

Proton Reduction Catalyst Grafted Covalent Organic Frameworks for Visible-Light-Driven Acceptorless Dehydrogenation of Cyclic Amines

Bin Wang ¹, Xinyu Shi ¹, Qianping Wang ¹, Xinrui Jiang ¹, Wanqi Wang ¹, Hui Chen ^{1 *}

1. Instrumentation

2. Methods

3. Supplementary Figures and Table

4. ^1H NMR Spectrum

1. Instrumentation

Powder X-ray diffraction (PXRD) data were collected using a D8 diffractometer from Bruker, Germany, at 40 kV and 30 mA with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The scanning range was set from 2° to 40° with a step size of 0.02° . X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo ESCALAB 250XI spectrometer from Thermo Fisher Scientific, USA. Fourier transform infrared (FT-IR) spectra was recorded using an IRPrestige-21 spectrometer from Shimadzu, Japan, in the range of $500\text{--}4000 \text{ cm}^{-1}$, with samples mixed with KBr powder and pressed into pellets for testing. The Brunauer Emmett Teller (BET) specific surface area and porous structure of the materials were measured using a JW-BK200C instrument from JWGB, China, through N₂ physical adsorption, with samples degassed at 120°C for 6 hours prior to testing. The surface morphology of the samples was analyzed using a Gemini SEM500 field emission scanning electron microscope (FE-SEM) from Carl Zeiss, Germany. The lattice fringe spacing of the samples was observed using a Talos F200X high-resolution transmission electron microscope (HR-TEM) from Thermo Fisher, USA. Ultraviolet-visible (UV-Vis) absorption spectra were obtained through diffuse reflectance spectroscopy (DRS) measurements in the range of $200\text{--}800 \text{ nm}$ using a Lambda850⁺ instrument from PerkinElmer, USA. Photoluminescence (PL) spectra were analyzed using an F-320 fluorescence spectrophotometer from Tianjin Gangdong, China. Thermal stability data were obtained in the range of 298 K to 1073 K using a TGA/DSC 3+thermogravimetric analyzer from Mettler Toledo, Switzerland, with a heating rate of $10^\circ\text{C}/\text{min}$.

2.Methods

2.1 Electrochemical measurement

All photoelectrochemical measurements, including transient photocurrent response, Mott-Schottky plots, and electrochemical impedance spectroscopy (EIS), were carried out on a CHI 660E electrochemical workstation with a conventional three-electrode setup, using 0.5 M aqueous sodium sulfate (Na_2SO_4) solution as the supporting electrolyte. A conductive glass substrate coated with the as-prepared catalyst slurry was used as the working electrode, a platinum foil was employed as the counter electrode, and a saturated Ag/AgCl electrode served as the reference electrode.

2.2 CV measurement

Three electrode systems comprising glassy carbon (3 mm dia.) was used as working electrode and Ag/AgCl (0.1 M Tetrabutylammonium in acetonitrile) as reference electrode and platinum wire was used as counter electrode, respectively. CVs were recorded in acetonitrile containing 0.1 M Tetrabutylammonium hexafluorophosphate as electrolytic medium. Solutions were purged with argon for 30 minutes before scans and also jacketed during the measurements.

2.3 EPR measurement

Electron paramagnetic resonance radical-trapping spectra were recorded at room temperature on a Bruker Elexsys E500 X-band spectrometer with 34W blue led irradiation source. Key parameters: microwave frequency 9.85 GHz, power 10 mW, modulation amplitude 1 G. 5,5-Dimethyl-1-pyrroline-N-oxide was used as the spin trap. The test solution contained tetrahydroquinoline (0.1 M), Co-PT-COF (8 mg) and DMPO (0.5 M) in deionized water. The solution was loaded into a quartz capillary, irradiated for 120 s and tested. Control experiments were performed under identical conditions without Co-PT-COF, light irradiation, or tetrahydroquinoline, respectively.

3. Supplementary Figures and Table

Table S1. The atomistic coordinates of PT-COF with AA stacking generated by calculations.

PT-COF AA Stacking Space group symmetry: <i>P1</i> $a = 53.272 \text{ \AA}$, $b = 25.047 \text{ \AA}$, $c = 3.838 \text{ \AA}$ $\alpha = 90.00^\circ$; $\beta = 89.94^\circ$; $\gamma = 90.48^\circ$							
Atom	x	y	z	Atom	x	y	z
C1	53.999	-227.674	0.526	C31	60.349	-217.274	1.825
C2	52.646	-227.594	0.104	C32	60.474	-214.917	1.823
C3	51.892	-228.777	-0.100	C33	62.450	-216.203	1.741
C4	52.032	-226.362	-0.138	C34	63.919	-216.254	1.642
C5	58.129	-218.390	1.868	C35	66.030	-215.078	1.418
C6	54.882	-226.487	0.760	C36	64.643	-215.058	1.542
C7	56.282	-226.639	0.761	H1	52.640	-225.410	0.016
C8	57.125	-225.542	0.968	H2	57.651	-217.361	1.980
C9	56.585	-224.270	1.183	H3	56.743	-227.667	0.593
C10	55.191	-224.111	1.203	H4	58.256	-225.683	0.961
C11	54.354	-225.208	0.999	H5	54.737	-223.081	1.386
C12	57.327	-219.528	1.796	H6	53.222	-225.074	1.026
C13	57.907	-220.789	1.658	H7	56.192	-219.430	1.850
C14	59.304	-220.909	1.603	H8	59.784	-221.938	1.498
C15	60.110	-219.766	1.677	H9	61.244	-219.865	1.633
C16	59.525	-218.496	1.804	H10	55.889	-221.808	1.583
C17	57.020	-221.947	1.527	H11	55.648	-203.573	1.055
C18	53.837	-204.723	0.133	H12	52.729	-207.197	1.168
C19	52.486	-204.638	0.133	H13	53.975	-209.347	1.561
C20	54.556	-203.536	0.731	H14	57.791	-207.248	0.981
C21	53.867	-207.197	1.110	H15	56.536	-205.085	0.572
C22	54.553	-208.391	1.334	H16	58.566	-208.871	1.533
C23	55.947	-208.421	1.282	N1	57.466	-223.151	1.348
C24	56.617	-209.671	1.471	N2	56.617	-209.671	1.471
C25	57.907	-209.793	1.471	N3	61.707	-217.343	1.767
C26	58.544	-211.103	1.622	N4	61.826	-214.997	1.766
C27	57.780	-212.273	1.728	N5	59.742	-216.058	1.852
C28	58.410	-213.517	1.813	N6	68.836	-215.217	1.071
C29	59.809	-213.604	1.792	N7	76.510	-224.268	-2.478
C30	59.938	-211.185	1.611	N8	85.635	-216.857	-1.742

