Supporting Information

Manganese-based metal-organic frameworks with nickel porphyrin for highly selective photocatalytic oxidation of benzylic C(sp^3)–H bonds

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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. Infrared (IR) spectra were performed on a PerkinElmer spectrum instrument with KBr tableting, and the range was 400-4500 cm^{-1}. Scanning electron microscopy (SEM) images were carried out on JSM-7610F. H^1 NMR spectra were collected on a Bruker AVANCE III 400 instrument. Thermogravimetric analyses (TGA) were performed at a ramp rate of 10 °C/min in a nitrogen flow with an SDTQ600 instrument. The solid UV−vis spectra were recorded on a Hitachi U-4100 UV−vis−NIR spectrophotometer. Liquid UV-vis spectra were recorded on a TU-1900 spectrophotometer. The solid-state fluorescence emission spectra were measured on an Edinburgh FLS1000 instrument. The time-resolved luminescence spectrum was measured on an Edinburgh FLS1000 spectrometer. Transient photocurrent tests were conducted on a CHI760E electrochemical workstation with a typical three-electrode cell. X-ray electron paramagnetic resonance (EPR) spectra were measured on an Electron Paramagnetic Resonance Spectrometer (E500) at 100 K. X-ray photoelectron spectroscopy (XPS) signals were collected on a Thermo ESCALAB Xi+ spectrometer. The light source was a 395 nm LED, which was purchased from Beijing China Education Aulight Co., Ltd.

Preparation

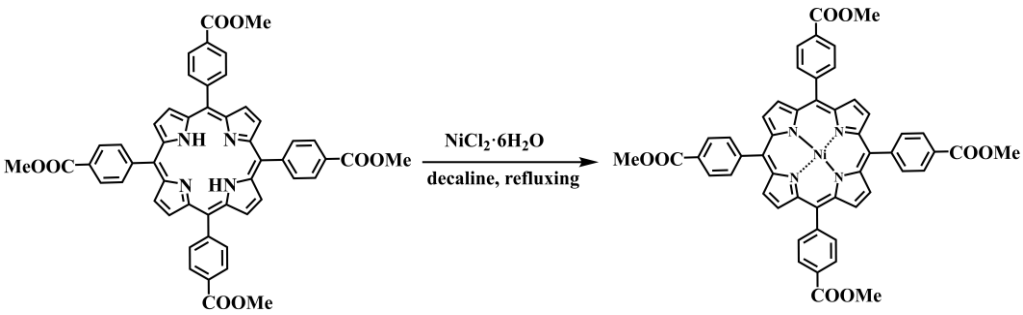
Synthesis of compound TPPCOOMe

The process was referred to the existing literature [1]. Methyl p-formyl benzoate (6.9 g, 42.0 mmol) in 100 mL of propionic acid was stirred until completely dissolved. Pyrrole (3 mL, 43.0 mmol) was added into the solution dropwise. Then, the mixture

was refluxed for 12 hours. After cooling down to room temperature, the precipitate was collected by filtration and washed successively with methanol, ethyl acetate, and tetrahydrofuran. The purple solid was dried under vacuum and collected. Yield: 1.9 g, 21%.

Synthesis of compound Ni (TPPCOOMe)

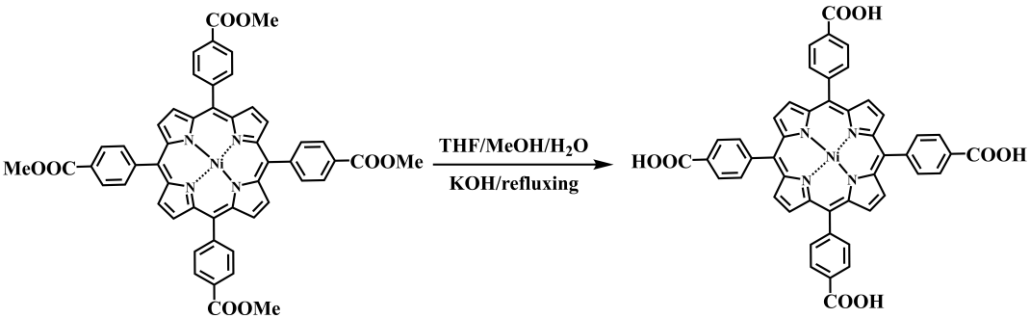
Scheme S1. Synthesis strategy for Ni (TPPCOOMe).



TPPCOOMe (854 mg, 1.0 mmol) and $NiCl_2 \cdot 6H_2O$ (3.1 g, 12.8 mmol) were refluxed in DMF (100 mL) for 6 hours, and then the reaction mixture was allowed to cool down to room temperature, 150 mL H_2O was added. The resulting precipitate was filtered and washed twice with 50 mL H_2O. The obtained solid was dissolved in $CHCl_3$, then washed three times with 1M HCl and twice with water. The organic layer was dried with anhydrous magnesium sulfate and evaporated to obtain quantitative dark red crystals.

Synthesis of compound Ni (TCPP)

Scheme S1. Synthesis strategy for Ni (TCPP).



Ni (TPPCOOMe) (500 mg, 0.5 mmol) was stirred in a mixed solvent of THF (20 mL) and MeOH (20 mL), to which a solution of KOH (1.75 g, 31.3 mmol) in H_2O (20 mL) was added. The mixture was then refluxed for 6 hours. After the mixture was cooled down to room temperature, THF and MeOH were evaporated. The remaining solution was acidified with 1 M HCl until no further precipitate was produced. The bright red solid was collected by filtration, washed with water three times and dried in a vacuum oven (419 mg, 89% yield).

Synthetic procedure of Mn-Ni (TCPP)

$MnCl_2$ (20 mg), Ni (TCPP) (5 mg), fluoroboric acid (0.5 mL) and N, N-dimethylformamide (DMF, 1 mL) were added into a Pyrex vial, and then the whole reaction mixture was ultrasonically dissolved. The reaction solution was heated in a 100 °C oven for 12 hours. After the mixture is cooled, red crystals are precipitated. The yield of Mn-Ni (TCPP) was 69% based on Ni (TCPP). Anal. Calcd (%) for Mn-Ni (TCPP) ($C_{30.75}H_{30.75}Mn_{1.25}N_{4.25}Ni_{0.5}O_{8.25}$): C, 53.48; H, 4.46; N, 8.62. Found: C, 52.01; H, 4.33; N, 8.57. IR (KBr): 2928 (w), 1690 (m), 1590 (s), 1460 (w), 1351 (s), 1028 (m), 1008 (m), 793 (s), 716 (w) cm^{-1}.

Experimental Section

General procedure for photocatalytic reactions

All catalytic reactions were carried out under a 395 nm LED. The reaction temperature was maintained at 298 K by circulating water through the outer packet of the reactor. For reactions 5.0 mg of Mn-Ni (TCPP) and 0.02 mmol substrates were dispersed in 3 mL of CH_3CN, derivatives in a 10.0 mL quartz test tube containing a stir bar. The illuminated area is about 4.5 cm^2 and the light intensity is 28.5 mW/cm^2. During the catalytic reaction, the catalyst is dispersed in the reaction solution under magnetic stirring. The reaction was carried out at ambient temperature for 12 h with O_2 bubbling under illumination from a 395 nm LED and magnetic stirring. After the specified time, Mn-Ni (TCPP) was removed by filtration, and the solvent was evaporated under reduced pressure, the yield was determined by ^1H NMR.

Photoelectrochemical Characterization

Photocurrent, electrochemical impedance spectra (EIS), and Mott-Schottky plots of Mn-Ni (TCPP) was obtained with a three-electrode system employing a photocatalyst-coated FTO working electrode, a Pt plate counter electrode, and an Ag/AgCl reference electrode. All measurements were made in a solution of 1.0 M potassium chloride at room temperature. A 395 nm LED was used as light source. A mixture solution containing 30.0 μL Nafion, and 270.0 μL of Isopropanol 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.

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 Mn-Ni (TCPP) aqueous

solution (1 mg/mL) was then added to the mixture solution with O_2 bubbling under 395 nm LED irradiation. The samples were taken at different time intervals for UV−Vis measurements. 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 superoxide radical

The ROS generated by Mn-Ni (TCPP) have been detected by EPR in the presence of TEMP, respectively. Typically, 10.0 μL TEMP in 1 mL CH_3CN was mixed with 0.5 mL CH_3CN solution (0.5 mg/mL) of Mn-Ni (TCPP). The formed mixture (400 μL) was added to the EPR tube.

Fluorescence Lifetime and Fluorescence Quenching Assays.

For fluorescence measurements, a 10.0 μM stock CH_3CN solution of Mn-Ni (TCPP) was added to a sample tube and capped with a septum. The sample tube was then degassed by bubbling argon for 15 min, and the emission spectra were continuously monitored when the solution exposed to O_2. Fluorescence was excited at 435 nm.

2. Single Crystal X-ray Crystallography

Intensities of Mn-Ni (TCPP) was collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation source; the data were acquired using the SMART and SAINT programs.[2, 3] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL version 5.1 software.[4] In the structural refinement of Mn-Ni (TCPP), all the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones are allowed to ride on the parent nonhydrogen atoms. The SQUEEZE subroutine in PLATON was used.[5] Crystallographic data for Mn-Ni (TCPP) has been deposited at the Cambridge Crystallographic Data Centre, CCDC number: **2543784**. The crystallographic data and structure refinement parameters are shown in Table S1.

Table S1. Crystal data and structure refinements.

Compound	**Mn-Ni (TCPP)**
Empirical formula	$C_{30.75}H_{30.75}Mn_{1.25}N_{4.25}Ni_{0.5}O_{8.25}$
Formula weight	689.87
Temperature/K	120.00
Crystal system	monoclinic
Space group	C2/m
a/Å	17.1722(17)
b/Å	34.041(3)
c/Å	18.2128(18)
α/°	90
β/°	113.085(3)
γ/°	90
Volume/Å^3	9794.0(16)
Z	8
ρ_{calc}/g·cm^{-3}	0.936
μ/mm^{-1}	0.554
F(000)	2850.0
Crystal size/mm^3	0.39×0.35×0.31
Radiation	MoK$_\alpha$ (λ=0.71073 Å)
2 theta range for data collection/°	4.42 to 50.264 (0.84 Å)
Index ranges	$-19 \le h \le 20$, $-40 \le k \le 40$, $-21 \le l \le 21$
Reflections collected	124302
Independent reflections	8868, R_{int} = 0.1412, R_{sigma} = 0.0814
Data/restraints/parameters	8868/ 363/ 399
Goodness-of-fit on F^2	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.1026, wR_2 = 0.2369
Final R indexes [all data]	R_1 = 0.1586, wR_2 = 0.2749
Largest diff. peak/hole / e Å^{-3}	0.82/ -0.53
CCDC number	2543784

3. Characterizations of Catalysts

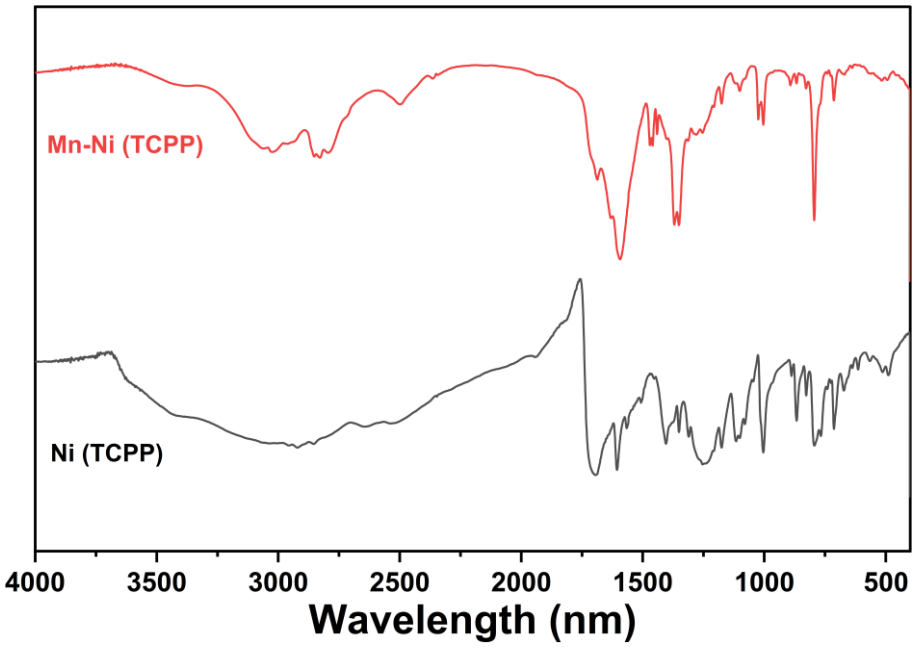


Figure S1. IR spectra of Ni (TCPP) (black line), Mn-Ni (TCPP) (red line).

