Supplementary Information (SI) for ChemComm.

Supporting Information

Carbazole-Functionalized MOFs for Efficient Selective Photocatalytic Oxidation of Thioethers to Sulfoxides

Contents

1. Experimental Section.

Materials and methods

The ligand H_4L was synthesized according to literature methods(Figure S1). All other requisite chemicals were purchased from commercial companies and used without further purification. ^1H NMR spectra were obtained relative to the internal standard tetramethyl silane at δ 0.0 ppm using Bruker AVANCE spectrometers (400 MHz). Fourier transform infrared spectra were recorded as KBr pellets on a NEXUS instrument in the range of 500−4000 cm^{-1}. Powder X-ray diffraction (PXRD) using a Bruker D8 Advance X-ray diffractometer (Cu Kα radiation, $\lambda = 1.5418$ Å) in the range of 5-50°(2θ). Solid UV−vis spectra were obtained using a Hitachi U-4100 UV−vis−NIR spectrophotometer and a white standard of $BaSO_4$ was used as a reference. Scanning electron microscope (SEM) experiments used JSM-7900F Plus record. GC analyses were carried out an Agilent Technologies 6890 N GC system, equipped with the FID detector and the chromatographic column of HP-50+, with N_2 used as the carrier gas. Electrochemical experiments were carried out on CHI760E workstation with three-electrode system. Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker E500 instrument. The spectra of the Advanced Fourier Transform Infrared Spectrometer were measured with a Thermo Fisher 6700 instrument (KBr pellets). N_2 sorption isotherm at 77.350 K was carried out on Automated Gas Sorption Analyzer.

Photoelectrochemical Characterization. Photocurrent curves, Electrochemical impedance spectra, Mott-Schottky plots for Co-H_4L and Mn- H_4L were carried out on a three-electrode system with the photocatalyst-coated FTO, a Pt plate and Ag/AgCl as the working electrode, counter electrode, reference electrode, respectively. All measurements were made in a solution of 1.0 M potassium chloride at room temperature. A 425 nm LED was used as light source. A mixture solution containing 20.0 µL Nafion, and 500.0 µL of ethanol was added to the catalyst (5.0 mg). The working electrode is prepared by dripping the mixture onto the surface of the FTO glass about one square centimeter and drying it naturally.

TMB Oxidation Measurement[1,2]**.** Typically, 5.0 mg of TMB was dissolved in 5.0 mL of H_2O and 5.0 mL of HAc/NaAc buffer solution (0.2 M). A total of 100.0 µL of Co-H_4L aqueous solution (1.0 mg/mL) was then added to the mixture solution with O_2 bubbling under 425 nm LED irradiation. The samples were taken at different time intervals for UV−Vis measurements.2 In order to verify specific ROS, various scavengers were added to the TMB solution before light irradiation: carotene (2.0 mg), mannite (2.0 mg), catalase (5.0 µL), and superoxide dismutase (SOD, 2.0 mg), respectively.

EPR detection of singlet oxygen and superoxide radical. The EPR spectra of singlet oxygen and superoxide radical were obtained in the presence of TEMPO and DMPO. Typically, 10.0 µL TEMPO/ DMPO was mixed with 1mL CH_3CN/CH_3OH of Co-H_4L (2.0 mg/0.5mL). The mixture were then added to EPR tube. EPR measurements were carried out under 425nm illumination for 3 minutes.

Synthesis of Ligand

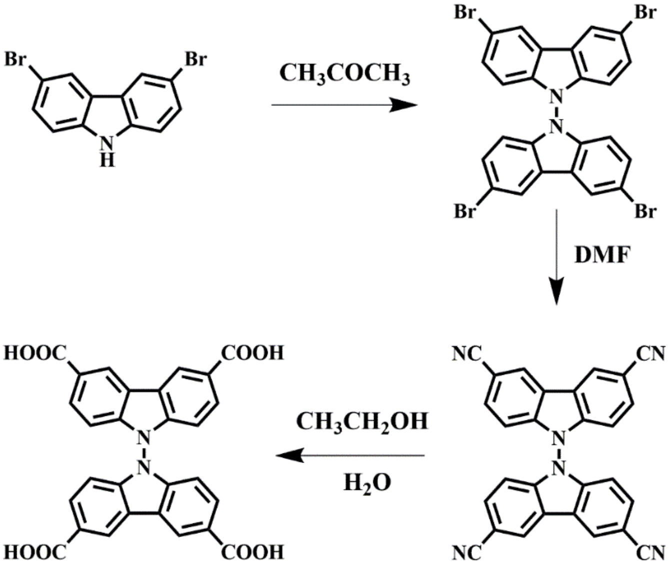


Figure S1 Schematic Diagram of the Synthetic Route for H_4L

Synthesis of 3,3',6,6'-tetrabromo-9,9'-bicarbazole(Br_4L)[3]: Add 3,6-dibromocarbazole (4 g, 12.30 M) into 80 mL of acetone and heat to 50 ℃. After reaching the temperature, add $KMnO_4$ (6 g, 0.038 M) slowly. Stir the solution for 4 hours, and subsequently add 100 mL of distilled water. Extract the solution with dichloromethane, then evaporate the solvent under reduced pressure to dryness. Wash the resulting solid with methanol, and dry it in a vacuum oven at 60 ℃ to yield white solid 1, with an approximate yield of 70%.

Synthesis of 3,3’,6,6’-tetracyano-9,9’-bicarbazole (CN_4L)[4]: Add CuCN (1.4 g, 16 M) and compound 1 (1 g, 1.55 M) into 40 mL of anhydrous DMF. Purge the solution with argon for 15 minutes. Maintain the reaction at 150 ℃ under an argon atmosphere for 48 hours, with additional argon purging once every 12 hours. Upon completion, cool the reaction mixture to room temperature, and then add 20 mL of concentrated hydrochloric acid and 16 g of anhydrous ferric chloride. Stir the mixture in an ice-water bath for 2 hours, then filter and dry under vacuum to obtain a gray-white solid, labeled as compound 3.

Synthesis of [9,9'-bicarbazole]-3,3',6,6'-tetracarboxylic acid (H_4L)[4]: Add compound 3 (0.67 g) to 30 mL of ethanol, followed by 30 mL of 10 mol/L NaOH solution. Stir and reflux the mixture at 78 ℃ for 24 hours. After completion, wash the resulting solid with methanol and water, then dry under vacuum to yield gray powder H_4L.

Synthesis of Co-H_4L: Add ligand H_4L (10 mg, 0.02 M) and $CoSO_4•7H_2O$ (25 mg, 0.105 M) to a 7 mL vial, followed by 2 mL of DMF, 1 mL of anhydrous ethanol, and 100 μL of concentrated hydrochloric acid. Dissolve the mixture using ultrasonic agitation. Maintain the reaction at 120 ℃ for 3 days. Subsequently, cool the mixture to room temperature at a controlled rate of 0.1 ℃/min to yield pink transparent block crystals.

Synthesis of Mn-H_4L: To a 7 mL vial, add ligand H_4L (10 mg, 0.02 M) and $MnCl_2•4H_2O$ (19.7 mg, 0.10 M), followed by 2 mL of DMF, 1 mL of anhydrous ethanol, 1 mL of water, and 30 μL of concentrated hydrochloric acid. Dissolve the mixture using ultrasonic agitation. Allow the reaction to proceed at 100 ℃ for 3 days, then cool to room temperature at a rate of 0.1 ℃/min to obtain brown transparent crystals.

2. Characterizations of Catalysts

Table S1 Crystal data and structure refinements

Compound	**Co-H_4L**	**Mn-H_4L**
Empirical formula	$C_{68}H_{52}Co_3N_8O_{20}$	$C_{74}H_{66}Mn_3N_{10}O_{22}$
Formula weight	1477.96	1612.18
Temperature [K]	302.30	170.00
Crystal system	monoclinic	monoclinic
Space group (number)	*C2/c* (15)	*C2/c* (15)
a [Å]	21.9250(15)	21.3652(9)
b [Å]	15.3495(11)	15.6738(6)
c [Å]	23.0003(19)	22.9732(10)
α [°]	90	90
β [°]	101.183(2)	98.797(2)
γ [°]	90	90
Volume [$Å^3$]	7593.5(10)	7602.6(5)
Z	4	4
ρ_{calc} [gcm^{-3}]	1.293	1.409
μ [mm^{-1}]	0.719	0.572
F(000)	3028	3324
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	4.70 to 48.99 (0.86 Å)	3.55 to 55.26 (0.77 Å)
Index ranges	$-25 \leq h \leq 21$ $-17 \leq k \leq 16$ $-26 \leq l \leq 26$	$-27 \leq h \leq 27$ $-20 \leq k \leq 20$ $-29 \leq l \leq 28$
Reflections collected	18124	58252
Independent reflections	5970 R_{int} = 0.0429 R_{sigma} = 0.0447	8676 R_{int} = 0.0790 R_{sigma} = 0.0548
Completeness to θ = 24.497°	94.4 %	98.8 %
Data / Restraints / Parameters	5970 / 0 / 358	8676 / 0 / 358
Absorption correction T_{min}/T_{max} (method)	0.6903 / 0.7455 (multi-scan)	0.6251 / 0.7519 (multi-scan)
Goodness-of-fit on F^2	1.069	1.033
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0459 wR_2 = 0.1528	R_1 = 0.0457 wR_2 = 0.1278
Final *R* indexes [all data]	R_1 = 0.0556 wR_2 = 0.1576	R_1 = 0.0729 wR_2 = 0.1395
Largest peak/hole [$eÅ^{-3}$]	0.61/−0.26	0.41/−0.44
CCDC number	2410416	2410417