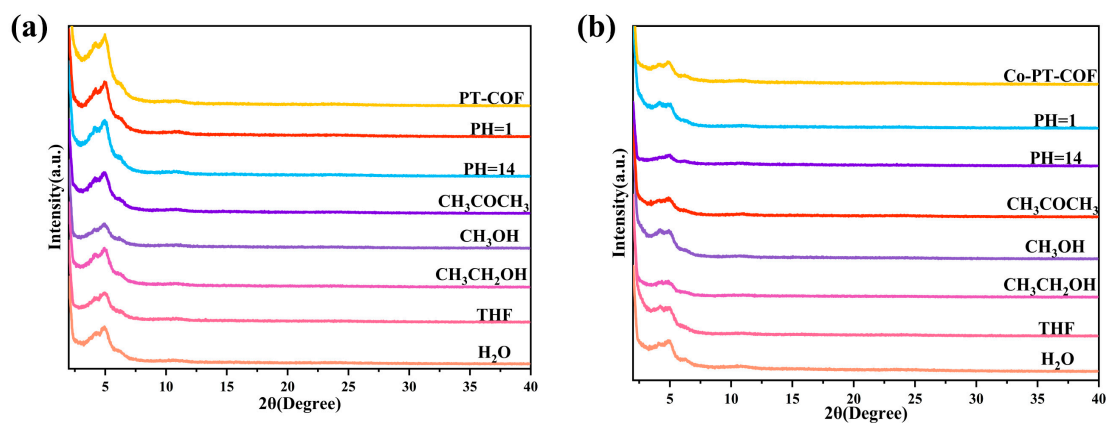


Figure S1. Comparative crystalline stability of (a) PT-COF and (b) Co-PT-COF in various solvents

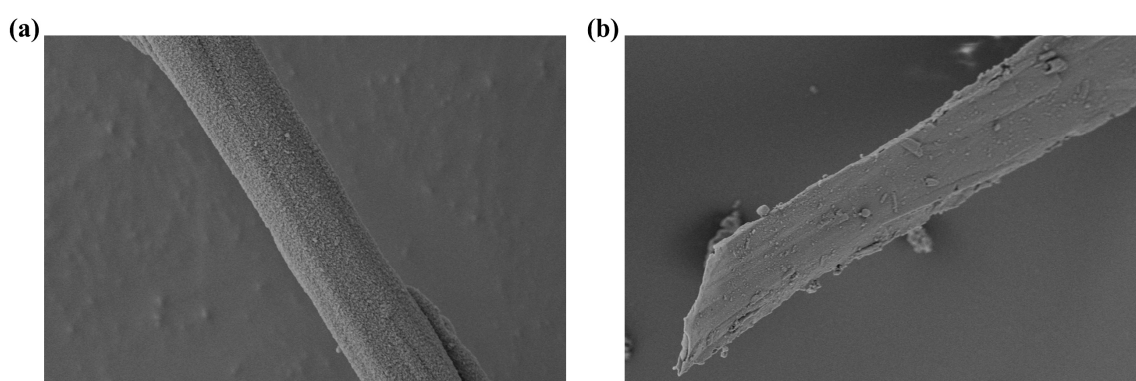


Figure S2. FE-SEM images of (a) PT-COF, (b) Co-PT-COF.

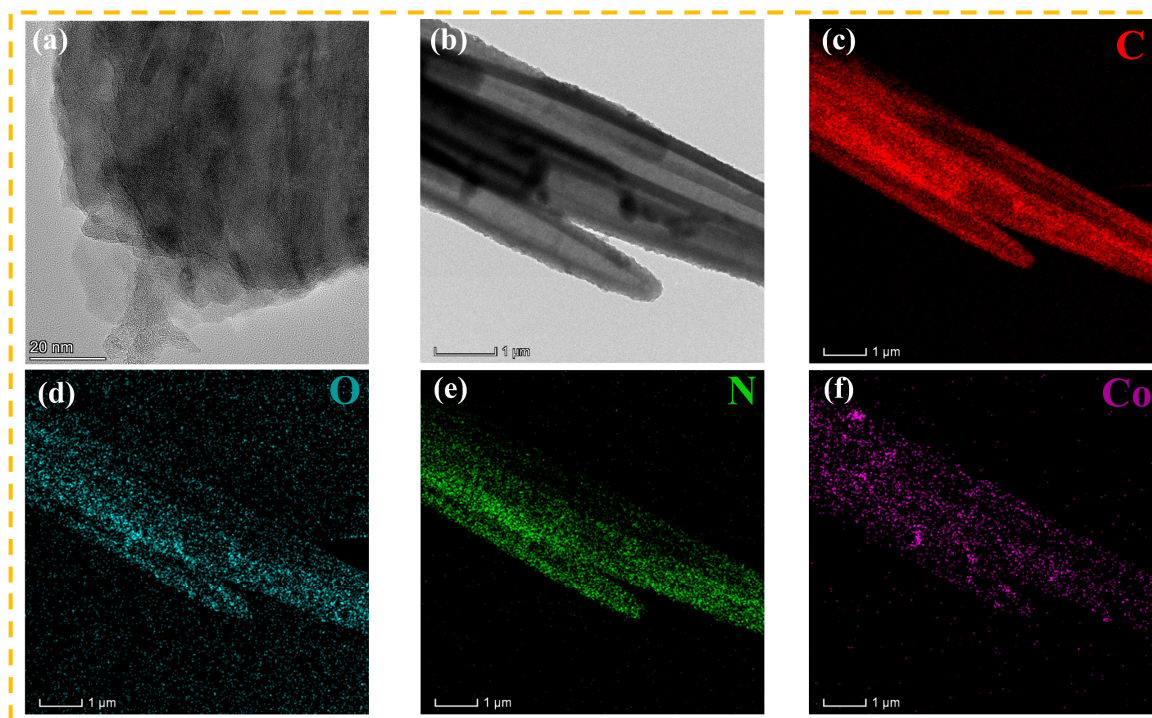


Figure S3. (a) The HRTEM image of Co-PT-COF. (b) The TEM image of Co-PT-COF. (c) ~ (f)

The EDX mapping of Co-PT-COF (Co: purple, C: red, O: cyan, N: Green).