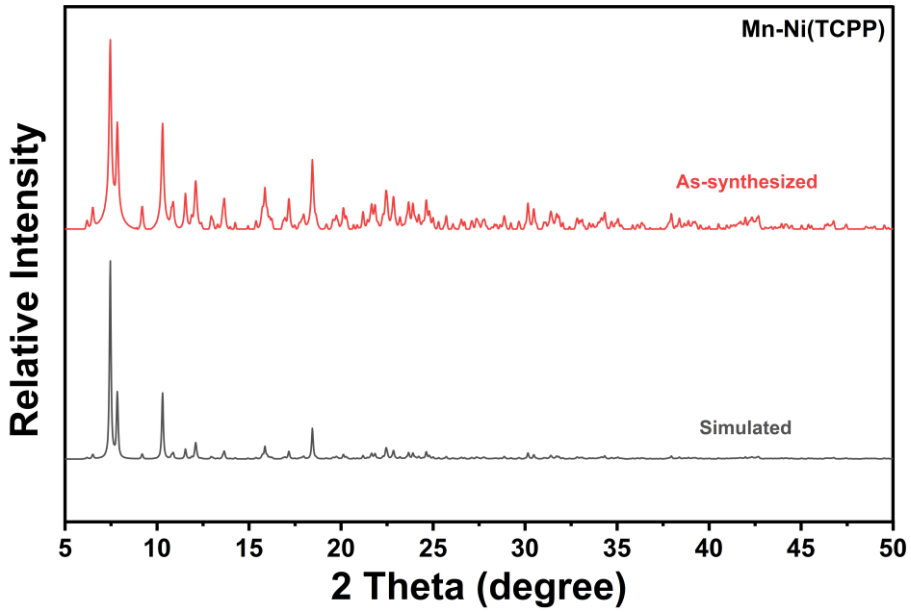


Figure S2. PXRD patterns of fresh as-synthesized Mn-Ni (TCPP) (red) and its calculated pattern based on the single-crystal simulation (black).

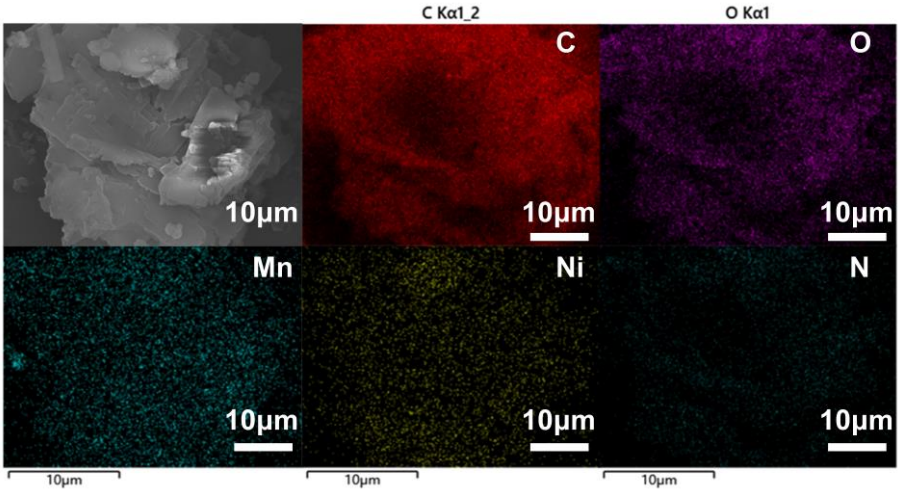


Figure S3. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) of Mn-Ni (TCPP).

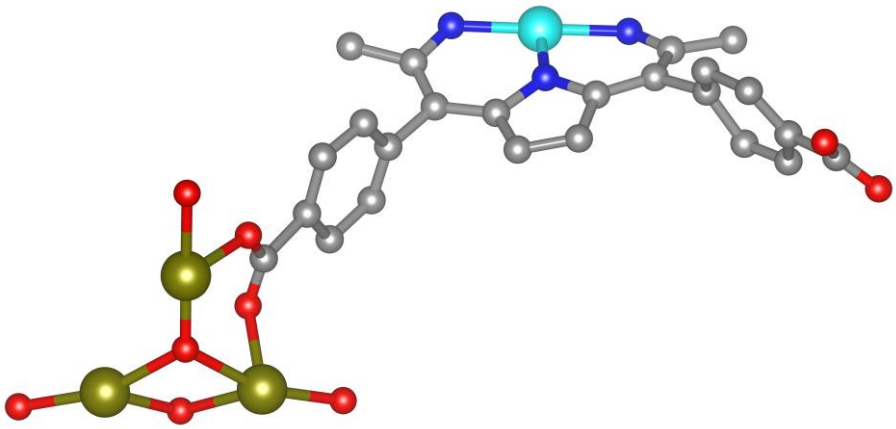


Figure S4. View of the asymmetric unit of Mn-Ni (TCPP) 1. C atoms, gray; N atoms, blue; O atoms, red; Ni atoms, cyan; Mn atoms, brown, H atoms were omitted for clarity.

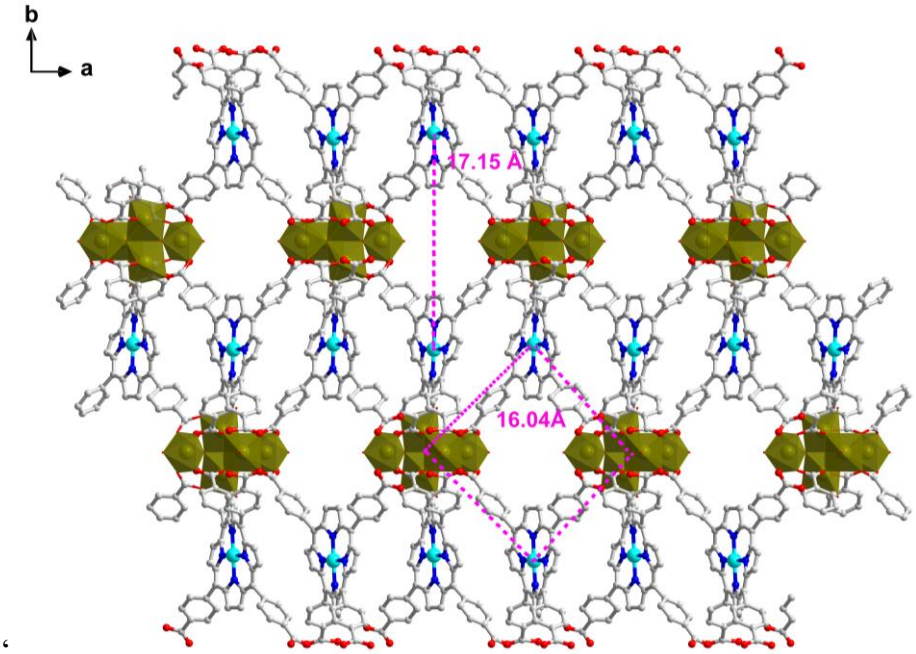


Figure S5. Structural view of Mn-Ni (TCPP) observed along the c-axis direction.

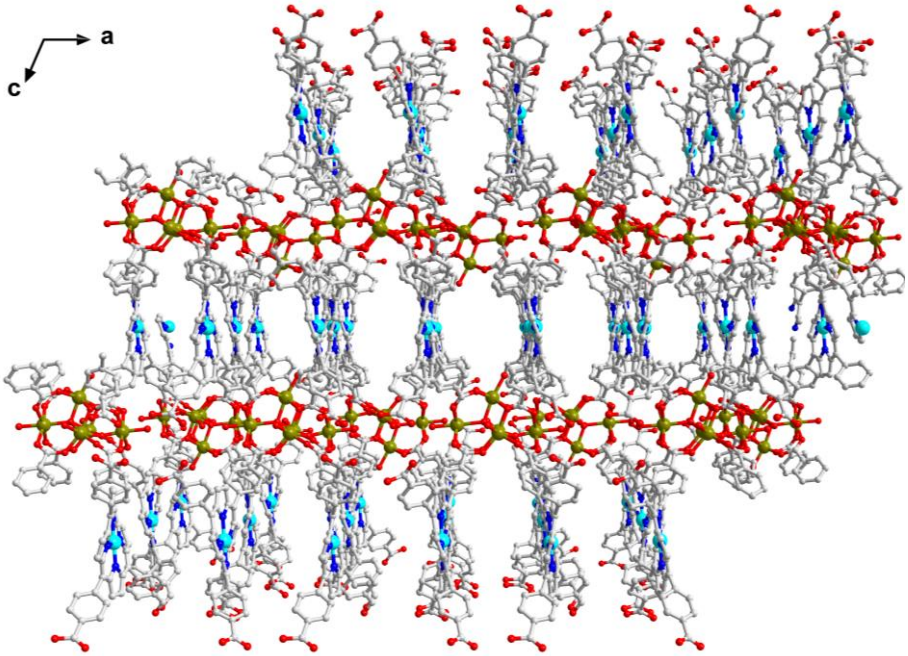


Figure S6. Structural view of Mn-Ni (TCPP) observed along the b-axis direction.

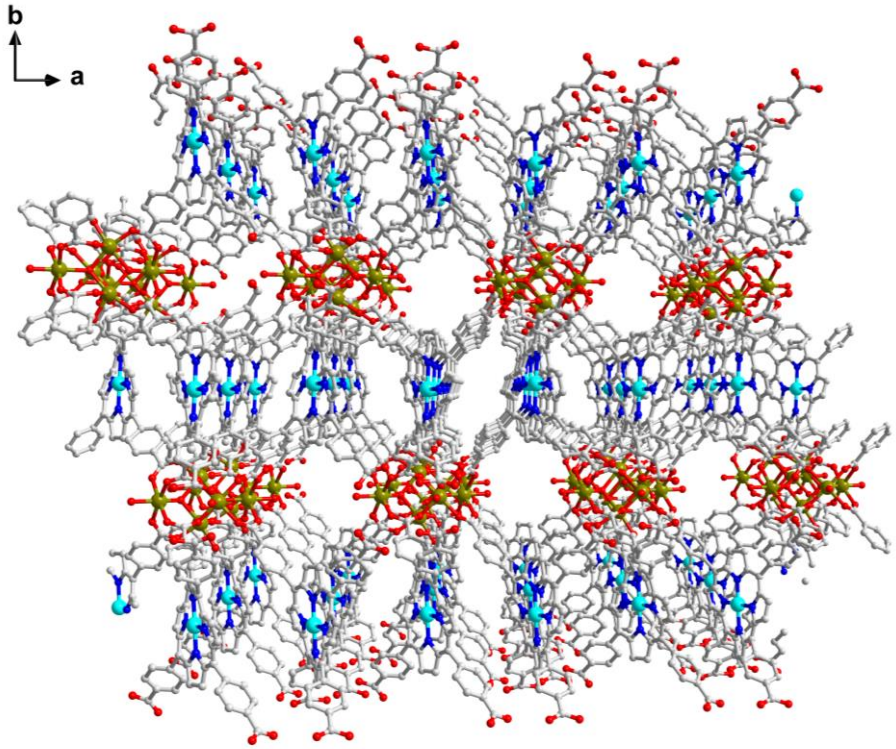


Figure S7. Structural view of Mn-Ni (TCPP) observed along the c-axis direction.

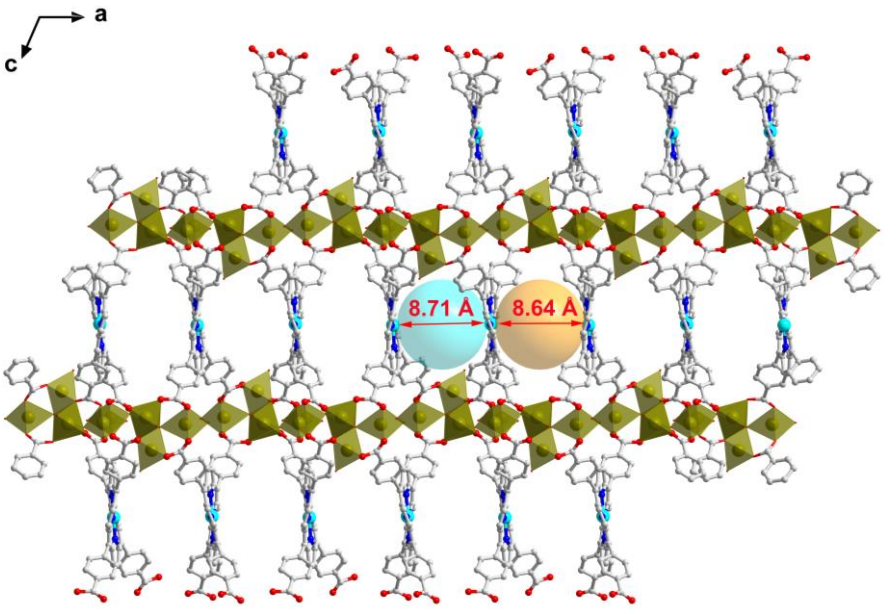


Figure S8. Distance between adjacent porphyrin centers of nickel in three-dimensional organic framework Mn-Ni (TCPP).

