

Supporting Information

Unveiling dual catalysis enhancement of a pyridinium-containing Zn(II) coordination polymer in aerobic photooxidation of organic substrates and selective photoreduction of CO₂

Youting Fang and Duobin Chao*

School of Materials Science and Chemical Engineering, Ningbo University, Ningbo, Zhejiang 315211, China

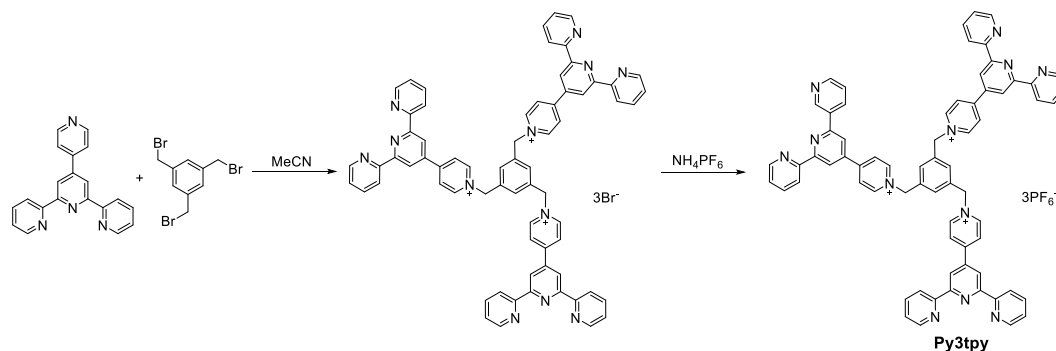
E-mail: chaoduobin@nbu.edu.cn

1. Experimental Section

1.1 Materials and instruments

All reagents including solvents and starting materials for synthesis were purchased from commercial suppliers (Energy Chemical and Macklin) and used as received. **Ph3tpy** was used as we previously synthesized.¹ ¹H-NMR spectra were recorded on a Bruker AVANCE III spectrometer (at 400 MHz) with chemical shifts recorded as ppm, and all spectra were calibrated against TMS. ¹³C-spectrum was recorded at a Bruker Ascend 500 MHz spectrometer. UV-vis spectra were recorded in a Edinburgh UV-visible Spectrophotometer DS5. The IR experiment measurements were carried out using FT-IR spectrophotometer (Nicolet 670) in the region 4000–500 cm⁻¹. High-resolution mass spectrometry was carried out using Shimadzu LCMS-IT-TOF. The PXRD patterns were measured by a D8 Advance Xray diffractometer with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) was carried out using Thermo Scientific K-Alpha with Al K α X-ray source (h ν = 1486.6 eV). The fluorescence tests were recorded on a fluorescence spectrometer RF6000. The measured spectral data excite light at 400 nm and emit light from 420 nm to 680 nm. Both excitation and emission light bandwidths are 5.0 nm. The fluorescence lifetime was measured by an Edinburgh FLS1000 instrument using an EPL laser (375 nm). photoelectrochemical experiments were carried out on CHI660E in a one-compartment cell equipped with glassy carbon or samples loaded FTO glass as working electrode, Ag/AgCl reference electrode, and platinum plate counter electrode at room temperature. N₂ adsorption tests were carried out on a Micromeritics ASAP 2460 fully automated specific surface and porosity analyser. EPR test recorded on a Bruker EMXplus-6/1 with a 300 W xenon lamp (365 nm). GC analysis for CO₂ reduction was performed on Shimadzu GC-2014 (packed column TDX-01, 2 m \times 3 mm, FID detector with Shimadzu Methanizer MTN-1 for CO and TCD detector for H₂, N₂ as carrier gas). SEM images were obtained on an instrument ZEISS Sigma 300. GC-MS experiment for ¹³CO₂ was carried out with Agilent 7890B-5977A.

1.2 Synthesis of Py3tpy



Scheme S1 Synthetic route of the ligand **Py3tpy**.

1,3,5-Tris(bromomethyl)benzene (328 mg, 0.46 mmol) was added into a solution of 4'-pyridin-4-yl)-2,2':6,2''-terpyridine (1.0 g, 1.61 mmol) in MeCN, and the solution was then heated at reflux for 24 h. The resulting precipitate was filtered and collected after washing with MeCN and CH₂Cl₂. The filter cake was then dissolved in a mixed solvent of ethanol and water (v/v = 2:1). NH₄PF₆ (450 mg, 2.76 mmol) dissolved in water was added and the suspension was stirred for 2 h. Next, the suspension was filtered to obtain a filter cake as **Py3tpy** after drying under vacuum at 60 °C for 12 h. Yield: 510 mg. ¹H NMR (400 MHz, CD₃CN) δ 8.84 – 8.77 (m, 6H), 8.62 (s, 6H), 8.58 (s, 6H), 8.50 (d, J = 9.0 Hz, 6H), 8.41 (s, 6H), 7.92 (s, 6H), 7.42 (s, 9H), 5.84 (s, 6H). ¹³C NMR (125 MHz, CD₃CN) δ 156.88, 155.73, 154.35, 149.49, 146.86, 144.11, 140.45, 136.53, 130.38,

128.19, 125.65, 122.46, 119.52, 66.43. ESI-TOF-MS: m/z 349.1451 $[M-3(PF_6^-)]^{3+}$ (calcd. 349.1448), 596.1982 $[M-2(PF_6^-)]^{2+}$ (calcd. 596.1995), 1337.3602 $[M-(PF_6^-)]^+$ (calcd.1337.3638).

1.3 Preparation of **Py3tpyZn** and **Ph3tpyZn**

Py3tpyZn: **Py3tpy** (510 mg, 0.34 mmol) and NH_4PF_6 (166 mg, 1.02 mmol) were dissolved in MeCN and $ZnBr_2$ (115 mg, 0.51 mmol) was then added. The reaction solution was stirred at reflux for 24 h. The resulting precipitate was filtered and the filter cake was washed with DMF and MeCN to afford **Py3tpyZn** after drying under vacuum at 60 °C for 12 h. Yield: 415 mg.

Ph3tpyZn: **Ph3tpy** (200 mg, 0.26 mmol) and NH_4PF_6 (127 mg, 0.78 mmol) were dissolved in MeCN and $ZnBr_2$ (88 mg, 0.39 mmol) was then added. The reaction solution was stirred at reflux for 24 h. The resulting precipitate was filtered and the filter cake was washed with DMF and MeCN to afford **Ph3tpyZn** after drying under vacuum at 60 °C for 12 h. Yield: 186 mg.

1.4 Photooxidation of organic substrates

General procedure: **Py3tpyZn** (2.0 mg) or **Ph3tpyZn** (2.0 mg) was dispersed in MeCN (5.0 mL) and then organic substrate (1.0 mmol) was added to form a suspension in a glass tube. The glass tube was not sealed and exposed to air during light irradiation. The light source is a blue LED light equipment (SMPC-LVWT, 395 nm, 3 W LEDs) supplied by Technical Institute of Physics and Chemistry & Chinese Academy of Sciences. After light irradiation for 5 h, 0.4 mL reaction solution was taken and mixed with 0.1 mL MeCN- d_3 in an NMR tube for 1H NMR test. Product yield was then calculated by integrating the characteristic peaks of organic substrate and corresponding product.

1.5 Photocatalytic CO_2 reduction

General procedure: **Py3tpyZn** (10.0 mg) or **Ph3tpyZn** (10.0 mg), 4CzIPN (0.8 mg), and TEA (0.28 M) were added into MeCN/ H_2O solution (5.0 mL, v/v = 4:1) in a glass tube. The mixed reaction solution was bubbled with N_2 for 10 min and then CO_2 for 20 min. Next, the glass tube was sealed up with a rubber septum before light irradiation. The light source is a white LED light equipment (SMPC-LVWT, 420–650 nm, 3 W LEDs) supplied by Technical Institute of Physics and Chemistry & Chinese Academy of Sciences. After light irradiation for 4 h, gaseous products were analyzed by injection of 100 μ L aliquots from headspace into the GC2014 instrument. Liquid products such as HCOOH were analyzed by 1H NMR.