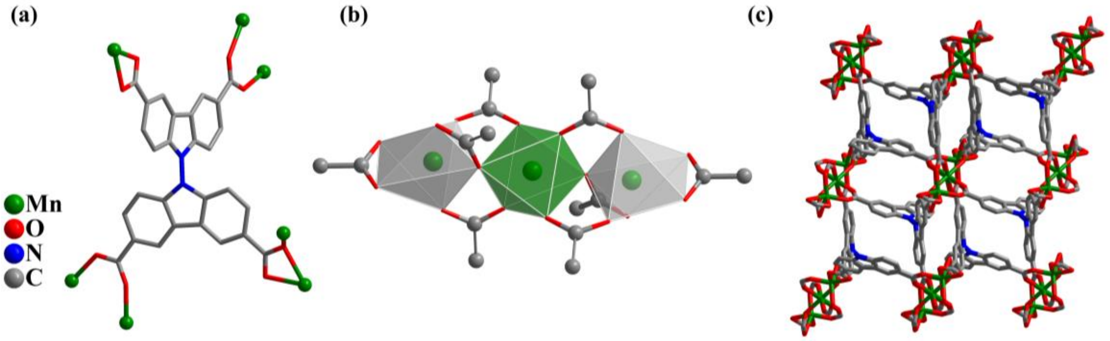


Figure S2 The structure of: (a) coordination mode of the L^{4-} ligand of Mn-H_4L; (b) $\{Mn_3C_8O_{16}\}$ trinuclear cluster; (c) The 3D framework structure of Mn-H_4L.

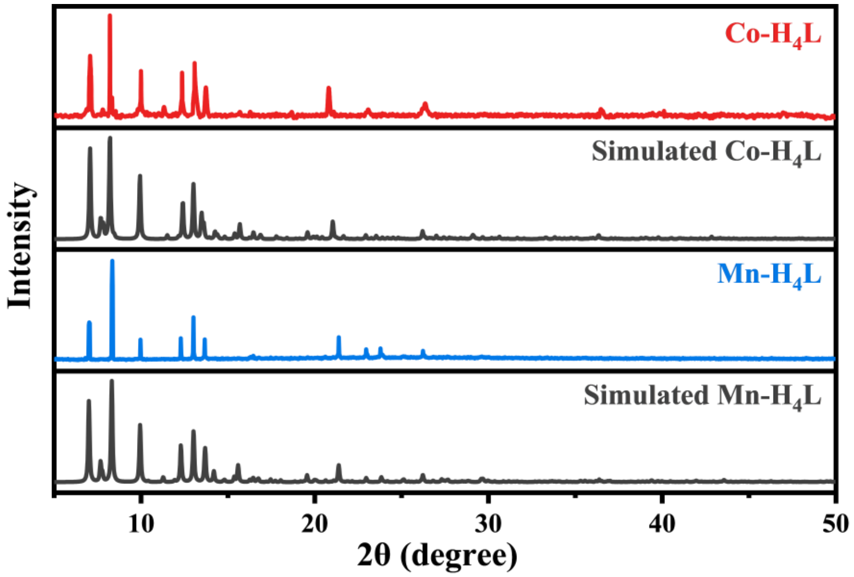


Figure S3 PXRD spectra of Co-H_4L and Mn-H_4L.

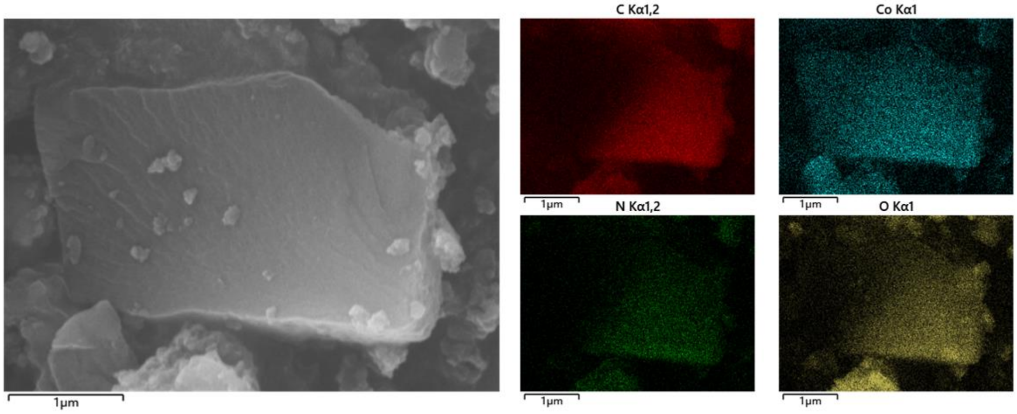


Figure S4 (a) Element maps for Co-H_4L, with N (green), O (yellow), Co (cyan) and C (red), manifesting that each element in Co-H_4L was uniformly dispersed throughout the entire structure.

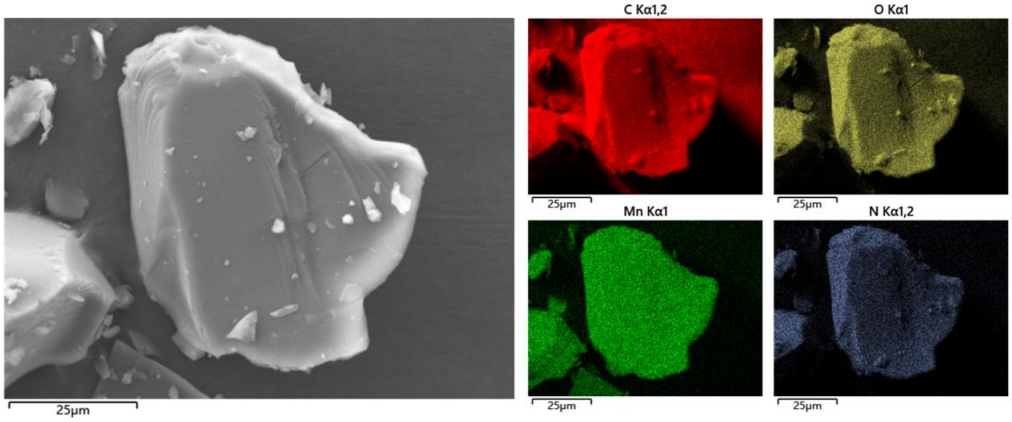


Figure S4 (b) Element maps for Mn-H_4L, with N (blue), O (yellow), Mn (green) and C (red), manifesting that each element in Mn-H_4L was uniformly dispersed throughout the entire structure.

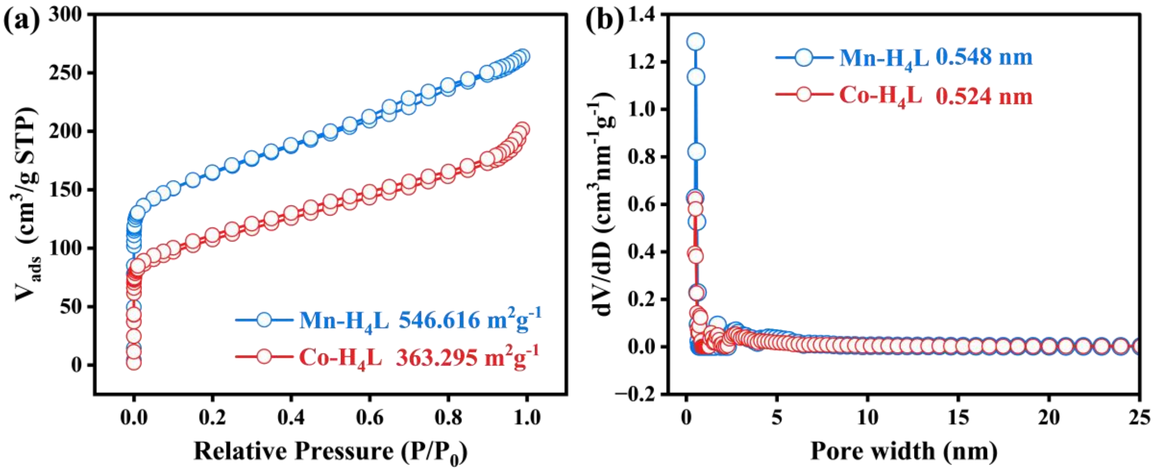


Figure S5 (a) Nitrogen sorption isotherm of Co-H$_4$L and Mn-H$_4$L measured at 77 K. (b) DFT pore size distribution for Co-H$_4$L and Mn-H$_4$L using data measured with nitrogen at 77 K.

