

## Supporting Information

# Binuclear Copper Iodine Clusters-Based Coordination Sheets as Photocatalytic Regulators to Decarboxylative Cyanation

### **Contents**

1. Experimental Section.
2. Single Crystal X-ray Crystallography.
3. Characterizations of Catalysts.
4. Catalysis Details.
5. References.

## 1. Experimental Section.

### Materials and methods

All substrates were used as received from commercial suppliers, unless otherwise stated. Chemicals were purchased from Sigma-Aldrich, Chempur, TCI, or Alfa Aesar. The ligand **Tpxa** (4,4',4''-(2,4,6-trimethylbenzene-1,3,5-triyl) tripyridine) was synthesized according to the previously reported procedure.<sup>S1</sup>

<sup>1</sup>H NMR data were collected on a Varian INOVA-600 MHz, Bruker Avance III 500 MHz, Vaian DLG400 MHz spectrometer at ambient temperature. FT-IR spectra were recorded as KBr pellets on JASCO FT/IR-430 spectrometer. The powder XRD diffractograms were obtained on a Rigaku D/Max-2400 X-ray diffractometer with a sealed Cu tube ( $\lambda = 1.54178 \text{ \AA}$ ). IR spectra were recorded as KBr pellets on a NEXUS instrument. Thermogravimetric analyses (TGA) were performed at a ramp rate of 10 °C/min in a nitrogen flow with an SDTQ600 instrument. Confocal Laser Scanning Microscopy micrographs were collected by Olympus Fluoview FV1000 with  $\lambda_{\text{ex}} = 617 \text{ nm}$ . 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. Liquid UV-*vis* spectra were performed on a TU-1900 spectrophotometer. The solid fluorescent spectrum was measured on an Edinburgh FS920 instrument. The time-resolved luminescence spectrum was measured on an Edinburgh FLS920 spectrometer.

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  $\text{Bu}_4\text{NPF}_6$  at a scan rate of  $100 \text{ mV s}^{-1}$ . 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.

(1) Synthesis of compound Cu-**Tpxa-1**

**Tpxa** (4,4',4''-(2,4,6-trimethylbenzene-1,3,5-triyl) tripyridine) (7mg, 0.02mmol), CuI (5.7mg, 0.03mmol) were added in *N,N*-Diethylformamide (DEF)/ $\text{CH}_3\text{CN}$  (v/v = 1/4) mixed solution in a teflon-lined autoclave. The resulting mixture was heated at  $120^\circ\text{C}$  for three days, then allowed to room temperature slowly. Light yellow crystals were obtained. Crystals were collected after filtration. Yield: 64% (based on **Tpxa**).

(2) Synthesis of compound Cu-**Tpxa-2**

**Tpxa** (7mg, 0.02mmol), CuI (5.7mg, 0.03mmol) were added in *N,N*-Dimethylformamide (DMF)/ $\text{CH}_3\text{CN}$  (v/v = 1/4) mixed solution in a teflon-lined autoclave. The resulting mixture was heated at  $120^\circ\text{C}$  for three days, then allowed to room temperature slowly. Chartreuse crystals were obtained. Crystals were collected after filtration. Yield: 62% (based on **Tpxa**).

**Dye uptake experiment** : The Cu-**Tpxa** crystals were immersed in the methanol saturated solution of malachite green for 12 hours, and the crystals were thoroughly washed with methanol until the solution was clarified.

**Photoelectrochemical Measurements:** Through CHI 760E electrochemical workstation, photocurrent was measured in a standard three-electrode system with the photocatalyst-coated FTO as the working electrode, Pt plate as the counter electrode and Ag/AgCl as the reference electrode. A 300 W xenon lamp with cutoff filter ( $\lambda >$

400 nm) was used as light source. A 3 M KCl solution was used as electrolyte. The catalyst (2 mg) was added into a mixed solution with 20  $\mu\text{L}$  of 5 wt% Nafion and 1 mL of ethanol, and the working electrodes were prepared by dropping the suspension (100  $\mu\text{L}$ ) onto the surface of a FTO plate with an area of  $1\text{cm}^2$ .

## 2. Single Crystal X-ray Crystallography

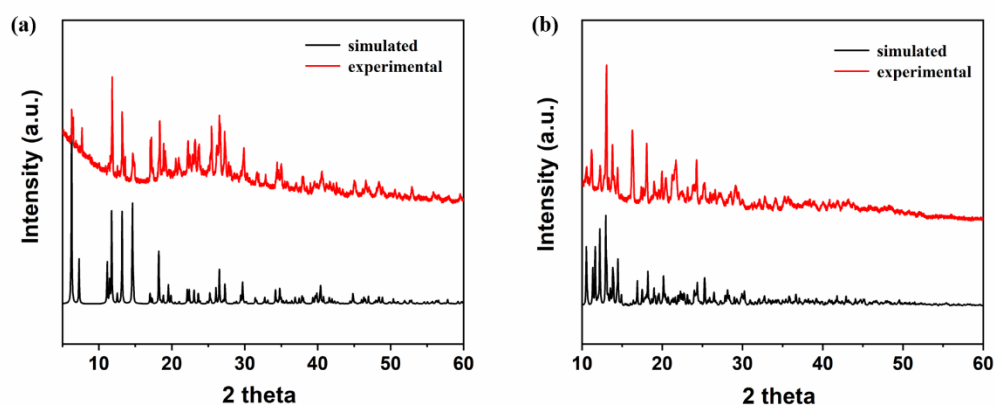
The intensities were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation source; the data were acquired using the SMART and SAINT programs. The structure was solved by direct methods and refined by full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

In the structural refinement of Cu-**Tpxa-1** and Cu-**Tpxa-2**, 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>S3</sup>

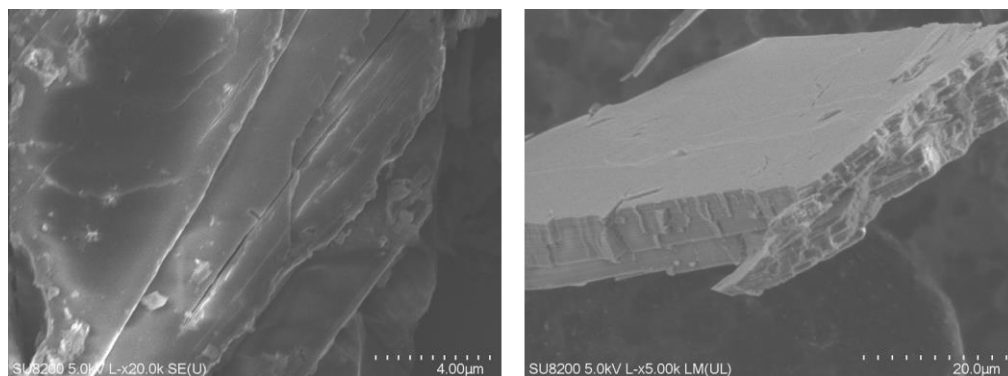
**Table S1.** Crystal data and structure refinements.

Compound	Cu-Tp $\alpha$ -1	Cu-Tp $\alpha$ -2
Empirical formula	C <sub>28</sub> H <sub>26</sub> N <sub>5</sub> Cu <sub>2</sub> I <sub>2</sub>	C <sub>98</sub> H <sub>87</sub> Cu <sub>6</sub> I <sub>6</sub> N <sub>13</sub>
Formula weight	813.42	2621.44
Temperature/K	120	130
Crystal system	Orthorhombic	Triclinic
Space group	Cmcm	P-1
a/Å	13.4390(16)	13.3961(9)
b/Å	28.091(4)	15.0316(9)
c/Å	9.4068(10)	33.541(2)
$\alpha$ /°	90	91.323(2)
$\beta$ /°	90	97.137(2)
$\gamma$ /°	90	114.728(2)
Volume/Å <sup>3</sup>	3551.2(8)	6066.0(7)
Z	4	2
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.521	1.435
$\mu/\text{mm}^{-1}$	2.957	2.603
F(000)	1572.0	2548.0
Crystal size/mm <sup>3</sup>	0.31 × 0.29 × 0.26	0.02 × 0.02 × 0.02
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 theta range for data collection/°	5.212 to 55.452	4.55 to 49.998
Index ranges	-13 ≤ h ≤ 17, -36 ≤ k ≤ 35, -11 ≤ l ≤ 12	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -39 ≤ l ≤ 39
Reflections collected	15098	61580
Independent reflections	2275 [R <sub>int</sub> = 0.0602, R <sub>sigma</sub> = 0.0438]	21331 [R <sub>int</sub> = 0.0734, R <sub>sigma</sub> = 0.0990]
Data/restraints/parameters	2275/13/118	21331/12/1139
Goodness-of-fit on F <sup>2</sup>	1.058	0.975
Final R indexes [I >= 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0458, wR <sub>2</sub> = 0.1245	R <sub>1</sub> = 0.0627, wR <sub>2</sub> = 0.1611
Final R indexes [all data]	R <sub>1</sub> = 0.0516, wR <sub>2</sub> = 0.1300	R <sub>1</sub> = 0.1011, wR <sub>2</sub> = 0.1778
Largest diff. peak/hole / e Å <sup>-3</sup>	1.63/-1.47	3.18/-1.04
CCDC number	2143067	2143068