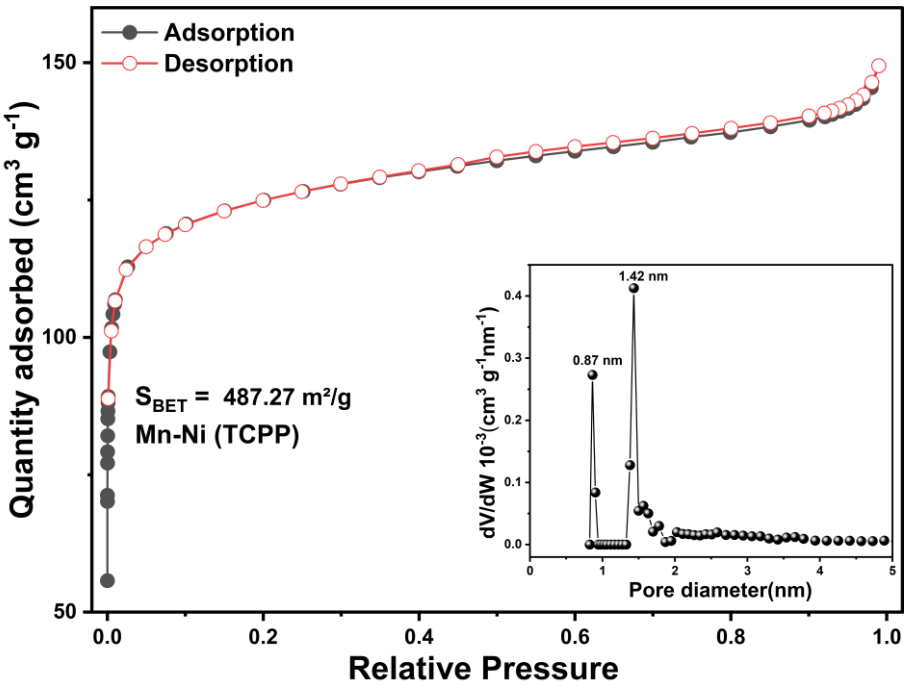


Figure S9. Nitrogen sorption isotherms and pore sizes of Mn-Ni (TCPP).

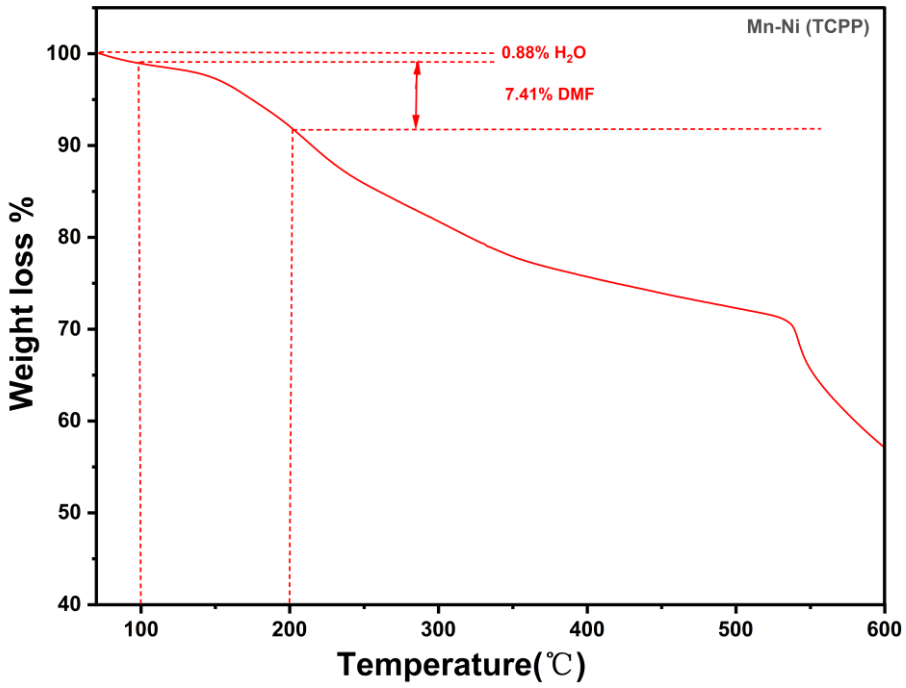


Figure S10. Thermogravimetric analysis plot of Mn-Ni (TCPP).

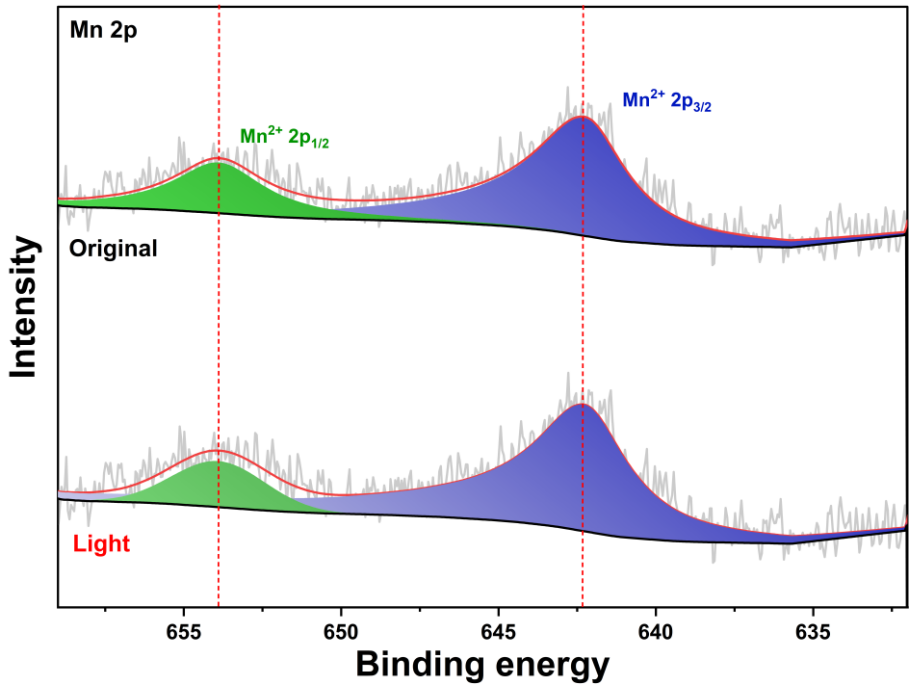


Figure S11. XPS spectra of the Mn 2p energies of Mn-Ni (TCPP) under light irradiation with the color lumps represented the simulating areas.

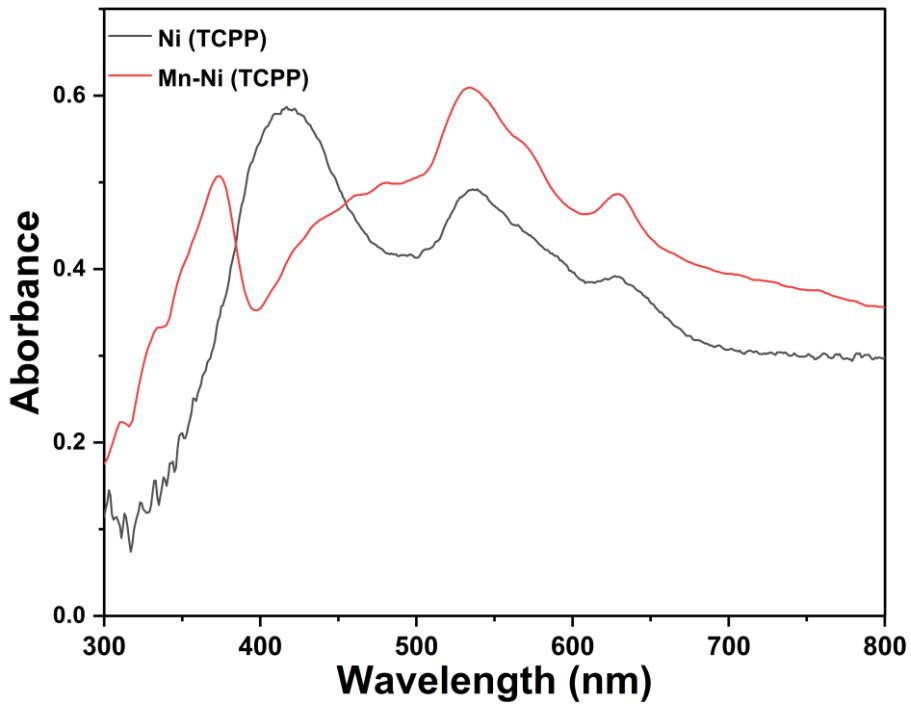


Figure S12. UV−vis absorption spectra of Ni (TCPP) (black), and Mn-Ni (TCPP) (red).

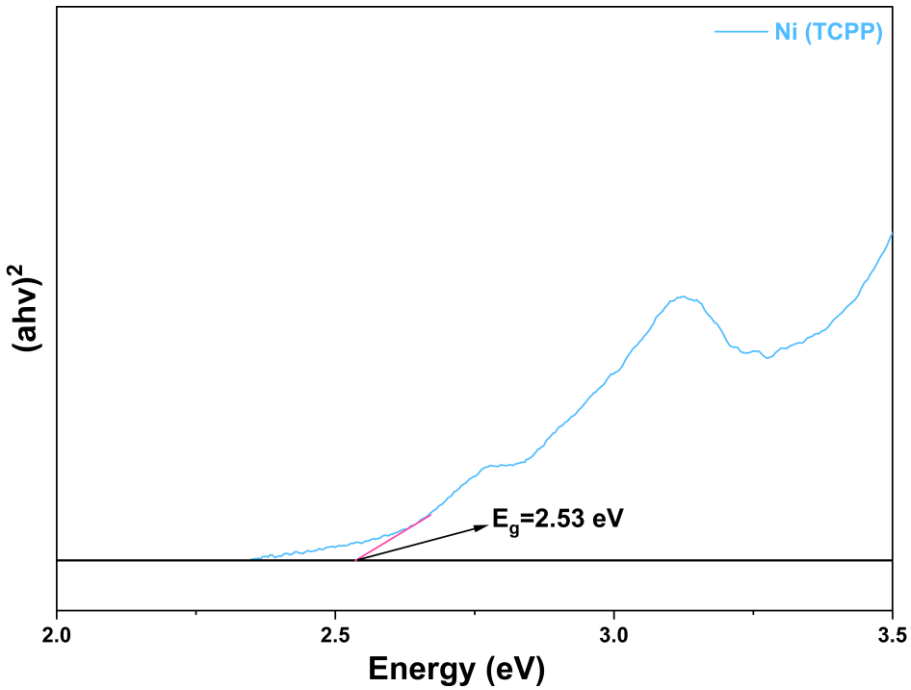


Figure S13. Tauc plots of Ni (TCPP).

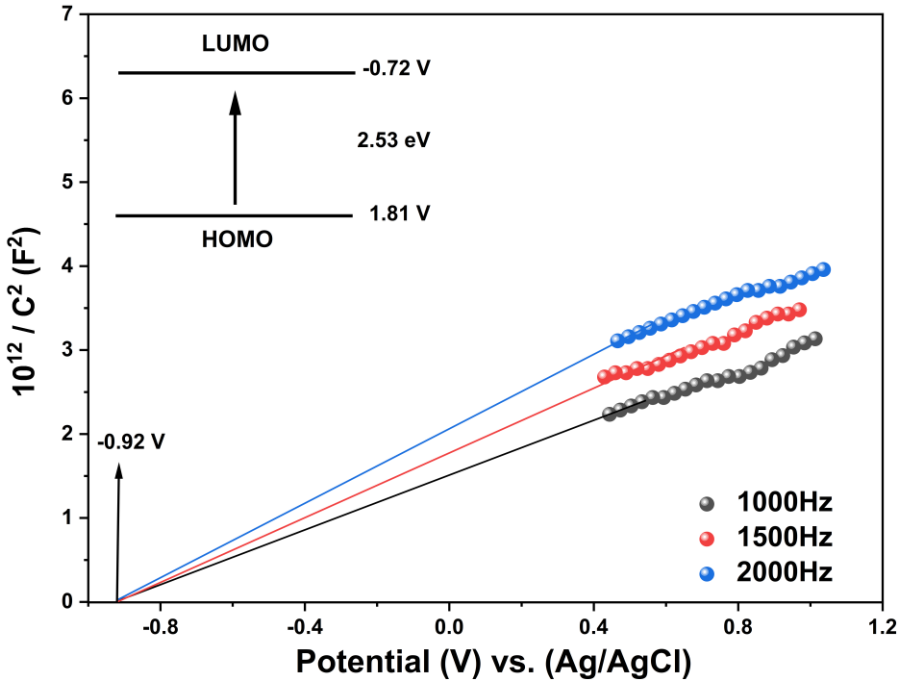


Figure S14. Mott-Schottky plots, VB and CB for Ni (TCPP)

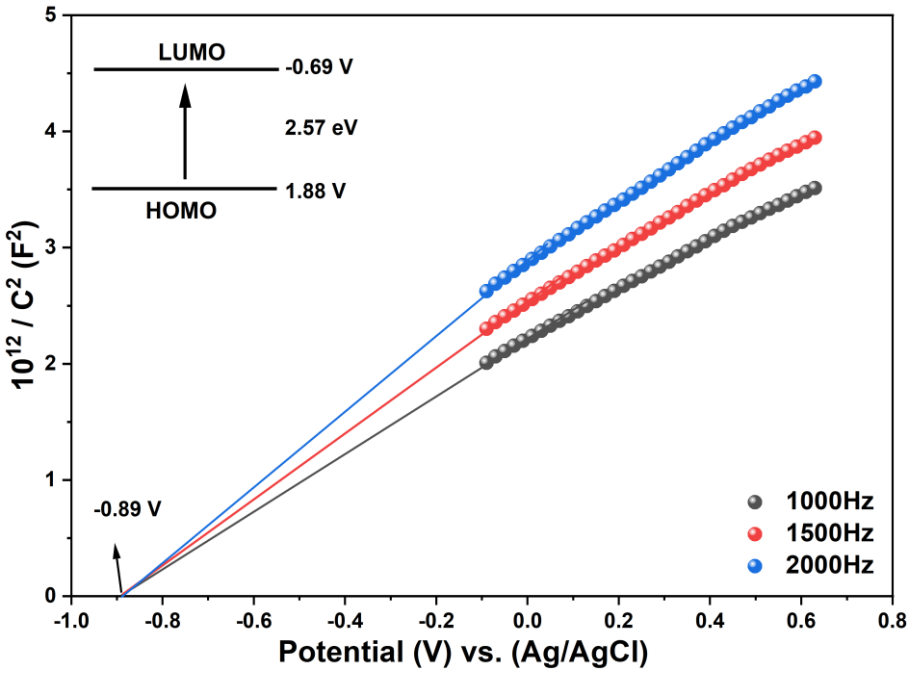


Figure S15. Mott-Schottky plots, VB and CB for Mn-Ni (TCPP).

