090352162	-0.30543919253931	-0.95235422961038
O	1.71984897095107	-0.64936731074498	-0.67115959153757
O	0.53052020262202	1.76207159135654	-0.23299006336775
N	-2.27524698623945	-0.00339591398007	-0.91395375569284
O	-0.36504704260871	0.16669527090536	-2.81890337086495
N	-0.64707922850642	-0.82273324973934	1.05976858672576
O	4.56017207162037	1.37889297476163	0.15675952493701
C	1.77445499267754	1.66558617273973	-0.20976891383564
C	2.41823328870370	0.38187504986080	-0.38029379553672
C	0.16683931308644	-0.83517300776102	2.11046060412627
H	1.21553382748325	-0.60096358882447	1.90498224929694
C	2.64863030818488	2.82331115048044	-0.02732512934915
O	-1.85619041359810	0.41657563427364	-4.47214557957362
C	-1.55029910134813	0.22316667211447	-3.31428422080076
C	4.02511860757838	2.62401659458757	0.10457286314418
C	-2.40057892327912	1.34916497181271	-0.31881328371692
H	-1.88375320426361	2.02325670558568	-1.01574631963210
H	-1.80422600593408	1.39075619884505	0.60255190542499
C	3.87163779097929	0.28011813578136	-0.25759465953669
C	-1.94354103001606	-1.11262467281486	1.21063121847954
C	2.14119486072329	4.13068536807337	-0.00034883251002
H	1.06110751868384	4.25579964272048	-0.09843620425353
C	-2.71742482410097	-1.13785814287114	-0.09475973221625
H	-3.80437889337433	-1.13089274128208	0.09717475696705
C	5.64849847642031	-3.32988481871828	1.24508288399411
H	6.10540171773245	-4.24300750504754	1.63712462731659
C	-1.64657423534571	-1.43332513463552	3.55930336155963
H	-2.04716030338199	-1.67963711932118	4.54579901318664
C	4.48177242893571	-0.97742066701349	0.25811927185485
C	-2.48732070845320	-1.43519025683896	2.44740142909999
H	-3.54692632268638	-1.68518167892415	2.53297487045931
C	4.89797221223273	3.70616969220970	0.22849349432727
H	5.96809903740348	3.50991054523986	0.31660027044502
C	-3.79735014543308	1.84418723800441	-0.03673392052089
C	4.37856207878005	4.99348516937649	0.23111314477614
H	5.05744220981215	5.84437887534819	0.31947622135888

C	-0.29820163517687	-1.13168017445686	3.39099959215981
H	0.39021985917444	-1.12614694807107	4.23647124112618
C	2.99724925457813	5.21156032506092	0.12343414848690
H	2.59691723238474	6.22794209527900	0.13120869077373
C	5.51742370493048	-0.91827635483491	1.20118780027549
H	5.87099098376832	0.05182073472181	1.55381861547210
C	4.04249438742110	-2.22955389911334	-0.19600067820396
H	3.23932789469281	-2.27556950911451	-0.92643992392896
C	4.62846473552578	-3.39426912542661	0.29573108294735
H	4.27156823106241	-4.35841256734358	-0.07874688409164
C	-4.42765913054960	2.74796056175586	-0.89851489083054
H	-3.91607579383950	3.06452245333095	-1.81190044439512
C	6.09107712938154	-2.08602906687511	1.69729702522152
H	6.89232543552887	-2.02150127591146	2.43734011405562
C	-4.45495414996418	1.47176766957287	1.14167647740217
H	-3.95452346835921	0.80111262193287	1.84584947940810
C	-5.67528618232434	3.28449738127214	-0.57910013287091
H	-6.14248684787121	4.00714191464437	-1.25194991196670
C	-5.71107397048799	1.98552830071170	1.45372361367125
H	-6.20850050997405	1.67792475099383	2.37702478516439
C	-6.31678813580322	2.90776846203625	0.60006299041307
H	-7.28306351023179	3.34493712792010	0.86551024712214
C	-2.71213584833928	-0.03099410913895	-2.31875098849173
H	-3.51428040383611	0.69697336168140	-2.50341335758943
H	-3.13497792345819	-1.01371908857411	-2.56846158208656
N	-1.10996234867770	-2.44828622054660	-1.32482071324450
C	-2.31747751665489	-2.45651474785860	-0.76982767066109
C	-2.59163183550944	-4.76925615612042	-1.31320023932164
H	-3.17634073341962	-5.69177047064446	-1.28935749542226
C	-1.34370116135340	-4.73750929608446	-1.92862426058913
H	-0.92197036471212	-5.61810433108194	-2.41683100199249
C	-3.10102917404503	-3.60632139183827	-0.73343919560260
H	-4.08651210621840	-3.59523130287527	-0.26353493016710
C	-0.63190302662574	-3.53895046367553	-1.90927914931289
H	0.35358389159798	-3.44111617124339	-2.37491995843931
O	4.06203166513061	-0.69059139902534	-2.65299944428543
O	4.38594972973472	0.31033765591962	-1.99400174513017

Table S13. Optimized coordinates of intermediate ^{4}**I1**

Cu	-0.15195238726899	-0.19979769165827	-0.92800727512246
O	1.80355117925599	-0.54570746292801	-0.83299707004425
O	0.63015286959671	1.85946059470794	-0.26386065338331
N	-2.22497345176867	-0.00660355171883	-0.87515417709297
O	-0.36261104289687	0.17913089213011	-2.80070320419082
N	-0.49626298845515	-0.51733581173632	1.12854265175696
O	4.57515150987412	1.24592066709899	0.45836805015941
C	1.87701775587324	1.73095777778011	-0.21733968465525
C	2.49491108558049	0.47230437912993	-0.52151135829549
C	0.36043784961692	-0.37694847841349	2.13558697812245
H	1.39296304171029	-0.13906154099005	1.86471952950549
C	2.77084960899634	2.82377105070868	0.19997176104485
O	-1.91234329947507	0.53621635266183	-4.37897046108172
C	-1.56387740578629	0.22038623774373	-3.26118480245438
C	4.09800093422484	2.52506312738759	0.52975464580789
C	-2.47281103203410	1.39870283992845	-0.46109143810025