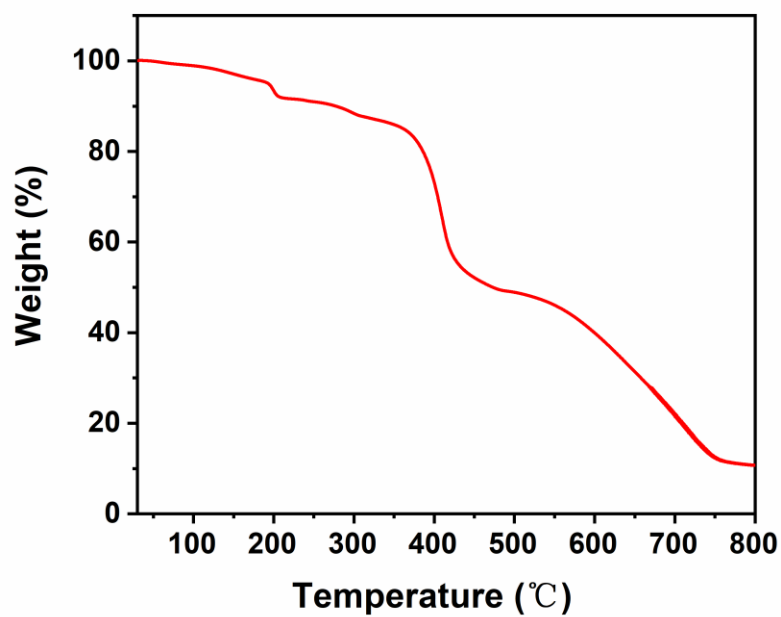
### 3. Characterizations of Catalysts



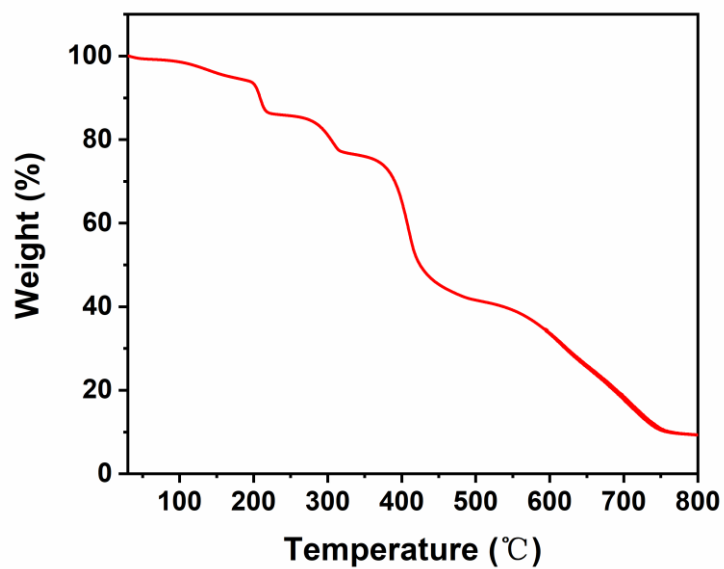
**Figure S1.** (a) X-ray powder diffraction (XRD) patterns of freshly prepared Cu-Tpax-1 (red) and its simulated pattern based on the reported single-crystal data (black); (b) X-ray powder diffraction (XRD) patterns of freshly prepared Cu-Tpax-2 (red) and its simulated pattern based on the reported single-crystal data (black).



**Figure S2.** A magnified SEM image of the as-synthesized photocatalyst Cu-Tpax-1

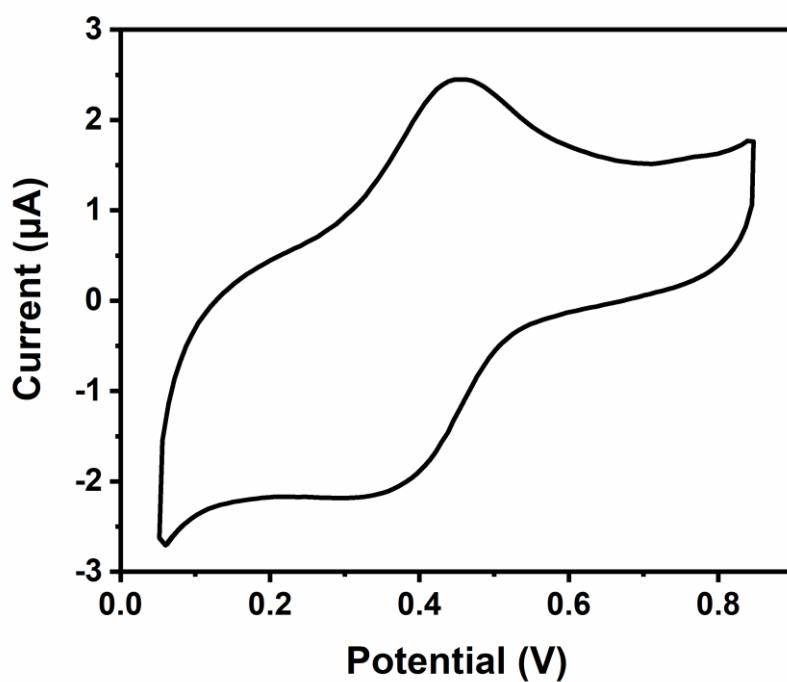


**Figure S3.** Thermogravimetric (TGA) figure of Cu-Tp $\alpha$ -1 with heating rates of 10°C /min.

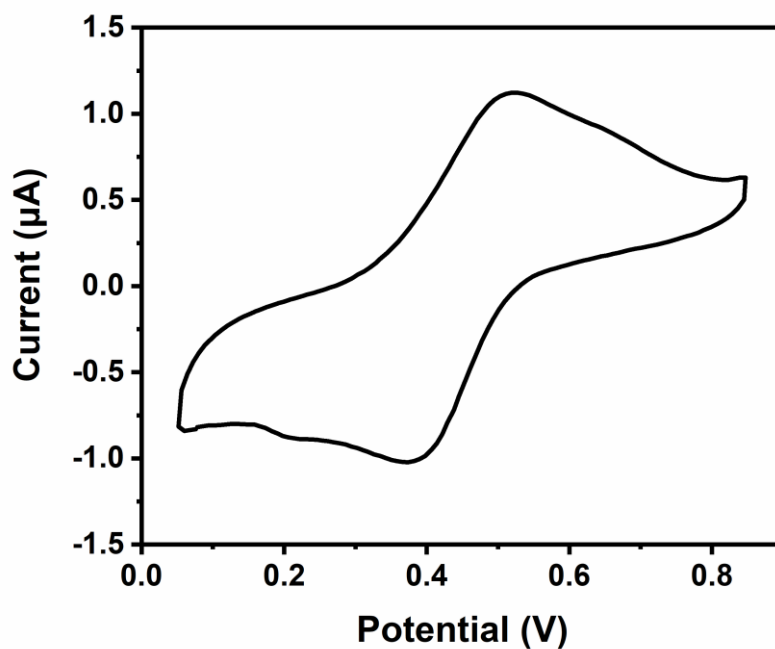


**Figure S4.** Thermogravimetric (TGA) figure of Cu-Tp $\alpha$ -2 with heating rates of 10°C /min.

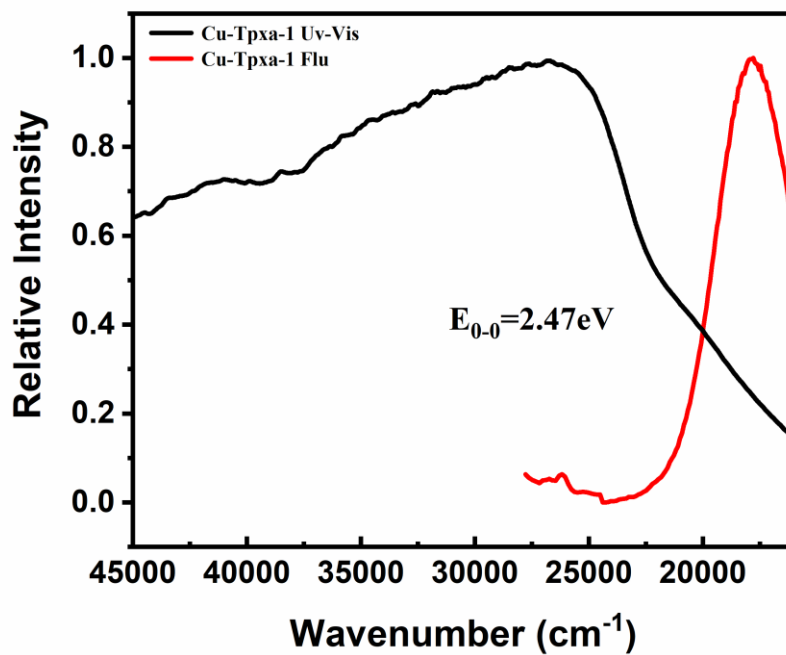




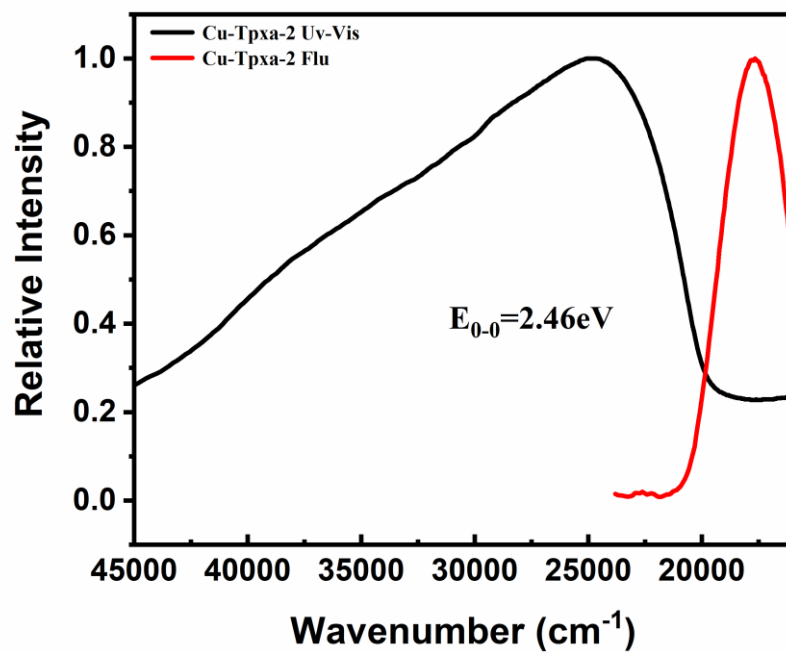
**Figure S5.** Solid-State cyclic voltammogram of Cu-Tpxa-1 with a scan rate of 100 mV/s in the scan range of 0 ~ 1 V.



