Supplementary Information

Integration of perylene diimide into a two-dimensional cobalt-organic framework for enhanced photocatalysis

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1. Materials and methods

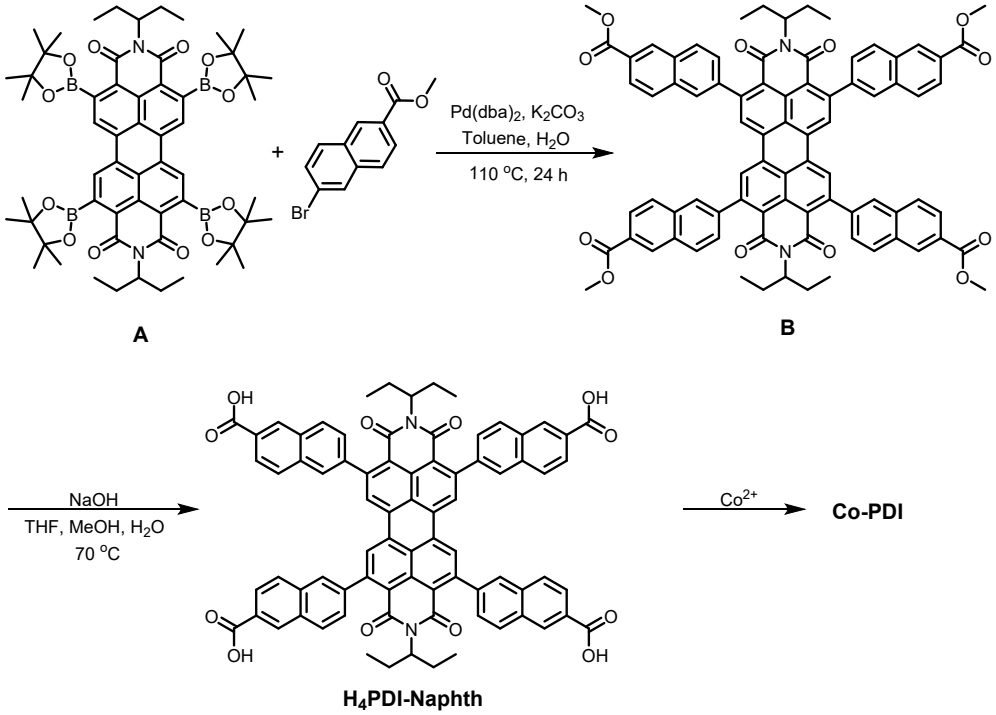
All commercially purchased chemicals and solvents are analytical grade without any further purification. Ultrapure water was prepared using a Hetai laboratory water purification system. NMR experiments were conducted on a Bruker AVANCE I 400 spectrometer. Chemical shifts (δ) are recorded in ppm using the residual proton resonance of the solvent as an internal standard ($CDCl_3$: δ = 7.26 ppm for ^1H spectra; DMSO-d_6: δ = 2.50 ppm for ^1H spectra). All coupling constants (J) are revealed in hertz (Hz) and only given for ^1H-^1H couplings unless stated otherwise. X-ray diffraction data were collected using a Bruker APEX area-detector X-ray diffractometer. ESI-MS spectra were recorded on an Agilent Quadrupole Time of Flight 6500 ion trap mass spectrometer. UV-*vis* spectra were measured with a Perses TU-1810 spectrometer. The steady-state photoluminescence spectrum (PL) was collected using a PerkinElmer FL-8500 Fluorescence spectrophotometer. Cyclic voltammetry was performed using a CHI 760E instrument. The femtosecond optical transient absorption spectroscopy measurements were performed with a regenerative amplified Ti:sapphire laser system from Coherent (800 nm, 35 fs, 6 mJ/pulse, and 1 kHz repetition rate), nonlinear frequency mixing techniques and the Helios spectrometer (Ultrafast Systems LLC). Photocatalytic reaction screening on WATTECS photocatalytic parallel reaction instrument (Model: WP-TEC-1020LC20W). Gas chromatography-mass spectrometry was performed using a SHIMADZU AOC-20i Plus instrument.

Photoelectrochemical Measurements

Electrochemical tests were measured using a three-electrode system: Ag/AgCl electrode as reference electrode, platinum silk as counter electrode, and photocatalyst coated glassy carbon as the working electrode. The working electrode was prepared by dropping the uniformly dispersed suspension liquid containing 2.0 mg of photocatalyst, 300 μL ethanol, 200 μL H_2O, and 10.0 μL Nafion onto the surface of the glassy carbon electrode, and then dried in air. Mott-Schottky plots were measured at 500, 750 and 1000 Hz, respectively. EIS plots were measured at a bias potential of -1.1 V under dark conditions. Transient photocurrent/time response signals were recorded at a bias potential of -0.5 V with a 300 W Xenon lamp as light source. All tests were performed

using a 0.1 M Na_2SO_4 aqueous solution as the electrolyte as the electrolyte.

2. Synthesis procedure and characterization data



Scheme S1 Synthetic route to the ligand **H_4PDI-Naphth** and complex **Co-PDI**.

Synthesis of Compound B

Compound **A** was synthesized according to literature methods.[1,2] Compound **A** (200 mg, 0.19 mmol), methyl 6-bromo-2-naphthoate (504 mg, 1.9 mmol), bis(dibenzylideneacetone)palladium (6.6 mg, 0.012 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (11.7 mg, 0.028 mmol), potassium carbonate (262.2 mg, 1.9 mmol), toluene (4 mL) and water (1 mL) were mixed in a 50 mL round bottom flask, and heated under nitrogen atmosphere for 24 h at 100 ℃. After cooling to ambient temperature, the solvent was removed under reduced pressure. The solid residue was washed three times with water and extracted with dichloromethane. The combined organic phases were concentrated under reduced pressure. The product was purified by column chromatography (CH_2Cl_2: EA = 80:1). Yield: 164 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 4H), 8.53 (s, 4H), 8.08 (d, J = 10.1 Hz, 4H), 8.03 (d, J = 8.5 Hz, 4H), 7.97 (s, 4H), 7.91 (d, J = 8.8 Hz, 4H), 7.57 (d, J = 8.3 Hz, 4H), 4.78 (m, 2H), 4.0 (s, 12H), 2.0 (m, 4H), 1.69 (m, 4H), 0.87 (t, J = 7.5 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 147.5, 142.3, 135.6, 132.9, 131.8, 131.2, 131.0, 129.1, 128.4, 127.8, 127.6, 126.1, 125.9, 125.7, 57.8, 52.4, 29.7, 24.6, 11.3 ppm.

Synthesis of Compound H_4PDI-Naphth

Compound **B** (2 g, 1.66 mmol) was dissolved in THF (140 mL) and MeOH (70 mL) in a round-bottom flask. Then the aqueous solution (70 mL) of NaOH (1.33 mg, 33.2 mmol) was added. The reaction mixture was stirred and refluxed at 70 °C for overnight. After cooling to ambient temperature, the solvent was removed under reduced pressure. The pH value of the resulting solution was adjusted to about 4.0 with hydrochloric acid (6 M). The red solid was filtered out, washed with water and dried in vacuo. The red solid ligand **H_4PDI-Naphth** was obtained, Yield: 1.93 g, 96%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.95 (s, 4H), 8.60 (s, 4H), 8.09 (s, 8H), 7.96 (s, 8H), 7.56 (d, J = 8.3 Hz, 4H), 4.50 (m, 2H), 1.83 (m, 4H), 1.54 (m, 4H), 0.77 (t, J = 6.9 Hz, 12H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.4, 163.1, 162.3, 146.7, 142.1, 134.9, 132.6, 131.3, 131.3, 130.2, 130.1, 128.2, 126.4, 125.3, 124.9, 120.8, 56.9, 35.8, 24.2, 11.1 ppm. ESI-MS: The molecular formula is $C_{78}H_{54}N_2O_{12}$: m/z = 1210.37 (calcd. for [**H_4PDI-Naphth** + H]$^+$ 1211.3688), 1233.36 (calcd. for [**H_4PDI-Naphth** + Na]$^+$ 1233.3552), 1248.93 (calcd. for [**H_4PDI-Naphth** + K]$^+$ 1248.9306).

Synthesis of Complex Co-PDI

The **Co-PDI** is synthesized using **H_4PDI-Naphth** (2 mg, 0.002 mmol) and $CoCl_2$ (2 mg, 0.015 mmol) in a mixture of N,N-diethylformamide (1.0 mL), ethanol (0.05 mL) and propionic acid (0.009 mg), which is degassed in a capped vial (10 mL). The mixture was heated at 100 °C for 72 h. The bright red crystals of complex **Co-PDI** suitable for X-ray crystallographic analysis were harvested after slow cooling to room temperature, collected, washed with ethanol, and dried in air. Yield: 4 mg, 56%. FTIR (KBr pellet): 3425.6 (m), 2958.9 (w), 2870.8 (w), 1704.0 (m), 1660.0 (s), 1593.9 (w), 1536.7 (w), 1479.5 (s), 1373.8 (s), 1329.8 (m), 1210.9 (m), 1083.2 (w), 1043.5 (w), 889.4 (w), 823.4 (w), 770.6 (w), 704.5 (w).

3. Characterization of Co-PDI and H_4PDI-Naphth

Single crystal X-ray crystallography

Single-crystal X-ray diffraction data for **Co-PDI** were collected at the BL17B macromolecular crystallography beamline of the National Facility for Protein Science at the Shanghai Synchrotron Radiation Facility (SSRF) at 173 K. The structures were solved with the SHELXT 2018/3 solution program using iterative methods and by using Olex2 1.5-dev as the graphical interface.[3,4] The model was refined with SHELXT 2018/3 using full matrix least squares minimisation on F^2. In the data, the disordered solvent molecules that could not be adequately restrained were removed using the SQUEEZE routine. These data are provided free of charge by The Cambridge Crystallographic Data Centre. Additional crystallographic details can be found in Tables S1 and S2 summarize the selected bond distances and angles. CCDC 2491993 contain the supplementary crystallographic data for this paper.

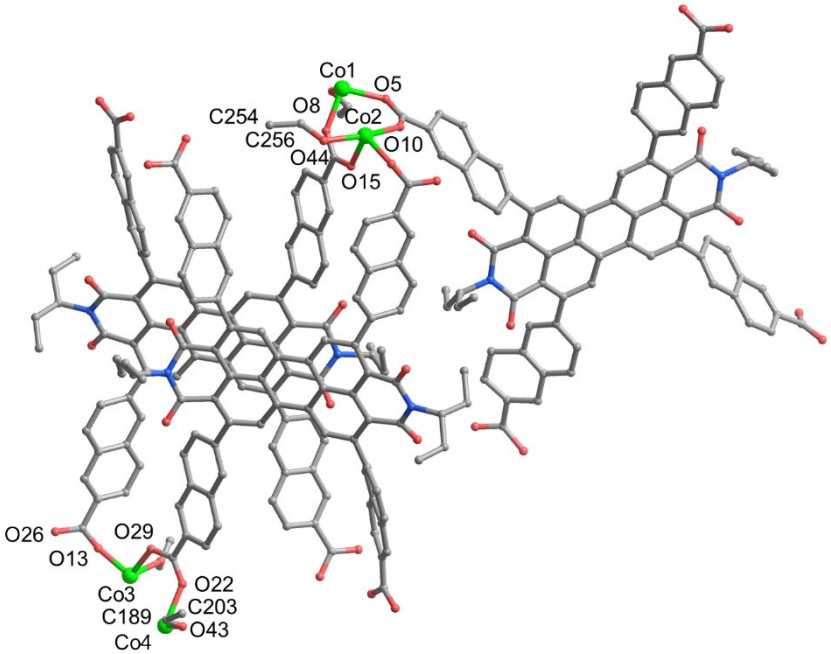


Figure S1 Asymmetric unit in the single-crystal structure of **Co-PDI**. All hydrogen atoms are omitted for clarity. Co, bright green; C, gray; N, blue; O, red.

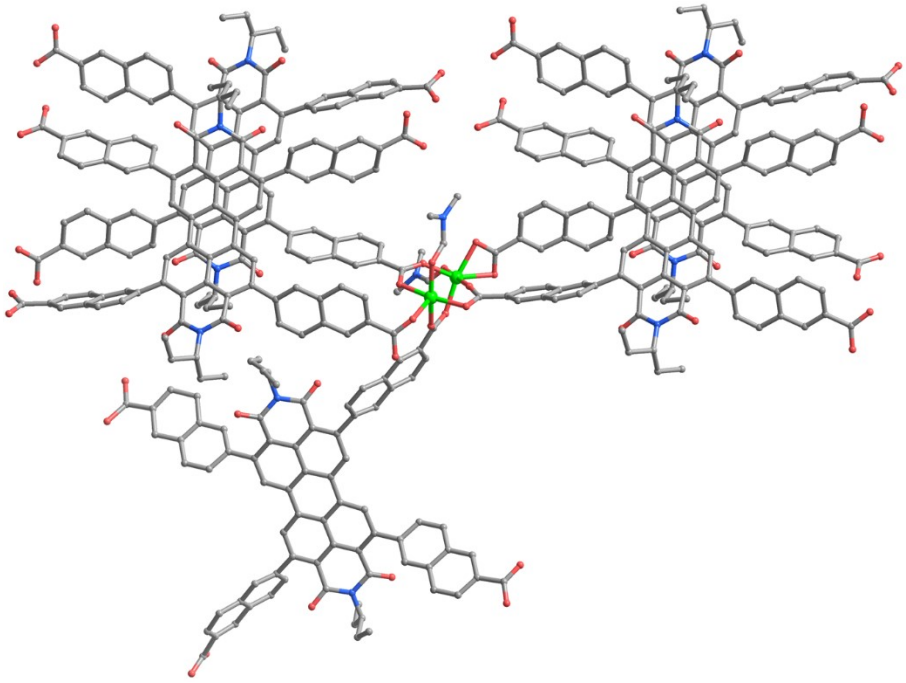


Figure S2 Coordination environments of Co(II) ions in **Co-PDI**.

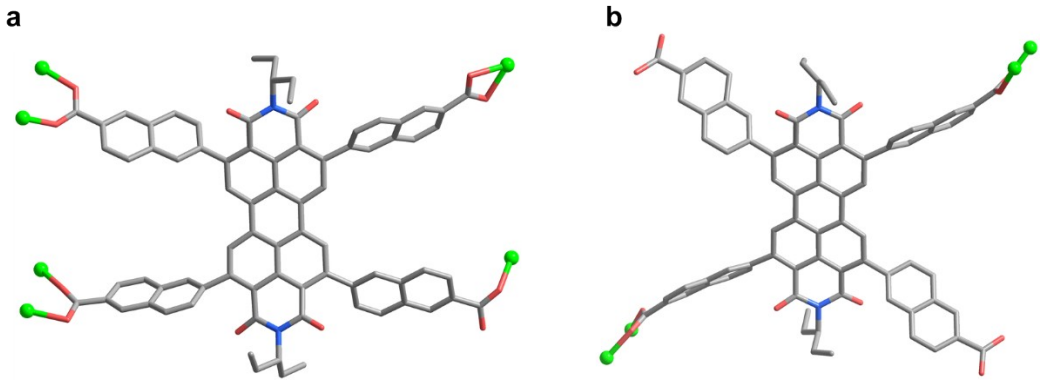


Figure S3 The coordination environment of **H_4PDI-Naphth** ligands in **Co-PDI**.

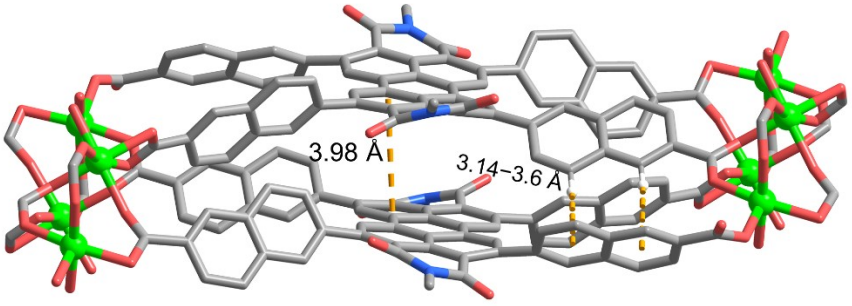


Figure S4 The interactions between adjacent ligands in **Co-PDI**.

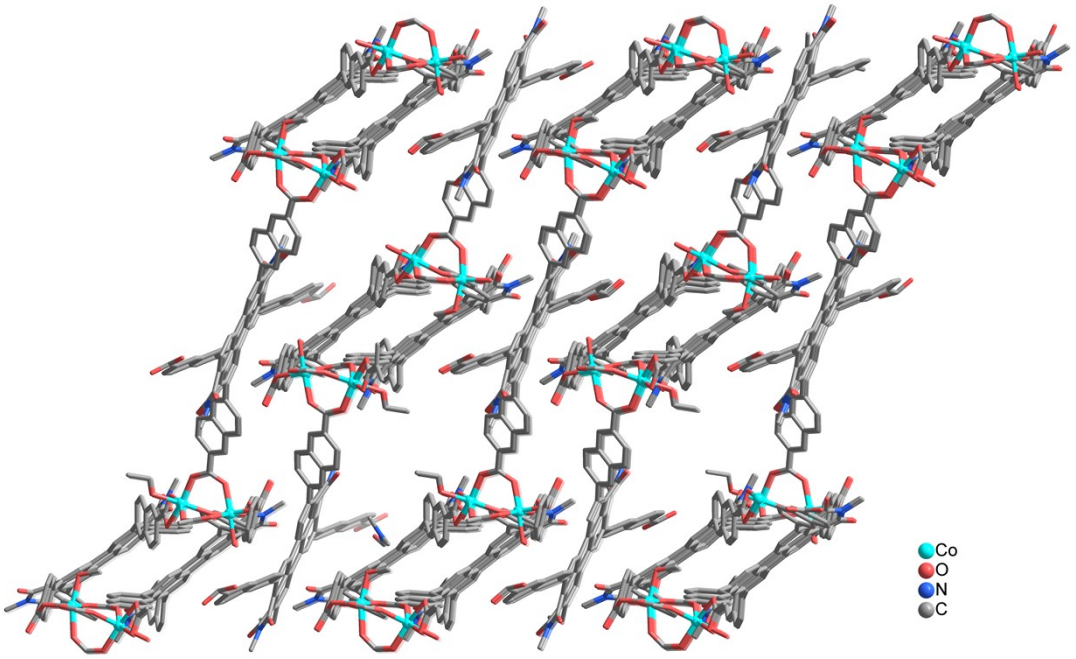


Figure S5 2D structure of the **Co-PDI**.

Table S1 Crystal data and structure refinement for complex **Co-PDI**.

complex	**Co-PDI**
formula	$C_{257}H_{205}Co_4N_{11}O_{45}$
F_w	4403.03
crystal system	Triclinic
space group	$P\bar{1}$
a (Å)	22.5652(6)
b (Å)	22.5982(6)
c (Å)	30.2731(8)
α (deg)	77.8250(10)
β (deg)	85.366(2)
γ (deg)	65.6610(10)
V (Å^3)	13748.6(6)
Z	2
D_c (g.cm^{-3})	1.064
F(000)	4584.0
μ (mm^{-1})	2.392
T (K)	173 K
reflns/unique	428551/50391
R_{int}	0.0901
data/restraints/params	50391/11159/ 2847
GOF on F^2	1.085
R_1, wR_2 ($I > 2\sigma(I)$)	0.1082, 0.2375
R_1, wR_2 (all data)	0.1397, 0.2525
largest diff. peak and hole (e.Å^{-3})	2.40, -1.20

Table S2 Selected bond lengths [Å] and angles [º] for complex **Co-PDI**.