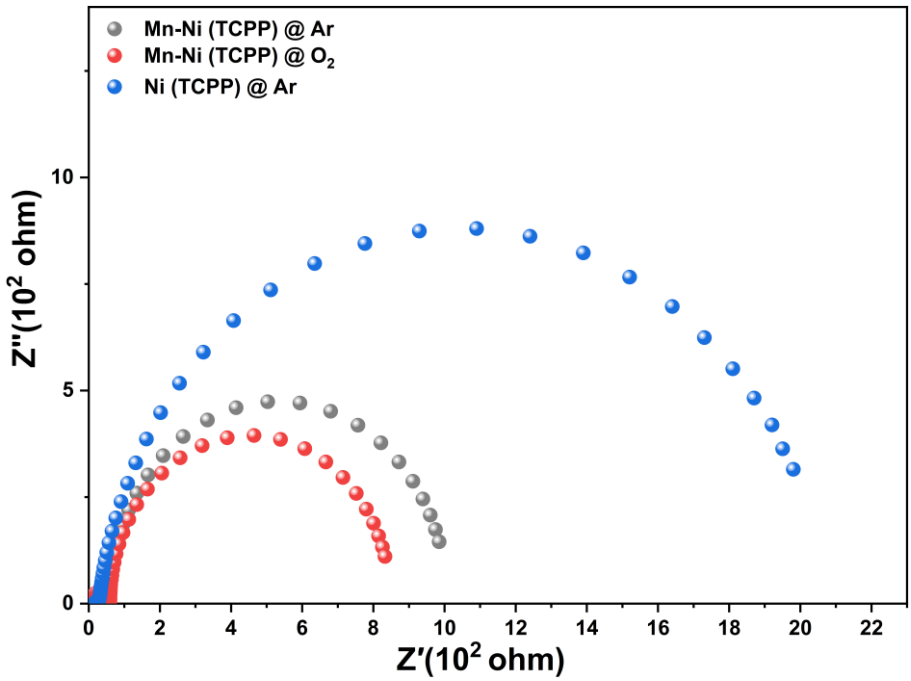


Figure S16. Electrochemical impedance spectroscopy (EIS) Nyquist plots of Ni (TCPP) and Mn-Ni (TCPP) (under an Ar and O_2 atmosphere).

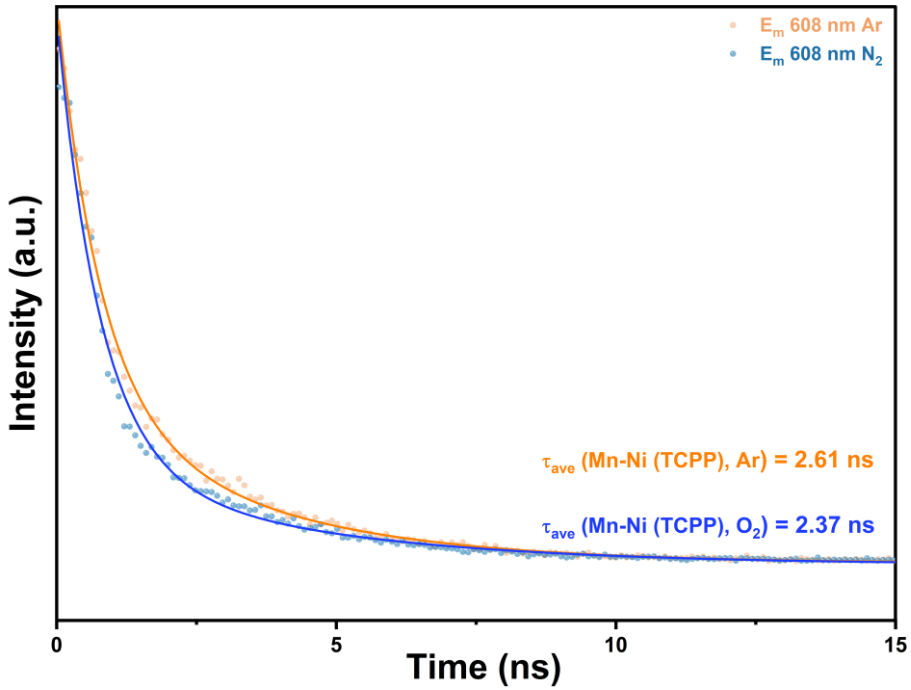


Figure S17. Luminescence decays of Mn-Ni (TCPP) suspensions with (orange line) Ar and (blue line) O_2 (4 min), the intensity was recorded at 608 nm with excitation at 435 nm.

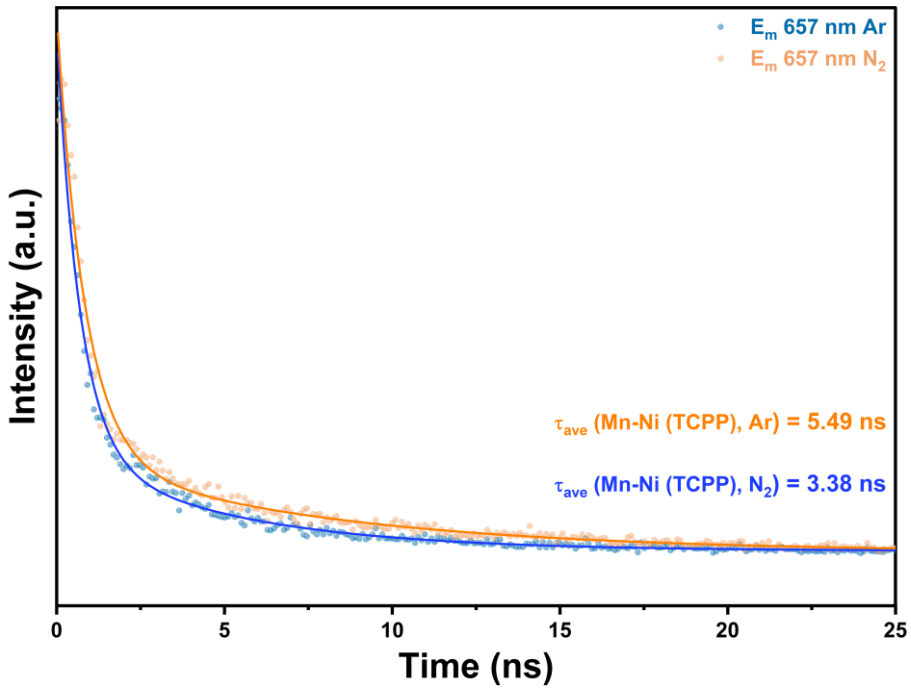


Figure S18. Luminescence decays of Mn-Ni (TCPP) suspensions with (orange line) Ar and (blue line) O_2 (4 min), the intensity was recorded at 657 nm with excitation at 435 nm.

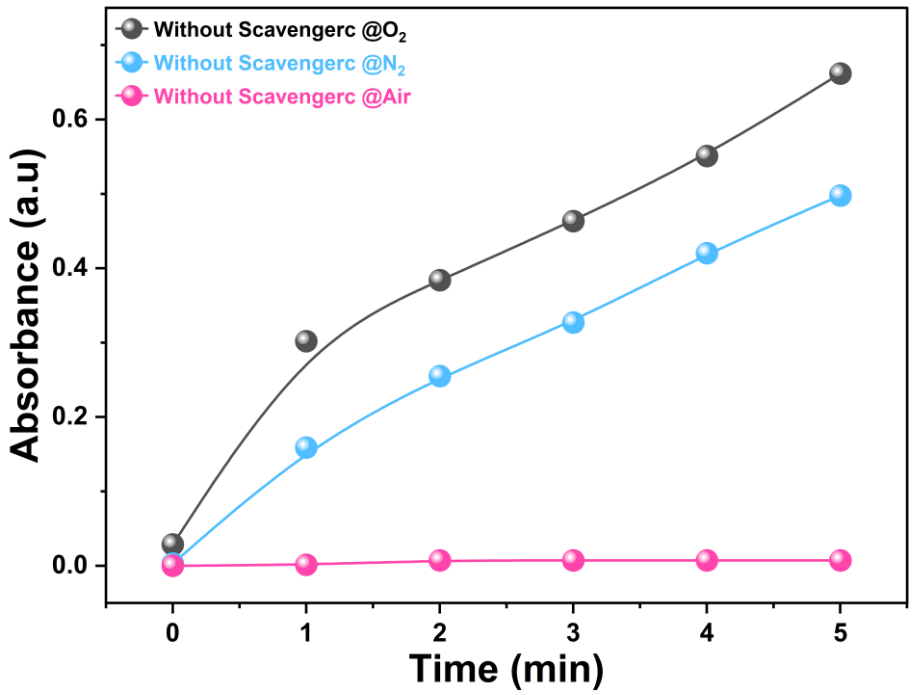


Figure S19. Absorbance variation of the TMB oxidation (650 nm) for Mn-Ni (TCPP) with different atmospheres with a 395 nm LED.

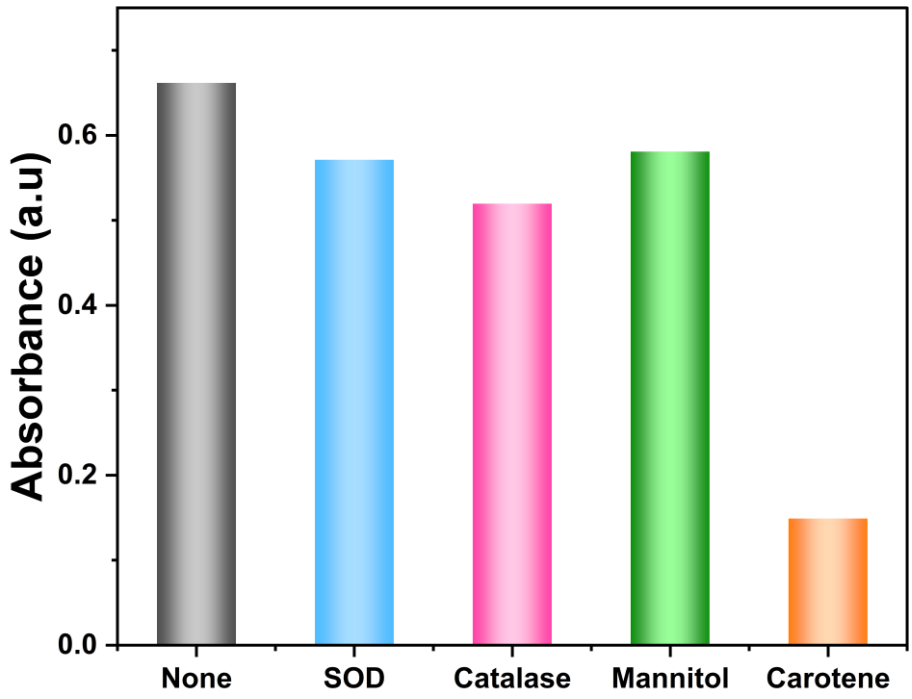


Figure S20. UV−vis spectra recording TMB oxidation by Mn-Ni (TCPP) with the absorbance of TMB in O_2, SOD, Catalase, Mannitol and Carotene after irradiation for 5 min.