1.6 Photoelectrochemical measurements

All photoelectrochemical measurements were carried out with a three-electrode electrochemical cell containing Ag/AgCl as the reference electrode, a platinum plate as the counter electrode, and FTO glass loaded with samples such as **Py3tpyZn** and **Ph3tpyZn** as the working electrode.

The FTO glass working electrodes were prepared as follows. 2.0 mg of **Py3tpyZn** and **Ph3tpyZn** were dispersed in C_2H_5OH (2.0 mL) containing 50 μ L of Nafion and then treated by sonication for 10 minutes to form inks of **Py3tpyZn** and **Ph3tpyZn**, respectively. The ink (1.0 mL) was dropped in batches onto the conductive surface of the FTO glass. The FTO glass was allowed to dry naturally at room temperature and then used as a working electrode.

Mott-Schottky plots, photocurrent responses and electro-chemical impedance spectra were all obtained with aqueous Na_2SO_4 solution (0.5 M) as the electrolyte. For Mott-Schottky plots, the open circuit voltage was 0.35 V. The initial potential was -1.5 V and the final potential is -0.4 V (at 800,1000,1200 Hz). The increment of potential was set as 0.05 V. For photocurrent responses, run time was 300 s with an interval of 20 s. The light source was the same white LEDs equipment as

that used for photocatalytic experiments. The potential for photocurrent test was set at open circuit potential. For electrochemical impedance spectra, the potential was set at open circuit potential and the frequency was set from 0.1 Hz to 100 kHz.

2. Supplementary Fig.s and tables.

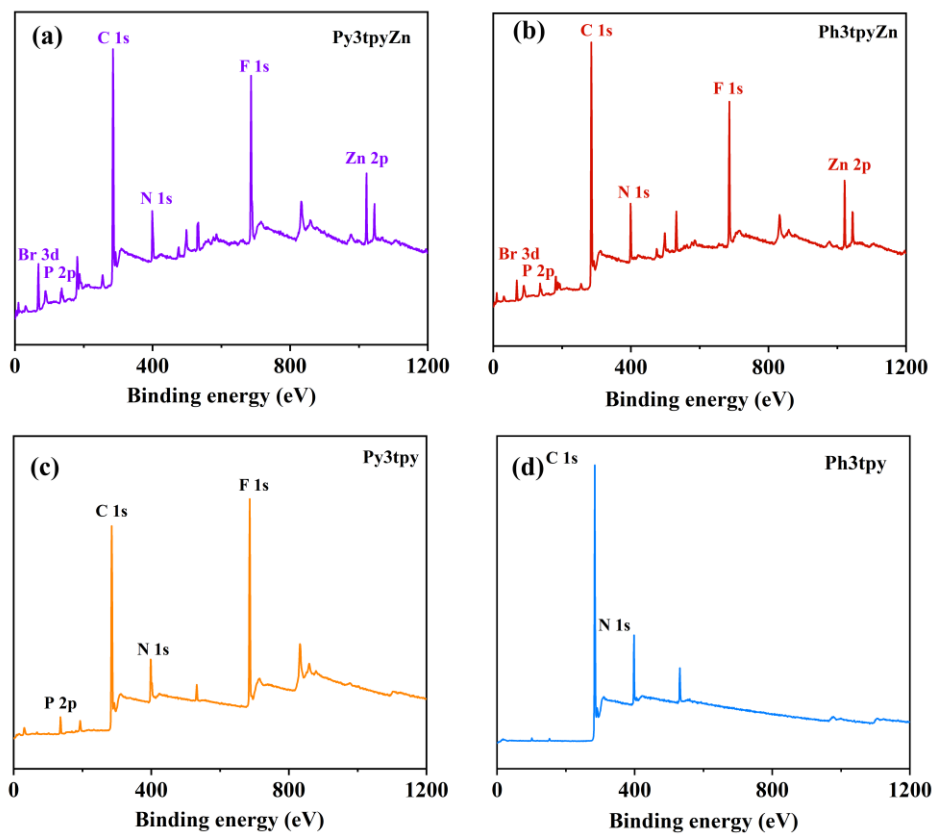


Fig. S1 XPS survey spectra of (a) **Py3tpyZn**, (b) **Ph3tpyZn**, (c) **Py3tpy**, and (d) **Ph3tpy**.

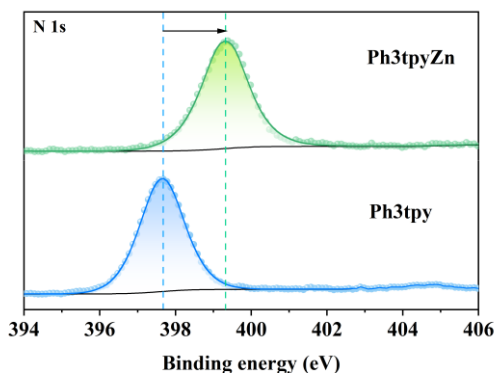


Fig. S2 High-resolution N 1s XPS spectra of ligand **Ph3tpy** and **Ph3tpyZn**.

Table S1 Binding energies of main elements for **Py3tpyZn**, **Ph3tpyZn**, **Py3tpy**, and **Ph3tpy**.

Sample	C 1s BE (eV)				N 1s BE (eV)		Zn 2p _{1/2} BE (eV)	Zn 2p _{3/2} BE (eV)	F 1s BE (eV)	P 2p BE (eV)	Br 3d BE (eV)
	C=C	C=N-	C-N ⁺ -	C=N ⁺ -	=N-	=N ⁺ -					
Py3tpyZn	284.6 (65)	285.8 (26)	285.1 (4)	286.1 (9)	399.3 (76)	401.6 (24)	1044.7	1021.7	686.2	135.3	68.1
Ph3tpyZn	284.8 (65)	286.0 (35)			399.4 (100)		1044.5	1021.5	686.1	135.9	68.3
Py3tpy	284.6 (65)	285.7 (26)	285.0 (4)	286.1 (9)	398.3 (75)	401.5 (25)			686.1	136.1	
Ph3tpy	284.6 (66)	285.6 (34)			398.6 (100)						

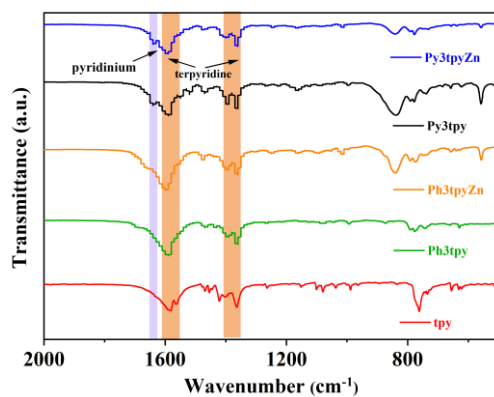


Fig. S3 Partial FT-IR spectra of **Py3tpyZn**, **Ph3tpyZn**, **Py3tpy**, **Ph3tpy**, and **tpy**.

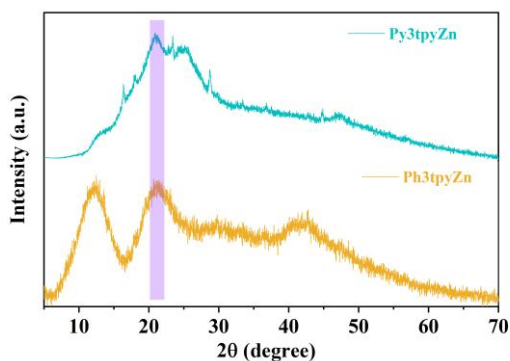


Fig. S4 PXRD patterns of **Py3tpyZn** and **Ph3tpyZn**.

