Supplementary Information

Photo-Mediated Aromatic C-H Activation by Cu(II)-Amido-Quinoline Complexes

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List of Contents

■ EXPERIMENTAL

Photo-mediated Benzene Hydroxylation with H_2O_2

A mixture of all three copper complexes (0.02 mM) in $H_2O/CHCl_3$ (1:5 v/v) 1mL and benzene 89 µL (1 M) was added to the solution, then 307 µL of 30% H_2O_2 was added slowly to the reaction mixture. This solution was stirred under irradiation at 50 ℃ for 6 hr. Then 500 µL of ethanol was added to convert the biphasic reaction mixture to single phase. A fraction of reaction mixture was analyzed by reverse phase HPLC, and conversion were calculated, and products were identified by GC-MS comparison with authentic standard compound.

Chromatographic Methods

Chromatographic separation of the various products shown in this work was performed using the following chromatographic methods: Agilent 5977B GC/MSD equipped with an HP-5 MS capillary column (30 m × 0.32 mm × 0.25 µm); Waters Alliance system (Milford, MA) consisting of e2695 separation module and a 2998 photodiode-array detector equipped with an column C 18 2.5µm (4.6 × 50 mm).

For Hydroxylation of Substituted Benzene (GC-MS):

	Rate (°C/min)	Temperature (°C)	Hold time (min)	Run time (min)
Initial		40	2	2
Ramp	5	50	2	6
Ramp	10	200	0	21
Inlet Septum purge flow- 3ml/min Total flow- 259 ml/min Split ratio- 100:1				

For Hydroxylation of Anthracene and Biphenyl (GC-MS):

	Rate (°C/min)	Temperature (°C)	Hold time (min)	Run time (min)
Initial		100	1	1
Ramp 1	15	200	0	7.67
Ramp 2	10	280	0	15.67
Ramp 3	5	310	0	21.67
Inlet Septum purge flow- 3ml/min Total flow- 259 ml/min Split ratio- 100:1				

For recording the data in HPLC, we follow the method below.

Sample taken = 10 µL

Time (min)	Flow (mL/min)	H_2O (%)	MeCN (%)
0-2	1.00	100	0.00
4-6	1.00	80	20
6-8	1.00	70	30
8-10	1.00	60	40
10-14	1.00	50	50
14-16	1.00	40	60
16-18	1.00	30	70
18-20	1.00	20	80
20-22	1.00	10	90
22-26	1.00	0.00	100
26-30	1.00	100	0.00

Synthesis of L2 and L3. 2-phenylmalonyl dichloride was synthesis according to the reported method.[1] To a solution of phenyl malonic acid (900mg, 5 mmol) in DCM (35 mL), 38 µL (0.5 mmol) of N, N-dimethylformamide (DMF) was added. oxalyl chloride (1.1 mL, 12.5 mmol) was added carefully using a dropping funnel over a period of 30 minutes at 0 ℃. After addition, the reaction was allowed to warm to room temperature, and the reaction was kept on stirring for an additional 4 hours to ensure a complete reaction. Then, the solvent was removed under reduced pressure, resulting in the formation of a colorless liquid. First, 2-phenylmalonyl dichloride was prepared by following the above procedure. Then a solution of 8-amino quinoline (500mg, 3.46 mmol) in dry THF (30 mL), triethylamine (580 µL, 4.16 mmol) was stirred under an N_2 atmosphere at 0 ℃, and the reaction was stirred for 15 minutes. Then the phenyl malonyl dichloride (319 uL, 2.08 mmol) pre-dissolved in 10 mL of dry THF was added dropwise at 0 ℃ over a period of 20 minutes. After this, the reaction mixture was brought to room temperature (RT) and was kept overnight. After 12 hours, the reaction mixture was filtered over celite. The filtrate was then

evaporated to dryness, then purified ligand **L3** was obtained after column chromatography using 5 % Ethyl acetate/ hexane to afford a pure yellowish powder.

Synthesis of L3 was carried out by a solution of 2-methylquinoline-8-amine (500mg, 3.16 mmol) in the presence of triethylamine (440 μL, 3.16 mmol) as a base in THF solvent, under an inert atmosphere, at 0 ℃, and the reaction was stirred for 15 minutes. Then the dimethyl malonyl chloride (320 uL, 1.896 mmol) pre-dissolved in 10 mL of dry THF was added dropwise at 0 ℃ over a period of 20 minutes. After this, the reaction mixture was brought to room temperature (RT) and was kept overnight. Under reduced pressure, the solvent was evaporated, and the ligand was further purified by column chromatography, and white colour powder was obtained for the ligand.

Synthesis of Cu (II) complexes (CuL1, CuL2 and CuL3). Copper complexes (**CuL1** and **CuL2**) were synthesized by reacting copper (II) chloride dihydrate $CuCl_2.2H_2O$ with the corresponding amido-quinoline ligands. $CuCl_2.2H_2O$ (19 mg, 0.11 mmol) was added to a reaction mixture containing either L1 (50.0 mg, 0.13 mmol) or L2 (50.0 mg, 0.11 mmol), triethylamine (NEt_3, 30 μL, 0.22 mmol), and 2 mL of dry tetrahydrofuran (THF), under a nitrogen atmosphere. The mixture was stirred at room temperature for 6 hours. Upon completion, the solution turned dark green and was filtered through a Celite pad. Under reduced pressure solvent was evaporated and the residue was dissolved in DCM, layered with Hexane, then left undisturbed for crystallization, yielding pure dark green colour crystals of the complexes within 15 days. For the synthesis of CuL3, the same procedure was followed, except that methanol (2 mL) was used instead of THF as the solvent.

Characterization of L1, L2 and L3

HR-MS

HR-MS m/z: calcd: 433.1659; found: 433.1645 $(M+H)^+$ for L2($C_{27}H_{20}N_4O_2$); HR-MS m/z: calcd: 413.1972; found: 413.1961 $(M+H)^+$ for L3($C_{25}H_{24}N_4O_2$).

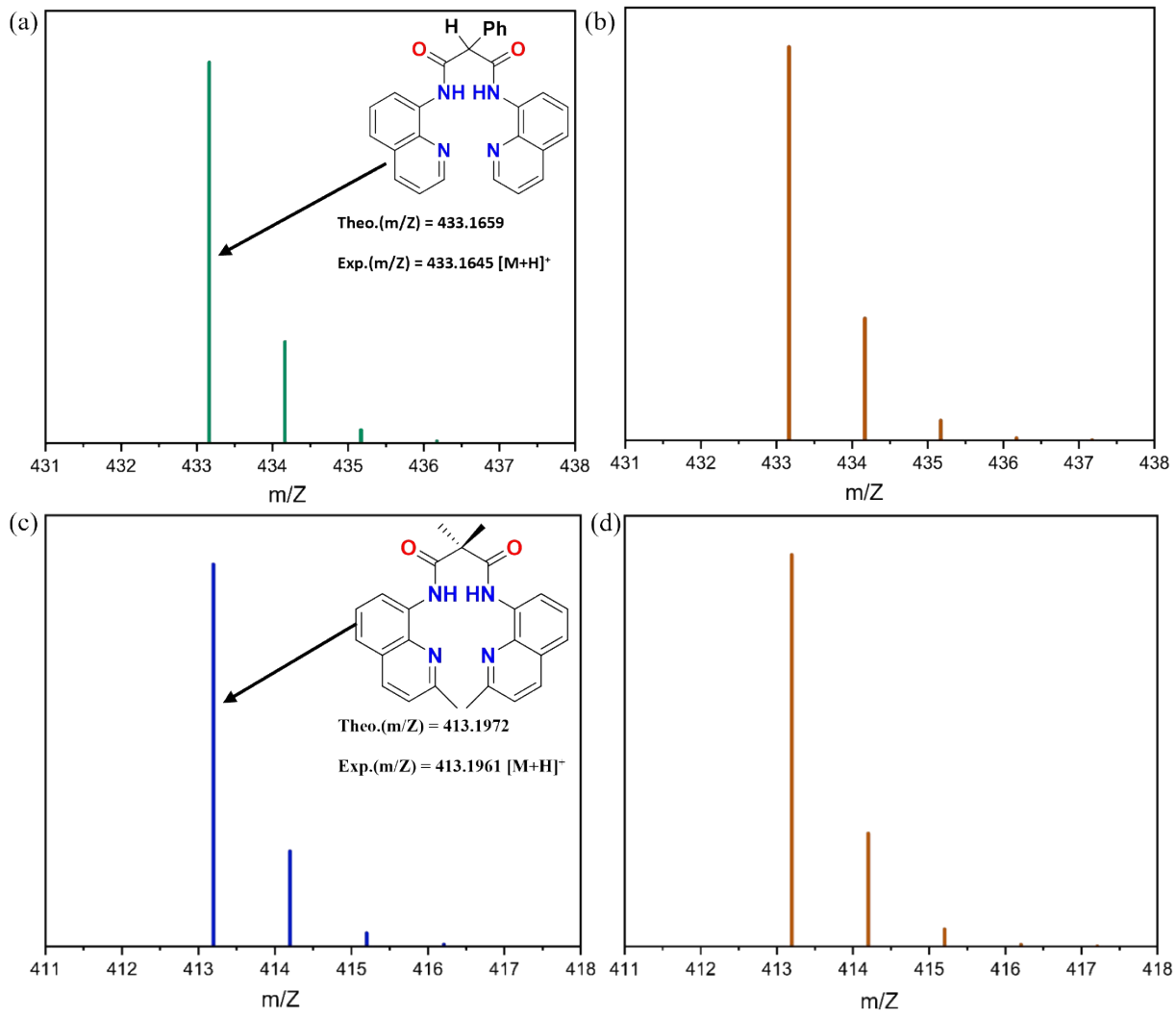


Figure S1. HR-MS Spectrum of experimental L2 and L3 (a and c) and theoretical calculated by Isotope Distribution Calculator (b and d).

^{1}H NMR

L1: L1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.93 (s, 2H), 8.84 (ddd, J = 9.0, 5.6, 1.9 Hz, 4H), 8.13 (dd, J = 8.3, 1.7 Hz, 2H), 7.56 – 7.47 (m, 4H), 7.44 (dd, J = 8.3, 4.2 Hz, 2H), 1.92 (s, 6H).

L2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 2H), 8.85 (dd, J = 5.5, 3.7 Hz, 4H), 8.14 (dt, J = 8.3, 1.5 Hz, 2H), 7.79 (d, J = 7.6 Hz, 2H), 7.55 – 7.50 (m, 4H), 7.47 – 7.42 (m, 4H), 7.39 – 7.33 (m, 1H), 4.99 (s, 1H).

L3:^{1}H NMR (400 MHz, $CDCl_3$) δ 10.96 (s, 2H), 8.79 (t, J = 4.6 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 4.6 Hz, 4H), 7.29 (d, J = 8.4 Hz, 2H), 2.70 (s, 6H), 1.91 (s, 6H).

^{13}C NMR

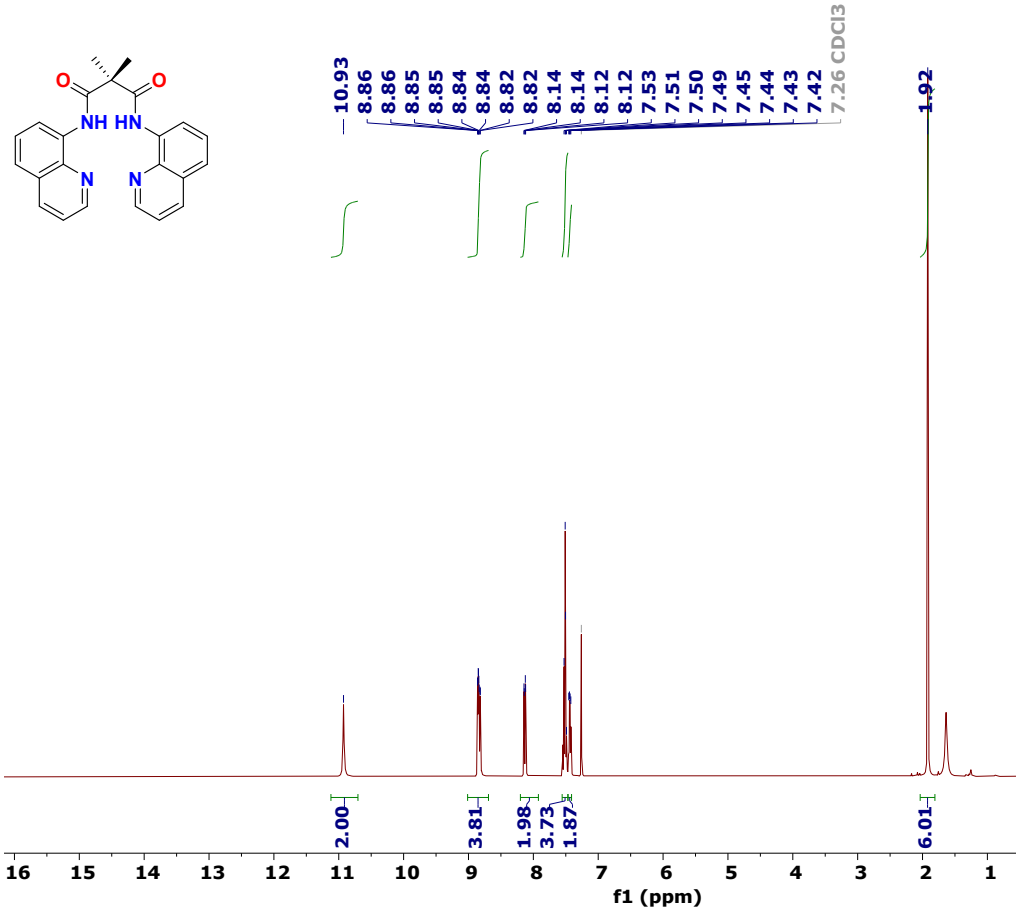
L1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.93 (s, 2H), 8.84 (ddd, *J* = 9.0, 5.6, 1.9 Hz, 4H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.56 – 7.47 (m, 4H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 2H), 1.92 (s, 6H).

L2: ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 148.73, 138.98, 136.34, 135.05, 134.43, 129.38, 128.65, 128.45, 128.06, 127.33, 122.31, 121.77, 117.25, 62.90, 31.07.

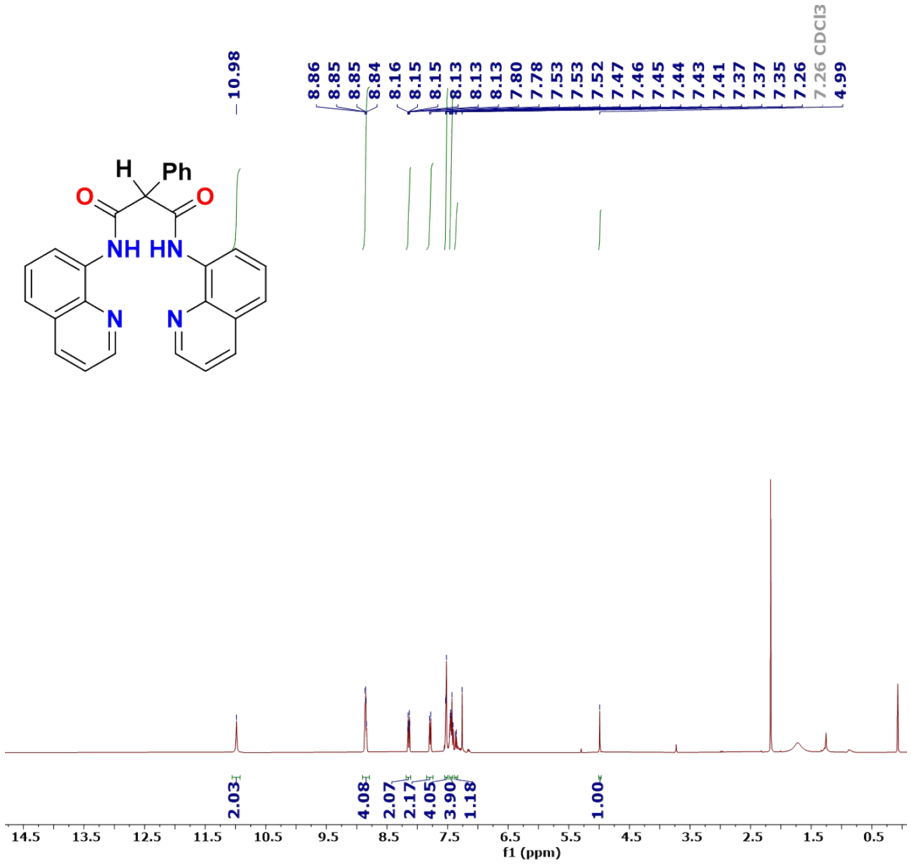
L3:^{13}C NMR (101 MHz, $CDCl_3$) δ 171.78, 157.51, 138.45, 136.36, 134.00, 126.32, 126.13, 122.52, 121.71, 116.76, 53.04, 25.42, 24.10, 1.16.