Co(1)-O(3)#1	2.141(4)	O(6)-Co(2)-O(7)#1	92.17(15)
Co(1)-O(4)#1	2.146(4)	O(6)-Co(2)-O(9)#1	148.51(14)
Co(1)-O(5)#2	2.038(4)	O(6)-Co(2)-O(10)#2	91.45(17)
Co(1)-O(8)	2.025(4)	O(6)-Co(2)-O(15)	96.87(16)
Co(1)-O(9)#1	2.146(4)	O(6)-Co(2)-O(45)	102.0(2)
Co(1)-O(12)	2.147(4)	O(7)#1-Co(2)-O(9)#1	57.86(15)
Co(2)-O(6)	2.020(4)	O(10)#2-Co(2)-O(7)#1	95.13(16)
Co(2)-O(7)#1	2.098(3)	O(10)#2-Co(2)-O(9)#1	82.70(15)
Co(2)-O(9)#1	2.382(4)	O(10)#2-Co(2)-O(45)	165.6(2)
Co(2)-O(10)#2	2.068(4)	O(15)-Co(2)-O(7)#1	170.85(17)
Co(3)-O(13)	2.029(4)	O(15)-Co(2)-O(9)#1	113.44(16)
Co(3)-O(19)#3	2.398(4)	O(15)-Co(2)-O(10)#2	86.04(18)
Co(3)-O(24)#3	2.100(4)	O(15)-Co(2)-O(45)	87.1(2)
Co(3)-O(29)	2.020(4)	O(45)-Co(2)-O(9)#1	88.4(2)
Co(4)-O(19)#3	2.147(5)	O(13)-Co(3)-O(19)#3	147.91(15)
Co(4)-O(21)#3	2.168(4)	O(13)-Co(3)-O(24)#3	91.58(17)
Co(4)-O(22)	2.014(4)	O(13)-Co(3)-O(32)	90.1(2)
Co(4)-O(25)#3	2.125(4)	O(24)#3-Co(3)-O(19)#3	57.78(17)
O(3)#1-Co(1)-O(4)#1	61.49(14)	O(29)-Co(3)-O(13)	103.42(17)
O(3)#1-Co(1)-O(9)#1	92.59(14)	O(29)-Co(3)-O(19)#3	108.17(18)
O(3)#1-Co(1)-O(12)	86.68(15)	O(32)-Co(3)-O(19)#3	84.71(17)
O(3)#1-Co(1)-C(102)#1	30.91(17)	O(32)-Co(3)-O(24)#3	96.52(19)
O(4)#1-Co(1)-O(9)#1	86.62(15)	O(44)-Co(3)-O(13)	91.4(2)
O(4)#1-Co(1)-O(12)	92.72(16)	O(44)-Co(3)-O(19)#3	95.63(18)
O(4)#1-Co(1)-C(102)#1	30.67(17)	O(19)#3-Co(4)-C(170)#3	90.3(2)
O(5)#2-Co(1)-O(3)#1	106.28(15)	O(21)#3-Co(4)-C(170)#3	30.33(18)
O(5)#2-Co(1)-O(4)#1	167.59(15)	O(22)-Co(4)-O(19)#3	92.58(19)
O(5)#2-Co(1)-O(9)#1	92.19(16)	O(22)-Co(4)-O(43)	86.9(2)
O(8)-Co(1)-O(3)#1	154.49(15)	O(22)-Co(4)-C(170)#3	124.8(2)
O(8)-Co(1)-O(4)#1	94.53(15)	O(25)#3-Co(4)-O(19)#3	93.46(18)
O(9)#1-Co(1)-O(12)	179.19(15)	O(25)#3-Co(4)-O(21)#3	61.06(16)
Co(1)#3-O(9)-Co(2)#3	101.61(13)	Co(4)#1-O(19)-Co(3)#1	101.88(15)

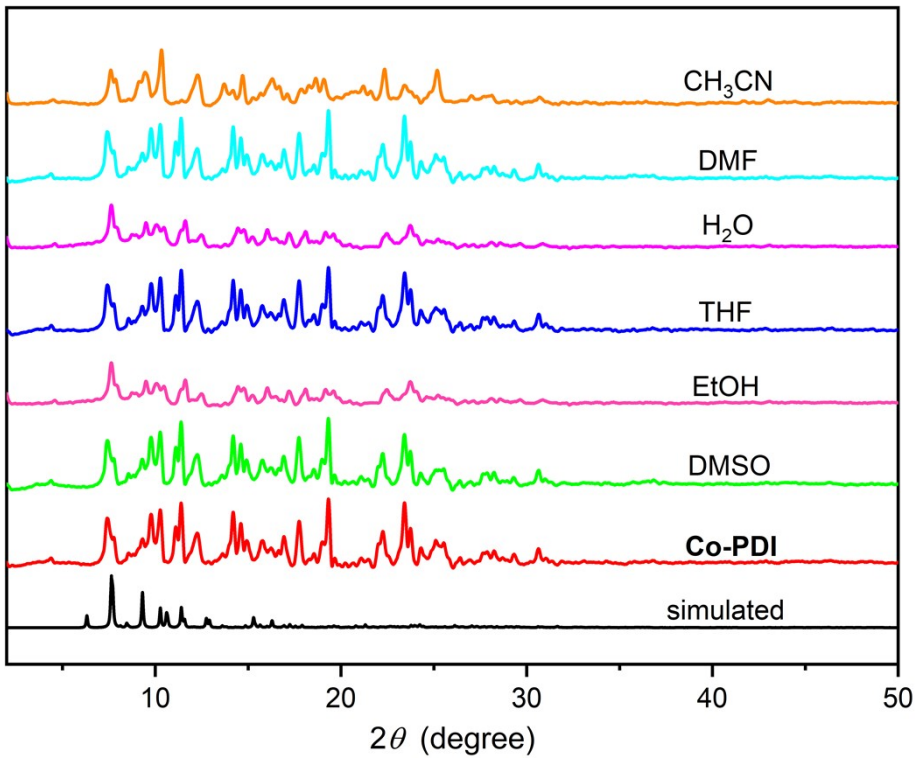


Figure S6 PXRD patterns of simulated and as-synthesized **Co-PDI** immersed in DMSO, EtOH, THF, H_2O, DMF and CH_3CN for 24 hours, respectively.

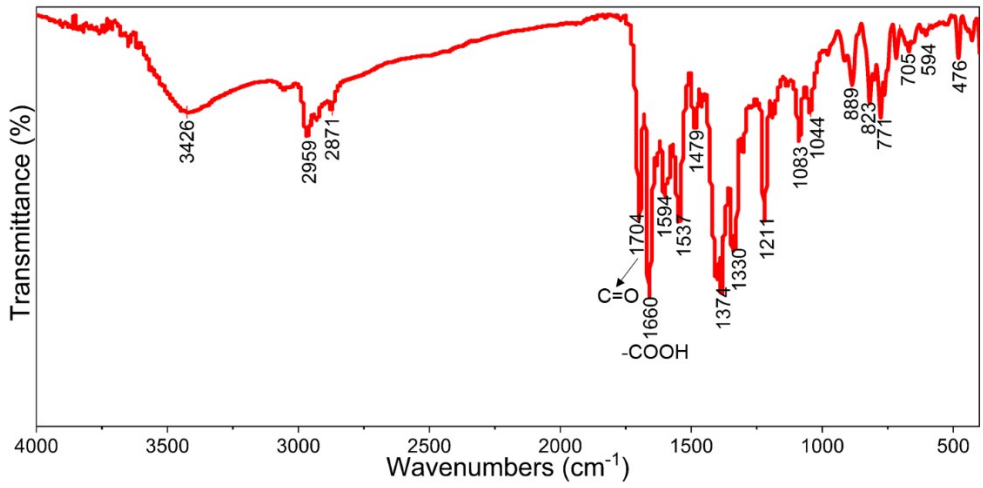


Figure S7 FT-IR spectrum of **Co-PDI**.

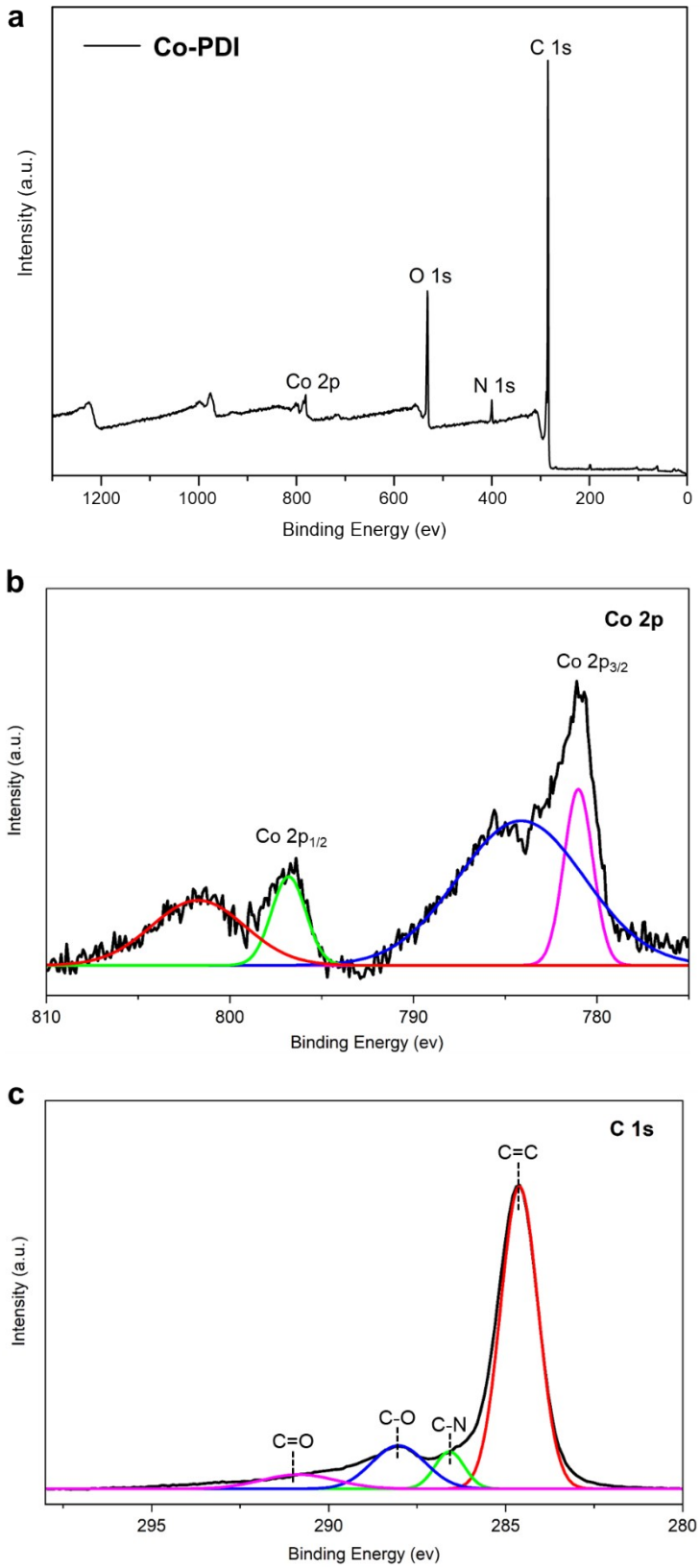


Figure S8 (a) XPS survey spectrum of complex **Co-PDI**. The high-resolution regional spectra of Co 2p (b) and C 1s (c).

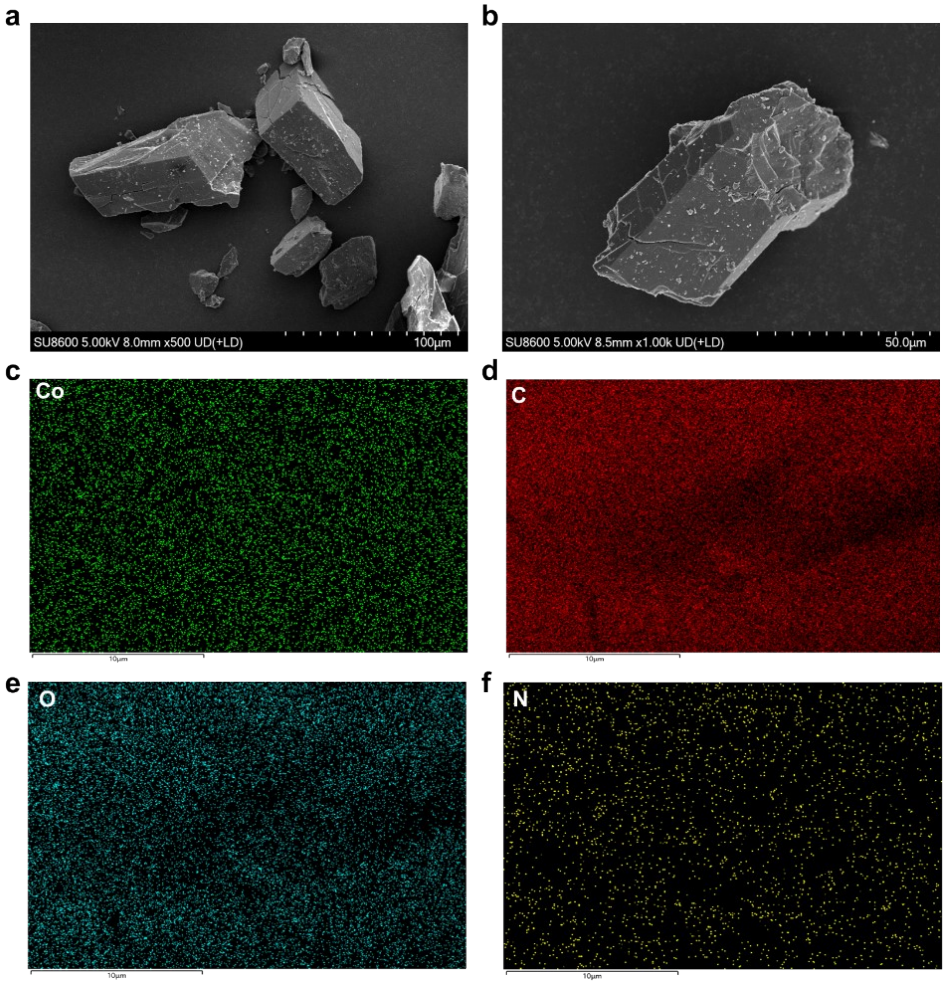
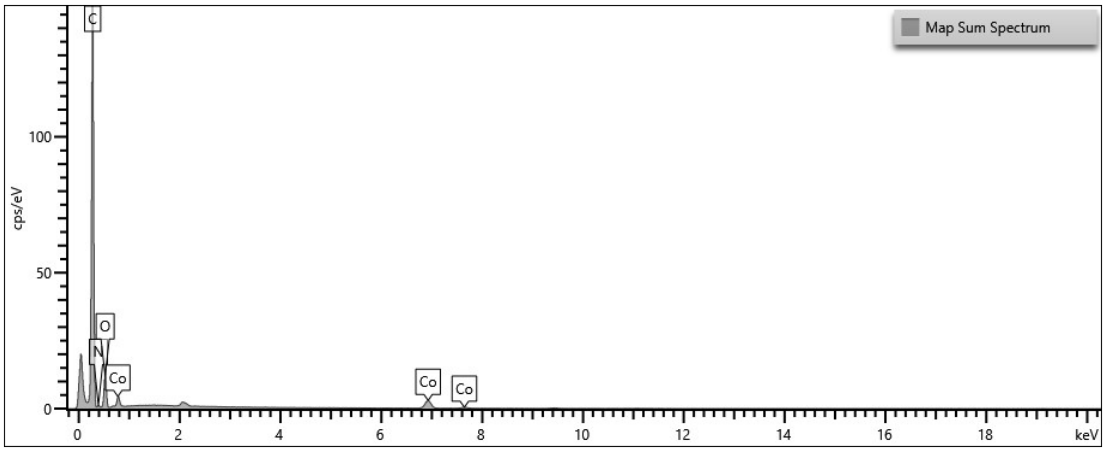


Figure S9 (a, b) SEM image of **Co-PDI**; (c-f) EDS elemental mapping images of **Co-PDI**.



Map Sum Spectrum		
Element	Wt%	Wt% Sigma
C	76.75	0.34
N	4.22	0.39
O	16.77	0.17
Co	2.26	0.03
Total:	100.00	

Figure S10 EDX pattern of **Co-PDI**. Elements observed for **Co-PDI**: C, N, O and Co.

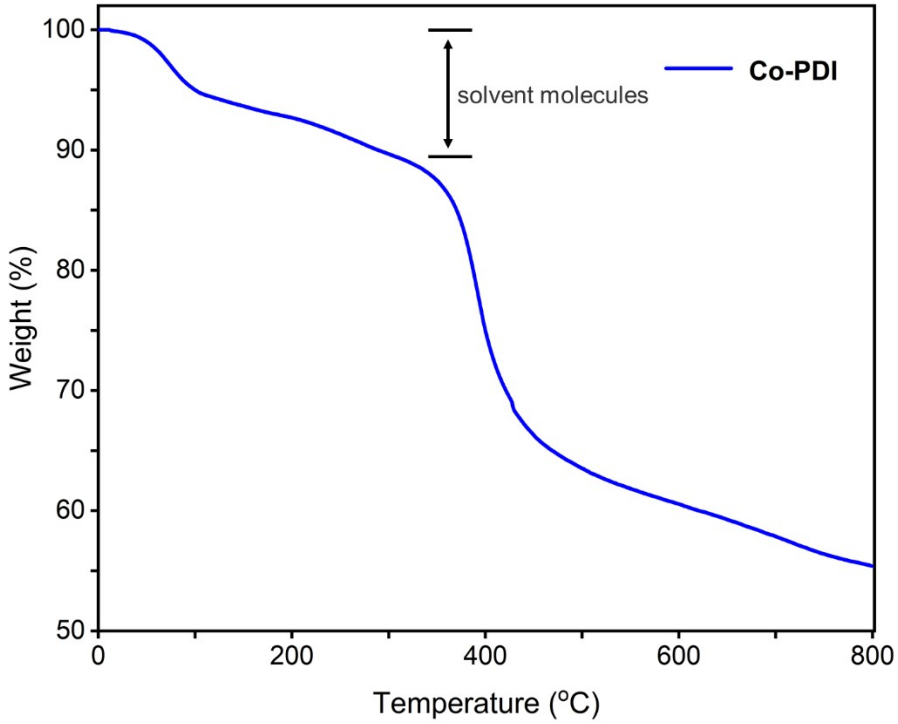


Figure S11 TGA curve for complex **Co-PDI**.

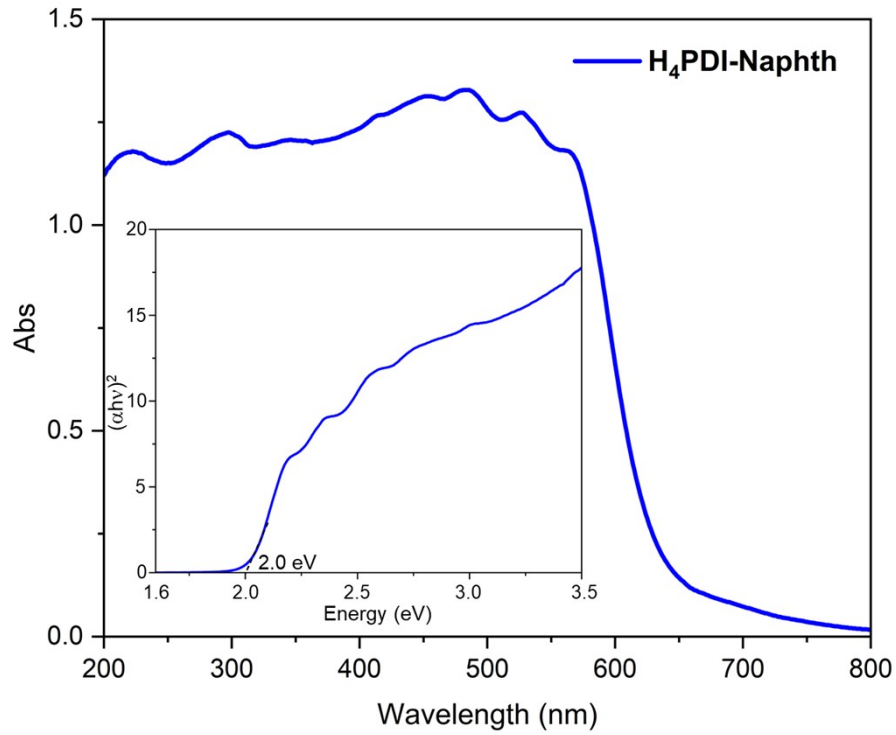


Figure S12 Solid-state UV-vis spectrum and the Tauc plot (inset) of **H_4PDI-Naphth**.