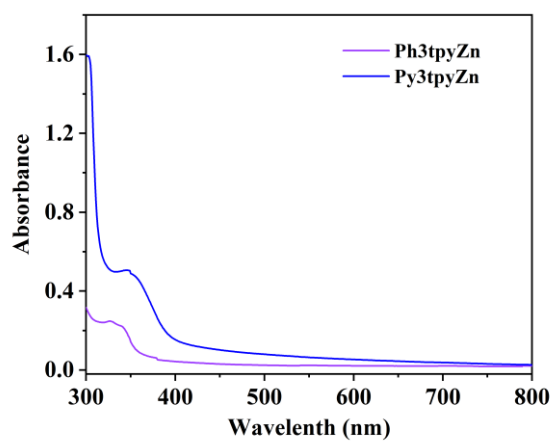


Fig. S5 UV-vis absorption spectra of **Py3tpyZn** and **Ph3tpyZn**.

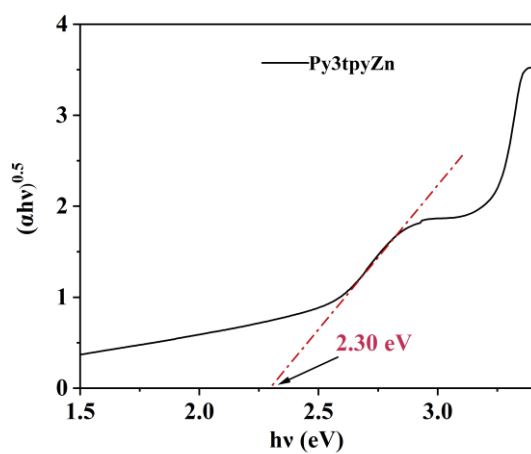


Fig. S6 Tauc plot of **Py3tpyZn**.

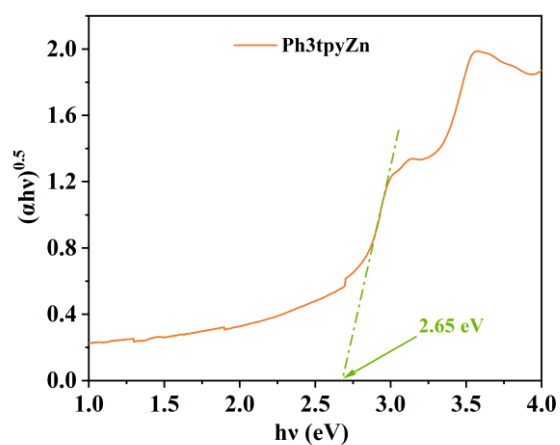


Fig. S7 Tauc plot of **Ph3tpyZn**.

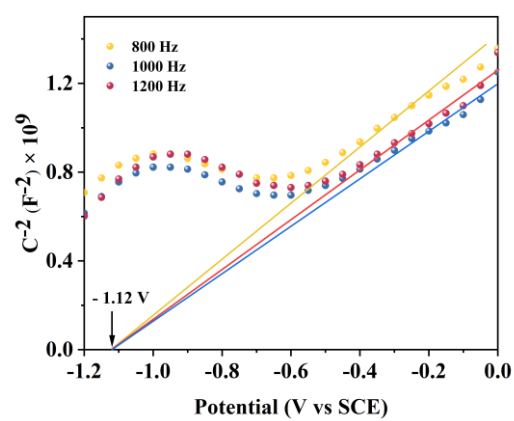


Fig. S8 Mott-Schottky plots of Ph₃tpyZn.

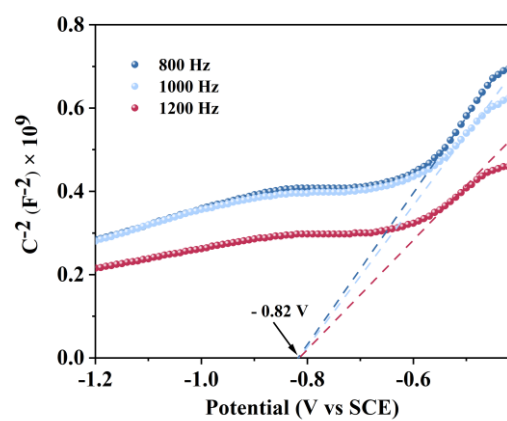


Fig. S9 Mott-Schottky plots of Py₃tpyZn.

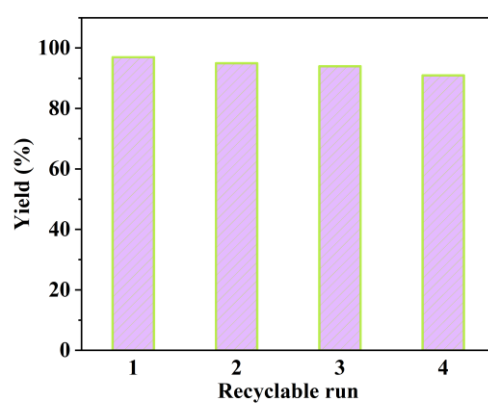


Fig. S10 Recyclable photooxidation of thioanisole using Py₃tpyZn under air.

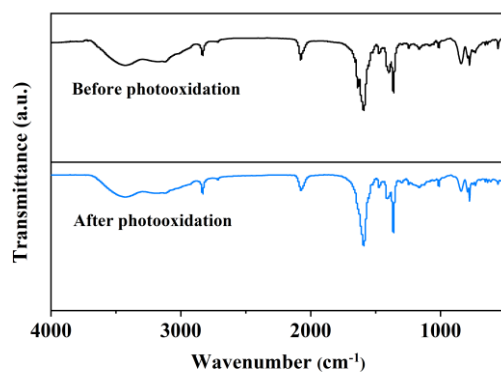


Fig. S11 FT-IR spectra of **Py3tpyZn** before and after photooxidation of thioanisole under air.

Table S2 Control experiments for photoreduction of CO₂ with **Py3tpyZn**.^[a]

Entry	Deviations for standard conditions	CO (μmol)	H ₂ (μmol)
1	None	1.23	0.05
2	Without Py3tpyZn	Trace	n.d.
3	Without photosensitizer 4CzIPN	n.d.	n.d.
4	Without TEA	n.d.	n.d.
5	N ₂ instead of CO ₂	n.d.	n.d.
6	Without light	n.d.	n.d.

[a] Standard conditions: **Py3tpyZn** (10.0 mg), 4CzIPN (0.8 mg), and TEA (0.28 M) in CO₂-saturated CH₃CN/H₂O solution (5.0 mL, v/v = 4.5:0.5) under light irradiation (420 – 650 nm) at room temperature for 120 min. n.d. = not detected. Trace = A trace amount of CO that was detected but could not be quantified by the instrument.

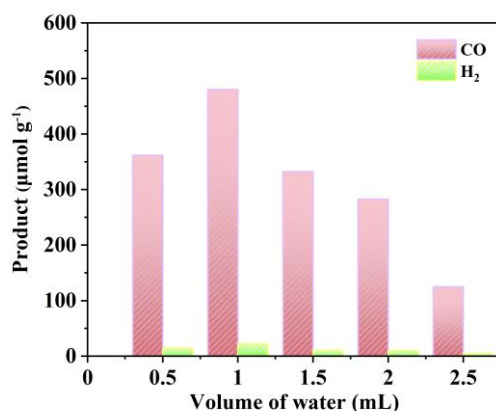


Fig. S12 Photoreduction of CO₂ for **Py3tpyZn** in mixed MeCN/H₂O (5.0 mL) solution with different volume of water.