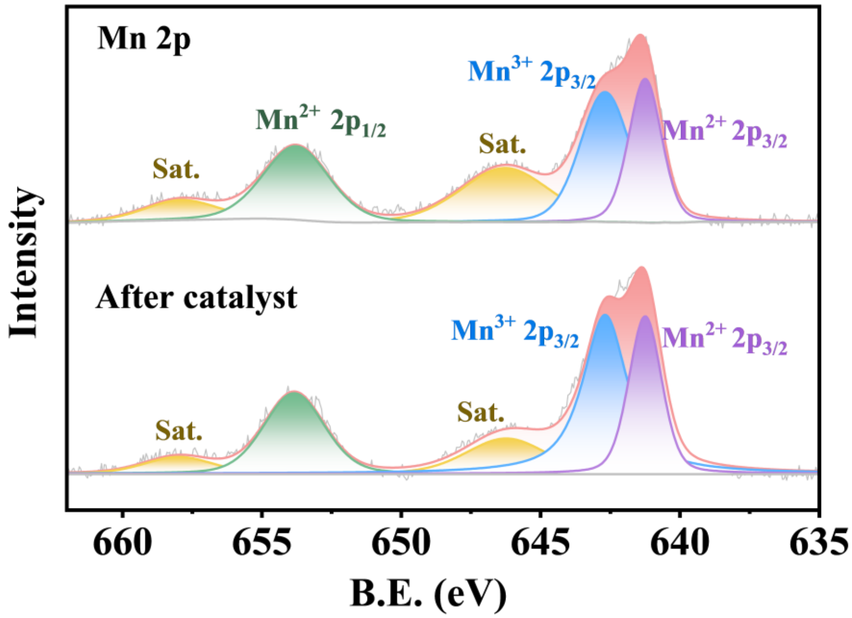


Figure S6 Mn 2p XPS data for the Mn-H_4L before and after adding catalyst.

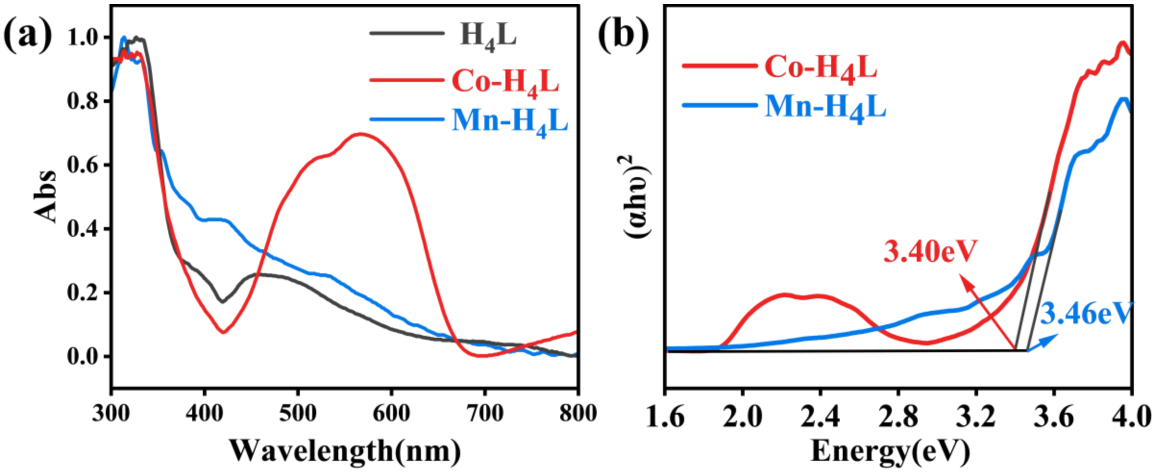


Figure S7 (a) The solid UV-vis spectrum of H_4L, Co-H_4L and Mn-H_4L measured at room temperature. (b) Tauc plots of Co-H_4L and Mn-H_4L.

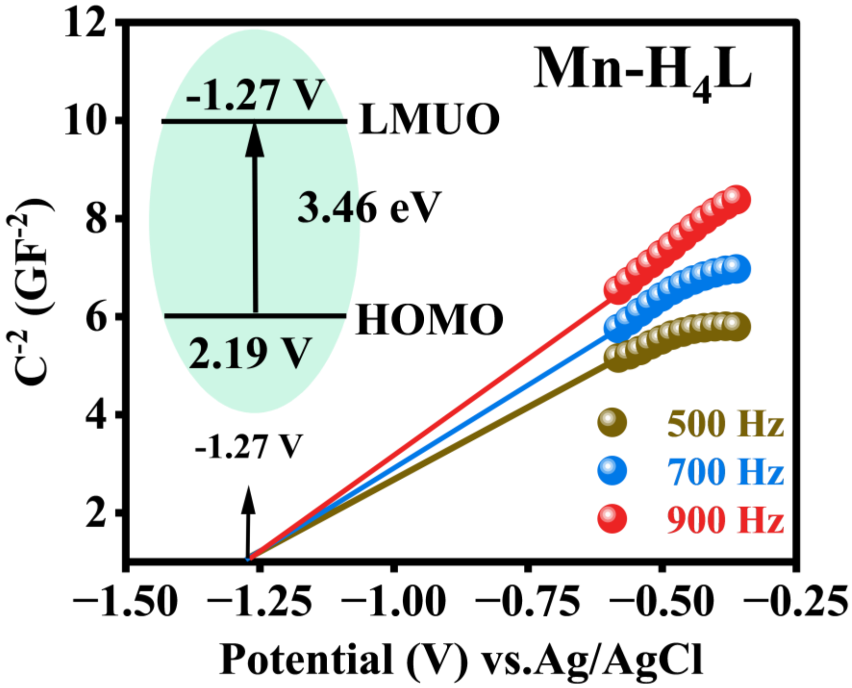


Figure S8 Mott–Schottky plots for Mn-H$_4$L respectively, in 0.1 M Bu$_4$NPF$_6$ CH$_3$CN solution (the inset is the energy diagrams of HOMO and LUMO levels).

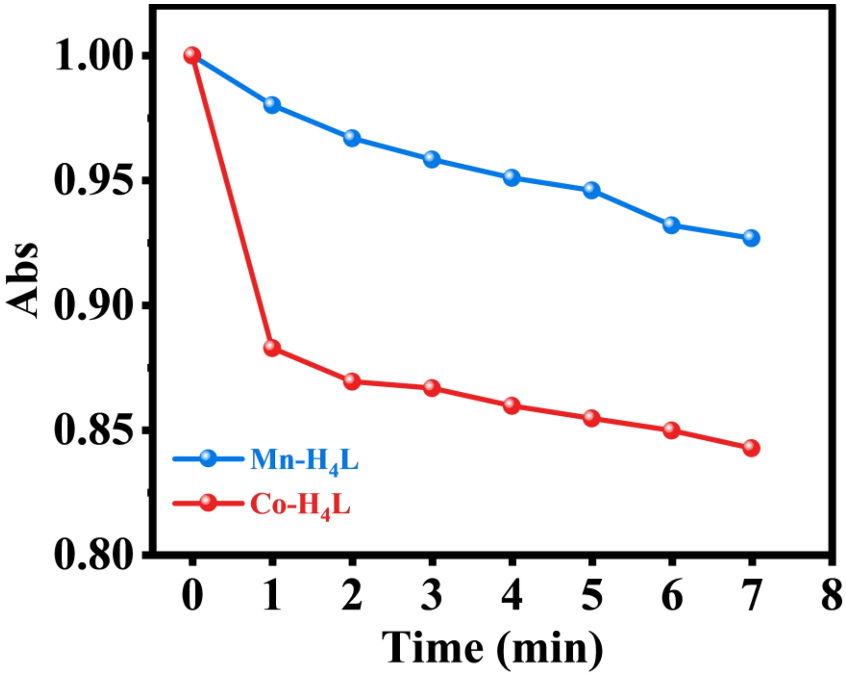
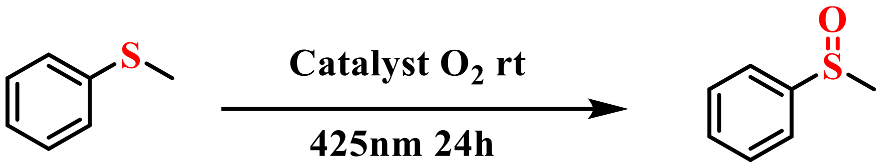


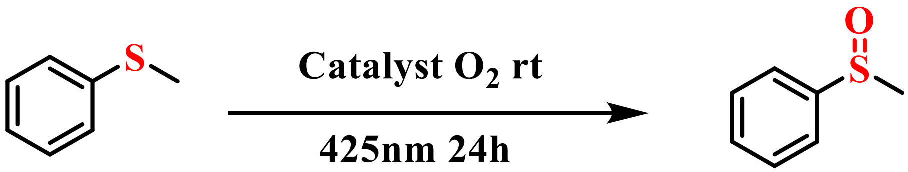
Figure S9 Comparison of the decay rate at 340 nm in presence of Co-H_4L and Mn-H_4L.

