

## Supporting Information

# A Novel Cu(I)-Based Coordination Polymer for Efficient Photocatalytic Oxidation of C(sp<sup>3</sup>)-H Bonds

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## 1. Experimental Section.

### Materials and methods

Unless otherwise specified, all substrates were received from commercial suppliers and had not been purified. Chemicals were purchased from Sigma-Aldrich, Chempur, TCI, or Alfa Aesar.

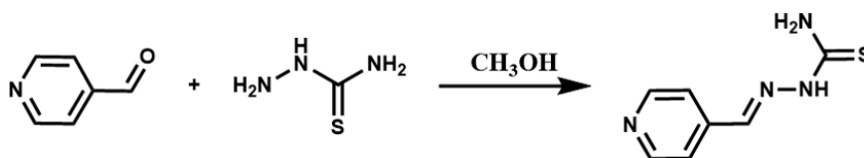
$^1\text{H}$  NMR data were collected on a Varian INOVA-600 MHz, Bruker Avance III 400 MHz spectrometer at ambient temperature. Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets on JASCO FT/IR-430 spectrometer. Powder XRD diffractograms were obtained on a Rigaku D/Max-2400 X-ray diffractometer with a sealed Cu tube ( $\lambda = 1.54178 \text{ \AA}$ ). The solid UV-vis spectra were recorded on a Hitachi U-4100 UV-vis-NIR spectrophotometer. Liquid UV-vis spectra were performed on a TU-1900 spectrophotometer. The solid UV-vis spectra were recorded on a Hitachi U-4100 UV-vis-NIR spectrophotometer. And thermogravimetric analyses (TGA) were performed at a ramp rate of  $10 \text{ }^\circ\text{C}/\text{min}$  in a nitrogen flow with an SDTQ600 instrument. The solid fluorescence spectrum and the time-resolved luminescence spectrum were measured on an Edinburgh FIS1000 instrument. The light sources are 455 nm LEDs (30 W), were purchased from Shenzhen Xinxingyuan Photoelectric Technology. Electron paramagnetic resonance (EPR) experiments were conducted on a Bruker E500 instrument, and the intensity was recorded at 100 K. X-ray photoelectron spectroscopy (XPS) signals were collected on a Thermo ESCALAB Xi<sup>+</sup> spectrometer. The microstructure and morphology observations of samples were performed with transmission electron microscope (TEM) of a JEM-1400Flash, scanning electron

microscope (SEM) of HITACHI UHR FE-SEM SU8220. The elemental analyses of C, H, N and S were performed on a Vario EL cube elemental analyzer.

### Preparation:

#### (1) The synthetic routes of the Pyhc

The mixture of 4-Pyridinaldehyde (1.07g, 10 mmol) and thiosemicarbazide (0.92 g, 10.1 mmol) in dry CH<sub>3</sub>OH solution (40 mL) was stirred over 8 h at 75 °C. The yellow precipitate was collected by filtration, washed with dry CH<sub>3</sub>OH and dried in vacuum.<sup>S1</sup> Yield: 1.66 g, 92%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 11.72 (s, 1H), 8.65 – 8.53 (m, 2H), 8.40 (s, 1H), 8.22 (s, 1H), 8.00 (s, 1H), 7.83 – 7.72 (m, 2H).



**Figure S1.** Synthesis route of Pyhc.

#### (2) The synthesis of CuCl-Pyhc

At room temperature, the 3 mL solution of 0.04 mM CuCl in acetonitrile (CH<sub>3</sub>CN) was slowly diffused into a 2.0 mL solution of 0.02 mM ligand Pyhc in N, N'-dimethylformamide (DMF). The interlayer solvent used was a 7.0 mL solution of DMF and CH<sub>3</sub>CN in a ratio of 1:6 (v / v). After approximately two weeks, block-shaped crystals with a yellow hue can be formed on the inner wall of the tube. These crystals can then be washed with ethanol and left to dry at room temperature, resulting in crystals that are suitable for X-ray structural analysis. Yield: 76% (based on ligand Pyhc). Elemental analysis calcd for C<sub>7</sub>H<sub>8</sub>ClCuN<sub>4</sub>S: C, 30.11; H, 2.887; N, 20.06; S, 11.48 (%). Found: C, 30.09; H, 2.727; N, 19.87; S, 11.38 (%).

**Electrochemical Experiment:** Solid-state cyclic voltammograms were measured on a Zahner PP211 instrument and measurements were performed on a three-electrode system with the photocatalyst-coated glassy carbon as the working electrode, Pt plate as the counter electrode, and an Ag/AgCl as a reference electrode were used in aqueous solution of KCl (1.0 M) at a scan rate of 100 mV s<sup>-1</sup>.

**Photoelectrochemical Measurements:** Using a CHI 760E electrochemical workstation, photocurrent was measured in a standard three-electrode system with the photocatalyst-coated FTO as the working electrode, a Pt plate as the counter electrode, and Ag/AgCl as the reference electrode. A 455 nm LED was used as light source. A 1.0 M KCl solution was used as the electrolyte. The catalyst (2.0 mg) was added to a mixed solution with 20.0  $\mu$ L of 5 wt % Nafion and 1 mL of ethanol, and the working electrodes were prepared by dropping the suspension (100  $\mu$ L) onto the surface of an FTO plate with an area of 1.0 cm<sup>2</sup>.

EIS was performed with a 20.0  $\mu$ L suspension on the working electrode, the measurements were carried out with KCl (1.0 M) as the supporting electrolyte, the Ag/AgCl electrode as the reference electrode, and Pt wire as the counter electrode.

**DPBF bleaching experiment:** DPBF (50  $\mu$ M) dissolved in 3 mL of acetonitrile solution, added CuCl-Pyhc (2 mg), under air atmosphere, irradiated with white visible light at 400 nm - 760 nm LED, and detected with liquid UV-*vis* spectra. All stock solutions and samples prepared were kept in the dark before the measurements.

**Ortho diphenol oxidation experiment:** 3,5-DTBC (20  $\mu$ M) dissolved in 4 mL of acetonitrile and added CuCl-Pyhc (2 mg), and the mixture was then transferred to a

15.0 mL quartz test tube. The reaction was carried out under air atmosphere using a 455 nm LED light for irradiation. After each reaction, filtered CuCl-Pyhc, and then detected the characteristic absorption peak of product 3,5-DTBQ at 410 nm using liquid UV-*vis* spectra.

**Substrate encapsulation experiments:** The synthesized CuCl-Pyhc was submerged in an acetonitrile solution containing 4-ethylphenol for a duration of 12 hours. The resulting crystalline powder was filtered, rinsed with acetonitrile, and subsequently air-dried. The substrate-loaded crystals were directly used for IR and digested with DMSO-*d*<sub>6</sub> and Sulfuric acid-*d*<sub>2</sub>, the amounts of released substrate molecules were quantified by <sup>1</sup>H NMR.

**General Procedure Photocatalytic Oxidation of C(sp<sup>3</sup>)-H Bonds:** Typically, the solution was prepared by dispersing 5.0 mg of CuCl-Pyhc in 4 mL of CH<sub>3</sub>CN, and then adding 0.1 mmol of substrates to a 15.0 mL quartz test tube containing a stir bar. The reaction was conducted at a temperature of 40 °C, with O<sub>2</sub> being bubbled under illumination using a 455 nm LED and magnetic stirring. Subsequently, 0.1 mmol of 1,3,5-trimethoxybenzene, employed as an internal standard substance, was added to the system after the completion of the reaction. The catalyst was filtered, and the solvent was evaporated under vacuum conditions. The reaction yield was determined by monitoring the corresponding <sup>1</sup>H NMR spectra.

**Procedure of the Recyclability Experiment:** The reaction conditions were as previously stated. After each reaction, the catalyst was thoroughly washed with DMF and ether, followed by drying under vacuum. Subsequently, the catalyst was monitored

by PXRD and subsequently reused for the next reaction.

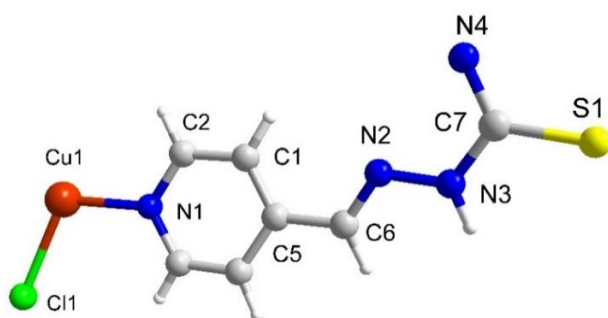
## **2. Single Crystal X-ray Crystallography**

The intensities were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation source; the data were acquired using the SMART and SAINT programs.<sup>S2,S3</sup> The structure was solved by direct methods and refined by full matrix least-squares methods by the program SHELXL-2014.<sup>S4</sup>

In the structural refinement of CuCl-Pyhc, all of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. The SQUEEZE subroutine in PLATON was used.<sup>S5</sup>

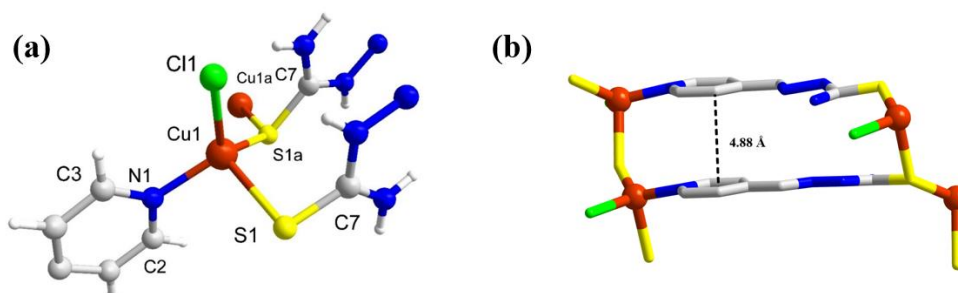
**Table S1.** Crystal data and structure refinements.

Compound	CuCl-Pyh
Empirical formula	C <sub>7</sub> H <sub>8</sub> ClCuN <sub>4</sub> S
Formula weight	279.22
Temperature/K	302.10
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	11.0800(12)
b/Å	12.3130(14)
c/Å	7.3157(8)
$\alpha$ /°	90
$\beta$ /°	95.985(4)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	992.63(19)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.868
$\mu/\text{mm}^{-1}$	2.641
F (000)	560.0
Crystal size/mm <sup>3</sup>	0.1 × 0.05 × 0.01
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 theta range for data collection/°	4.96 to 53.428
Index ranges	-13 ≤ h ≤ 13, 0 ≤ k ≤ 15, 0 ≤ l ≤ 9
Reflections collected	2083
Independent reflections	2083 [Rint = ?, Rsigma = 0.0286]
Data/restraints/parameters	2083/0/122
Goodness-of-fit on F <sup>2</sup>	1.090
Final R indexes [ $I \geq 2\sigma(I)$ ]	R1 = 0.0667, wR2 = 0.1462
Final R indexes [all data]	R1 = 0.0796, wR2 = 0.1566
Largest diff. peak/hole / e Å <sup>-3</sup>	2.28/-1.67
CCDC number	2329162



**Figure S2.** Asymmetric unit of CuCl-Pyh.

Selected bond distances (Å): Cu1-Cl1 2.355(6), Cu1-N1 1.996(19), N1-C2 1.35(4), C2-C1 1.39(5), C5-C1 1.33(5), C6-C5 1.44(3), N2-C6 1.26(3), N3-N2 1.37(3), N3-C7 1.35(3), N4-C7 1.32(3), S1-C7 1.71(2).