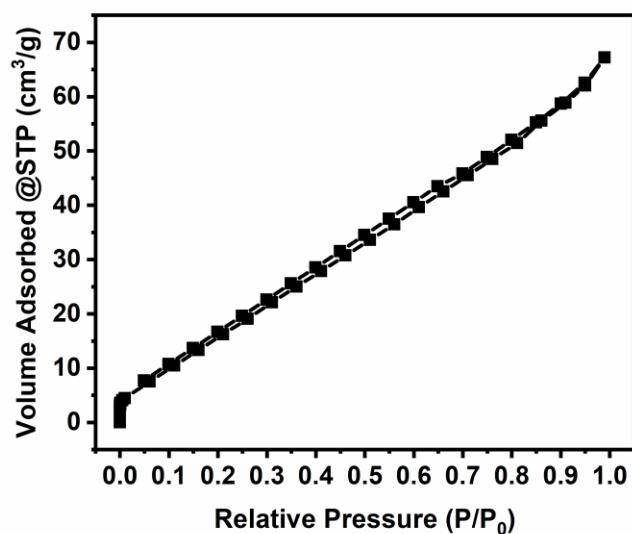
**Figure S6.** Solid-State cyclic voltammogram of Cu-Tpxa-2 with a scan rate of 100 mV/s in the scan range of 0 ~ 1 V.



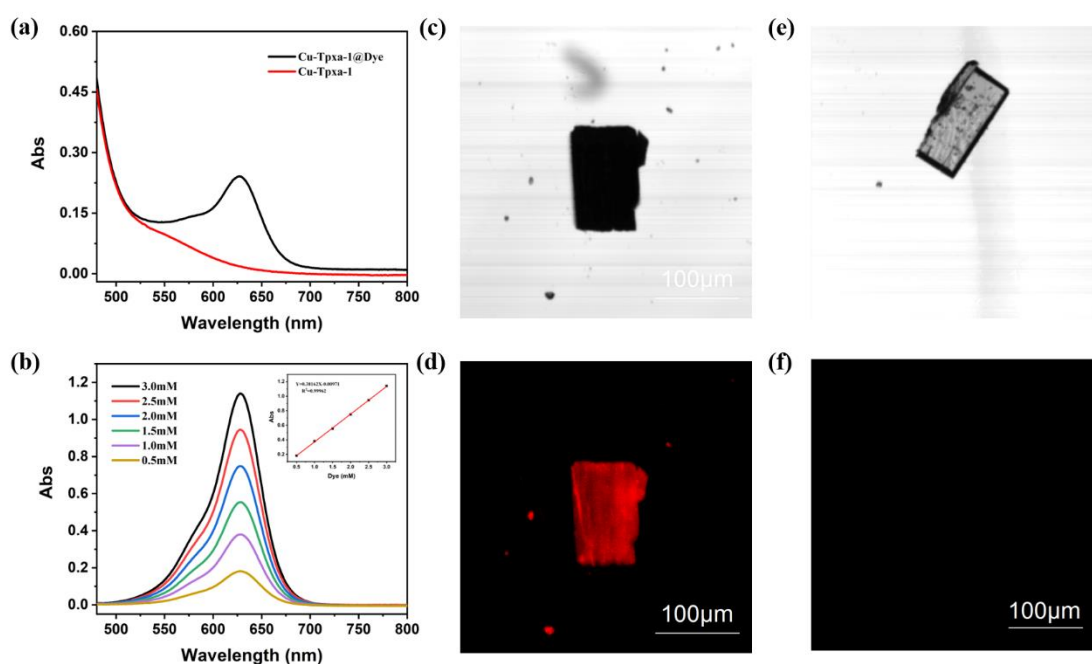
**Figure S7.** Cu-Tpxa-1 normalized ultraviolet-visible absorption (black) and emission spectra (red).



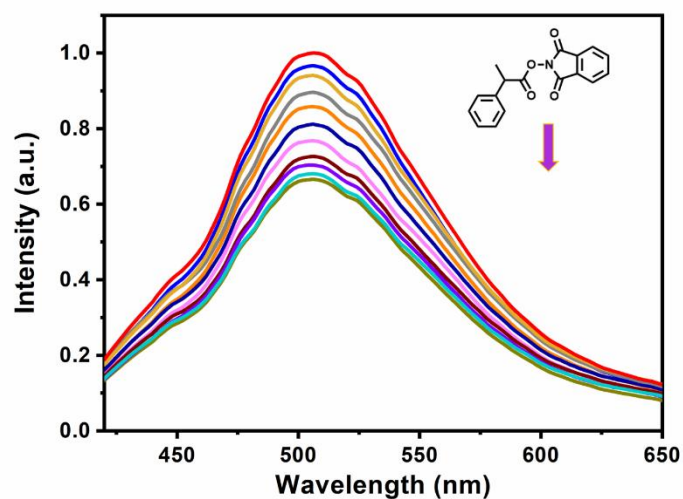
**Figure S8.** Cu-Tpxa-2 normalized ultraviolet-visible absorption (black) and emission spectra (red).



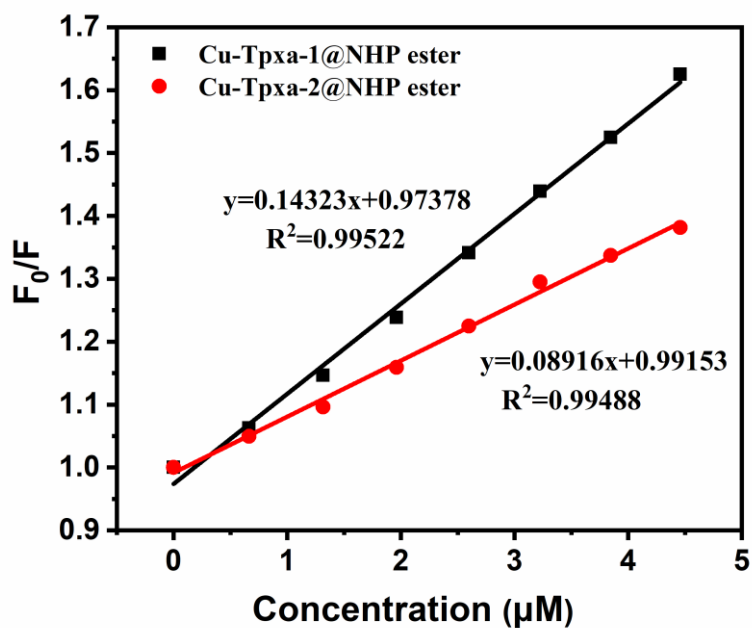
**Figure S9.** N<sub>2</sub> adsorption-desorption isotherms of Cu-Tpxa-1.



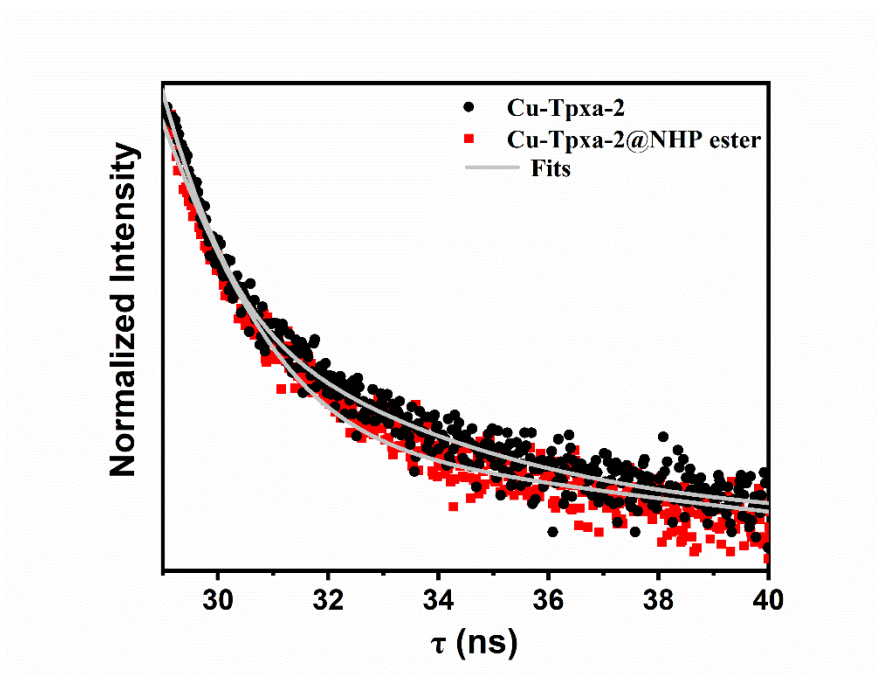
**Figure S10.** (a) The ultraviolet-visible absorption spectrum of malachite green released by Cu-Tpxa-1; (b) the ultraviolet-visible absorption spectrum of malachite green without concentration, the inner figure is the standard curve of concentration and absorption intensity; Cu-Tpxa-1 crystals adsorbed (c, d) and (e, f) unadsorbed malachite green.