Table S2 Aerobic photocatalytic oxidative of Methylphenyl sulfide into sulfoxide under different conditions.



Entry	Solvent	Atmospheres	Catalyst	Yield(%)	Sel.(%)
1	CH_3OH	O_2	5.0 mg	56.7	79.5
2	CH_3CN	O_2	5.0 mg	99.9	99.9
3	CH_3CH_2OH	O_2	5.0 mg	81.5	80.3
4	DMF	O_2	5.0 mg	75.7	78.4
5	CH_3CN	O_2	3.0 mg	86.9	99.4
6	CH_3CN	O_2	10.0 mg	90.8	90.4
7	CH_3CN	O_2	7.0 mg	90.1	98.2

Table S3 Aerobic photocatalytic oxidative of Methylphenyl sulfide into sulfoxide under different conditions.



Entry	**Variation from standard condition**	**Yield(%)**	**Sel.(%)**
1	Co-H_4L	99.9	99.9
2	Mn-H_4L instead of Co-H_4L	24.4	99.9
3	No catalyst	N.R.	N.R.
4	No light	N.R.	N.R.
5	Ar instead of O_2	N.R.	N.R.
6	Air instead of O_2	10.2	80.8
7	H_4L instead of Co-H_4L	25.4	50.5
8	$CoCl_2$	N.R.	N.R.
9	$MnCl_2$	N.R.	N.R.

[a] Standard conditions: methylphenyl sulfide (0.1 mmol), Co-H_4L (catalyst, 5.0 mg) in CH_3CN (2.0 mL) irradiated with 425 nm LED at room temperature under O_2 atmosphere.

Table S4 Comparison of MOF-based photocatalysts for selective oxidation of sulfides under light irradiation.

Catalyst	**Condition**	**Yield (%)**	**Sel. (%)**	**Ref.**
Co-H_4L	sulfide, CH_3CN, 425 nm, O_2, rt	99.9	99.9	this
Zn-AcTA	sulfide, MeOH, 427 nm, O_2, rt, 9h	-	96.0	S5[5]
CoBW$_{12}$-TPT	sulfide, MeOH, LED light, O_2, 16 h	99.0	99.0	S6[6]
MOF/BA/textile	CEES, no solvent, simulated sunlight, air, 30min	91.0	91.0	S7[7]
MOF/BA/textile	CEES, no solvent, Blue LED, O_2, 30min	95.0	95.0	S7[7]
LCU-20	sulfide, MeOH, white LED, O_2, 36 h	99.0	99.0	S8[8]

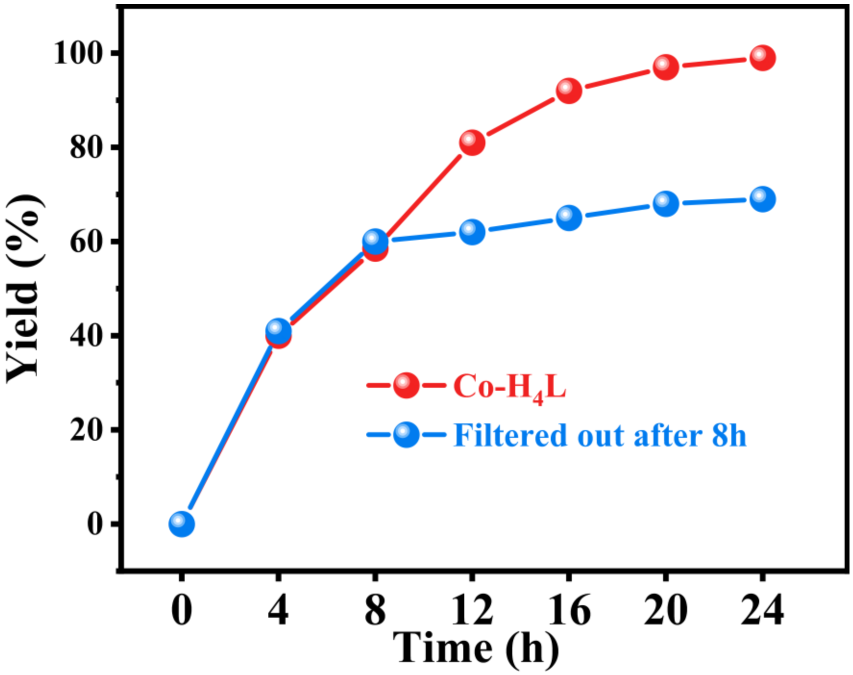


Figure S10 Catalytic performed under optimal conditions with the catalyst Co-H_4L filtered after 8h.

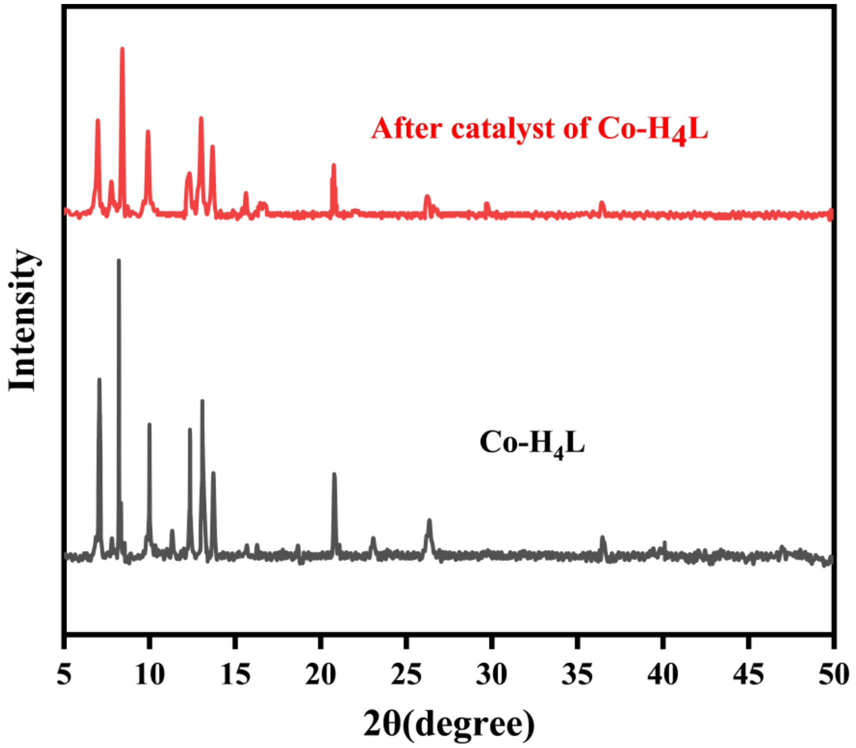


Figure S11 The PXRD spectra of Co-H_4L and after catalyst of Co-H_4L.