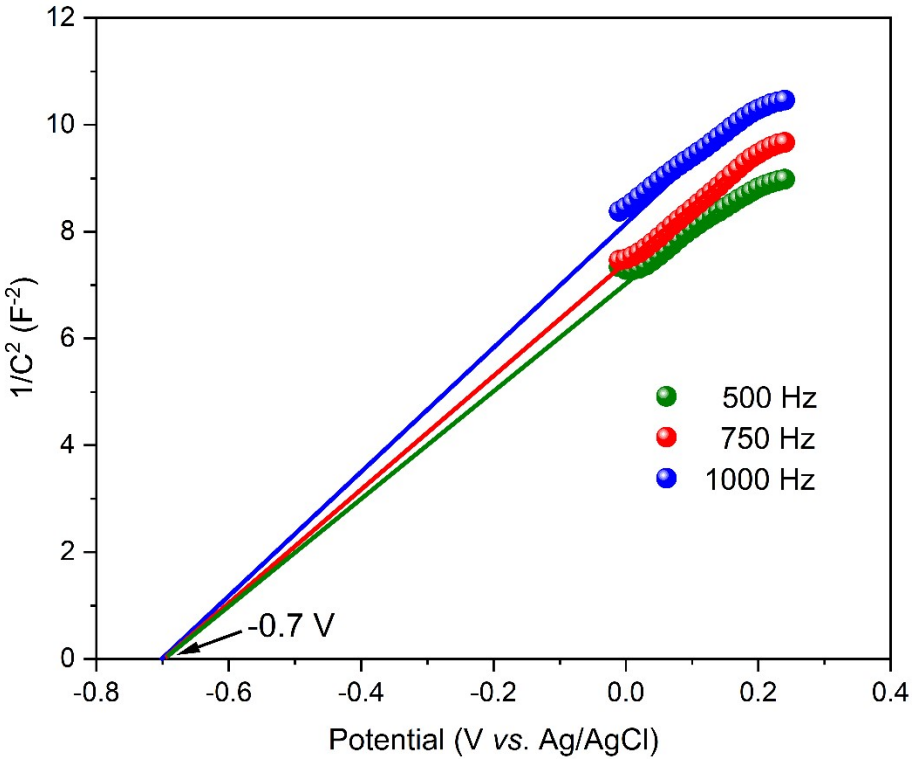


Figure S13 Mott–Schottky plots of **H_4PDI-Naphth**.

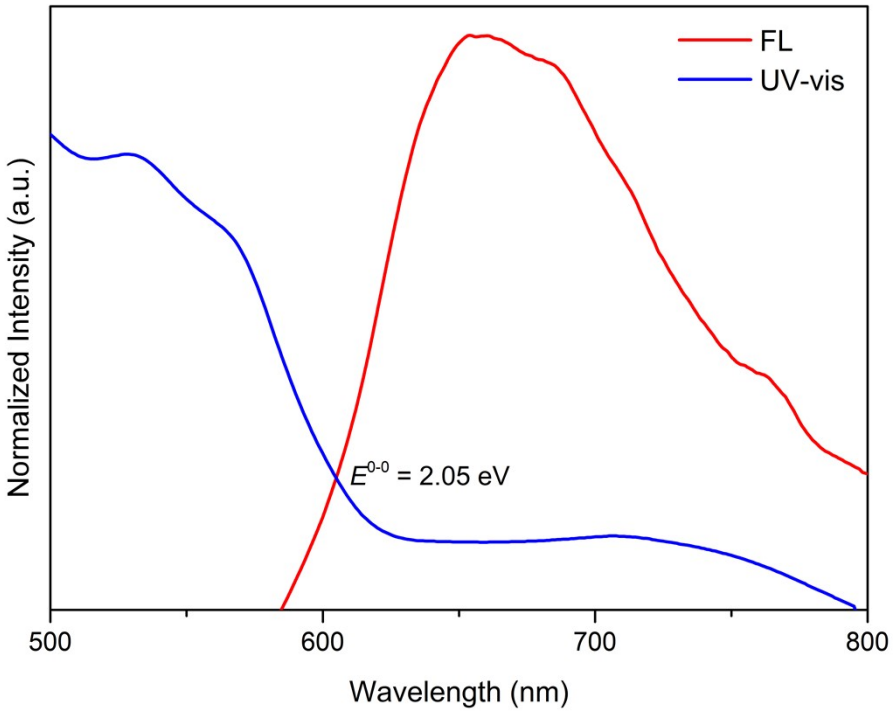


Figure S14 Normalized absorption (blue line) and emission spectra (red line) of compound **Co-PDI**, excited at 605 nm.

4. Photocatalysis activity measurement

General procedure photocatalytic thiocyanation of indoles

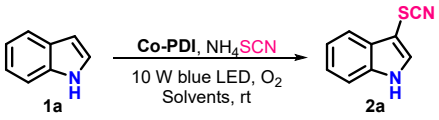
Before the photocatalytic experiment, the single crystal of **Co-PDI** was soaked in acetone for 24 h and then heated at 60 °C for 10 h in a vacuum oven. A mixture of **Co-PDI** (4.0 mg), indole (28.1 mg, 0.24 mmol) and ammonium thiocyanate (36.5 mg, 0.48 mmol) were dissolved in 3 mL acetonitrile. The reaction mixture was degassed with O_2 bubbling for 15 min, and then the resulting mixture was irradiated with 10 W blue LED at room temperature for 8 h. After the reaction, the mixture was centrifuged at 8000 rpm for 5 min. The solution was collected, and the solvent was removed under reduced pressure. The product was purified by column chromatography. In the photocatalytic cycle experiment, the photocatalysts were washed with CH_3CN for the next tests.

General procedure photocatalytic oxidative coupling of benzylamines

A mixture of **Co-PDI** (4.0 mg), 2-aminobenzenethiol (37.5 mg, 0.3 mmol) and benzaldehyde (31.8 mg, 0.3 mmol) was dissolved in 3 mL ethanol. The reaction mixture was irradiated with 10 W blue LED under air atmosphere for 8 h. After the reaction,

the mixture was centrifuged at 8000 rpm for 5 min. The solution was collected, and the solvent was removed under reduced pressure. The product was purified by column chromatography. In the photocatalytic cycle experiment, the photocatalysts were washed with EtOH for the next tests.

Table S3 Optimization of reaction conditions for the photocatalytic thiocyanation of indoles.[a]



Entry	Catalyst	Amount (mmol%)	Solvent	Time (h)	Yield (%)[c]
1	**Co-PDI**	0.2	CH_3CN	8	99
2	**Co-PDI**	0.2	THF	8	66
3	**Co-PDI**	0.2	DMF	8	60
4	**Co-PDI**	0.2	DMSO	8	62
5	**Co-PDI**	0.2	EtOH	8	42
6	**Co-PDI**	0.2	MeOH	8	45
7	—	—	CH_3CN	8	trace
8[b]	**Co-PDI**	0.2	CH_3CN	8	trace
9	**Co-PDI**	0.3	CH_3CN	8	99
10	**Co-PDI**	0.1	CH_3CN	8	76
11	**Co-PDI**	0.2	CH_3CN	4	47
12	**Co-PDI**	0.2	CH_3CN	12	99
13	$CoCl_2$	0.2	CH_3CN	8	10%
14	**H_4PDI-Naphth**	0.2	CH_3CN	8	28%
15	**H_4PDI-Naphth**/ $CoCl_2$	0.2	CH_3CN	8	30%

[a]Reaction conditions: indole (0.24 mmol), ammonium thiocyanate (0.48 mmol), **Co-PDI** (0.2 mmol%), 10 W blue light, room temperature, oxygen, CH_3CN = 3 mL. [b]In the dark. [c]Isolated yields.

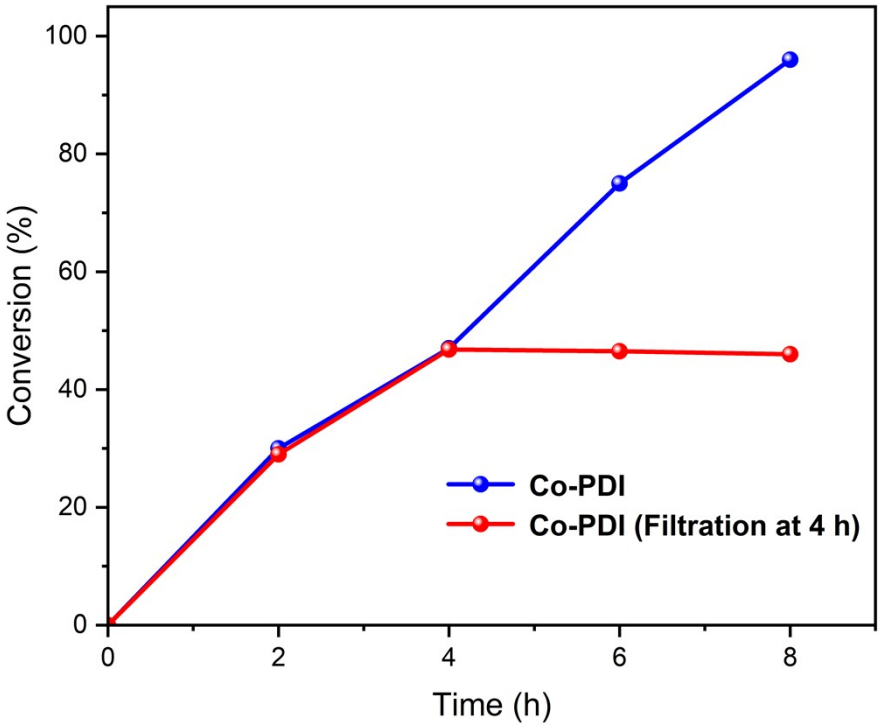
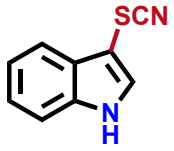


Figure S15 Kinetic curves of the thiocyanation reaction catalyzed by **Co-PDI** at room temperature.

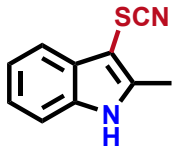
NMR data for the products 2a–l

2a. 3-Thiocyanato-1*H*-indole[5,6]



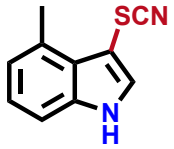
The product was purified by column chromatography with petroleum ether as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 7.80 (m, 1H), 7.46 (d, J = 2.9 Hz, 1H), 7.41 (m, 1H), 7.31 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 131.3, 127.7, 123.8, 121.9, 118.6, 112.4, 112.3, 91.7 ppm.

2b. 2-Methyl-3-thiocyanato-1*H*-indole[5,6]



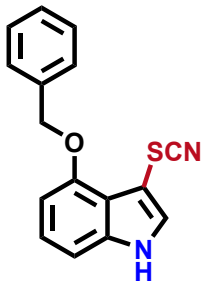
The product was purified by column chromatography with petroleum ether as eluent. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.95 (s, 1H), 7.56 (m, 1H), 7.43 (m, 1H), 7.20 (m, 2H), 2.54 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.0, 135.3, 128.3, 122.2, 120.8, 117.1, 112.1, 111.8, 86.6, 11.7 ppm.

2c. 4-Methyl-3-thiocyanato-1*H*-indole[5,6]



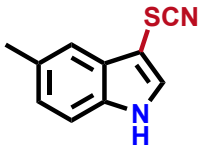
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 7.52 (d, J = 2.8 Hz, 1H), 7.26 (m, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 7.2 Hz, 1H), 2.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 132.1, 131.3, 125.7, 124.2, 123.7, 113.2, 110.1, 92.7, 19.3 ppm.

2d. 4-(Benzyloxy)-3-thiocyanato-1*H*-indole[5,6]



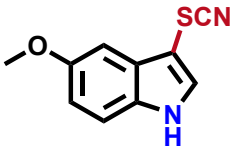
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.61 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.36 (m, 2H), 7.16 (t, J = 8.1 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 5.27 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 138.2, 137.0, 129.0, 128.7, 128.0, 127.5, 125.0, 117.3, 113.0, 105.4, 103.1, 70.4 ppm.

2e. 5-Methyl-3-thiocyanato-1*H*-indole[5,6]



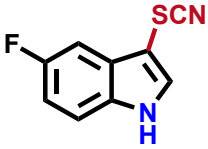
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.58 (s, 1H), 7.43 (d, J = 2.8 Hz, 1H), 7.31 (d, J = 8.3 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 2.51 (s, 3H) ppm.

2f. 5-Methoxy-3-thiocyanato-1*H*-indole[5,6]



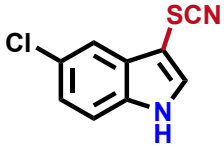
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 7.49 (d, J = 2.9 Hz, 1H), 7.32 (d, J = 8.9 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 6.96 (dd, J = 8.9, 2.4 Hz, 1H), 3.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 131.4, 130.9, 128.7, 114.8, 113.1, 112.0, 100.0, 91.9, 56.0 ppm.

2g. 5-Fluoro-3-thiocyanato-1*H*-indole[5,6]



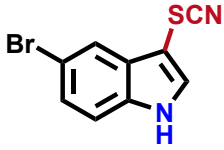
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (s, 1H), 7.57 (d, J = 2.9 Hz, 1H), 7.44 (dd, J = 8.8, 2.4 Hz, 1H), 7.37 (dd, J = 8.8, 4.1 Hz, 1H), 7.08–7.03 (m, 1H) ppm.

2h. 5-Chloro-3-thiocyanato-1*H*-indole[5,6]



The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 7.77 (s, 1H), 7.55 (d, J = 2.8 Hz, 1H), 7.35 (d, J = 8.7 Hz, 1H), 7.27 (d, J = 9.0 Hz, 1H) ppm.

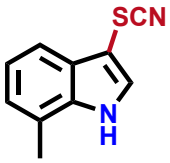
2i. 5-Bromo-3-thiocyanato-1*H*-indole[5,6]



The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.94 (s, 1H), 7.54 (d, J = 2.7 Hz, 1H), 7.41

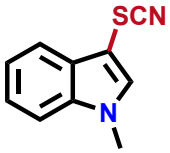
(dd, J = 8.6, 1.7 Hz, 1H), 7.31 (d, J = 8.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.8, 132.1, 129.6, 127.3, 121.7, 115.7, 113.7, 111.4, 92.6 ppm.

2j. 7-Methyl-3-thiocyanato-1*H*-indole[5,6]



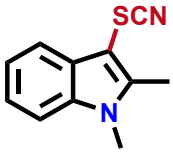
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 2.9 Hz, 1H), 7.24 (m, 1H), 7.13 (d, J = 7.2 Hz, 1H), 2.51 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.8, 130.7, 127.5, 124.6, 122.2, 121.4, 116.6, 111.9, 93.1, 16.5 ppm.

2k. 1-Methyl-3-thiocyanato-1*H*-indole[5,6]



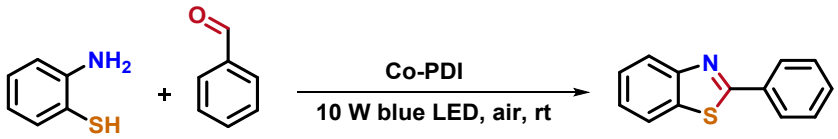
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 7.9 Hz, 1H), 7.41–7.30 (m, 4H), 3.84 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 135.2, 128.6, 123.6, 121.8, 119.1, 112.0, 110.3, 90.1, 33.6 ppm.

2l. 1,2-Dimethyl-3-thiocyanato-1*H*-indole[5]



The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (m, 1H), 7.38–7.30 (m, 3H), 3.77 (s, 3H), 2.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.0, 128.4, 122.8, 121.6, 118.4, 112.0, 109.7, 88.1, 30.6, 11.2 ppm.

Table S4 The optimization of the condensation promoted by **Co-PDI**.[a]



Entry	Catalyst	Amount (mmol%)	Solvent	Time (h)	Yield (%)[c]
1	**Co-PDI**	0.5	EtOH	8	93
2	**Co-PDI**	0.5	THF	8	20
3	**Co-PDI**	0.5	DMF	8	25
4	**Co-PDI**	0.5	DMSO	8	20
5	**Co-PDI**	0.5	CH_3CN	8	42
7	—	—	EtOH	8	trace
8[b]	**Co-PDI**	0.5	EtOH	8	trace
9	$CoCl_2$	0.5	EtOH	8	trace
10	**H_4PDI-Naphth**	0.5	EtOH	8	15%
11	**H_4PDI-Naphth/** $CoCl_2$	0.5	EtOH	8	18%

[a]Reaction conditions: 2-aminobenzenethiol (0.3 mmol), benzaldehyde (0.3 mmol), **Co-PDI** (0.2 mmol%), 10 W blue light, room temperature, air, EtOH = 3 mL. [b]In the dark. [c]Isolated yields.

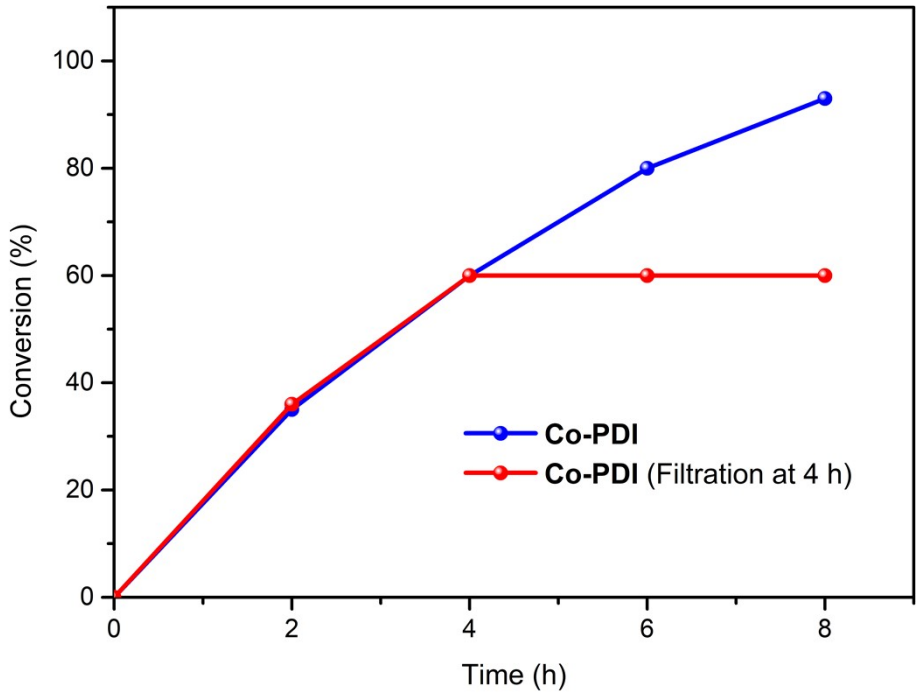
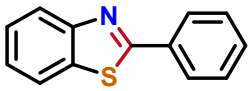


Figure S16 Kinetic curves of the condensation reaction catalyzed by **Co-PDI** at room temperature.

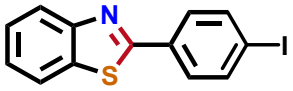
NMR data for the products 5a–i

5a. 2-Phenylbenzothiazole[7]



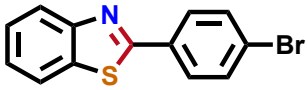
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12–8.06 (m, 4H), 7.58–7.52 (m, 4H), 7.45 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.3, 153.6, 134.5, 132.9, 131.4, 129.4, 127.2, 126.6, 125.5, 122.9, 122.3 ppm.

5b. 2-(4-Iodophenyl)benzothiazole[7]



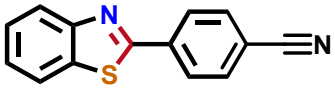
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.6 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.82 (m, 4H), 7.50 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 154.2, 138.3, 135.1, 133.2, 129.0, 126.6, 125.6, 123.5, 121.8, 97.6 ppm.

5c. 2-(4-Bromophenyl)benzothiazole[7]



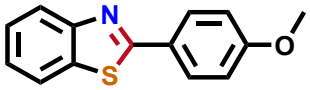
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.6 Hz, 2H), 7.91 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.50 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 8.1 Hz, 1H) ppm.

5d. 2-(4-Cyanophenyl)benzothiazole[7]



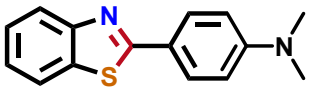
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.21–8.15 (m, 3H), 8.08 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.1 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.3, 153.4, 136.6, 134.9, 133.2, 127.8, 127.0, 126.2, 123.4, 122.6, 118.3, 113.3 ppm.

5e. 2-(4-Methoxyphenyl)benzo[d]thiazole[7]



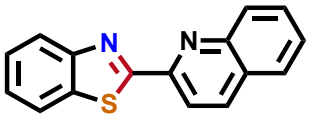
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.9 Hz, 3H), 7.87 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 8.8 Hz, 2H), 3.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 162.1, 154.4, 135.0, 129.2, 126.6, 126.3, 124.9, 123.0, 121.6, 114.5, 55.6 ppm.