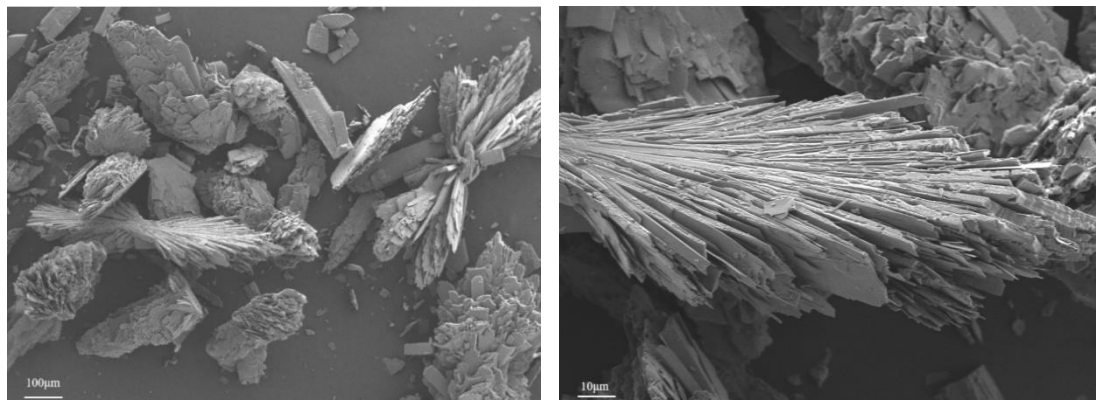


**Figure S3.** (a) Coordination geometry of the Cu atom in CuCl-Pyh. (b) The shortest C...C distances of CuCl-Pyh is 4.88 Å, and adjacent benzene rings are parallel to each other.

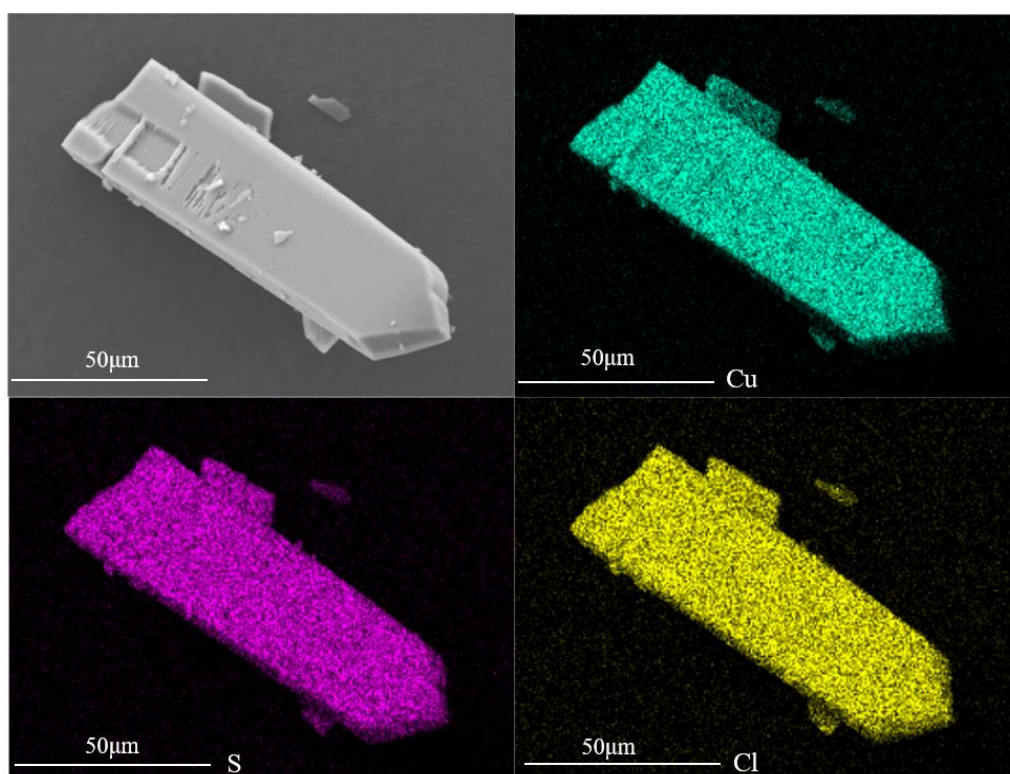
Cu-S bond distances (Å) and angles (°): Cu1-S1 2.241(6), Cu1-S1a 2.498(6); Cl1-Cu1-S1 98.1(2), S1-Cu1-C1 116.9(2), S1-Cu1-S1a 103.72(17), N1-Cu1-Cl1 111.4(6), N1-Cu1-S1 122.0(6), N1-Cu1-S1a 99.2(6), C7-S1-Cu1 109.2(8), C7-S1-Cu1a 95.0(8), Cu1-S1-Cu1a 129.4(3), C3-N1-Cu1 121.3(17), C2-N1-Cu1 121.8(19).



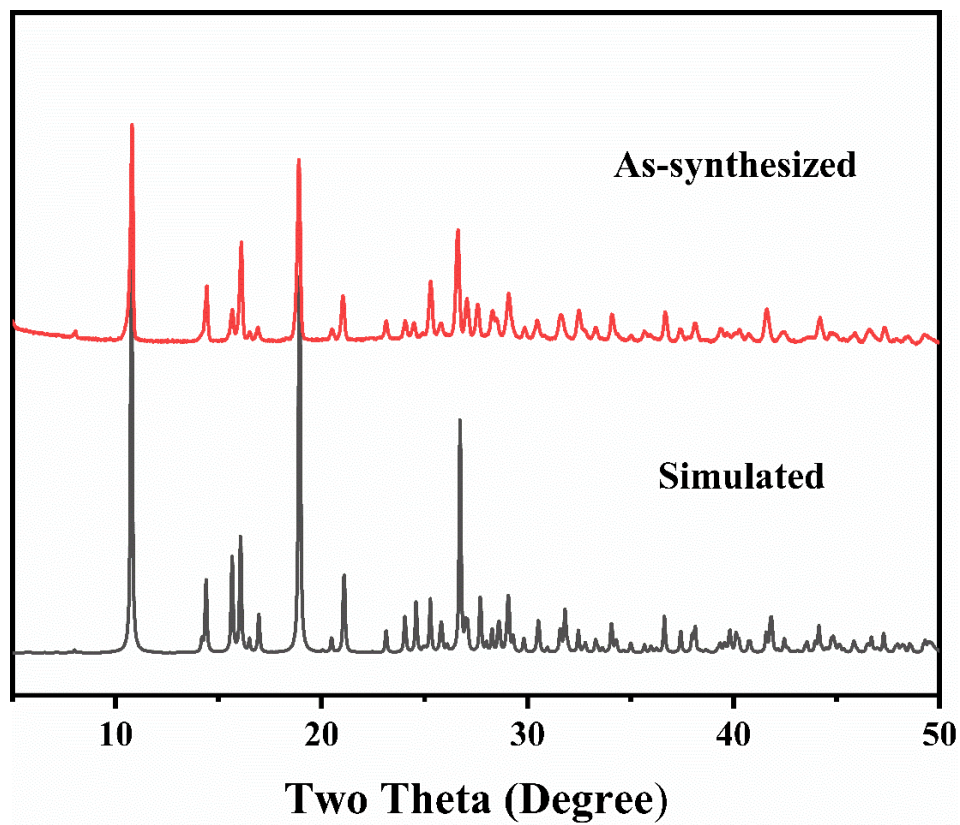
### 3. Characterizations of Catalysts



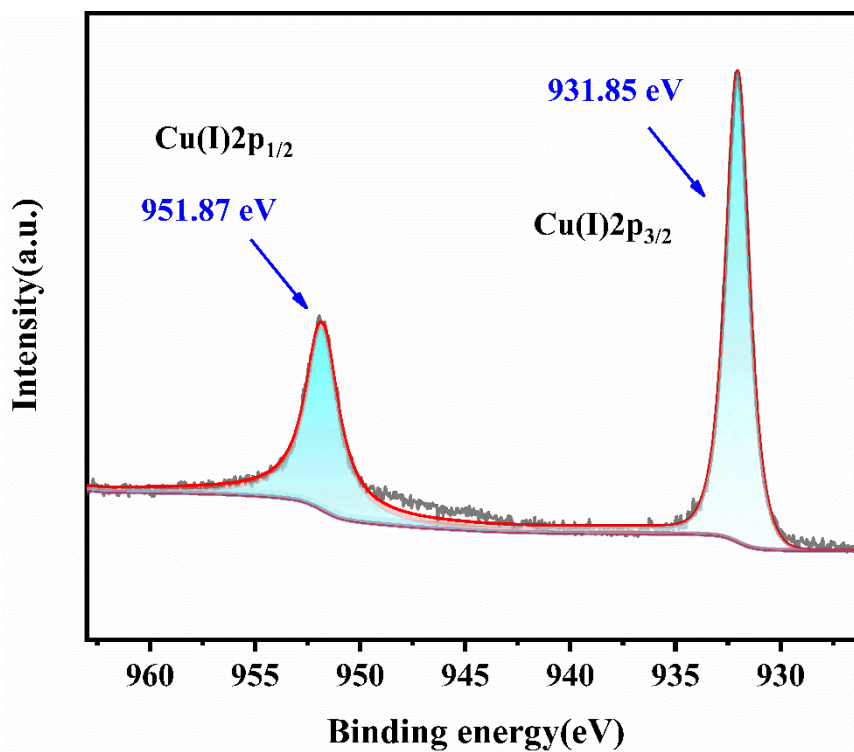
**Figure S4.** The overall SEM image and lateral details of CuCl-Pyhc.