H	-1.98333906718122	2.02864579616558	-1.21757934247086
H	-1.92680640070504	1.58542875050725	0.47387681084456
C	4.00992032115664	0.37354695877167	-0.45665484335377
C	-1.77916696333577	-0.81011107290993	1.36901536341719
C	2.31684594379354	4.14021398433453	0.34259697533441
H	1.27551746452706	4.34867014659199	0.08747375231896
C	-2.61310443949270	-1.02254861262495	0.11337162660749
H	-3.68911003057655	-0.98719222430974	0.35617704429717
C	5.37566603878205	-3.63360208760996	0.34208743908389
H	5.71831937605201	-4.65188614711544	0.54381537393838
C	-1.37077574543534	-0.82917230873246	3.72518394578699
H	-1.71816857538873	-0.94858801123353	4.75421712155531
C	4.50525709355569	-1.02961876722806	-0.17950397954436
C	-2.26149409746852	-0.97670890625176	2.66212279086391
H	-3.31367360309930	-1.21600213495253	2.83034285110779
C	4.96144788001499	3.51195237398729	0.99870815842089
H	5.98921292255532	3.23946954557262	1.24516512319727
C	-3.92930563838779	1.77104519602602	-0.30935255448354
C	4.49360554124826	4.81574962842482	1.12998104704296
H	5.17049909694431	5.59504670570829	1.48890744587121
C	-0.03808096921399	-0.52722980455126	3.46138106876713
H	0.68785270961391	-0.40453113531886	4.26649237222878
C	3.17210402443400	5.13463646981092	0.79955312232264
H	2.81488868503435	6.16177402861005	0.90180122710775
C	5.17047970675181	-1.32181616341398	1.01183609384415
H	5.35300136377274	-0.52327314909414	1.73228734684719
C	4.27434394510651	-2.04660821497421	-1.11256730185768
H	3.74985465084319	-1.81429115220111	-2.04039139688854
C	4.71329465609794	-3.34082228520497	-0.85080917166214
H	4.53653044692000	-4.12905327372428	-1.58702429223670
C	-4.65248584527090	2.29353177841920	-1.38881277209688
H	-4.14676626672429	2.46253189634940	-2.34450483106085
C	5.60285589979014	-2.62224850519709	1.27197344818675
H	6.12617067480704	-2.84179407022659	2.20608407529707
C	-4.58426315710123	1.60111528124466	0.91647326600764
H	-4.02011031717674	1.23591508064077	1.78079859856558
C	-6.00305970101852	2.60990097327824	-1.25290835820444
H	-6.55214085854740	3.01698255518804	-2.10539602137108
C	-5.93483240365361	1.91640349640624	1.05599691595807
H	-6.42947954218883	1.78298150975209	2.02148842582338
C	-6.64862372793597	2.41606397071495	-0.03237628540643
H	-7.70680524724930	2.66727554731855	0.07435775818423
C	-2.64933190457427	-0.25062593225660	-2.26271687069186
H	-3.61304833754015	0.22328046016174	-2.49321324612691
H	-2.77765223284385	-1.32819893504314	-2.42884506429177
N	-1.01783762513466	-2.51837140319551	-0.90235514407931
C	-2.24940435953533	-2.41346955872295	-0.40324262213892
C	-2.66524936139628	-4.73663945172829	-0.78126134198869
H	-3.31875463716157	-5.61129401469819	-0.73732193809147
C	-1.38036377133399	-4.83966948376309	-1.30417062748662
H	-0.99512768338761	-5.78947108653939	-1.67931402404961
C	-3.11563306197177	-3.49890242892860	-0.31983090223354
H	-4.12243228403176	-3.37713499696450	0.08568075187367
C	-0.58715334315702	-3.69173288833872	-1.34692829160304
H	0.42975644764286	-3.71032397058559	-1.75119851745812
O	3.94206659958299	0.45283332158274	-2.78862389738882
O	4.58588348314887	0.85148034023936	-1.74846619441261

Table S14. Optimized coordinates of the minimum energy crossing point (MECP)