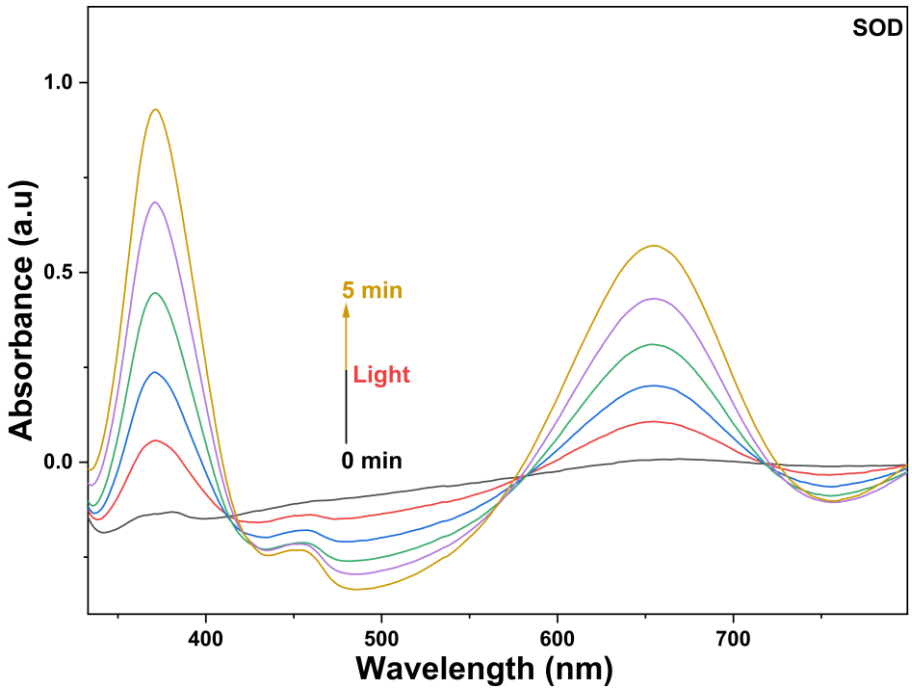


Figure S21. UV−vis spectra recording TMB oxidation by Mn-Ni (TCPP) with the absorbance of SOD irradiation for 5 min.

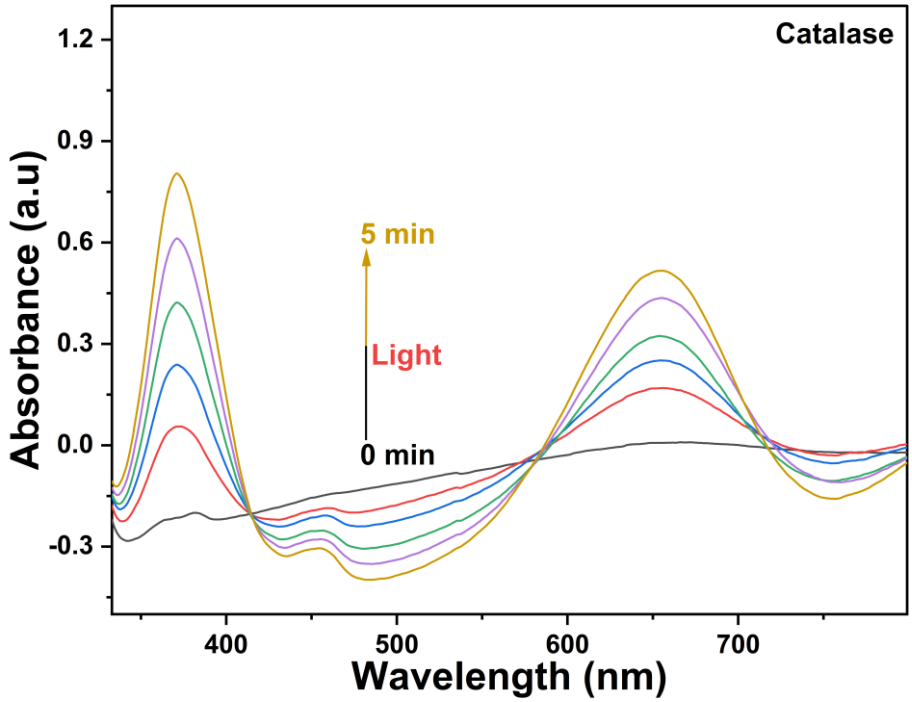


Figure S22. UV−vis spectra recording TMB oxidation by Mn-Ni (TCPP) with the absorbance of Catalase irradiation for 5 min.

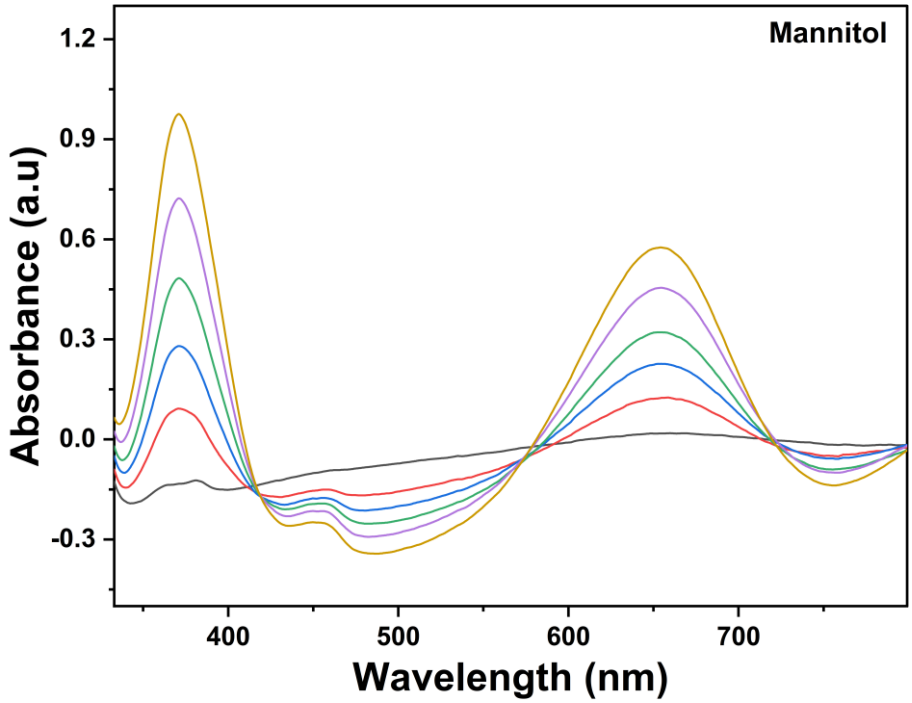


Figure S23. UV−vis spectra recording TMB oxidation by Mn-Ni (TCPP) with the absorbance of Mannitol irradiation for 5 min.

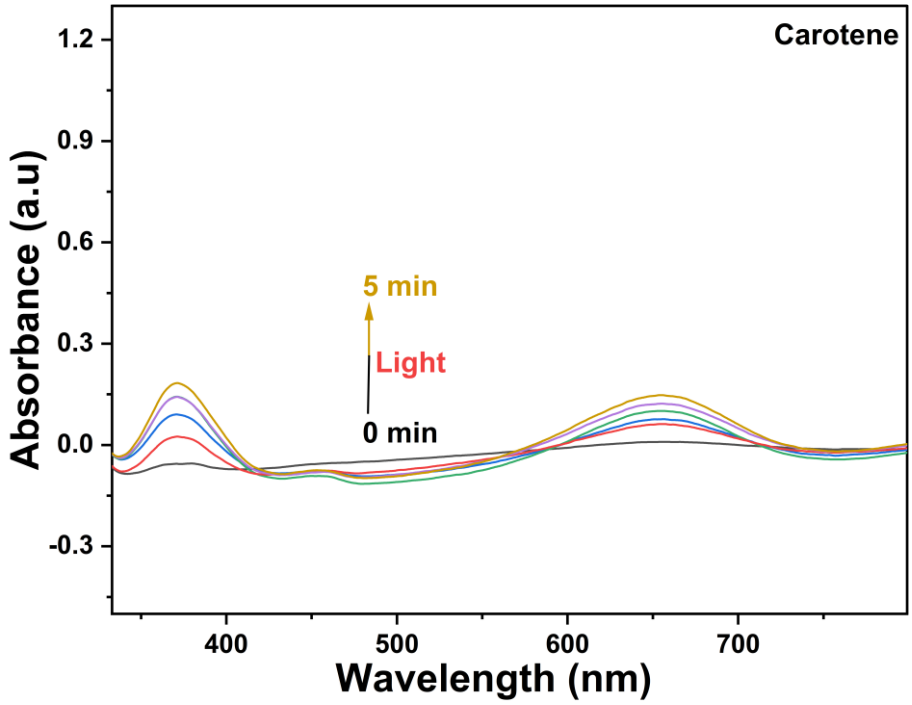


Figure S24. UV−vis spectra recording TMB oxidation by Mn-Ni (TCPP) with the absorbance of Carotene irradiation for 5 min.

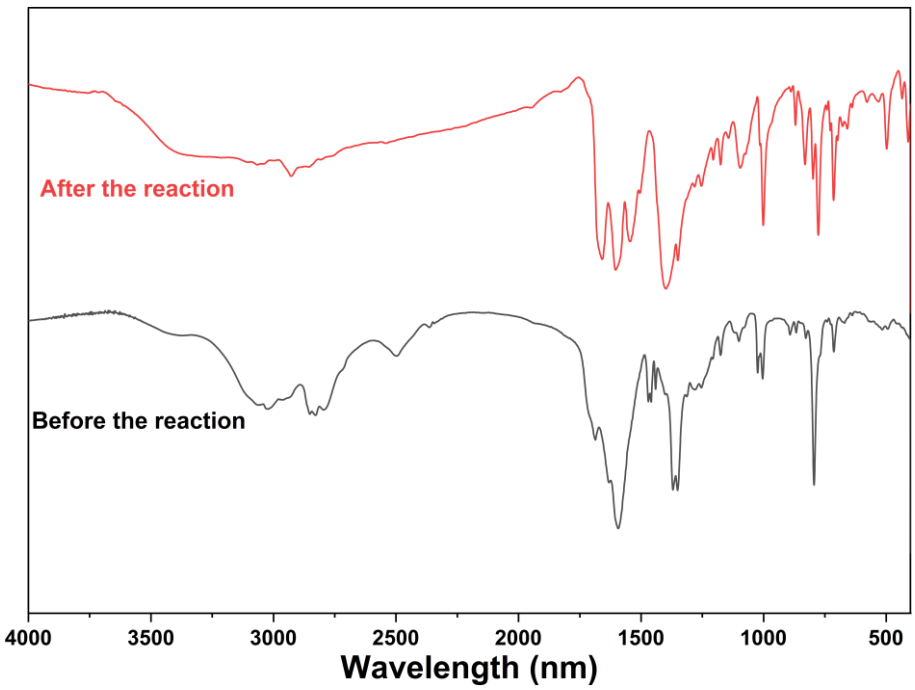


Figure S25. IR spectra of before the reaction Mn-Ni (TCPP) (black line) and after the reaction Mn-Ni (TCPP) (red line).

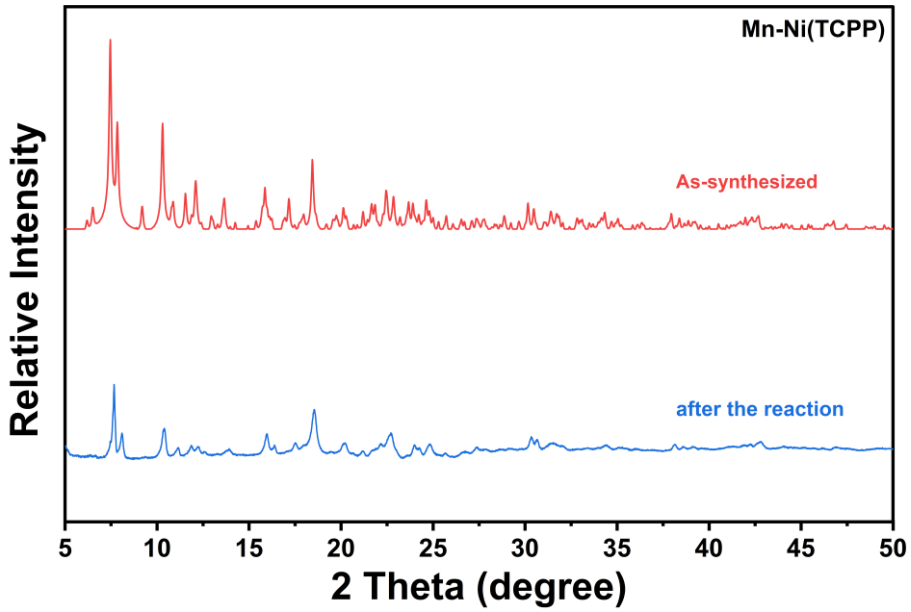


Figure S26. PXRD patterns of fresh as-synthesized Mn-Ni (TCPP) (red) and after the reaction Mn-Ni (TCPP) (blue line).