5f. 4-(Benzo[*d*]thiazol-2-yl)-N,N-dimethylaniline[7]



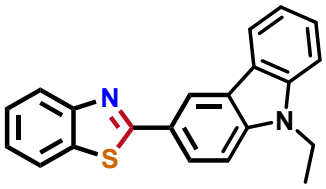
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.03 (d, J = 7.9 Hz, 1H), 7.91 (m, 3H), 7.47 (m, 1H), 7.35 (m, 1H), 6.81 (d, J = 8.6 Hz, 2H), 3.01 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.2, 151.3, 129.6, 127.6, 121.4, 117.2, 111.8, 65.6 ppm.

5g. 2-Benzothiazol-2-yl-quinoline[7]



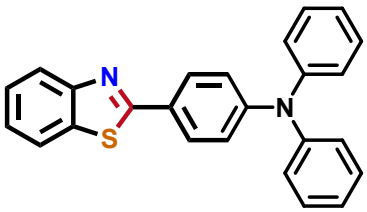
The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.61 (d, J = 8.6 Hz, 1H), 8.46 (d, J = 8.5 Hz, 1H), 8.21–8.09 (m, 4H), 7.87 (t, J = 7.5 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.62–7.52 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.8, 148.8, 147.2, 137.5, 130.5, 128.8, 128.3, 128.1, 127.3, 119.3 ppm.

5h. 3-(2-Benzothiazolyl)-9-ethyl-9*H*-carbazole[7]



The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.92 (s, 1H), 8.36 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 8.6 Hz, 1H), 8.10–8.03 (m, 2H), 7.71–7.63 (m, 2H), 7.52 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.27 (t, J = 7.4 Hz, 1H), 4.45 (m, 2H), 1.31 (m, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.5, 153.9, 141.2, 140.3, 134.3, 126.6, 126.5, 125.1, 124.9, 123.9, 122.7, 122.3, 122.2, 122.1, 121.1, 119.7, 119.7, 109.7, 109.6, 37.2, 13.7 ppm.

5i. 4-(Benzothiazol-2-yl)-N,N-diphenylaniline[8]



The product was purified by column chromatography with petroleum ether and ethyl acetate as eluent. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.06 (d, J = 8.0 Hz, 1H), 7.99–7.93 (m, 3H), 7.49 (t, J = 7.7 Hz, 1H), 7.37 (m, 5H), 7.14 (m, 6H), 6.99 (d, J = 8.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.0, 153.8, 150.1, 146.2, 134.2, 129.9, 128.5, 126.5, 125.5, 125.4, 125.0, 124.5, 122.4, 122.2, 120.7 ppm.

5. Stability test of Co-PDI

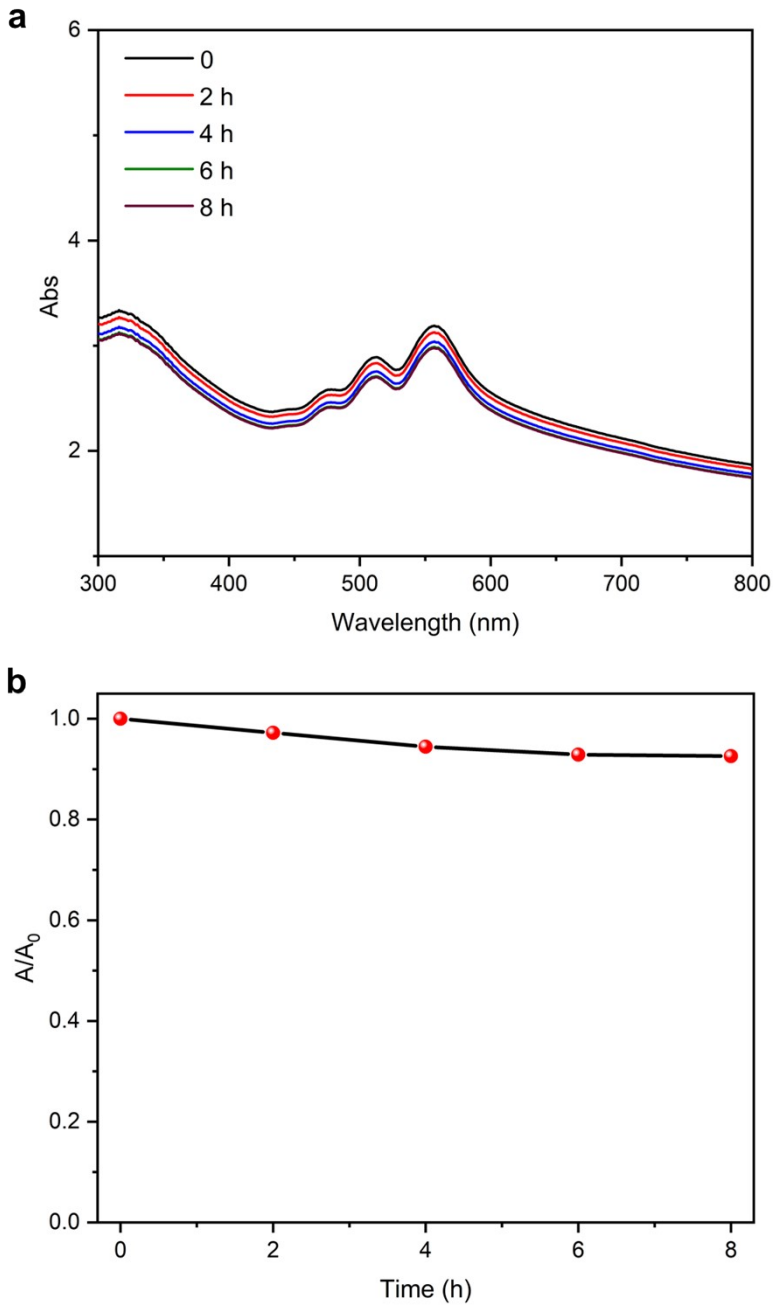


Figure S17 The UV/vis spectra of **Co-PDI** by the continuous irradiation with UV light (455 nm).

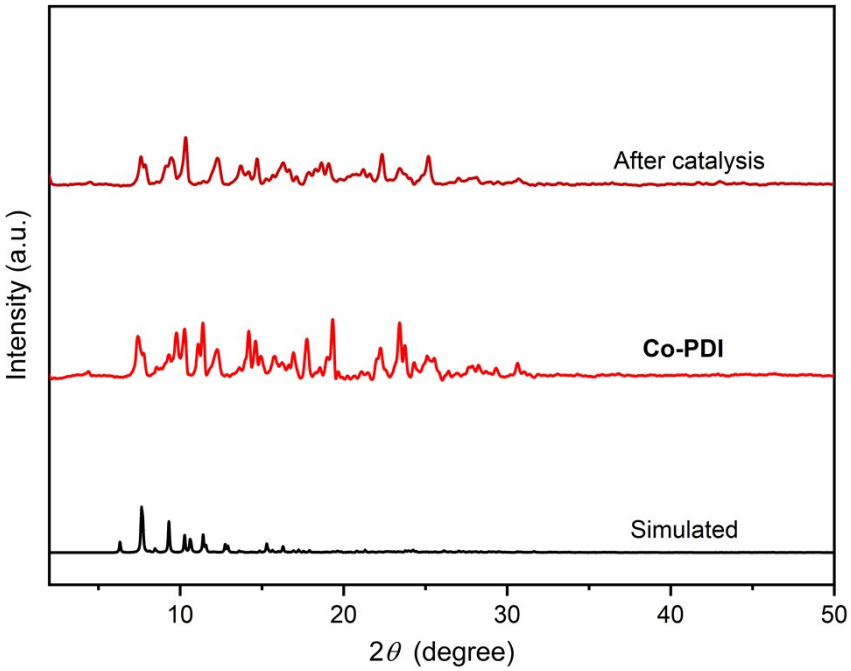


Figure S18 PXRD patterns of **Co-PDI** after the photocatalytic reaction.

6. The fluorescence lifetimes of Co-PDI and H_4PDI-Naphth

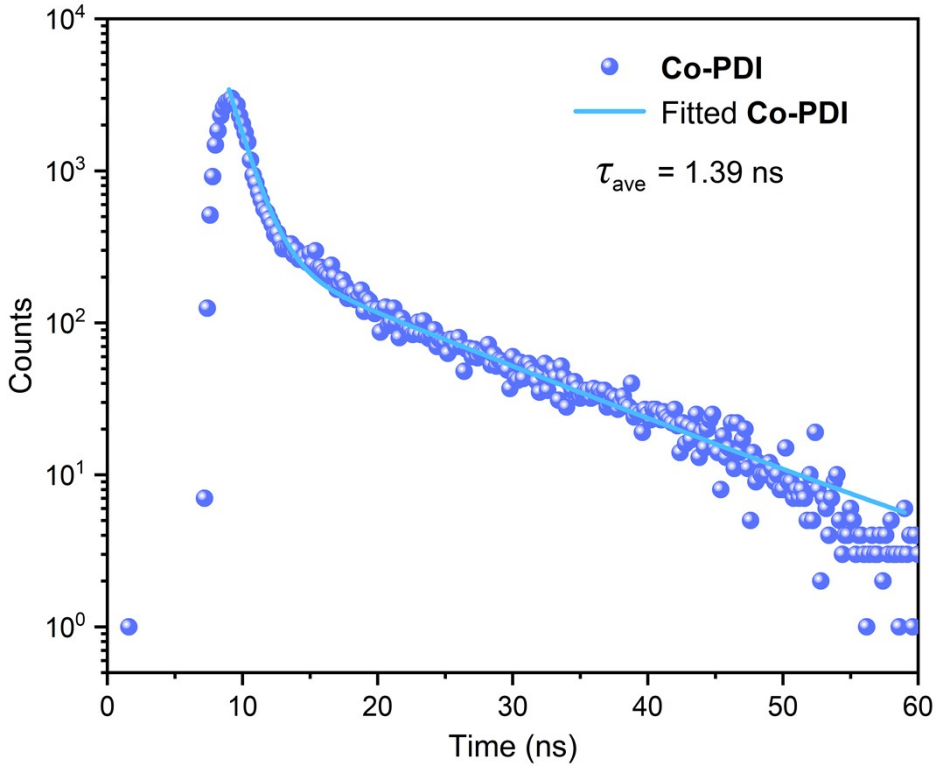


Figure S19 Fluorescence decay profiles of **Co-PDI**.

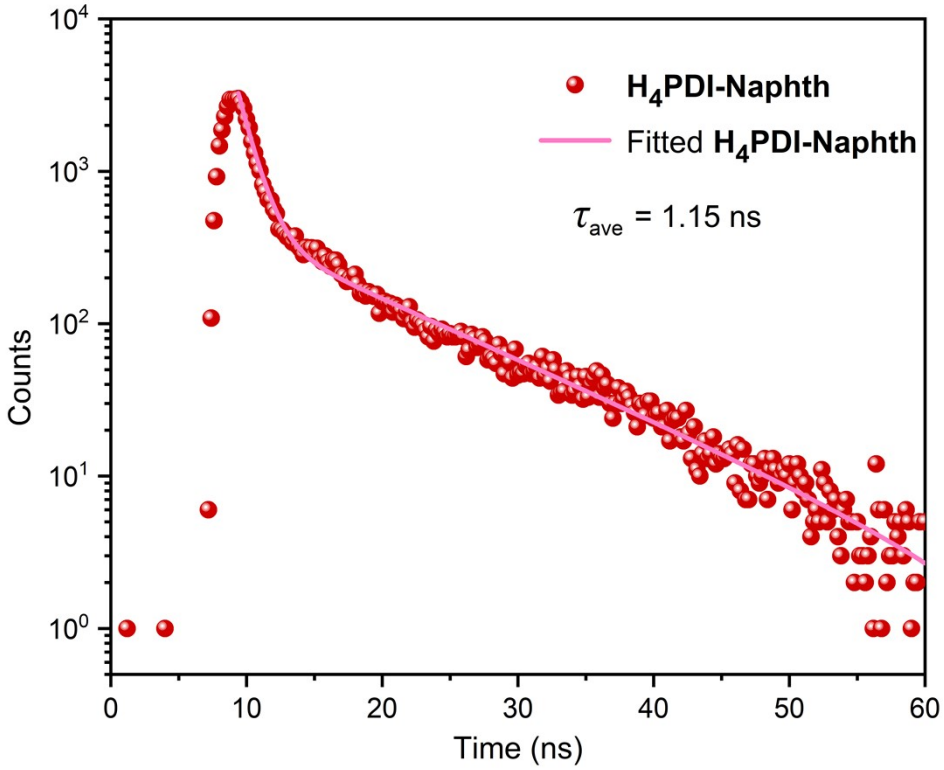


Figure S20 Fluorescence decay profiles of **H_4PDI-Naphth**.

7. Fluorescence quenching experiment

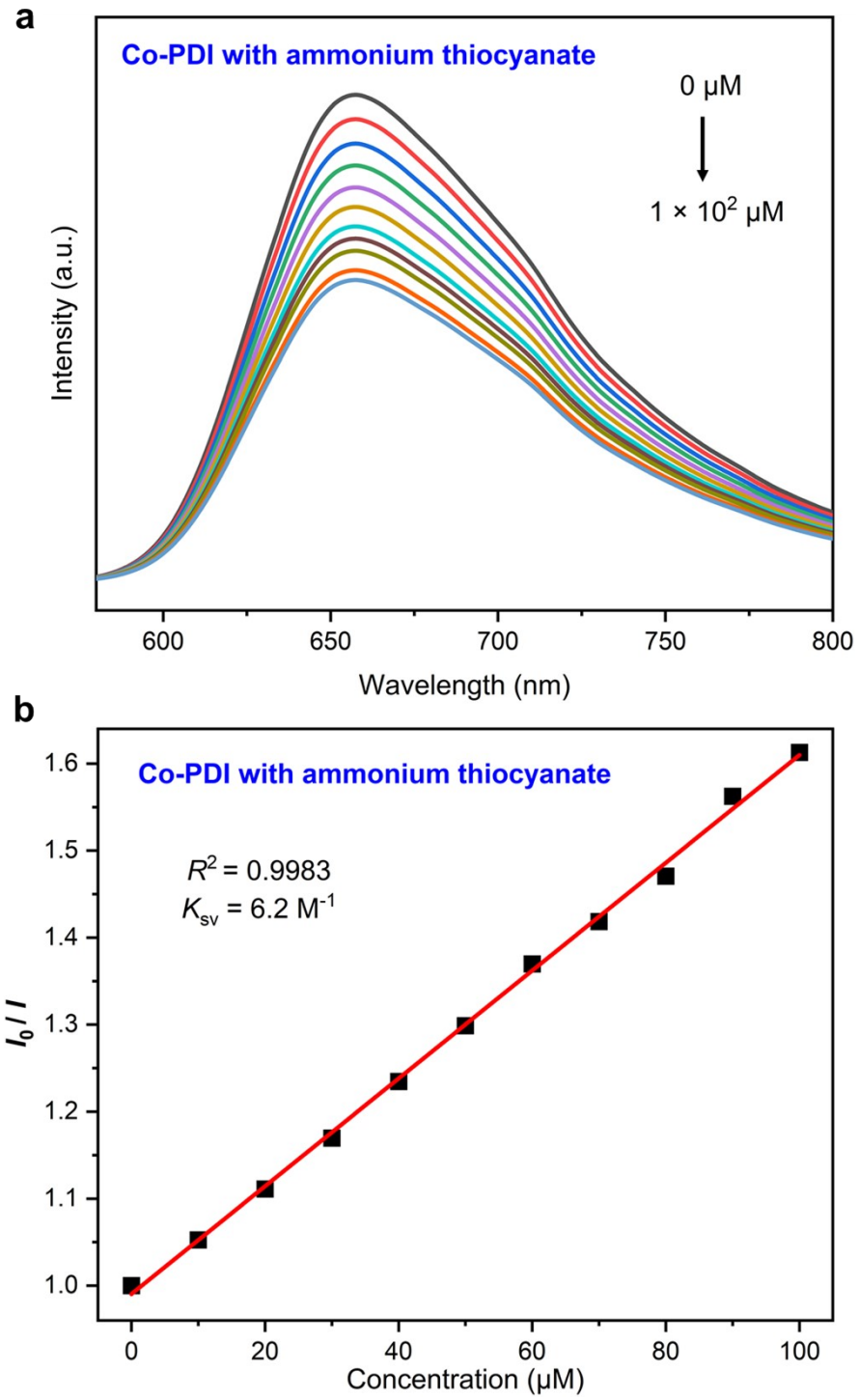


Figure S21 (a) Fluorescence quenching spectrum of **Co-PDI** (λ_{ex} = 470 nm, c = 2 × 10^{-4} M, T = 298 K) in CH_3CN after the addition of different amounts of ammonium thiocyanate. (b) The Stern-Volmer plot of **Co-PDI** *vs*. the concentration of ammonium thiocyanate.

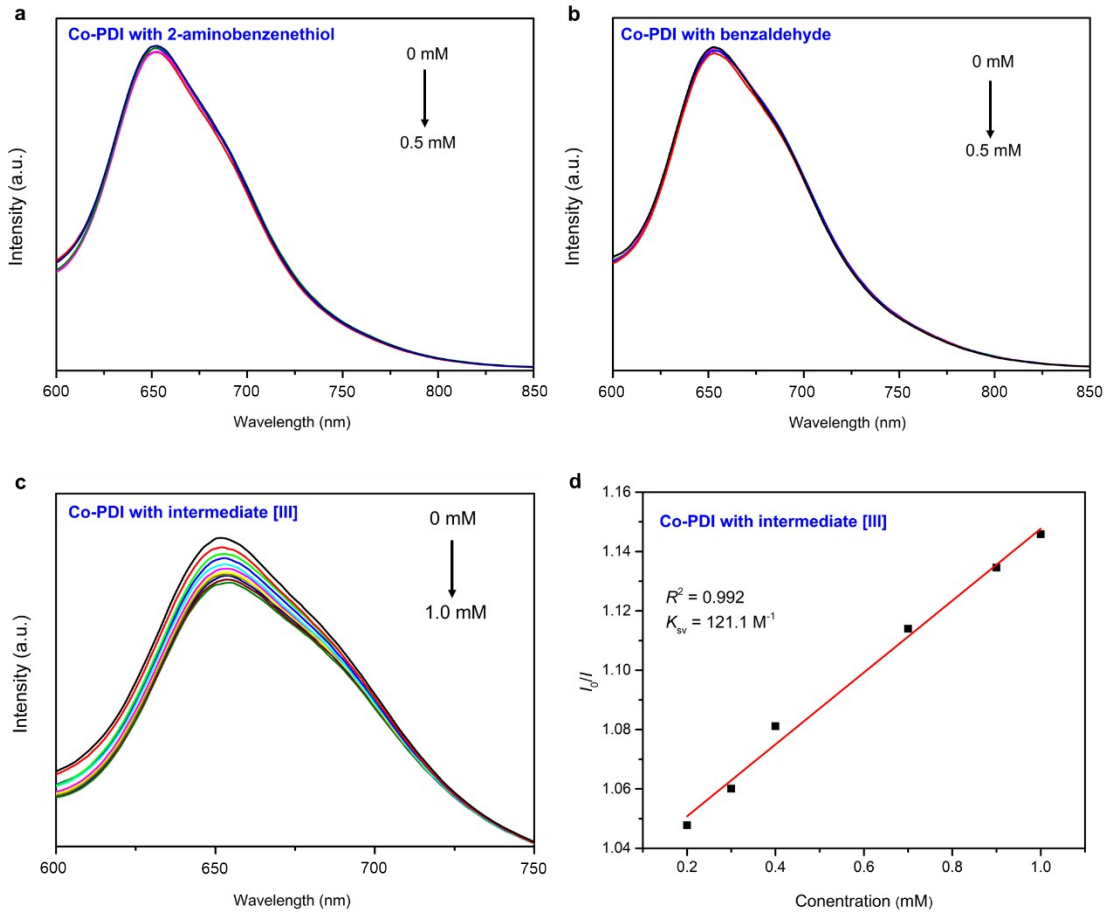
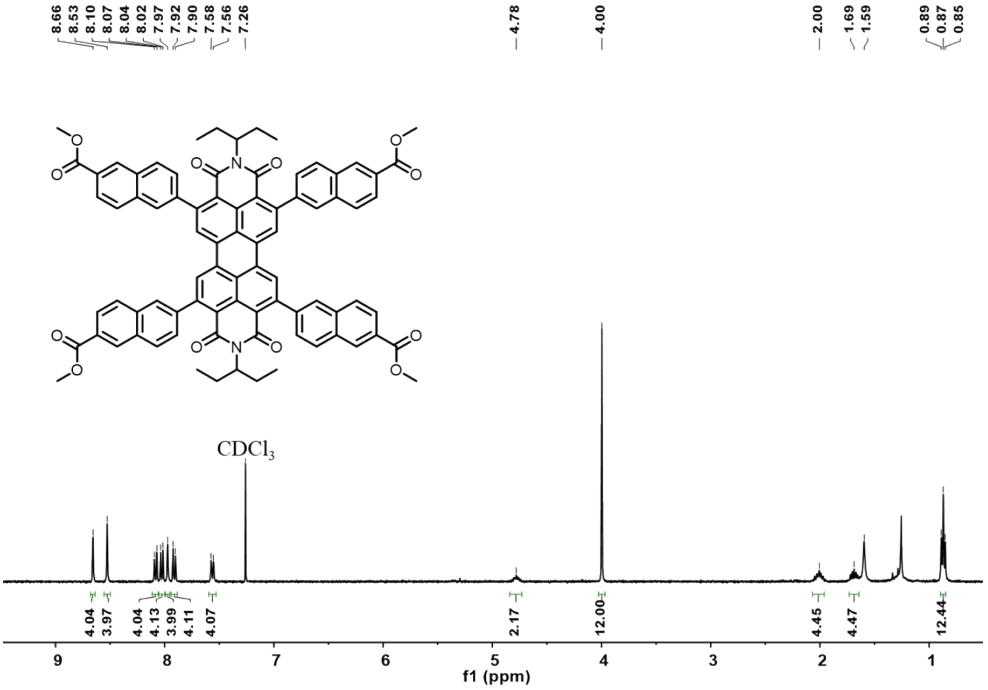
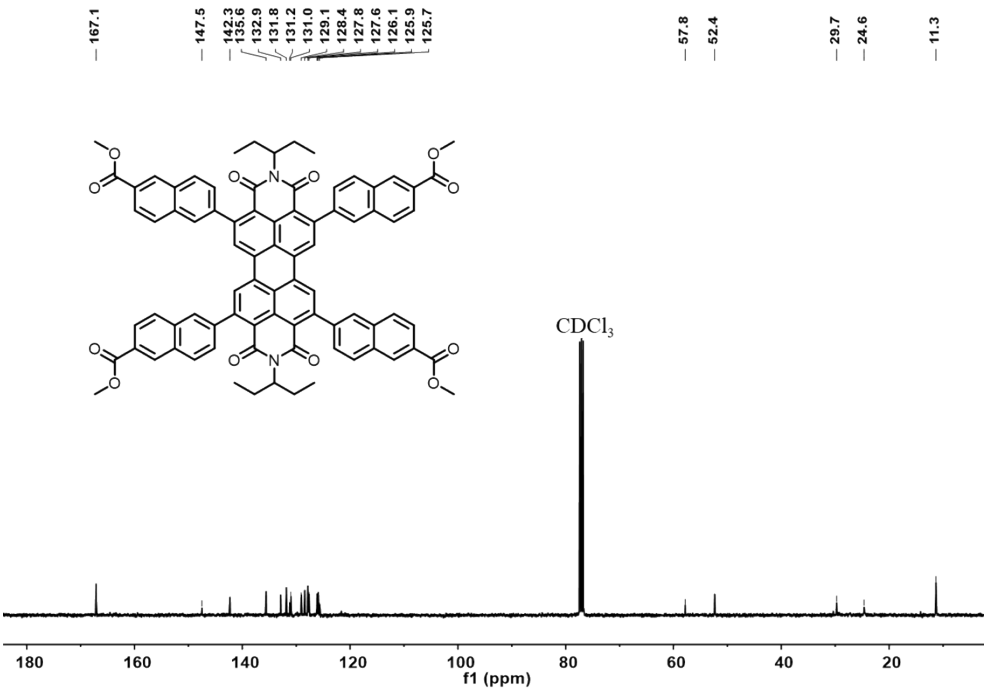