^{1}H NMR

(a)



(b)


10.98
8.86
8.85
8.85
8.84
8.16
8.15
8.15
8.13
8.13
8.13
7.80
7.78
7.53
7.53
7.52
7.47
7.46
7.45
7.44
7.43
7.41
7.37
7.37
7.35
7.26
7.26 CDCl3
4.99
H
Ph
O
O
NH HN
N
N
2.03
4.08
2.07
2.17
4.05
3.90
1.18
1.00
14.5 13.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

(c)

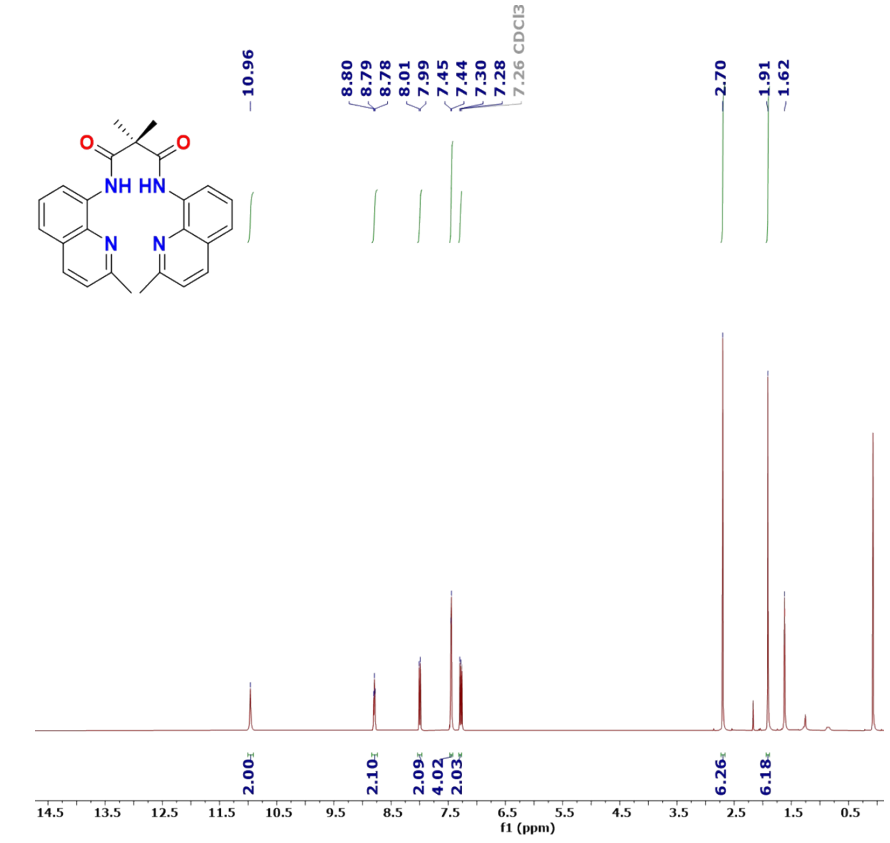
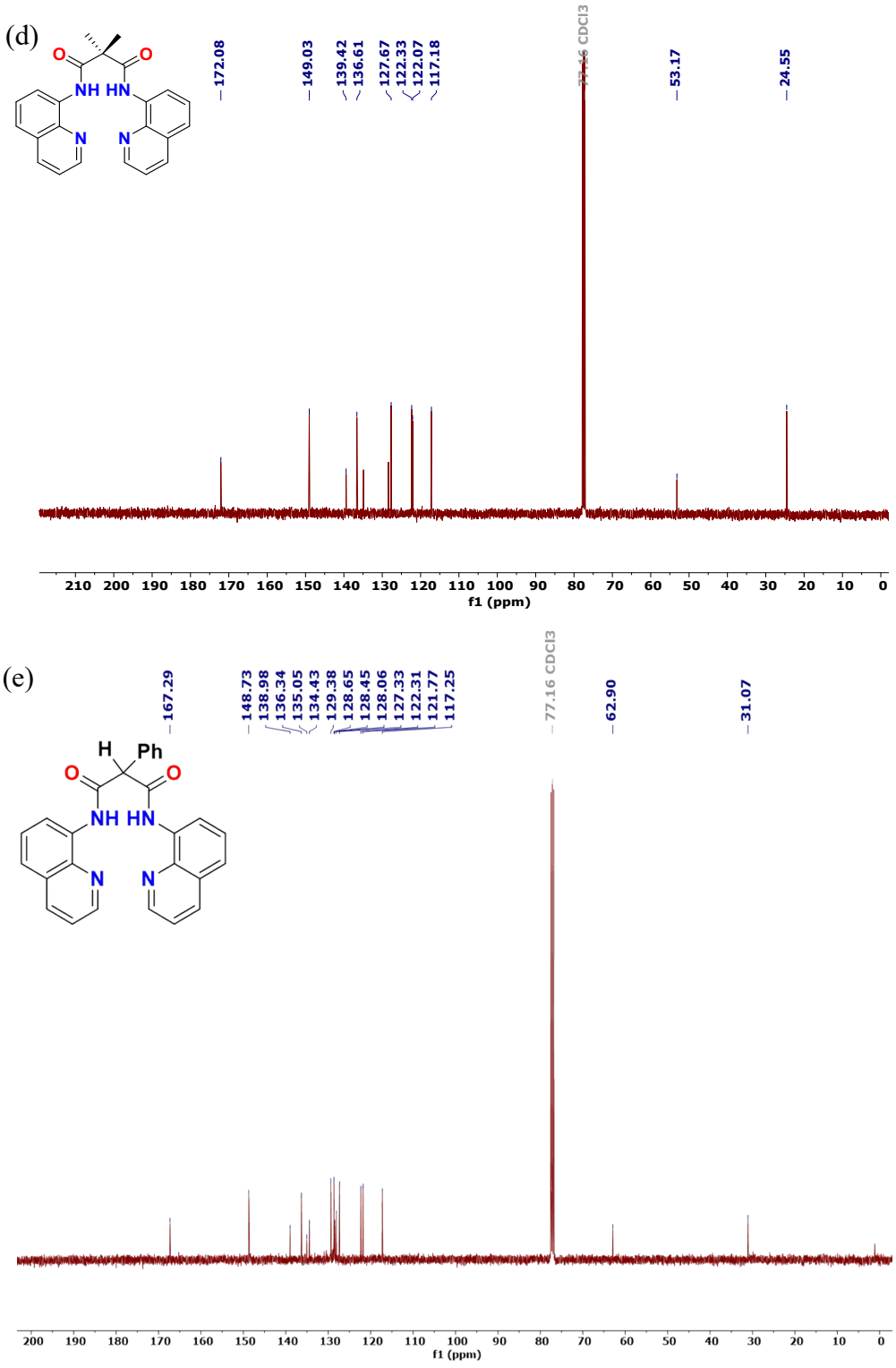

10.96
8.80
8.79
8.78
8.01
7.99
7.45
7.44
7.30
7.28
7.26 CDCl3
2.70
1.91
1.62
O
O
NH HN
N
N
2.00
2.10
2.09
4.02
2.03
6.26
6.18
14.5 13.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

Figure S2. ^{1}H NMR Of L1(a), L2(b) and L3(c) in $CDCl_3$.



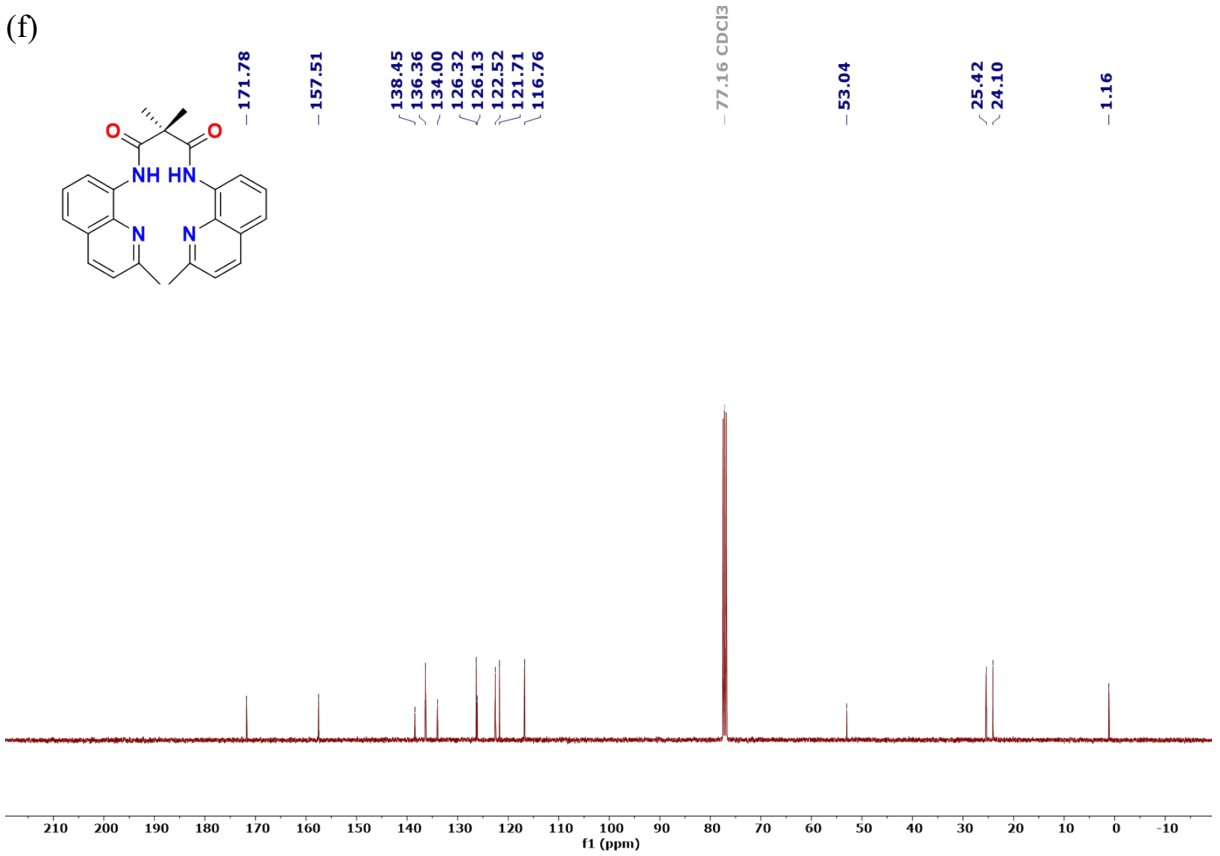
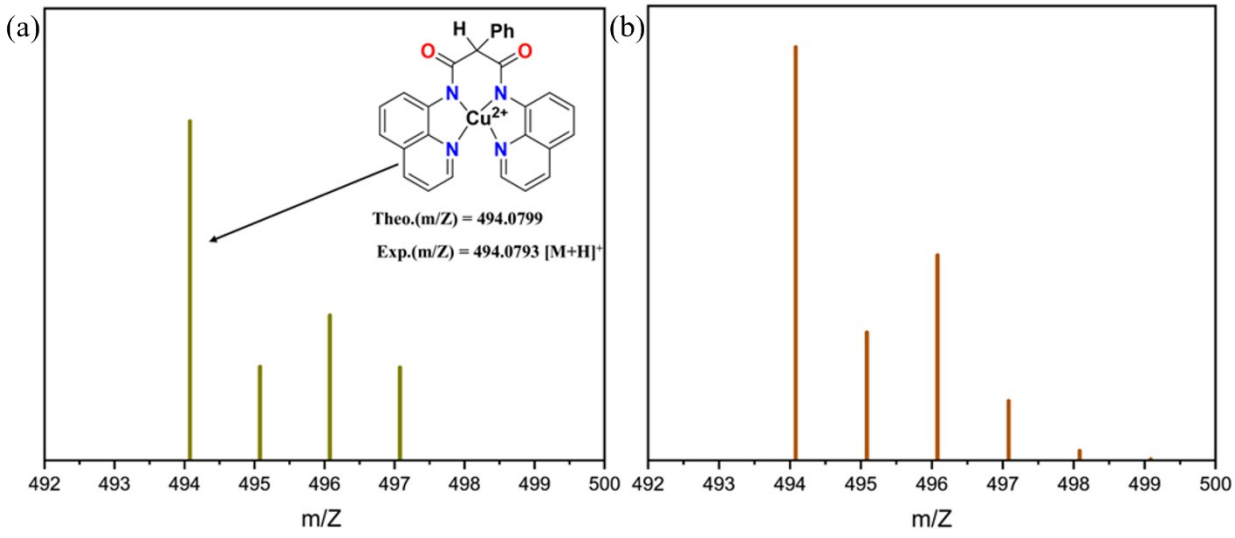


Figure S3. ^{13}C NMR of L1(d), L2(e) and L3(f) in $CDCl_3$.

Characterization of Cu complexes

HR-MS

HR-MS m/z: calcd for CuL3: 494.0799; found: 494.0793 $(M+H)^+$ for CuL2; HR-MS m/z: calcd: 474.1112; found: 474.1132$(M+H)^+$for CuL3.



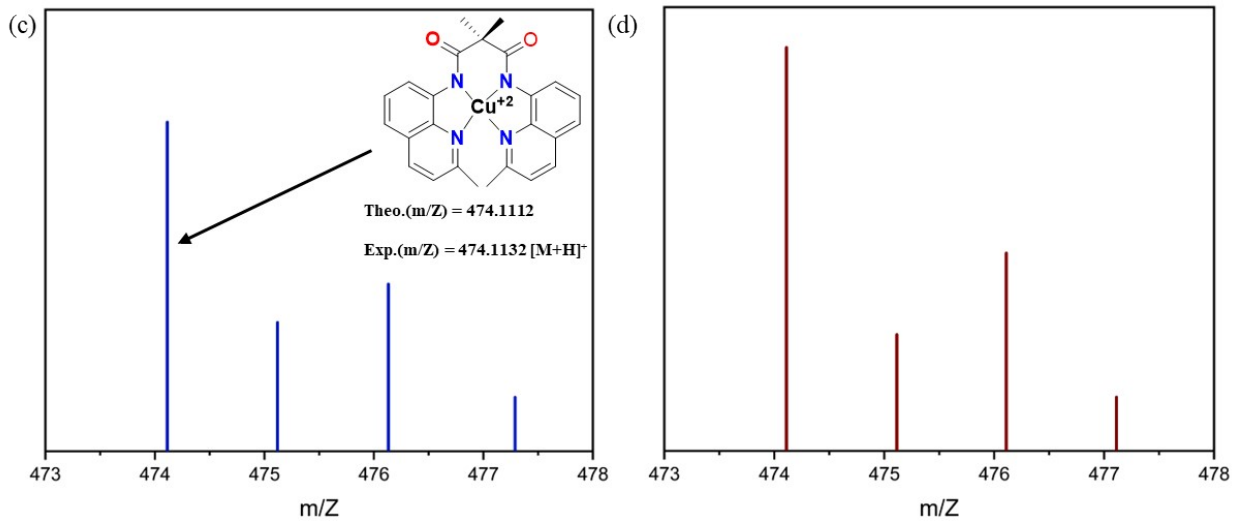


Figure S4. HR-MS Spectrum of experimental CuL2 and CuL3 (a and C) and theoretical calculated by Isotope Distribution Calculator (b and d).

UV-Vis

UV-Vis (CuL1): 392 nm (λ_{max}); ε = 8751 $M^{-1}cm^{-1}$ in $CHCl_3$.

UV-Vis (CuL2): 372 nm (λ_{max}); ε = 5956 $M^{-1}cm^{-1}$ in $CHCl_3$.

UV-Vis (CuL3): 376 nm (λ_{max}); ε = 4565 $M^{-1}cm^{-1}$ in $CHCl_3$.

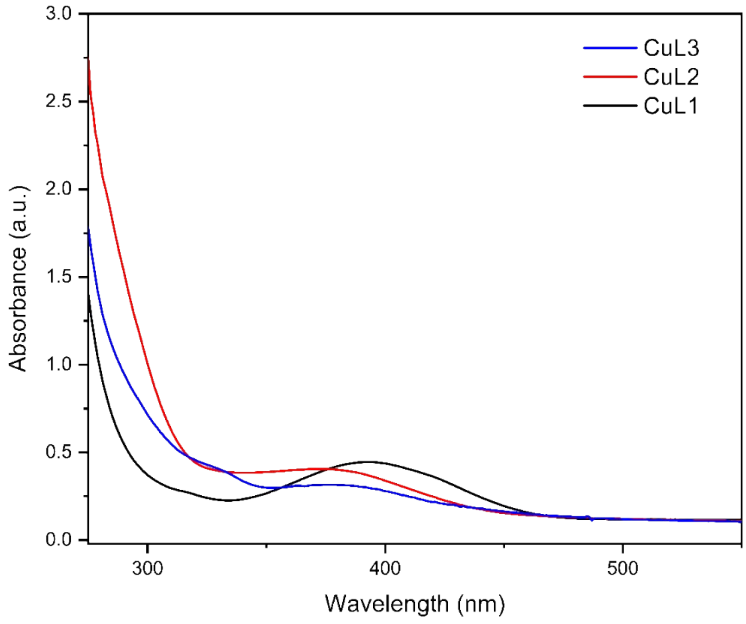


Figure S5. UV-Vis spectra CuL1 (0.04 mM),CuL2 (0.06 mM) and CuL3(0.06 mM) in ACN.

CV

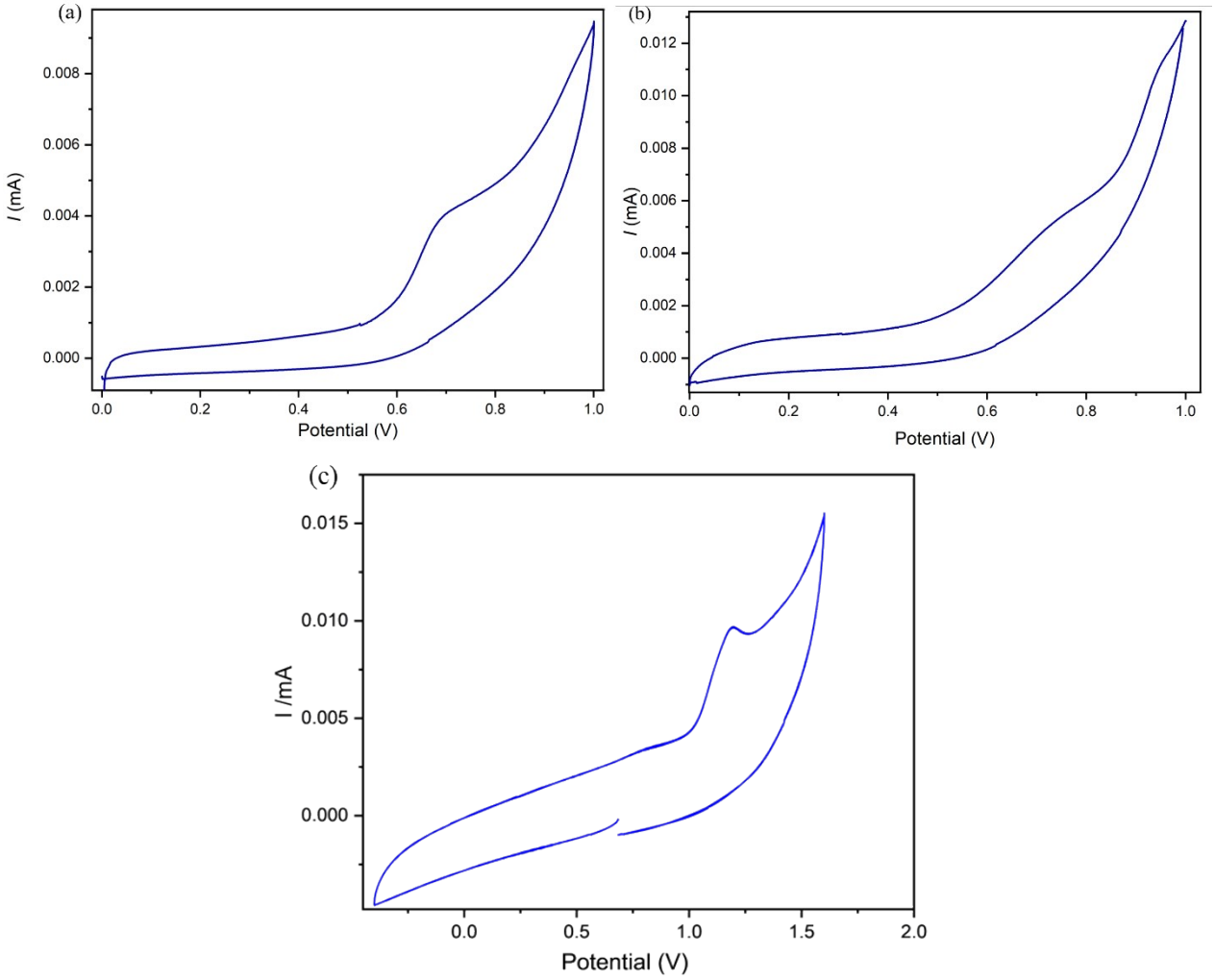


Figure S6. Cyclic voltammogram of **CuL2** (a), **CuL3** (b) and **L2** (c) 0.5 mM in DMF. Supporting electrolyte: $^{n}Bu_4NPF_6$ (0.1 M); Reference electrode: Ag/Ag^{+} (0.54 V *vs.* NHE); Working electrode: glassy carbon; Counter electrode: Pt wire; Scan rate: 0.05 Vs^{-1}.

Distortion parameters

Table S1. Crystal data and structure refinement parameters of complexes.