Cu	-0.15172470081382	-0.24348763029064	-0.77835526525677
O	1.80236877488369	-0.60062023292565	-0.65333535467151
O	0.61998449681023	1.79746714555692	-0.06317658641480
N	-2.22469425770299	-0.03193033920139	-0.80793893380153
O	-0.28446964706686	0.17542021419202	-2.65113033403017
N	-0.58158367328641	-0.58173051729661	1.25477582860745
O	4.61600579760510	1.26291515195154	0.42098194017850
C	1.87016863671960	1.68857229825531	-0.08057185880794
C	2.49151017571642	0.43570557574429	-0.40262293092472
C	0.23529935275969	-0.44319072823575	2.29416877368081
H	1.27946047926646	-0.21587455534436	2.06157718040990
C	2.76651964253804	2.80186233475169	0.27027810287963
O	-1.76973954289901	0.58693737915500	-4.27761641630808
C	-1.46666197133793	0.23579873199455	-3.15709230377380
C	4.11791159843854	2.53237820559908	0.51715348748448
C	-2.47146441831685	1.37283450533899	-0.39131944231142
H	-1.91811137179357	2.00219273837473	-1.10284940062269
H	-1.98634208252782	1.53501805593349	0.58103659584618
C	4.00925144257735	0.37939991890258	-0.45591084515264
C	-1.87705452131289	-0.85604589179925	1.44368299247756
C	2.29589444274469	4.11046707833107	0.43009683198704
H	1.23692173007588	4.29656117203869	0.23837762828028
C	-2.66244403758738	-1.05267366642086	0.15446048512729
H	-3.74719881504854	-1.00985639994519	0.35380945285826
C	5.58854402421339	-3.58161862703446	0.15171315807956
H	5.98884297572277	-4.58756544663704	0.30262628712635
C	-1.56479196515024	-0.86413436342542	3.81433625542190
H	-1.95651519371374	-0.96992944666031	4.82880906482851
C	4.57291101766951	-1.00814589549734	-0.24188320946686
C	-2.41340450348892	-1.00856656847440	2.71678961894884
H	-3.47487410423496	-1.23128895149324	2.84462941700469
C	4.98928307818901	3.54034873533552	0.92159173709542
H	6.03650954280373	3.29148333750190	1.10210331133122
C	-3.92554924163536	1.77815404817945	-0.33487474020769
C	4.50385183792450	4.83549896099198	1.07325676535625
H	5.18635474443450	5.63127701445550	1.38165389080804
C	-0.21896457054072	-0.57927235388811	3.60369872199846
H	0.47394107378138	-0.45596376733104	4.43729171776811
C	3.15790565666044	5.12519220516915	0.82512675925741
H	2.78691559735333	6.14584206727283	0.94194108673651
C	5.36337550630538	-1.28728612436593	0.87331724881707
H	5.58541673666384	-0.49123412463650	1.58524899433046
C	4.28833197633659	-2.02310438535097	-1.16241195636704
H	3.66745124431975	-1.79992716456186	-2.03113466660762
C	4.79963494229881	-3.30195069115176	-0.96480820154633
H	4.58077856625089	-4.08786546404055	-1.69212657769939
C	-4.55243955159816	2.34227551360973	-1.45288511557544
H	-3.97282016397121	2.51158267041157	-2.36570264680245
C	5.86891833411145	-2.57246524848308	1.06926189692084
H	6.49121407555583	-2.78216304681669	1.94295041985215
C	-4.67329733043173	1.60271682717054	0.83549556528771
H	-4.18684660847279	1.20512978718468	1.73219902142773
C	-5.89980798299053	2.69499883398150	-1.41005449192729
H	-6.37219010313814	3.13419821083587	-2.29197226424653
C	-6.02108919753157	1.95528894122470	0.88186147685163
H	-6.58875646233811	1.82007981313978	1.80596959636008
C	-6.63858983267915	2.49670995290365	-0.24442570598536

H	-7.69429572900253	2.77678446255046	-0.20961322626760
C	-2.59114271246554	-0.25717042212454	-2.21459764680625
H	-3.54659345908352	0.21604377610489	-2.47843117629542
H	-2.70542425407260	-1.33265342836011	-2.40169829389381
N	-1.04476932035018	-2.54770568870845	-0.82643941900441
C	-2.28948843993158	-2.44150999719949	-0.36141312130411
C	-2.70549450328769	-4.75786238957839	-0.77835071273494
H	-3.36348286477710	-5.63010356663544	-0.76270124492135
C	-1.40765417972652	-4.86148665895273	-1.26805373549302
H	-1.01682269048809	-5.80812596339384	-1.64546480531874
C	-3.16247500281222	-3.52337716965758	-0.31448391569187
H	-4.17942158275685	-3.40151597474774	0.06459677303841
C	-0.60752657019289	-3.71771621592280	-1.27329745255368
H	0.42048657134939	-3.73702939409703	-1.64824808720970
O	3.75809738953570	0.47722668962073	-2.77588693640510
O	4.46595069894092	0.88978714692210	-1.78399006205666

Table S15. Optimized coordinates of transition state ^{2}**TS2**

Cu	-0.17217596831368	0.04605732907498	-0.95867338330394
O	1.77505963099799	-0.51717977790720	-1.05090553484997
O	0.91124493788437	2.01633282138591	-0.51164827670362
N	-2.25465032101697	0.03555763977466	-0.90227120990496
O	-0.43240654554917	0.10359692026730	-2.86165475590286
N	-0.59364246429561	0.30468512897976	1.21605223813299
O	4.52022605317588	0.53505069026344	0.69315893976432
C	2.09943467130348	1.68769652816647	-0.29919926999535
C	2.57296925518409	0.37928253235357	-0.71710791587904
C	0.11168962777794	0.93813127943489	2.15178580485781
H	1.13603869633882	1.21344790243567	1.89674584075129
C	2.98687122003764	2.41242267807289	0.62560830699350
O	-2.03524279881239	-0.03399128144664	-4.42315519035404
C	-1.62873106596744	-0.12616545605000	-3.28445568686776
C	4.12609687322770	1.76529635680321	1.13744211364289
C	-2.73543969923563	1.44354637564014	-0.87066875497184
H	-2.34099498272358	1.91971098924401	-1.77945296609850
H	-2.25664384457998	1.95146029796550	-0.02269022693463
C	4.08843126047714	0.16746320083017	-0.58595221777420
C	-1.85924886820303	-0.04076858014989	1.47660370619506
C	2.59048457506816	3.63256863927411	1.18590677629155
H	1.69111522259114	4.09921083989513	0.77750978332547
C	-2.55949595423750	-0.73101276588249	0.31688834185422
H	-3.64417431537163	-0.79232531213900	0.50904833545577
C	5.56190330629830	-3.70874554084827	-1.70571810541900
H	5.96575437283606	-4.67331971334985	-2.02667752193442
C	-1.73383264615704	0.89227370552696	3.67599230792865
H	-2.19125728680933	1.14318840992057	4.63660426154431
C	4.57836176874352	-1.21673437980988	-0.92321289770676
C	-2.46348924712252	0.20917415776045	2.70463003918824
H	-3.49421760065058	-0.10405046873056	2.88522166311001
C	4.84507117754587	2.32698364407359	2.19241020632144
H	5.71344849828535	1.79056354723236	2.58005222394238
C	-4.23938938640096	1.58568009273685	-0.79633952423214
C	4.42719232971396	3.53450223911221	2.74161442310931
H	4.99208633094584	3.97163779908376	3.56876621448464
C	-0.42420880576418	1.26589165352742	3.39504873946875
H	0.18328643226704	1.81081812473842	4.11909523031954