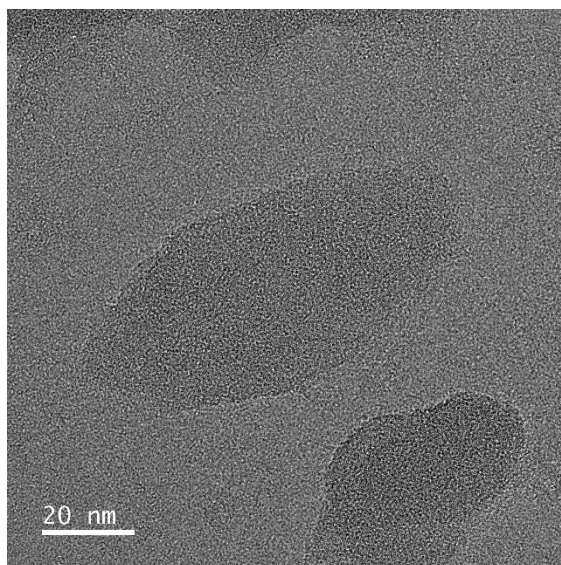
**Figure S11.** The fluorescence quenching curve of Cu-Tpxa-2 suspension with different concentrations of NHP ester.



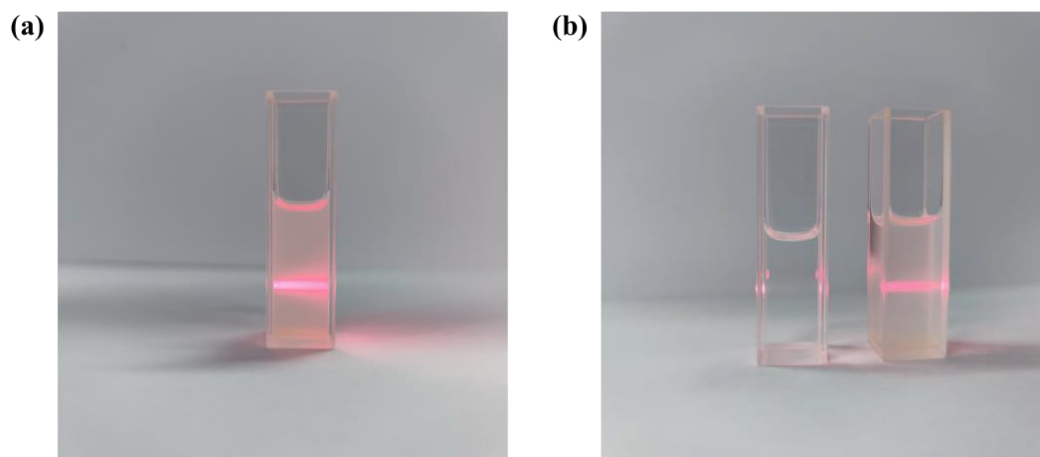
**Figure S12.** Stern-Volmer equation of Cu-Tpxa-1 (black) and Cu-Tpxa-2 (red) fluorescence quenching curve.



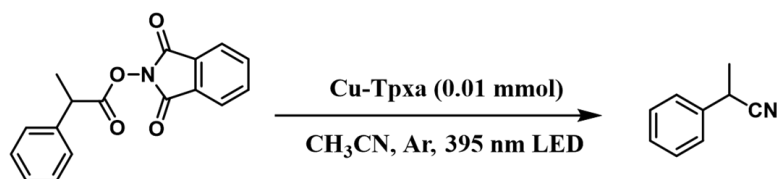
**Figure S13.** Time-dependent luminescence decays of Cu-Tpxa-2 suspension before and after the addition of NHP ester.



**Figure S14.** A magnified TEM image Cu-Tpxa-1 after four cycles of reaction, showing the step-like cross section of the laminated thin layers



**Figure S15.** (a) Tyndall effect of Cu-**Tpax**-1 after stripping; (b) Comparison of the Tyndall effect of the stripped Cu-**Tpax**-1 (right) and the blank sample (Acetonitrile, left).

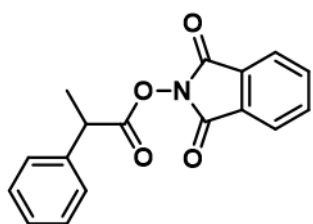
**Table S1. Optimization of Reaction Conditions<sup>a</sup>**

Entry	Conditions	Yield (%) <sup>b</sup>
1 <sup>a</sup>	Standard conditions	70
2	No light	0
3	No Cu-Tpaxa-1	0
4	Air instead of Ar	trace
5	Cu-Tpaxa-2 instead of Cu-Tpaxa-1	61
6	Tpaxa instead of Cu-Tpaxa-1	0
7	CuI instead of Cu-Tpaxa-1	15
8	CuI and Tpaxa instead of Cu-Tpaxa-1	17
9	455 nm LED instead of 395 nm LED	trace

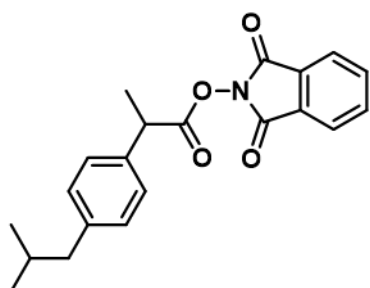
<sup>a</sup>Standard conditions: NHP ester (0.1 mmol), TMSCN (0.15 mmol), NaCO<sub>3</sub> (0.1 mmol), Cu-Tpaxa-1 (0.01 mmol), ultradry CH<sub>3</sub>CN (3mL); The mixture was irradiated with 395 nm LED; <sup>b</sup>Yield of 2-phenylpropanenitrile were determined by GC chromatogram.

#### 4. Catalysis Details

**Synthesis and Characterization of N-(Acyloxy)phthalimides :** In a round bottom flask, alkyl carboxylic acid (10 mmol), *N,N*-dimethylpyridine (DMAP, 1.0 mmol) and *N*-hydroxyphthalimide (NHP, 11.0 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The solution was cooled under an ice-water bath, then a solution of *N,N*-dicyclohexylcarbodiimide (DCC) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added dropwise. The reaction mixture was allowed to stir overnight at room temperature. After that, the heterogeneous mixture was filtered through a pad of silica gel and rinsed with CH<sub>2</sub>Cl<sub>2</sub> (or EA in the case of highly polar product). The filtrate was concentrated under reduced pressure, and further purification via silica gel chromatography to afford the pure products.



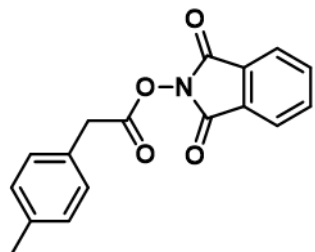
**1,3-dioxoisindolin-2-yl 2-phenylpropanoate (1a):** Purified by chromatography (petroleum ether / ethyl acetate = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.86 (s, 2H), 7.78 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.45 – 7.35 (m, 4H), 7.33 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H).



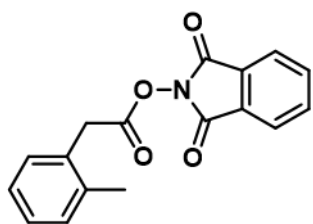
**1,3-dioxoisindolin-2-yl 2-(4-isobutylphenyl)propanoate (1b):** Purified by chromatography (petroleum ether / ethyl acetate = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ



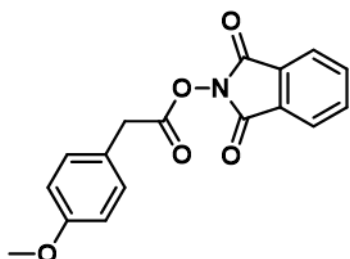
7.86 (s, 2H), 7.77 (dd, J = 5.4, 3.0 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 4.10 (q, J = 7.1 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 1.87 (dt, J = 13.4, 6.8 Hz, 1H), 1.66 (d, J = 7.2 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H).



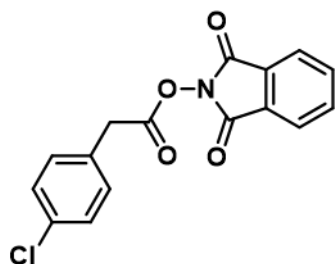
**1,3-dioxoisindolin-2-yl 2-(p-tolyl)acetate (1c):** Purified by chromatography (petroleum ether / ethyl acetate = 5:1). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.09 – 7.83 (m, 4H), 7.28 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 4.14 (s, 2H), 2.30 (s, 3H).