Figure S22 (a) Fluorescence quenching spectrum of **Co-PDI** ($c = 1 \times 10^{-5}$ M) in EtOH after the addition of different amounts of 2-aminobenzenethiol. (b) Fluorescence quenching spectrum of **Co-PDI** ($c = 1 \times 10^{-5}$ M) in EtOH after the addition of different amounts of benzaldehyde. (c) Fluorescence quenching s spectrum of **Co-PDI** ($c = 1 \times 10^{-5}$ M) in EtOH after the addition of different amounts of intermediate [III]. (d) The inset represents the Stern-Volmer plot of **Co-PDI** *vs*. the concentration of intermediate [III].

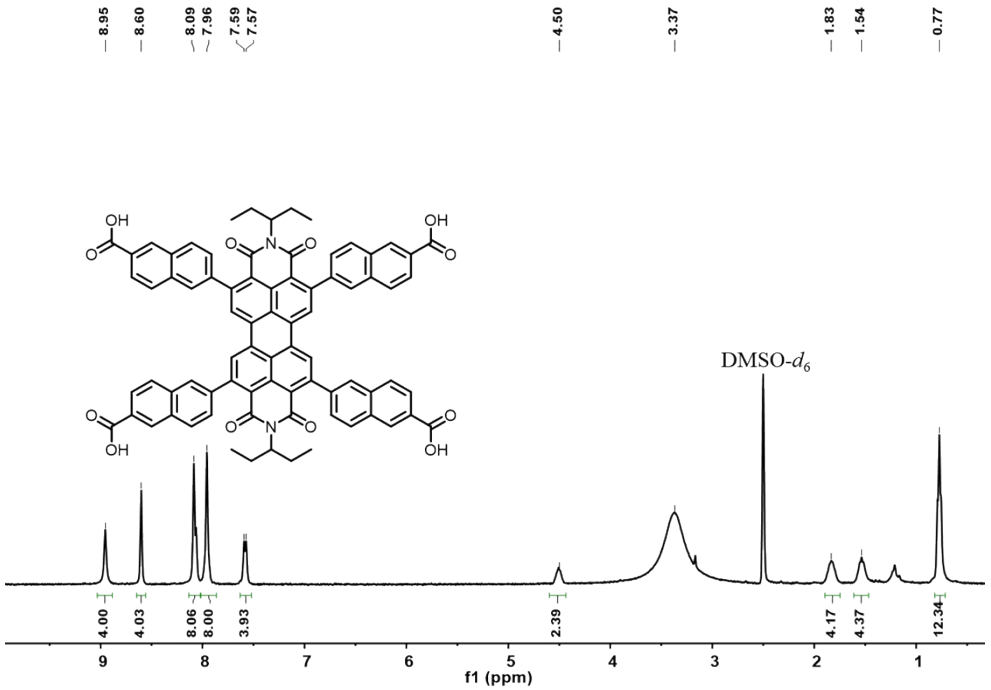
8. Selected NMR spectra for compounds



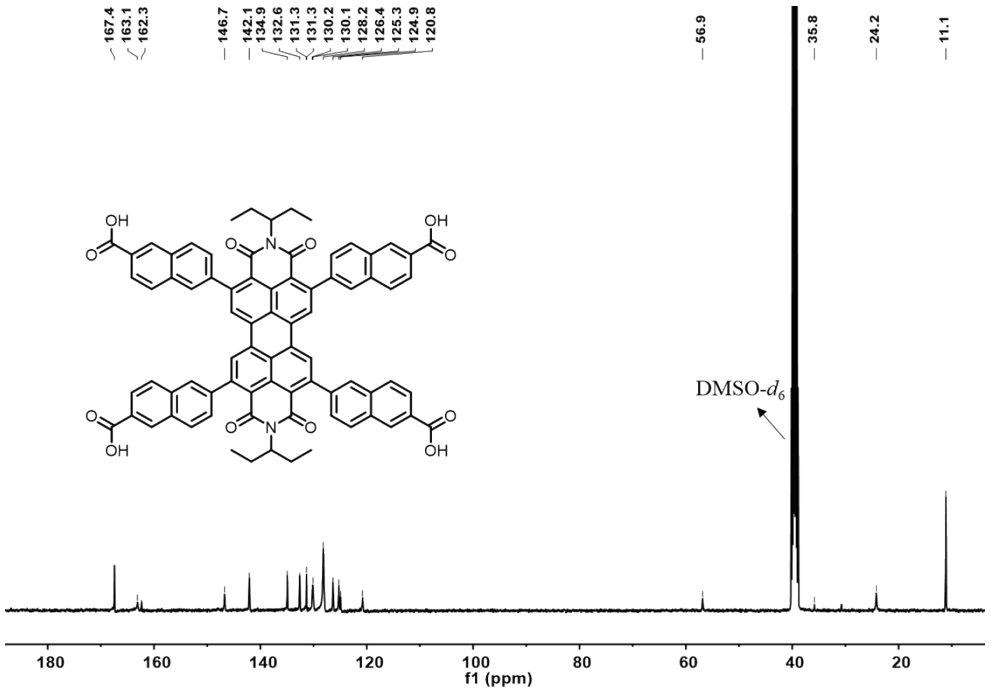
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **B**.



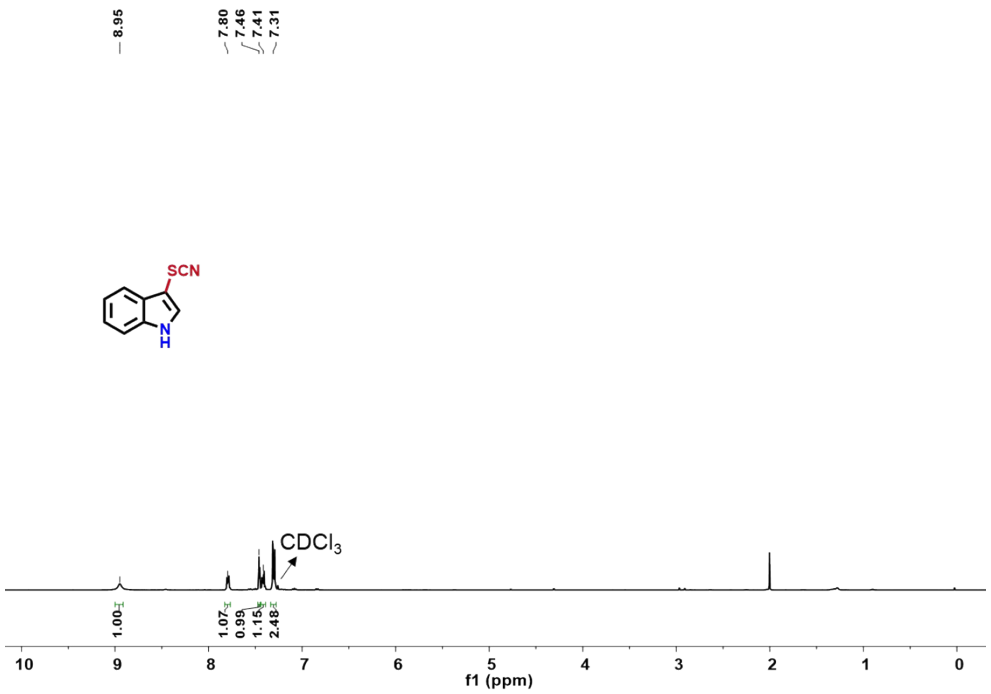
^{13}C NMR spectrum (100 MHz, $CDCl_3$, ppm) of the compound **B**.



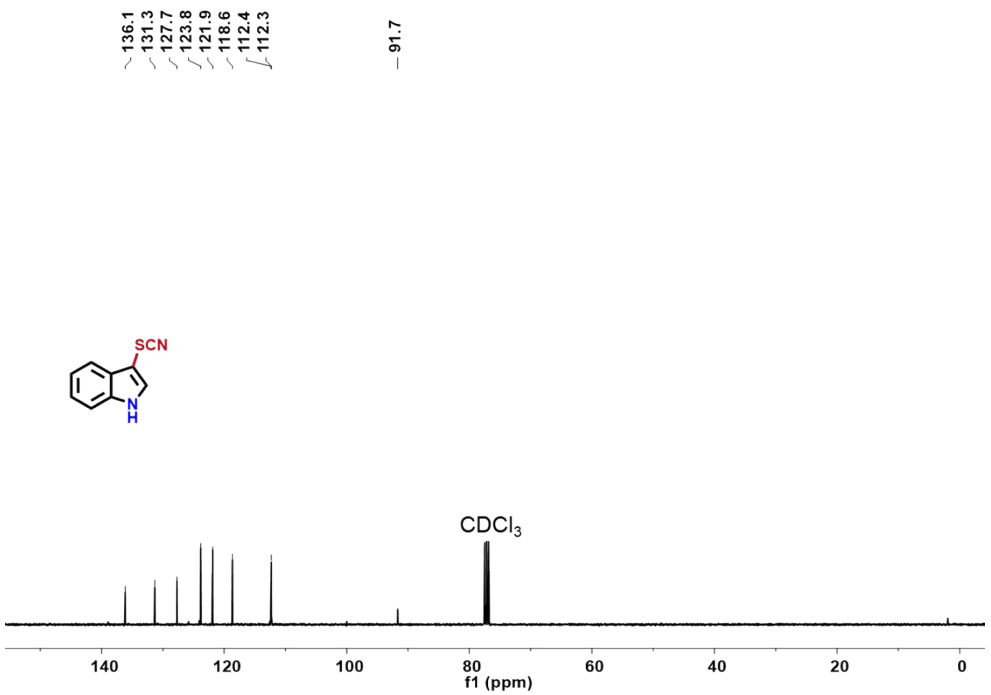
^{1}H NMR spectrum (400 MHz, DMSO-d_6, ppm) of the compound **H_4PDI-Naphth**.



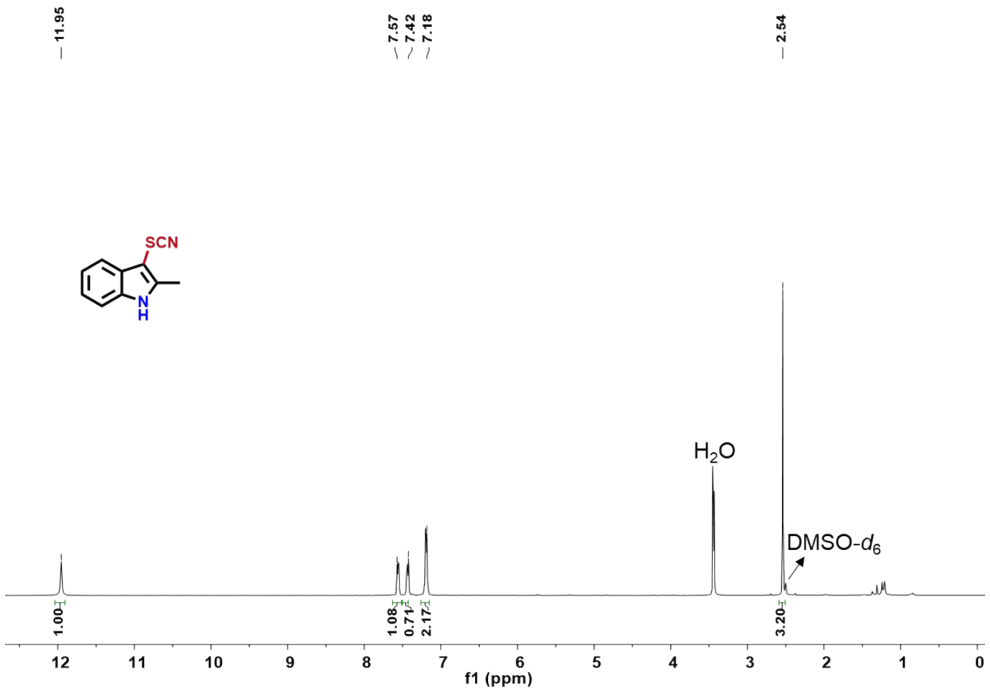
^{13}C NMR spectrum (100 MHz, DMSO-d_6, ppm) of the compound **H_4PDI-Naphth**.



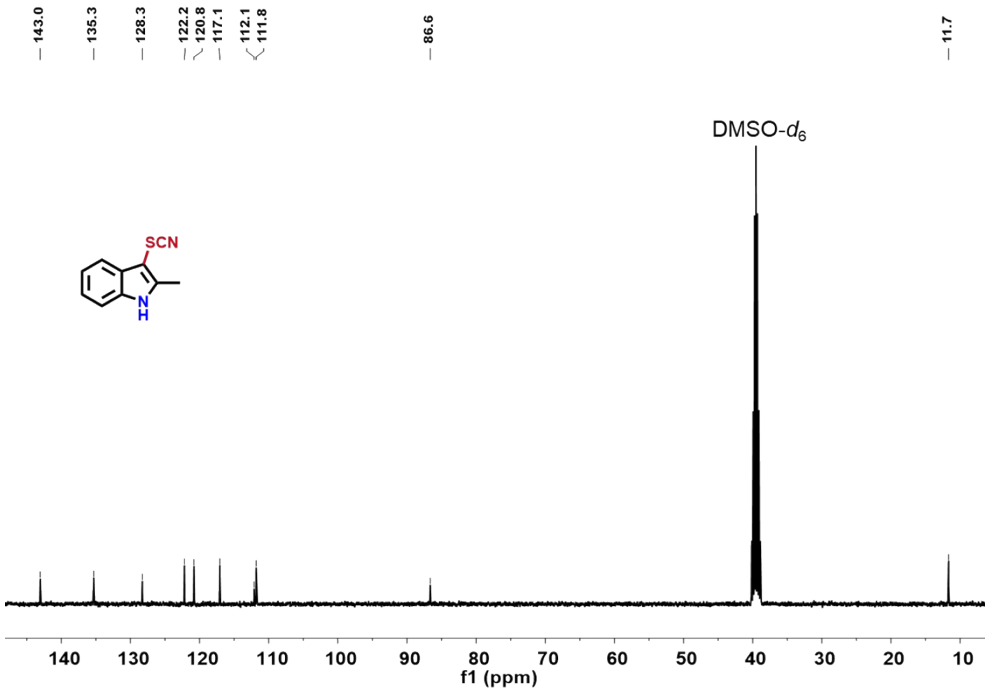
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2a**.



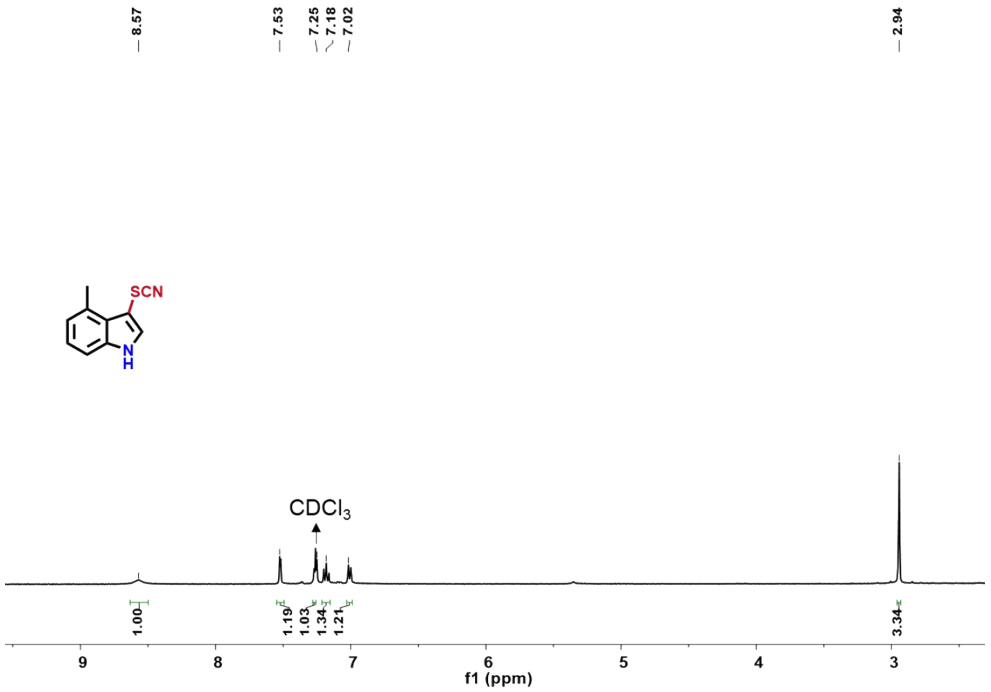
^{13}C NMR spectrum (100 MHz, $CDCl_3$, ppm) of the compound **2a**.



