Supporting Information for

Covalent organic framework as photocatalyst for window ledge cross-dehydrogenative coupling reactions

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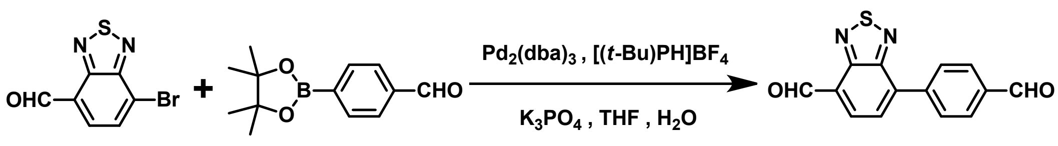
Contents

1. Materials and measurements

The synthetic procedures were performed under argon atmosphere. Commercial chemicals (from sigma-Aldrich, JK Chemical and TCI) were used as received. Compound 1 and TPPy were purchased from Zhi-yan Inc., Nanjing.

^{1}H-NMR and ^{13}C-NMR spectra of intermedia products, monomers and catalytic products were recorded at 400MHz on a Bruker Avance spectrometer with tetramethylsilane (TMS) as the internal standard. Powder X-ray diffraction (PXRD) data were collected using a D8 ADVANCE X-ray with Cu Kα radiation (λ = 1.5405 Å). Gas chromatography (GC) analysis was performed on an Agilent 7890B GC. Fourier Transform Infrared (FT-IR) spectra in the region of 400-4000cm^{-1} were obtained with a Perkin-Elmer 1600 FT-IR spectrometer. Ultraviolet–visible (UV−vis) absorption spectra were recorded on a Shimadzu UV-2600 Double Beam UV−vis Spectrophotometer. Cyclic voltammetry (CV) measurement was performed on a CHI660E electrochemical workstation in a three-electrode system. The working electrode was prepared by dropcasting an 5% Nafion (50 uL) suspension of COF (0.2 mg) and carbon black (0.7 mg) onto a glassy carbon electrode. The auxiliary electrode and reference electrode were platinum-wire and Ag/$AgNO_3$, and the electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, Ferrocene was used as a standard to calculate the energy levels vs. vacuum. Thermogravimetric analysis (TGA) was performed on a TGA/DSC 3+ in the temperature range of 30-800 ºC under an nitrogen atmosphere and a heating rate of 10 °C/min. Transmission electron microscopy (TEM) analysis was performed on a JEOL 2100 Electron Microscope at an operating voltage of 200 kV. Scanning electron microscopy (SEM) images were performed on a SUB010 scanning electron microscope with acceleration voltage of 20 kV. Solid state ^{13}C CP-MAS spectrum was acquired at 100.38 MHz using a 4 mm MAS NMR probe with a spinning rate of 8 kHz and a 2 s recycle delay. N_2 adsorption-desorption isotherm was obtained using an ASAP 2020/TriStar 3000 (Micromeritics) apparatus measured at 77 K, the sample was degassed at 100 ºC for 12 h under high vacuum before analysis. Highresolution mass spectrometry (HRMS) analysis was detected by Bruker maXis ultrahigh-resolution-TOF mass spectrometer. The models of LED lamp is PL-SX100A. Electron paramagnetic resonance (EPR) spectra was measured by Bruker A300 EPR Spectroscopy. The elemental analysis was determined by Elementar Vario EL (Germany). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 X-ray photoelectron spectrometer with a monochromatized Al Kα X-ray source (1486.71 eV). the CHNS analysis was performed by Elementar: UNICUBE. The electrochemical impedance spectra (EIS) was performed by Correst Electrochemical Workstation CS310H.

2. Synthesis of PBT and TPPy-PBT-COF



1 2 PBT

Scheme S1 Chemical Structure of **PBT** and its synthetic route.