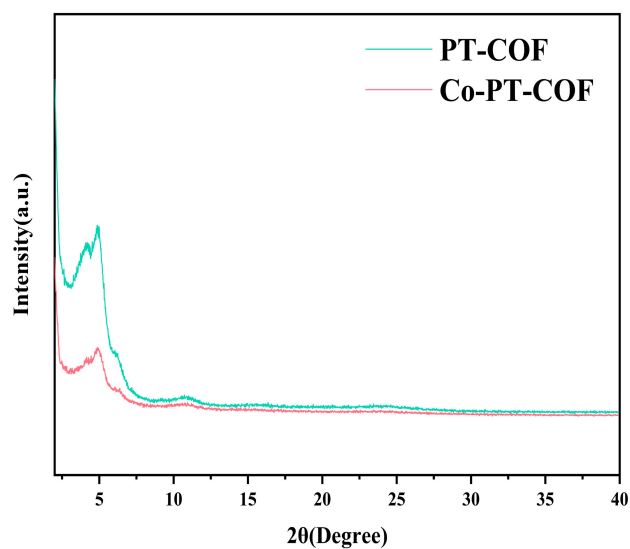


Figure S4. PXRD pattern of experimental PT-COF (green) and Co-PT-COF (pink).

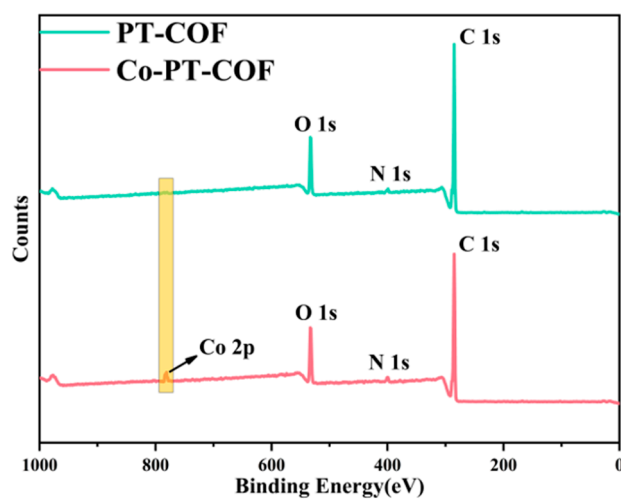


Figure S5. XPS spectra of PT-COF and Co-PT-COF.

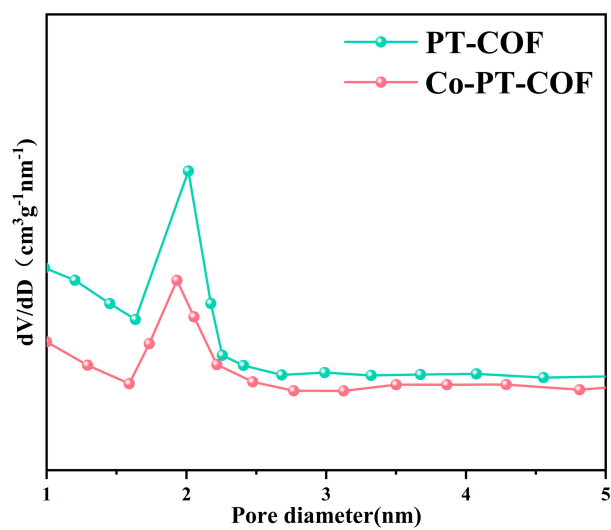


Figure S6. The pore size distribution of PT-COF and Co-PT-COF.

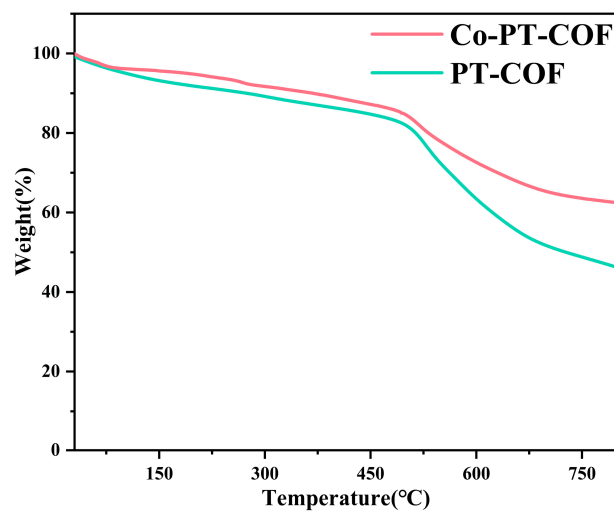


Figure S7. TGA of PT-COF and Co-PT-COF.

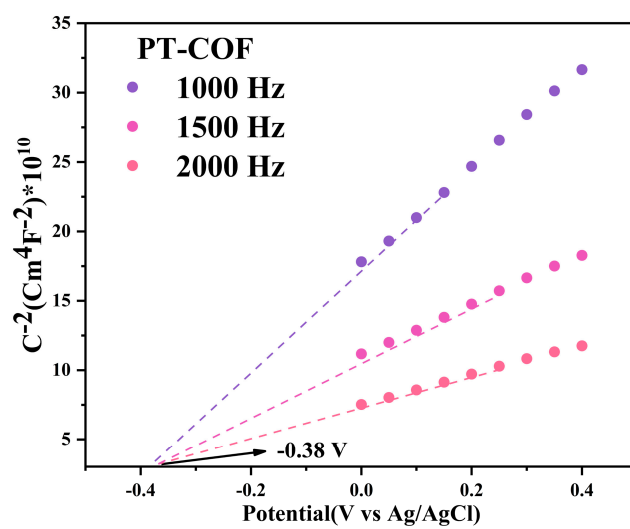


Figure S8. Mott-Schottky curves of PT-COF.