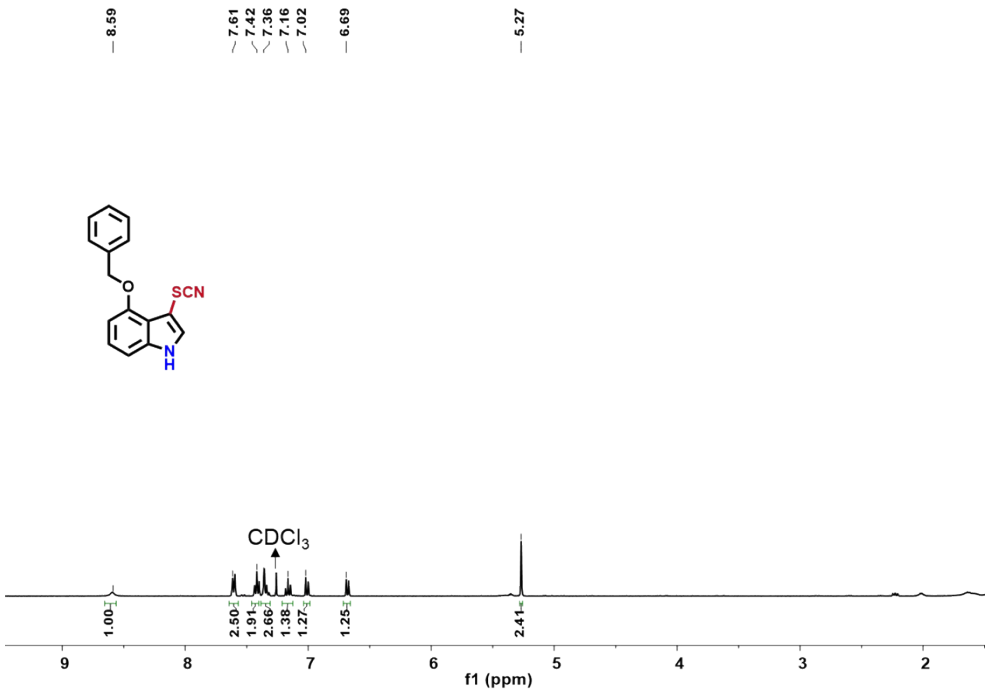
^{1}H NMR spectrum (400 MHz, DMSO-d_6, ppm) of the compound **2b**.



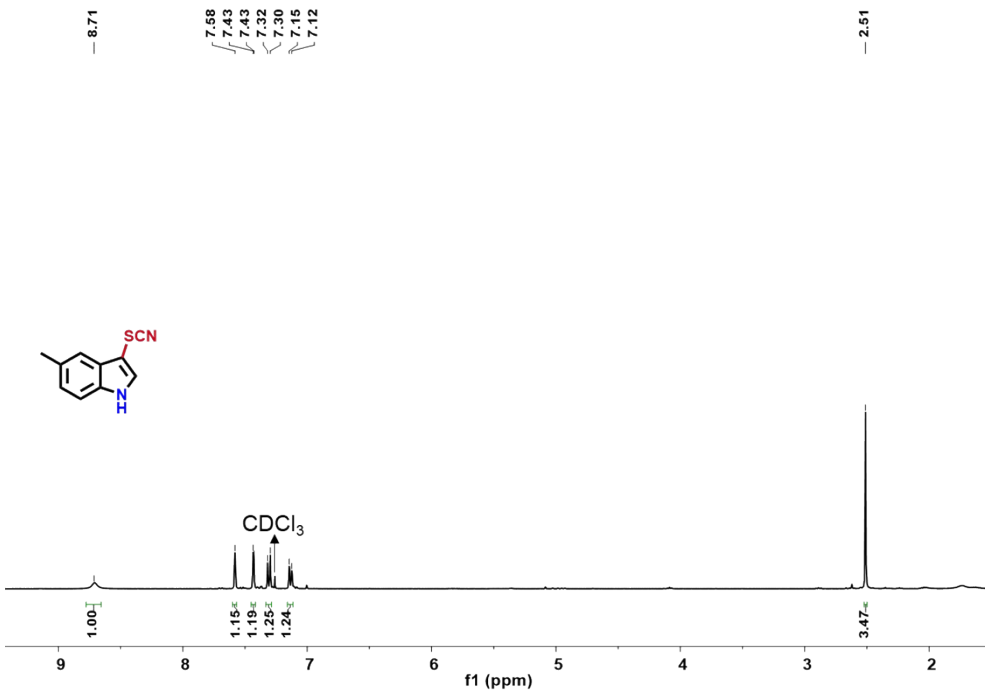
^{13}C NMR spectrum (100 MHz, DMSO-d_6, ppm) of the compound **2b**.



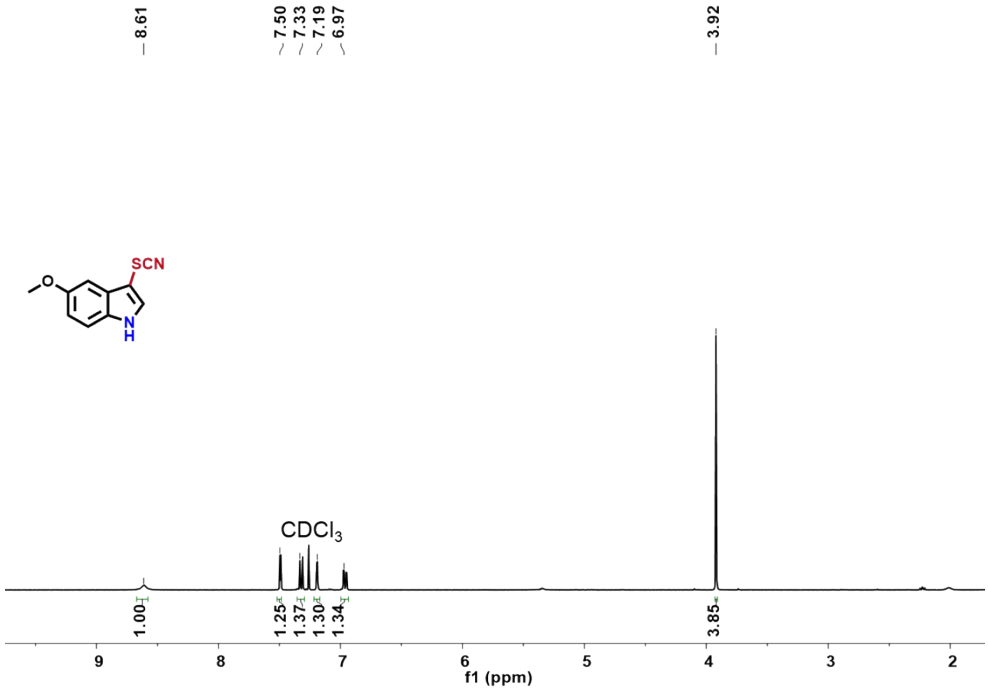
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2c**.



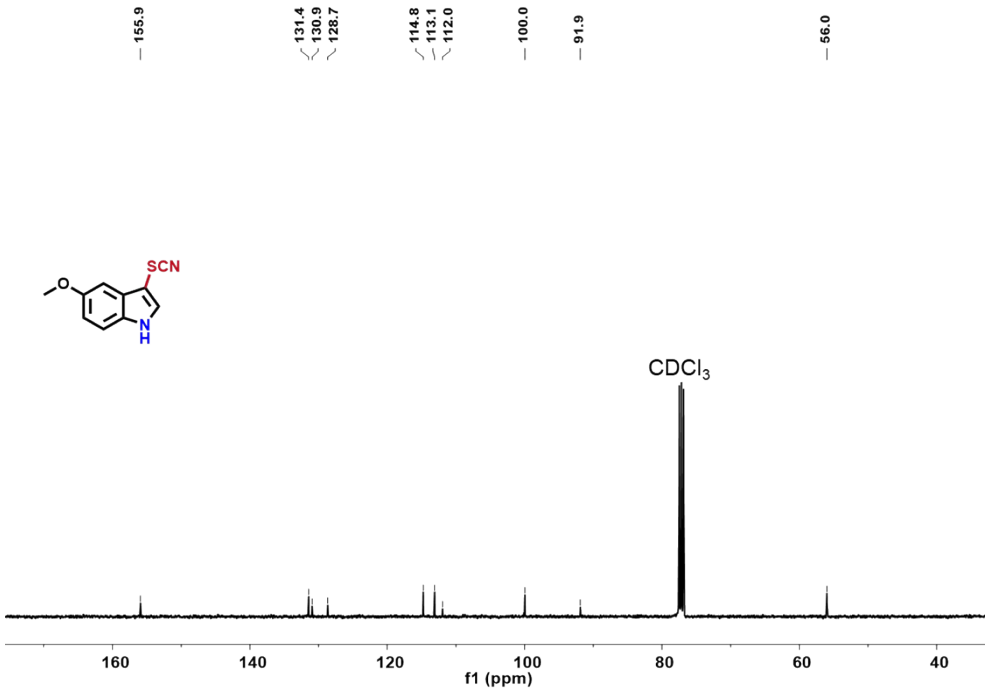
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2d**.



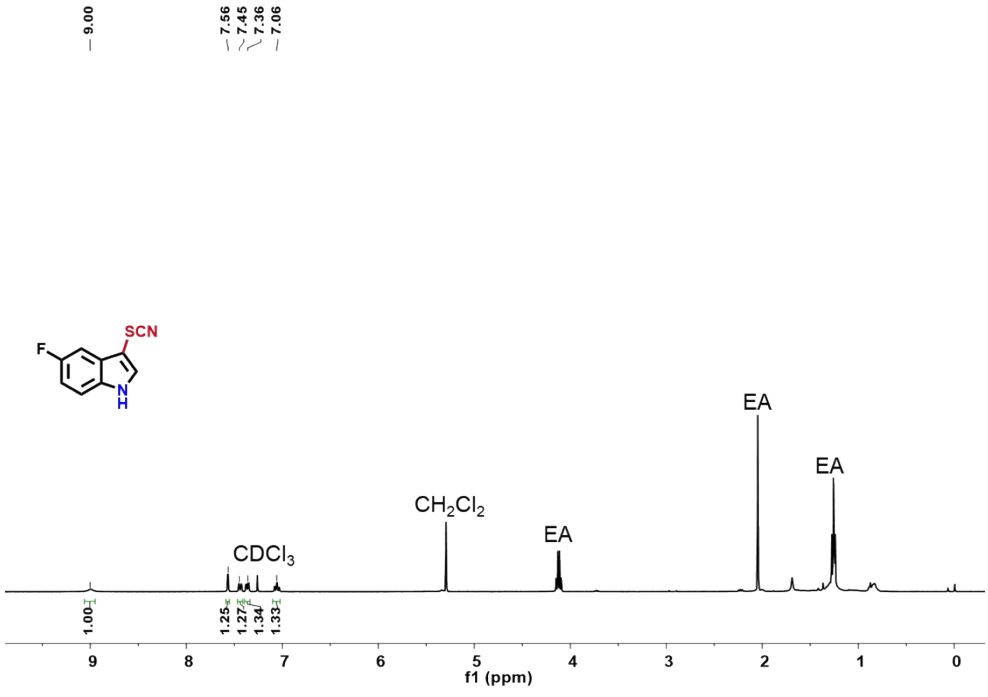
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2e**.



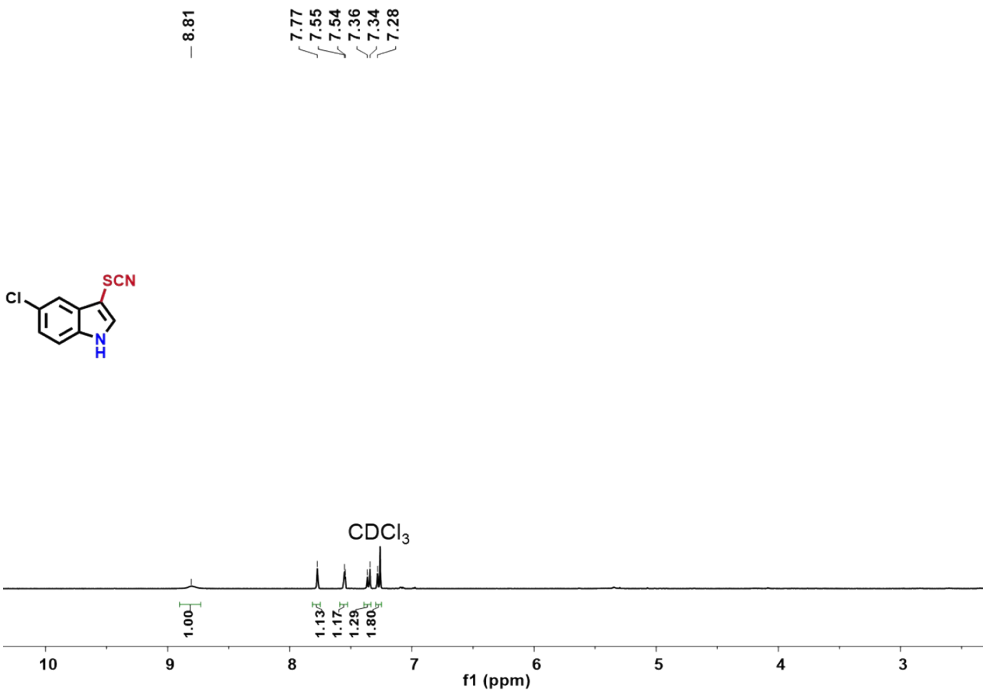
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2f**.



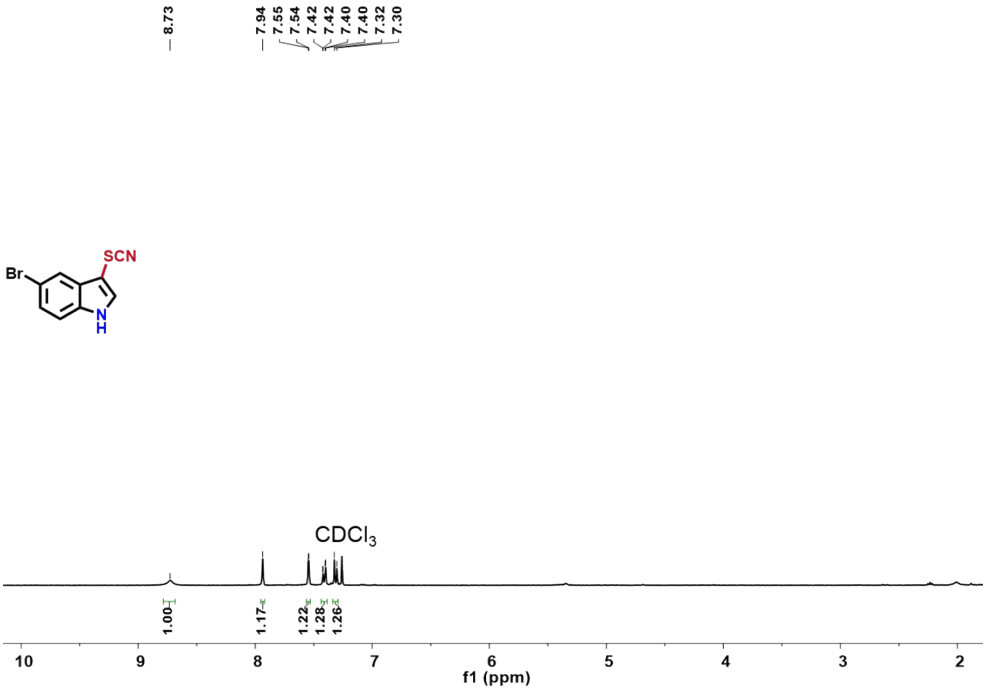
^{13}C NMR spectrum (100 MHz, $CDCl_3$, ppm) of the compound **2f**.



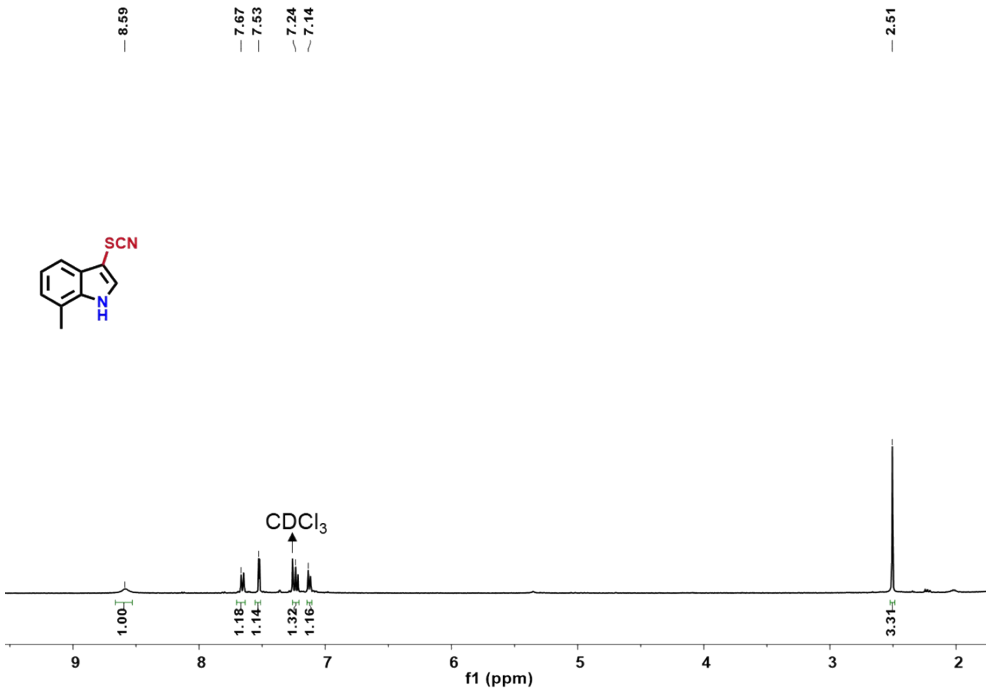
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2g**.



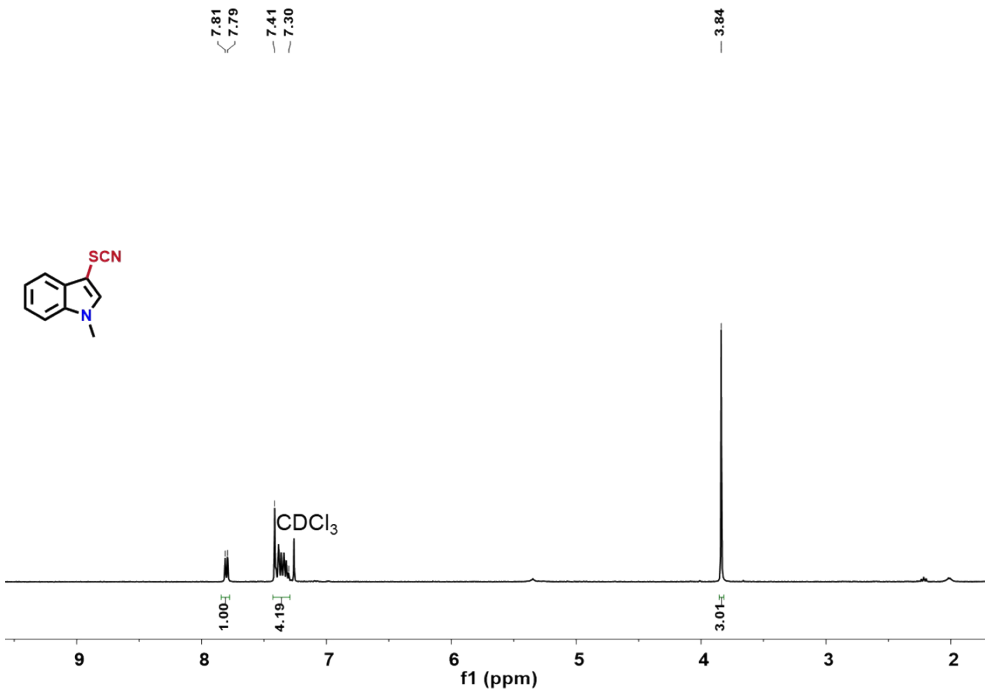
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2h**.