Compounds	**CuL2**	**CuL3**
Empirical formula	$C_{27}H_{18}N_4CuO_2$	$C_{25}H_{22}N_4CuO_2$ 1[H_2O]
Formula weight	494.00	492.02
Temperature (K)	298	295
Wavelength (Å)	0.71073	0.71073

Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)/α (°)	18.9830(12)/90	13.507(11)/90
b (Å)/β (°)	10.4621(7)/ 108.076(2)	13.173(15)/99.26(4)
c (Å)/γ (°)	22.4265(12)/90	12.659(16)/90
Volume ($Å^3$)	4234.1(5)	2223(4)
Z	8	4
Density (calc) (Mg/m^{-3})	1.550	1.470
Absorption coefficient (μ) (mm^{-1})	1.067	1.018
F(000)	2024	1020
Crystal size (mm^3)	0.23 x 0.15 x 0.12	0.5 x 0.5 x 0.5
Theta ranges for data collection	1.89-26.42°	2.173 - 26.462°
Index ranges	-23<=h<=23, -13<=k<=13, -28<=l<=24	-16<=h<=15, -16<=k<=16, -15<=l<=15
Reflections collected	80159	32886
Independent reflections	8670 [R(int) = 0.0759]	4554 [R(int) = 0.0685]
Data/restraints/parameters	8670/0/613	4554/0/305
Goodness-of-fit on F^2	3.698	1.106
Final R indices [I>2sigma(I)]	R1 = 0.1184	R1 = 0.0451
	wR_2 = 0.1912	wR_2 = 0.0963
R indices (all data)	R1 = 0.2320	R1 = 0.0776
	wR_2 = 0.2043	wR_2 = 0.1214
Largest diff peak and hole (e $Å^{-3}$)	1.333 and -1.106	0.746 and -0.469
CCDC No.	2491828	2477383

Table S2. Distortion parameter from Selected bond lengths (Å) and bond angles (°) of CuL2 and CuL3 complex.

Bond Length [Å]	Bond Angle [°]	Bond Length [Å]	Bond Angle [°]
CuL2	**CuL2**	**CuL3**	**CuL3**
1.941 [Cu(1)-N(4)]	83.0 [N(4)-Cu(1)-N(5)]	1.997 [Cu(1)-N(1)]	83.6 [N(1)-Cu(1)-N(2)]
2.015 [Ni(1)-N(5)]	98.7 [N(4)-Cu(1)-N(6)]	1.912 [Cu(1)-N(2)]	105.9 [N(1)-Cu(1)-N(4)]
1.941 [Ni(1)-N(6)]	172.9 [N(4)-Cu(1)-N(8)]	2.003 [Cu(1)-N(3)]	156.4 [N(1)-Cu(1)-N(3)]
1.989 [Ni(1)-N(8)]	159.3 [N(5)-Cu(1)-N(6)]	1.914 [Cu(1)-N(2)]	148.0 [N(2)-Cu(1)-N(4)]
	97.7 [N(5)-Cu(1)-N(8)]		98.4 [N(2)-Cu(1)-N(3)]
	83.2 [N(6)-Cu(1)-N(8)]		84.9 [N(4)-Cu(1)-N(3)]

Equation for the calculation of τ_4 and τ_δ

$$\tau_4 = \frac{360^\circ - (\alpha + \beta)}{141^\circ}$$

$$\tau_4 = 0.14 \; for \; CuL2$$

$$\tau_4 = 0.39 \; for \; CuL3$$

α = largest L-Ni-L angles

β = second largest L-Ni-L angles

$$\tau_\delta = \frac{360^\circ - (\alpha + \beta)}{141^\circ}\delta$$

$$\delta = \frac{\beta}{\alpha}$$

EPR data.

EPR spectra were recorded using JEOL Model No. X320. X band EPR spectra for CuL1 recorded for 1 Mm solution in DMF at 123 K, similar spectra were observed as reported earlier by our group. From the magnetic field, its g values are (g_x= 2.0344, g_y= 2.0721, g_z= 2.1955). Similar features were observed for CuL2 and CuL3, and their g values are (g_x= 2.0432, g_y= 2.0721, g_z= 2.1952) and (g_x= 2.0408, g_y= 2.0721, g_z= 2.1957), respectively.

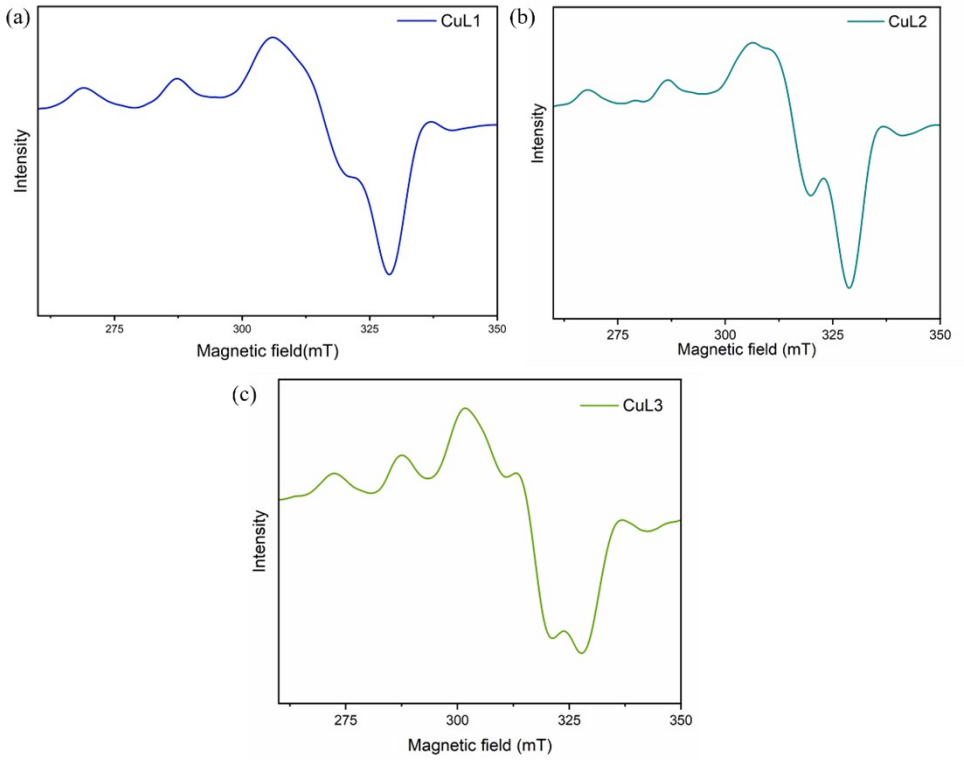


Figure S7. EPR spectrum of **CuL1** (a), **CuL2** (b) and **CuL3** (c) in DMF at 123K at X-band frequency and magnetic field modulation of 100 KHz, microwave power of 0.988 mW, Sweep width 100 mT and modulation width 0.25 mT in DMF at 123K.

HPLC Analysis

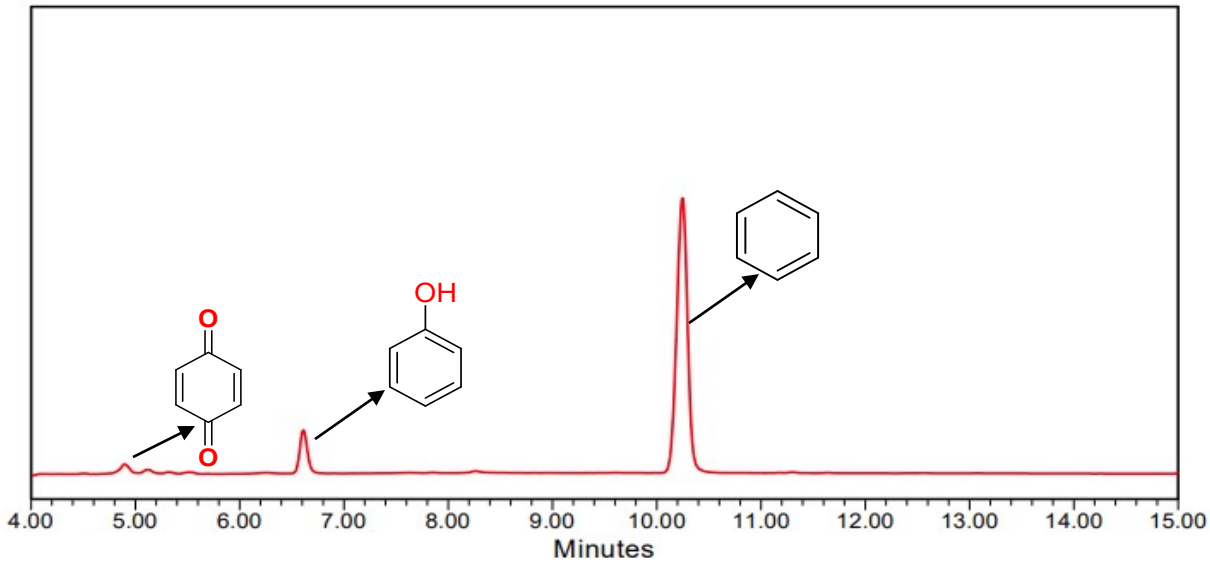


Figure S8. Reversed-phase HPLC chromatogram (recorded at 254 nm) of benzene.

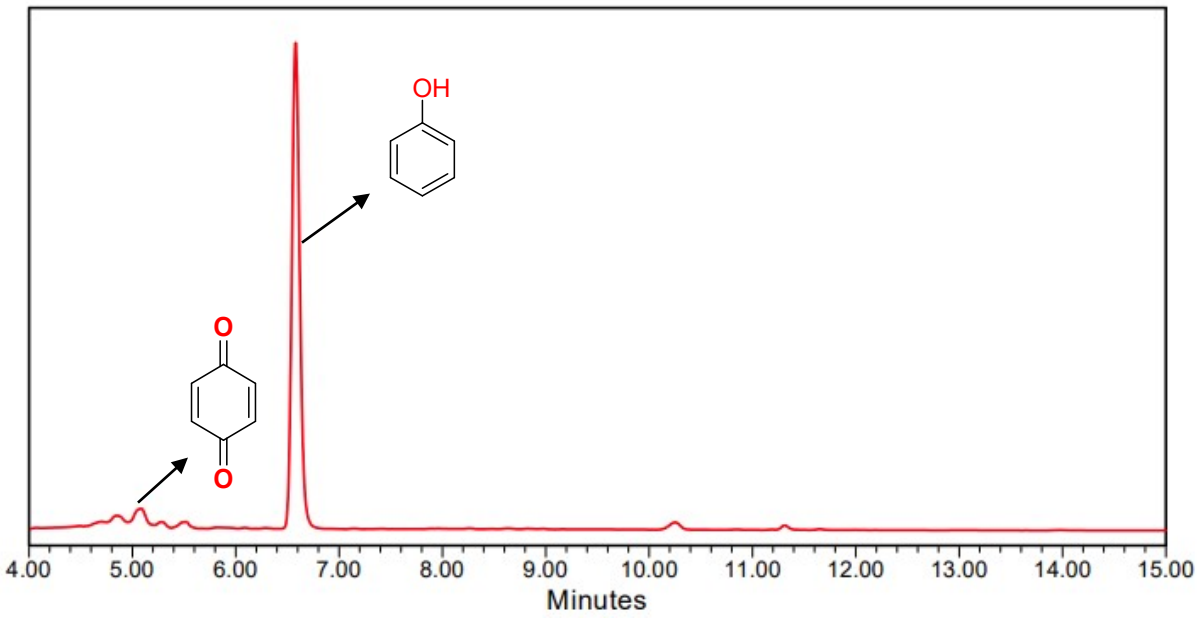
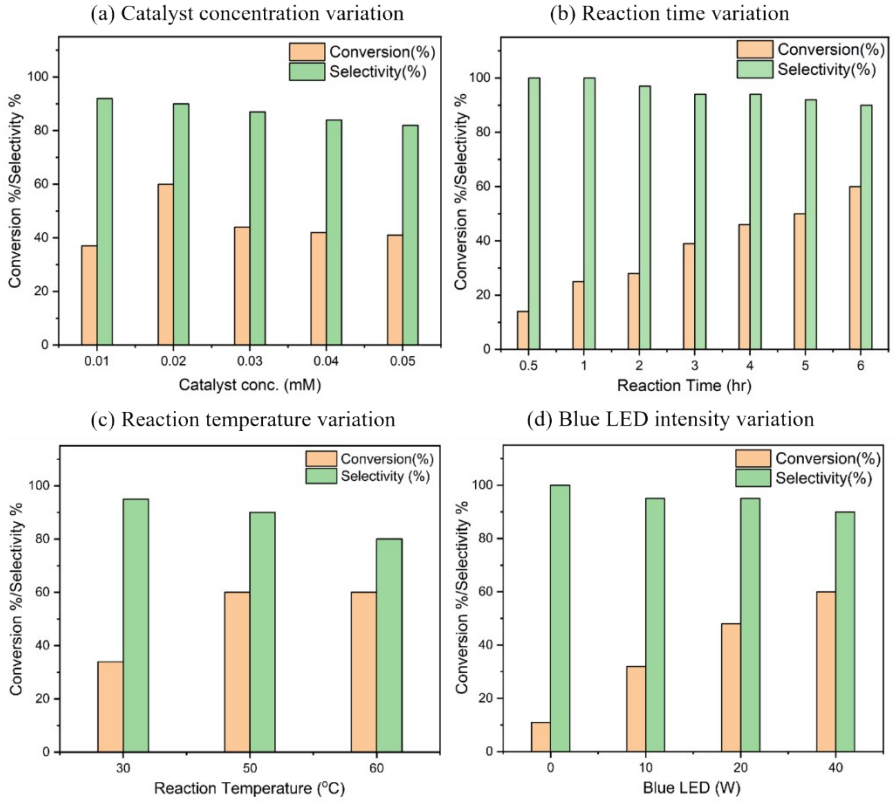


Figure S9. Reversed phase HPLC chromatogram (recorded at 272 nm) of phenol.

Optimization of the reaction conditions.



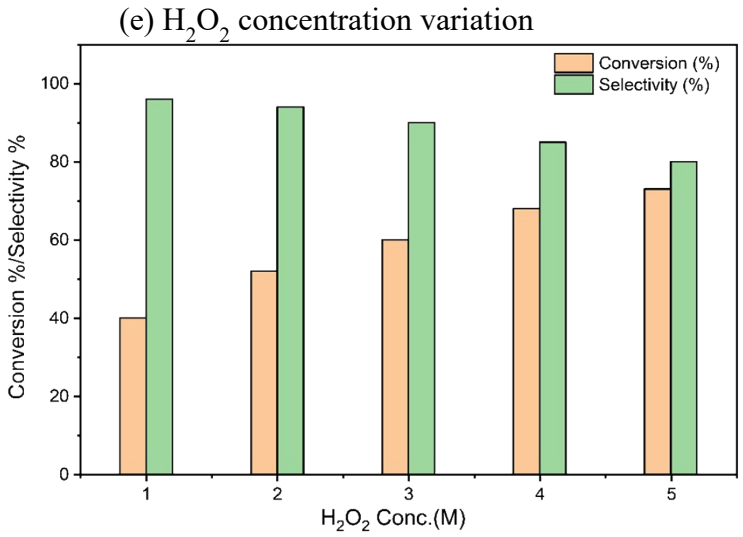


Figure S10. (a) Conversion of benzene and selectivity of phenol with respect to catalyst variation; (b) Effect of reaction time on benzene conversion and product selectivity; (c) Effect of temperature; (d) Intensity of blue LED in aromatic hydroxylation; (e) H_2O_2 concentration variation.

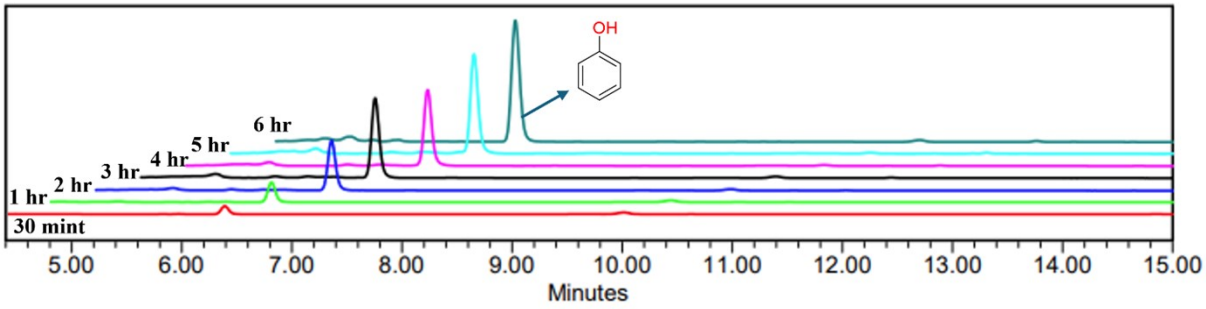


Figure S11. HPLC overlay chromatogram shows effect of reaction time on phenol formation over a period of 30mint - 6 hr (at 272 nm)

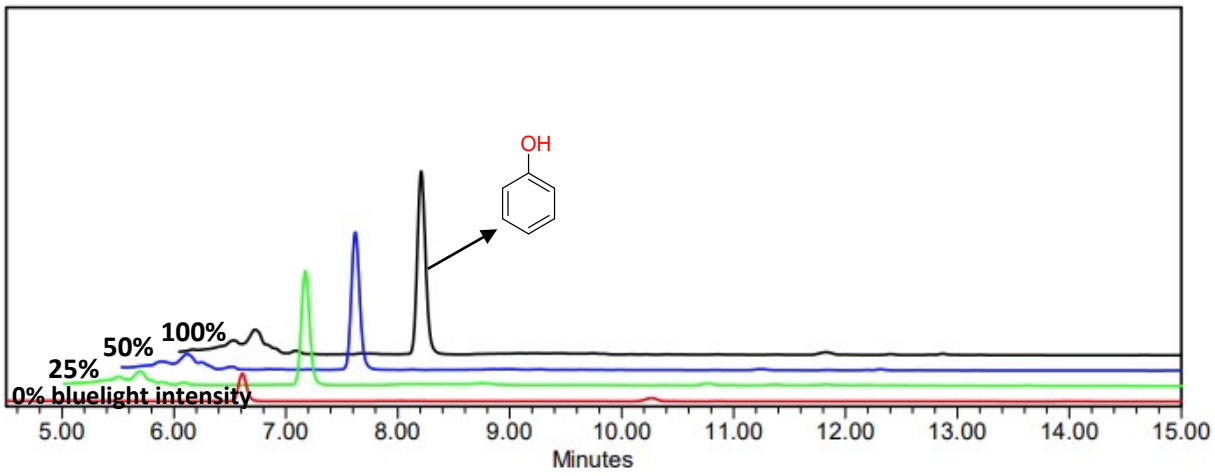


Figure S12a. HPLC overlay chromatogram shows effect of blue light intensity on phenol formation (at 272 nm).

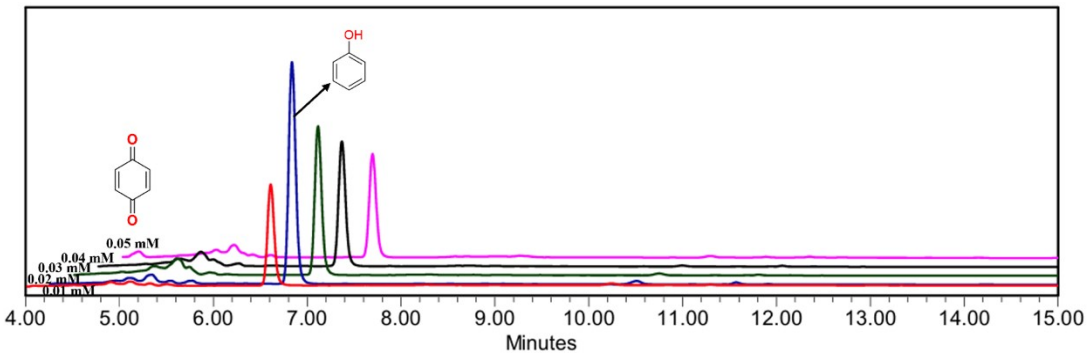


Figure S12b. HPLC overlay chromatogram shows effect of Catalyst concentration on phenol formation (at 272 nm).