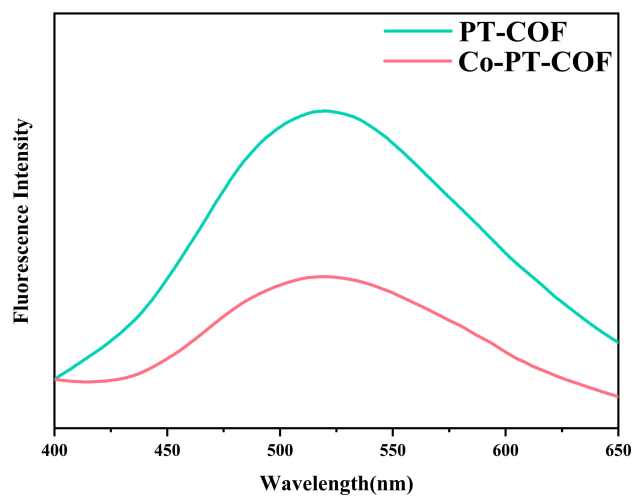
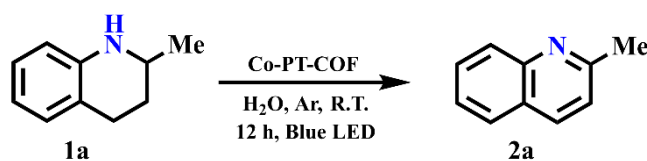
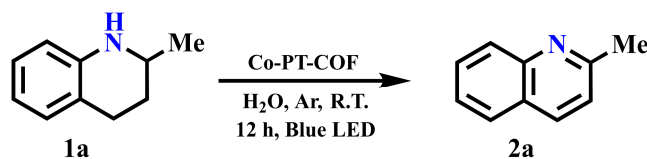


Figure S9. PL spectra of PT-COF and Co-PT-COF.

Table S2. Influence of solvents in the reaction

Entry	Variation from the standard conditions	GC yield ^[b]
1	Methanol instead of water	~ 86%
2	Ethanol instead of water	~ 92%
3	Acetone instead of water	N. R.
4	Acetonitrile instead of water	N. R.
5	Toluene instead of water	N. R.
6	Tetrahydrofuran instead of water	N. R.
7	1,4-Dioxane instead of water	N. R.
8	N,N-Dimethylformamide instead of water	N. R.
9	Dimethyl sulfoxide instead of water	N. R.
10	N-Methylpyrrolidone instead of water	N. R.

Reaction conditions: **1a** (0.25 mmol), Co-PT-COF (10 mg), water (8 mL), Ar atmosphere, visible-light irradiation from blue LED at room temperature for 12 h. ^[b] GC yield using toluene as an internal standard. N.R. = No Reaction.

Table S3. Control experiments at varying pH

Entry	Variation from the standard conditions	GC yield ^[b]
1	standard conditions ^[a]	~ 95%
2	pH = 4	~ 53%
3	pH = 7	~ 92%
4	pH = 9	~ 86%

Reaction conditions: **1a** (0.25 mmol), Co-PT-COF (10 mg), water (8 mL), Ar atmosphere, visible-light irradiation from blue LED at room temperature for 12 h. ^[b] GC yield using toluene as an internal standard. N.R. = No Reaction.

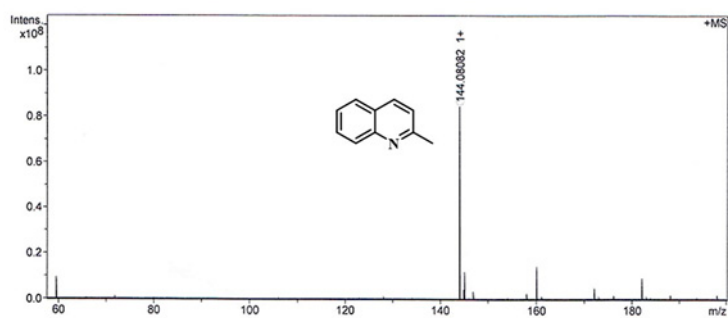


Figure S10. High-resolution mass spectrometry of 2-methylquinoline

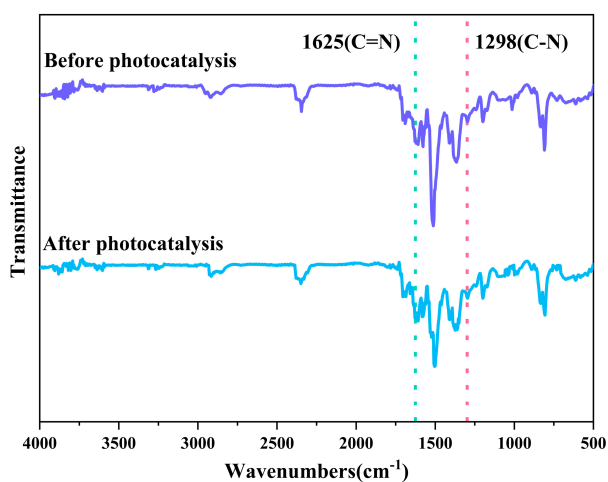


Figure S11. FT-IR spectra of Co-PT-COF before and after photocatalysis.

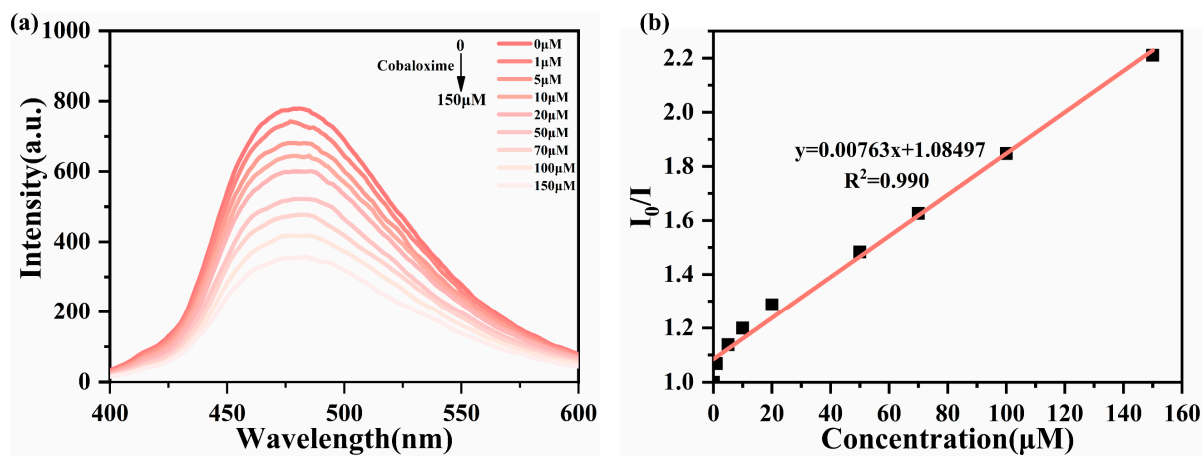


Figure S12. (a) Steady-state emission quenching of PT-COF* with cobaloxime. (b) Stern-Volmer analysis of the results.