C	3.29643735051786	4.19187814440330	2.24157353472166
H	2.95992863224946	5.12991761132464	2.69007671902042
C	5.48287696310946	-1.89625451686953	-0.10856044956628
H	5.80922409023345	-1.44272569308872	0.82833085301133
C	4.15269959368652	-1.79175401638666	-2.12554877939178
H	3.44883429673821	-1.25186598986379	-2.76094117367537
C	4.63450936189665	-3.03949602026855	-2.50674863043287
H	4.28201893028119	-3.48977224188571	-3.43853301800116
C	-5.01505836901596	1.63552361420810	-1.96117738774205
H	-4.52233715491085	1.64898969081213	-2.93809753632651
C	5.98314708093011	-3.13627253842680	-0.50770278131248
H	6.70339473815574	-3.65894955287028	0.12664586408170
C	-4.88690535714487	1.63433900118489	0.44408387106692
H	-4.28780740052209	1.65936568887073	1.35776389500667
C	-6.40581208652247	1.67118035554000	-1.88282052844075
H	-6.99975997915290	1.70132161930287	-2.79893829537183
C	-6.27700964336166	1.66912308477977	0.52596157588763
H	-6.77052418464693	1.70438679825201	1.50086439693476
C	-7.03855875742034	1.67412945174459	-0.64092574303650
H	-8.12953769157051	1.69989960084660	-0.57980078866789
C	-2.59567709162241	-0.60900406176677	-2.18205390214378
H	-3.63817332527795	-0.42331667096488	-2.47503574449562
H	-2.45721921699710	-1.69508244020575	-2.09606843972857
N	-0.78325587152070	-2.22197539733374	-0.34793375861670
C	-1.97937169775951	-2.13482973351947	0.22897373287810
C	-1.99849991085046	-4.47916570425923	0.68704527688600
H	-2.47947563676349	-5.36605090302907	1.10741297252362
C	-0.76461938353485	-4.57074772175865	0.05087136971502
H	-0.25206559023567	-5.52737698422445	-0.06607453363080
C	-2.62330705960426	-3.23649811607909	0.78077891902866
H	-3.59473139703324	-3.12142661261491	1.26721128153180
C	-0.18409857111891	-3.40258945552414	-0.44356359958802
H	0.79426853700382	-3.40198882713565	-0.93352333354046
O	3.67448990156911	1.49011316990691	-2.33385805610575
O	4.64445146072655	1.14903711963868	-1.47608984032827

Table S16. Optimized coordinates of intermediate ^{2}**I2**

Cu	-0.15312883844894	-0.06202747389305	-0.99691282698326
O	1.72191826536025	-0.44103559054363	-1.04459167896955
O	0.87899775685899	2.10036198225399	-0.44920126759073
N	-2.22626890800114	0.03167671145928	-0.86237463591335
O	-0.52987621415652	0.31490872321128	-2.87496041336078
N	-0.56050868840771	0.21420973207315	1.27419322615754
O	4.64703935677612	0.75394141715379	0.41086866669845
C	2.04680994265043	1.78239544172634	-0.30570058986087
C	2.57479314608040	0.53870362366972	-1.02791072654797
C	0.15641379058304	0.79332804028365	2.23236833495954
H	1.19451851163288	1.03336266797818	1.99240489111874
C	2.94777111279021	2.46853627817091	0.63056133272099
O	-2.20580983858752	0.23428995060523	-4.36772726174189
C	-1.72699238484680	0.05651383317500	-3.26458758742870
C	4.16157983898313	1.86604346366257	0.99457243731046
C	-2.66529160627991	1.45091360551122	-0.78520629470063
H	-2.20459566437861	1.95822285773752	-1.64341415731178
H	-2.22421770585607	1.90211989408042	0.11262096691351

C	4.08210629745377	0.25785184198364	-0.76785898033574
C	-1.83558423468531	-0.10354441377174	1.51604995779240
C	2.50567380510011	3.60827385194207	1.32031125822777
H	1.55386353966343	4.04167575521722	1.00346145572491
C	-2.53980003706983	-0.75848650690527	0.33572192561237
H	-3.62521109104556	-0.82076838760366	0.52603950479755
C	5.48803100726842	-3.74390787706958	-1.48354409134542
H	5.87722982341455	-4.74175160598419	-1.70701168476194
C	-1.70244051740409	0.76761561032398	3.74027713130315
H	-2.16052473962655	1.00533739737986	4.70389079416425
C	4.54961530184018	-1.16486282843172	-0.95834718801570
C	-2.44515273071787	0.13430930681009	2.74458390123419
H	-3.48601317599607	-0.15343432240302	2.90882595520941
C	4.90114751073044	2.38597690818956	2.06527426347764
H	5.82509276494510	1.87999083145968	2.35285135130506
C	-4.16567462091680	1.62720873041231	-0.79356637807213
C	4.43806492397152	3.50434995165543	2.74329175457745
H	5.02246459574710	3.90282490116693	3.57652358149159
C	-0.37752496520739	1.10495436069742	3.48185247376769
H	0.24007524867140	1.60661934831848	4.22828523765135
C	3.23845153134770	4.13151192507991	2.37134140530867
H	2.88123117053373	5.00942095253052	2.91355008079763
C	5.42860514893619	-1.78438953354343	-0.07006691142750
H	5.76231832520961	-1.24948636252439	0.81967189622374
C	4.12400868340705	-1.84787672733189	-2.10421112494011
H	3.43219233848727	-1.35667402391060	-2.79010421633728
C	4.58417232183688	-3.13566452420813	-2.35816350130393
H	4.23941911596535	-3.66463175336614	-3.25028302700687
C	-4.86391333989451	1.69988297126046	-2.00660163321811
H	-4.30690854622465	1.69757714047388	-2.94901583516776
C	5.90290619316584	-3.07108356725892	-0.33653772236593
H	6.60389453764025	-3.54426337173575	0.35562599563987
C	-4.88642546664020	1.67070761706974	0.40525666439014
H	-4.34489421575859	1.67061939536714	1.35517142178882
C	-6.25633450667014	1.74968781864214	-2.01553305917160
H	-6.79274679730501	1.78938046765772	-2.96643906835687
C	-6.27908415821828	1.72612418133132	0.39860370698005
H	-6.83209050331300	1.75687466133627	1.34080114290601
C	-6.96508257331071	1.75040769112002	-0.81439091581468
H	-8.05729626305560	1.78652723062181	-0.82431668824533
C	-2.60891015423576	-0.56114286593994	-2.15458884155897
H	-3.67457617159999	-0.42050786477191	-2.38047760546711
H	-2.40414565410408	-1.64013179920198	-2.13601605449641
N	-0.77060594870430	-2.21754612511182	-0.40174340497364
C	-1.95322838408668	-2.15681632722088	0.20894180895273
C	-1.91116215149317	-4.50510253373303	0.64515517475296
H	-2.36473729816559	-5.40510235382441	1.06848697610019
C	-0.68901554676737	-4.56532840469559	-0.01850076609403
H	-0.15704782041999	-5.50931601126030	-0.15044502833149
C	-2.56016219560734	-3.27667106491521	0.76548286361475
H	-3.52021736821989	-3.18616263264223	1.27841864383339
C	-0.14389231413551	-3.38229926998494	-0.51845133988867
H	0.82536494386043	-3.35024621453308	-1.02516423166504
O	3.02474473886577	1.09891119854918	-2.33375023248185
O	4.40124774978553	1.08212206897141	-1.87856321225133