Synthesis of PBT. To a 100 mL pressure tube was added 7-bromo-benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (**1**, 500 mg, 2.06 mmol), 4-formylphenylboronic acid pinacol cyclic ester (**2**, 525.13 mg, 2.26 mmol), [(*t*-Bu)PH]BF_4 (41.77 mg, 0.14 mmol), 1 mL K_3PO_4 aqueous solution (2M) and 10 mL THF. Then the mixture was degassed-inflated with nitrogen three times before $Pd_2(dba)_3$ (37.67 mg, 0.04 mmol) was added. The reaction system was heated up to 80 °C for 24 h. Then the mixture was cooled to room temperature and poured into water, a yellowish solid precipitated, and then the precipitate was filterd and dried in a vacuum oven. The crude product was purified by silica gel chromatography (dichloromethane : petroleum ether, v/v = 1 : 1 as eluent) to obtain **PBT** as a yellowish powder (380 mg, 69% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 10.77 (s, 1H), 10.07 (s, 1H), 8.29-8.27 (d, *J* = 8.0 Hz, 1H), 8.11-8.01 (dd, *J* = 32.0, 8.0 Hz, 4H), 7.91-7.89 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 191.68, 188.81, 153.75, 153.71, 142.06, 138.73, 136.62, 131.99, 130.25, 130.00, 127.87, 127.16. (EI): Found: 269.04. (calcd for $C_{14}H_8N_2O_2S$+H: 269.04).

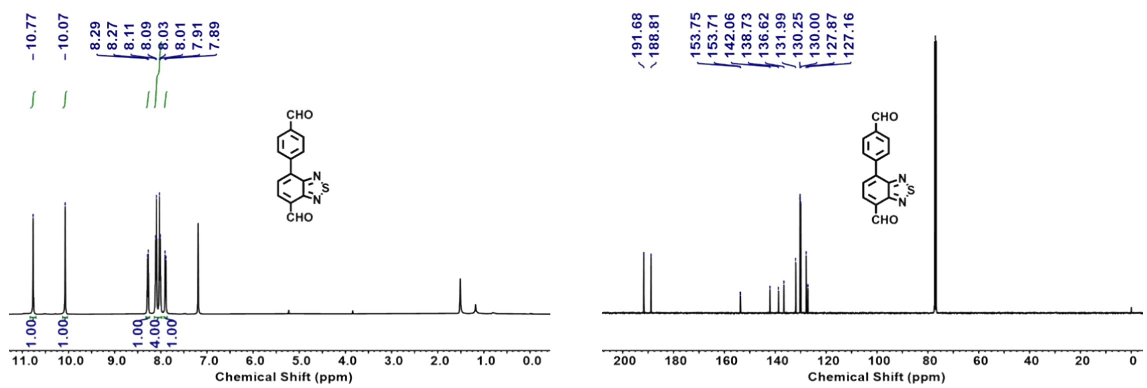


Fig. S1 ^{1}H-NMR and ^{13}C-NMR of the monomer **PBT**.

Synthesis of TPPy-PBT-COF. A 10 mL Pyrex tube was charged with 1,3,6,8-tetra (4-aminophenyl) pyrene (TPPy, 28 mg, 0.04 mmol), 7-(4-formylphenyl)benzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (**PBT,** 21.6 mg, 0.08 mmol), and *o*-dichlorobenzene/EtOH (3:1 v/v, 2 mL). After the mixture was sonicated for 1 min, a yellowish suspension was obtained. Subsquently, 0.2 mL of acetic acid (6 M) were added and the mixture was sonicated for another 20s again. Afterwards, the tube was flash frozen at 77 K using a liquid N_2 bath and degassed by three freeze-pump-thaw cycles, sealed under vacuum and then heated at 120 °C for 3 days. A red precipitate was formed, which was collected by sucking filtration and throughly washed with acetone, anhydrous ethanol, tetrahydrofuran, and dichloromethane, respectively. The collected sample was dried under vacuum at 120°C for 24 h to give an red powder (44 mg, 95% yield). Elemental analysis (%): Anal. Calcd. For $(C_{68}H_{38}N_8S_2)_n$: C, 79.20; H, 3.71; N, 10.87; S, 6.22. Found: C, 77.50; H, 4.02; N, 10.19; S, 5.82.