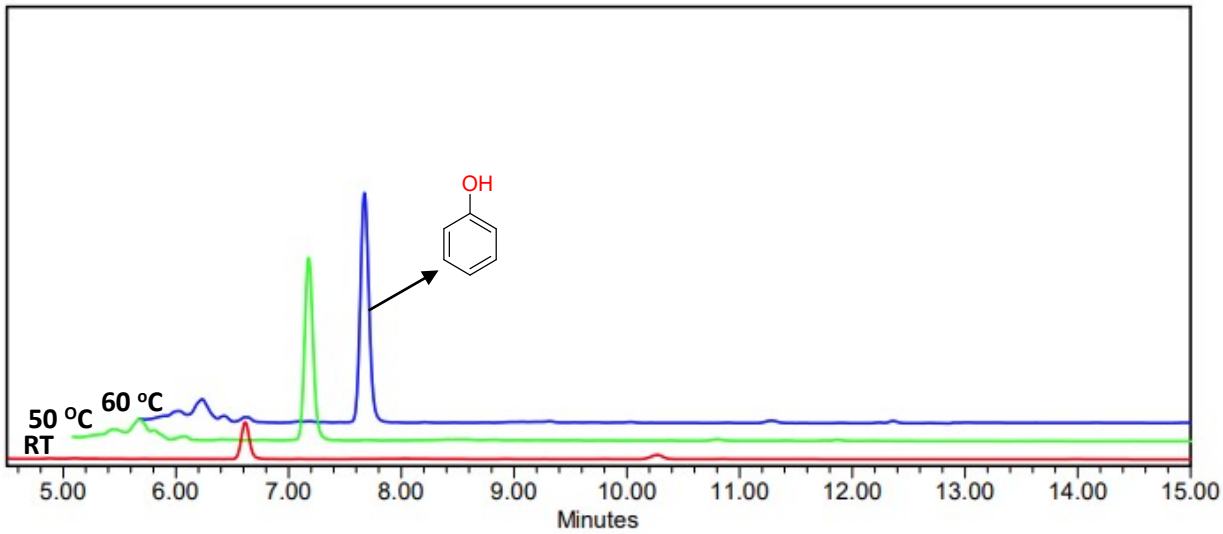


Figure S13a. HPLC overlay chromatogram shows effect of Temperature in aromatic hydroxylation on phenol formation (at 272 nm).

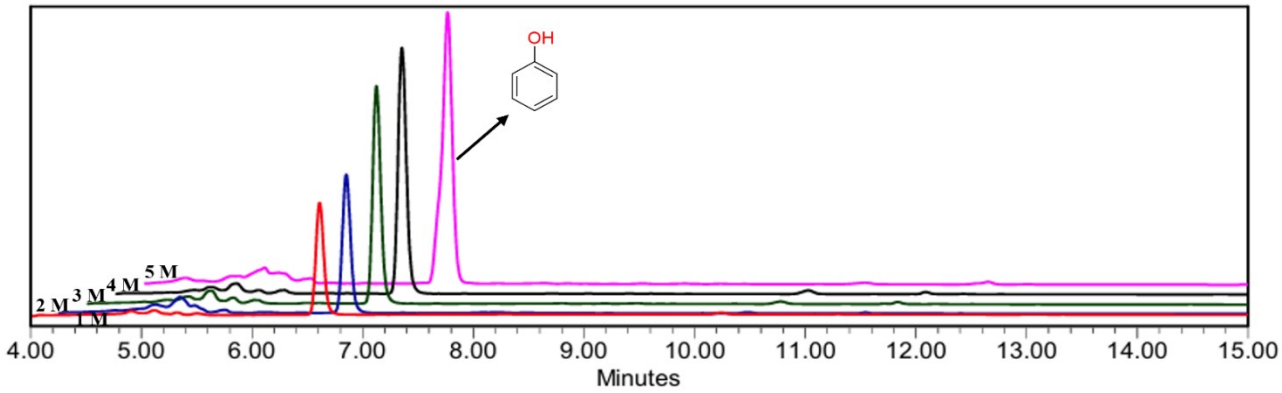


Figure S13b. HPLC overlay chromatogram shows effect of H_2O_2 variation in aromatic hydroxylation on phenol formation (at 272 nm).

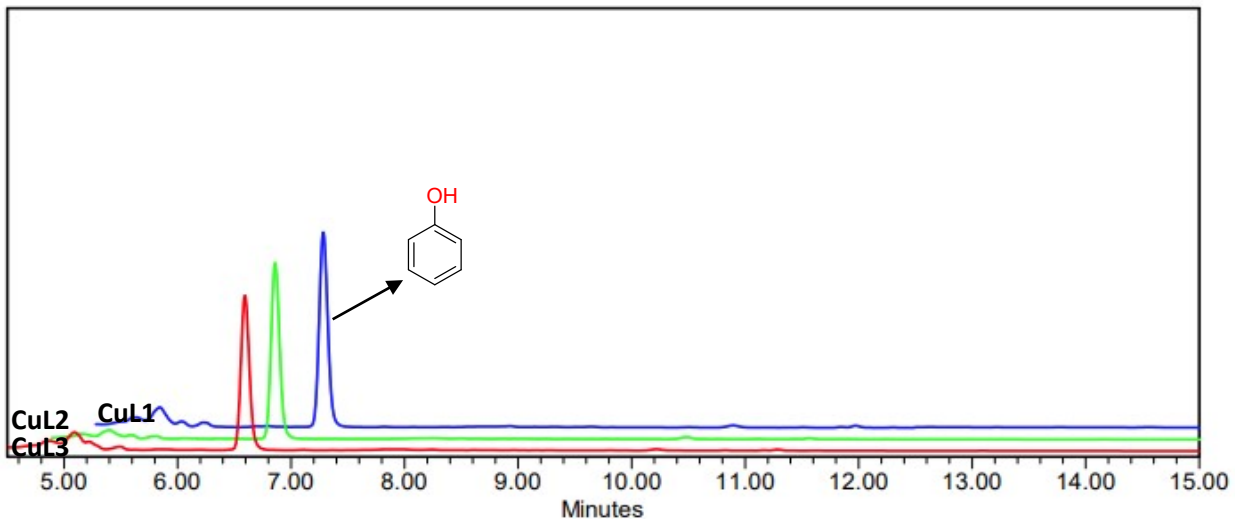
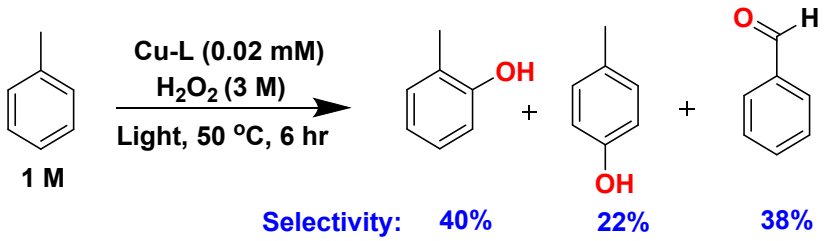


Figure S14. HPLC overlay chromatogram shows comparison of three catalysts in aromatic hydroxylation on phenol formation (at 272 nm).

GC-MS Analysis

Scheme S1. Product distribution of photo-mediated hydroxylation of toluene using catalyst CuL1.



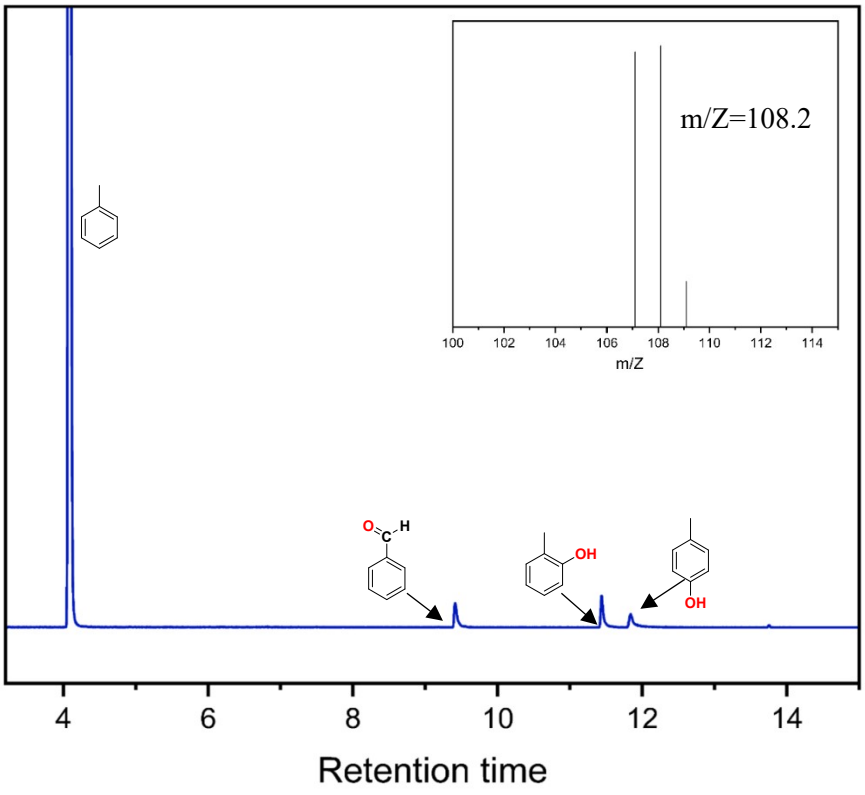


Figure S15a. GC-MS trace for hydroxylation of toluene using **CuL1**. The inset shows the GC-MS spectra for *ortho*-Cresol.

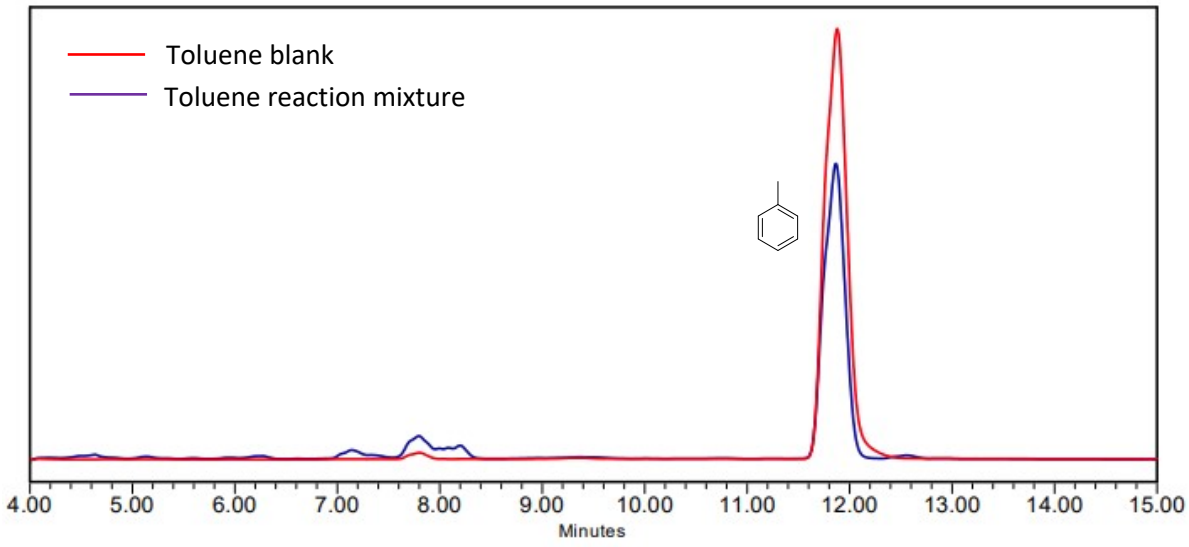
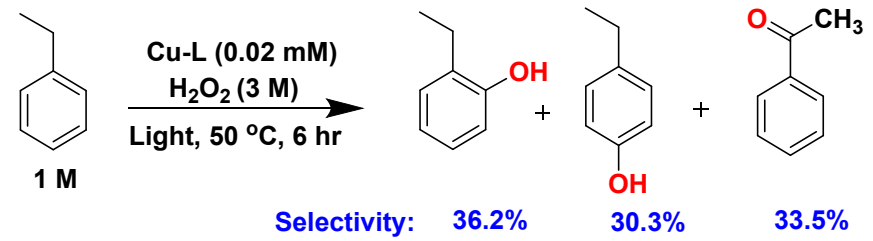


Figure S15b. Reverse phase HPLC chromatogram for hydroxylation of toluene using **CuL1** (recorded at 254 nm).

Scheme S2. Product distribution of photo-mediated hydroxylation of ethylbenzene using catalyst **CuL1**.



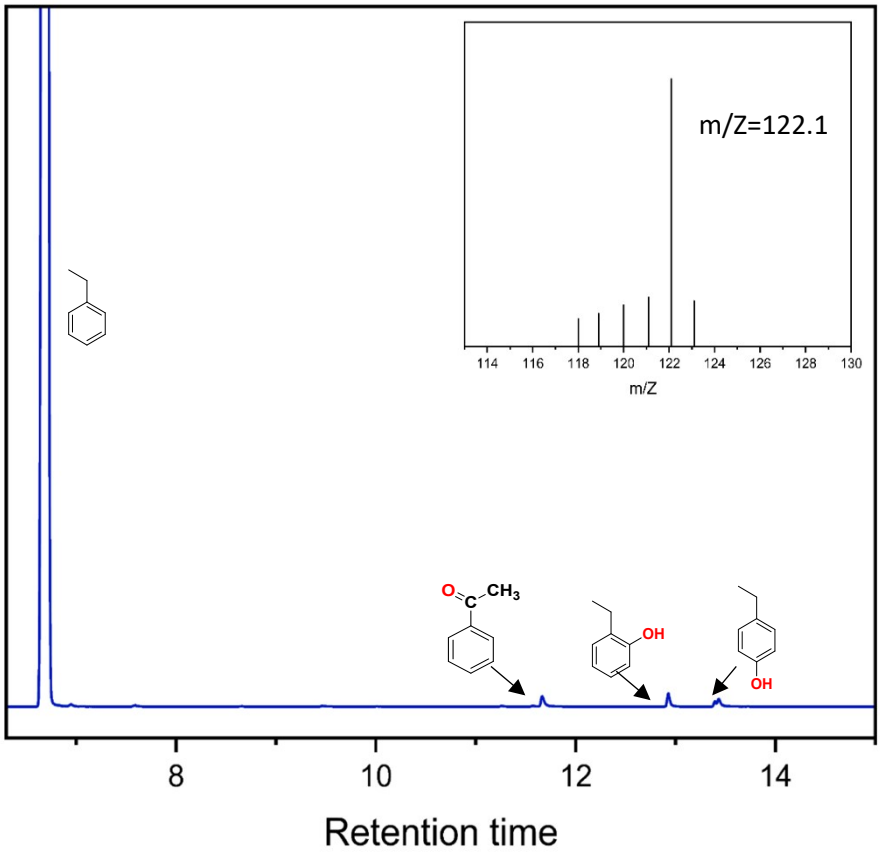


Figure S16a. GC-MS trace for hydroxylation of ethylbenzene using **CuL1**. The inset shows the GC-MS spectra of O-ethyl phenol.

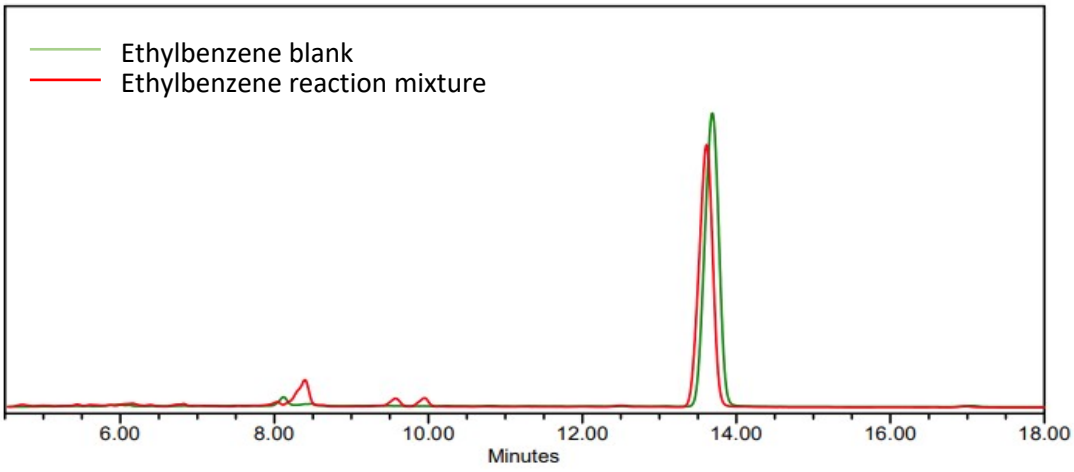
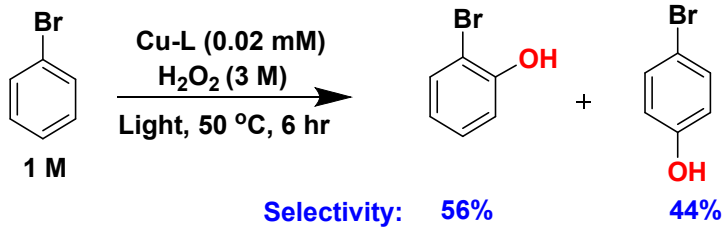


Figure S16b. Reverse phase HPLC chromatogram for hydroxylation of Ethylbenzene using **CuL1** (recorded at 254 nm).

Scheme S3. Product distribution of photo-mediated hydroxylation of bromobenzene using catalyst **CuL1**.



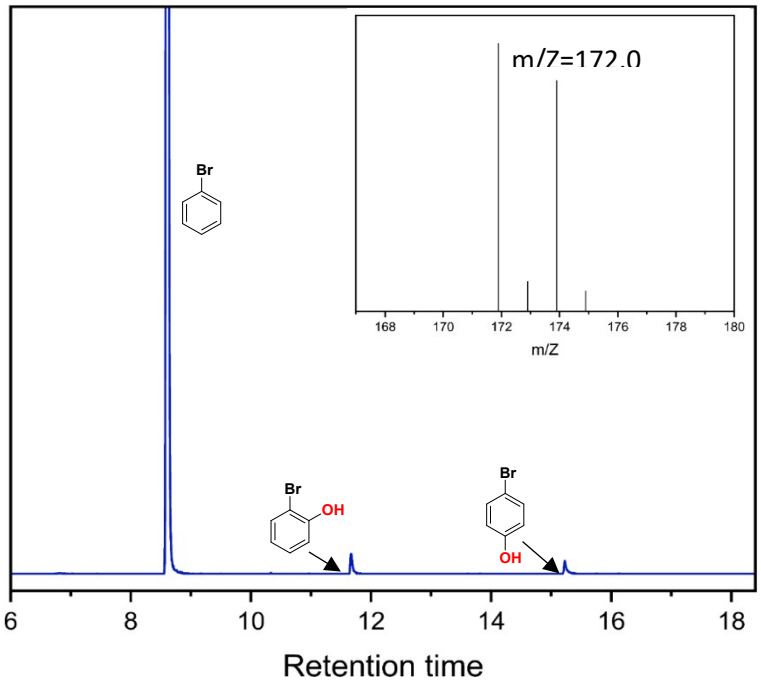
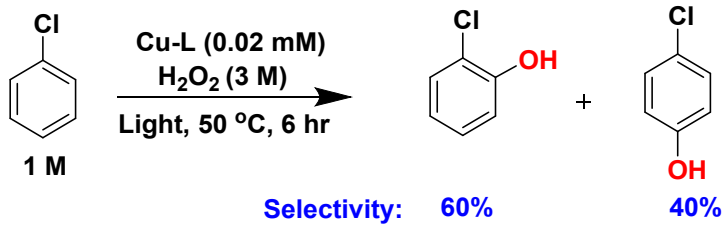


Figure S17. GC-MS trace for hydroxylation of bromobenzene using **CuL1**. The inset shows the GC-MS spectra for 2-bromophenol.

Scheme S4. Product distribution of photomediated hydroxylation of chlorobenzene using catalyst **CuL1**.