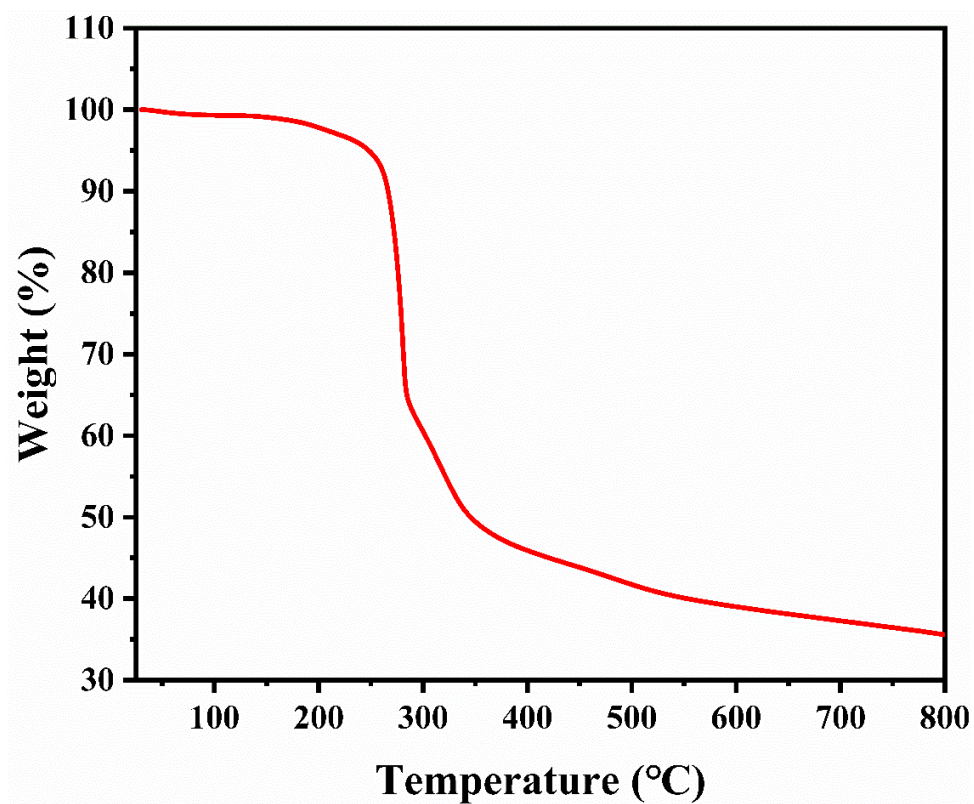
**Figure S5.** A magnified SEM image of CuCl-Pyhc and the elemental mapping images of CuCl-Pyhc.



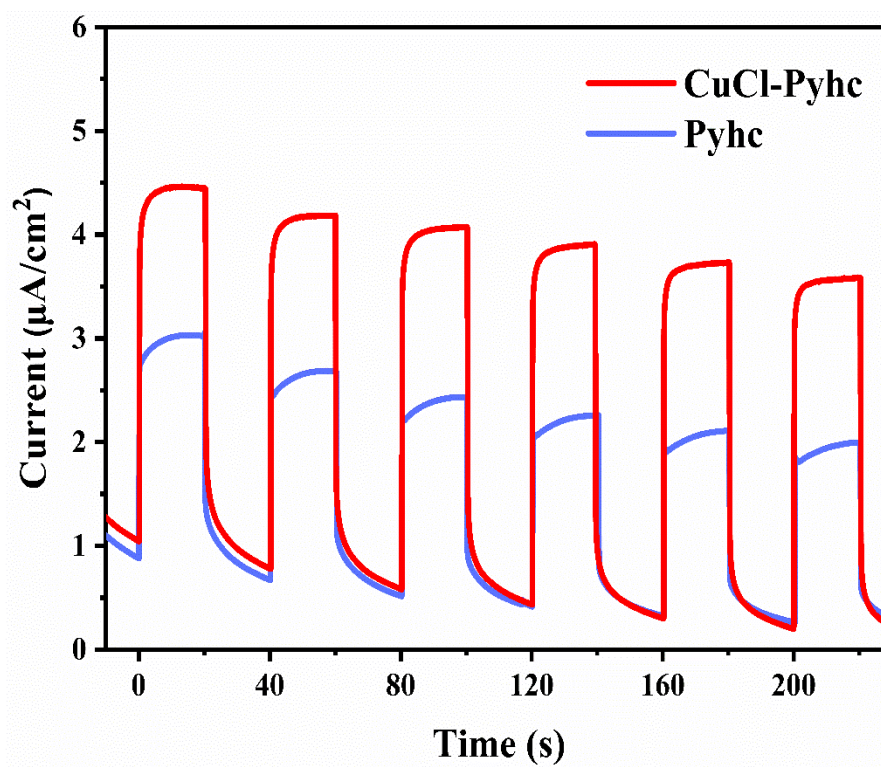
**Figure S6.** X-ray powder diffraction (XRD) patterns of freshly as-synthesized CuCl-Pyhc (red) and its simulated pattern based on the reported single-crystal data (black).



**Figure S7.** XPS spectra of Cu  $2p$  for freshly as-synthesized CuCl-Pyhc, two Voigt doublets at 931.85 eV and 951.87 eV assigned to Cu(I) species.



**Figure S8.** Thermogravimetric (TGA) figure of CuCl-Pyh<sub>c</sub> with heating rates of 10 °C/min.



**Figure S9.** Electrochemical photocurrent response testing of the catalysts CuCl-Pyhc and Pyhc.

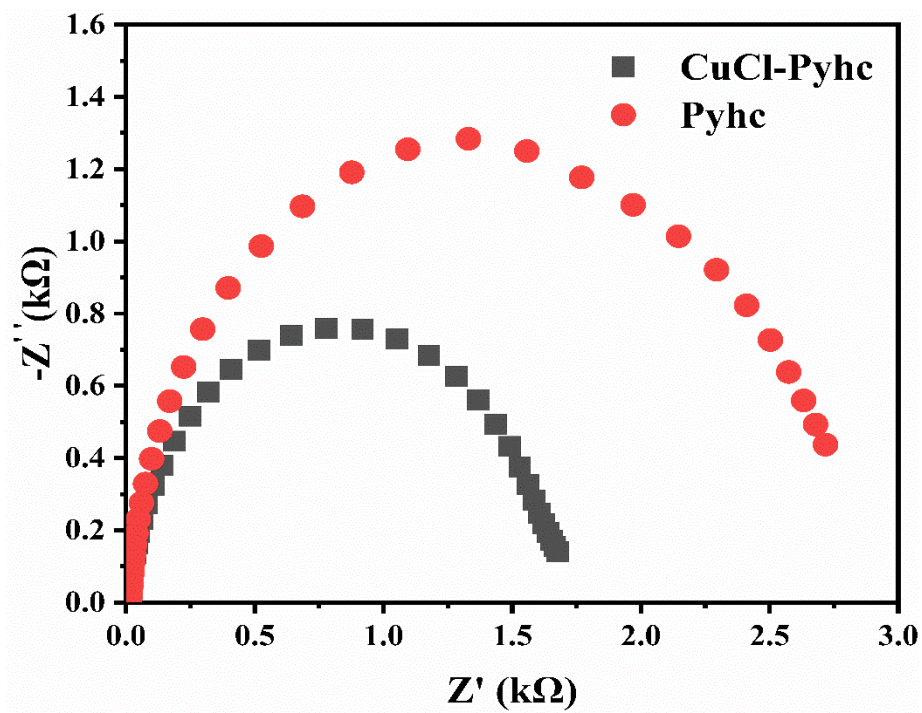
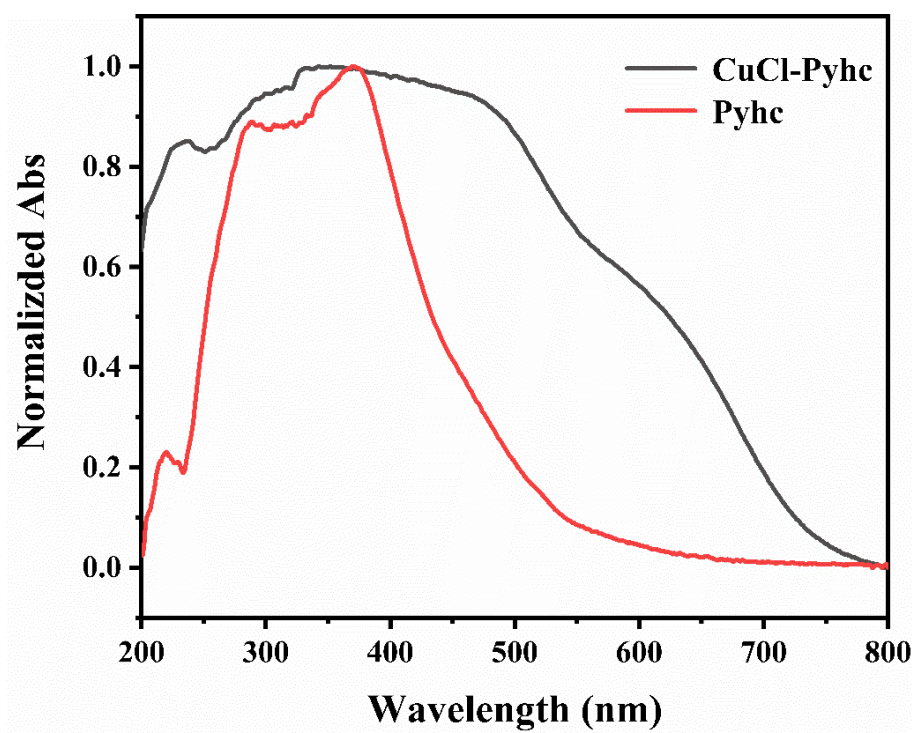
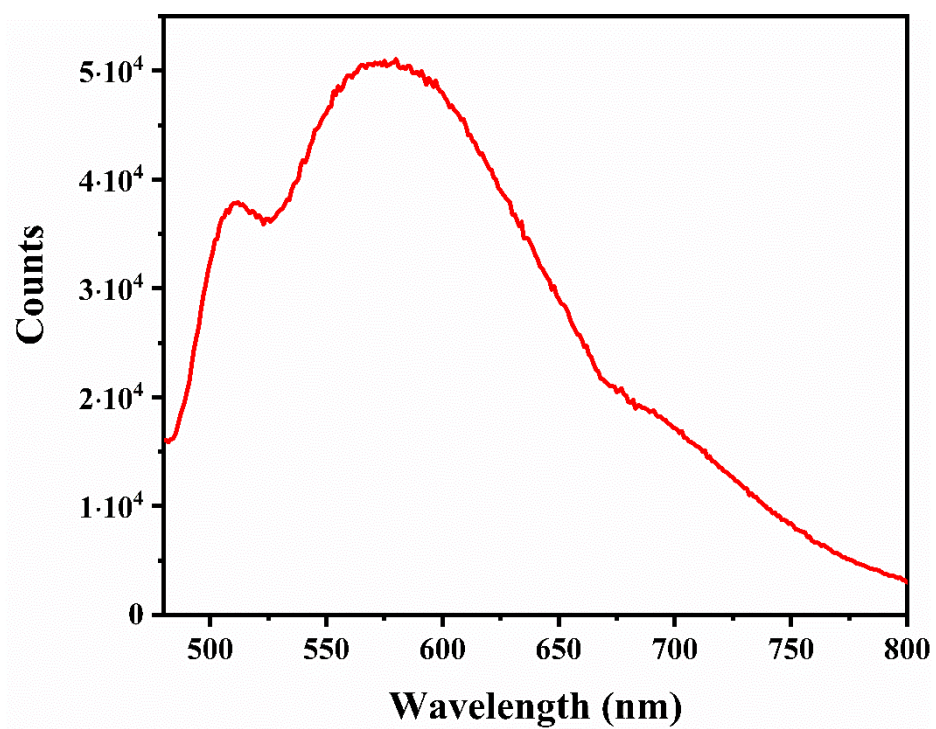


Figure S10. EIS plots of CuCl-Pyhc and Pyhc.