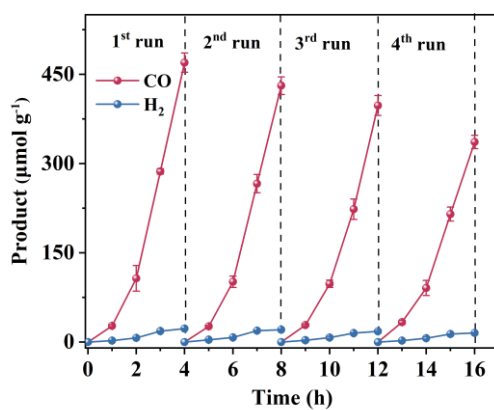


Fig. S13 Recyclable photoreduction of CO₂ using **Py3tpyZn**.

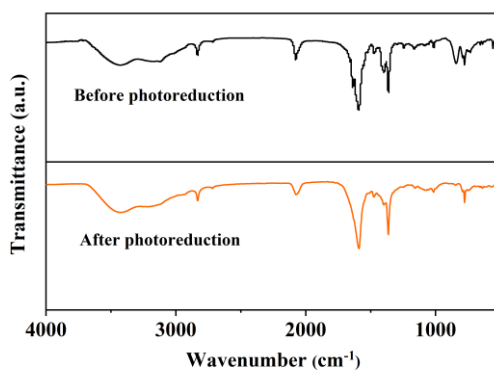


Fig. S14 FT-IR spectra of **Py3tpyZn** before and after photoreduction of CO₂.

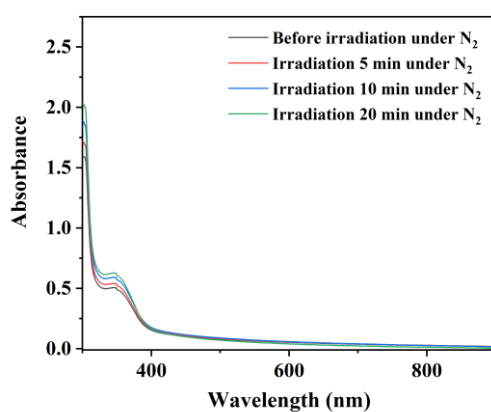


Fig. S15 UV-vis absorption spectra of **Py3tpyZn** without thioanole upon light irradiation under N₂.

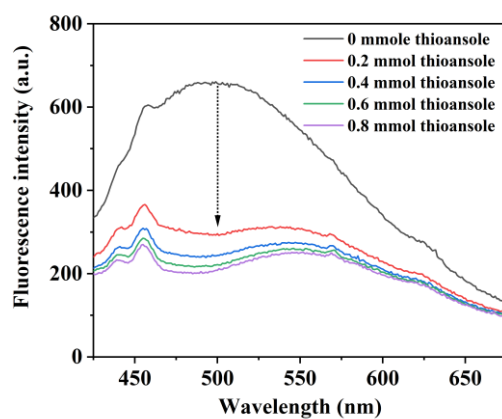


Fig. S16 Fluorescence spectra of **Py3tpyZn** upon addition of thioansole. The excited wavelength is 400 nm.

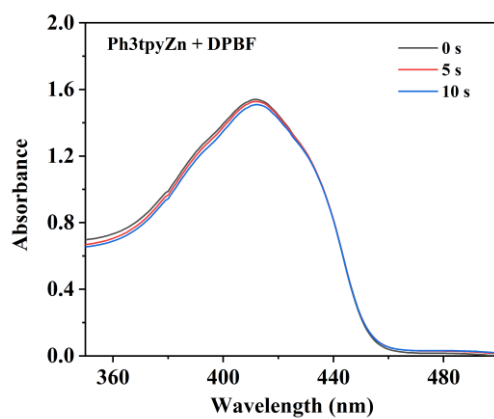


Fig. S17 UV-vis absorption spectra of the MeCN solution containing DPBF ($5.0 \mu\text{M}$) and **Ph3tpyZn** (0.4 mg mL^{-1}) upon light irradiation under air.

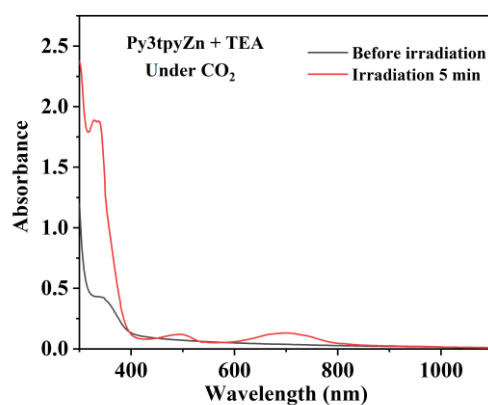


Fig. S18 UV-vis absorption spectra of **Py3tpyZn** (0.4 mg mL^{-1}) in the presence of TEA (1.0 mmol) upon light irradiation under CO_2 .

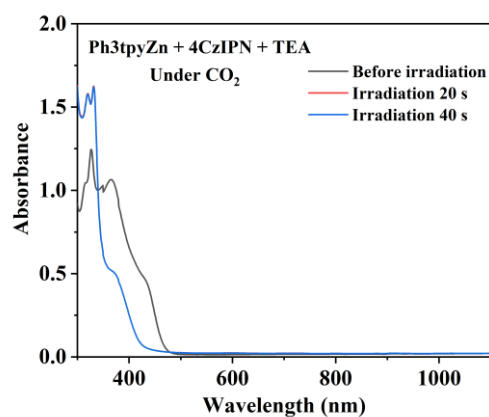


Fig. S19 UV-vis absorption spectra of **Ph3tpyZn** (0.4 mg mL^{-1}) in the presence of TEA (1.0 mmol) and 4CzIPN ($50 \text{ }\mu\text{M}$) upon light irradiation under CO_2 .

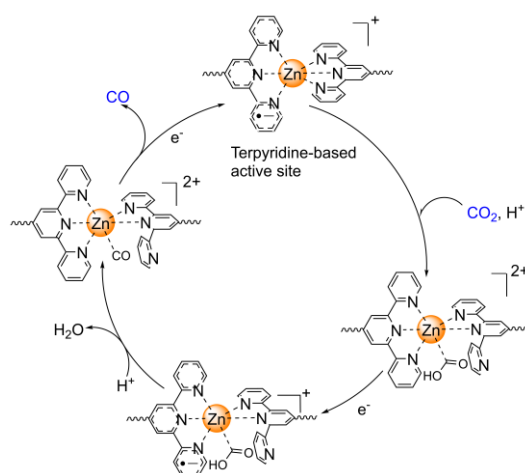


Fig. S20 Probable conversion of CO_2 to CO at the terpyridine-based active site for **Py3tpyZn** and **Ph3tpyZn**.

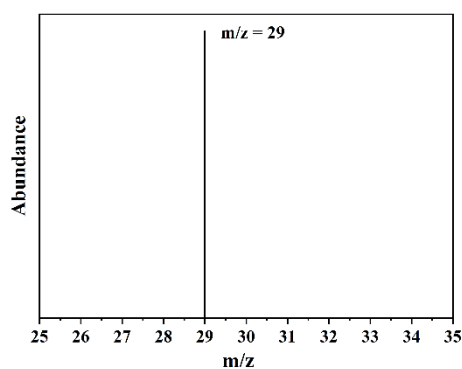


Fig. S21 Isotopic labelling experiment with $^{13}\text{CO}_2$ for photocatalytic CO_2 reduction using **Py3tpyZn**.