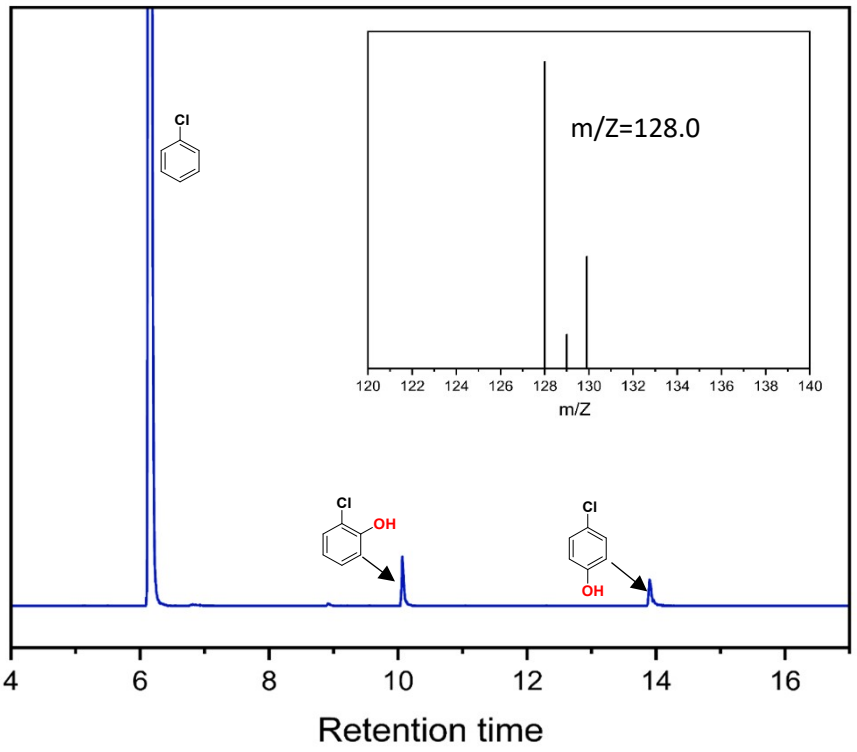
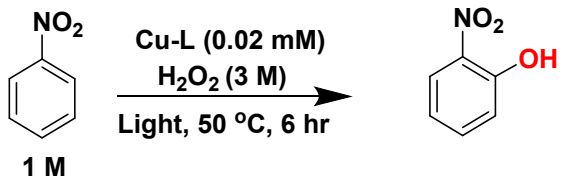


Figure S18. GC-MS trace for hydroxylation of chlorobenzene using **CuL1**. The inset shows the GC-MS spectra for 2-chlorophenol.

Scheme S5. Product distribution of photo-mediated hydroxylation of nitrobenzene using catalyst **CuL1**.



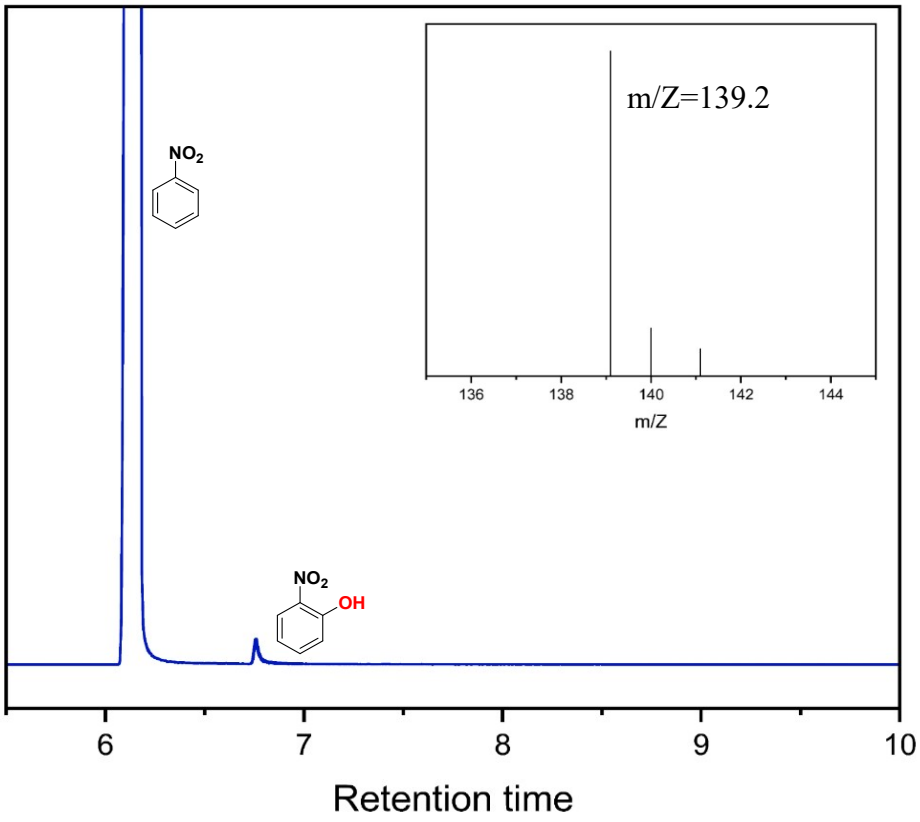
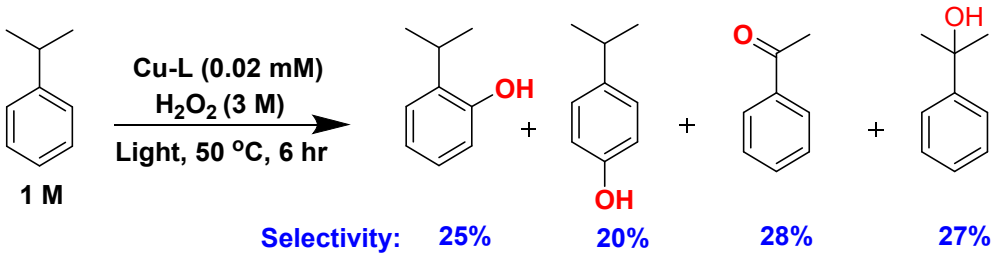


Figure S19. GC-MS trace for hydroxylation of nitrobenzene using **CuL1**. The inset shows the GC-MS spectra for 2-nitrophenol.

Scheme S6. Product distribution of photo-mediated hydroxylation of cumene using catalyst **CuL1**.



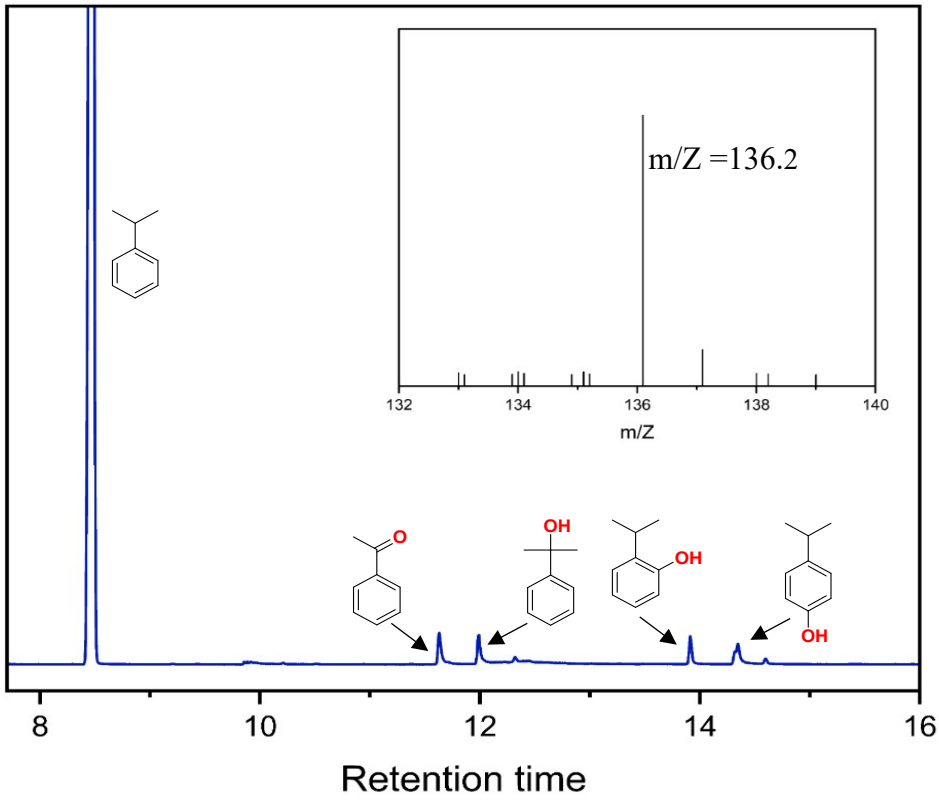
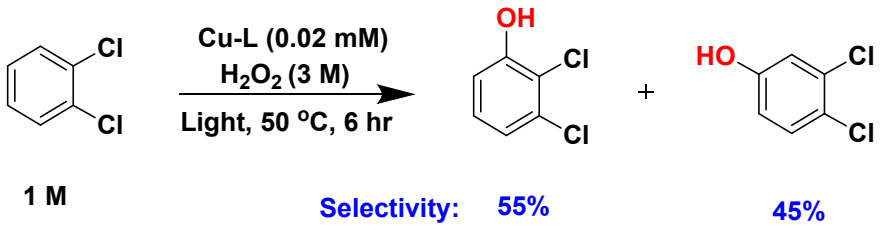


Figure S20. GC-MS trace for hydroxylation of cumene using **CuL1**. The inset shows the GC-MS spectra for 2-isopropylphenol.

Scheme S7. Product distribution of photo-mediated hydroxylation of 1,2-dichlorobenzene using catalyst **CuL1**.



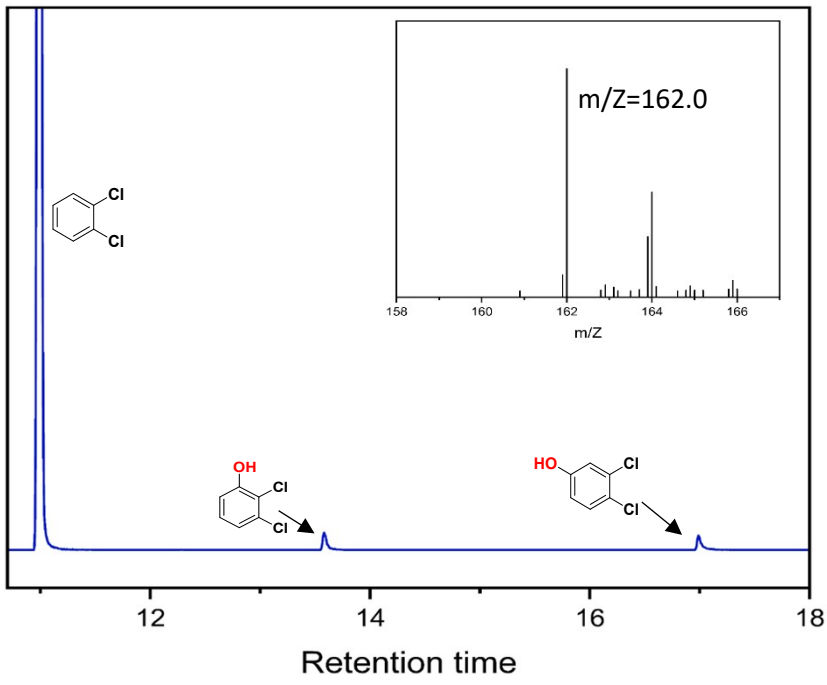
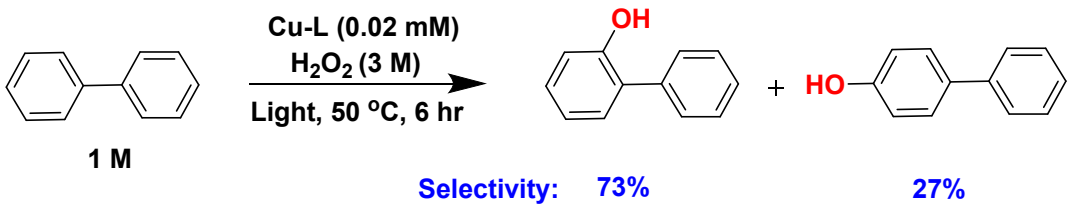


Figure S21. GC-MS trace for hydroxylation of 1,2-dichlorobenzene using **CuL1**. The inset shows the GC-MS spectra for 2,3-dichlorophenol

Scheme S8. Product distribution of photo-mediated hydroxylation of biphenyl using catalyst **CuL1**.



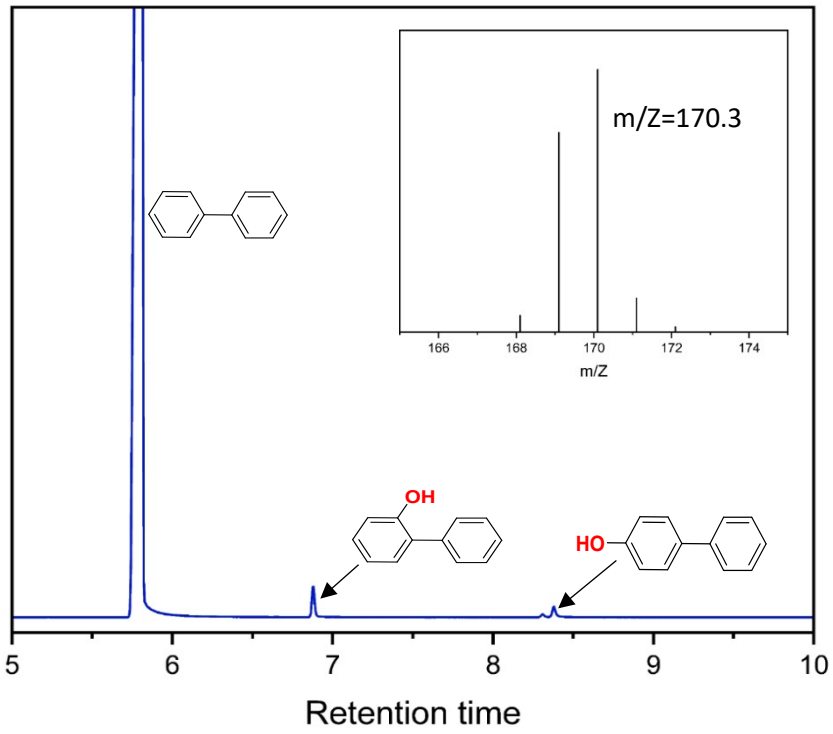
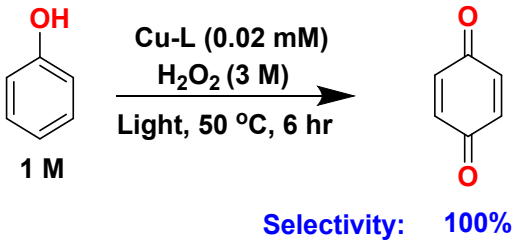


Figure S22. GC-MS trace for hydroxylation of biphenyl using **CuL1**. The inset shows the GC-MS spectra for the Ortho-hydroxylated product.

Scheme S9. Product distribution of photo-mediated hydroxylation of phenol using catalyst **CuL1**.



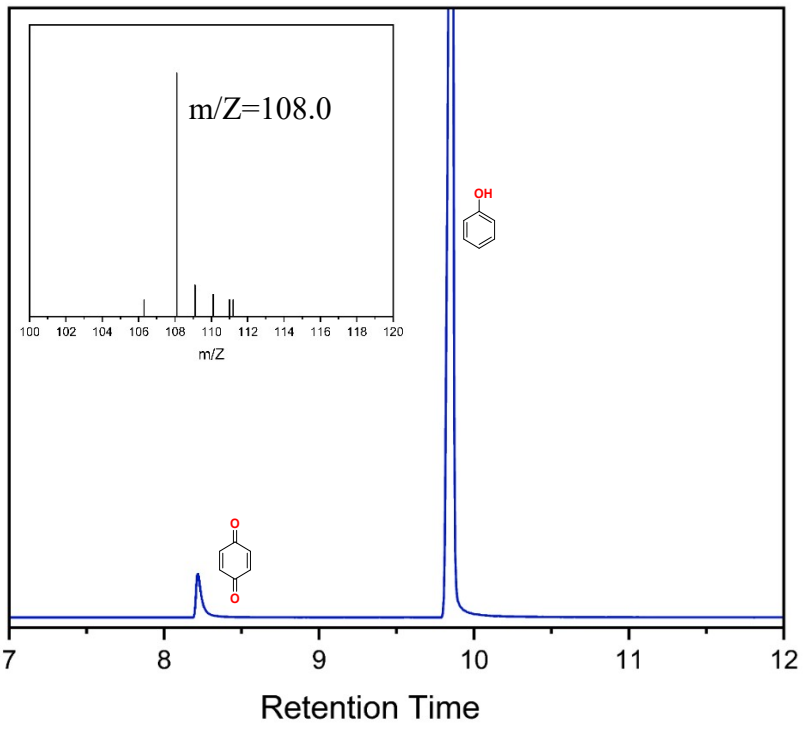
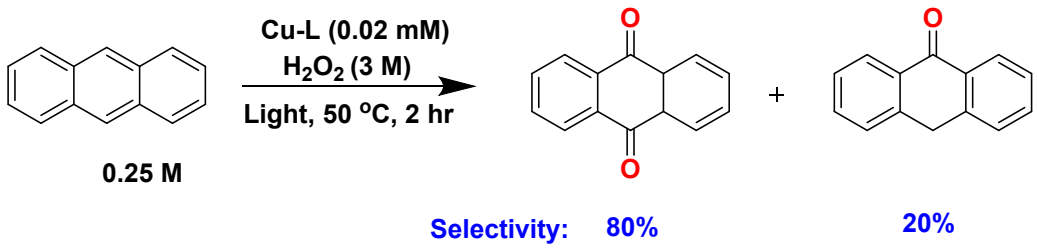


Figure S23. GC-MS trace for oxidation of phenol using **CuL1**. The inset shows the GC-MS spectra for Benzoquinone.

Scheme S10. Product distribution of photo-mediated hydroxylation of anthracene using catalyst **CuL1**.



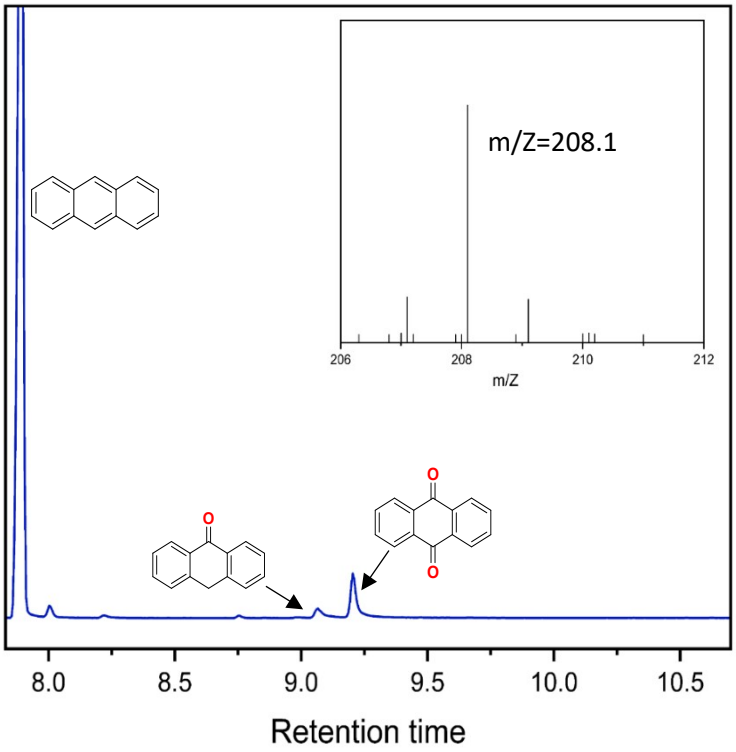
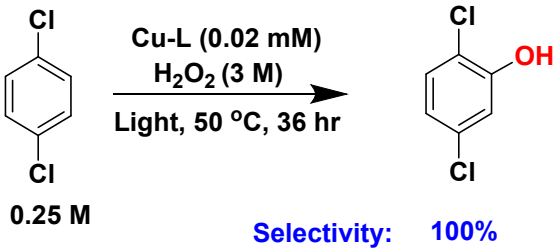


Figure S24. GC-MS trace for oxidation of anthracene using **CuL1**. The inset shows the GC-MS spectra for 9,10-Anthroquinone.