3. Simulated stacking models

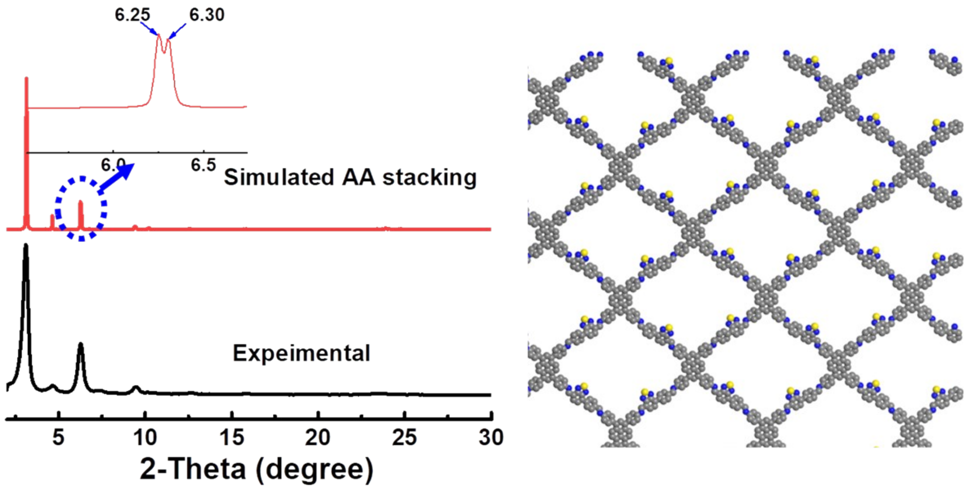


Fig. S2 Comparision of the experimental (black) and simulated (red) AA stacking PXRD patterns of **TPPy-PBT-COF** and the top view of the simulated structure of AA stacking model.

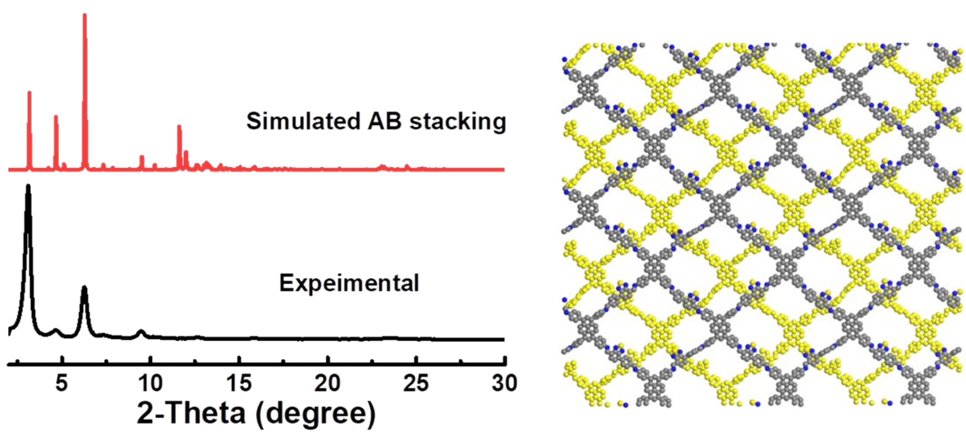


Fig. S3 Comparision of the experimental (black) and simulated (red) AB stacking PXRD patterns of **TPPy-PBT-COF** and the top view of the simulated structure of AB stacking model.

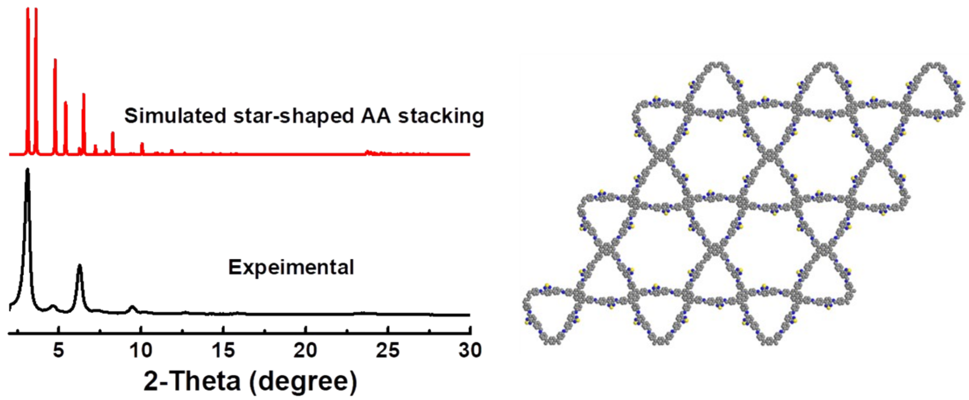


Fig. S4 Comparision of the experimental (black) and simulated (red) star-shaped AA stacking PXRD patterns of **TPPy-PBT-COF** and the top view of the simulated structure of star-shaped AA stacking model.