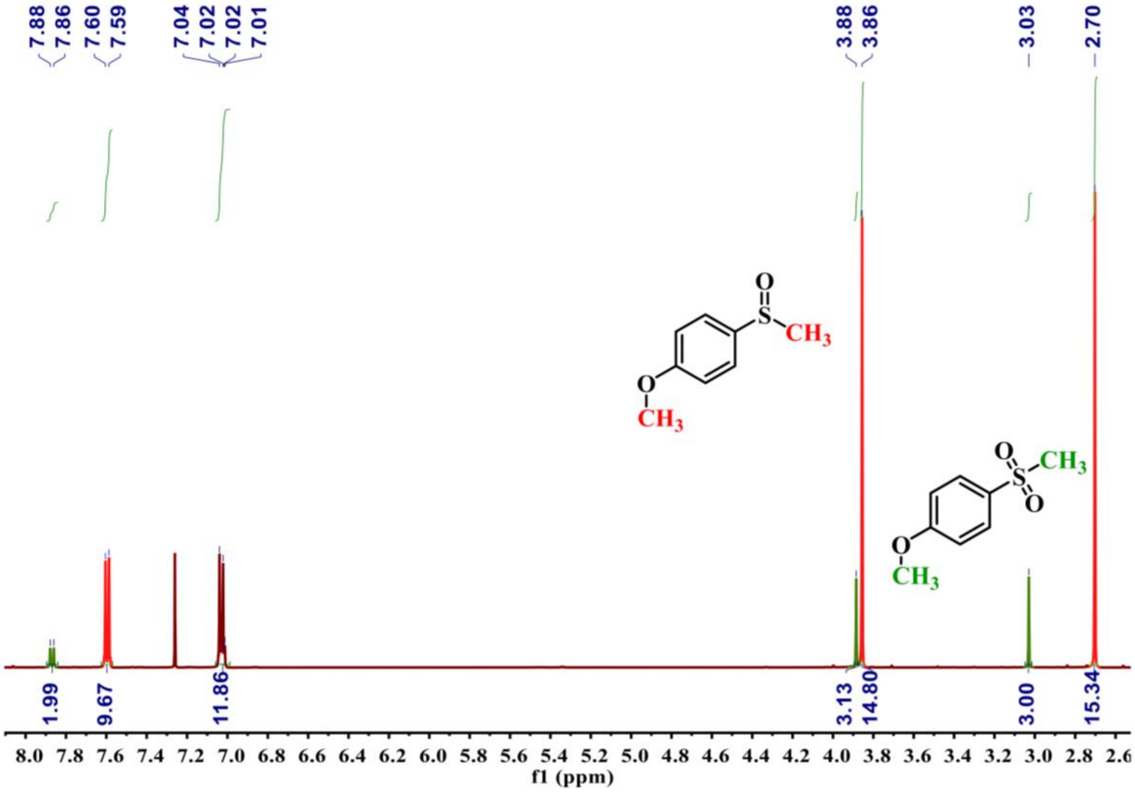


Figure S12 NMR spectrum after catalysis of 4-methoxyphenyl thioacetate.

note: red: 4-Methoxyphenyl methyl sulfoxide; green: 4-Methoxyphenyl methyl sulfone

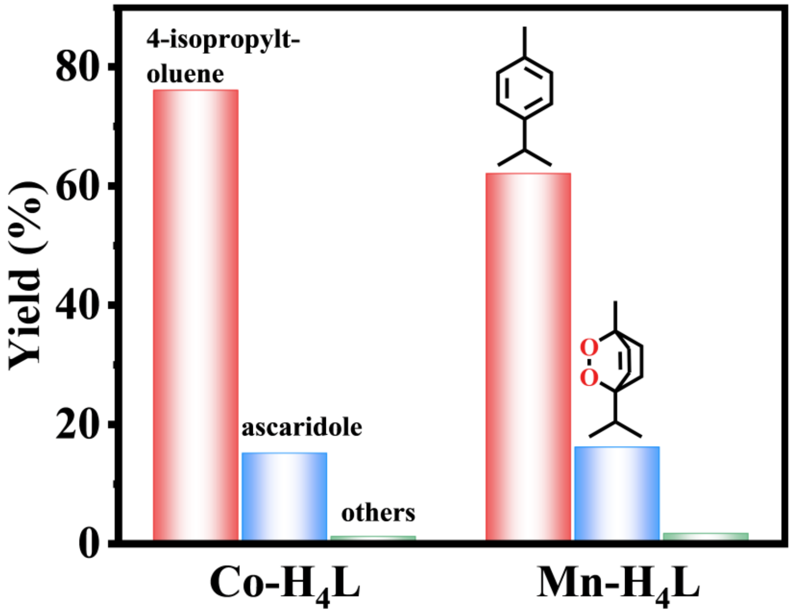


Figure S13 Conversion of α-terpinene into 4-isopropyltoluene, ascaridole, and others catalysed by Co-H_4L and Mn-H_4L.

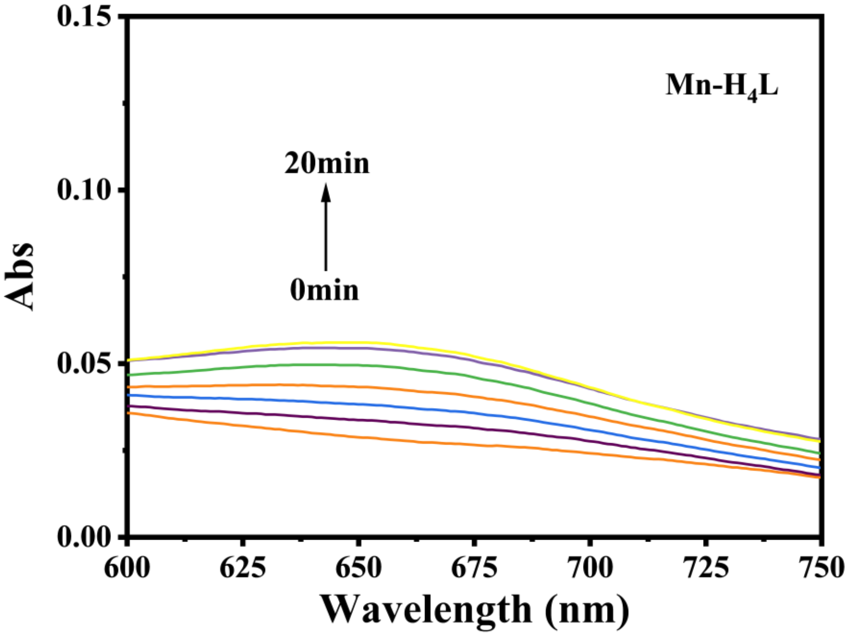


Figure S14 The change in the UV-Vis spectrum at an absorbance of 650 nm for the oxidation of TMB by Mn-H_4L in air.

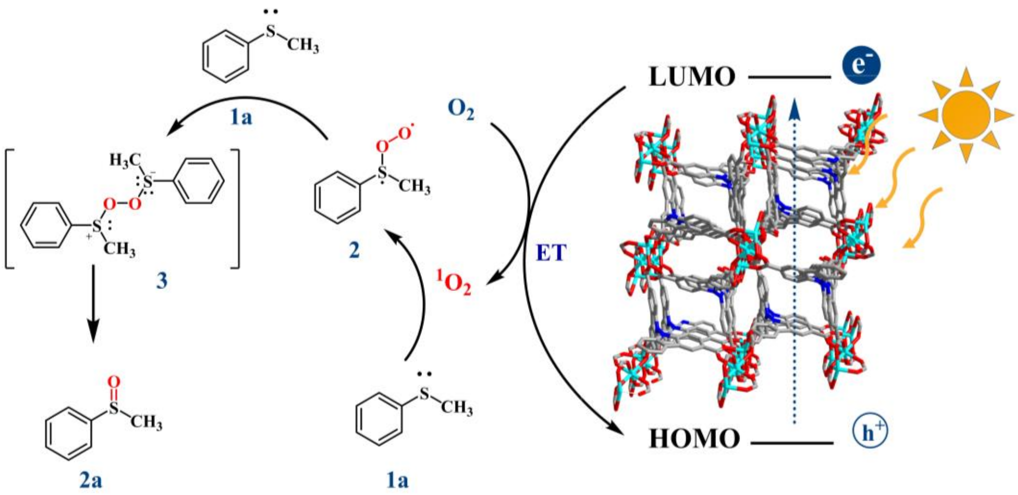
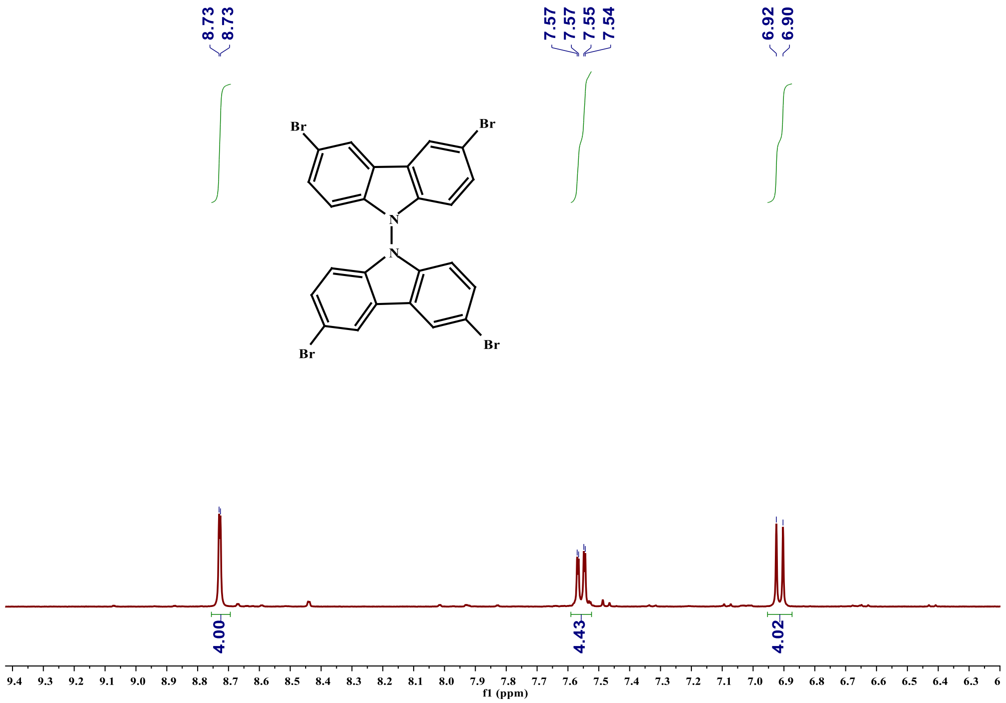