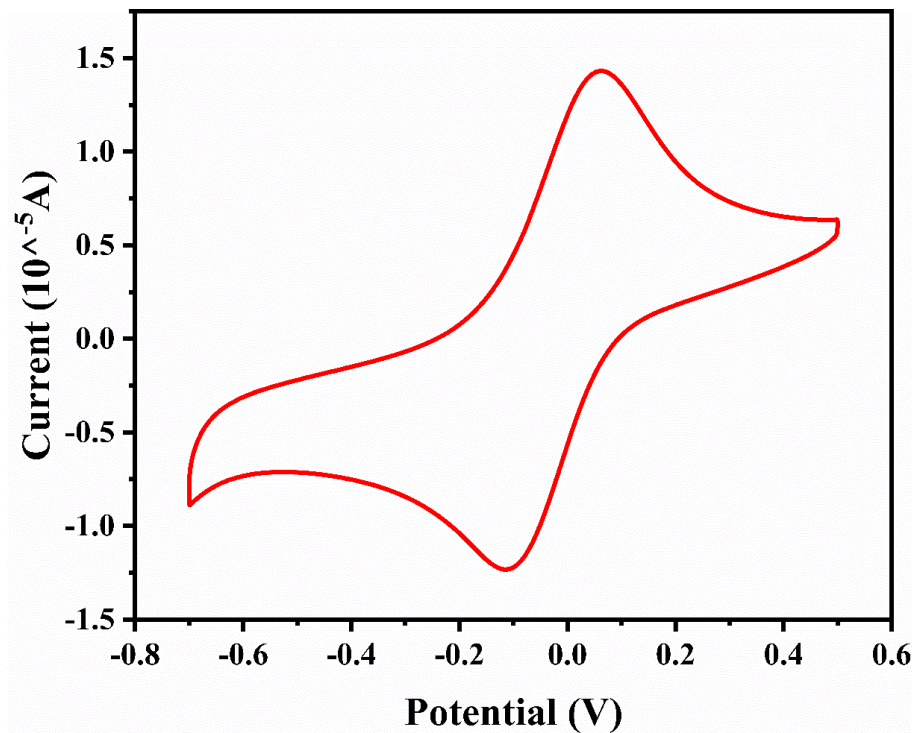


**Figure S11.** Solid UV-*vis* spectra of the free ligand Pyhc and the CuCl-Pyhc.



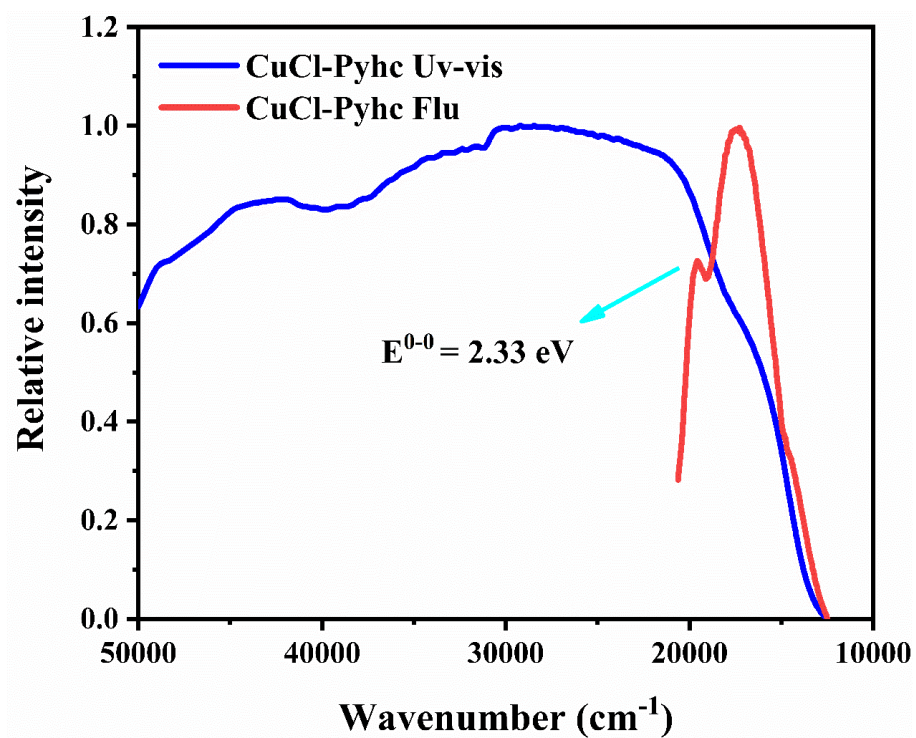
**Figure S12.** Fluorescence emission spectrum for CuCl-Pyhc excited by  $\lambda_{\text{ex}} = 455$  nm.





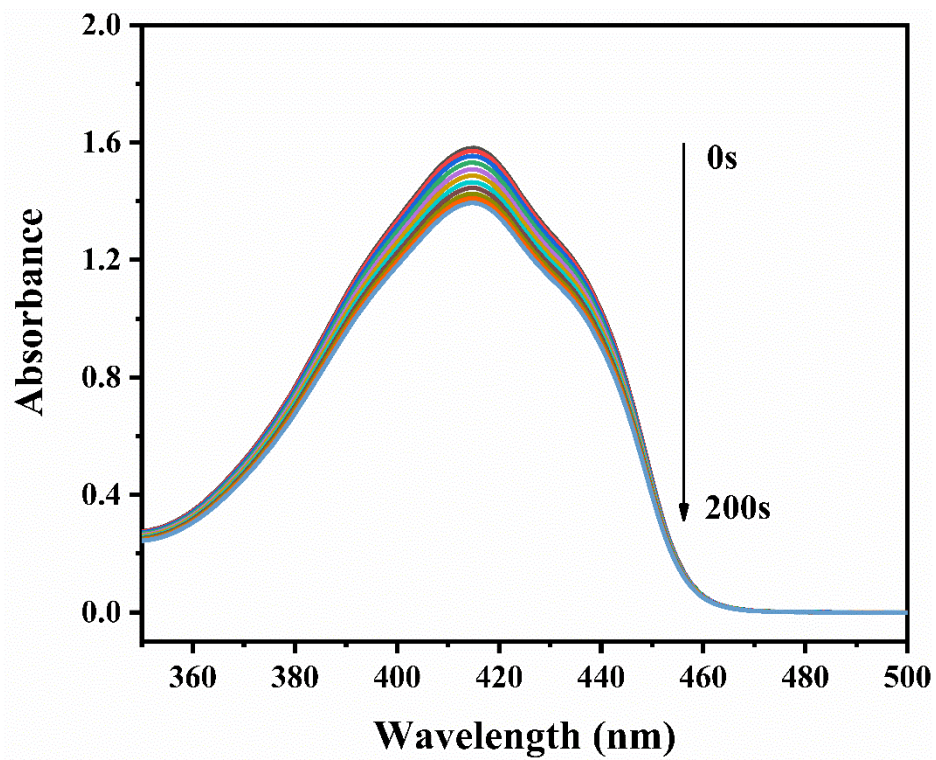
**Figure S13.** Solid-State cyclic voltammogram of CuCl-Pyhc with a scan rate of 100 mV/s in the scan range of -0.8 ~ 0.6 V.

$$E_{1/2} (\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}) = (E_{\text{pc}} + E_{\text{pa}})/2 = (-0.12 + 0.06)/2 = -0.03 \text{ V.}$$

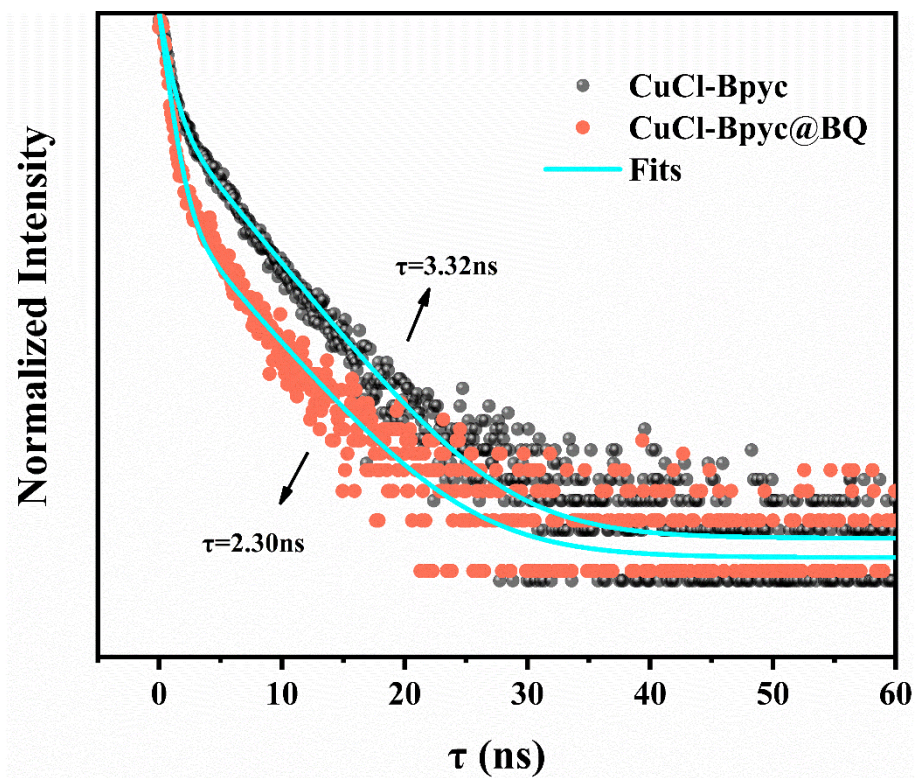


**Figure S14.** Normalized absorption and emission spectra of CuCl-Pyhc ( $E^{0-0} = 2.33$  eV). The Method of Calculation of the Excited-State Reduction Potential  $E_{red}^*$ :