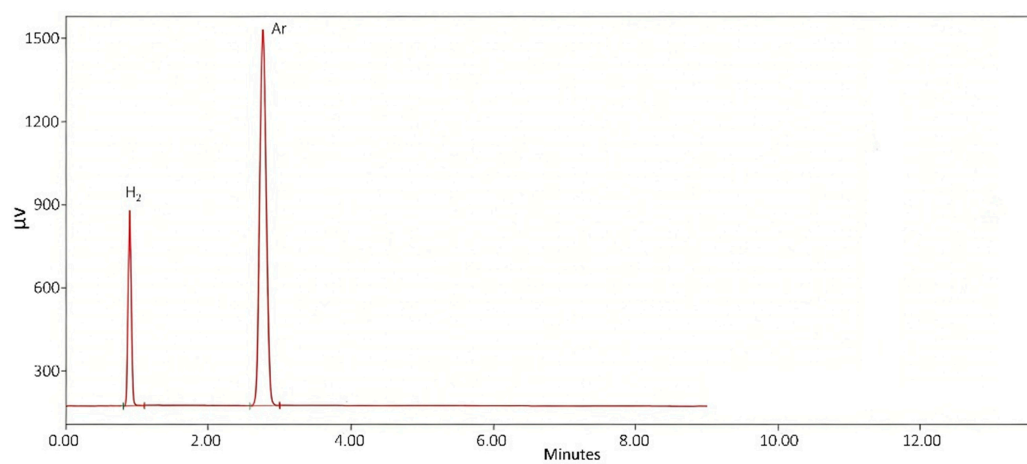


Figure S13. GC analysis.

Chemical structure: 2-methyl-1H-indole (Cc1c[nH]c2ccccc12)

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (6.8-8.1 ppm) and a methyl singlet (2.5 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
8.05	1.00
8.00	1.05
7.73	1.06
7.72	0.95
7.71	1.00
7.21	0.91
2.50	3.18

Chemical structure: 2-methyl-1H-indole (Cc1c[nH]c2ccccc12)

¹H NMR spectrum (CDCl₃) data:

Chemical Shift (ppm)	Integration
8.65 (d, 1H)	1.00
8.05 (d, 1H)	1.04
7.95 (d, 1H)	1.05
7.75 (d, 1H)	2.11
7.65 (d, 1H)	1.04
7.25 (s, 1H)	-
2.35 (s, 3H)	3.13

Figure S15. ^1H NMR spectrum of 3-methylquinoline.

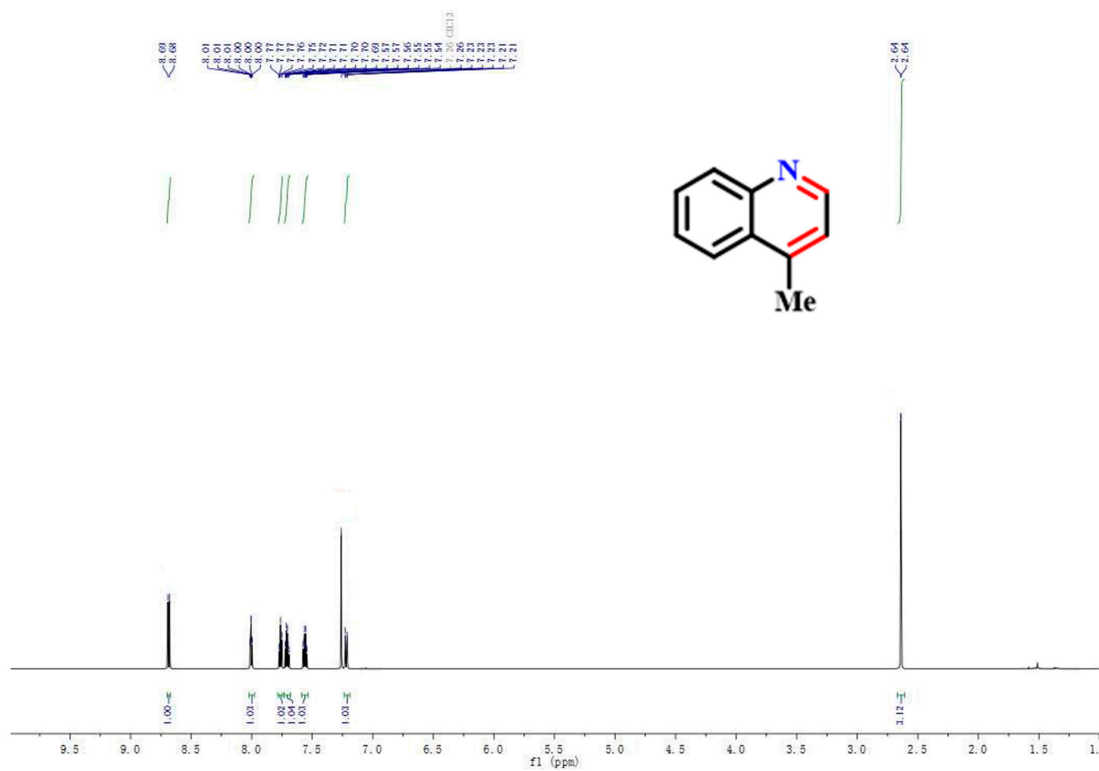


Figure S16. ^1H NMR spectrum of 4-methylquinoline.