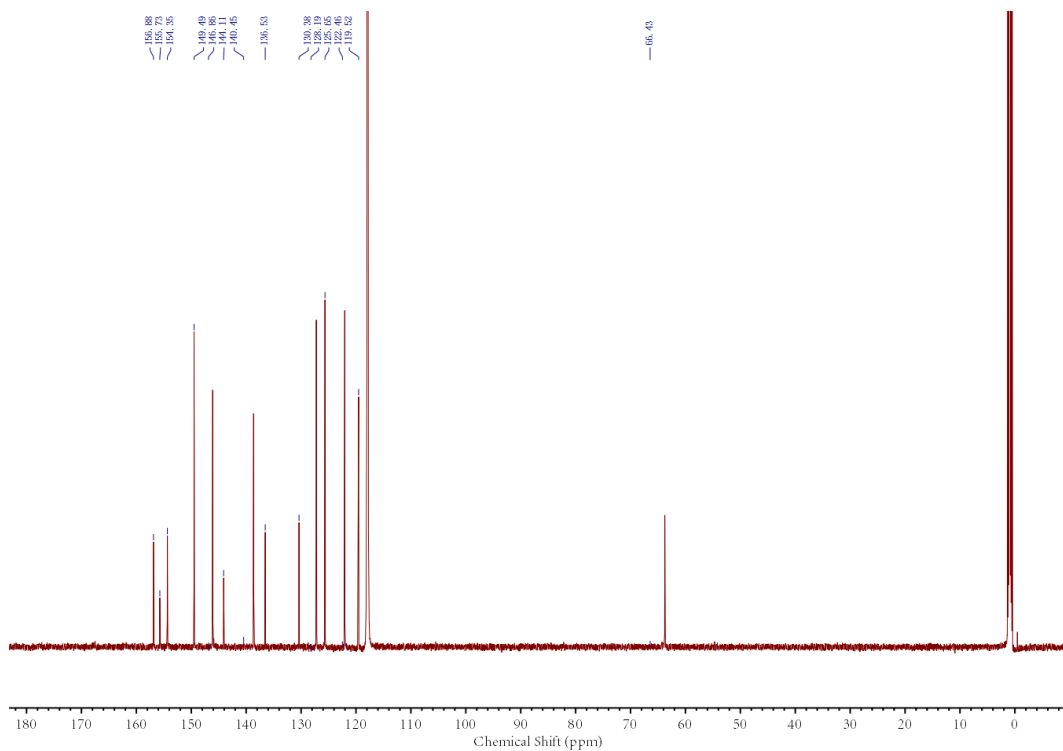


Fig. S25 ^{13}C NMR spectrum of Py3tpy in MeCN- d_3 .

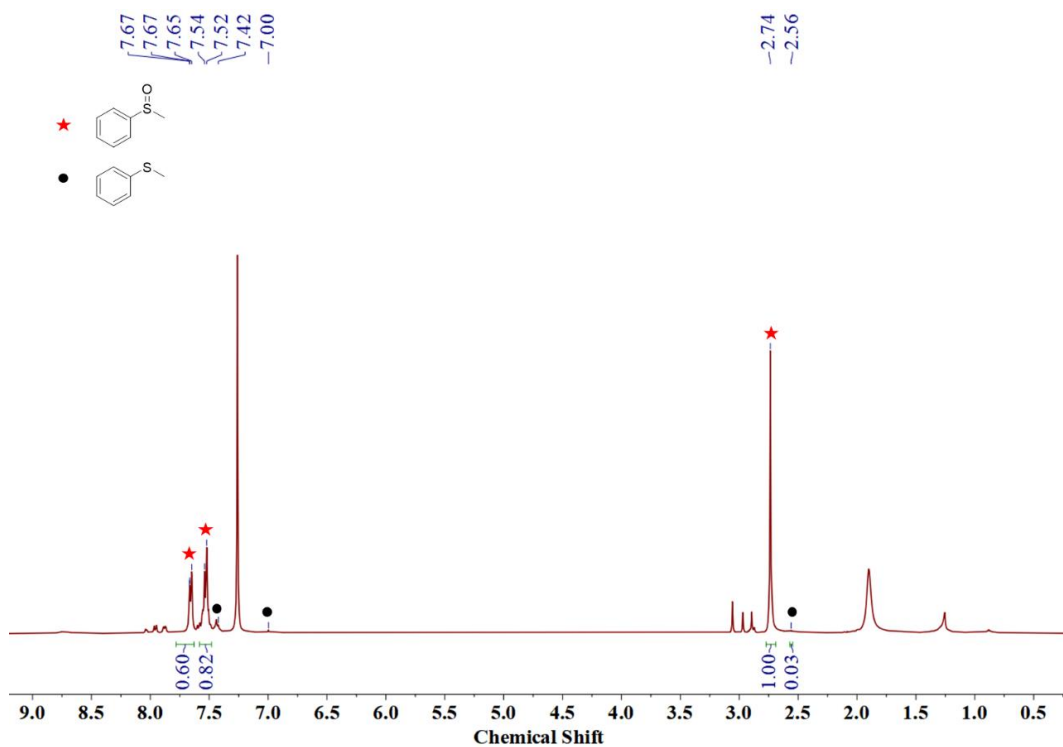


Fig. S26 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of thioansole with Py3tpyZn.

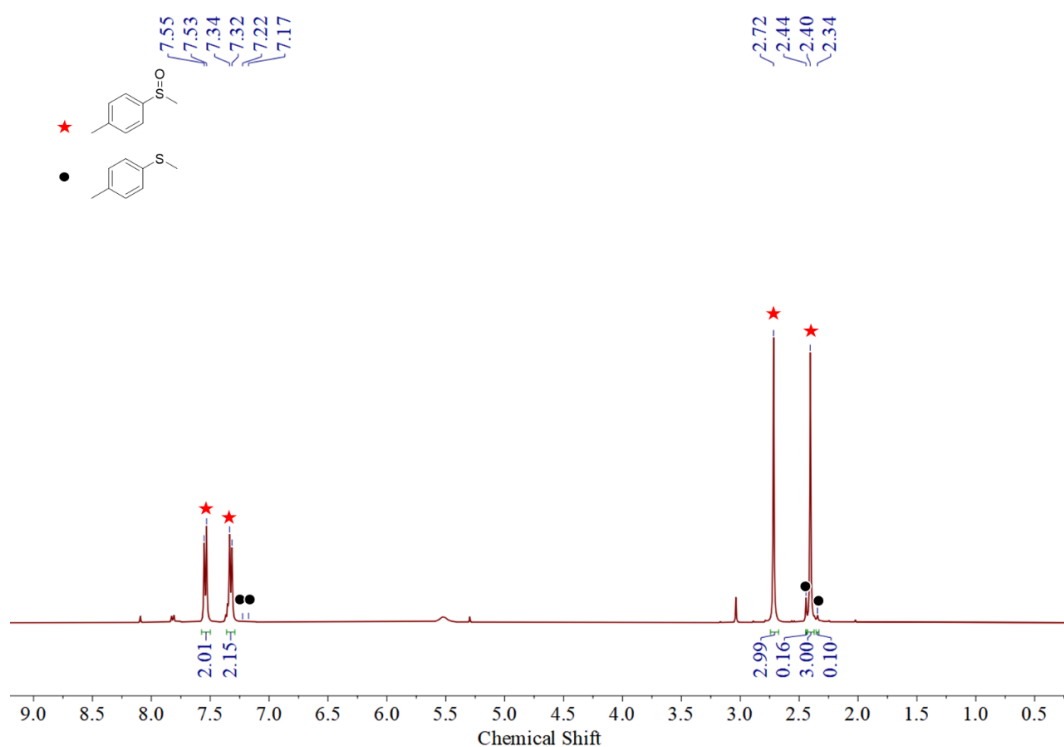


Fig. S27 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of methyl(*p*-tolyl)sulfane with **Py3tpyZn**.