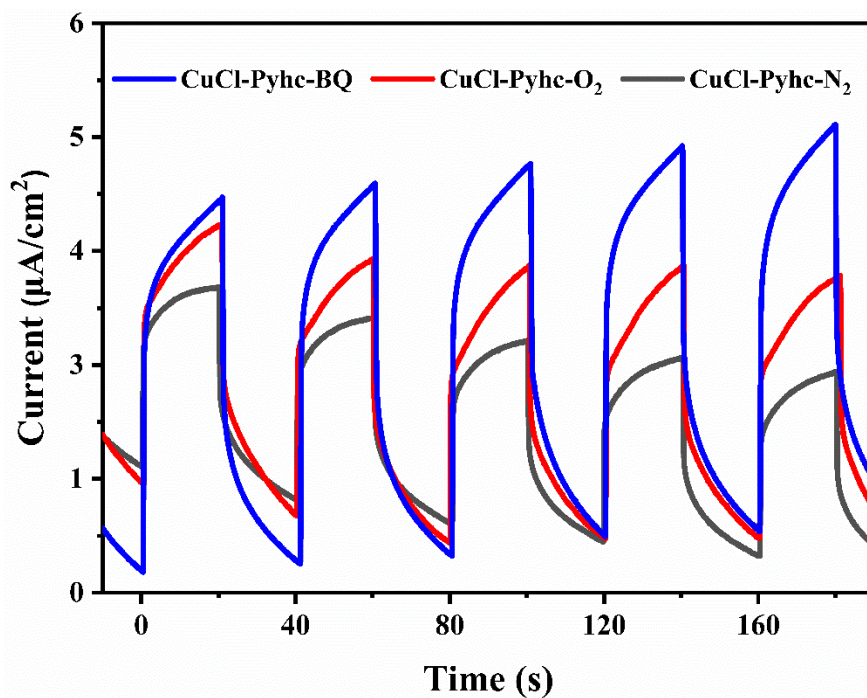
$$E_{red}^* = E_{1/2}(\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}) - E^{0-0} = -0.03 - 2.33 = -2.36 \text{ (V vs Ag/AgCl)}.$$



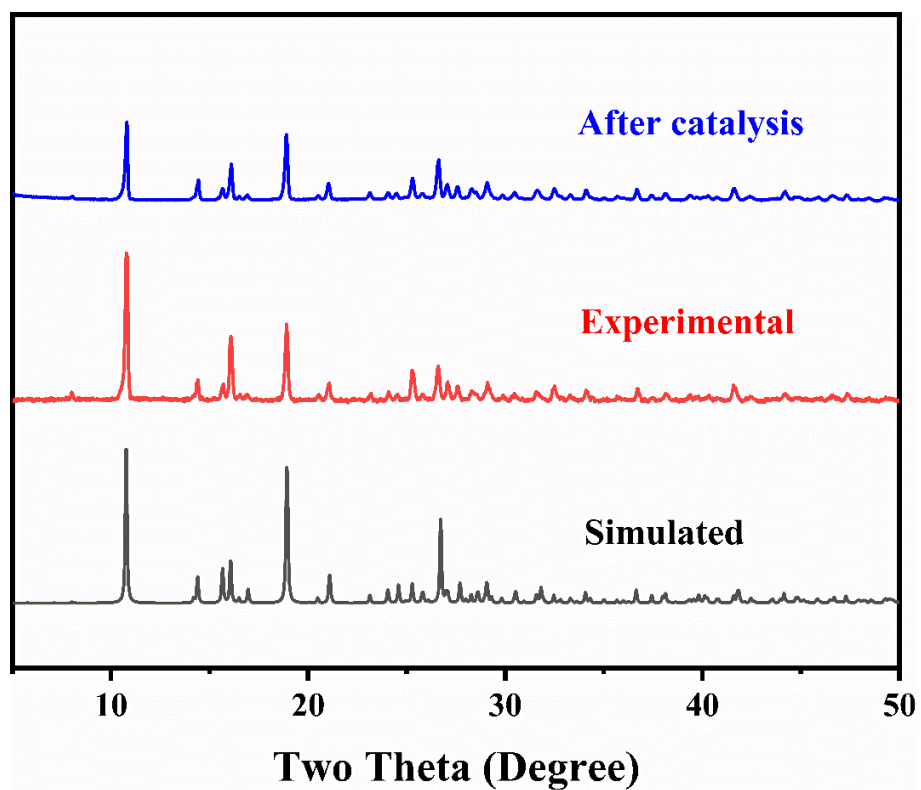
**Figure S15.** UV-vis Absorbance decay of DPBF without CuCl-Pyhc under illumination



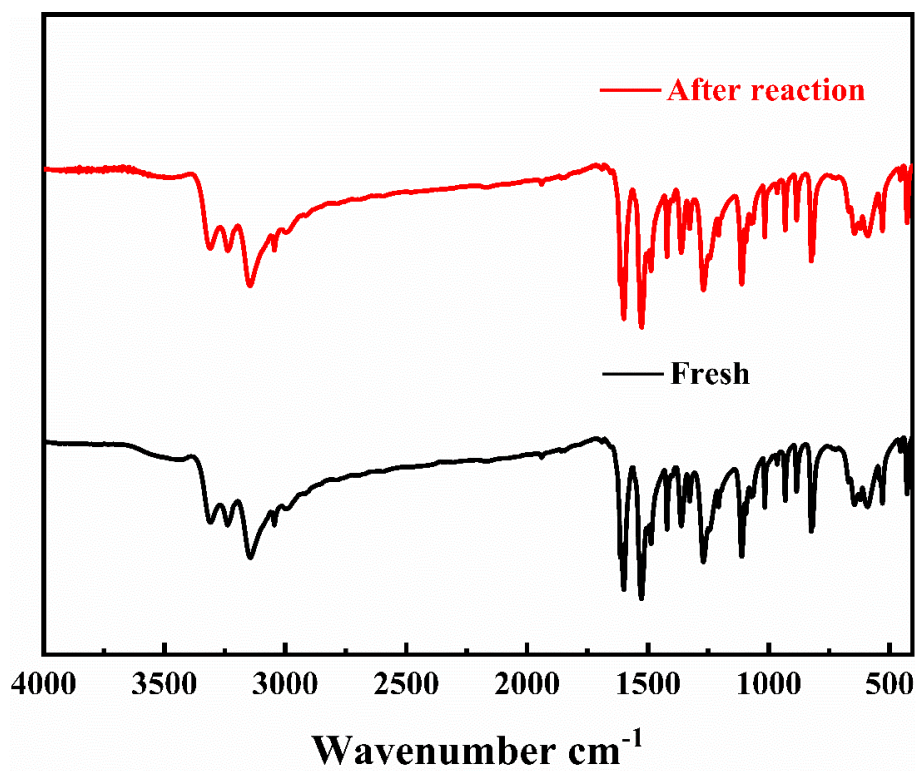
**Figure S16.** Time-dependent luminescence decays of the CuCl-Pyhc (black) suspension before and after the addition of BQ (red). The intensity was recorded at 570 nm with excitation at 455 nm.



**Figure S17.** Photocurrent responses of CuCl-Pyhc in N<sub>2</sub> (black line) and O<sub>2</sub> (red line) atmospheres and CuCl-Pyhc@BQ (blue line).



**Figure S18.** The PXRD spectra. Simulated CuCl-Pyhc (black bar); freshly prepared CuCl-Pyhc (red bar); CuCl-Pyhc of after catalysis (blue bar).



**Figure S19.** IR spectra of freshly prepared CuCl-Pyhc (black) and CuCl-Pyhc after reaction (red).

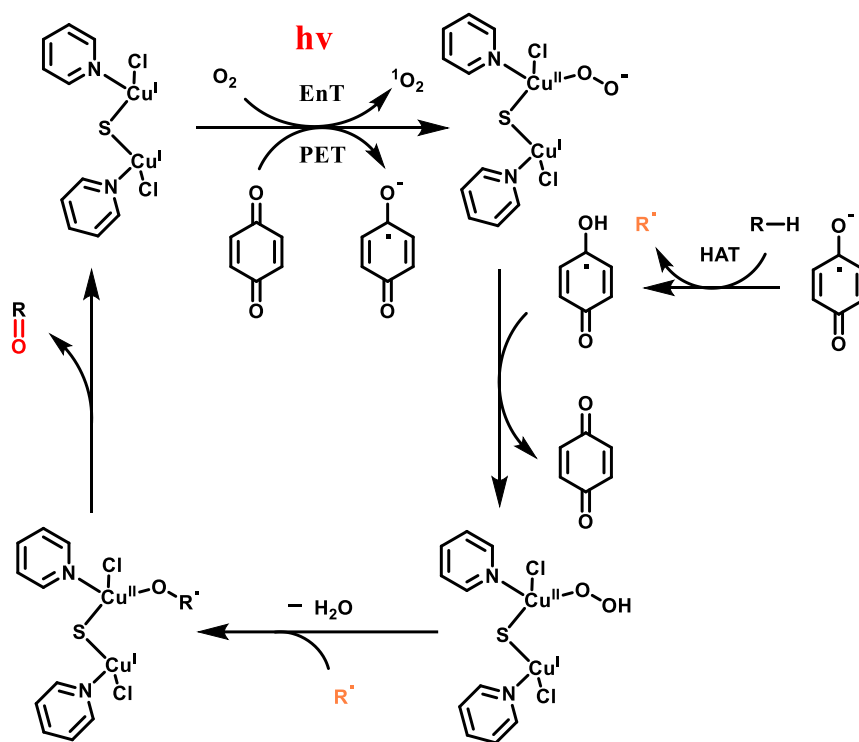
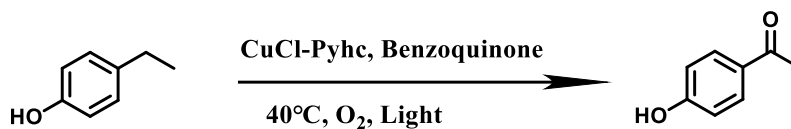


Figure S20. Possible reaction mechanism.