4. Characterization of TPPy-PBT-COF

4.1. XPS spectra of the COF

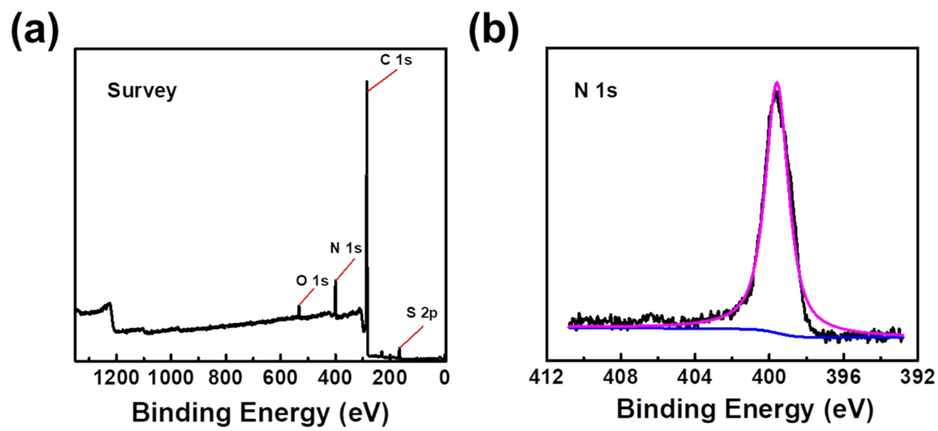


Fig. S5 (a) Survey and (b) N1s spectrum of **TPPy-PBT-COF**. The single peak at 399.5 eV is ascribed to C=N linkage.

4.2. BET surface area and pore sizes distribution

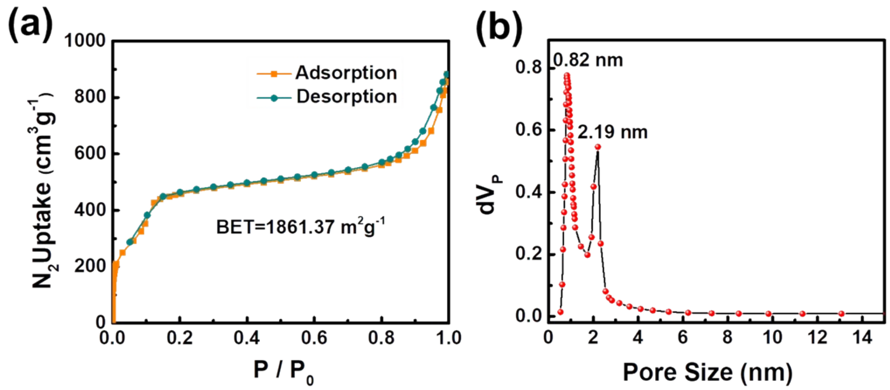


Fig. S6 (a) N_2 adsorption-desorption isotherms. (b) Pore size distribution profile.

4.3. TGA curve of TPPy-PBT-COF

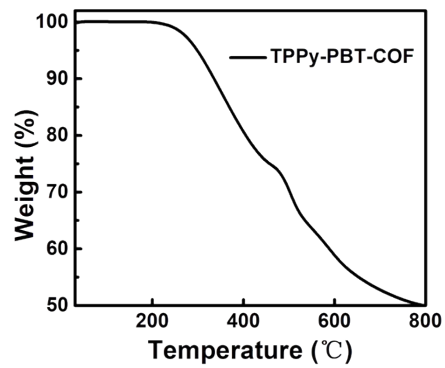


Fig. S7 TGA curve of **TPPy-PBT-COF**.

4.4. SEM and TEM images of TPPy-PBT-COF

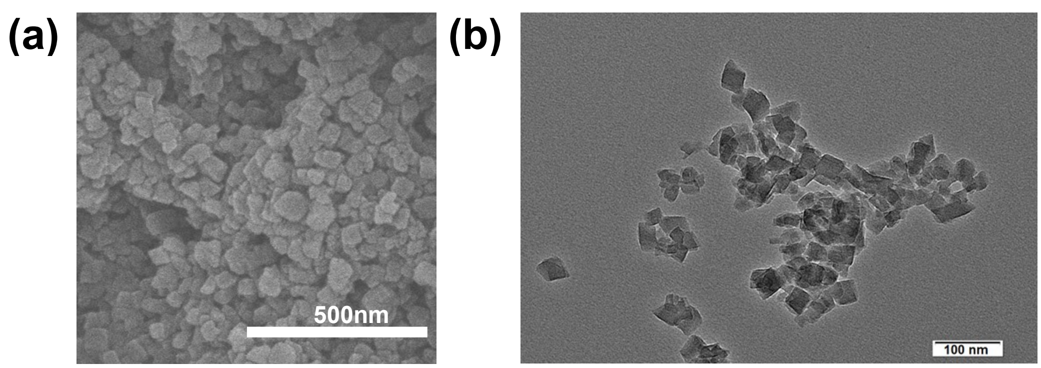


Fig. S8 Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of **TPPy-BPT-COF**.