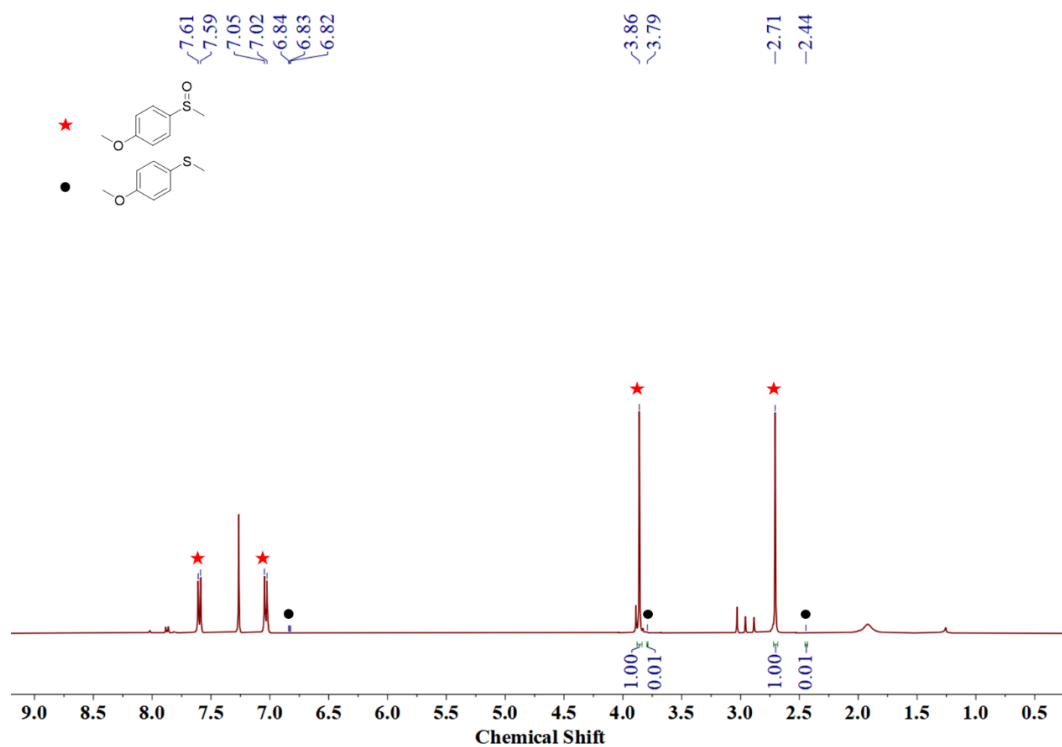


Fig. S28 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of (4-methoxyphenyl)(methyl)sulfane with **Py3tpyZn**.

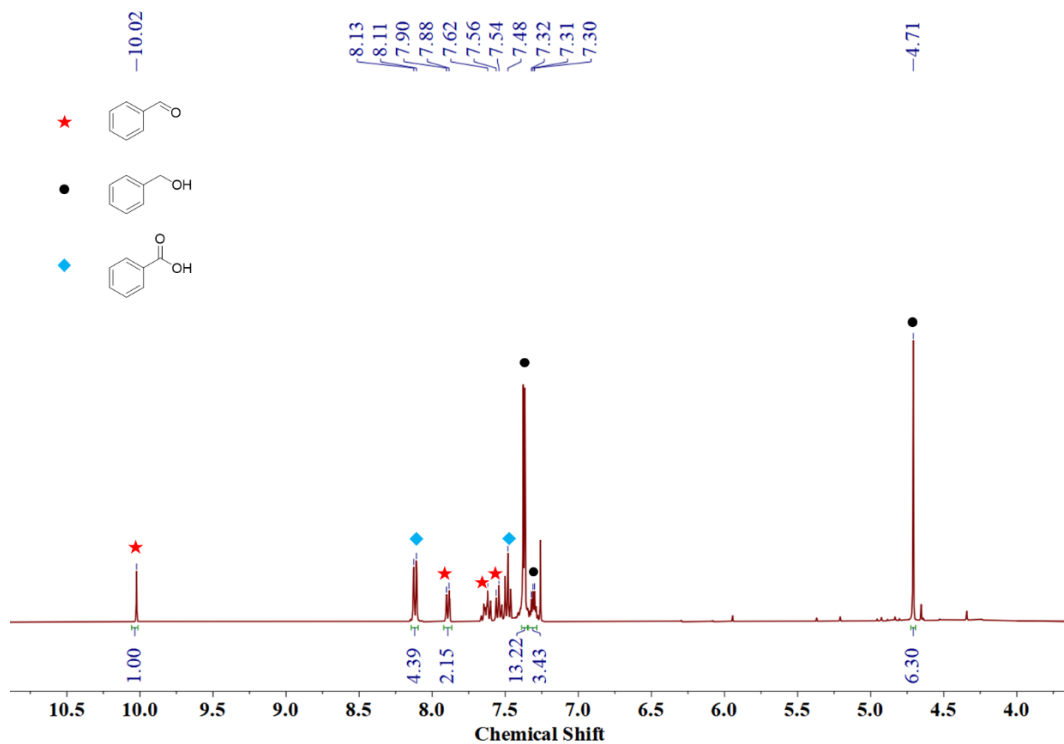


Fig. S29 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of phenylmethanol with Py3tpyZn.

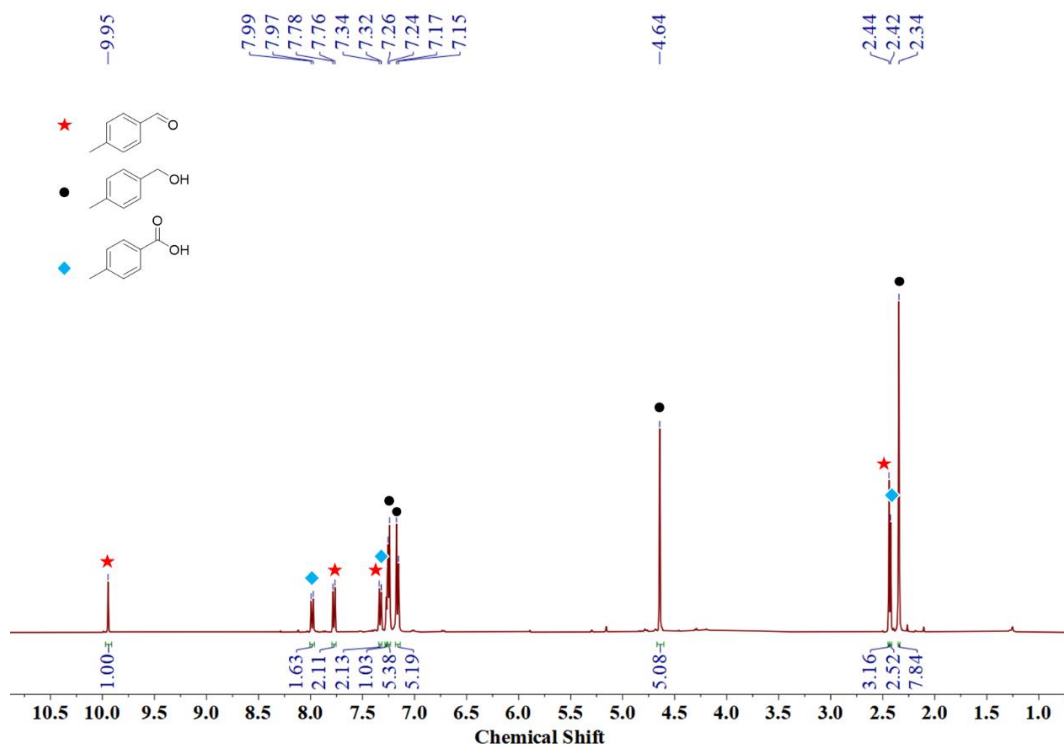


Fig. S30 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of *p*-tolylmethanol with Py3tpyZn.