## 4. Optimization of the Different Reaction Conditions

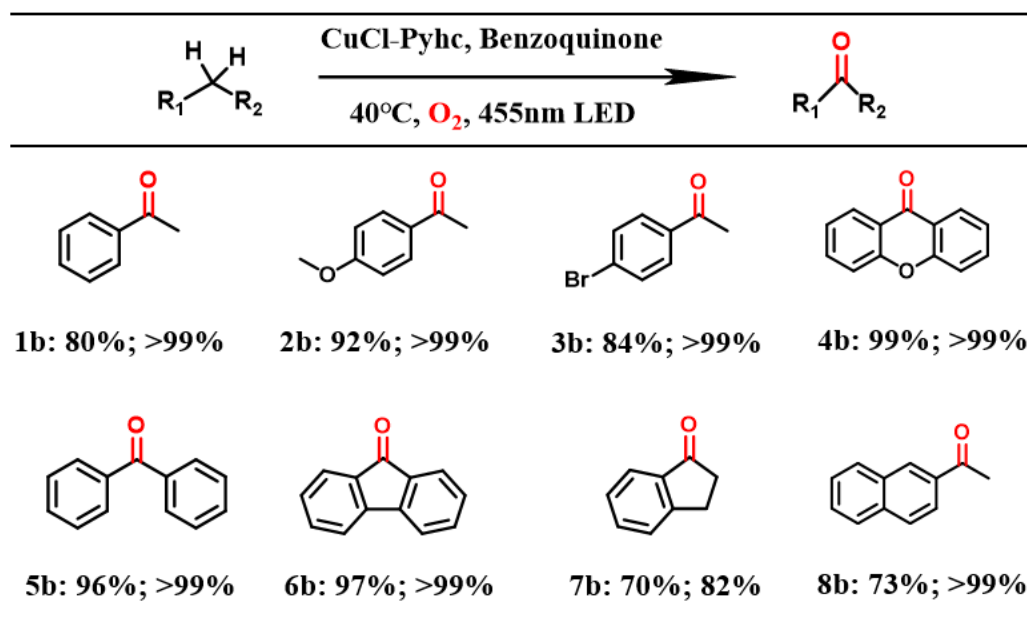
**Table S2.** Optimization of the Different Reaction Conditions for the Oxidation of 4-ethylphenol.



<sup>a</sup> Entry	Sol.	Light	<sup>b</sup> Yield (%)
1	MeOH	455nm	26
2	CH <sub>3</sub> CN	455nm	84
3	H <sub>2</sub> O	455nm	N.R.
4	acetone	455nm	36
5	CH <sub>3</sub> CN	395nm	40
6	CH <sub>3</sub> CN	365nm	32
7	CH <sub>3</sub> CN	White	N.R.

<sup>a</sup>Reaction conditions: CuCl-Pyhc (5mg), solvent (4mL), benzoquinone (0.1mmol), 4-ethylphenol (0.1mmol), O<sub>2</sub> balloon, and 40°C, t = 8h. <sup>b</sup>Yields of isolated products.

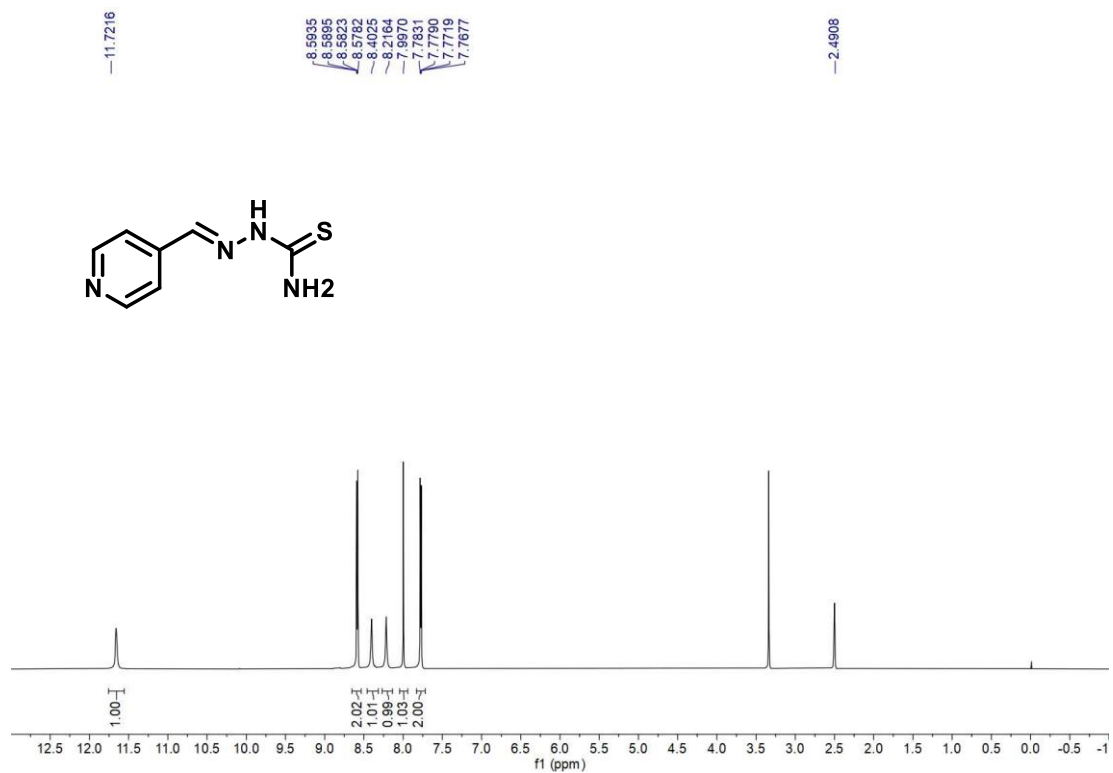
**Table S3.** Scopes of the Catalytic Oxidation of C-H Bonds<sup>a</sup>



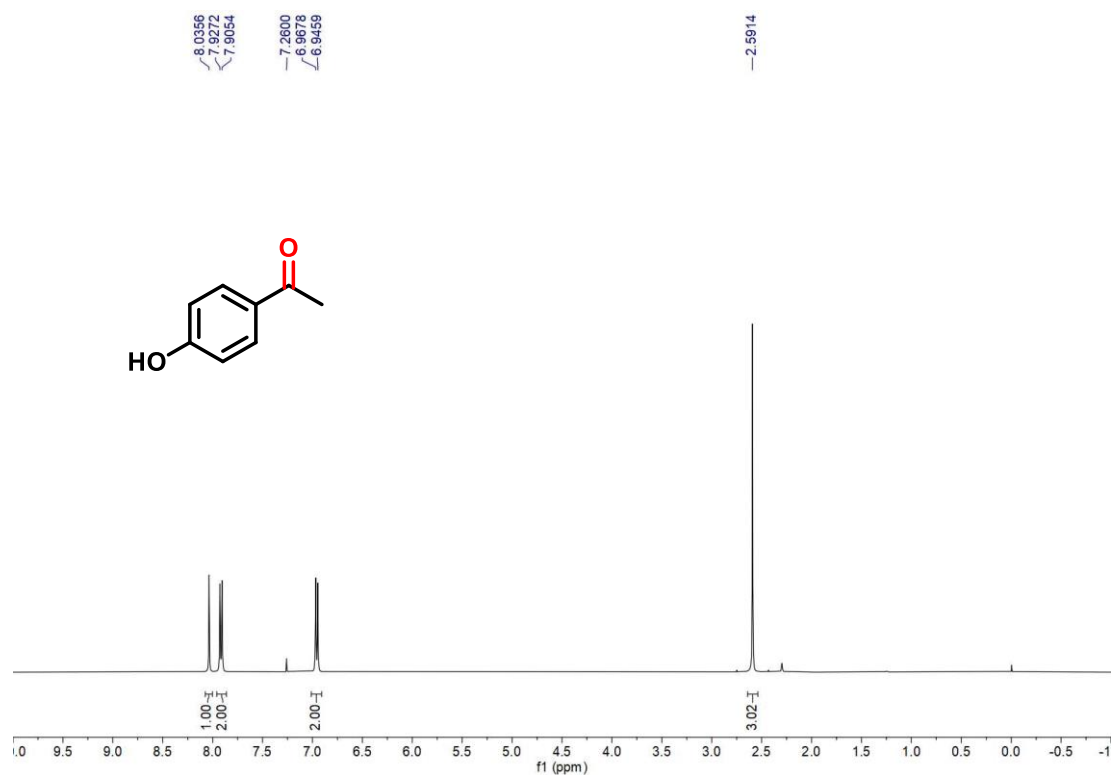
<sup>a</sup>Reaction conditions: CuCl-Pyhc (5 mg), substrate (0.1 mmol), benzoquinone (0.1 mmol), CH<sub>3</sub>CN (4 mL), 455 nm LED, O<sub>2</sub>, 40 °C, 8 h. This table displayed the yield (left) and selectivity (right) of the products. <sup>b</sup>The yields were determined using <sup>1</sup>H NMR spectroscopy.

## 6. $^1\text{H}$ NMR Spectrum

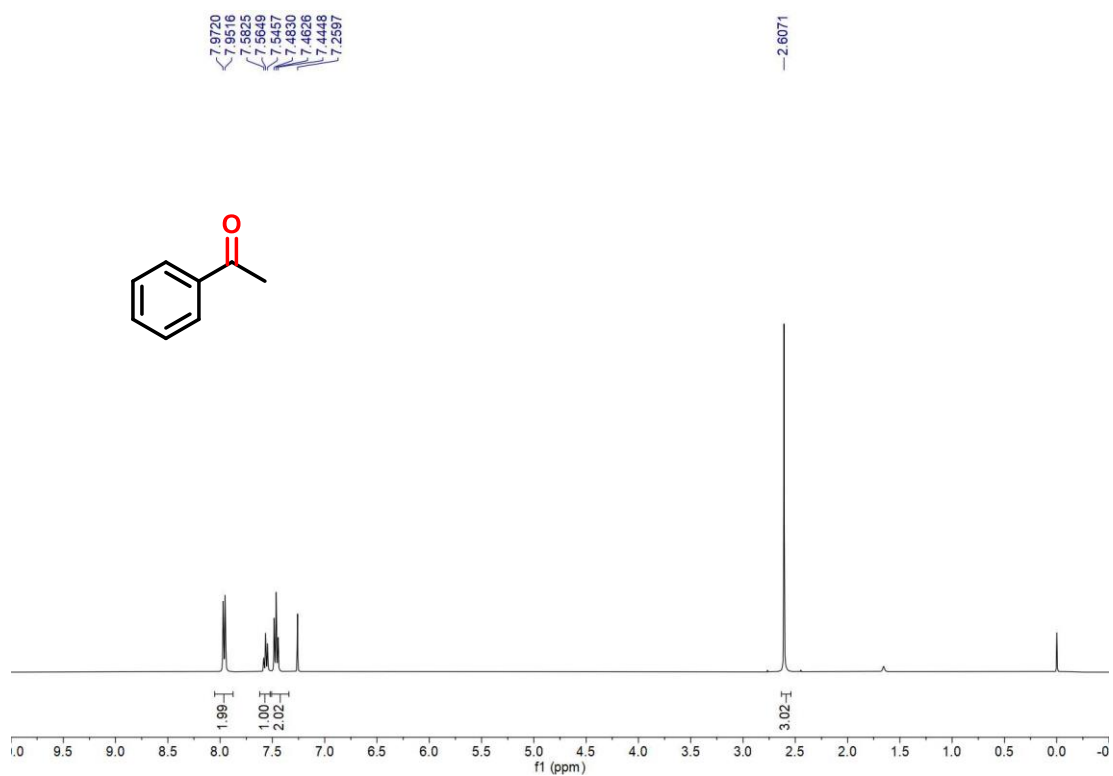
Pyhc ((E)-2-(pyridin-4-ylmethylene) hydrazine-1-carbothioamide):  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  11.72 (s, 1H), 8.65 – 8.53 (m, 2H), 8.40 (s, 1H), 8.22 (s, 1H), 8.00 (s, 1H), 7.83 – 7.72 (m, 2H).