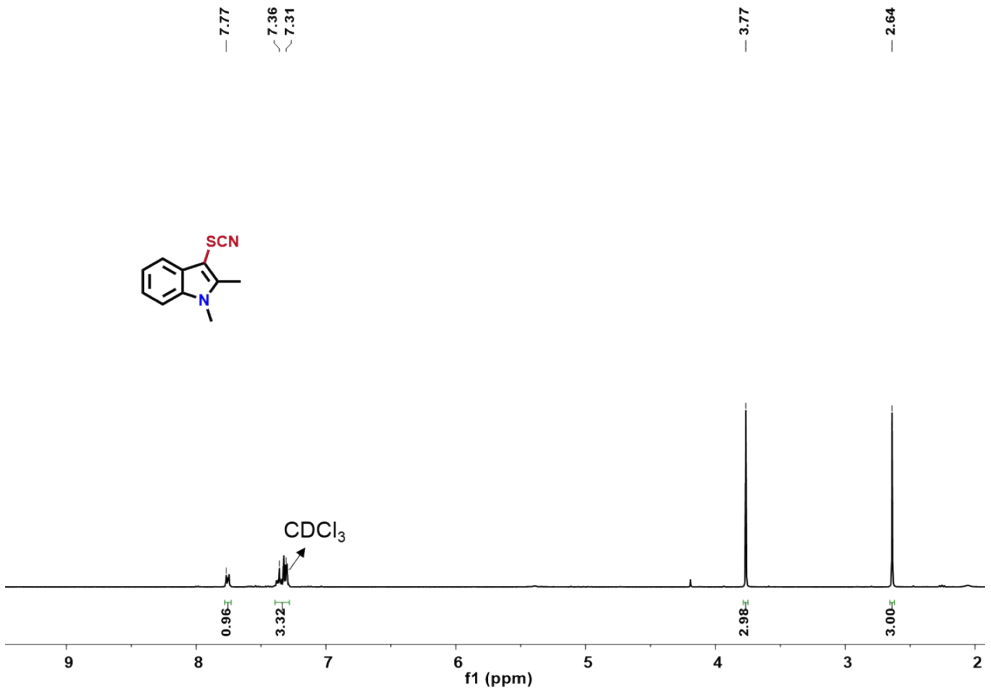
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2i**.



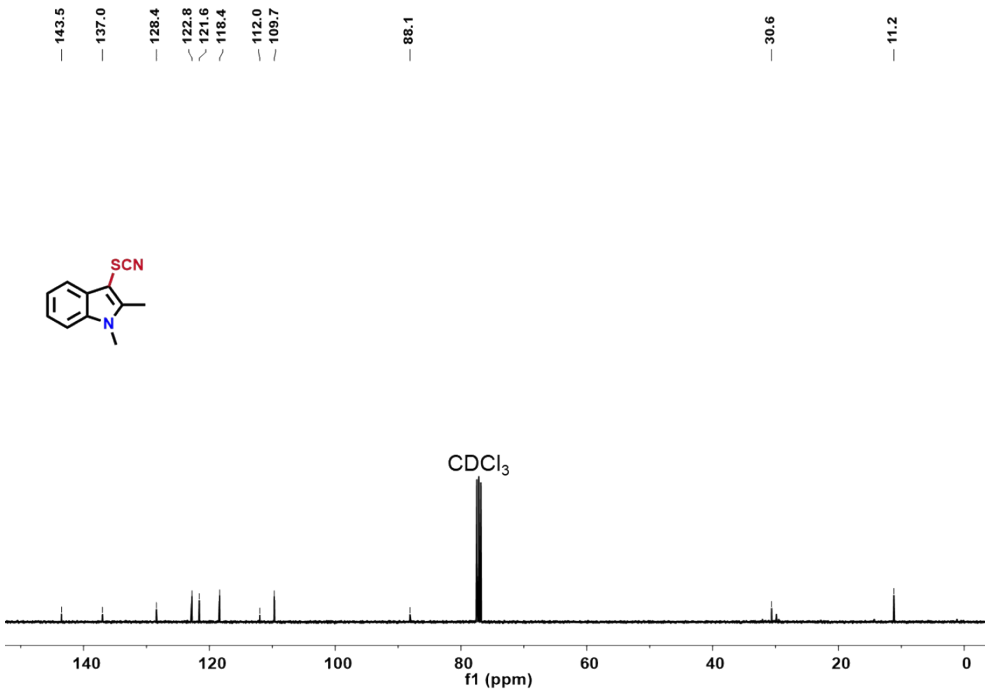
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2j**.



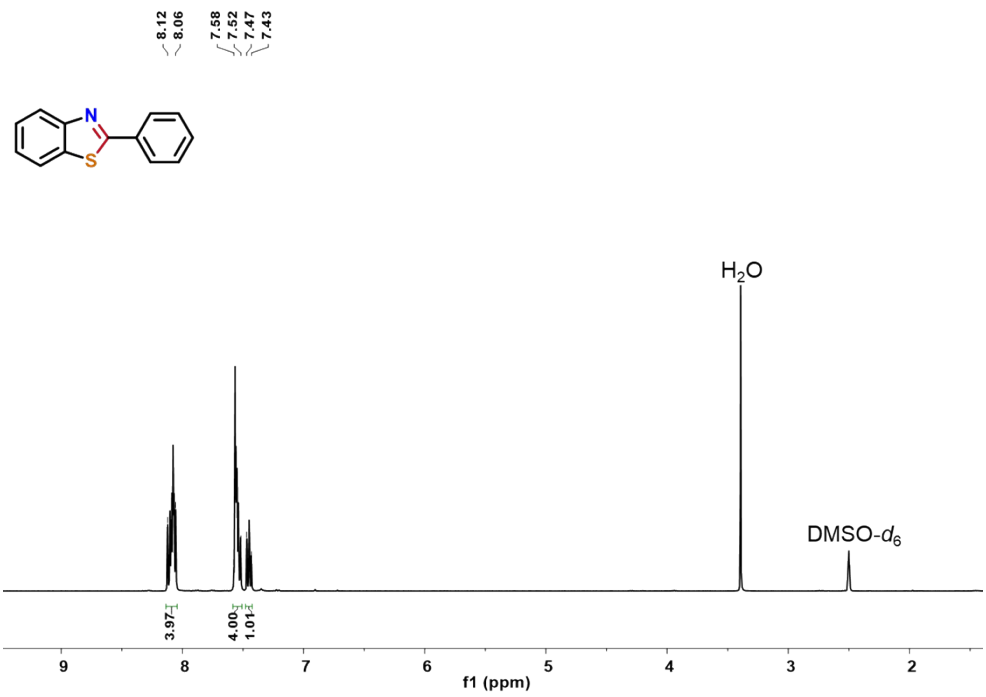
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2k**.



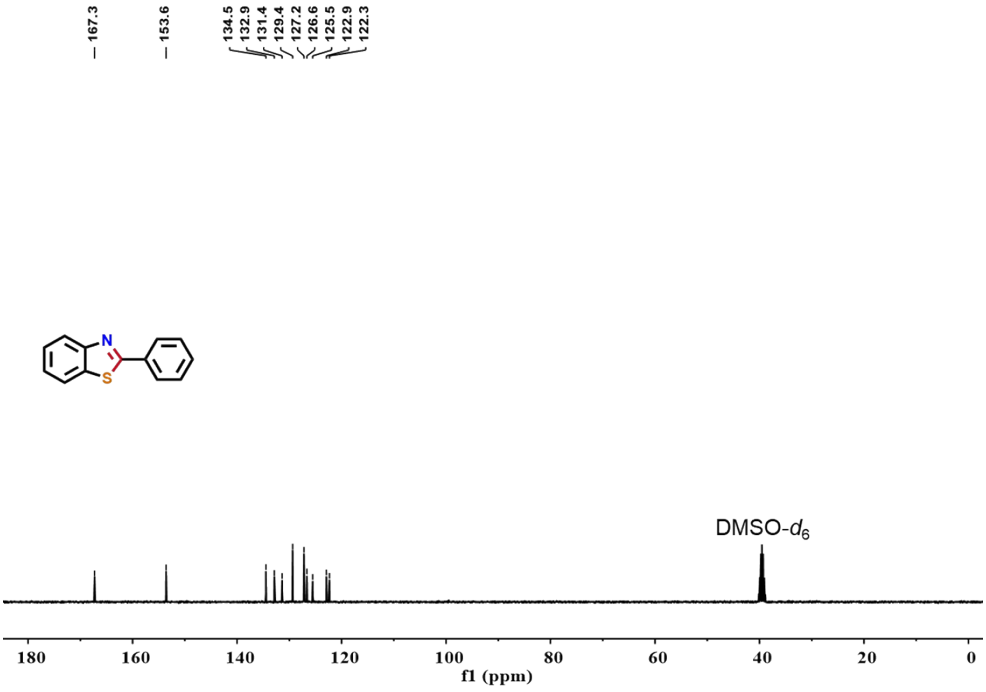
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **2l**.



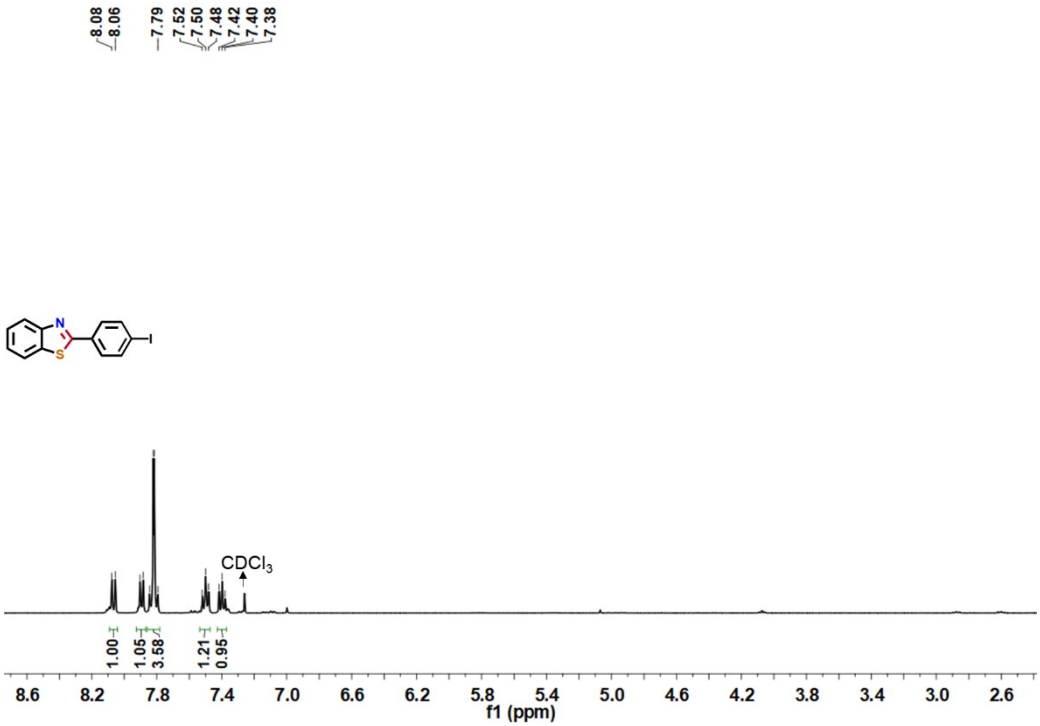
^{13}C NMR spectrum (100 MHz, $CDCl_3$, ppm) of the compound **2l**.



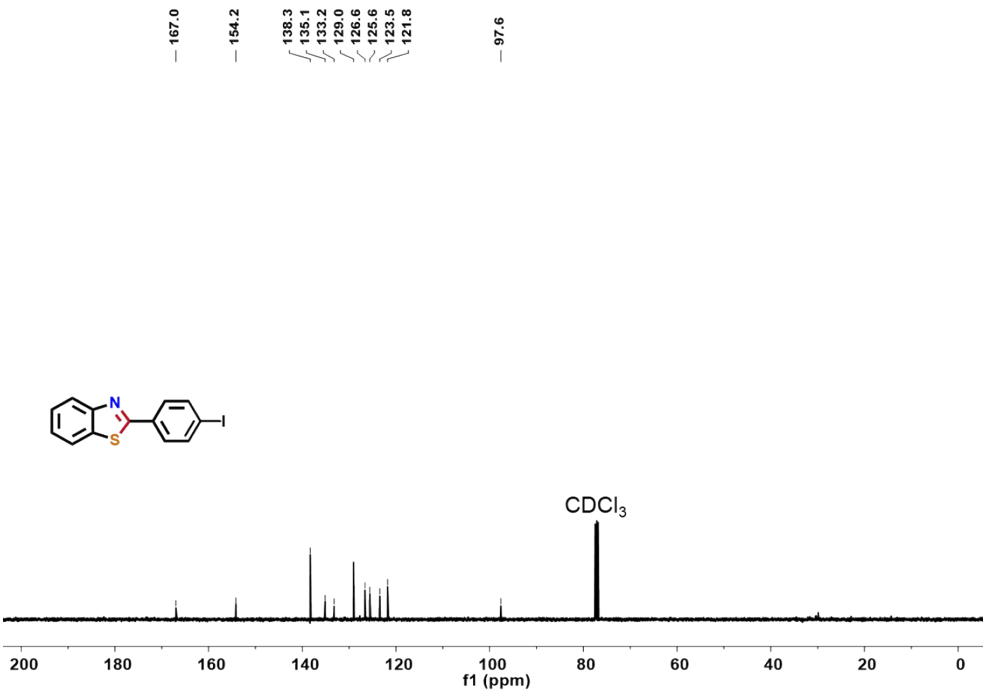
^{1}H NMR spectrum (400 MHz, DMSO-d_6, ppm) of the compound **5a**.



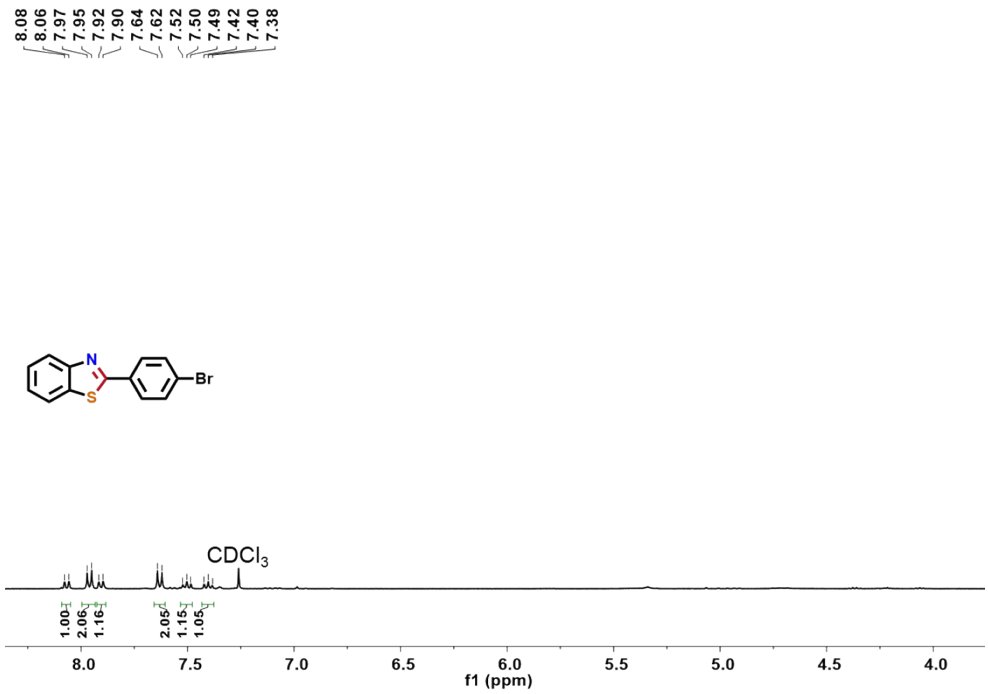
^{13}C NMR spectrum (100 MHz, DMSO-d_6, ppm) of the compound **5a**.



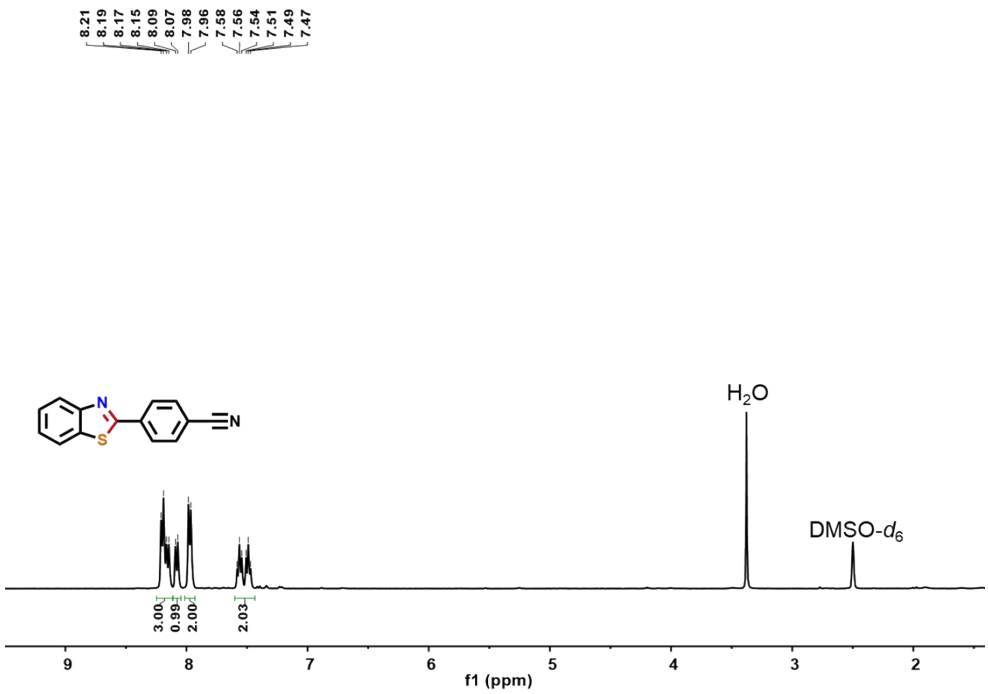
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **5b**.



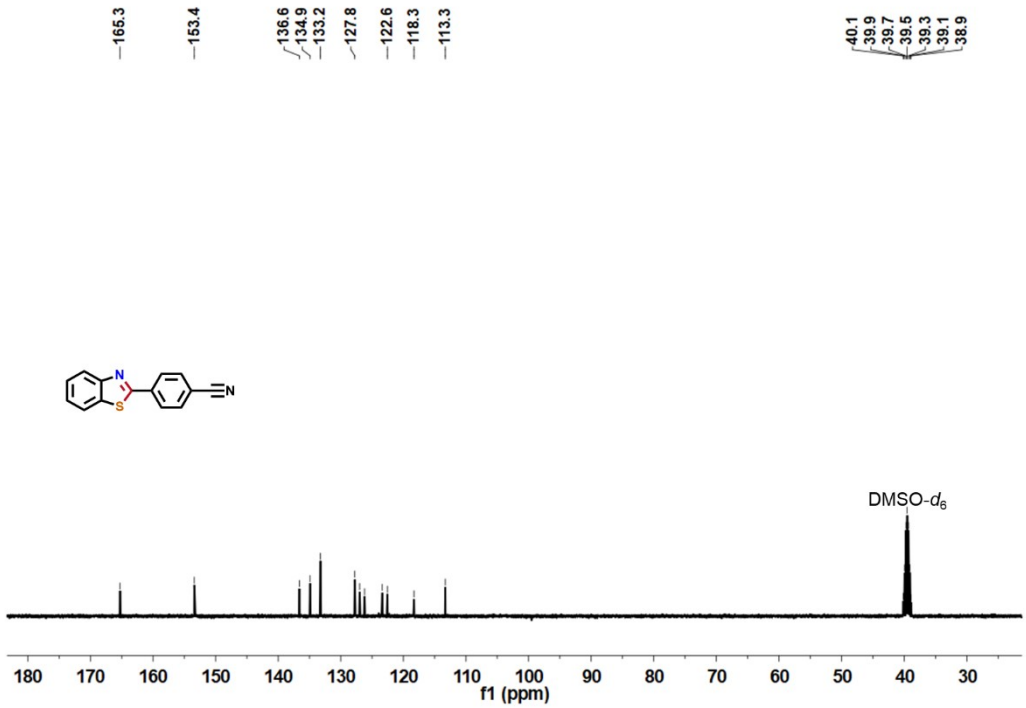
^{13}C NMR spectrum (100 MHz, $CDCl_3$, ppm) of the compound **5b**.