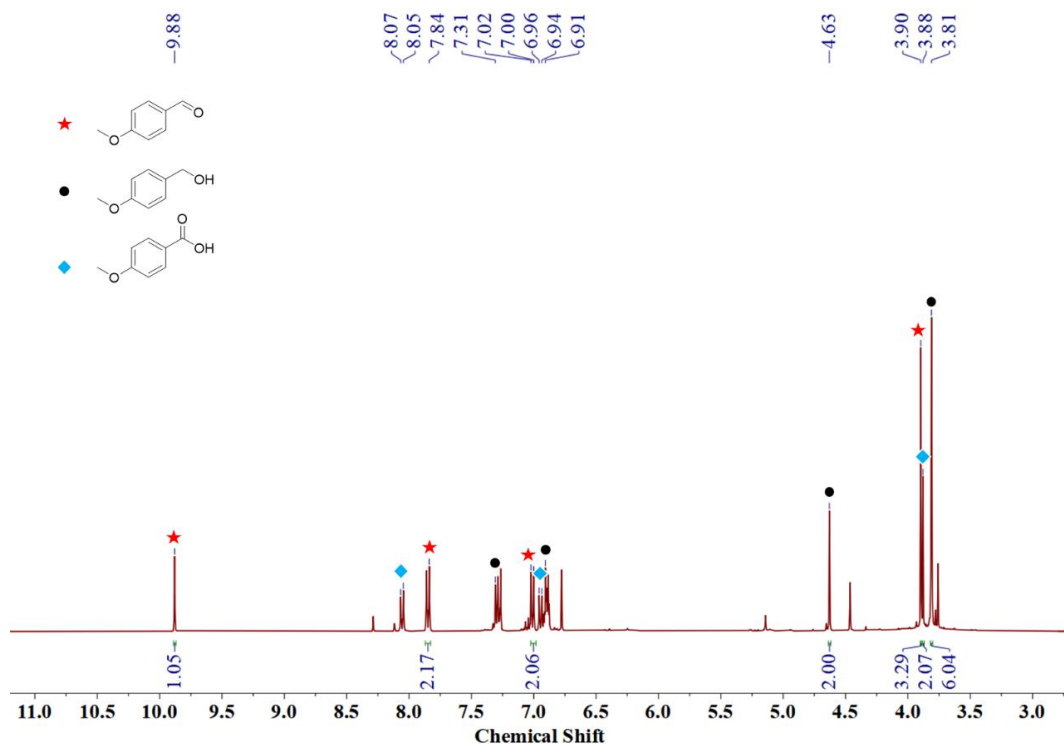


Fig. S31 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of (4-methoxyphenyl)methanol with **Py3tpyZn**.

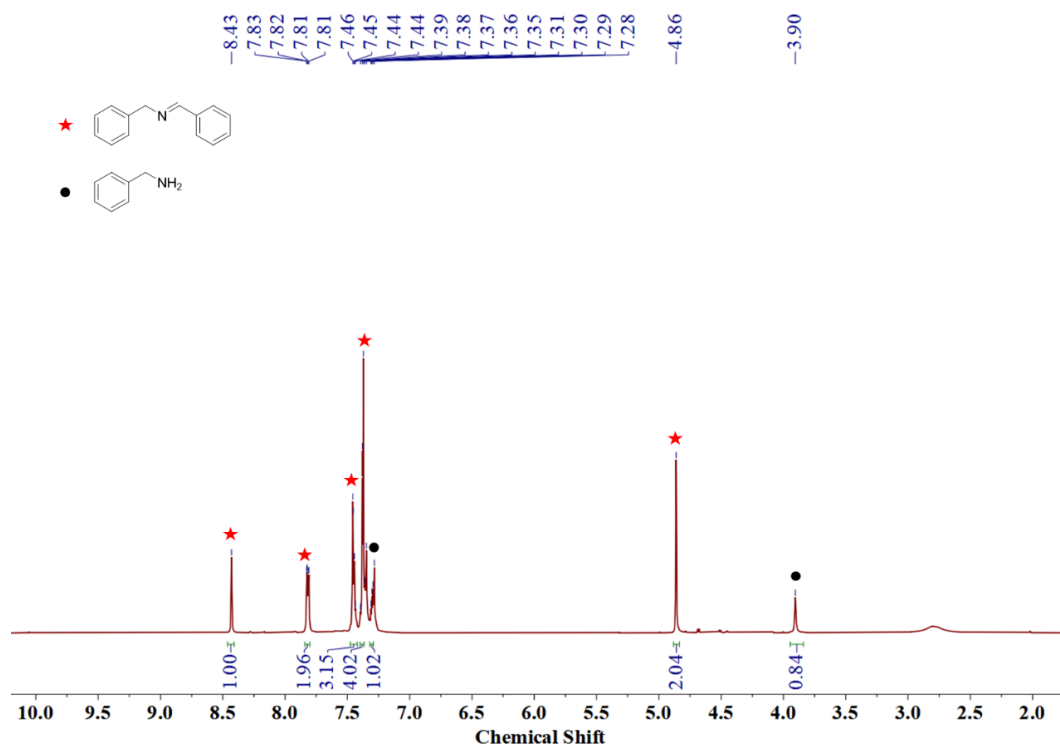


Fig. S32 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of N-benzyl-1-phenylmethanimine with **Py3tpyZn**.

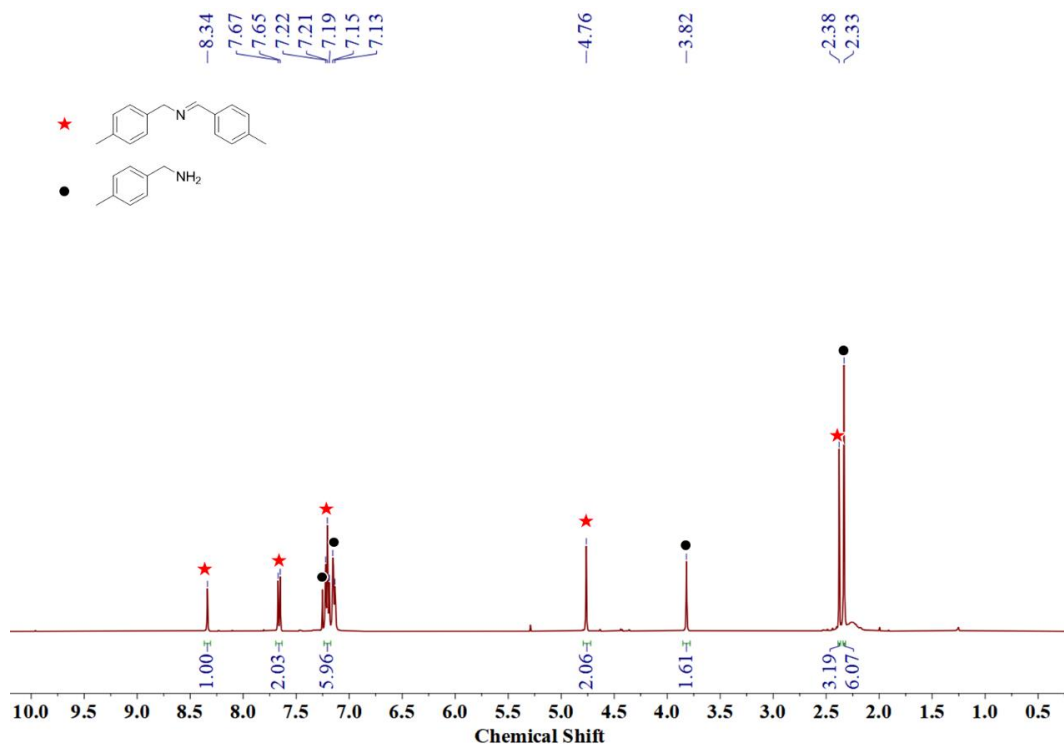


Fig. S33 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of *p*-tolylmethanamine with **Py3tpyZn**.