Table S17. Optimized coordinates of transition state ^{2}**TS3**

Cu	-0.19238948453682	0.17621586773731	-0.66024275158889
O	1.75034055541677	-0.63750118874317	-0.66022505511530
O	1.00145499169723	1.99311504936719	-0.32322883771986
N	-2.27969267563455	0.06221403577399	-0.77229275875660
O	-0.29940614176828	0.16170510753265	-2.57426618573068
N	-0.75491806181088	0.48193509021403	1.38984422355438
O	4.68564703701835	0.48279005194177	0.59084484187176
C	2.20001530854703	1.65937178420707	-0.22710044272062
C	2.58344632973077	0.26598813475786	-0.57839104074677
C	-0.10213489686193	1.14466641206809	2.34310634237620
H	0.87906366150729	1.54116433184144	2.07338765332358
C	3.15455918434628	2.36159377206895	0.66879293300845
O	-1.77815941028571	-0.00659472865709	-4.25179610530495
C	-1.45423896064384	-0.09814102109924	-3.08671068700533
C	4.30515100410698	1.68411395720061	1.10643293002732
C	-2.80235469000535	1.45174655339777	-0.81892609113418
H	-2.33132686401674	1.92718622628452	-1.69132901169721
H	-2.43518737478976	1.99183635793443	0.06437879294047
C	4.11106133590426	0.12328979827009	-0.64862362843699
C	-1.99006135266280	0.02230285407061	1.62605129756959
C	2.79762353638345	3.57096217295834	1.26710902010889
H	1.89043177620531	4.05936417188728	0.90323009033453
C	-2.63304183953562	-0.68738816968942	0.44393869746114
H	-3.72392983405999	-0.75886719873452	0.59216537948409
C	5.60288033067075	-3.63953474833129	-2.07164382271770
H	6.00693918273440	-4.57202823554323	-2.47580699409490
C	-1.92457314337992	0.85297378890013	3.86861501388347
H	-2.39059416677528	1.00664060347198	4.84510496693560
C	4.62827696932505	-1.22024402753033	-1.08446411145973
C	-2.60759287429793	0.17035026321351	2.86308793774433
H	-3.61070585200761	-0.22993579152993	3.02613407529709
C	5.07272887690868	2.21259078332386	2.14658791979304
H	5.95253423320812	1.66107267181736	2.48339457494527
C	-4.30688854074962	1.55191496411470	-0.90965242144880
C	4.68967225472460	3.40930692497875	2.74526144478974
H	5.29070825414001	3.81385981650316	3.56360583244489
C	-0.65443418496988	1.35603504607513	3.60428950812597
H	-0.09415031056322	1.91336836127070	4.35580215700406
C	3.55221840983305	4.09714246980004	2.30902216038518
H	3.24875082416152	5.02905107523974	2.79199447016185
C	5.63731829097877	-1.89437188319487	-0.40031993627906
H	6.04621576047931	-1.46108135809645	0.51351895980811
C	4.08629559982035	-1.76851995822833	-2.25260608739343
H	3.29327091506710	-1.23410124638771	-2.78116399874472
C	4.56765677085695	-2.97922465883994	-2.73811604059745
H	4.13316564372342	-3.40915043201728	-3.64440728473414
C	-4.94571768120462	1.58381037544161	-2.15592194599279
H	-4.34346113515614	1.59279643544854	-3.06957999593506
C	6.13228953832609	-3.09874898438474	-0.90232722580357
H	6.93464506756166	-3.61800339060253	-0.37244477596052
C	-5.08822828502471	1.59146809417380	0.25151424390407
H	-4.59702982926725	1.62445210162474	1.22886145130426
C	-6.33716232284716	1.60364822491863	-2.23621813726790
H	-6.82743254204501	1.62273477916099	-3.21254973937377
C	-6.47935810995773	1.60975963993643	0.17372519681650
H	-7.07796317792306	1.63843202458086	1.08738248593120
C	-7.10474108273279	1.60591701716558	-1.07220824129167