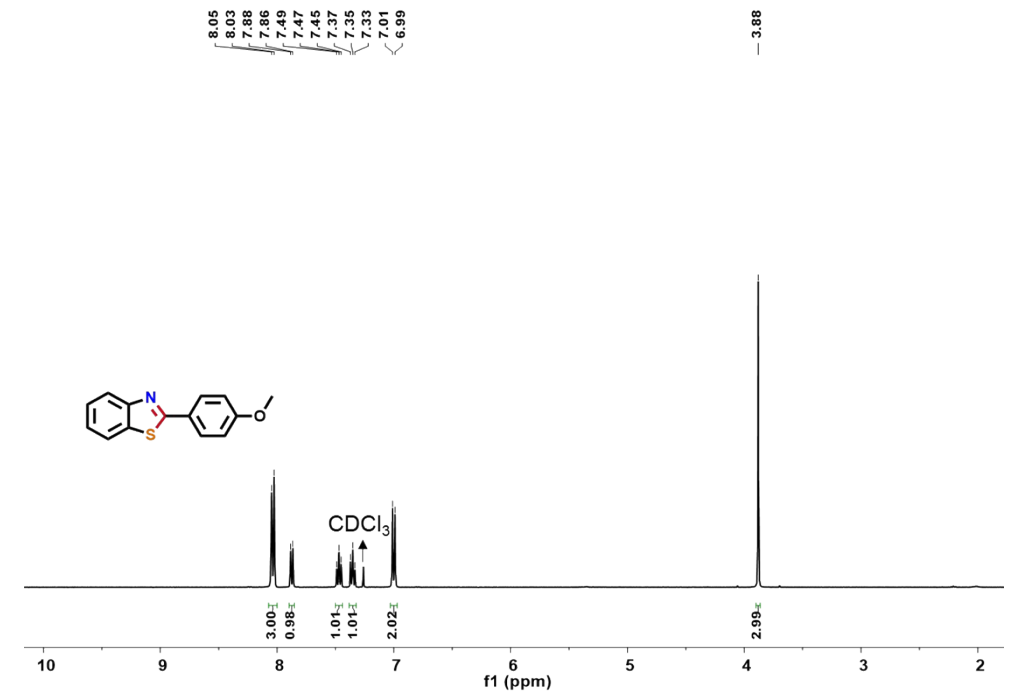
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **5c**.



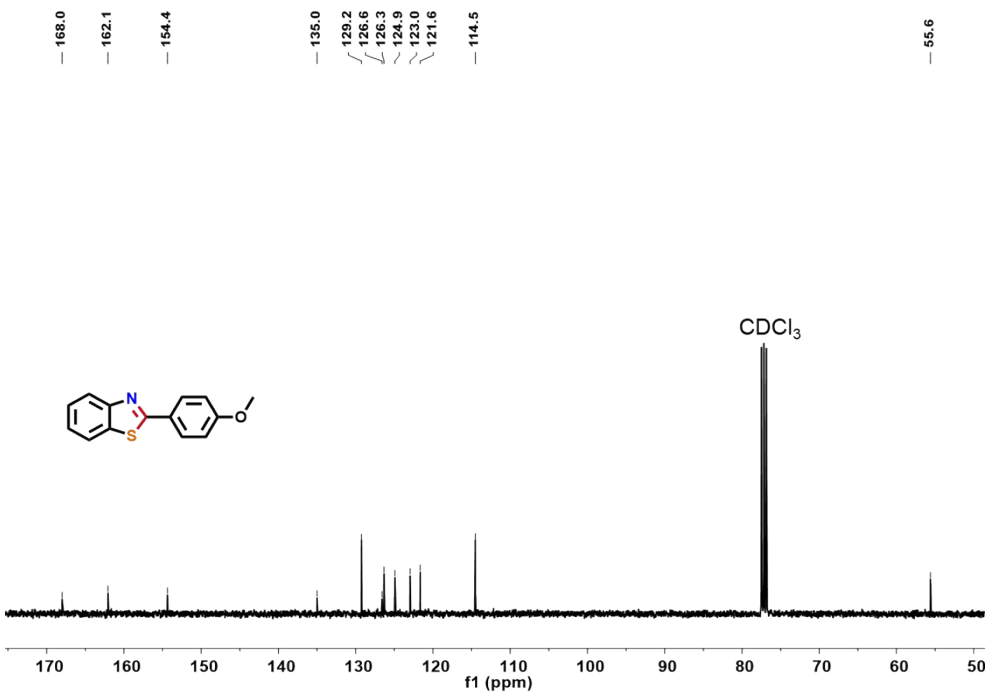
^{1}H NMR spectrum (400 MHz, DMSO-d_6, ppm) of the compound **5d**.



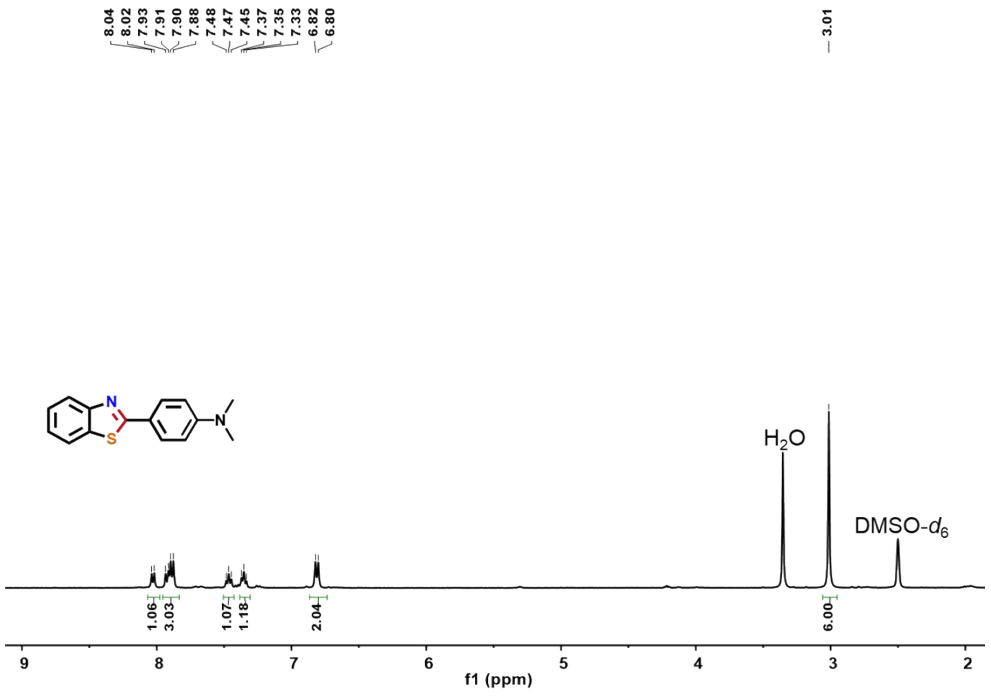
^{13}C NMR spectrum (100 MHz, DMSO-d_6, ppm) of the compound **5d**.



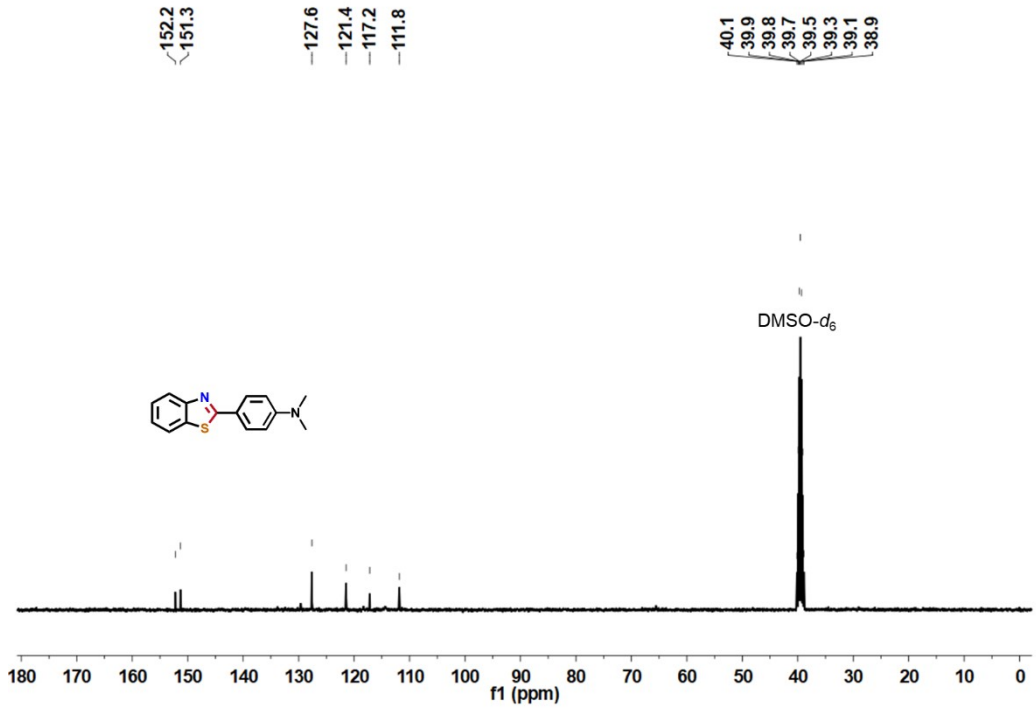
^{1}H NMR spectrum (400 MHz, $CDCl_3$, ppm) of the compound **5e**.



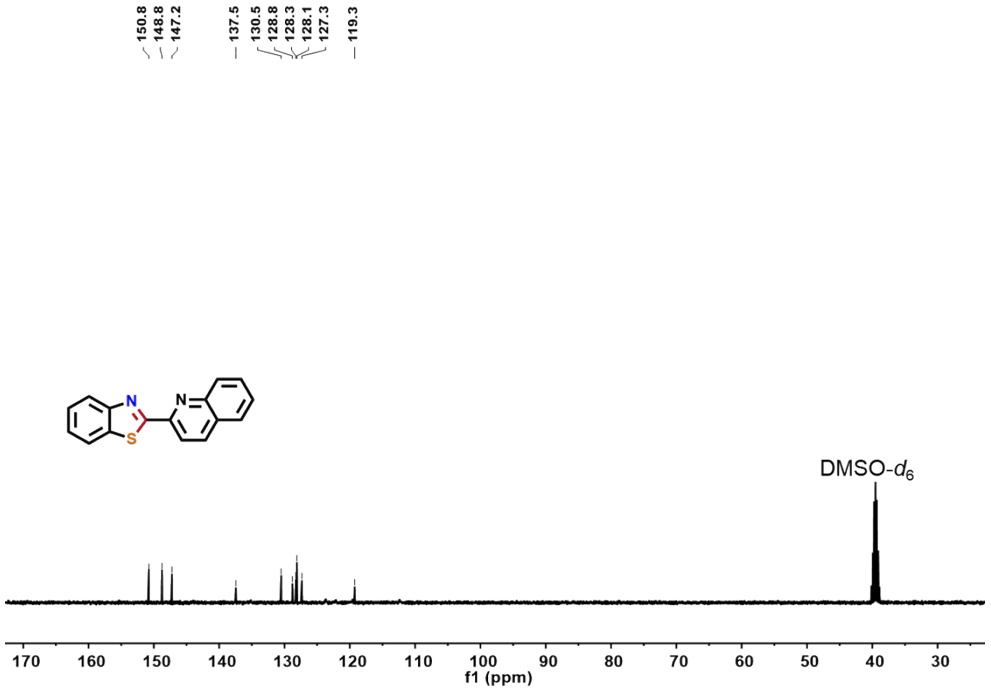
^{13}C NMR spectrum (100 MHz, $CDCl_3$, ppm) of the compound **5e**.



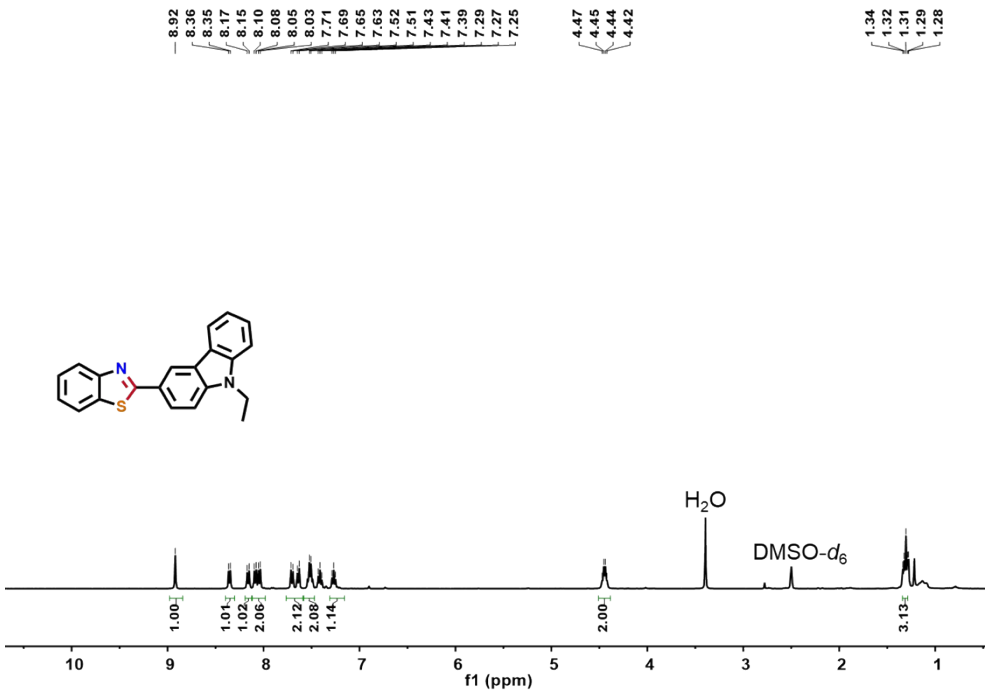
^{1}H NMR spectrum (400 MHz, DMSO-d_6, ppm) of the compound **5f**.



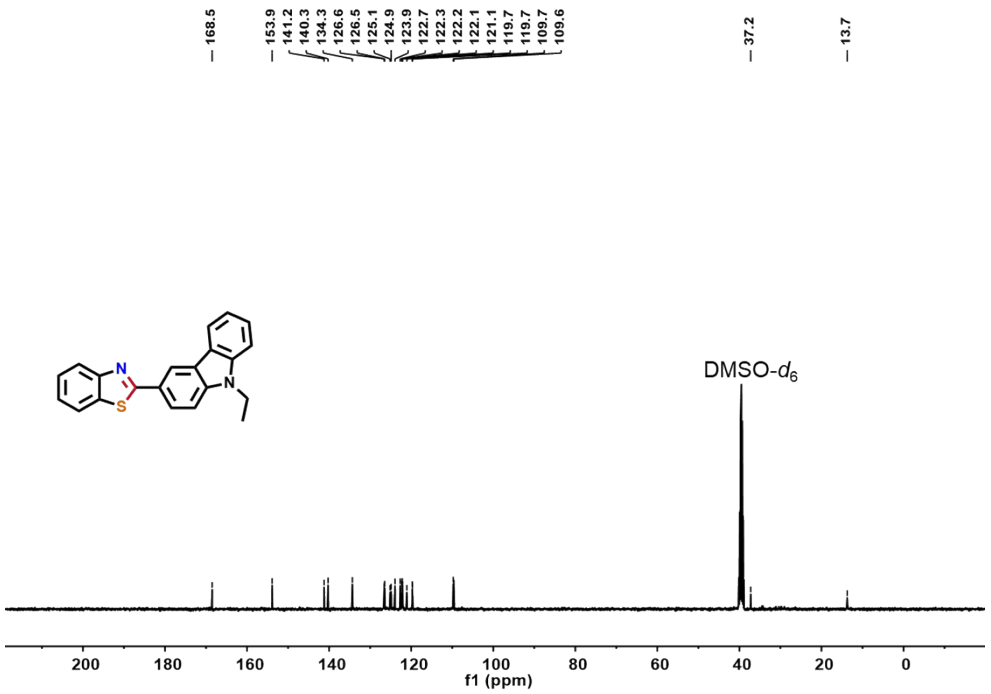
^{13}C NMR spectrum (100 MHz, DMSO-d_6, ppm) of the compound **5f**.



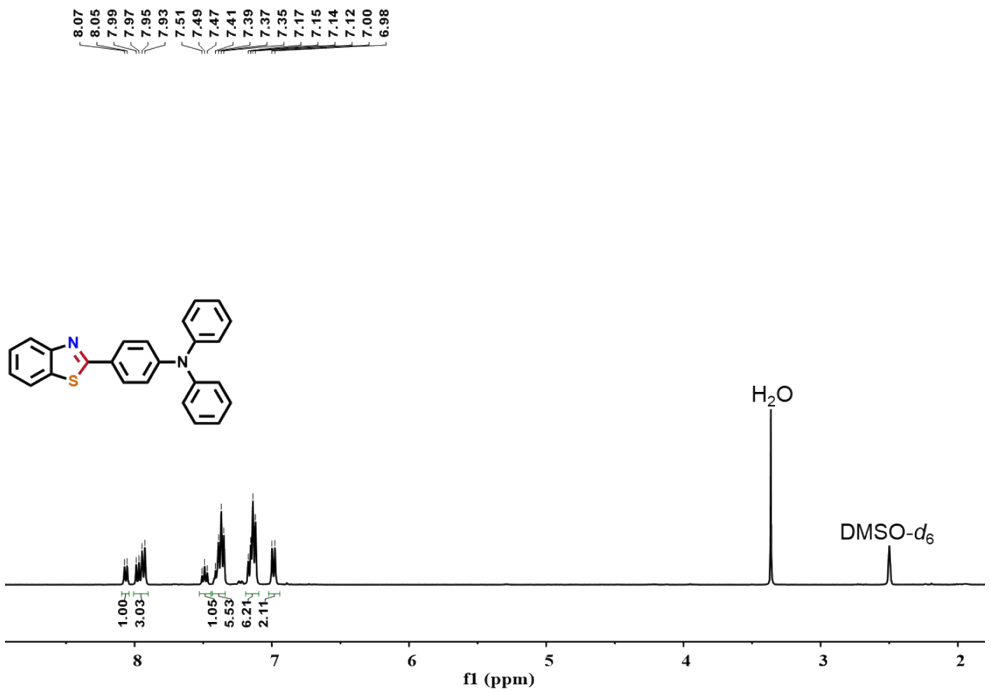
^{13}C NMR spectrum (100 MHz, DMSO-d_6, ppm) of the compound **5g**.



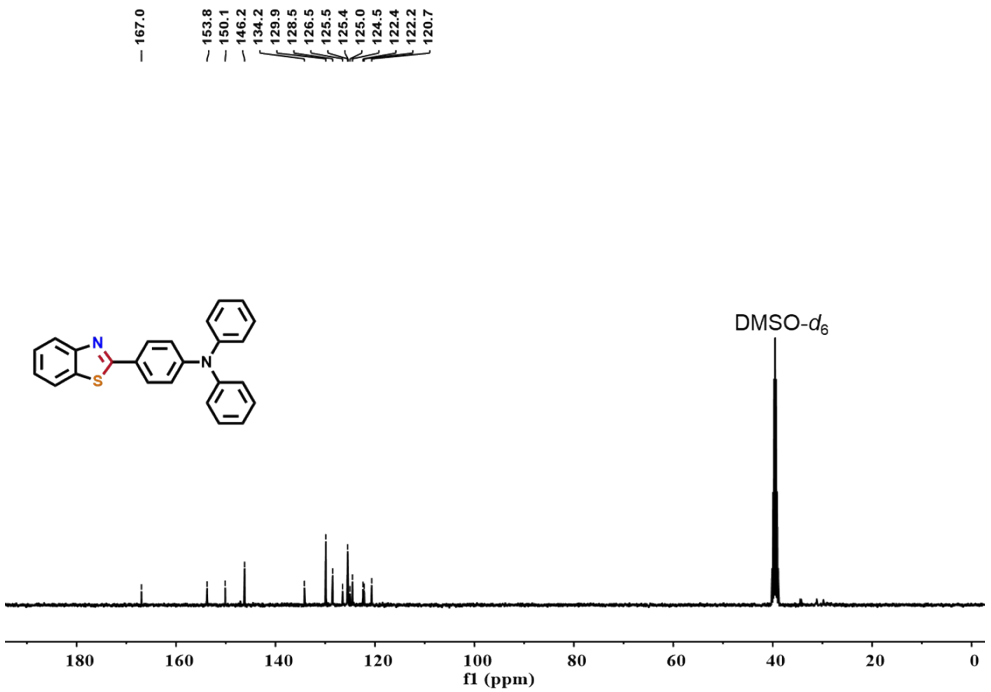
^{1}H NMR spectrum (400 MHz, DMSO-d_6, ppm) of the compound **5h**.



^{13}C NMR spectrum (100 MHz, DMSO-d_6, ppm) of the compound **5h**.



^{1}H NMR spectrum (400 MHz, DMSO-d_6, ppm) of the compound **5i**.



^{13}C NMR spectrum (100 MHz, DMSO-d_6, ppm) of the compound **5i**.

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