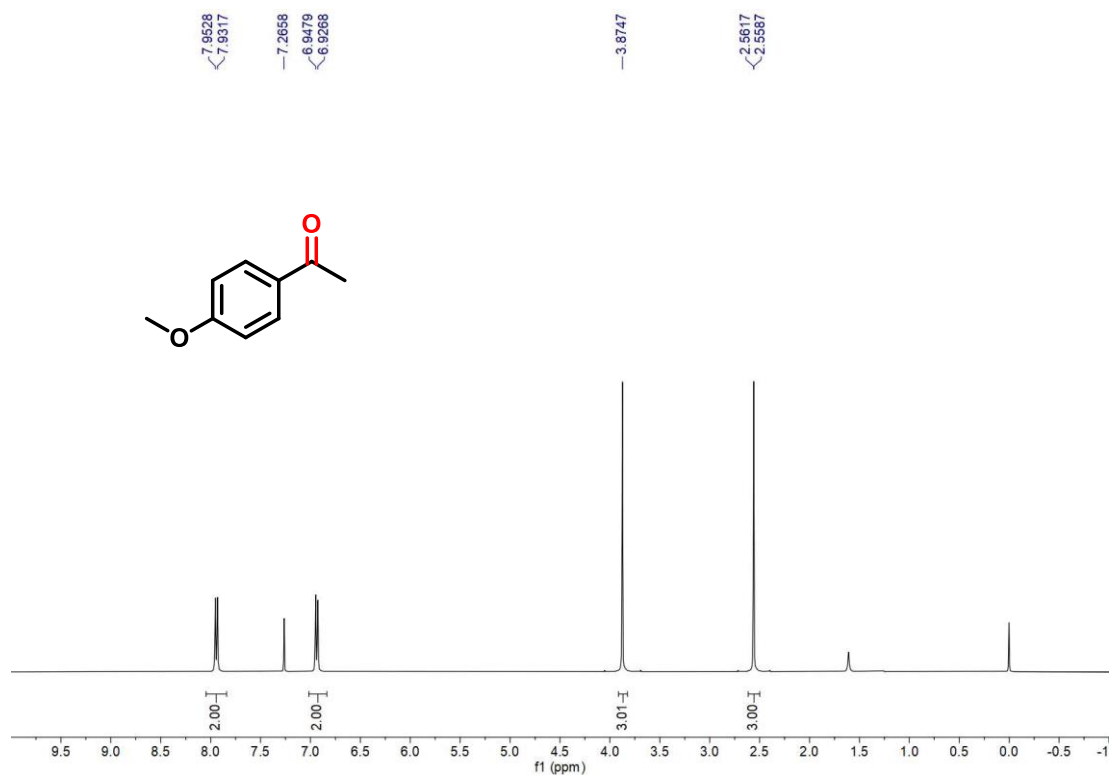
**1-(4-hydroxyphenyl) ethan-1-one:**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.04 (s, 1H), 7.92 (d,  $J = 8.7$  Hz, 2H), 6.96 (d,  $J = 8.8$  Hz, 2H), 2.59 (s, 3H).



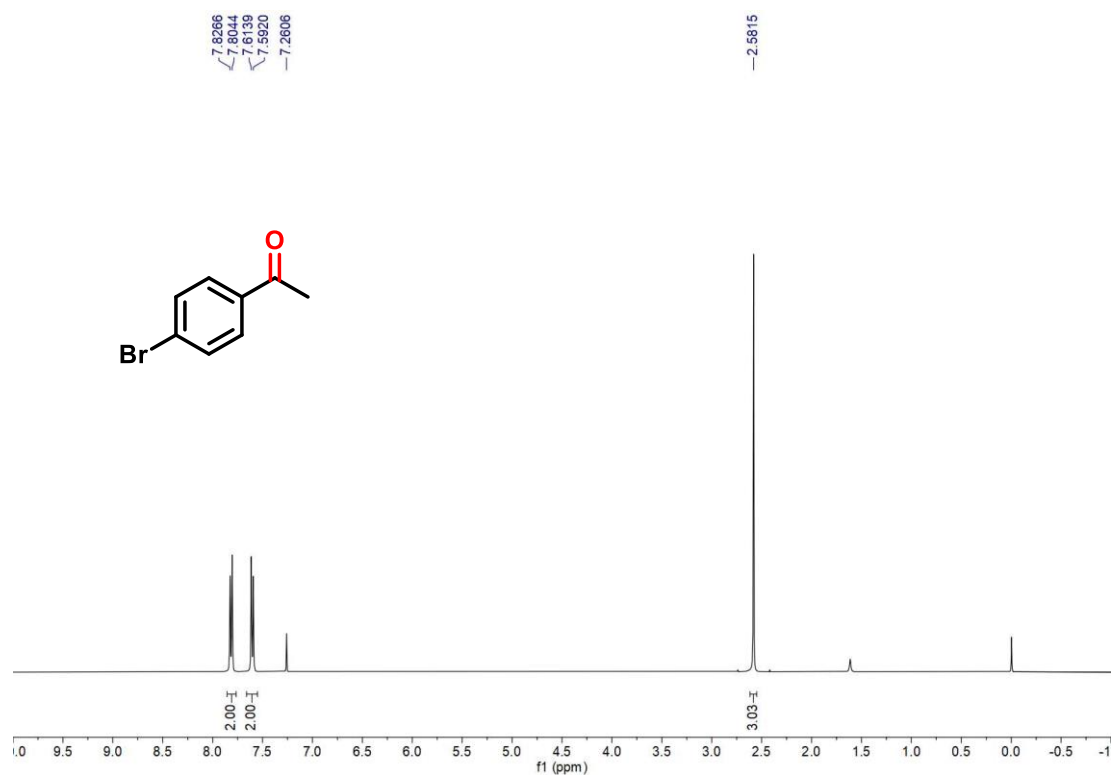
**Acetophenone (1b):**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.96 (d,  $J = 8.2$  Hz, 2H), 7.56 (t,  $J = 7.4$  Hz, 1H), 7.51 – 7.34 (m, 2H), 2.61 (s, 3H).



**1-(4-methoxyphenyl) ethan-1-one (2b):**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.94 (d,  $J = 8.4$  Hz, 2H), 6.94 (d,  $J = 8.4$  Hz, 2H), 3.87 (s, 3H), 2.56 (d,  $J = 1.2$  Hz, 3H).

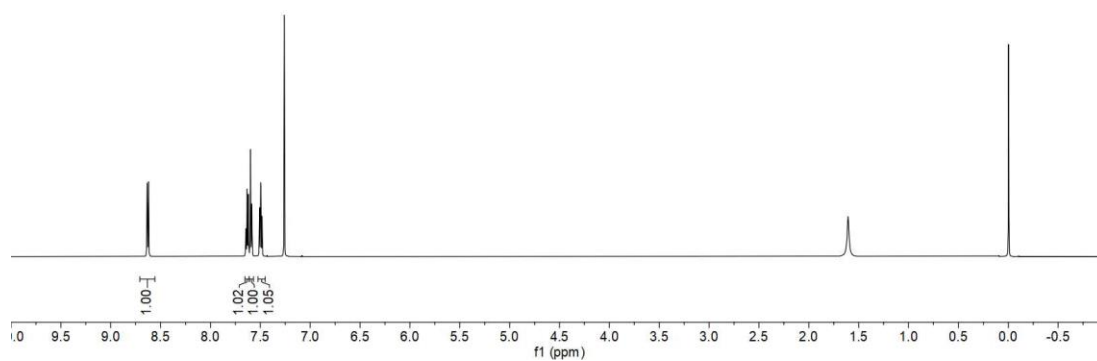
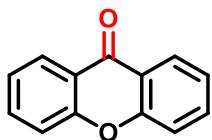


**1-(4-bromophenyl) ethan-1-one (3b):**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.82 (d,  $J = 8.9$  Hz, 2H), 7.60 (d,  $J = 8.8$  Hz, 2H), 2.58 (s, 3H).



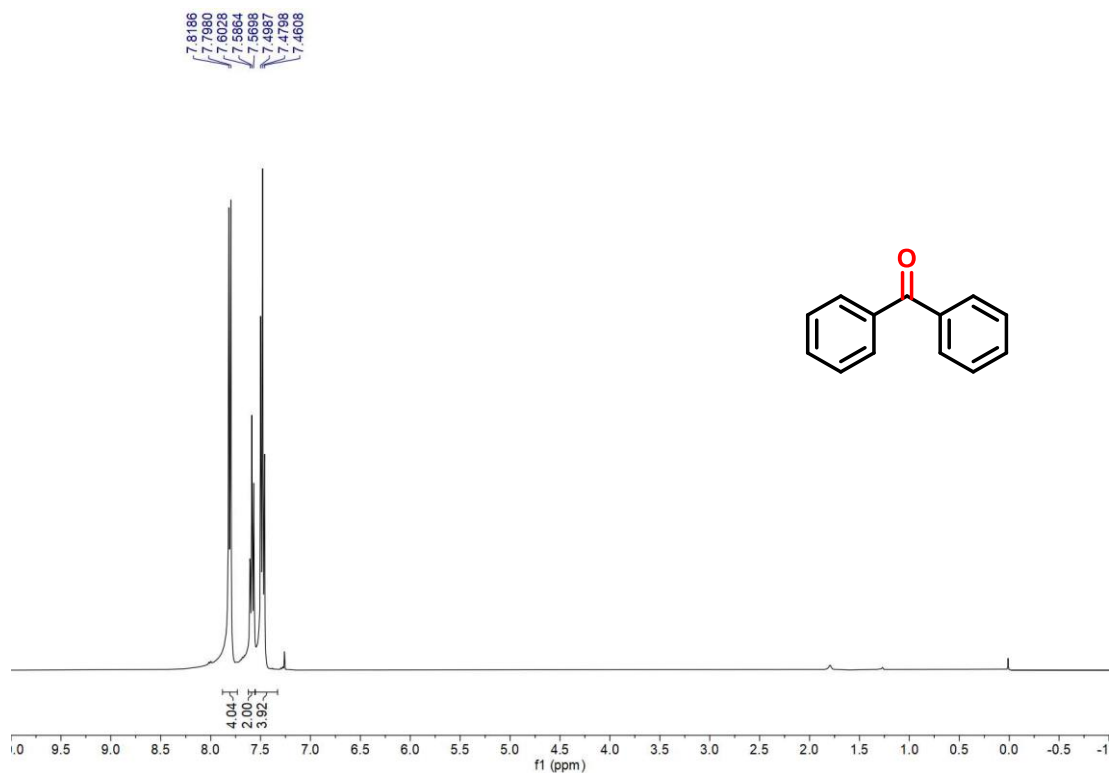
**9H-xanthen-9-one (4b):**  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  8.63 (d,  $J = 7.9$  Hz, 1H), 7.65 – 7.61 (m, 1H), 7.59 (d,  $J = 8.0$  Hz, 1H), 7.52 – 7.45 (m, 1H).