Scheme S11. Product distribution of photo-mediated hydroxylation of 1,4-dichlorobenzene using catalyst **CuL1**.



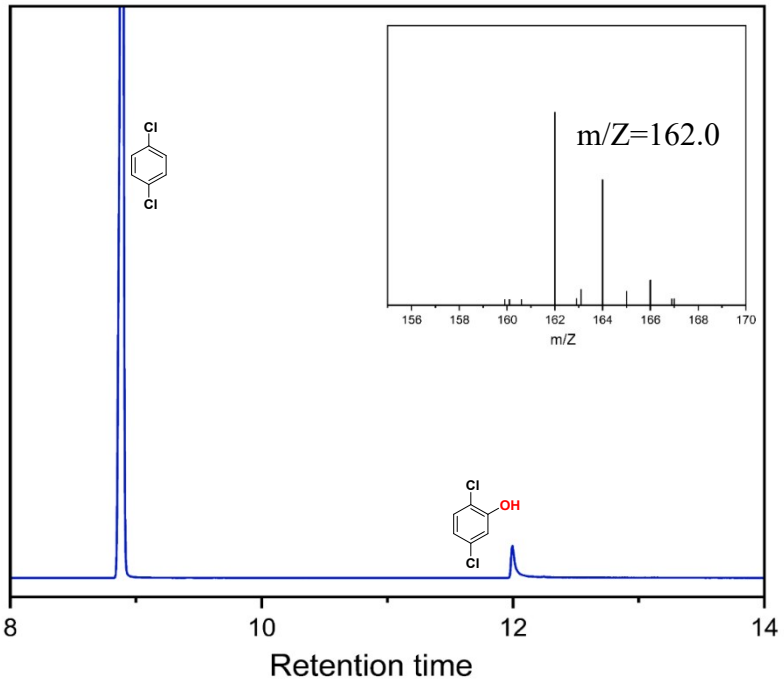


Figure S25a. GC-MS trace for hydroxylation of 1,4-dichlorobenzene using **CuL1**. The inset shows the GC-MS spectra for 2,5-dichlorophenol.

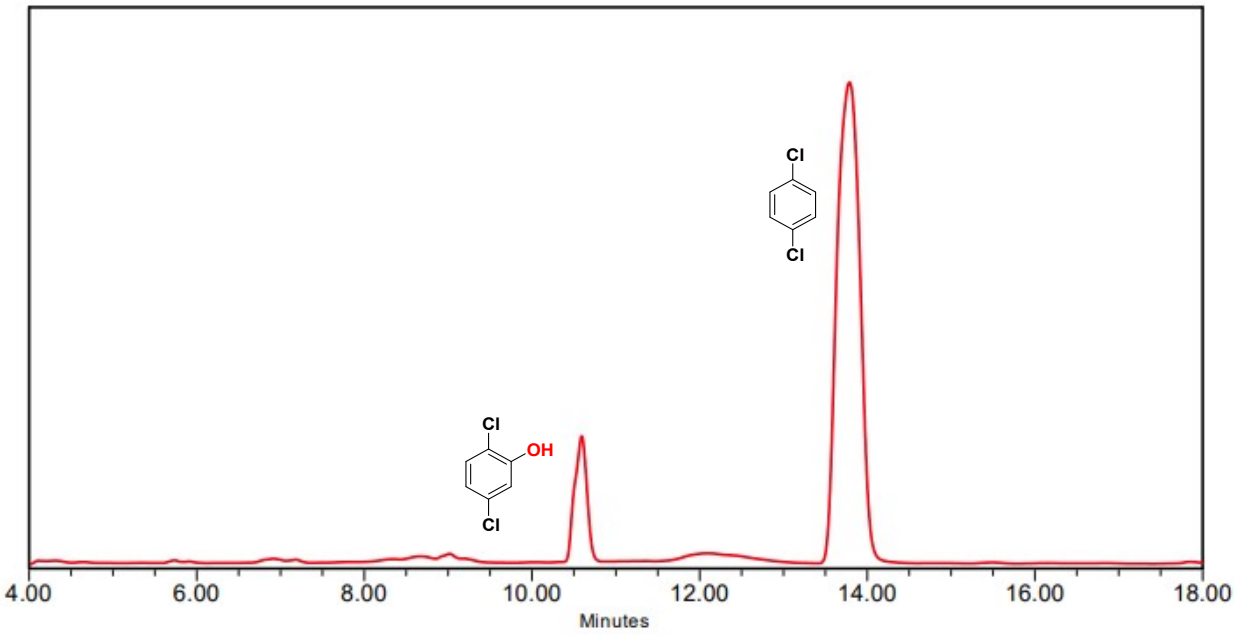


Figure S25b. Reverse phase HPLC chromatogram for hydroxylation of 1,4-dichlorobenzene using CuL1 (recorded at 235 nm).

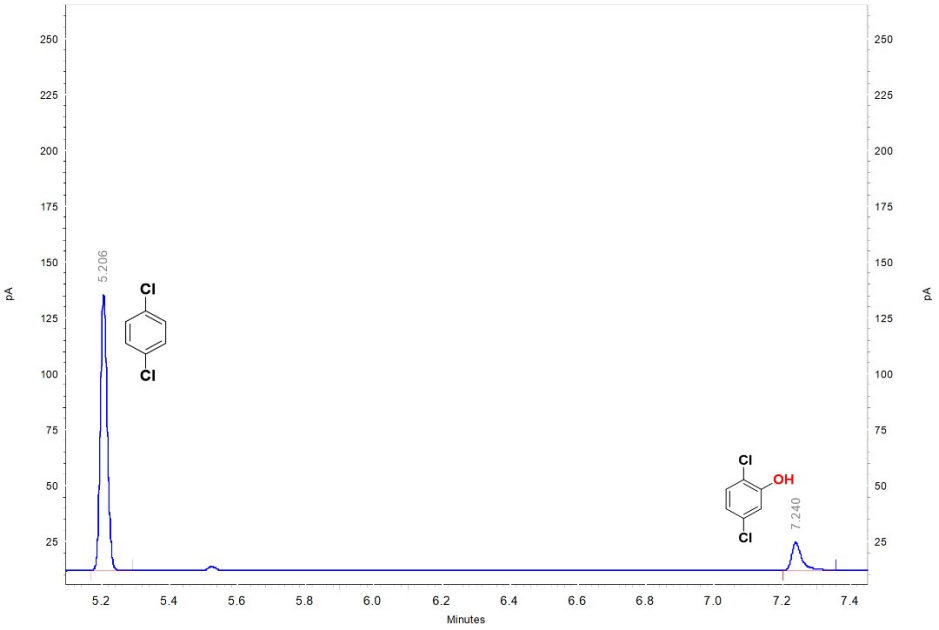


Figure S25c. GC chromatogram for hydroxylation of 1,4-dichlorobenzene using **CuL1** (36 hr).

Evidences for Fenton-pathway

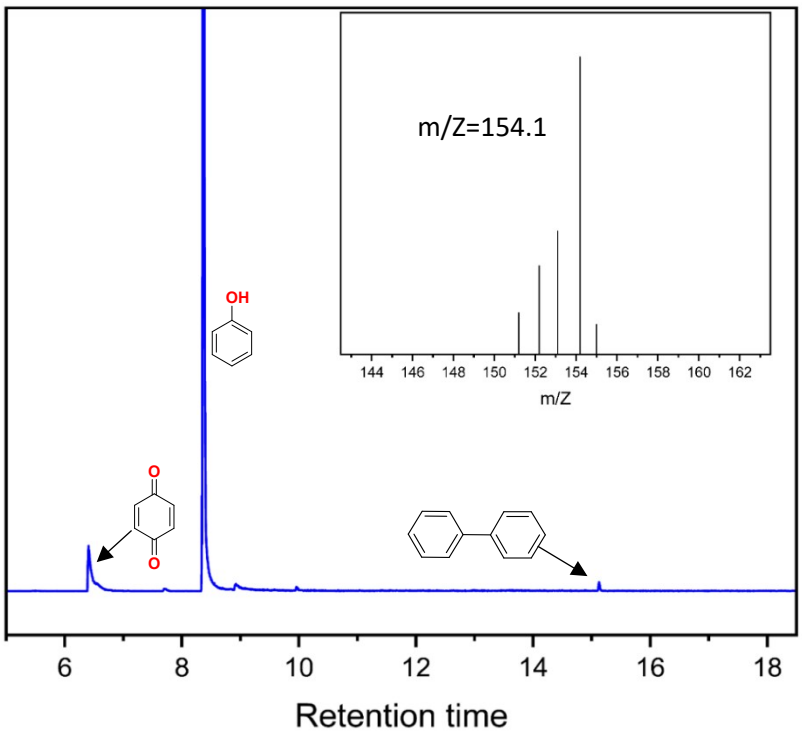


Figure S26. GC-MS trace for hydroxylation of benzene using **CuL1**. The inset shows the GC-MS spectra for Biphenyl.

Photo-mediated benzene hydroxylation in the presence of radical trap CCl_4

In a typical reaction, 0.02 mM of **CuL1** in H_2O: CH_3CN (5:1) and benzene 89 µL (1 M) then 307 µl of H_2O_2 and 290 µl of CCl_4 were added to the reaction mixture, and the reaction mixture was stirred under irradiation for 6 hours at 50 °C. A portion of the reaction mixture was analyzed by GC-MS and product identification by comparison with an authentic standard.

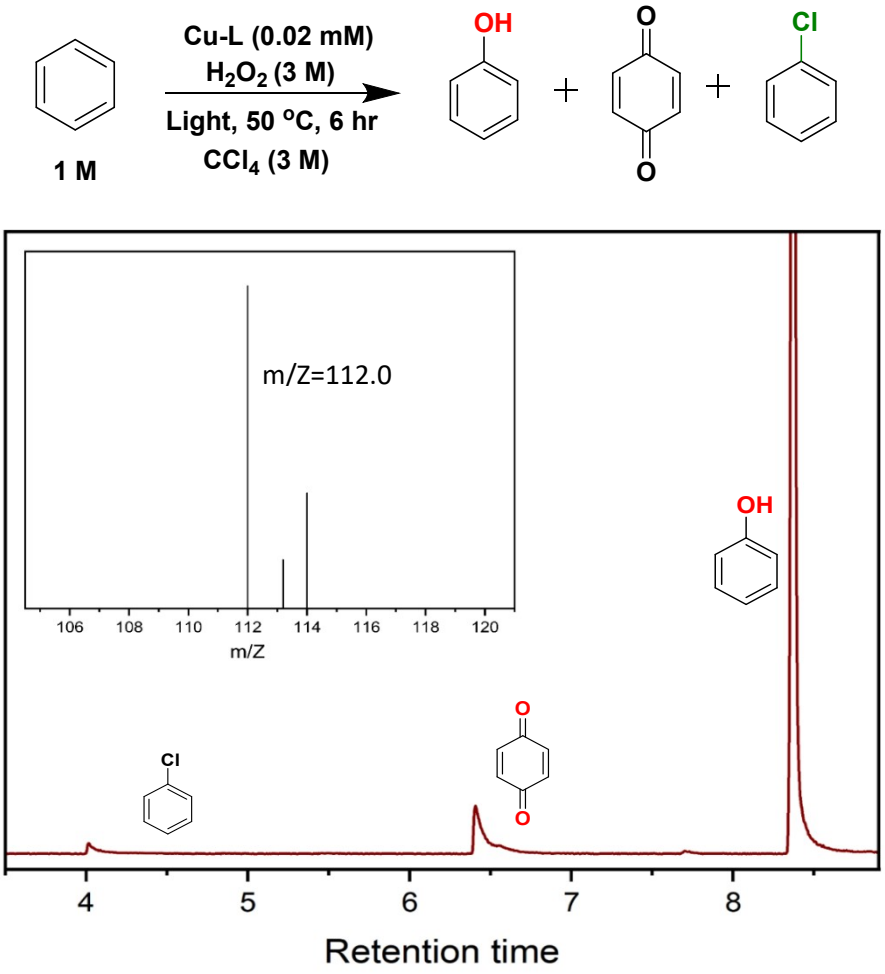


Figure S27. GC-MS trace for hydroxylation of benzene using **CuL1** in presence of CCl_4. The inset shows the GC-MS spectra for chlorobenzene.

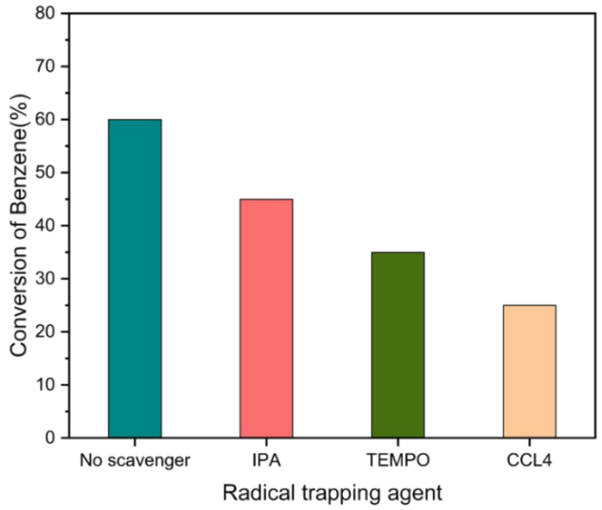


Figure S28. Radical trapping experiments using **CuL1**.

Determination of the Kinetic Isotope Effect (KIE)

A solution of **CuL1** (0.02 mM) in $H_2O/CHCl_3$ (1:5 v/v) 1mL and benzene 44.5 µL (0.5 M) and deuterated benzene 44.5 µL (0.5 M) was added to the solution, then 307 µL of 30% H_2O_2 was added slowly to the reaction mixture. This solution was stirred under irradiation at 50 ℃ for 6 hr. The product distribution was calculated by GC-MS. The Kinetic isotope effect (KIE) value was calculated by the ratio $K_H/K_D = 1.75 \pm 0.2$.

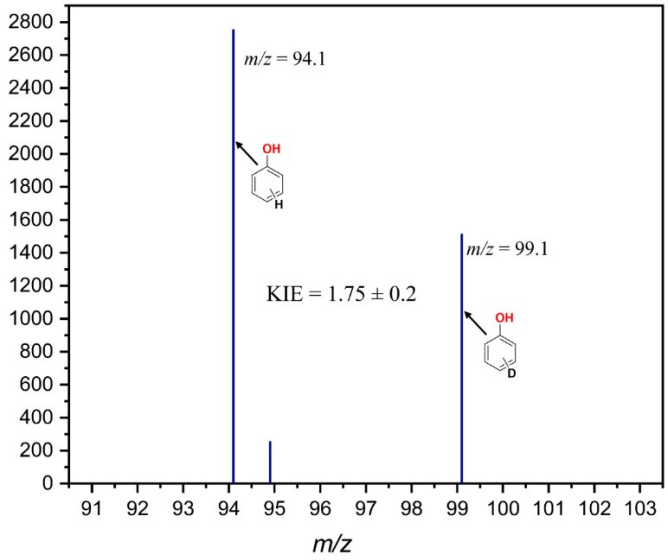


Figure S29. GC-MS spectra for measurement of KIE using C_6H_6 and C_6D_6 and **CuL1** as a catalyst.

EPR Data.

EPR spectrum was recorded in the absence of blue light, with **CuL1** catalyst by adding DMPO and we observed very small peak. Moreover, changing the intensity of the blue light (100% to 25%), we found less intense peak for EPR experiment.

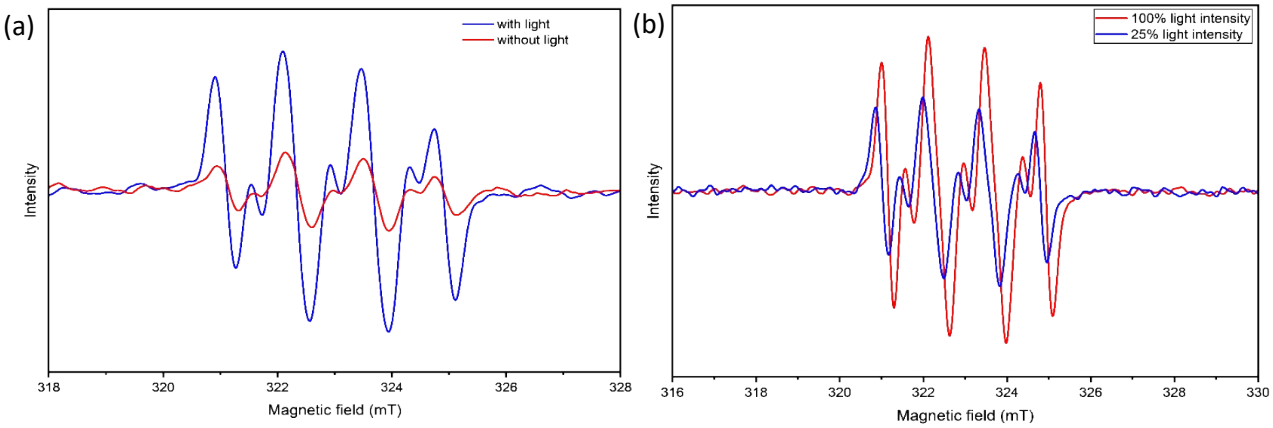


Figure S30. (a) A solution of **CuL1** (0.02 mM), H_2O_2 (3 M), benzene (1 M) and DMPO (0.2 mmol) was irradiated under blue LED or without blue LED in acetonitrile, and then an EPR spectrum was recorded. (b) A solution of **CuL1** (0.02 mM), H_2O_2 (3 M), benzene (1 M) and DMPO (0.2 mmol) was irradiated under blue LED (40 W) and blue LED (10W).

DFT.

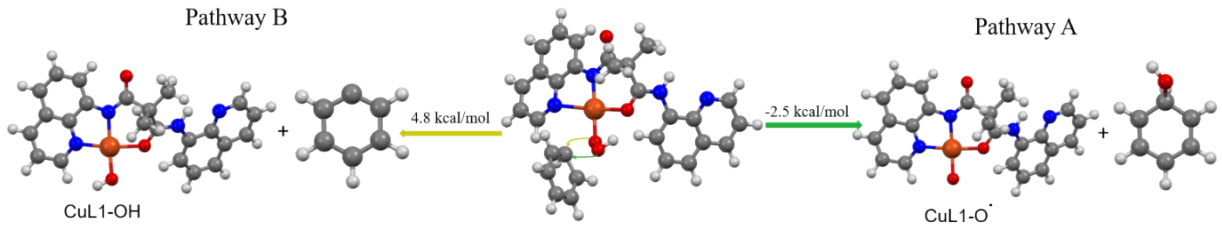


Figure S31. Reactivity of **CuLX-O•** or the OH• radical species towards the benzene ring.