**1,3-dioxoisindolin-2-yl 2-(o-tolyl)acetate (1d):** Purified by chromatography (petroleum ether / ethyl acetate = 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (td, J = 5.2, 2.0 Hz, 2H), 7.82 – 7.74 (m, 2H), 7.34 – 7.29 (m, 1H), 7.25 – 7.17 (m, 3H), 3.99 (s, 2H), 2.40 (s, 3H).



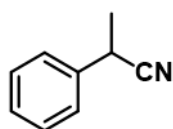
**1,3-dioxoisindolin-2-yl 2-(4-methoxyphenyl)acetate (1e):** Purified by chromatography (petroleum ether / ethyl acetate = 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (dt, J = 7.1, 3.6 Hz, 2H), 7.79 (td, J = 5.2, 2.0 Hz, 2H), 7.32 – 7.28 (m, 2H), 6.94 – 6.88 (m, 2H), 3.94 (s, 2H), 3.81 (s, 3H).



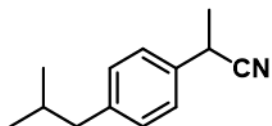
**1,3-dioxoisindolin-2-yl 2-(4-chlorophenyl)acetate (1f):** Purified by chromatography (petroleum ether / ethyl acetate = 5:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.85 (m, 2H), 7.83 – 7.75 (m, 2H), 7.40 – 7.29 (m, 4H), 3.97 (s, 2H).

**Decarboxylative cyanation :** The NHP ester (0.1 mmol),  $\text{TMSCN}$  (0.15 mmol),  $\text{NaCO}_3$  (0.1 mmol),  $\text{Cu-Tpax-1}$  (0.01 mmol), ultradry  $\text{CH}_3\text{CN}$  (3mL) were added to an oven-dried 10 mL quartz test tube which contained a stir bar. Rubber spacers were installed in the test tube, the joint was wrapped with sealing film, and freeze the test tube under liquid nitrogen, then was evacuated and backfilled with nitrogen (3 cycles). The resulting mixture was stirred and equipped with water bath and irradiated with a 395 nm LED for 10 h under room temperature. The catalyst was recovered by centrifugation and filtration, then the solvent was removed under reduced pressure, and the desired products were obtained through column chromatography.

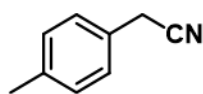
**Photocatalytic products:**



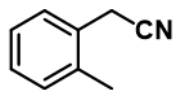
**2-phenylpropanenitrile (2a):** Purified by chromatography (petroleum ether / ethyl acetate = 10:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.28 (m, 5H), 3.89 (q,  $J = 7.3$  Hz, 1H), 1.64 (d,  $J = 7.3$  Hz, 3H).



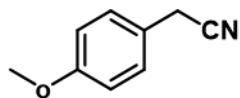
**2-(4-isobutylphenyl)propanenitrile (2b):** Purified by chromatography (petroleum ether / ethyl acetate = 10:1).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  7.30 (d,  $J$  = 8.0 Hz, 2H), 7.19 (d,  $J$  = 8.0 Hz, 2H), 4.25 (q,  $J$  = 7.2 Hz, 1H), 2.44 (d,  $J$  = 7.2 Hz, 2H), 1.83 (dt,  $J$  = 13.5, 7.1 Hz, 1H), 1.52 (d,  $J$  = 7.2 Hz, 3H), 0.86 (dd,  $J$  = 6.5, 3.7 Hz, 6H).



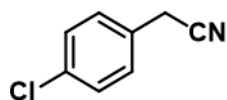
**2-(p-tolyl)acetonitrile (2c):** Purified by chromatography (petroleum ether / ethyl acetate = 10:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (q,  $J$  = 8.3 Hz, 4H), 3.69 (s, 2H), 2.34 (s, 3H).



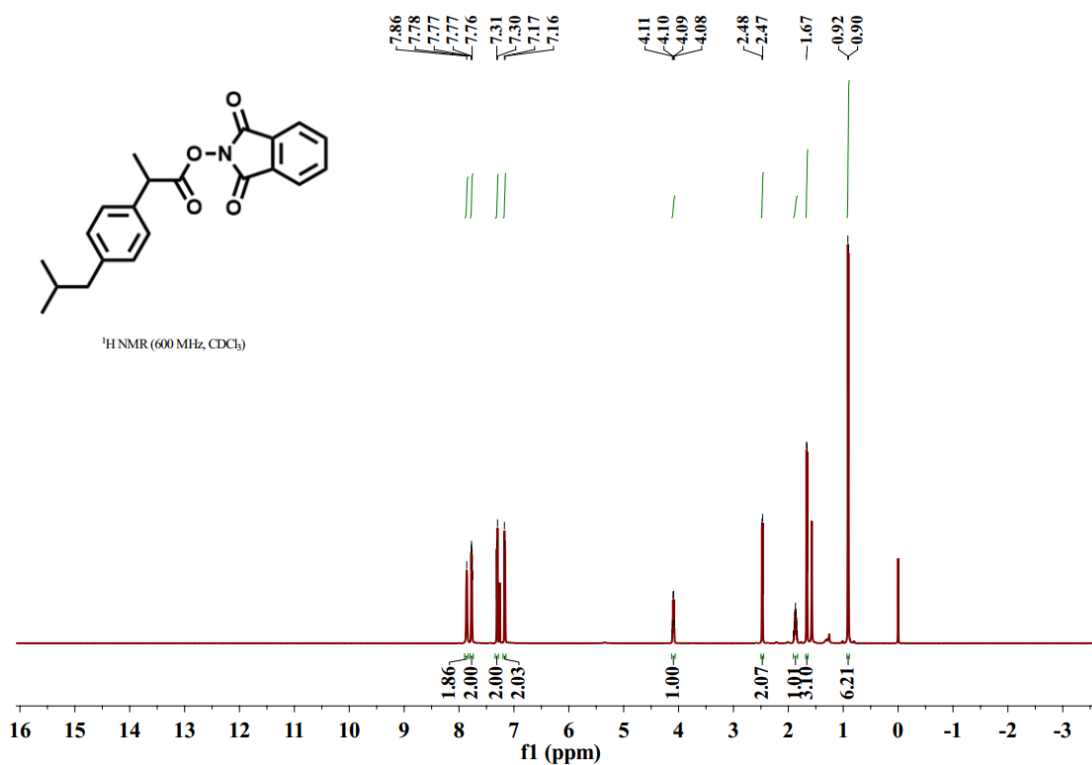
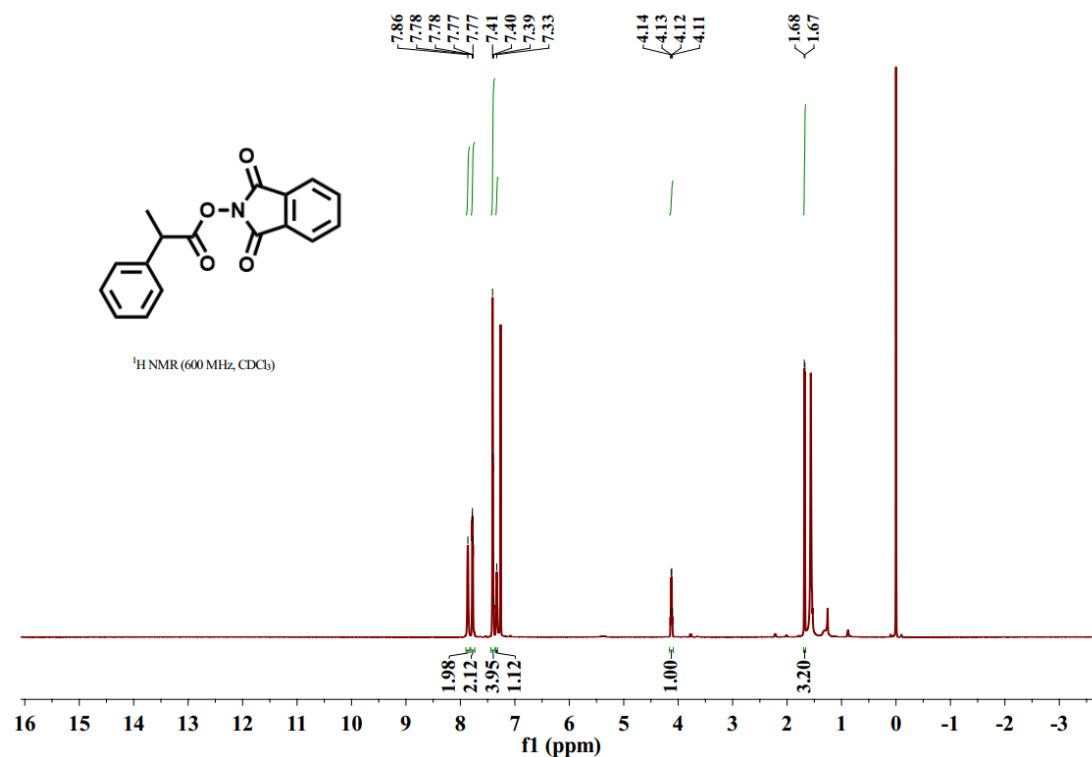
**2-(o-tolyl)acetonitrile (2d):** Purified by chromatography (petroleum ether / ethyl acetate = 10:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.30 (m, 1H), 7.22 (dq,  $J$  = 8.8, 3.1 Hz, 3H), 3.64 (s, 2H), 2.38 – 2.26 (m, 3H).