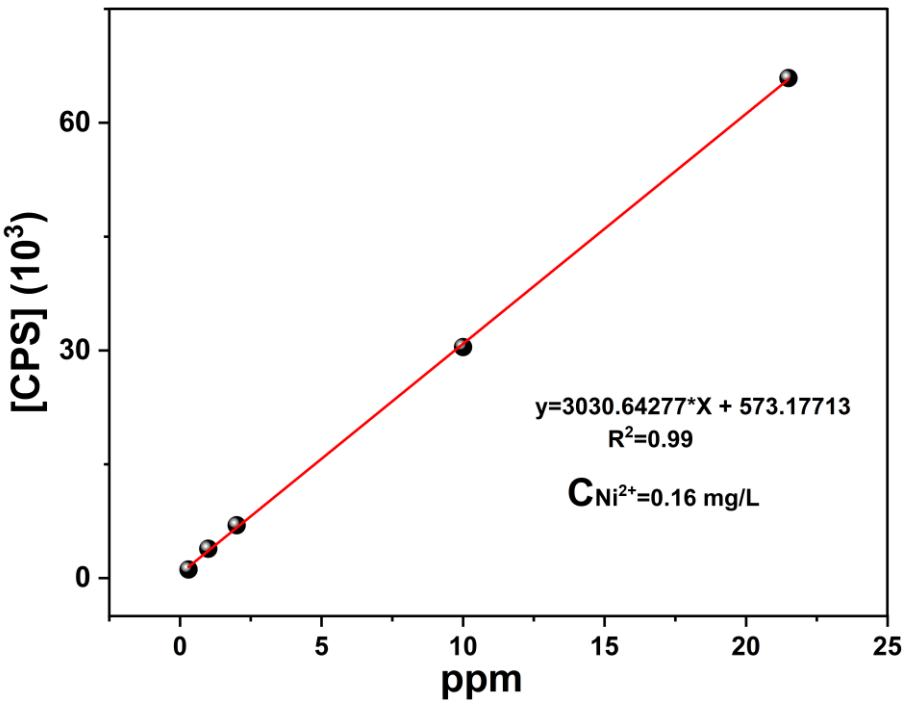
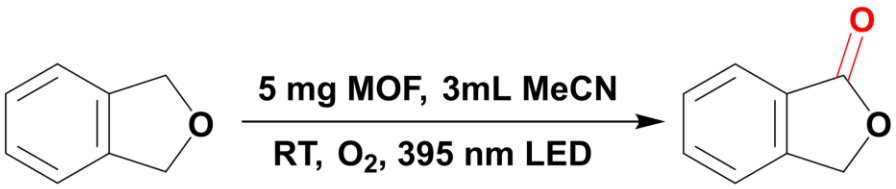


Figure S27. ICP-MS calibration curve for manganese ions and the content of Ni^{2+} in the mother liquor.

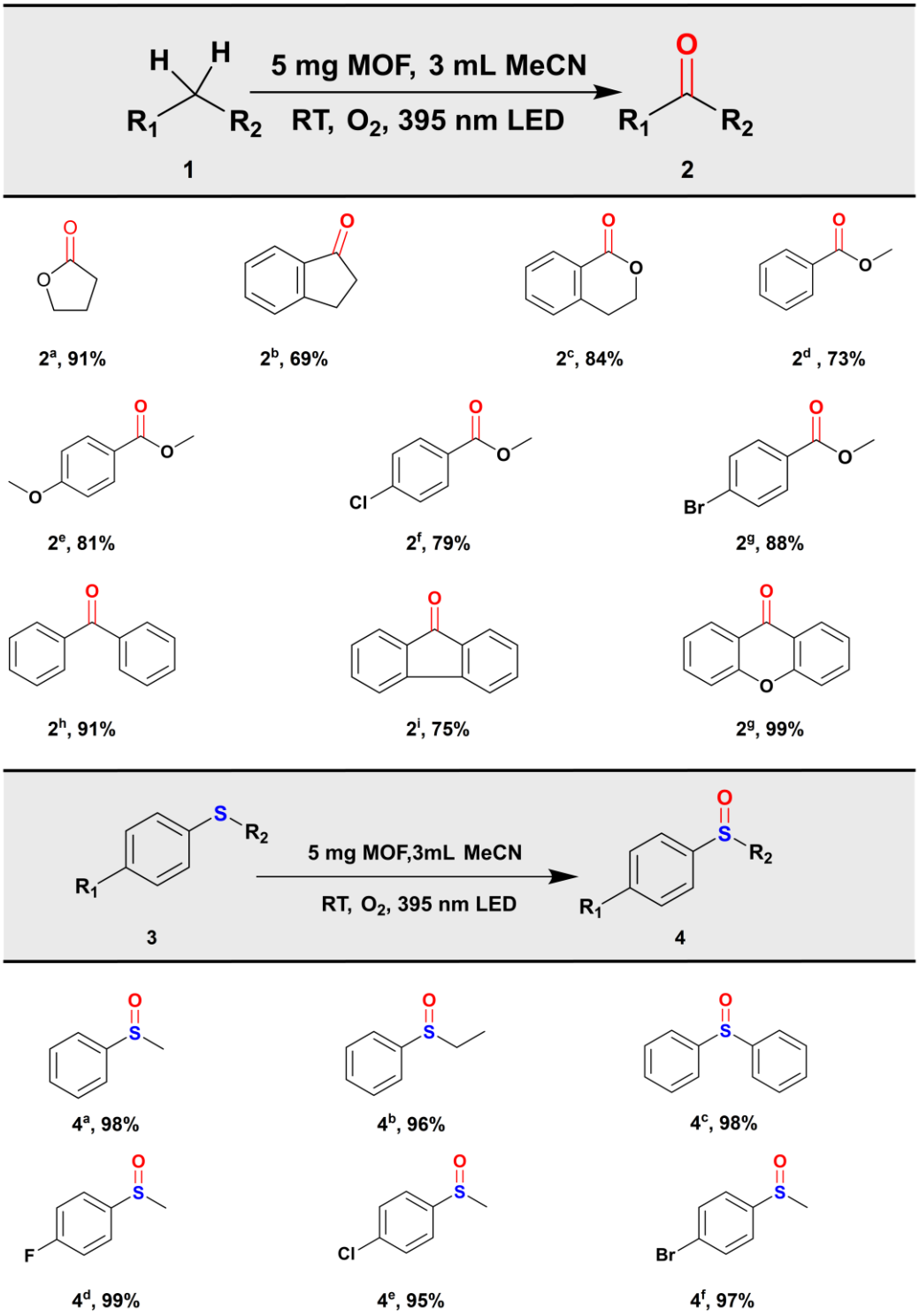
Table S2. Catalytic Oxidation of the C-H Bond of Phthalan.



entry	variation from standard conditions [a]	yield (%) [b]
1	none	93
2	no Mn-Ni (TCPP)	N.R.
3	Ar without O_2	N.R.
4	no Light	N.R.
5	$MnCl_2$	N.R.
6	Ni (TCPP)	14
7	$MnCl_2$ + Ni (TCPP)	17
8	405 nm LED	67
9	DMF	54
10	Air	82
11	CH_3OH	67
12	CH_3CH_2OH	74

Standard conditions: phtalan (0.2 mmol), Mn-Ni (TCPP) (catalyst, 5.0 mg) in CH_3CN (3.0 mL) irradiated with 395 nm LED at room temperature under O_2 atmosphere. Yields were determined by ^1H NMR.

Table S3. Scopes of the Catalytic Oxidation of C-H Bonds and Sulfides.



Reaction conditions: Mn-Ni (TCPP) (5mg), substrate (0.02 mmol), CH_3CN (3 mL), 395 nm LED, O_2, and isolated yields. Yields of the products were analyzed by ^1H NMR.

4. ^{1}H NMR Spectra

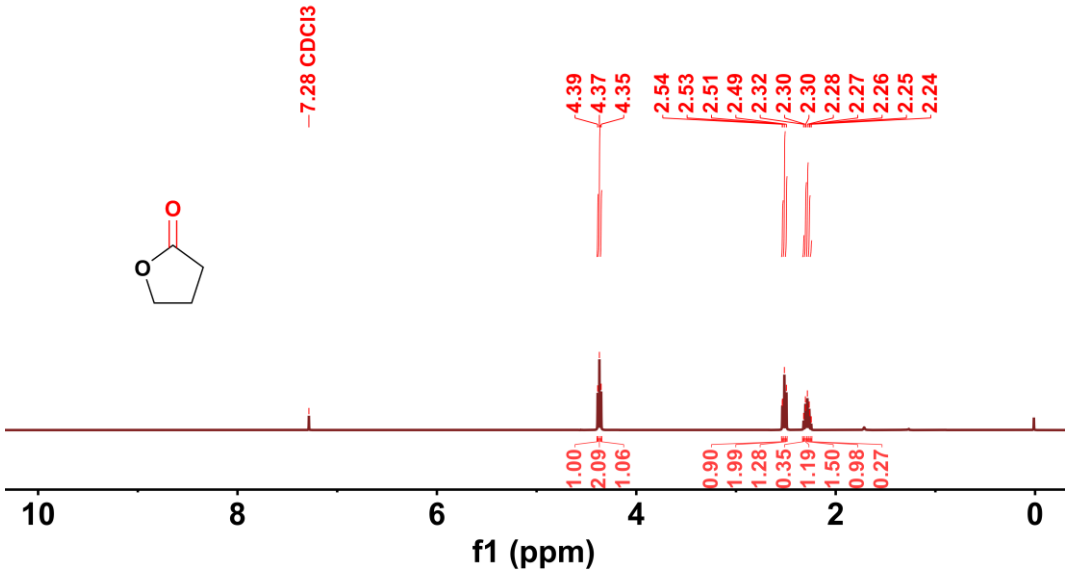


Figure S28. ^{1}H NMR spectrum of 2a in $CDCl_3$.

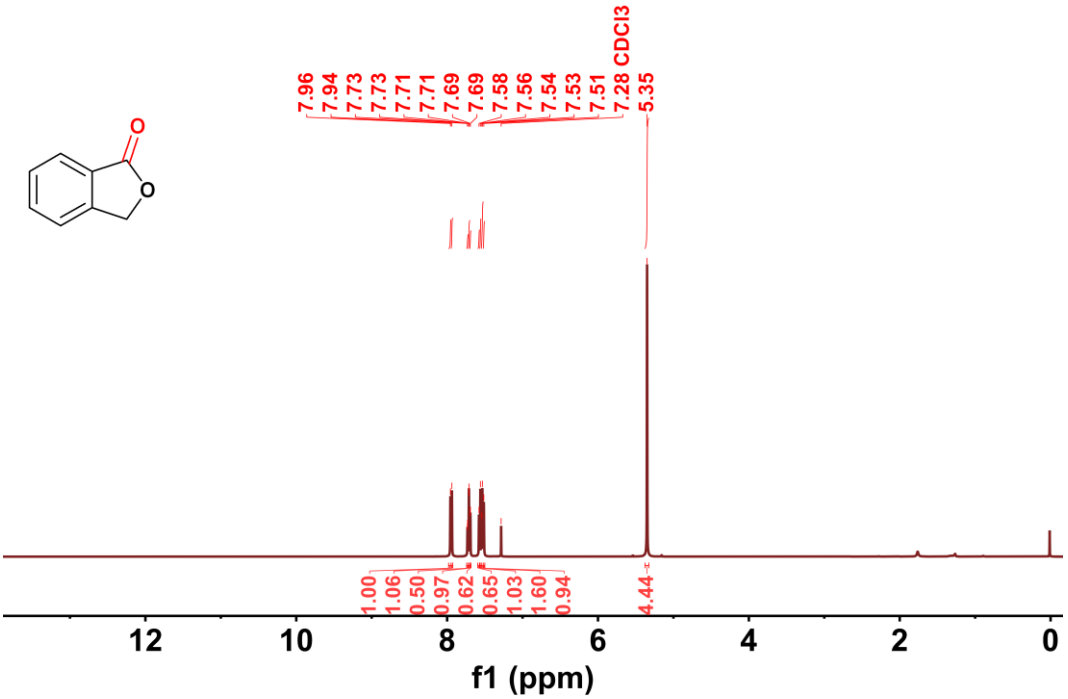


Figure S29. ^{1}H NMR spectrum of 2b in $CDCl_3$.

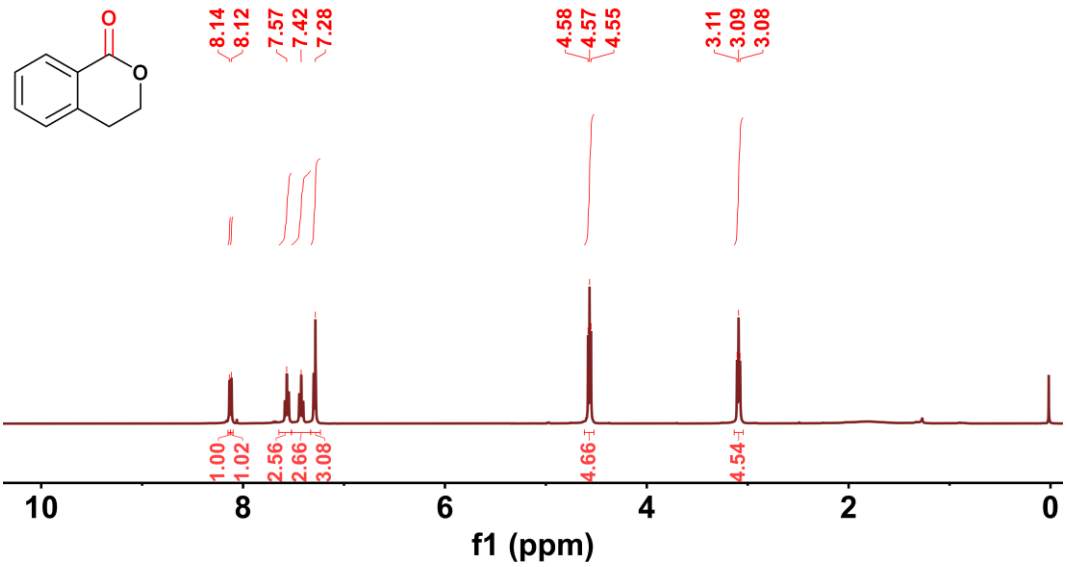


Figure S30. ^{1}H NMR spectrum of 2c in $CDCl_3$.