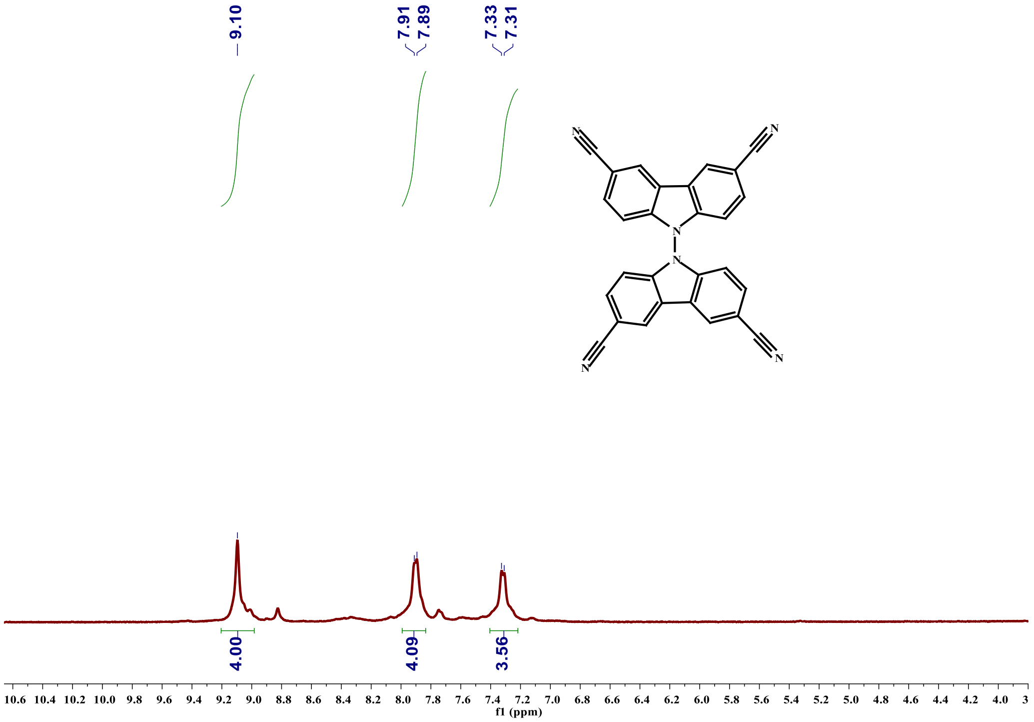
Figure S15 Proposed mechanisms for the photocatalytic oxidative thioanisole reaction over Co-H_4L.

3. Supporting Information Spectra

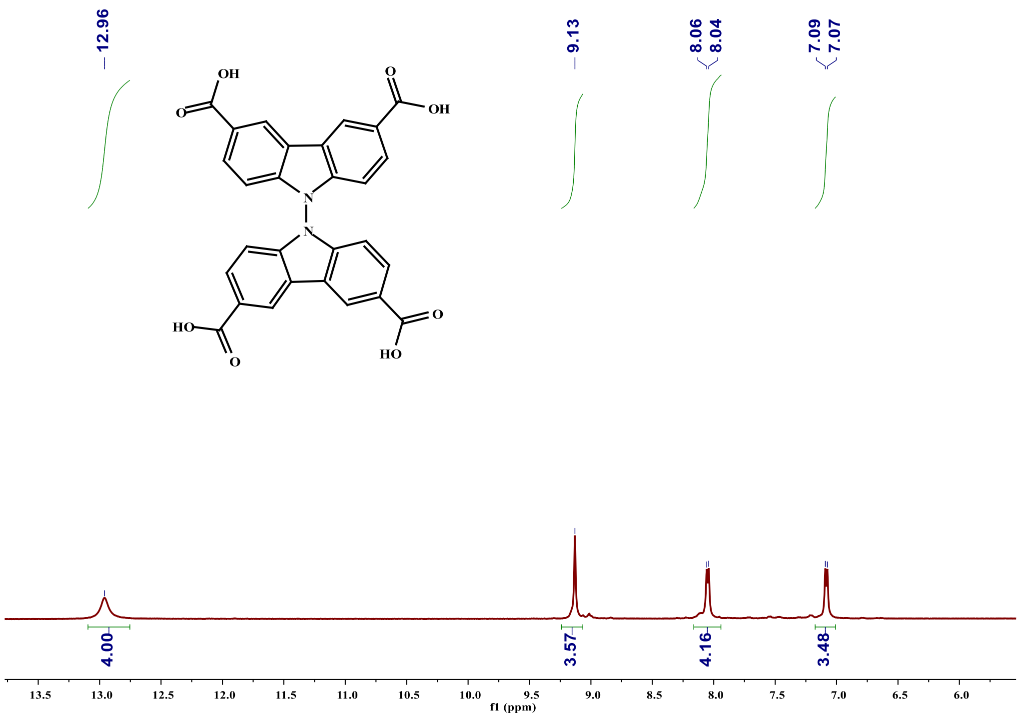
3,3',6,6'-tetrabromo-9,9'-bicarbazole(Br_4L)： ^1H NMR (400 MHz, DMSO-d_6) δ 8.73 (d, *J* = 1.8 Hz, 4H), 7.56 (dd, *J* = 8.6, 1.9 Hz, 4H), 6.91 (d, *J* = 8.6 Hz, 4H).



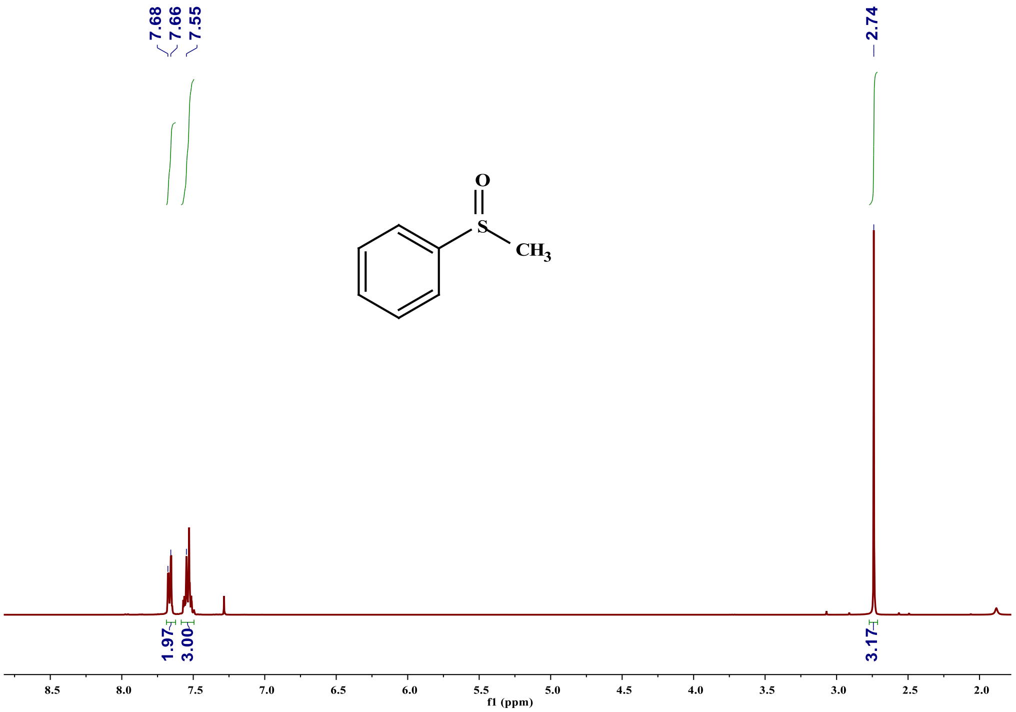
3,3',6,6'-tetracyano-9,9'-bicarbazole (CN_4L)： ^1H NMR (400 MHz, DMSO-d_6) δ 9.10 (s, 4H), 8.08 – 7.83 (m, 4H), 7.32 (d, *J* = 7.2 Hz, 4H).