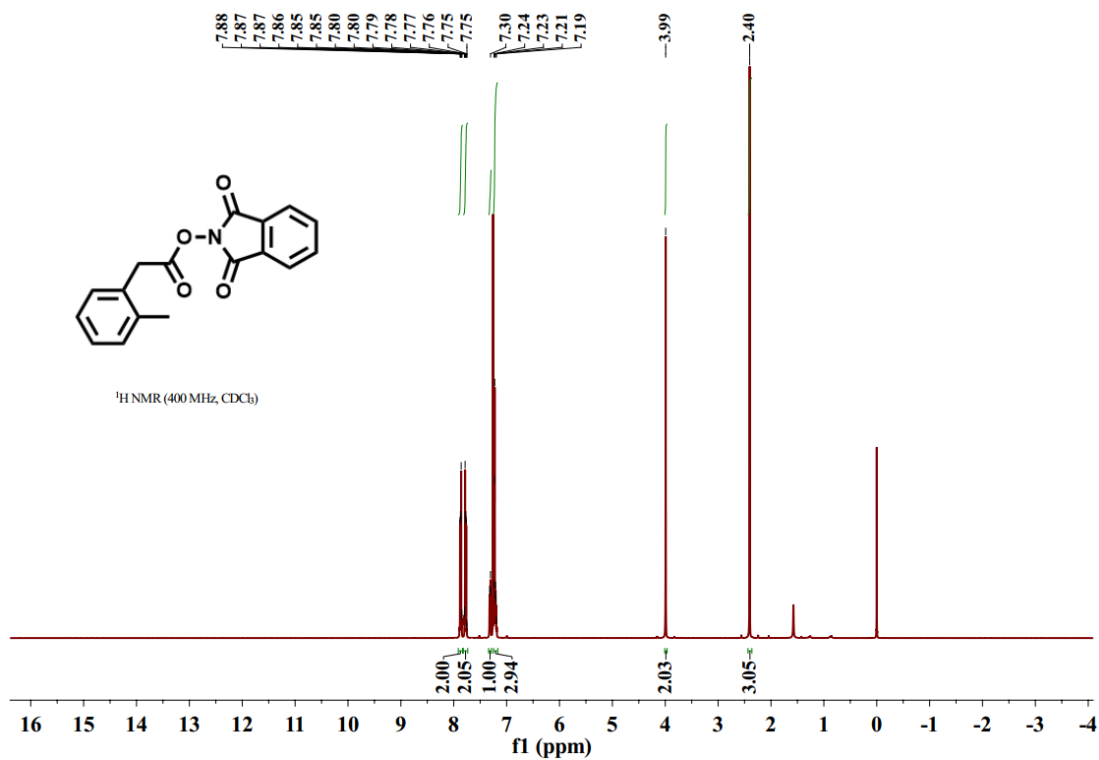
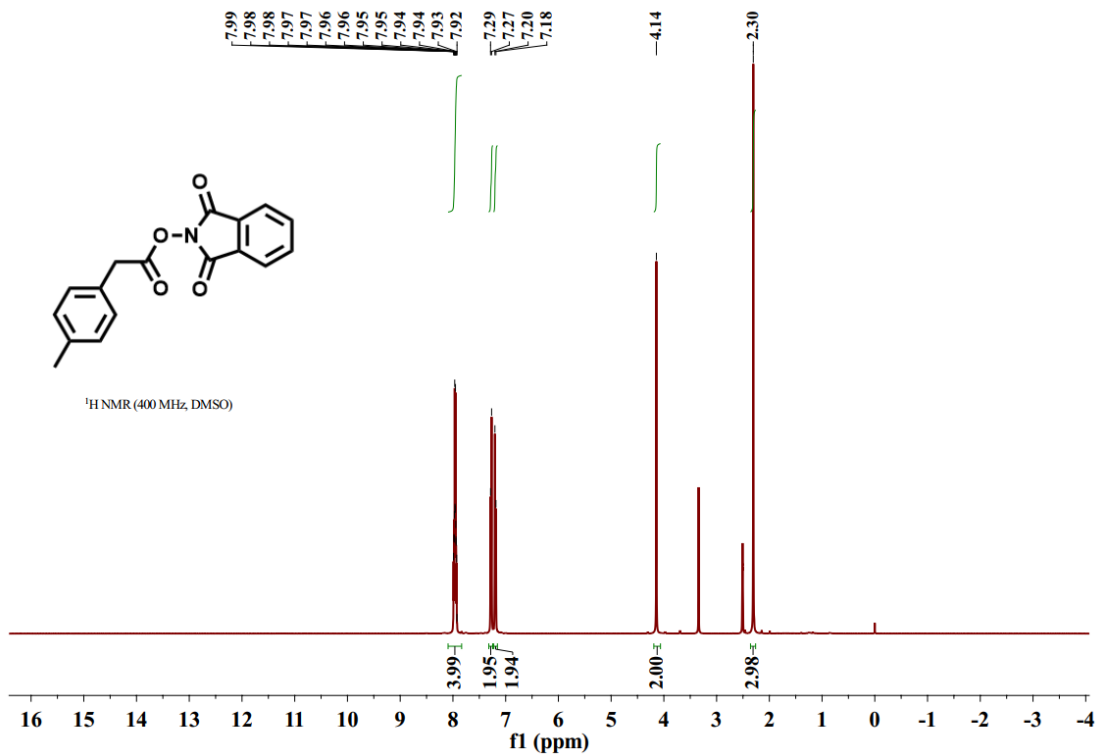


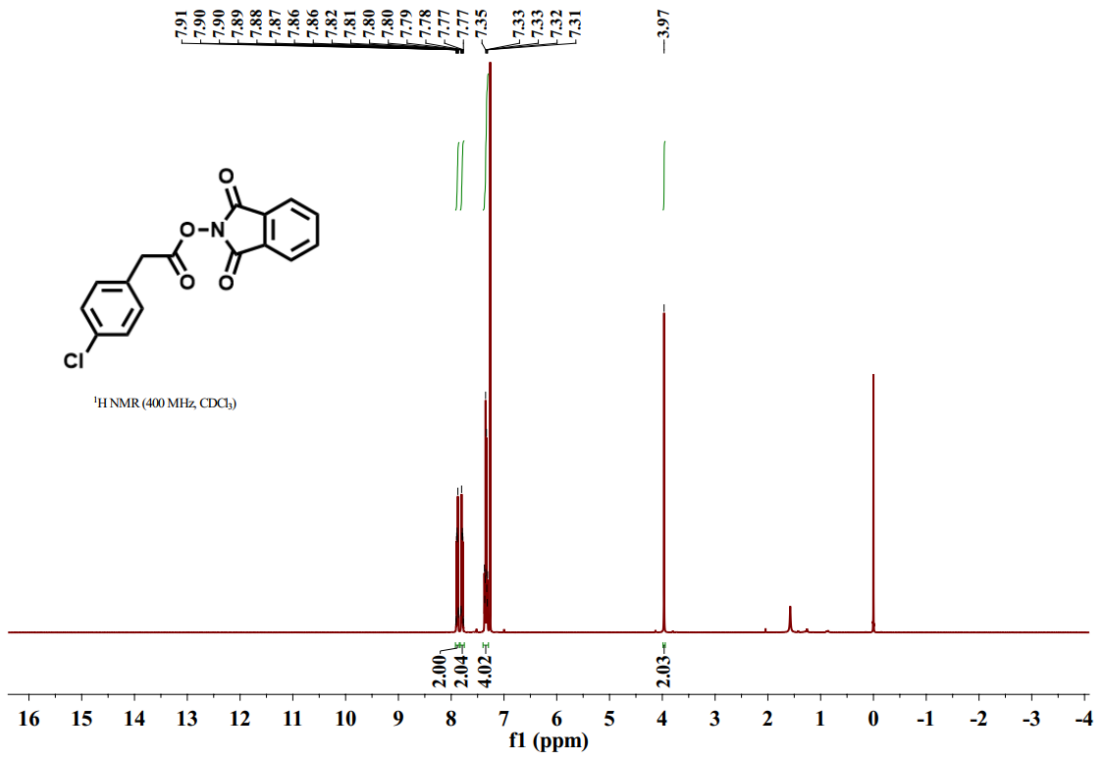
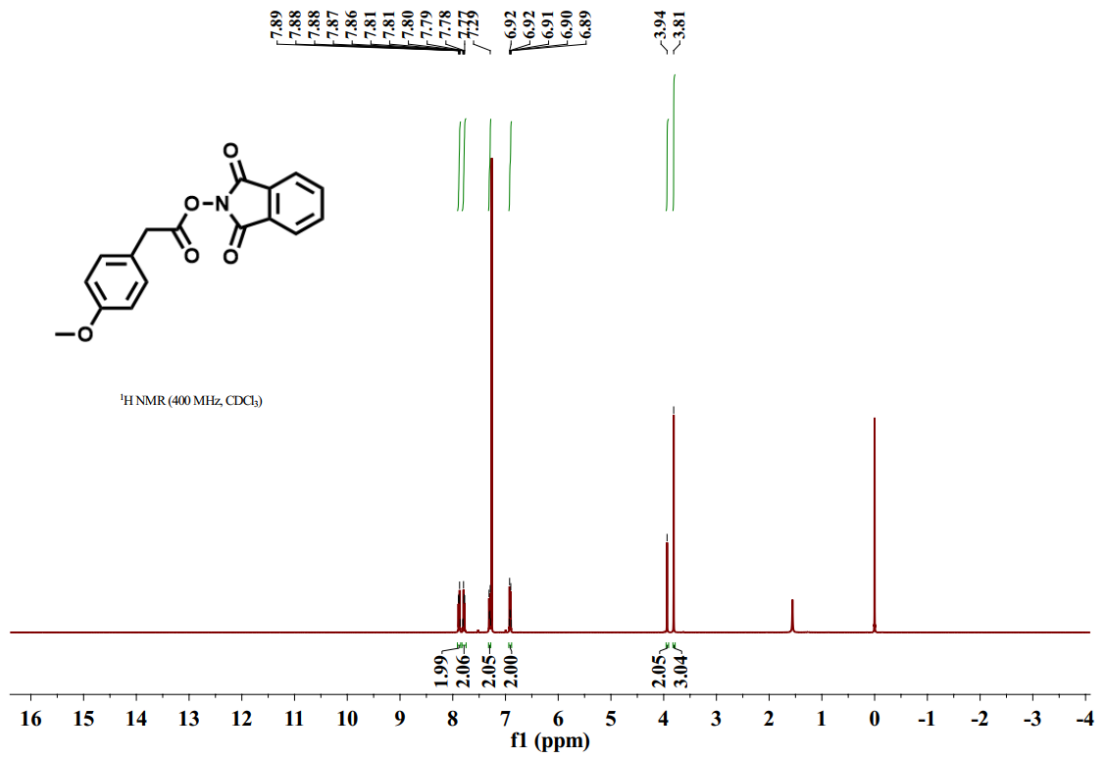
**2-(4-methoxyphenyl)acetonitrile (2e):** Purified by chromatography (petroleum ether / ethyl acetate = 10:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.19 (m, 2H), 6.93 – 6.85 (m, 2H), 3.80 (s, 3H), 3.66 (d,  $J$  = 12.4 Hz, 2H).