H	-8.19547662288061	1.62077257704310	-1.13841454036471
C	-2.48025531023688	-0.62136778912697	-2.05792575736432
H	-3.50519636933327	-0.50865695187086	-2.43740345848893
H	-2.27455003790901	-1.69345963603682	-1.93771046098116
N	-0.74806467775528	-2.10930826753826	0.02729306297647
C	-2.02798714708167	-2.08317462711379	0.39106164424162
C	-2.05896775606064	-4.45499212703510	0.66204918592705
H	-2.58246877956518	-5.38056974807194	0.91359626932089
C	-0.72401031053990	-4.47734693662292	0.27158645638755
H	-0.17059431039889	-5.41463779173963	0.19213055318997
C	-2.72961982043215	-3.23290064621532	0.73198792364708
H	-3.77438170494103	-3.17308877782862	1.04558933137923
C	-0.10048748360044	-3.26512943472236	-0.03321822818775
H	0.94505535553052	-3.20600980456360	-0.35379498040120
O	3.00735276752397	1.47925225961493	-1.93211713112705
O	4.35216538981105	1.12516753276403	-1.59933111643720

Table S18. Optimized coordinates of intermediate ^{2}**I3**

Cu	-0.24819352460616	0.44021677297269	-0.42427025638325
O	2.05155756423586	-0.92376874278098	-0.04574691540188
O	1.10704544735019	1.79676688779716	-0.17902480790952
N	-2.34173540835298	0.15287035776331	-0.80819511869464
O	0.00503868874400	-0.08872220625242	-2.22880795029045
N	-1.01832954300425	0.83826857923516	1.43186559867535
O	4.94671139357828	0.37335918417270	0.41651270828451
C	2.38213861383208	1.49133842348894	-0.27013182236321
C	2.74498344030301	0.01316347930179	-0.31369877390097
C	-0.41285890395514	1.53580808945390	2.38981512434918
H	0.57064094799042	1.93059704979040	2.11998747168387
C	3.26688889449871	2.06265932736549	0.84590795419646
O	-0.94312479275053	-1.33734129070368	-3.81755734599174
C	-0.97653135631487	-0.71610104226101	-2.77747744496816
C	4.48780276714880	1.44222228382507	1.14211425766176
C	-2.92613266886740	1.49706707795039	-1.02401746139134
H	-2.46332069928937	1.89163935858217	-1.93960268993514
H	-2.60237277350237	2.15783320933450	-0.20668641190499
C	4.20430466019182	0.06631823801511	-0.75909853473495
C	-2.23504104763901	0.31753136931243	1.62152556055442
C	2.85508470814381	3.15926334569567	1.59557204119646
H	1.91407064398837	3.63413971386294	1.30609287588178
C	-2.75618357852848	-0.49857091473032	0.44339896038822
H	-3.85015597187725	-0.61705914775695	0.52250891190546
C	5.72535913981057	-3.42638327970683	-2.72738349652027
H	6.11396973912772	-4.30631717571204	-3.24687664070117
C	-2.27732106226265	1.18987979693509	3.84925287705519
H	-2.77925472208442	1.33318083904914	4.80913477082298
C	4.76115876509016	-1.15958468756738	-1.42442311972873
C	-2.90027063630726	0.46195335943334	2.83465883610083
H	-3.88651195264093	0.01525935363160	2.97958486911913
C	5.25699851626116	1.88714076840590	2.21676056481138
H	6.19242078950191	1.37334269898849	2.44714449010861
C	-4.43590088984019	1.52742758526175	-1.12790003615367
C	4.81580525066733	2.97048507346840	2.97661030154412
H	5.42452831589447	3.32095252569188	3.81367750920256
C	-1.01840691170258	1.74177579021163	3.62637875004354
H	-0.50698020435426	2.32218965051921	4.39501606004142

C	3.61868398982693	3.61893903870092	2.66592273937203
H	3.28035181603838	4.47393240543843	3.25584135853672
C	5.89530988003139	-1.80906651984207	-0.94061644733556
H	6.39708181799934	-1.42092768973652	-0.05357387884480
C	4.09844141290335	-1.64938459771863	-2.55418869397076
H	3.20441302029481	-1.14005329412280	-2.92505289761146
C	4.57988136242541	-2.78391660226453	-3.20092217197946
H	4.05505182124661	-3.17206439670852	-4.07725256976325
C	-5.08280947324982	1.47839251324373	-2.36818806685364
H	-4.49202198588496	1.47146569946703	-3.28836119916017
C	6.37595318330272	-2.94317523991316	-1.59409666036434
H	7.26286240680021	-3.45299590409574	-1.20922349306125
C	-5.21933298214952	1.59384319671446	0.03233774585270
H	-4.72932206449111	1.69417590193559	1.00540410367582
C	-6.47498193935600	1.45853661711192	-2.44488947618175
H	-6.96779574548837	1.42353444287184	-3.41945341340010
C	-6.60988931231448	1.55831248772079	-0.03880817366191
H	-7.20513075680991	1.60345896406158	0.87644833946403
C	-7.24002075832868	1.48591272464201	-1.28050834605543
H	-8.33084493759257	1.46431715266382	-1.34252081908805
C	-2.34380903322004	-0.67092450233458	-2.03363575222765
H	-3.09451895622627	-0.30573923700832	-2.74780749838231
H	-2.63181402915785	-1.70690145321676	-1.81114408596503
N	-0.80733402737234	-1.87291338427858	0.19772285641818
C	-2.08881487762823	-1.86140489116792	0.55438736111709
C	-2.04223326038239	-4.19324572059206	1.06154104826313
H	-2.53025569404901	-5.10403354382143	1.41727310514821
C	-0.71856441740778	-4.21377269738190	0.63384574806321
H	-0.14062168346536	-5.13927788419072	0.61970656350696
C	-2.74940551726108	-2.99167341659615	1.02101257009907
H	-3.79290827073824	-2.93280759362525	1.33916148667113
C	-0.13237768018987	-3.01735016520207	0.21572761450537
H	0.90648909258873	-2.95939509550475	-0.12129403903988
O	2.94972766518207	1.86831660800566	-1.55563760943507
O	4.21133929564538	1.15661237470004	-1.64286401496493