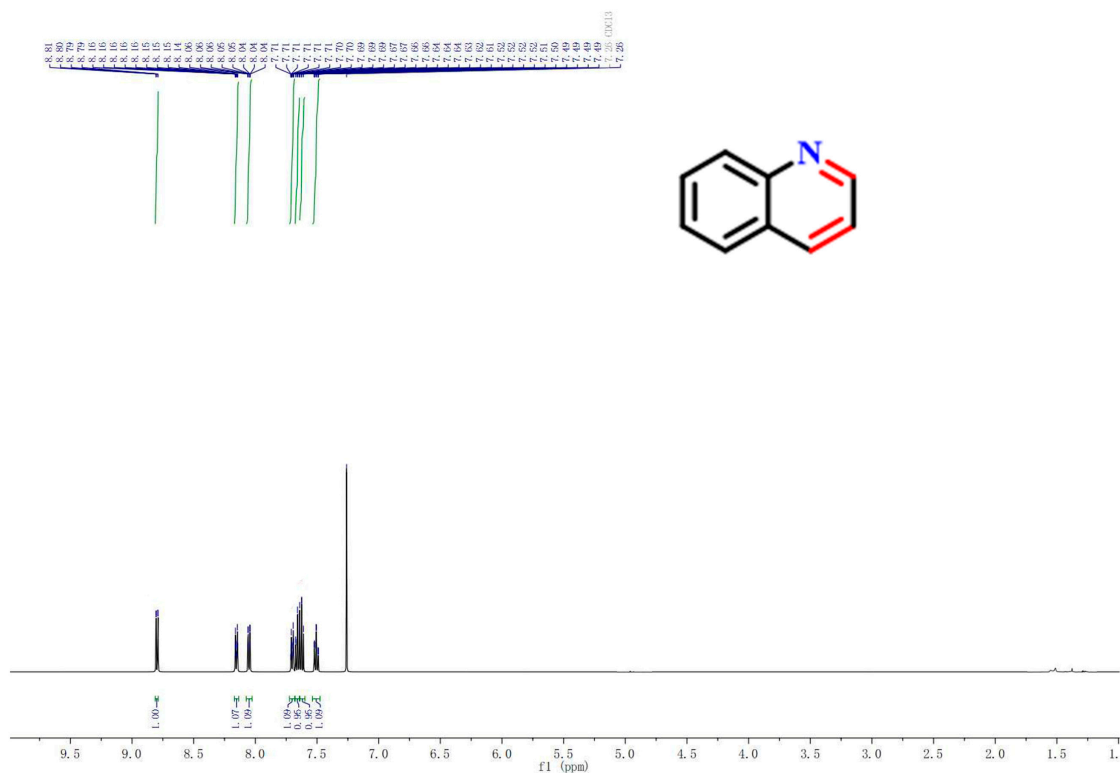
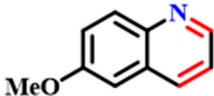


Figure S17. ^1H NMR spectrum of quinoline.



Chemical structure: Clc1ccc2ncncc2c1

¹H NMR spectrum (ppm):

Chemical Shift (ppm)	Integration
8.80, 8.79, 8.78	1.00
8.11, 8.10, 8.09, 8.09	1.09
7.85, 7.84, 7.83, 7.74, 7.73, 7.68, 7.66, 7.65, 7.62, 7.61, 7.50, 7.25	1.10, 1.08, 1.12, 1.12
0.00	Reference

Figure S21. ^1H NMR spectrum of 6-chloroquinoline.

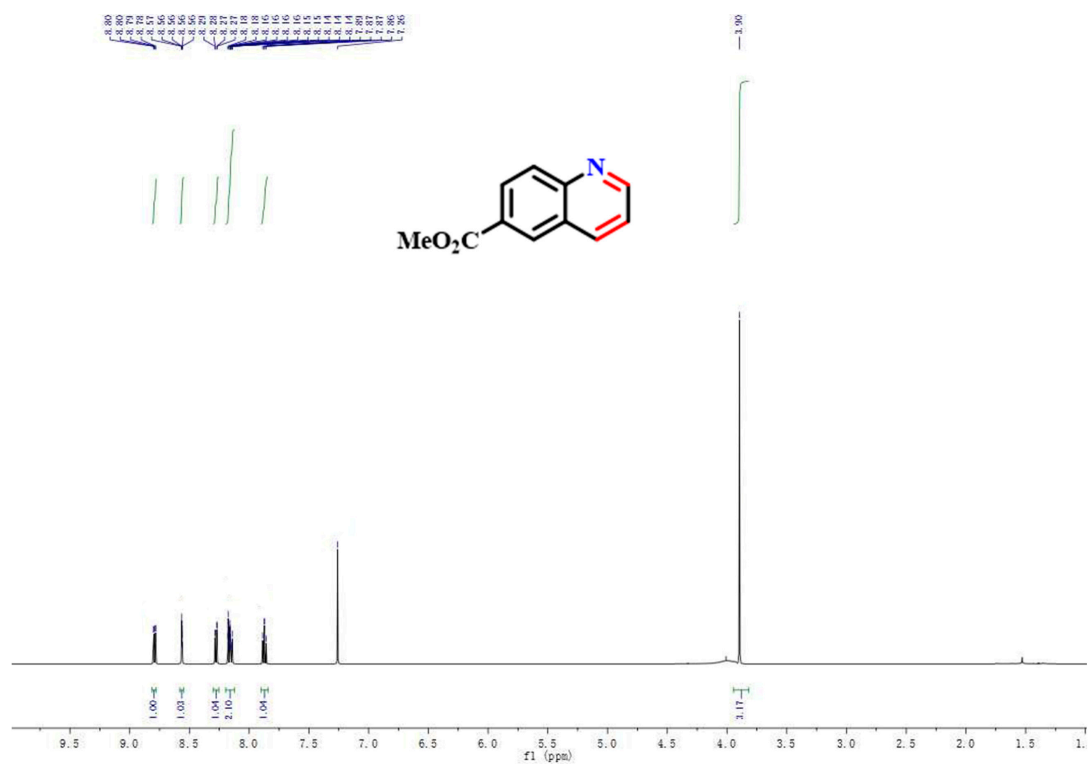


Figure S24. ¹H NMR spectrum of methyl quinoline-6-carboxylate.