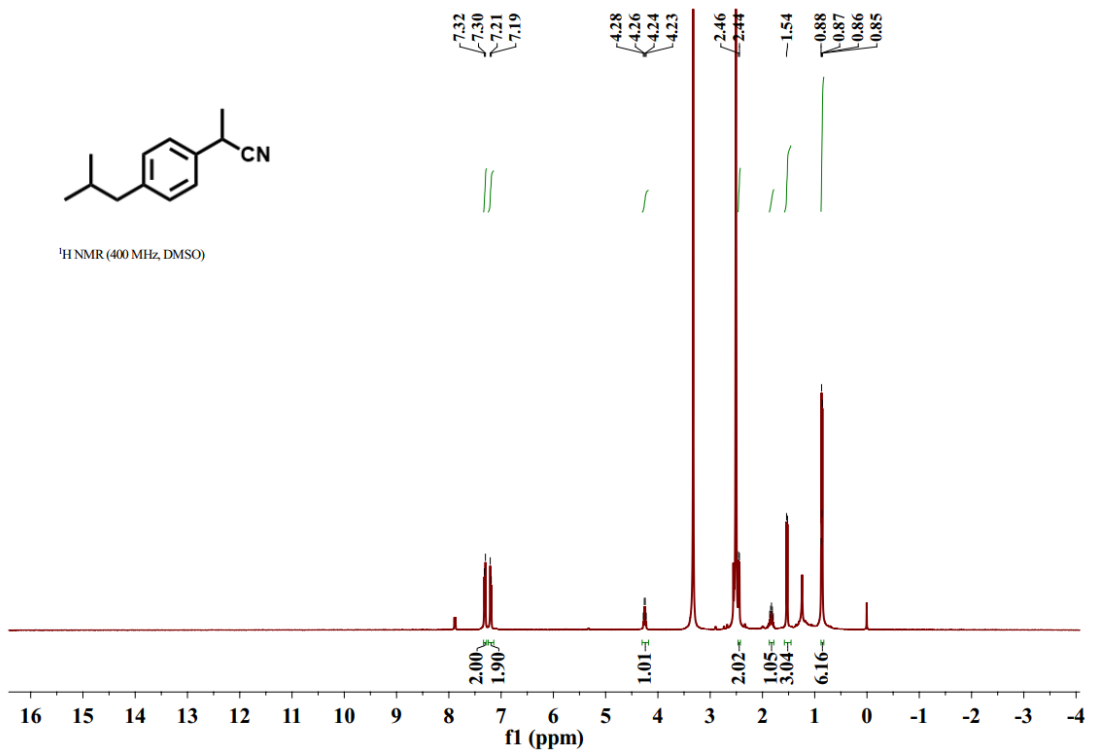
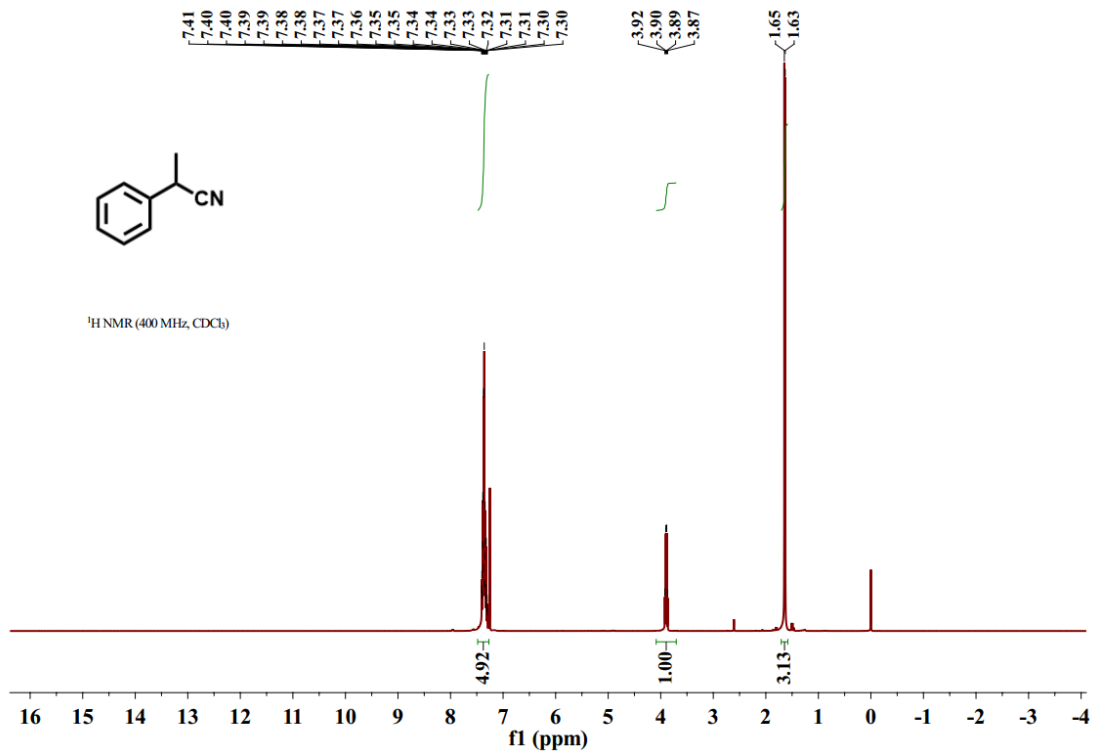


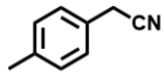
**2-(4-chlorophenyl)acetonitrile (2f):** Purified by chromatography (petroleum ether / ethyl acetate = 10:1).  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.59 – 7.23 (m, 4H), 4.05 (s, 2H).



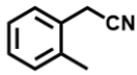
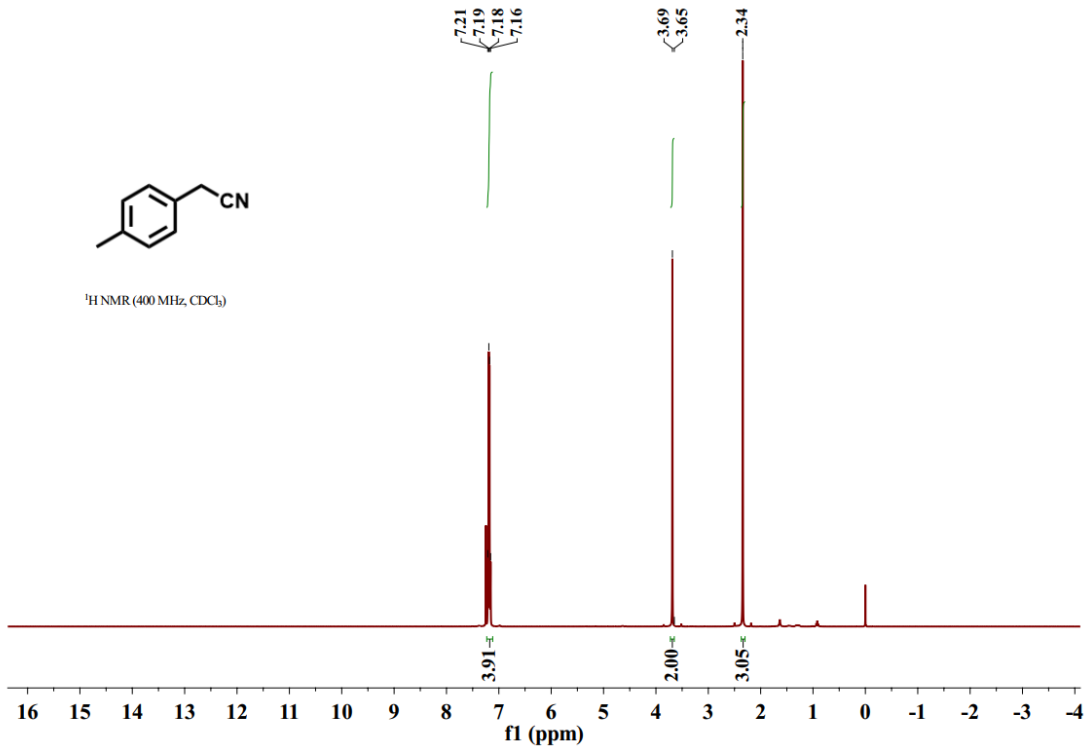