Table S19. Optimized coordinates of transition state ^{2}**TS4**

Cu	-0.31724842109239	0.38549631843977	0.27197061719522
O	2.50690011428000	-1.06357924282924	0.38606937763923
O	1.19368502831497	1.25841589426338	1.02066588237520
N	-2.30268730357355	0.10255869589241	-0.42488503885657
O	0.19302569400926	-0.12605559407136	-1.50225075050100
N	-1.35700246674054	0.73862524533937	2.00464523231405
O	5.06000535660286	0.83671963166423	-0.36175418846039
C	2.27454366160493	1.47527192815660	0.26626374115192
C	2.87871727084115	-0.06171500152421	-0.07400057732686
C	-0.86272539333964	1.32468215085451	3.09193776446147
H	0.14421012312117	1.73778995274947	2.97102824243413
C	3.46931413615575	2.10634309236381	0.99313191003935
O	-0.59186511212031	-0.92149022696892	-3.43783969185306
C	-0.72818903262945	-0.55996189680945	-2.28779248353510
C	4.77173255374037	1.79405577724001	0.57149809629404
C	-2.83683199299013	1.46068517180192	-0.68775685018568
H	-2.13573958323039	1.93651886508932	-1.39004492287905
H	-2.78923275300422	2.03784199230047	0.24648284636022
C	4.00492731921676	0.27964883017625	-1.16131360177332

C	-2.56578002914270	0.17112530743718	2.00747891259663
C	3.28805830956247	3.07020770031258	1.98312423589771
H	2.26729299655930	3.31066786489102	2.29229356048623
C	-2.89684086195989	-0.59369503023494	0.72858203049056
H	-3.98721431052638	-0.73267975021035	0.62843812628347
C	5.32671705076804	-3.41803878570918	-2.91485151222373
H	5.67759948590557	-4.34117507552084	-3.38470092464674
C	-2.84803581024880	0.77300957104455	4.30593745293626
H	-3.43817928979820	0.76958456106844	5.22523314000872
C	4.47617411917181	-1.03273923521531	-1.76597723200708
C	-3.35532461611616	0.17293622143479	3.15235157776932
H	-4.33746573097172	-0.30371466349785	3.14791457618367
C	5.86632065632662	2.43899426731668	1.15128934220928
H	6.86304541523908	2.16653264223635	0.79558084095323
C	-4.23866644616927	1.50342100289381	-1.25160935935397
C	5.66619018615362	3.40149199694952	2.13871405425428
H	6.52637752723948	3.90891514586694	2.58338491556424
C	-1.58823641676855	1.36561642580054	4.27897766622153
H	-1.16258658188847	1.84790595263808	5.16053662299825
C	4.37498815304269	3.72434863477750	2.55955390183073
H	4.21318822575165	4.48379635361389	3.32764714340762
C	5.62230203817445	-1.66202578919358	-1.28284992069710
H	6.18231152653026	-1.20278453857422	-0.46773525912264
C	3.72691720416291	-1.60532023827363	-2.79550855000833
H	2.81284573916332	-1.11234371510039	-3.13837673240194
C	4.16211691455986	-2.79767860413442	-3.37080159276387
H	3.58453845341161	-3.24711528057926	-4.18198507854990
C	-4.44610840047812	1.53280090245117	-2.63627724616253
H	-3.58477602469269	1.57172125211097	-3.30918285690170
C	6.04535203188238	-2.85814698570230	-1.85991214310396
H	6.94253746260263	-3.35247932571441	-1.47766649302497
C	-5.35579770375875	1.50760677811117	-0.40822827588809
H	-5.21101521395953	1.54095290087930	0.67721118285315
C	-5.73453533697367	1.52176757009306	-3.16563129506182
H	-5.87783536029311	1.53996318587351	-4.24860959577220
C	-6.64707122742918	1.49867704651159	-0.93466268877917
H	-7.50907553976331	1.50489123321515	-0.26398849409148
C	-6.83867271662695	1.49753434977241	-2.31571768839176
H	-7.84821869616206	1.49152022010040	-2.73437257068625
C	-2.14673942817786	-0.67900024358967	-1.66657404426624
H	-2.88568984568142	-0.39081133276227	-2.42376945059558
H	-2.32328723833506	-1.74501464890078	-1.47143817371061
N	-0.88144302278830	-1.89714545776009	0.84046695552473
C	-2.21324256648138	-1.95152927355451	0.87225144391022
C	-2.17481367353655	-4.33064737419553	1.06408147251332
H	-2.68933091709991	-5.29044525681628	1.15239226642613
C	-0.78678178659971	-4.27194196470715	0.99485781275218
H	-0.17938834294444	-5.17779226459474	1.01992925598601
C	-2.91043451967939	-3.14546876754208	1.00694399472874
H	-4.00187122743898	-3.14711311144703	1.04434646616208
C	-0.17535237421046	-3.02017324354014	0.88956660826174
H	0.91079085570507	-2.90208178706870	0.82451980052654
O	2.11629106009048	1.97610033365563	-0.93594380061352
O	3.44929764553102	1.08144073895508	-2.00131498580521

Table S20. Optimized coordinates of products (^{2}**P**)