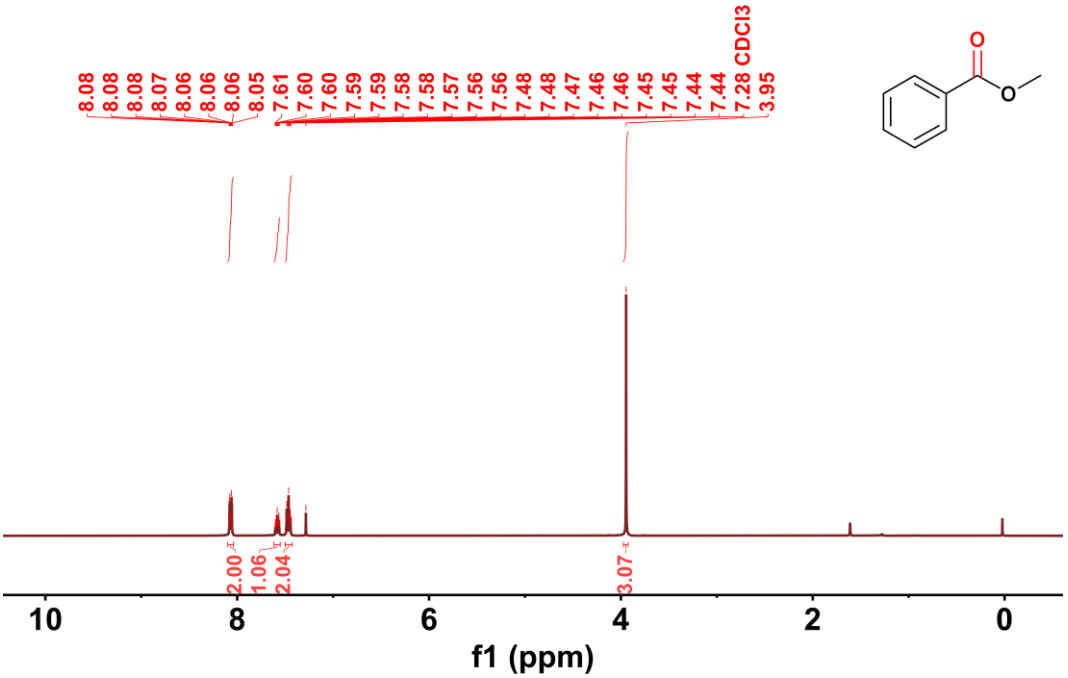


Figure S31. ^{1}H NMR spectrum of 2d in $CDCl_3$.

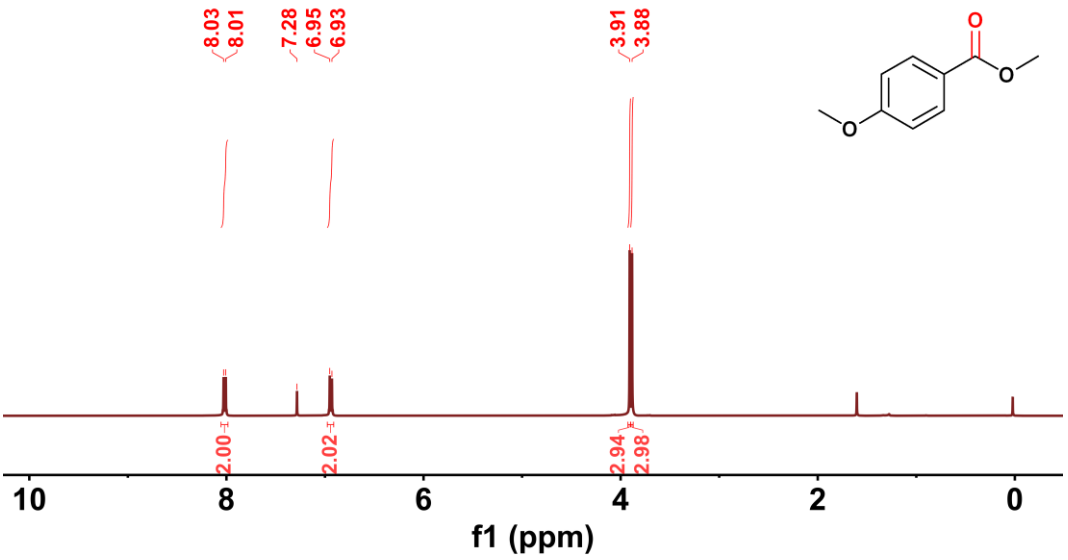


Figure S32. ^{1}H NMR spectrum of 2e in $CDCl_3$.

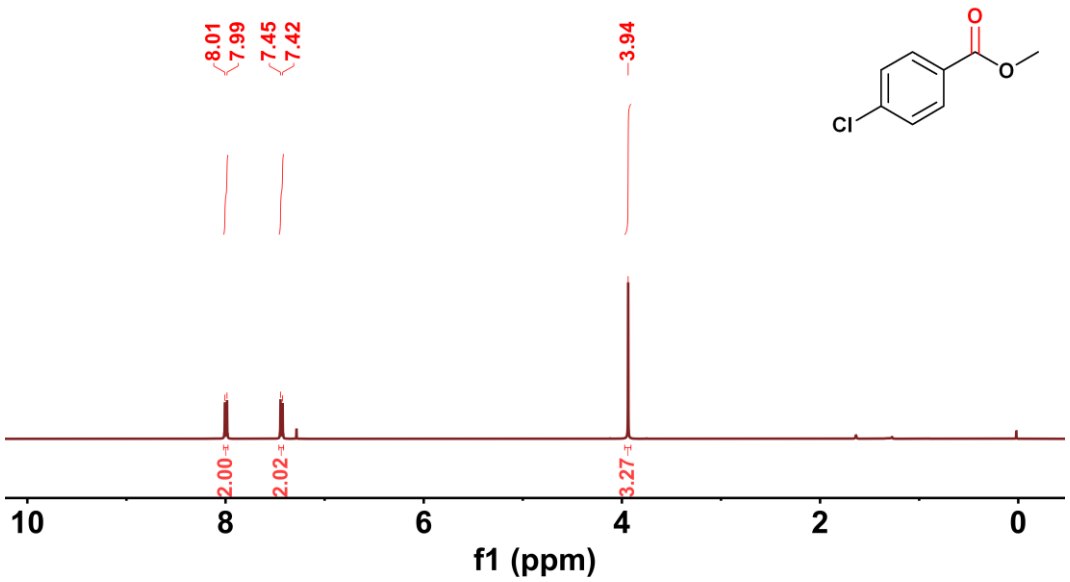


Figure S33. ^{1}H NMR spectrum of 2f in $CDCl_3$.

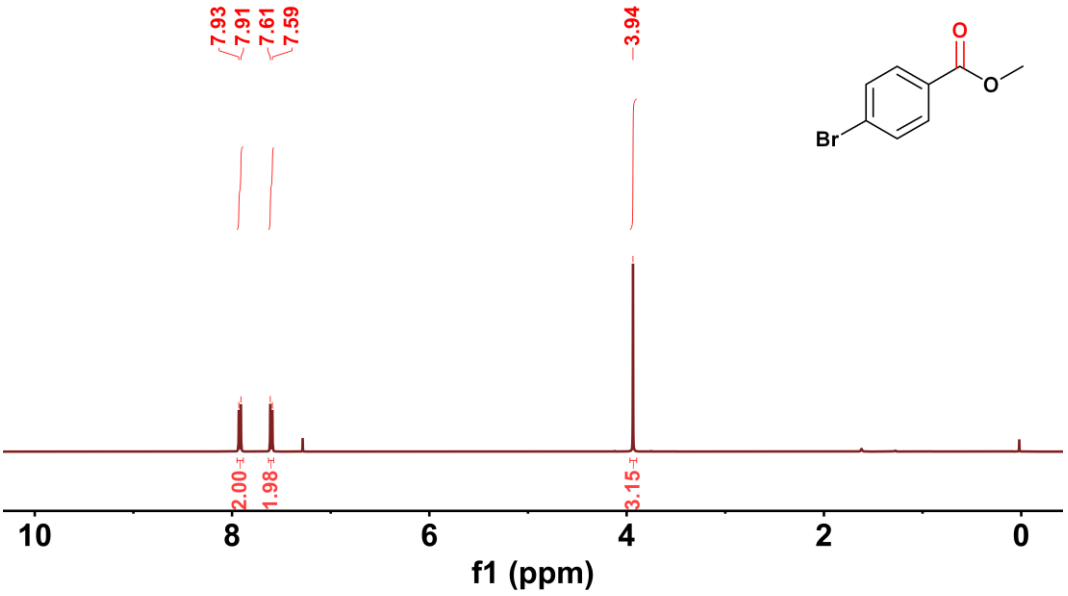


Figure S34. ^{1}H NMR spectrum of 2g in $CDCl_3$.

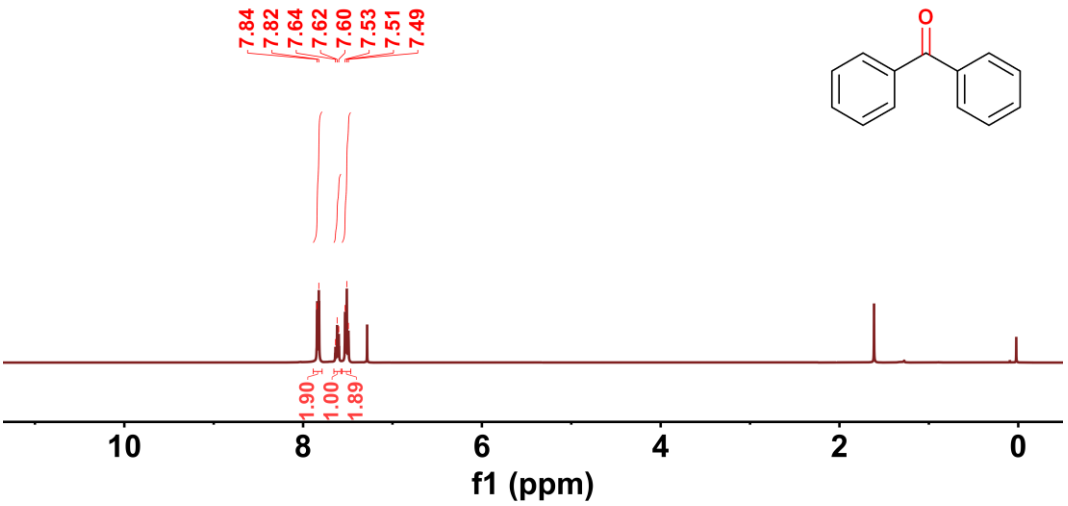


Figure S35. ^{1}H NMR spectrum of 2h in $CDCl_3$.

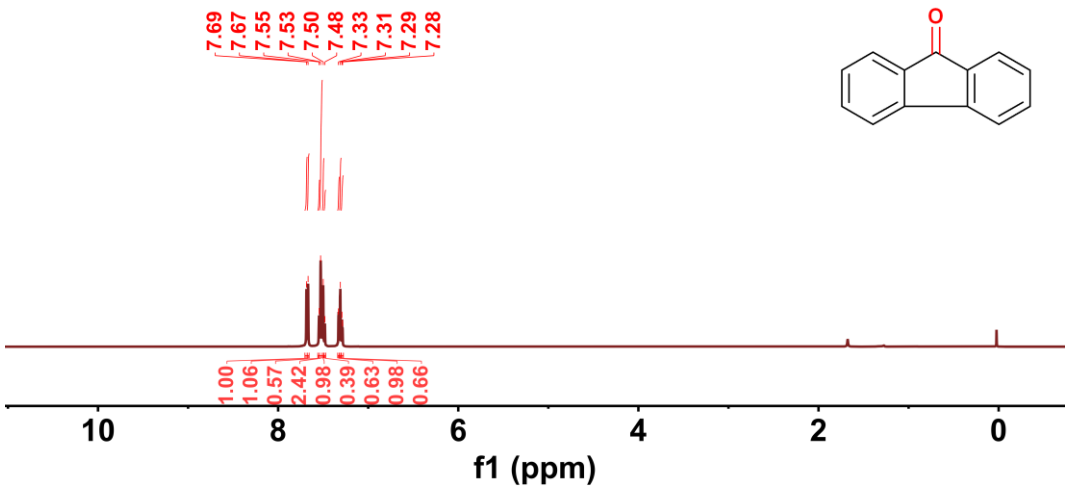


Figure S36. ^{1}H NMR spectrum of 2i in $CDCl_3$.