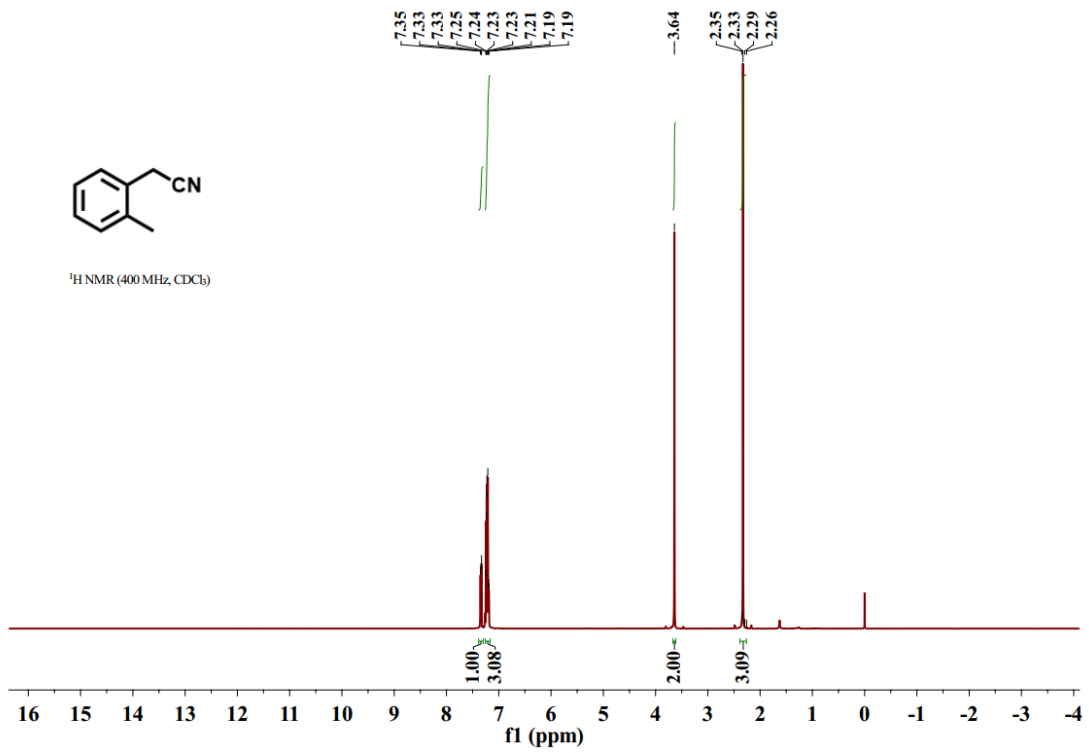




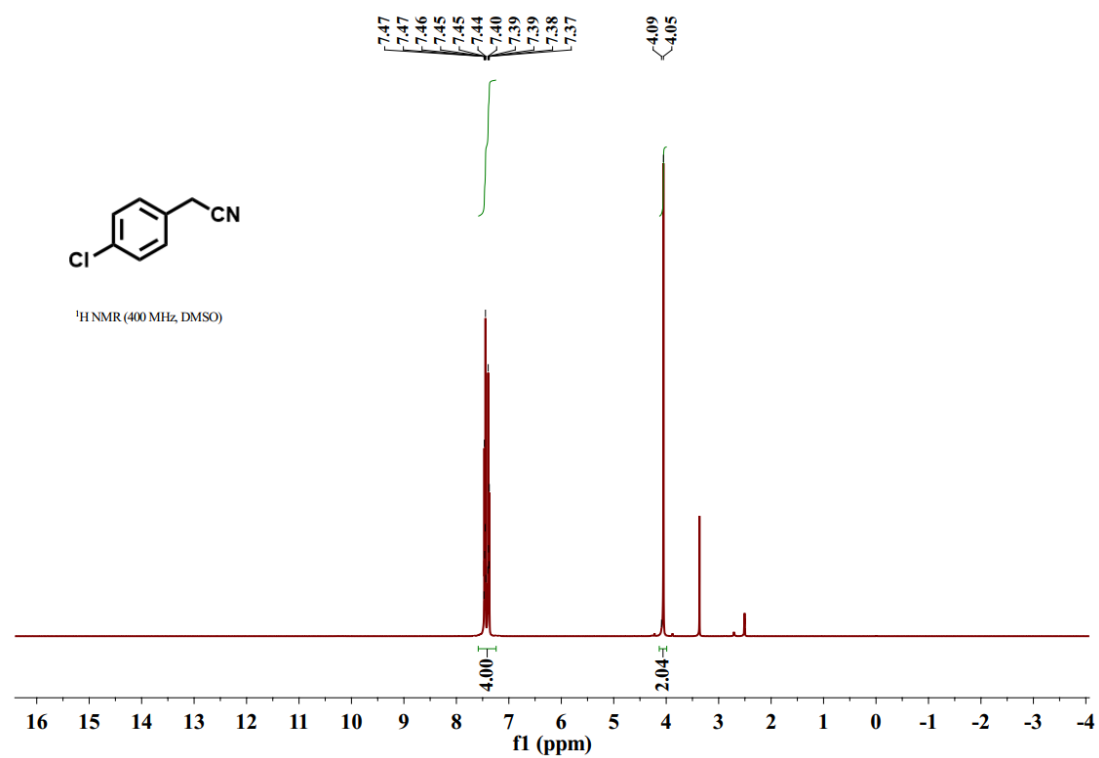
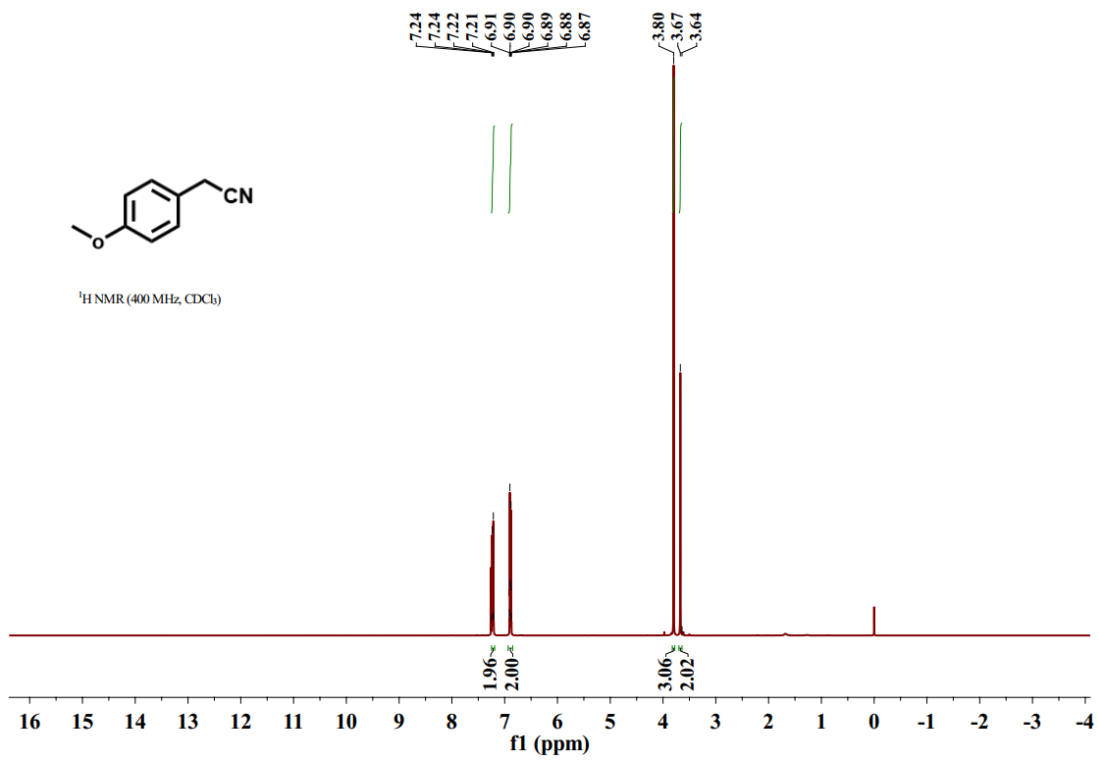
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)







## References

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