4.5. DFT calculations

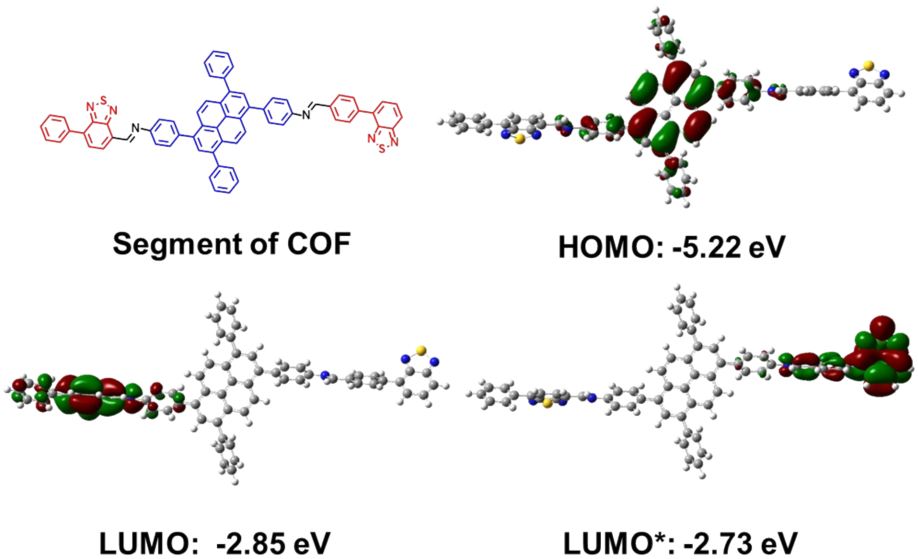


Fig. S9 Optimized molecular geometries and frontier molecular orbitals for the segment of **TPPy-PBT-COF** at B3LYP/6-311G(d, p) level, LUMO and LUMO* are degenerate orbital energy levels.

4.6. CV curves

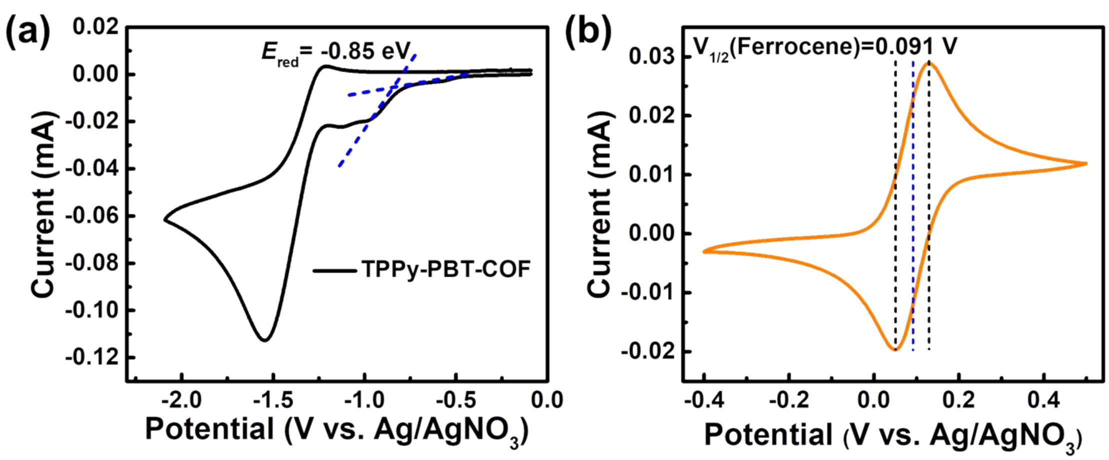


Fig. S10 Cyclic voltammetry graph of (a) **TPPy-PBT-COF**, (b) ferrocene.

The energy level of TPPy-PBT-COF vs. vacuum were derived from the following equations.