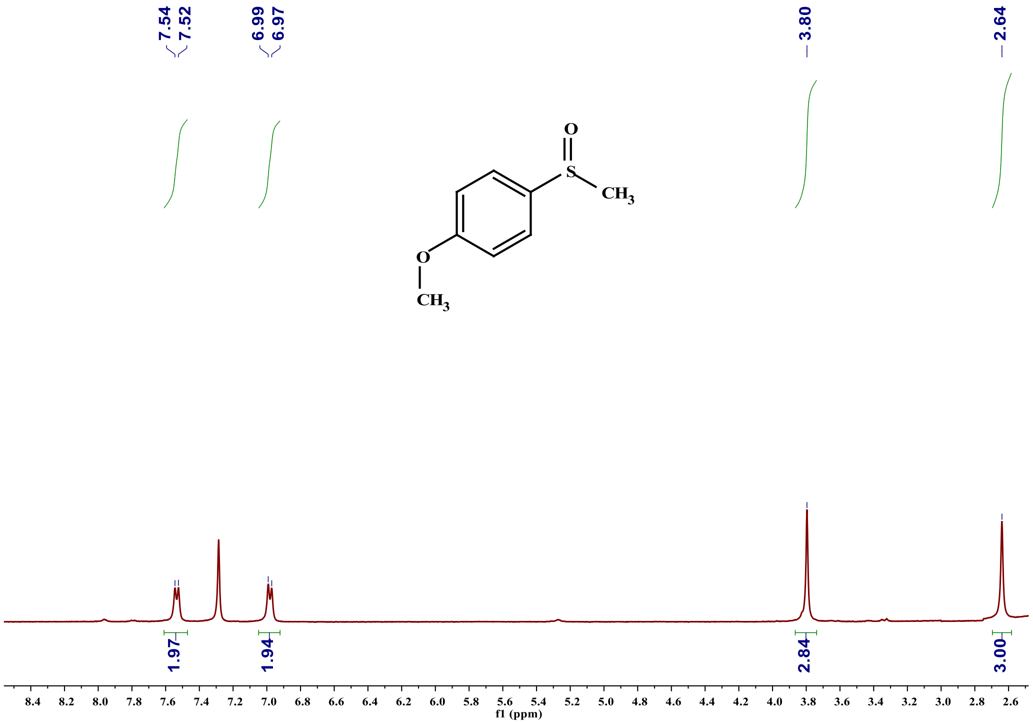
[9,9'-bicarbazole]-3,3',6,6'-tetracarboxylic acid (H_4L): ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.96 (s, 4H), 9.13 (s, 4H), 8.05 (d, *J* = 8.0 Hz, 4H), 7.08 (d, *J* = 8.3 Hz, 4H).



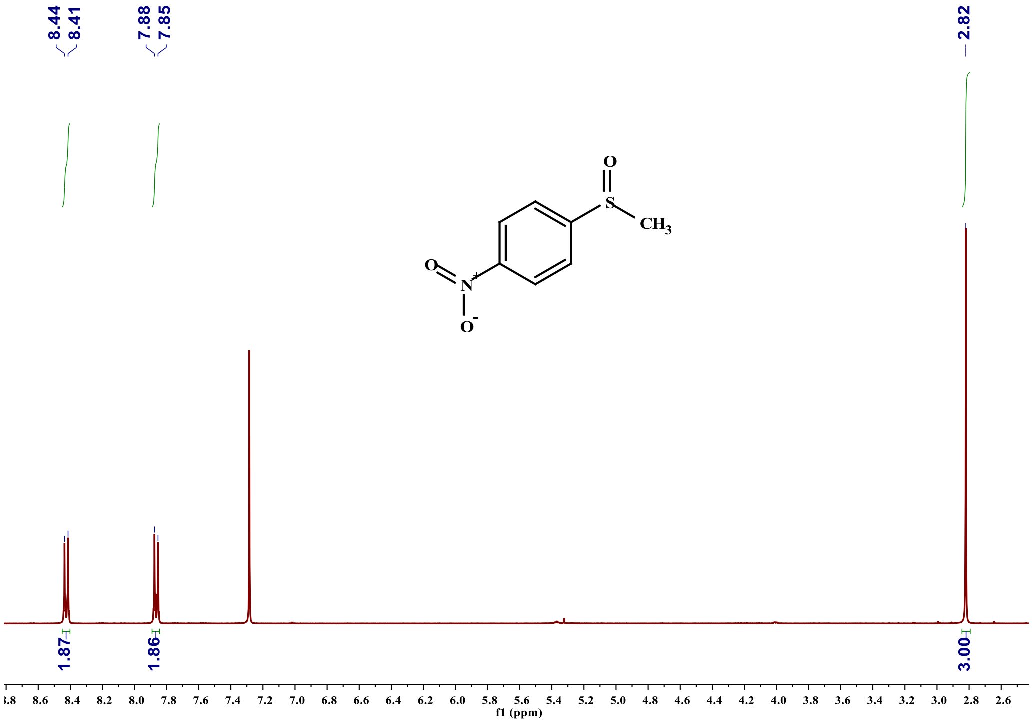
(methyl sulfinyl) benzene: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.55 (s, 3H), 2.74 (s, 3H).



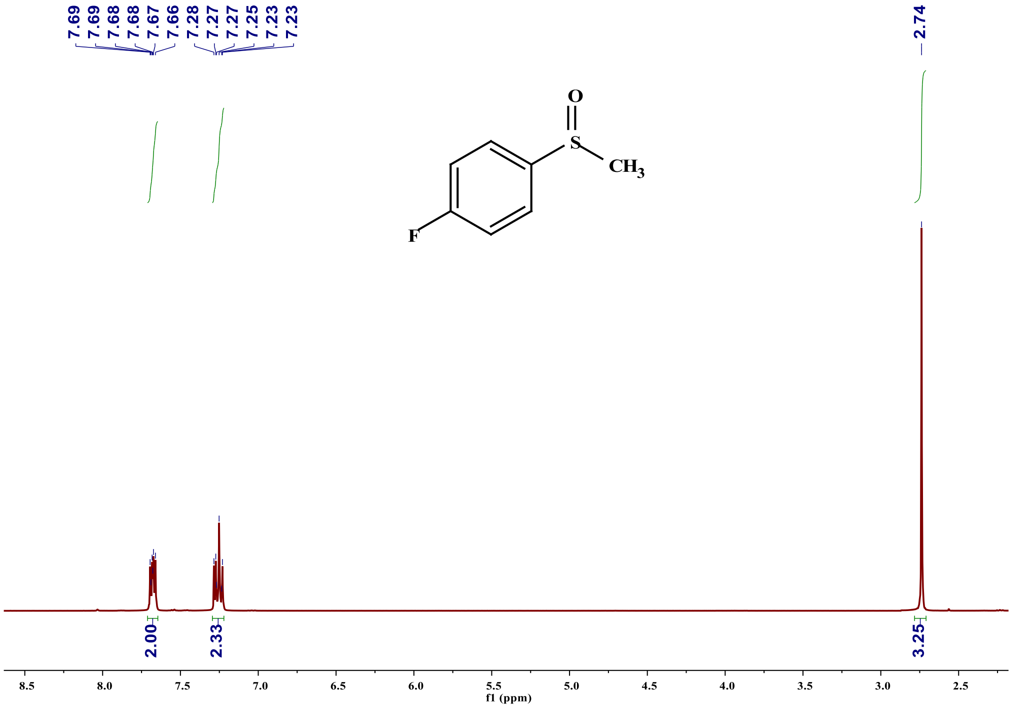
4-Methoxyphenyl methyl sulfoxide: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H), 2.64 (s, 3H).



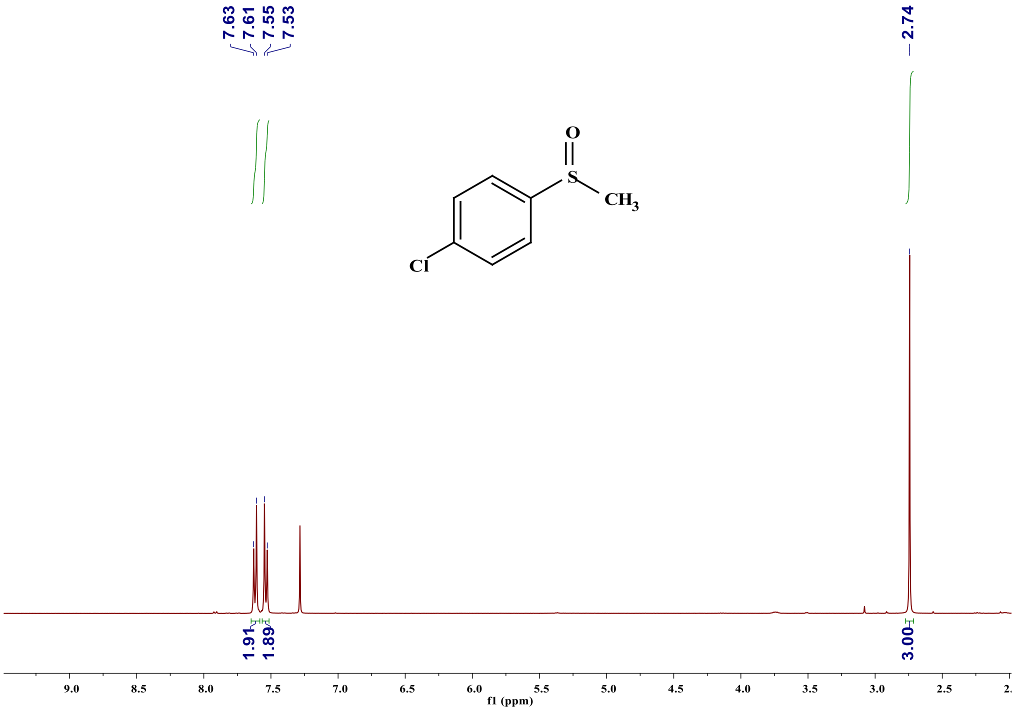
1-(Methyl sulfinyl)-4-nitrobenzene: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 8.9 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 2H), 2.82(s, 3H).