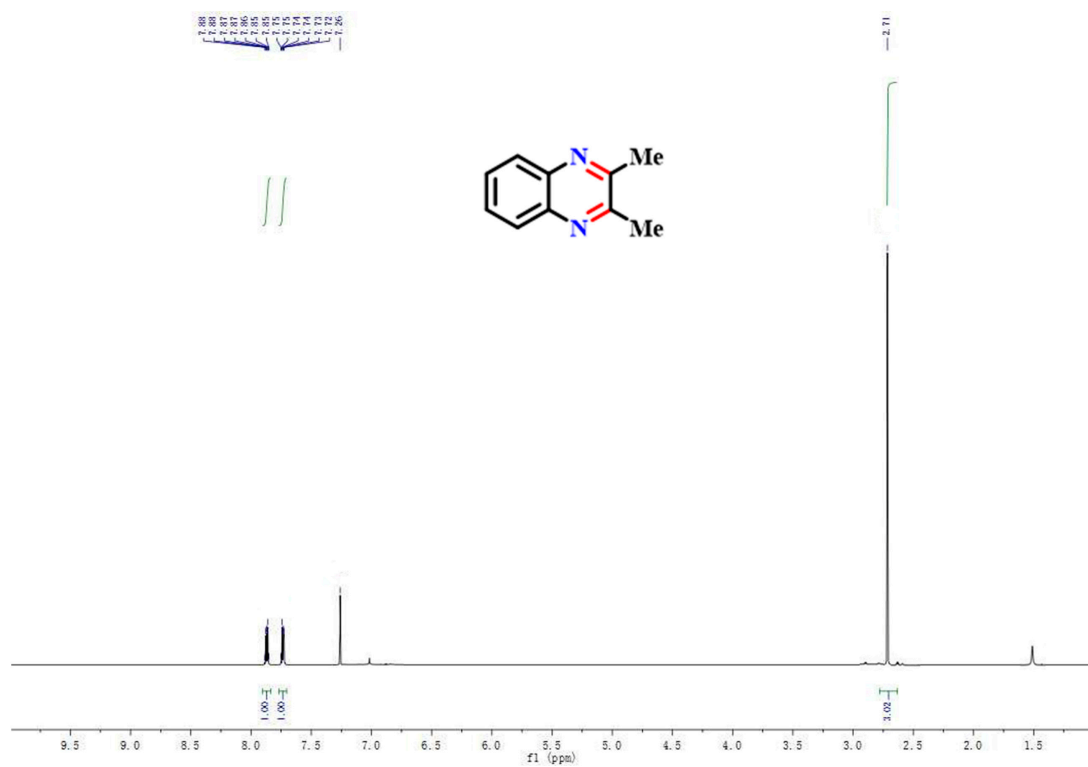


Figure S25. ¹H NMR spectrum of 2,3-dimethylquinoxaline.

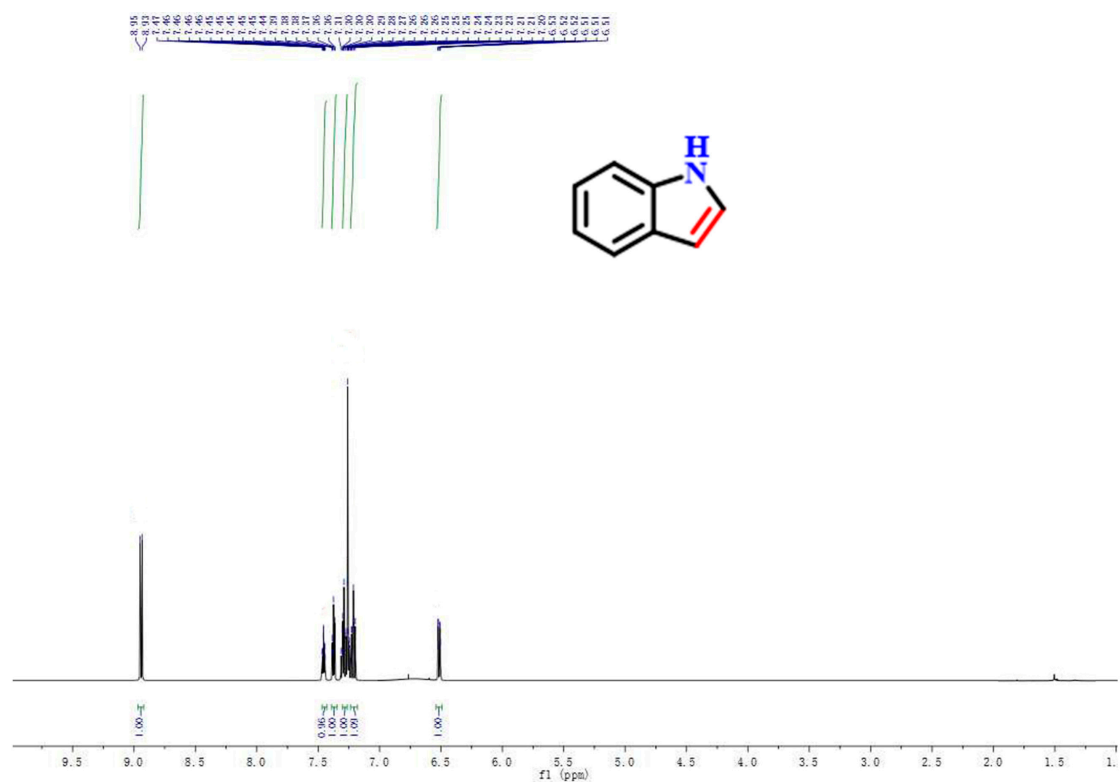


Figure S26. ¹H NMR spectrum of indole.

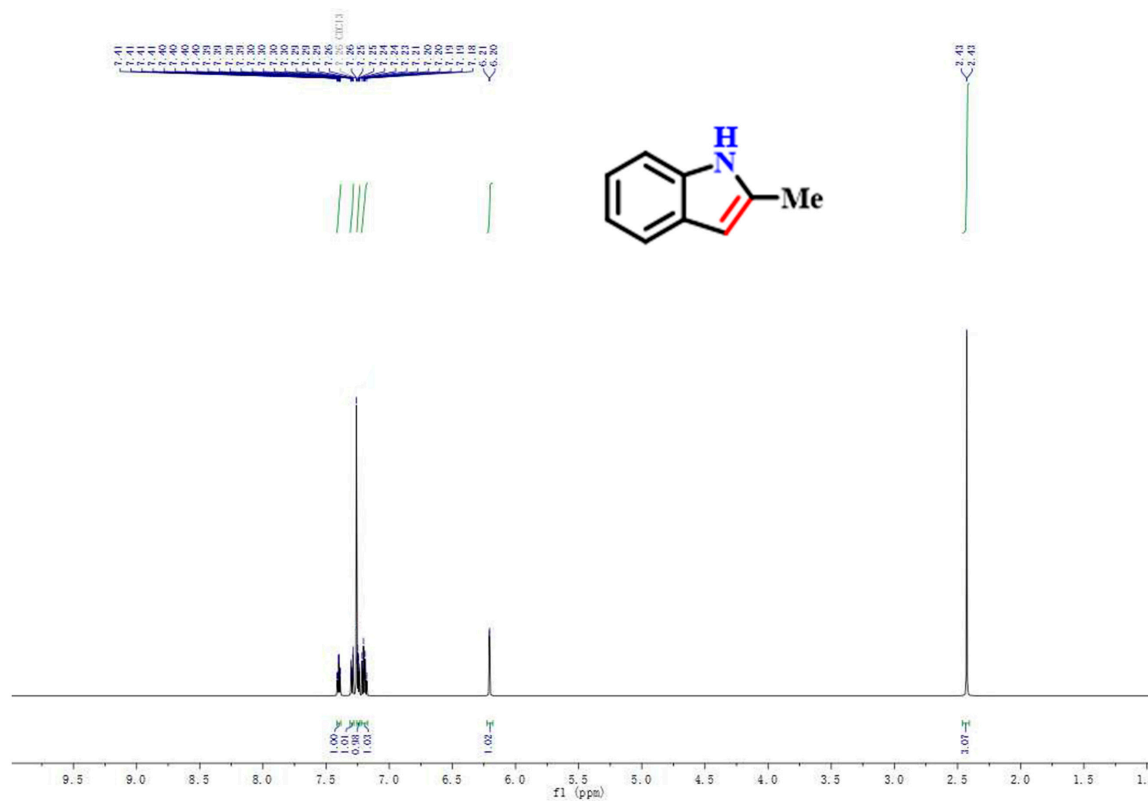


Figure S27. ¹H NMR spectrum of 2-methylindole.