$$E_{\mathrm{LUMO}} = -(E_{\mathrm{red}}(\mathrm{onset}) - E_{1/2}(\mathrm{Fc}) + 4.8)\ \mathrm{eV}$$

$$E_{\mathrm{HOMO}} = E_{\mathrm{LUMO}} - E_{\mathrm{g}}$$

4.7. Electrochemical impedance spectra (EIS) of COF

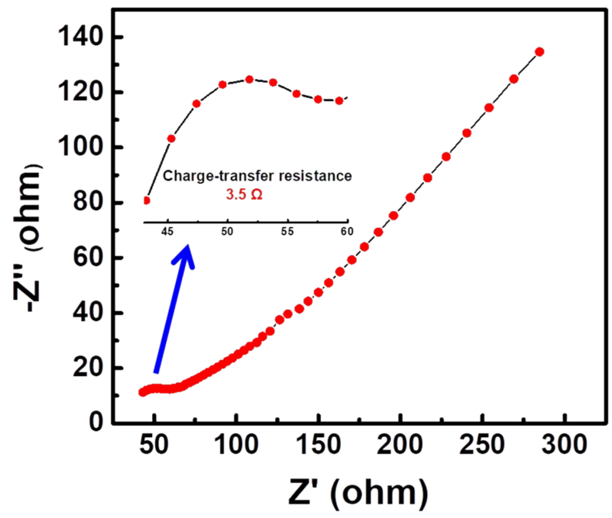


Fig. S11 Electrochemical impedance spectroscopy (EIS) Nyquist plots of **TPPy-PBT-COF**.

5. Typical synthesis of 3a with the irradiation of LED lamp and natural sunlight

5.1. The synthetic procedure for substrate 1a

The compound **1a** used in the photocatalysis were synthesized according to the literature.[1]

1a: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.35-7.30 (m, 2H), 7.25-7.18 (m, 4H), 7.04-7.02 (d, *J* = 8.0 Hz, 2H), 6.89-6.85 (t, *J* = 8.0 Hz, 1H), 4.45 (s, 2H), 3.62-3.59 (t, *J* = 5.8 Hz, 2H), 3.04-3.01 (t, *J* = 5.8 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 150.56, 134.89, 134.48, 129.23, 128.55, 126.56, 126.35, 126.05, 118.69, 115.17, 50.75, 46.55, 29.14.

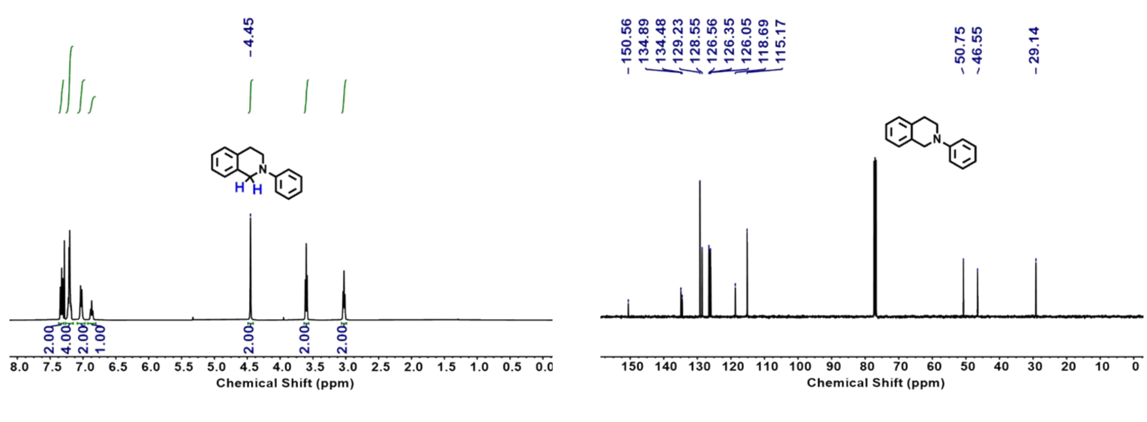


Fig. S12 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **1a**.

5.2. The synthetic procedure for 3a.

A 10 mL quartz tube was charged with **1a** (0.2 mmol), L-proline (0.06 mmol), **TPPy-PBT-COF** (5 mg), acetone (0.5 mL) and methanol (2 mL). The mixture was bubbled with oxygen and stirred, then the tube was irradiated with LED lamp or natural sunlight in room temperature. After reaction, the solution was centrifuged and the supernatant was removed by rotary evaporation. Yields were determined by GC and ^{1}H-NMR spectroscopy with 0.2 mmol diphenylacetonitrile (DPAT) as internal standard.

3a: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.20-7.15 (m, 2H), 7.12-7.04 (m, 4H), 6.87-6.85 (d, J = 8.0 Hz, 2H), 6.72-6.69 (t, J = 7.2 Hz, 1H), 5.34-5.31 (t, J = 5.7 Hz, 1H), 3.60-3.55 (m, 1H), 3.49-3.42 (m, 1H), 3.02-2.94 (m, 2H), 2.78-2.72 (m, 2H), 2.00 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 207.33, 148.88, 139.38, 134.46, 129.39, 128.71, 126.85, 126.32, 118.28, 114.78, 54.82, 50.23, 42.08, 31.16, 27.23.