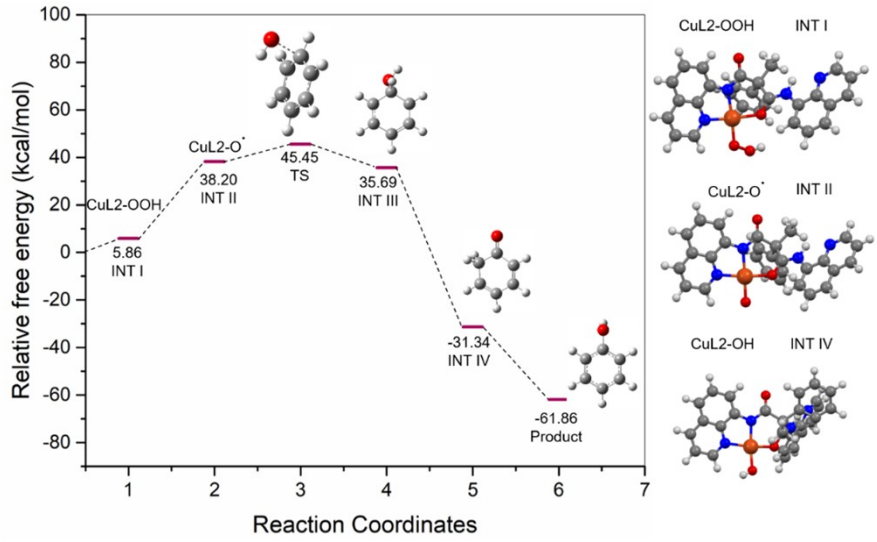


Figure S32. Gibbs free energy in kcal/mol of the Fenton-type mechanism for **CuL2**.

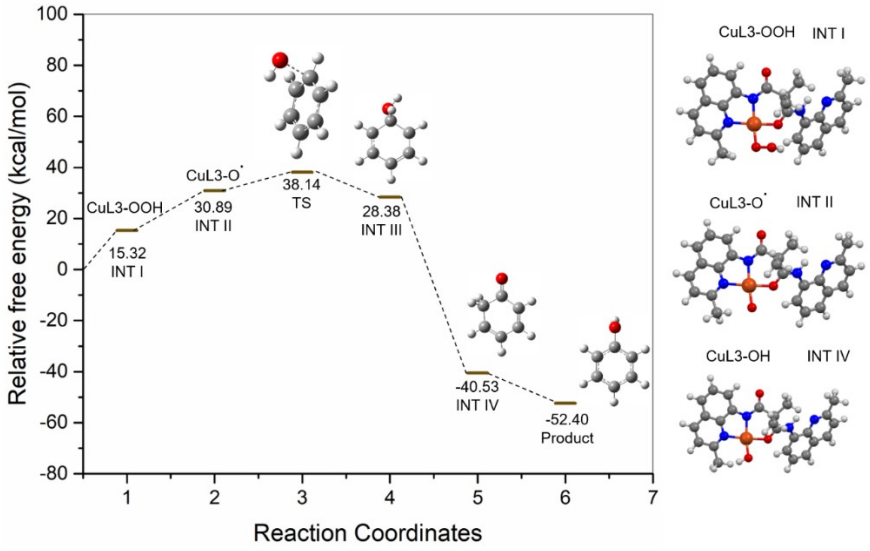


Figure S33. Gibbs free energy in kcal/mol of the Fenton-type mechanism for **CuL3**.

(I)

(II)

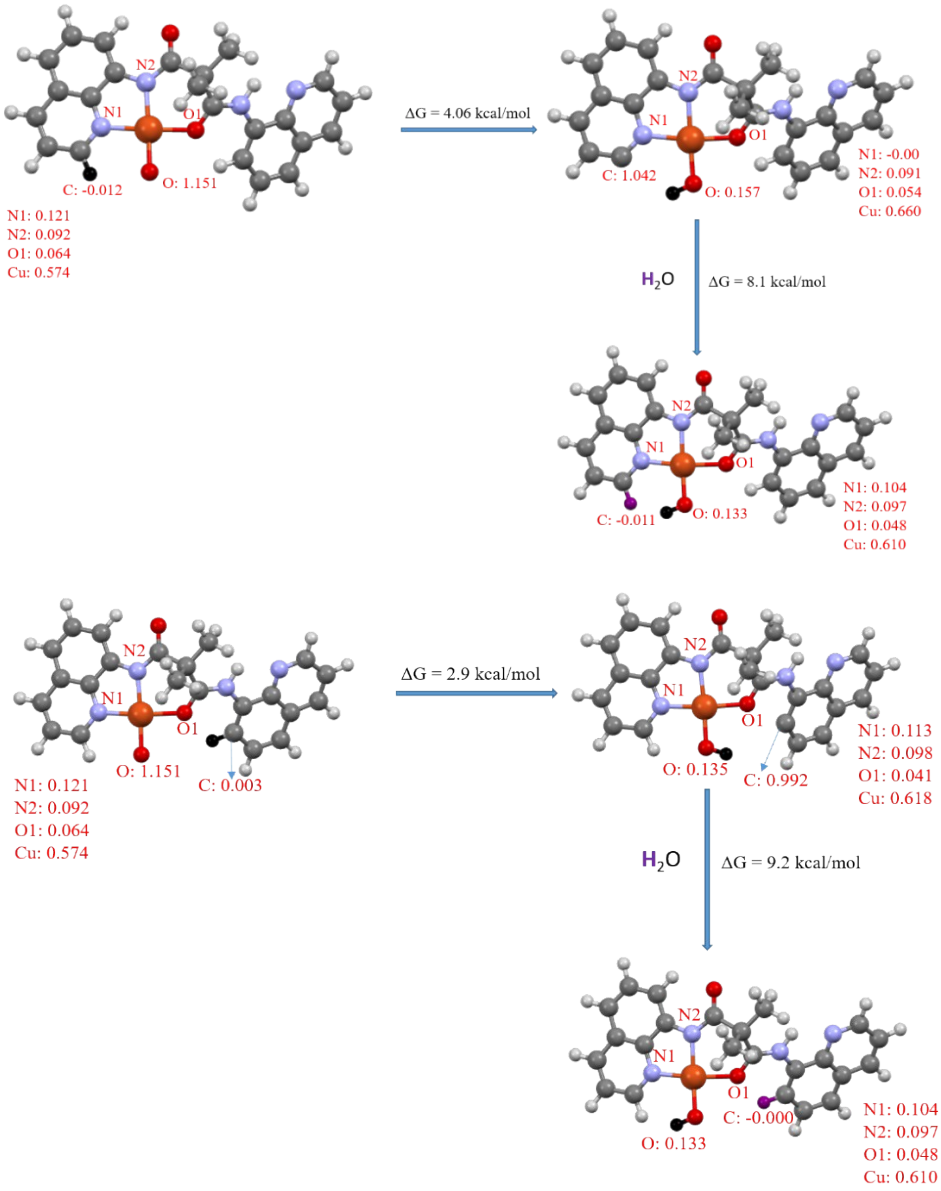
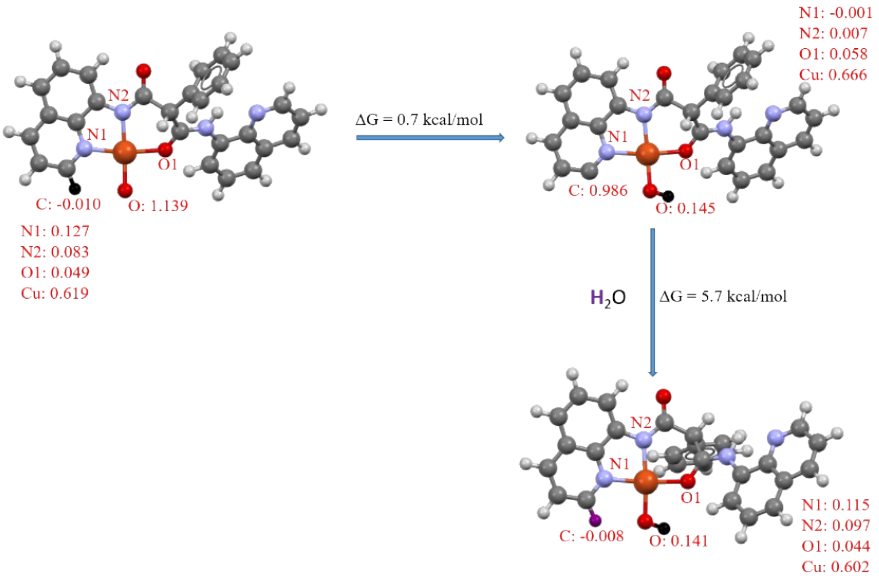


Figure S34. The thermodynamic barrier and Mulliken spin (of the selected atoms) for the intermolecular PCET oxidation and its conversion to the **CuL1˙-OH** species for **CuL1** (I), hydrogen abstraction from the metal-attached quinoline unit (II), and hydrogen abstraction from the free quinoline unit.

(I)



(II)

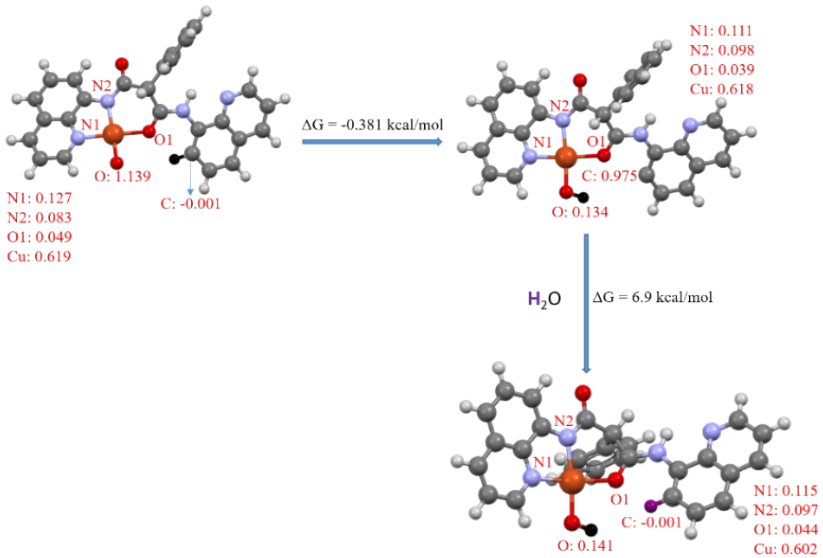


Figure S35. The thermodynamic barrier and Mulliken spin (of the selected atoms) for the intramolecular ligand oxidation and its conversion to the **CuL2˙-OH** species for **CuL2** (I), hydrogen abstraction from the metal-attached quinoline unit (II), and hydrogen abstraction from the free quinoline unit.

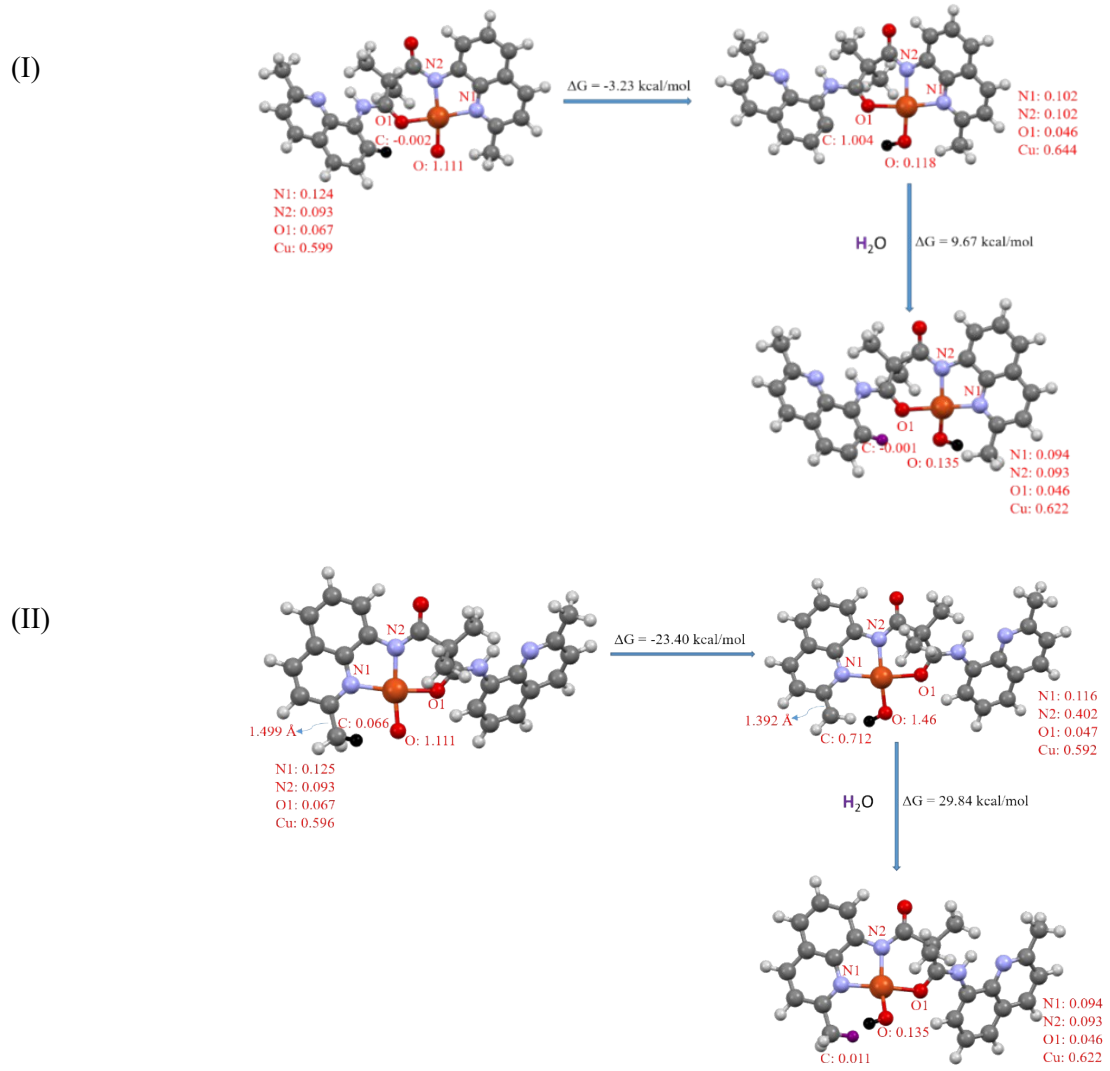


Figure S36. The thermodynamic barrier and Mulliken spin (of the selected atoms) for the intramolecular ligand oxidation and its conversion to the **CuL3'-OH** species for **CuL3**; (I) abstraction of quinoline hydrogen; (II) abstraction of $-CH_3$ hydrogen attached to the quinoline ring.

Table S3: Energy associated with H-atom abstraction in Kcal/mol for CuL1, CuL2 and CuL3.

Catalyst	Energy associated with H-atom abstraction Kcal/mol
CuL1	
H-atom abstraction from the metal-attached quinoline unit	4.06
H-atom abstraction from the free quinoline unit	2.9

CuL2 H-atom abstraction from the metal-attached quinoline unit H-atom abstraction from the free quinoline unit	 0.70 -0.38
CuL3 H-atom abstraction from the metal-attached quinoline unit H-atom abstraction of $-CH_3$ hydrogen attached to the quinoline ring.	 -3.23 -23.40

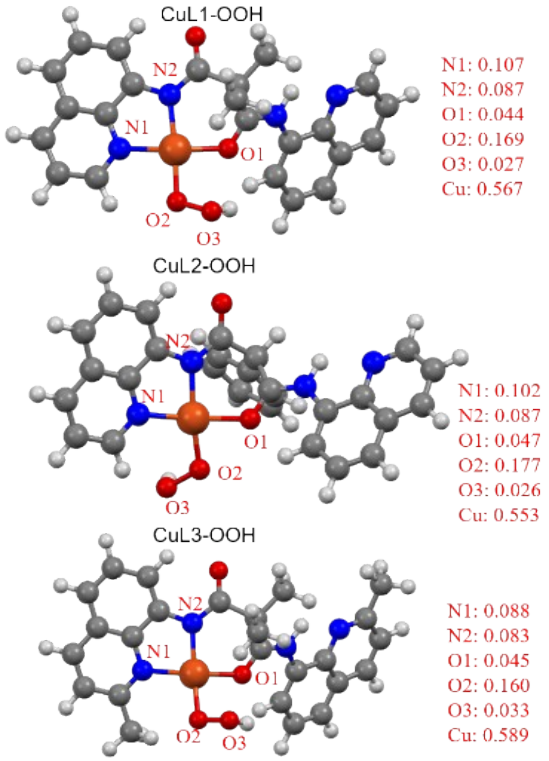


Figure S37. Mulliken spin density of selected atoms in the **LXCuOOH** intermediate.

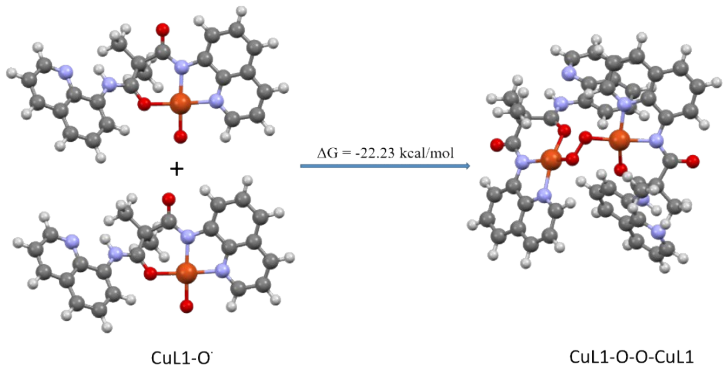


Figure S38. Thermodynamic barrier for dimerization of L1CuO˙.