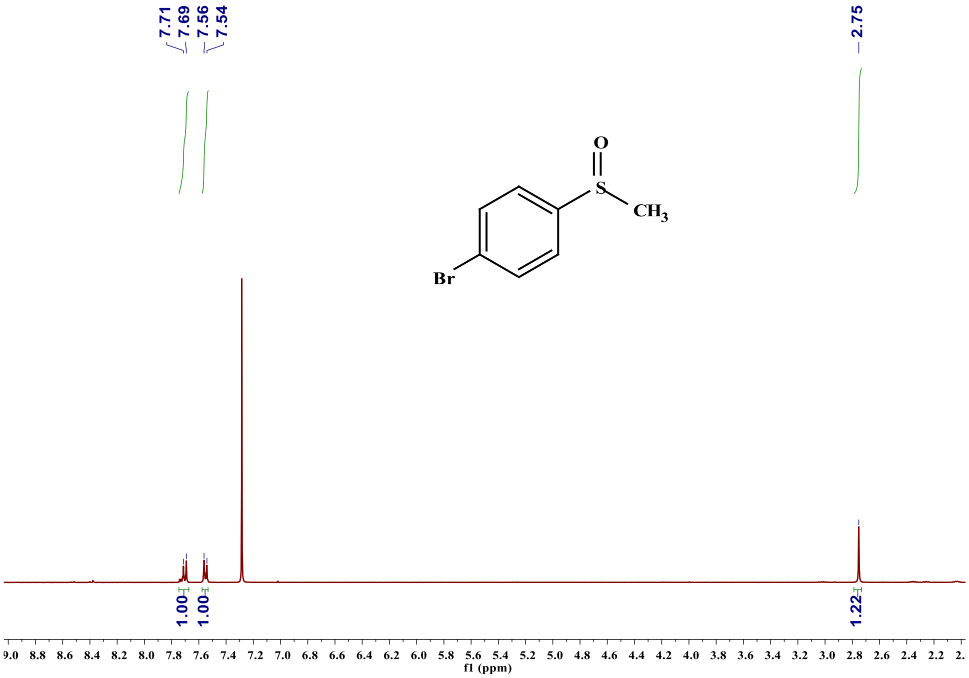
4-Fluorophenyl methyl sulfoxide: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (ddd, *J* = 8.2, 5.1, 2.5 Hz, 2H), 7.26 (td, *J* = 8.8, 2.6 Hz, 2H), 2.74 (m, 3H).



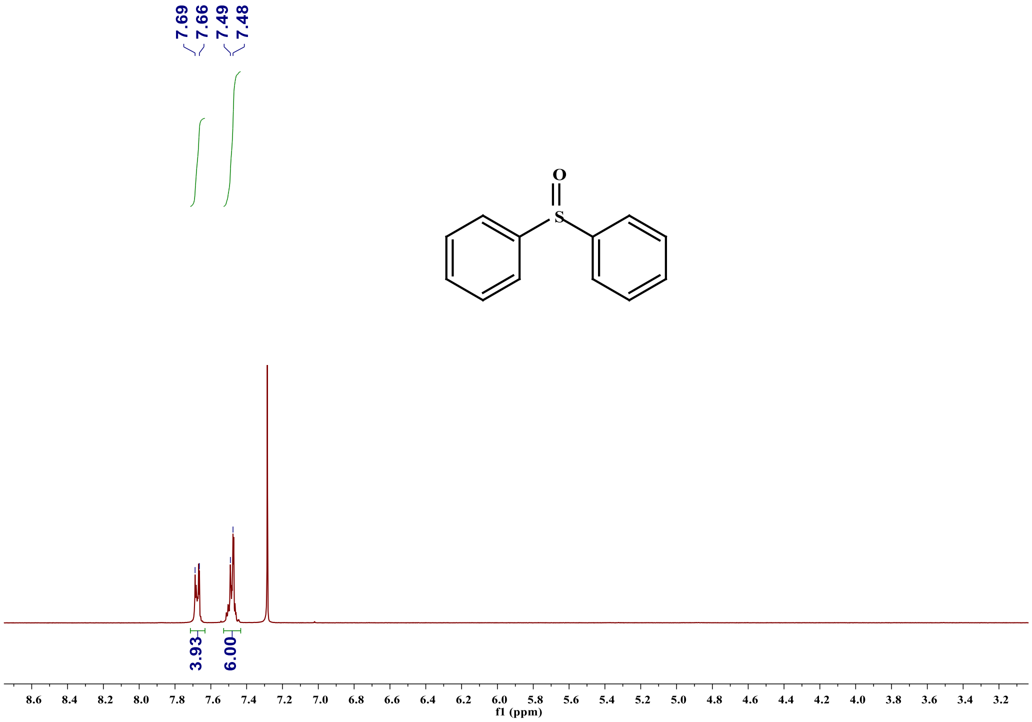
4-Chlorophenyl methyl sulfoxide: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 2.74 (s, 3H).



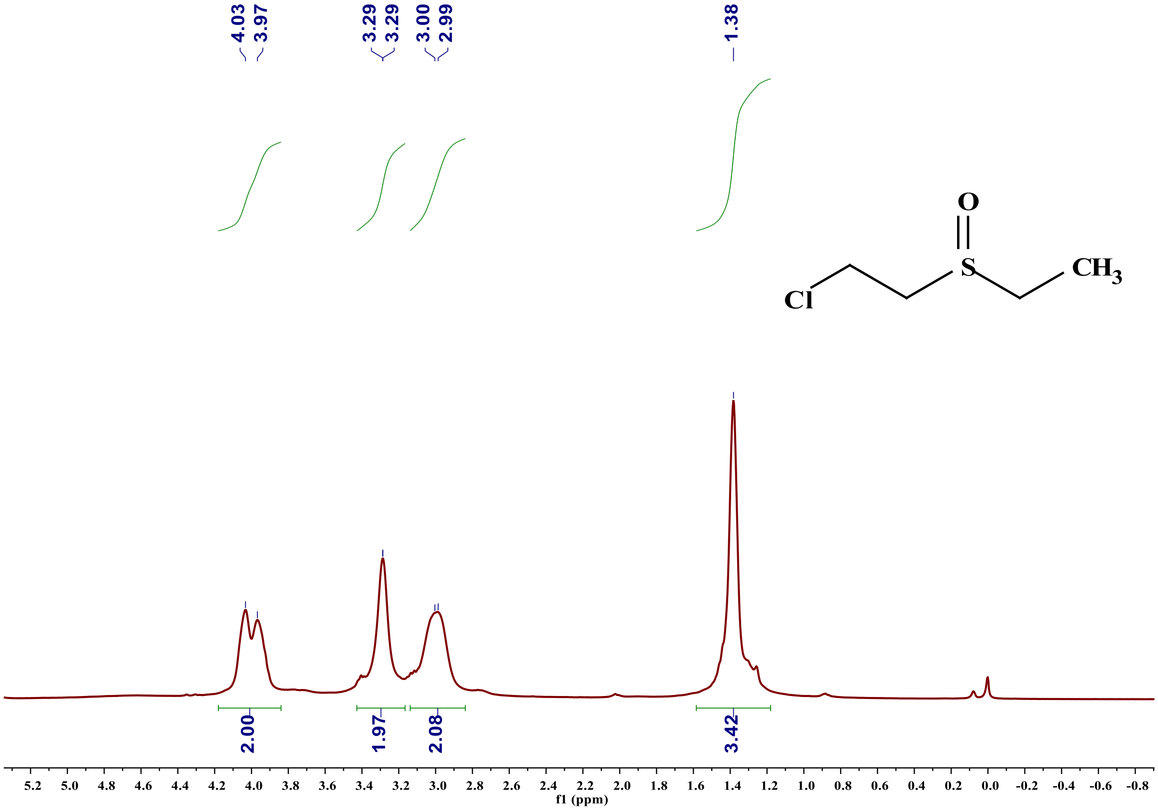
4-Bromophenyl methyl sulfoxide：^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.65 (m, 1H), 7.59 – 7.49 (m, 1H), 2.75 (s, 1H).



Diphenyl sulfoxide：^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 9.6 Hz, 4H), 7.48 (d, *J* = 5.9 Hz, 6H).



2-Chloroethyl ethyl sulfoxide:^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.00 (d, *J* = 25.8 Hz, 2H), 3.43 – 3.17 (m, 2H), 3.14 – 2.84 (m, 2H), 1.38 (s, 3H).



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