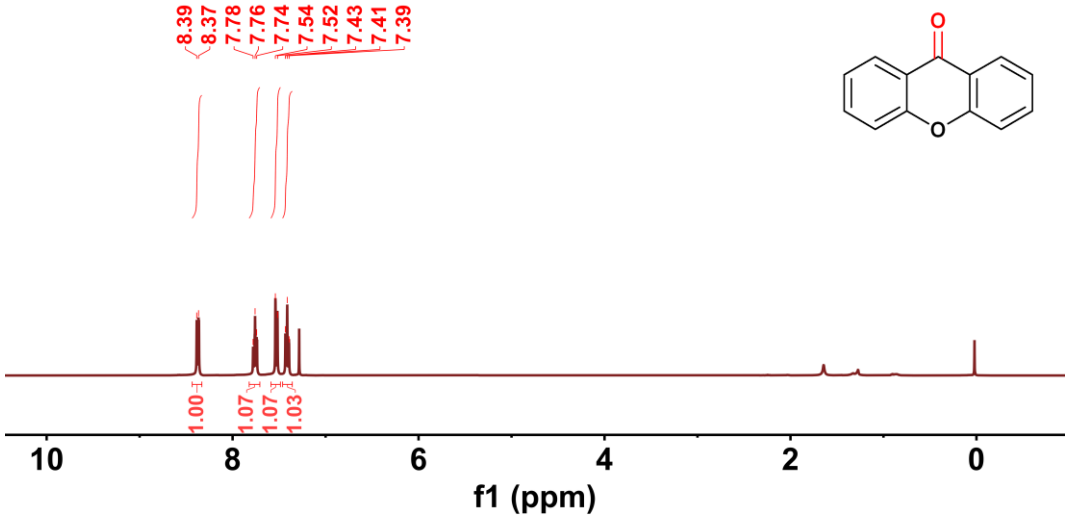


Figure S37. ^{1}H NMR spectrum of 2j in $CDCl_3$.

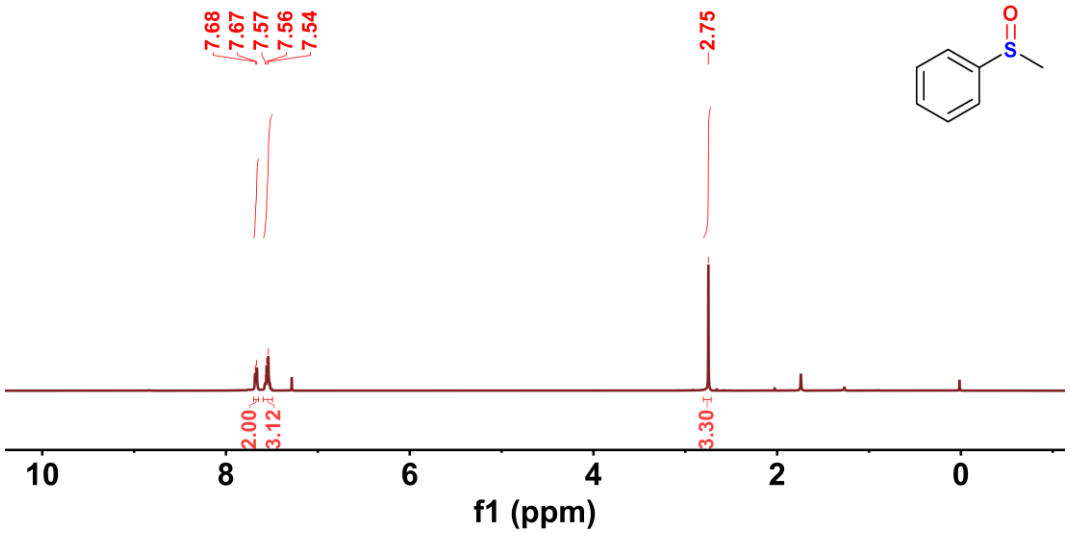


Figure S38. ^{1}H NMR spectrum of 4a in $CDCl_3$.

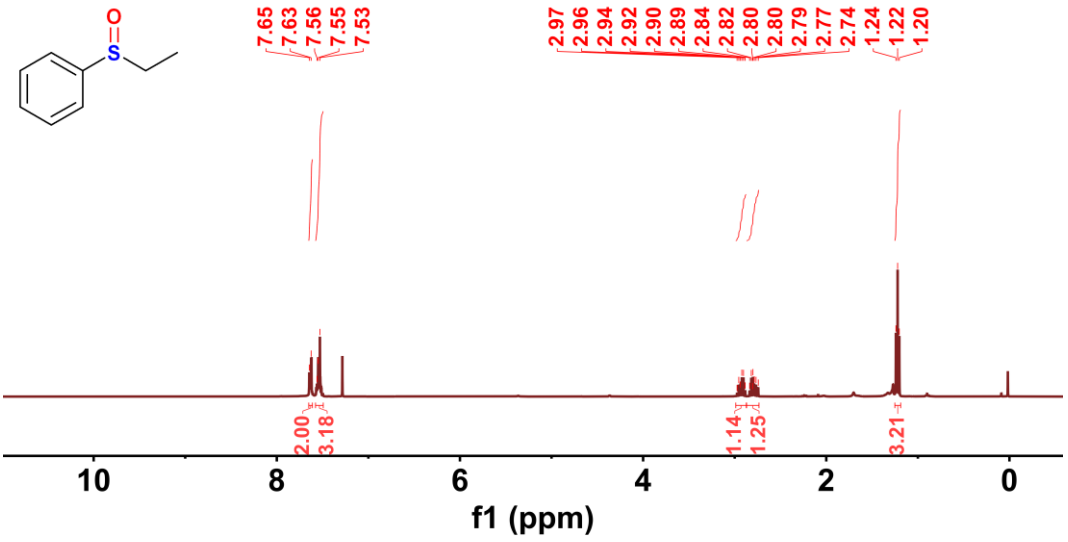


Figure S39. ^{1}H NMR spectrum of 4b in $CDCl_3$.

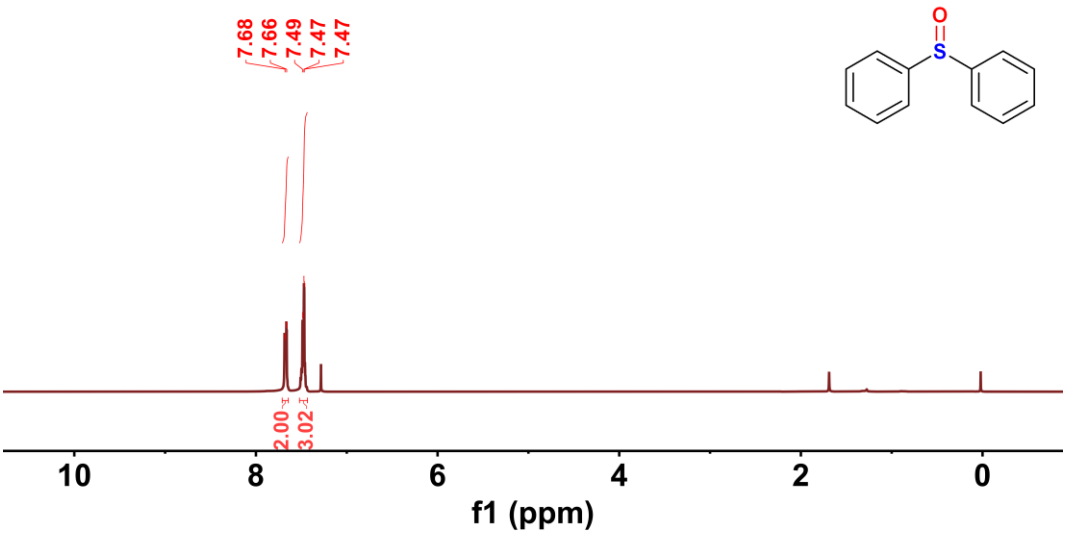


Figure S40. ^{1}H NMR spectrum of 2c in $CDCl_3$.

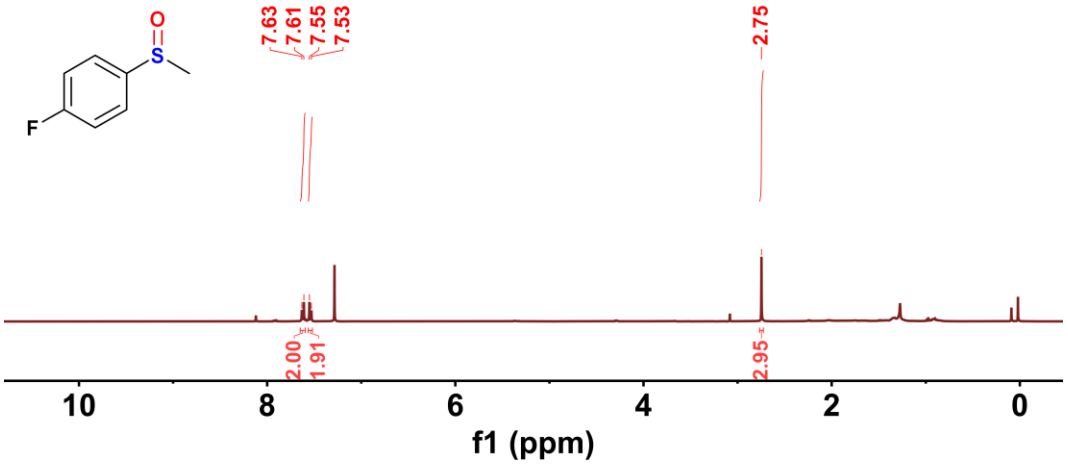


Figure S41. ^{1}H NMR spectrum of 2d in $CDCl_3$.

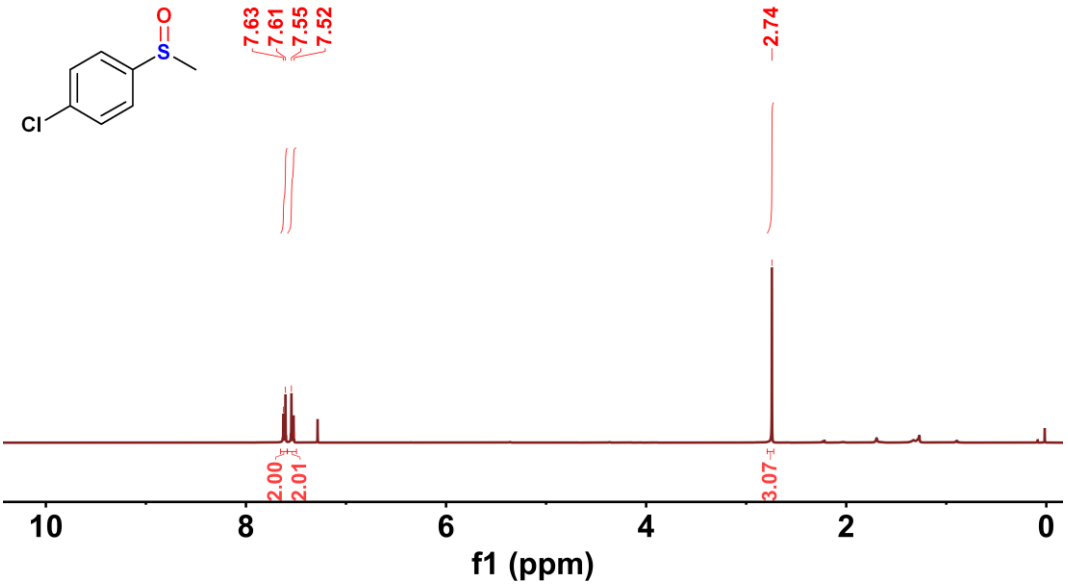


Figure S42. ^{1}H NMR spectrum of 2e in $CDCl_3$.

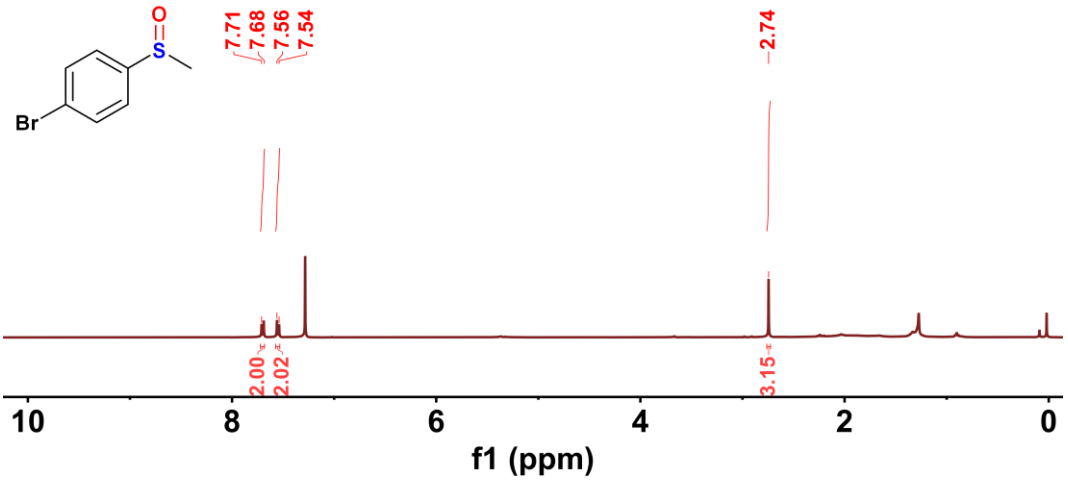


Figure S43. ^{1}H NMR spectrum of 4f in $CDCl_3$.

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