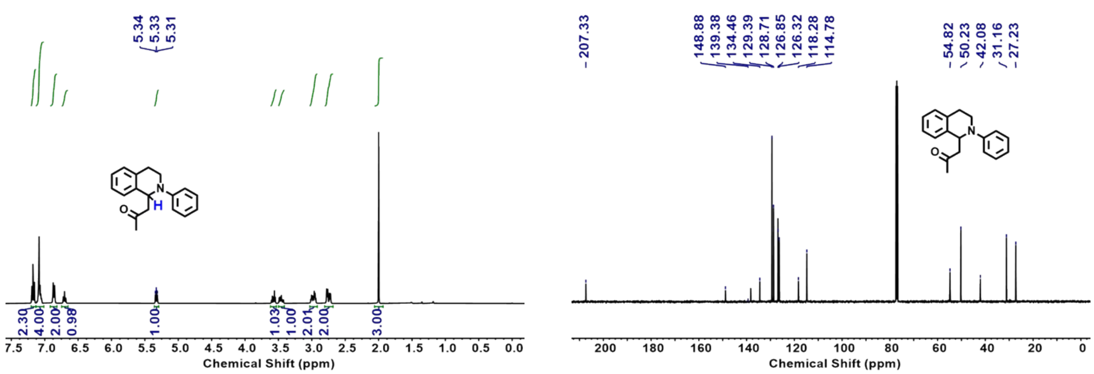


Fig. S13 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3a**.

5.3. Yields of 3a determined by ^{1}H-NMR and GC analysis

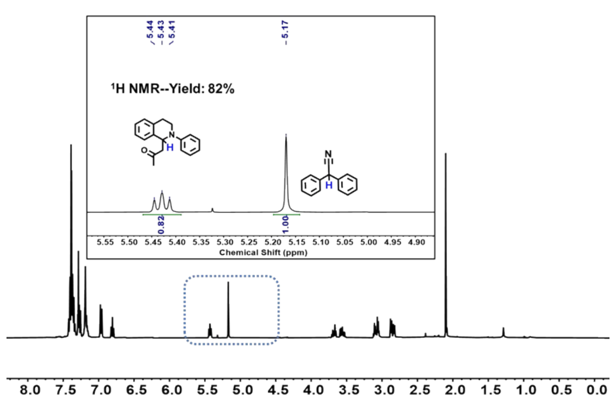


Fig. S14 Yield of **3a** determined by ^{1}H-NMR with DPAT as internal standard (**with white LED**).

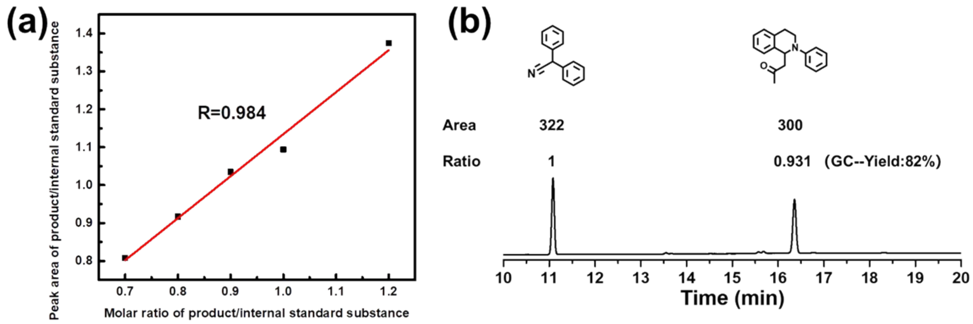


Fig. S15 Yield of **3a** determined by GC with DPAT as internal standard (**with white LED**).

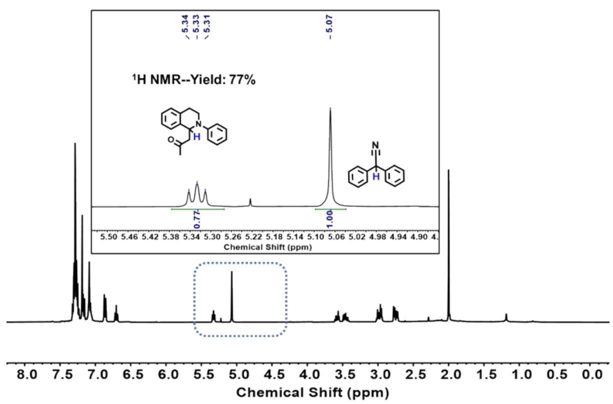


Fig. S16 Yield of **3a** determined by ^{1}H-NMR with DPAT as internal standard (**with blue LED**).