8.6346  
8.6214  
7.6449  
7.6312  
7.6200  
7.5982  
7.5849  
7.5074  
7.4961  
7.4824

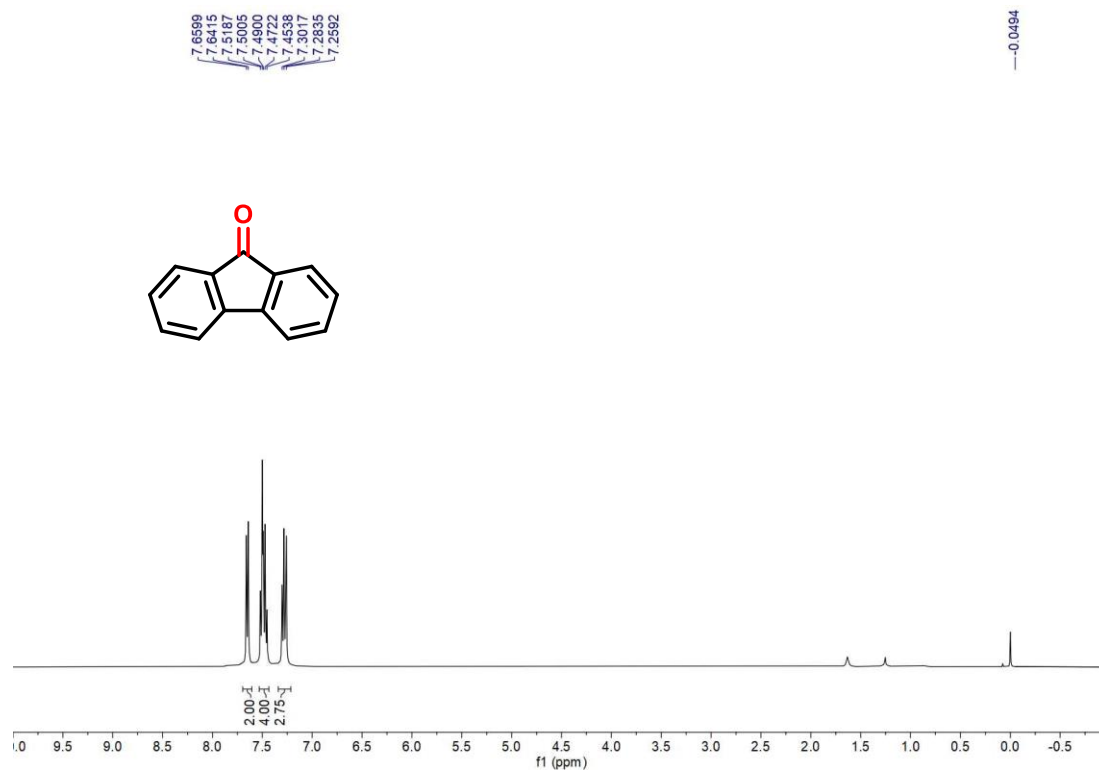




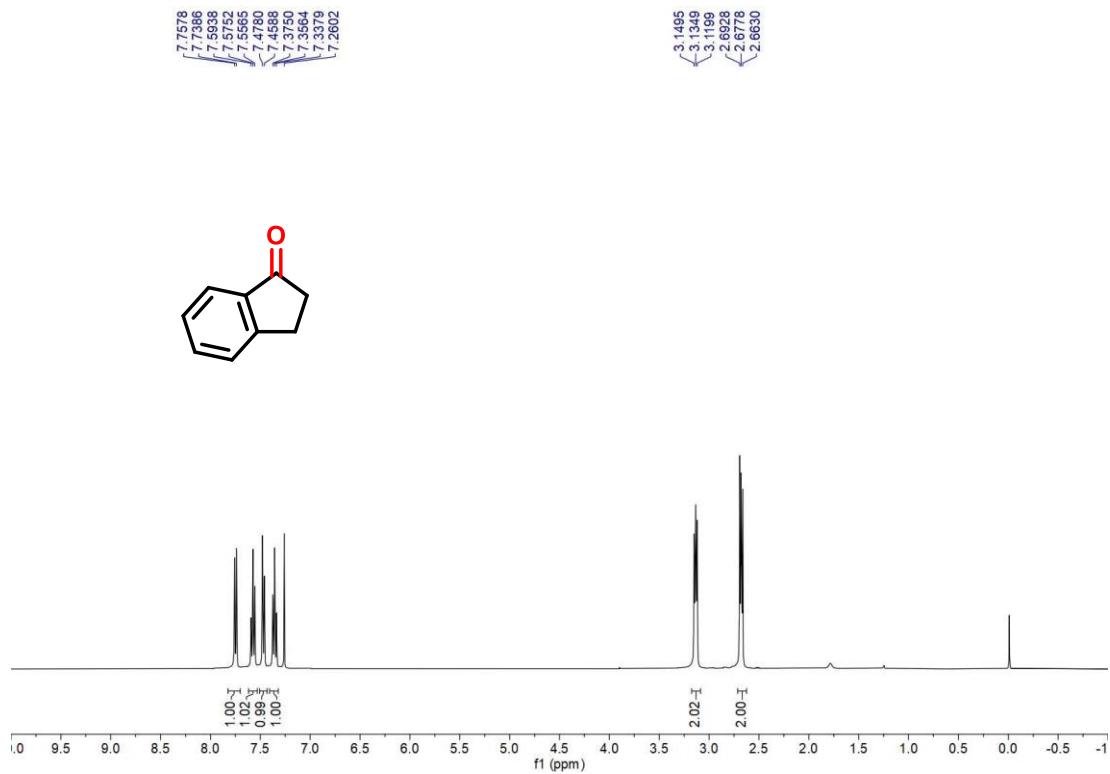
**Benzophenone (5b):**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.81 (d,  $J = 8.2$  Hz, 4H),  
7.62 – 7.56 (m, 2H), 7.48 (t,  $J = 7.6$  Hz, 4H).



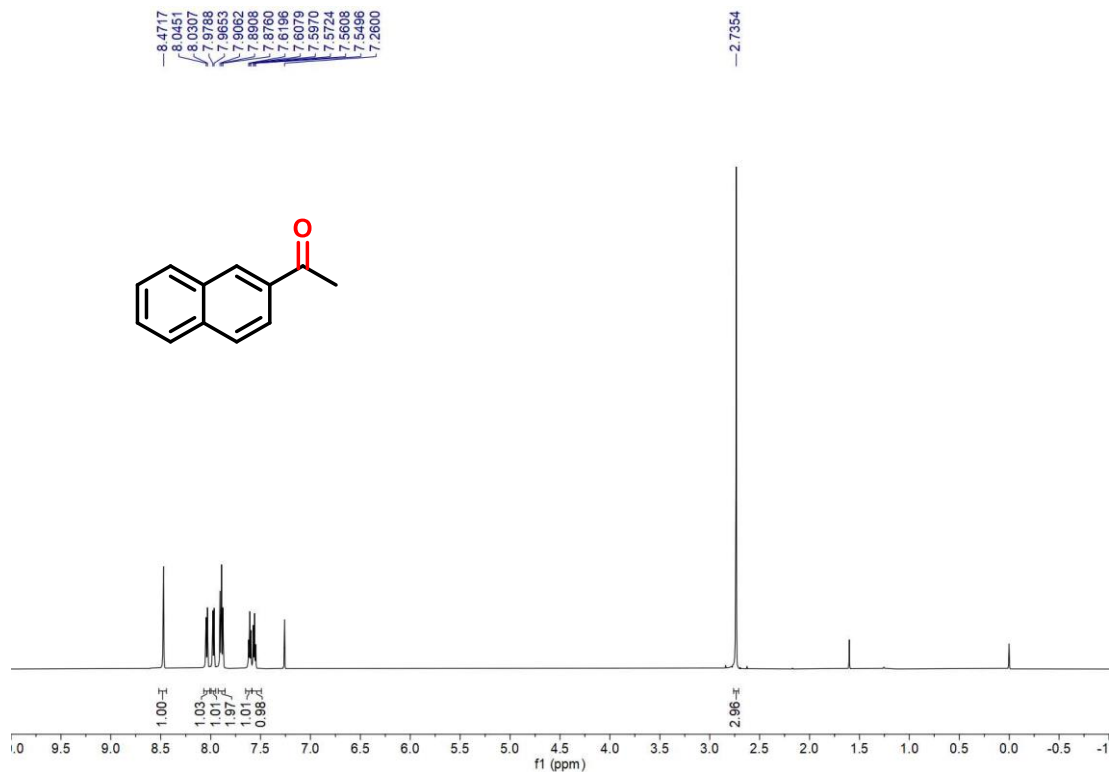
**9H-fluoren-9-one (6b):**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.65 (d,  $J = 7.3$  Hz, 2H), 7.53 – 7.43 (m, 4H), 7.34 – 7.21 (m, 3H).



**2,3-dihydro-1H-inden-1-one (7b):**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.75 (d,  $J = 7.7$  Hz, 1H), 7.58 (t,  $J = 7.4$  Hz, 1H), 7.47 (d,  $J = 7.7$  Hz, 1H), 7.36 (t,  $J = 7.4$  Hz, 1H), 3.17 – 3.09 (m, 2H), 2.71 – 2.62 (m, 2H).



**1-(naphthalen-2-yl) ethan-1-one (8b):**  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.47 (s, 1H), 8.04 (d,  $J = 8.6$  Hz, 1H), 7.97 (d,  $J = 8.1$  Hz, 1H), 7.89 (t,  $J = 9.1$  Hz, 2H), 7.65 – 7.59 (m, 1H), 7.56 (t,  $J = 6.8$  Hz, 1H), 2.74 (s, 3H).



## 7. References

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