Cu	-0.00366370147796	-0.60426085834486	0.20069936103943
O	2.41815343672317	-3.41067501445924	0.30018671100144
O	1.78411628002208	-0.41438224771043	0.98162155825211
N	-1.95598193351898	-0.44653163389173	-0.49938367064924
O	0.36879755897622	-1.22921379561780	-1.57917851694081
N	-0.91005982220766	0.29406834599679	1.89637344723809
O	3.60710477134863	3.06813535524412	-0.58574256029300
C	2.07555629948509	0.77925348268458	0.61599910194676
C	3.38331379700307	-2.82293540459269	0.27727082693660
C	-0.33482903016437	0.98898442973596	2.87301026247206
H	0.75758157171658	0.95800512431930	2.90354039428080
C	3.37457072684712	1.32915264640941	1.12754121622736
O	-0.61391185848280	-1.87017590896432	-3.47805400987846
C	-0.64432601995665	-1.52277773244092	-2.31438637502772
C	4.02502741184787	2.42716638713958	0.54080562707768
C	-2.12038346322090	0.94009901465969	-1.02485312032591
H	-1.26480351534616	1.13036682975776	-1.68910638810225
H	-2.01200849611146	1.64048128457000	-0.18548681665144
C	3.11676297648664	2.47834554707079	-1.72642162388066
C	-2.24390594132187	0.23433090217142	1.80583898928062
C	3.94487009454400	0.74784141305986	2.26665942405963
H	3.44286050669654	-0.12649015608853	2.68674106450790
C	-2.72259401470282	-0.72747799829078	0.72317026423194
H	-3.81298283196054	-0.64335376457830	0.57752056536196
C	4.32754845189450	-1.47763712893479	-2.85583330895428
H	4.63146556574644	-2.47938317427020	-3.17342490038323
C	-2.47255864357113	1.67263286753736	3.70282514424369
H	-3.09423085977199	2.23045115520801	4.40629115998385
C	3.57237252979813	1.09030443516678	-2.05948681174461
C	-3.06827815662096	0.91645428810567	2.69086976893691
H	-4.15482578200709	0.85980762505525	2.59128848674063
C	5.17677380218314	2.95301713590866	1.13198886093560
H	5.65344369088317	3.80569572153528	0.64483965384895
C	-3.42388693565755	1.15936770904617	-1.75829329192504
C	5.70503363804729	2.38206104879018	2.28320238076580
H	6.60094790499359	2.81312917110327	2.73718100936945
C	-1.08531977162222	1.70424027374745	3.80475105804824
H	-0.58109598938279	2.27161550716175	4.58790054293764
C	5.09694527553561	1.26080662782251	2.84980217360642
H	5.52558448664529	0.78326784889618	3.73388172992952
C	4.79637988817853	0.55461221283956	-1.64030822047277
H	5.47021251844182	1.13635870777250	-1.00985016333190
C	2.72977494546858	0.32633546918230	-2.87110018061870
H	1.76502984181458	0.73659882844022	-3.17314324297983
C	3.10350746735200	-0.95412123881281	-3.26714592977902
H	2.40996913706122	-1.54830822649483	-3.86502551805518
C	-3.46250375559097	1.11863496768055	-3.15600588591426
H	-2.52907944176986	1.00407339790768	-3.71572902129579
C	5.16820840971088	-0.72711710420612	-2.03313364075617
H	6.11208558843531	-1.14843567701891	-1.67733055009641
C	-4.62597096412539	1.33166752064199	-1.06174065826961
H	-4.60540308082806	1.43993107686741	0.02714285911440
C	-4.67709239697525	1.18634235989587	-3.83557113402334
H	-4.68989830972353	1.13876185444932	-4.92725218778341
C	-5.84421404049504	1.37885944440784	-1.73626159103310
H	-6.77393183881646	1.49518045047069	-1.17415164938027
C	-5.87240815729431	1.29325220812180	-3.12746427661927

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H   -6.82383142198801       1.32395731247186      -3.66419344465667
C   -2.01393497600235      -1.43998678341603      -1.58931981817782
H   -2.80607852505309      -1.21003920773481      -2.31570910549225
H   -2.22549329220452      -2.43341751168423      -1.17284938166617
N   -1.14448563317018      -2.53930464217122       1.06377012055996
C   -2.38080610229051      -2.10531882985871       1.29839749588043
C   -2.81236858660578      -3.95737428435374       2.75064189512662
H   -3.47027506307691      -4.50935035917235       3.42591148361791
C   -1.52765559534671      -4.41960110069072       2.47916812882602
H   -1.14397480371069      -5.33524952973112       2.93321228429219
C   -3.25792384766055      -2.78616763605010       2.14071043314345
H   -4.25745547898500      -2.39284346849633       2.34378218542478
C   -0.72890491390698      -3.67837182448353       1.61034012599495
H   0.27951793520346      -3.99865877186657       1.33279495221060
O   1.31082037093506       1.47788875825260      -0.05866251984013
O   2.42640477604381       3.13763616142982      -2.44288408095664
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Table S21. Energies in a.u.

	ωB97XD3/def2-SVP					ωB97XD3/def2-TZVP	ωB97XD(COSMO)/def2-SVP
Name	Total Energy	Gibbs Free Energy	Free energy correction	ZPE	NImag	Total Energy	Total Energy
^{4}R	-3679.09631	-3678.60242	0.49389	0.56210	0	-3681.52526	-3679.13534
^{4}TS1	-3679.04955	-3678.55595	0.49360	0.56071	1	-3681.47927	-3679.09579
^{4}I1	-3679.06187	-3678.56484	0.49702	0.56340	0	-3681.49114	-3679.10815
MECP	-3679.06172	-3678.56242	0.49887	0.56289	0	-3681.49090	-3679.10801
^{2}TS2	-3679.03478	-3678.53526	0.49952	0.56271	2[a]	-3681.47238	-3679.09289
^{2}I2	-3679.08869	-3678.58328	0.50541	0.56709	1	-3681.51859	-3679.13649
^{2}TS3	-3679.06649	-3678.55850	0.50799	0.56945	1	-3681.49637	-3679.11522
^{2}I3	-3679.08807	-3678.58355	0.50452	0.56634	1	-3681.51870	-3679.13453
^{2}TS4	-3679.05869	-3678.55838	0.50031	0.56282	1	-3681.48855	-3679.10713
^{2}P	-3679.21551	-3678.71977	0.49574	0.56141	1	-3681.65828	-3679.26766

[a]The value of the second negative frequency is very small, -14.54 cm^{-1} and hence ignored.