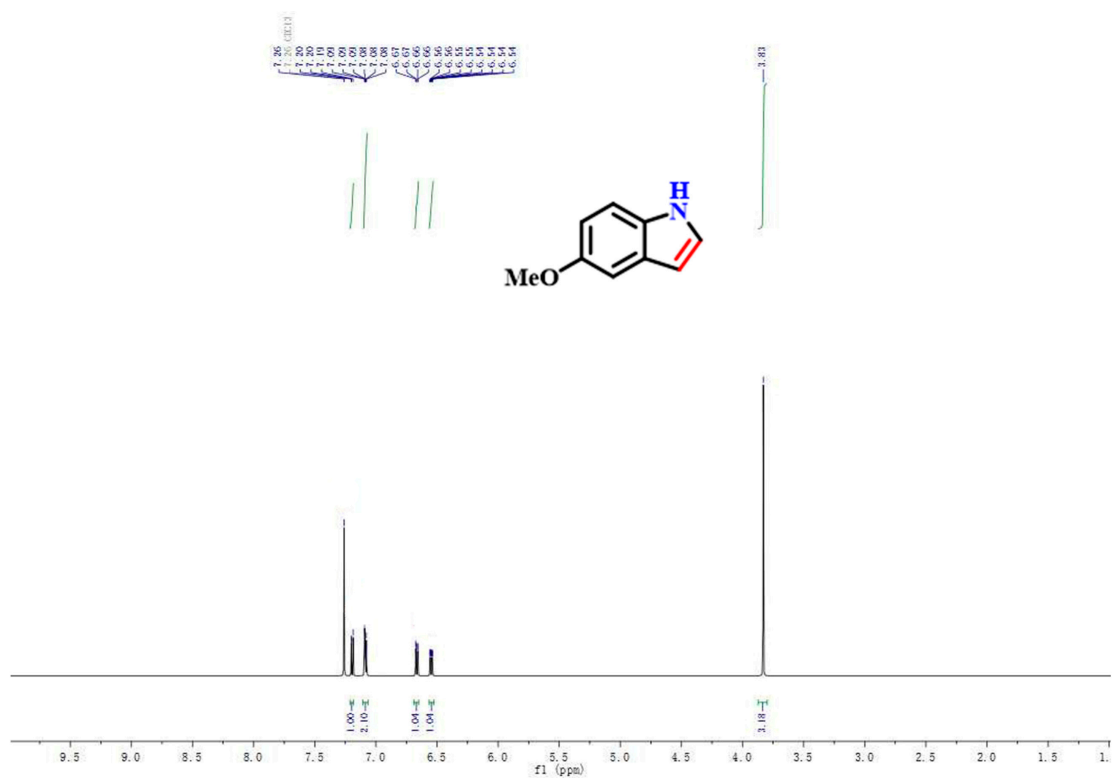


Figure S28. ¹H NMR spectrum of 5-methoxyindole.

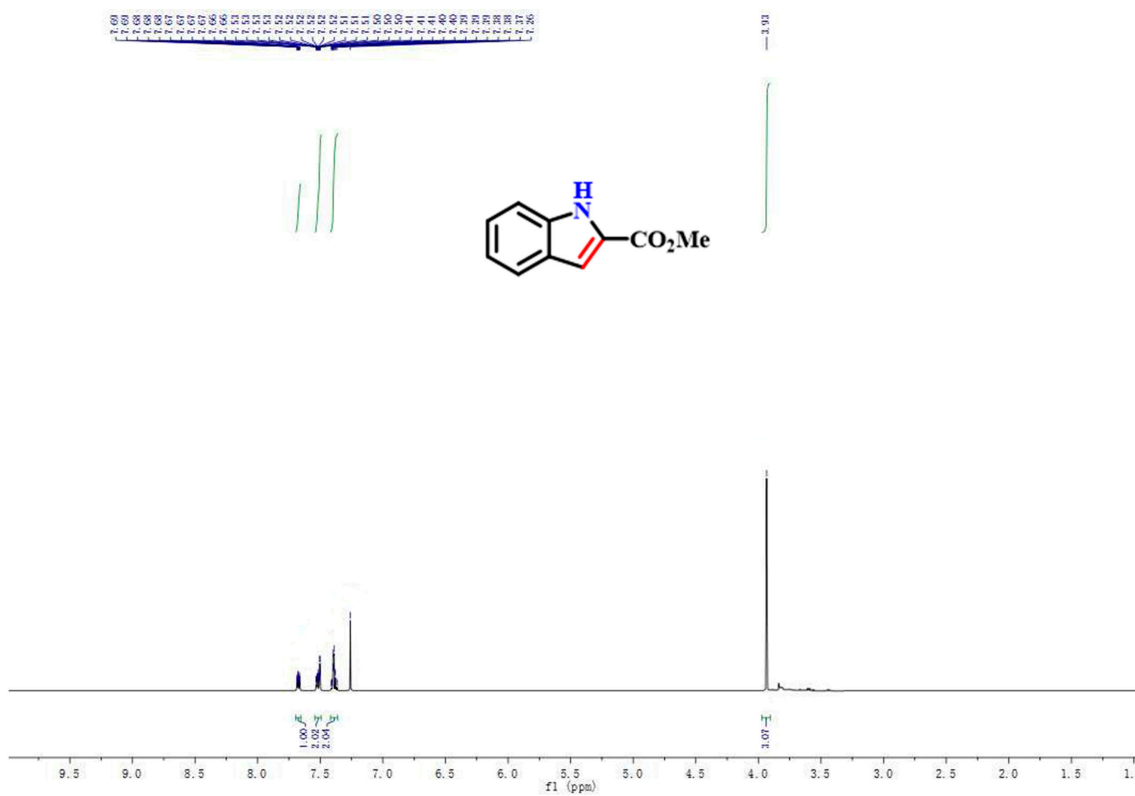


Figure S29. ¹H NMR spectrum of methyl 1H-indole-2-carboxylate.