Cartesian Coordina

CuL1

0.0132	3.0303	0.4461	C
1.3755	2.4169	0.009	C
-1.2187	2.4536	-0.3142	C
2.2676	3.1717	-0.3925	O
-1.9897	3.2263	-0.8937	O
1.5184	1.0689	0.1582	N
-1.4116	1.1132	-0.1992	N
2.7559	0.438	0.0055	C
2.7004	-0.9844	-0.1595	C
4.0207	1.0213	0.0385	C
3.8817	-1.7619	-0.329	C
5.1905	0.2417	-0.0917	C
4.108	2.0888	0.1553	H
1.35	-2.8643	-0.4114	C
3.7232	-3.1496	-0.5553	C
5.1429	-1.1193	-0.2829	C
6.1499	0.7458	-0.0528	H
2.4638	-3.6976	-0.6143	C
0.349	-3.2731	-0.4503	H
4.6038	-3.7676	-0.6918	H
6.0456	-1.7057	-0.4063	H
2.3109	-4.7516	-0.805	H
-3.7767	1.0332	-1.0468	C
-3.9384	-1.5891	-0.0297	C
-3.7475	2.0411	-1.4265	H
-1.6367	-2.5947	1.1279	C
-3.9472	-2.8761	0.5589	C
-2.8103	-3.3684	1.1568	C
-0.723	-2.9638	1.5773	H
-4.8615	-3.4591	0.5445	H
-6.0019	-1.5504	-0.6906	H
-2.7954	-4.3387	1.6355	H
1.4623	-1.5658	-0.1723	N
0.0057	-0.1948	0.1904	Cu
-5.0735	-0.9943	-0.6357	C
-4.9712	0.2824	-1.1355	C
-5.8328	0.7451	-1.6043	H
-1.5874	-1.3977	0.5612	N
0.0606	4.5498	0.2311	C
0.889	4.9795	0.7954	H
0.1963	4.806	-0.8195	H
-0.8714	5.0011	0.5735	H
-0.1816	2.7616	1.9642	C
-1.1147	3.2179	2.3062	H

CuL2

CuL3

0.0416	3.2453	0.3209	C
1.4187	2.5805	0.0235	C
-1.1787	2.6393	-0.4385	C
2.3672	3.2984	-0.3121	O
-1.9382	3.391	-1.0603	O
1.5136	1.236	0.2231	N
-1.3875	1.3085	-0.2658	N
2.7465	0.5747	0.1674	C
2.6997	-0.7993	-0.2254	C
3.9886	1.1084	0.4974	C
3.8892	-1.5679	-0.3349	C
5.1598	0.3254	0.4374	C
4.0577	2.143	0.7952	H
1.376	-2.5441	-1.0601	C
3.7587	-2.8866	-0.8349	C
5.1297	-0.9857	0.0193	C
6.1036	0.7829	0.7126	H
2.5299	-3.3534	-1.2191	C
4.6423	-3.5075	-0.9356	H
6.0357	-1.5756	-0.0551	H
2.4173	-4.3422	-1.6458	H
-2.6167	0.684	-0.4803	C
-2.7129	-0.6323	0.0847	C
-3.7527	1.1972	-1.1035	C
-3.9378	-1.3465	0.0822	C
-3.7095	2.1795	-1.5448	H
-1.6318	-2.2902	1.3467	C
-3.9583	-2.5875	0.7663	C
-2.8355	-3.036	1.4116	C
-4.8762	-3.1646	0.7919	H
-6.0006	-1.334	-0.5798	H
-2.8458	-3.9643	1.9689	H
1.4667	-1.3268	-0.5322	N
0.0111	-0.0052	0.1163	Cu
-5.0669	-0.7841	-0.5628	C
-4.9545	0.4567	-1.1463	C
-5.8117	0.8958	-1.6449	H
-1.5809	-1.149	0.6678	N
0.1328	4.7427	-0.0068	C
0.9417	5.2	0.5633	H
0.3269	4.9124	-1.0665	H
-0.805	5.2362	0.2497	H
-0.2335	3.0934	1.8441	C
-1.1732	3.5886	2.1045	H
-0.2996	2.0484	2.1447	H
0.5684	3.5689	2.4156	H
0.0495	-3.0725	-1.5281	C
-0.3051	-3.8786	-0.8794	H
-0.7078	-2.2937	-1.5681	H
0.1639	-3.4979	-2.5282	H
-0.4131	-2.7793	2.0758	C
-0.1732	-3.8081	1.7958	H
0.4535	-2.1484	1.8883	H
-0.6105	-2.7782	3.1522	H

CuL1-OOH

0.3968	1.5351	1.4223	C
-0.8144	1.9718	0.5069	C
1.0958	0.3236	0.7968	C
-0.8747	3.1577	0.1671	O
0.506	-0.7761	0.6873	O
-1.7193	1.0083	0.2214	N
-2.918	1.2801	-0.4509	C
-3.794	0.1507	-0.6022	C
-3.3645	2.4947	-0.9657	C
-5.0631	0.2659	-1.235	C
-4.6243	2.6029	-1.5985	C
-2.7379	3.3661	-0.8758	H
-4.1266	-2.1275	-0.2027	C
-5.8551	-0.9046	-1.3245	C
-5.4683	1.5274	-1.738	C
-4.9227	3.5727	-1.9811	H
-5.3942	-2.095	-0.8111	C
-3.7144	-3.0372	0.2184	H
-6.8276	-0.8483	-1.8012	H
-6.4321	1.6242	-2.2237	H
-5.9829	-3.0013	-0.8662	H
3.2267	-0.4563	-0.2385	C
4.5522	0.0417	-0.4707	C
2.8986	-1.7394	-0.6275	C
5.515	-0.8014	-1.0949	C
1.9019	-2.1153	-0.4632	H
6.0477	1.7807	-0.292	C
6.8082	-0.2594	-1.2997	C
7.0767	1.0271	-0.9001	C
6.2402	2.8004	0.0286	H
7.5713	-0.8687	-1.7714	H
5.8833	-2.7561	-1.952	H
8.0542	1.4706	-1.0426	H
-3.3672	-1.0482	-0.1098	N
5.1472	-2.1168	-1.478	C
3.8686	-2.5621	-1.2469	C
3.5824	-3.5651	-1.5406	H
4.832	1.3145	-0.0818	N
-0.1483	1.12	2.8148	C
-0.7252	1.9456	3.2364	H
-0.795	0.2439	2.7714	H
0.6799	0.8986	3.4925	H
1.3349	2.7364	1.6131	C
2.1725	2.4713	2.2633	H
1.7149	3.1256	0.667	H
0.7884	3.5482	2.0908	H
2.3626	0.4699	0.378	N
2.8239	1.363	0.5305	H
-1.5089	-0.9359	0.6224	Cu
-1.4728	-2.778	1.0987	O
-0.5317	-3.0013	2.1853	O
0.3253	-2.8996	1.7463	H

CuL2-OOH

CuL3-OOH

CuL1-O

0.3692	1.5966	1.2732	C
-0.8536	1.9038	0.3235	C
1.0808	0.3245	0.8017	C
-0.9333	3.0394	-0.1553	O
0.4972	-0.7834	0.7995	O
-1.7509	0.9035	0.165	N
-2.9686	1.0894	-0.5022	C
-3.8383	-0.0544	-0.4971	C
-3.4399	2.2341	-1.1402	C
-5.127	-0.019	-1.0995	C
-4.719	2.2627	-1.7419	C
-2.8179	3.1127	-1.1714	H
-4.1357	-2.2767	0.1587	C
-5.9112	-1.1957	-1.0315	C
-5.558	1.1745	-1.7306	C
-5.0366	3.1805	-2.2245	H
-5.4229	-2.319	-0.4049	C
-3.7051	-3.1397	0.6529	H
-6.8986	-1.1987	-1.48	H
-6.5367	1.21	-2.1942	H
-6.0031	-3.23	-0.3407	H
3.2426	-0.5707	-0.0592	C
4.5531	-0.0857	-0.3848	C
2.9482	-1.9103	-0.2155	C
5.5347	-0.9973	-0.8671	C
6.967	0.3411	-1.1495	C

1.9651	-2.2789	0.0297	H
6.0041	1.6951	-0.5127	C
6.8117	-0.4651	-1.1737	C
7.0486	0.8766	-0.9982	C
6.1722	2.7582	-0.3672	H
7.5879	-1.1257	-1.5442	H
5.9503	-3.0592	-1.3842	H
8.013	1.3142	-1.2232	H
-3.384	-1.1882	0.1117	N
5.2004	-2.3679	-1.017	C
3.937	-2.8008	-0.6963	C
3.6776	-3.8469	-0.8089	H
4.8022	1.2406	-0.2156	N
-0.1616	1.3488	2.7113	C
-0.7426	2.2149	3.0346	H
-0.8005	0.4688	2.7789	H
0.6741	1.2184	3.4033	H
1.2932	2.8232	1.3088	C
2.1343	2.6526	1.9858	H
1.6681	3.0935	0.3203	H
0.7376	3.6824	1.6815	H
2.3599	0.4232	0.407	N
2.8086	1.3351	0.4352	H
-1.5066	-0.978	0.7788	Cu
-1.3979	-2.6626	1.5467	O
5.5874	3.2475	0.0651	H
7.2662	2.738	0.3464	H

CuL2-O

CuL3-O

-0.4154	-1.4143	1.4061	C
-1.0142	-0.1424	0.7985	C
0.7546	-1.9267	0.4797	C
-0.3227	0.8902	0.6523	O
0.724	-3.1116	0.1302	O
1.7268	-1.0312	0.1916	N
-3.0978	0.8554	-0.1399	C
-4.4522	0.4657	-0.4023	C
-2.6773	2.1346	-0.4508	C
-5.3451	1.4064	-0.9823	C
-3.5813	3.0555	-1.0277	C
-1.6597	2.4303	-0.2523	H
-6.0654	-1.1937	-0.3083	C
-6.6715	0.9612	-1.2176	C
-4.8856	2.7107	-1.292	C
-3.2251	4.0518	-1.2617	H
-7.0282	-0.3191	-0.8866	C
-7.3909	1.6426	-1.6589	H
-5.5717	3.4238	-1.735	H
-8.0359	-0.6778	-1.0588	H
2.8807	-1.3787	-0.5219	C
3.8967	-0.3646	-0.5707	C
3.1445	-2.5822	-1.1737	C
5.1313	-0.6071	-1.2323	C
2.3989	-3.3588	-1.1572	H
4.5664	1.7968	0.0667	C
6.0959	0.4275	-1.2066	C
5.8224	1.6028	-0.5601	C
7.0511	0.2743	-1.697	H
6.2955	-2.0235	-2.3815	H
6.5528	2.4008	-0.5211	H
-4.8241	-0.8041	-0.0787	N
5.3532	-1.8489	-1.8755	C
4.3666	-2.804	-1.8432	C
4.5198	-3.7581	-2.3353	H
3.6429	0.8374	0.0469	N
-1.4447	-2.5411	1.5785	C
-2.2544	-2.225	2.2413	H
-1.8612	-2.8762	0.6271	H
-0.9617	-3.4042	2.0339	H
0.1566	-1.0657	2.8067	C
0.6652	-1.941	3.2156	H
0.8705	-0.2421	2.7812	H
-0.6541	-0.7908	3.486	H
-6.451	-2.6006	0.0592	C
-6.821	-3.1413	-0.817	H
-5.5956	-3.1353	0.4702	H
-7.2571	-2.5989	0.7993	H
4.2799	3.108	0.7364	C
3.7974	3.7926	0.0317	H
3.6073	2.9864	1.5877	H
5.2084	3.5737	1.0701	H
1.7074	0.8798	0.7058	Cu
1.606	2.5688	1.4528	O
-2.3064	-0.159	0.435	N
-2.8423	-1.0119	0.5746	H

CuL1-OH

0.3857	1.603	1.3125	C
-0.8419	1.9204	0.3746	C
1.0818	0.3298	0.8184	C
-0.9178	3.0592	-0.098	O
0.4852	-0.7669	0.8099	O
-1.7437	0.9242	0.2066	N
-2.938	1.1113	-0.5016	C
-3.7943	-0.041	-0.5569	C
-3.3932	2.2639	-1.1382	C
-5.0478	-0.0089	-1.2309	C
-4.6411	2.2914	-1.8011	C
-2.7807	3.1493	-1.1228	H
-4.0956	-2.2804	0.0258	C
-5.8154	-1.1981	-1.2408	C
-5.4631	1.192	-1.8577	C
-4.9464	3.216	-2.2786	H
-5.3434	-2.3305	-0.6194	C
-3.6871	-3.1542	0.5179	H
-6.7745	-1.2034	-1.7468	H
-6.4162	1.2234	-2.3722	H
-5.9073	-3.254	-0.6174	H
3.2248	-0.5702	-0.0832	C
4.5358	-0.0957	-0.423	C
2.9141	-1.905	-0.251	C
5.5002	-1.0123	-0.9308	C
1.9307	-2.2652	0.0049	H
6.0044	1.6708	-0.553	C
6.778	-0.4902	-1.2509	C
7.0323	0.8467	-1.0638	C
6.1864	2.7303	-0.3981	H
7.5411	-1.1548	-1.6409	H
5.8861	-3.0723	-1.4776	H
7.998	1.2765	-1.2987	H
-3.3599	-1.1803	0.0585	N
5.1491	-2.3774	-1.0914	C
3.886	-2.8003	-0.7565	C
3.6137	-3.8423	-0.877	H
4.8022	1.2259	-0.2426	N
-0.1288	1.3483	2.755	C
-0.7059	2.2126	3.0897	H
-0.7654	0.4666	2.828	H
0.7152	1.2145	3.4362	H
1.3162	2.8247	1.3465	C
2.1644	2.6437	2.0119	H
1.681	3.1005	0.3557	H
0.7703	3.6843	1.7326	H
2.3588	0.4253	0.4076	N
2.8146	1.3329	0.442	H
-1.544	-0.9375	0.8854	Cu
-1.385	-2.5168	1.8912	O
-2.2362	-2.8397	2.2026	H

CuL2-OH

CuL3-OH

0.4335	1.6118	1.3319	C
1.0038	0.2678	0.8617	C
-0.769	2.0214	0.3968	C
0.3061	-0.7667	0.8837	O
-0.7357	3.1482	-0.1092	O
-1.7659	1.1146	0.2603	N
3.0448	-0.8461	-0.0396	C
4.3853	-0.5009	-0.4136	C
2.6118	-2.1527	-0.1641	C
5.2502	-1.5128	-0.9104	C
3.4882	-3.1448	-0.6599	C
1.605	-2.4146	0.1192	H
6.0004	1.148	-0.6094	C
6.5633	-1.1084	-1.2642	C
4.7781	-2.8439	-1.0279	C
3.1223	-4.1611	-0.7467	H
6.9348	0.2017	-1.1169	C
7.2609	-1.8445	-1.6492	H
5.4434	-3.6113	-1.4073	H
7.9329	0.5299	-1.3816	H
-2.9391	1.3908	-0.4547	C
-3.825	0.2754	-0.6381	C
-3.3394	2.6183	-0.9816	C
-5.042	0.4255	-1.3569	C
-2.695	3.4726	-0.8622	H
-4.1939	-2.0247	-0.3273	C
-5.8338	-0.7334	-1.5427	C
-5.4093	-1.938	-1.0525	C
-6.7678	-0.6556	-2.0883	H
-6.3376	1.8018	-2.4107	H
-5.9894	-2.8394	-1.205	H
4.7718	0.7977	-0.2729	N
-5.406	1.6945	-1.8675	C
-4.5626	2.7609	-1.6691	C
-4.8272	3.7396	-2.0539	H
-3.4503	-0.9416	-0.1166	N
1.4737	2.742	1.3287	C
2.3092	2.4965	1.9895	H
1.8514	2.9611	0.3286	H
1.0152	3.6572	1.7006	H
-0.0861	1.4392	2.7846	C
-0.579	2.3602	3.1029	H
-0.7963	0.619	2.8863	H
0.7512	1.2476	3.4605	H
6.4017	2.5885	-0.4438	C
6.7166	3.0145	-1.4012	H
5.5699	3.1733	-0.0531	H
7.2503	2.6766	0.2414	H
-3.7585	-3.3645	0.1931	C
-3.9129	-4.1258	-0.575	H
-2.7155	-3.359	0.5005	H
-4.3702	-3.6519	1.0551	H
-1.7457	-0.7215	0.9866	Cu
2.2798	0.2358	0.4375	N
2.8185	1.0977	0.4427	H
-1.754	-2.0611	2.2972	O
-2.6394	-2.3608	2.5236	H

TS

-2.2104	0	0.797	O
1.5899	0	1.5422	H
0.1662	1.224	-0.477	C
0.8476	0	-0.7256	C
0.1662	-1.224	-0.477	C
-1.0931	-1.2174	0.0975	C
-1.7248	0	0.3915	C
-1.0931	1.2174	0.0975	C
0.6564	2.1588	-0.7204	H
1.7075	0	-1.3805	H
0.6564	-2.1588	-0.7204	H
-1.5984	-2.1522	0.3108	H
-2.7117	0	0.8397	H
-1.5984	2.1522	0.3108	H

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6 2.8858 H
4 0.3375 N
3 -0.1555 H
8 1.3914 Cu
9 3.0589 O
4 3.3309 H
2 0.568 C
3 1.3801 C
8 1.3393 C
8 0.494 C
7 -0.2933 C
2 -0.2548 C
9 2.0681 H
1 1.9753 H
9 0.458 H
3 -0.9442 H
1 -0.874 H

Benzene

-1.017	-0.9558	0	C
0.3194	-1.3586	0.0001	C
1.3362	-0.4029	-0.0001	C
1.0169	0.9559	0	C
-0.3192	1.3586	0.0001	C
-1.3363	0.4028	-0.0001	C
-1.8071	-1.6985	-0.0001	H
0.5673	-2.4142	0.0001	H
2.3744	-0.7156	-0.0001	H
1.8072	1.6984	0	H
-0.5675	2.4142	0	H
-2.3744	0.7158	0	H

Cyclohexa-2,4-dien-1-ol

-1.154	-1.2137	0.0463	C
0.1821	1.2566	0.2278	C
0.2106	-1.2476	0.2276	C
-1.125	-1.2383	-0.0547	C
-1.8365	-0.0202	-0.1923	C
-1.7075	2.1399	-0.1607	H
0.7025	2.2024	0.3297	H
0.7486	-2.184	0.3357	H
-1.6551	-2.1769	-0.1793	H
-2.8956	-0.0317	-0.4182	H
1.003	0.0162	0.3995	C
1.4538	0.0258	1.4059	H
2.1101	0.0846	-0.5525	O
2.7913	-0.5345	-0.2624	H

Cyclohexa-2,4-dien-1-one

-1.0337	1.2715	0	C
0.3212	1.2752	-0.0002	C
1.0767	0.0267	0	C
-1.2098	-1.148	0.0001	C
-1.8186	0.0492	0.0001	C
-1.567	2.2171	0	H
0.887	2.1998	-0.0002	H
-1.7867	-2.0668	0.0002	H
-2.8992	0.1267	0.0004	H
2.3077	0.0025	0.0002	O
0.2798	-1.2703	-0.0002	C
0.606	-1.8617	0.8658	H
0.6055	-1.8609	-0.8669	H

Phenol

-1.1286	1.2196	0	C
-0.2662	-1.1988	0	C
-0.9382	0.0257	0	C
-0.2184	1.2229	0	C
1.1739	1.1884	0	C
1.8564	-0.03	0	C
1.6439	-2.1736	0	H
-0.8288	-2.1269	0	H
-0.7553	2.1643	0	H
1.7276	2.1207	0	H
2.9397	-0.0511	0	H
-2.3063	0.1132	0	O
-2.6941	-0.7702	0	H

Benzene

-1.017	-0.9558	0	C
0.3194	-1.3586	0.0001	C
1.3362	-0.4029	-0.0001	C
1.0169	0.9559	0	C
-0.3192	1.3586	0.0001	C
-1.3363	0.4028	-0.0001	C
-1.8071	-1.6985	-0.0001	H
0.5673	-2.4142	0.0001	H
2.3744	-0.7156	-0.0001	H
1.8072	1.6984	0	H
-0.5675	2.4142	0	H
-2.3744	0.7158	0	H

Cyclohexa-2,4-dien-1-ol

-1.154	-1.2137	0.0463	C
0.1821	1.2566	0.2278	C
0.2106	-1.2476	0.2276	C
-1.125	-1.2383	-0.0547	C
-1.8365	-0.0202	-0.1923	C
-1.7075	2.1399	-0.1607	H
0.7025	2.2024	0.3297	H
0.7486	-2.184	0.3357	H
-1.6551	-2.1769	-0.1793	H
-2.8956	-0.0317	-0.4182	H
1.003	0.0162	0.3995	C
1.4538	0.0258	1.4059	H
2.1101	0.0846	-0.5525	O
2.7913	-0.5345	-0.2624	H

Cyclohexa-2,4-dien-1-one

-1.0337	1.2715	0	C
0.3212	1.2752	-0.0002	C
1.0767	0.0267	0	C
-1.2098	-1.148	0.0001	C
-1.8186	0.0492	0.0001	C
-1.567	2.2171	0	H
0.887	2.1998	-0.0002	H
-1.7867	-2.0668	0.0002	H
-2.8992	0.1267	0.0004	H
2.3077	0.0025	0.0002	O
0.2798	-1.2703	-0.0002	C
0.606	-1.8617	0.8658	H
0.6055	-1.8609	-0.8669	H

Phenol

-1.1286	1.2196	0	C
-0.2662	-1.1988	0	C
-0.9382	0.0257	0	C
-0.2184	1.2229	0	C
1.1739	1.1884	0	C
1.8564	-0.03	0	C
1.6439	-2.1736	0	H
-0.8288	-2.1269	0	H
-0.7553	2.1643	0	H
1.7276	2.1207	0	H
2.9397	-0.0511	0	H
-2.3063	0.1132	0	O
-2.6941	-0.7702	0	H