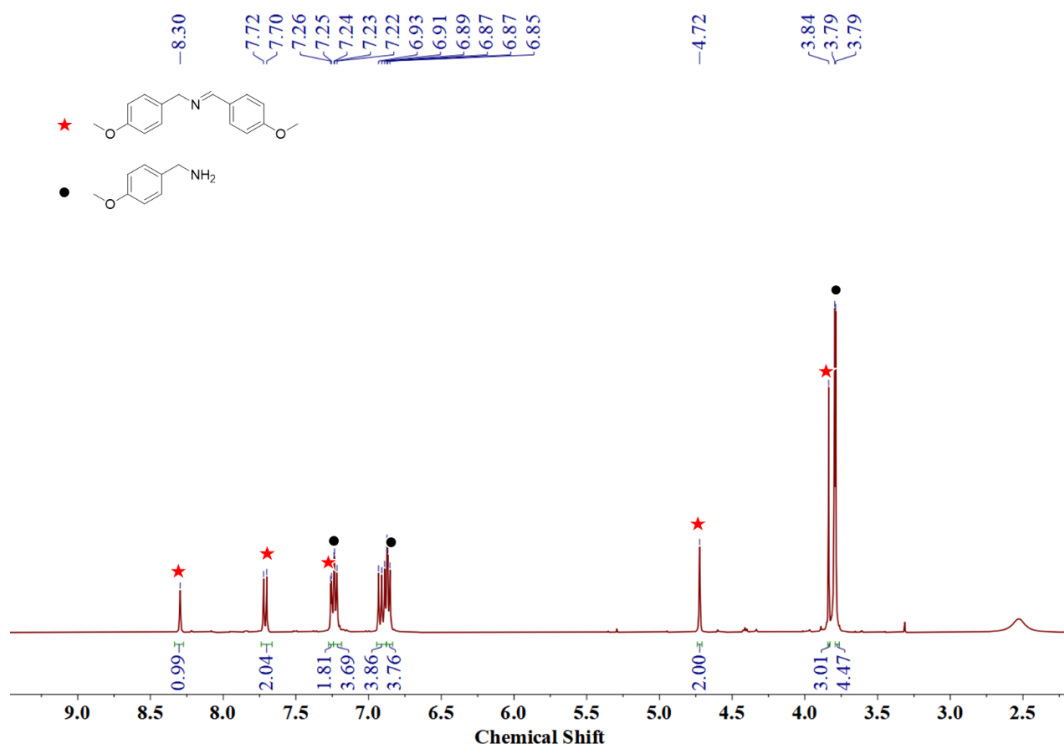


Fig. S34 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of (4-methoxyphenyl)methanamine with **Py3tpyZn**.

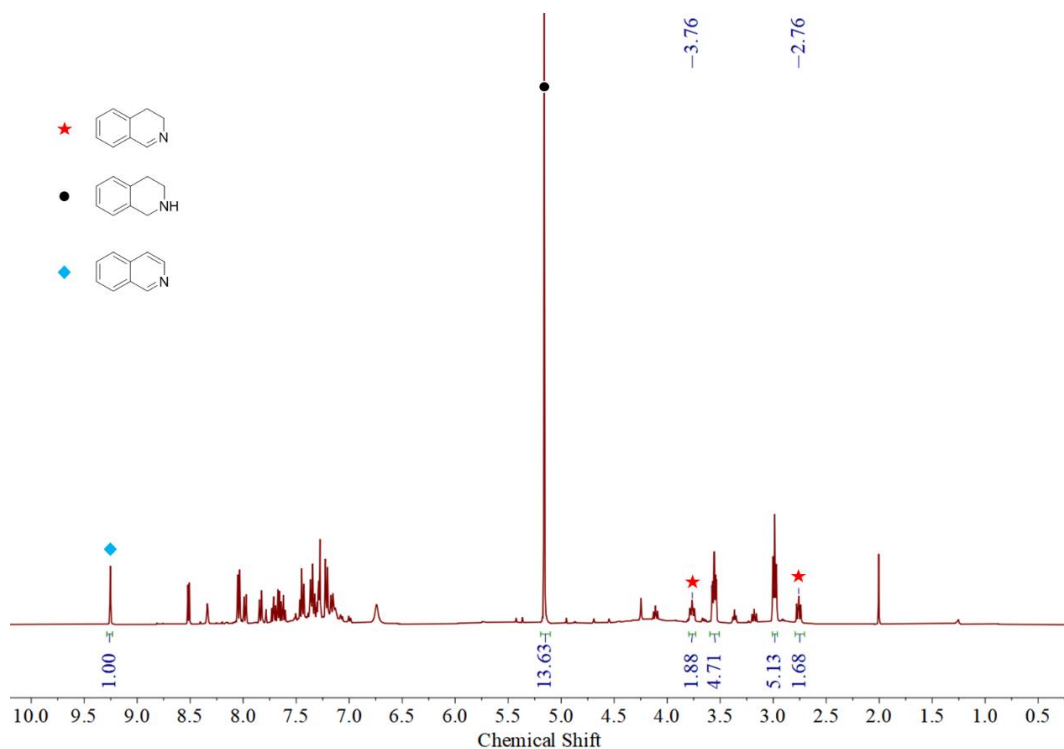


Fig. S35 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of 1,2,3,4-tetrahydroisoquinoline with **Py3tpyZn**.

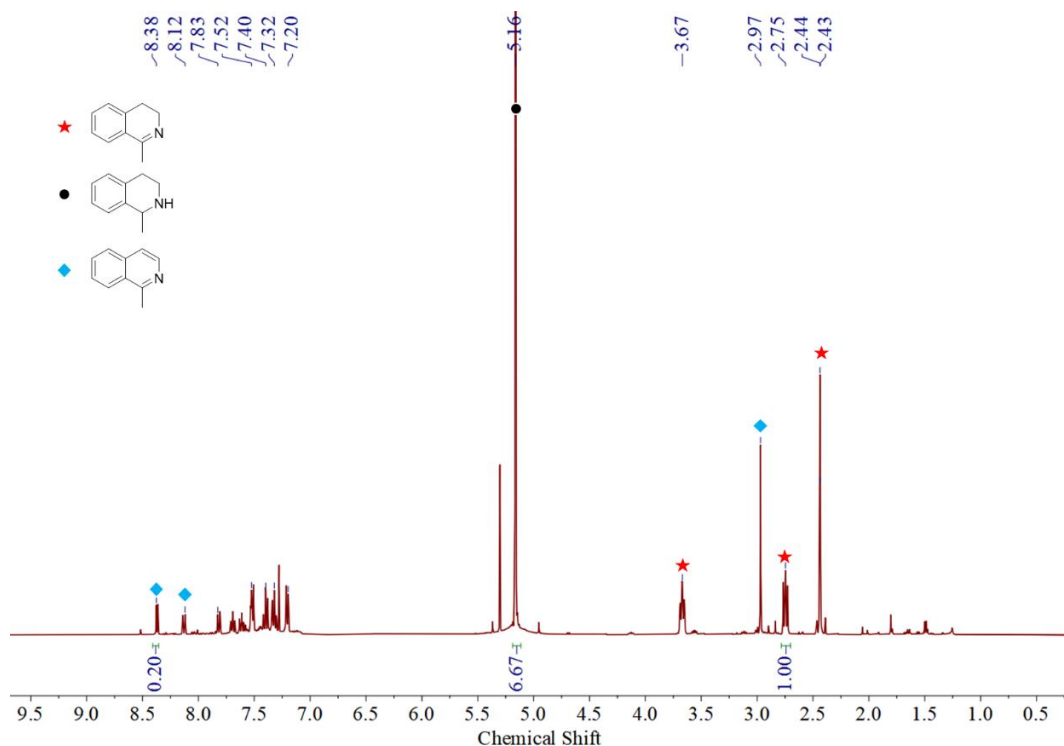


Fig. S36 ^1H NMR spectrum of the reaction solution after aerobic photooxidation of 1-methyl-1,2,3,4-tetrahydroisoquinoline with **Py3tpyZn**.

References

1. L. Chen, T. Liu and D. Chao, *Nano Res.*, 2022, **15**, 5902-5911.