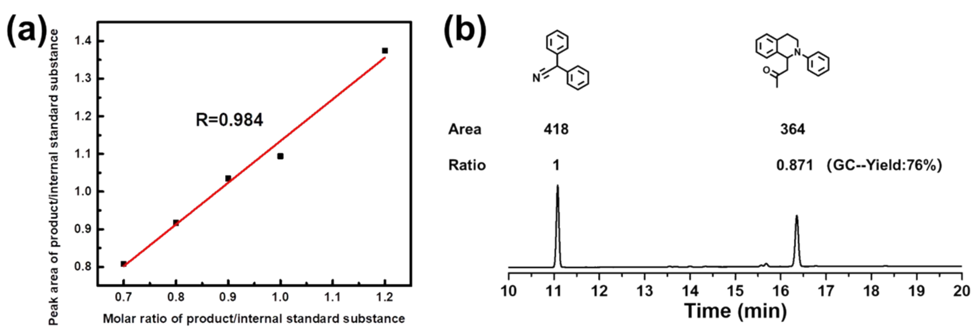


Fig. S17 Yield of **3a** determined by GC with DPAT as internal standard (**with blue LED**).

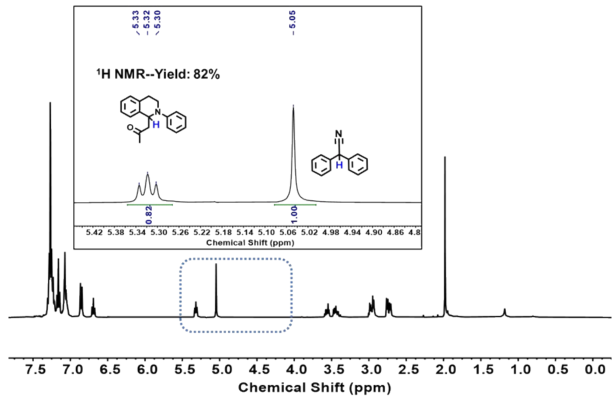


Fig. S18 Yield of **3a** determined by ¹H-NMR with DPAT as internal standard (**with green LED**).

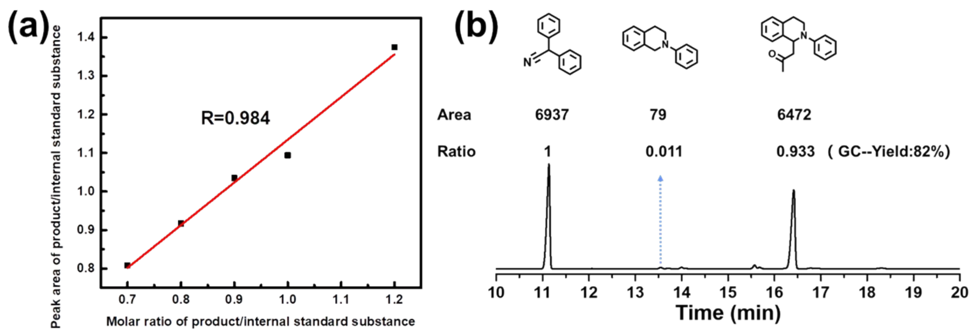


Fig. S19 Yield of **3a** determined by GC with DPAT as internal standard (**with green LED**).

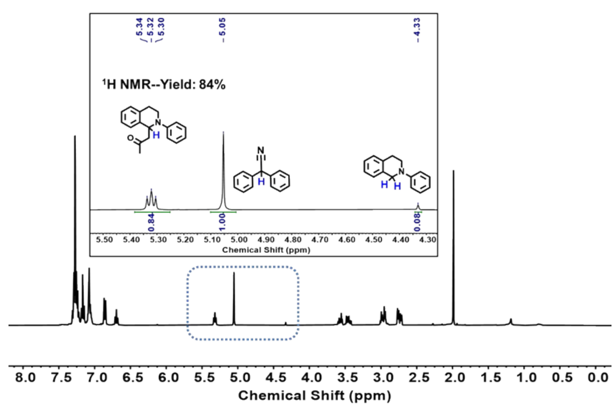


Fig. S20 Yield of **3a** determined by ¹H-NMR with DPAT as internal standard (**with sunlight**).

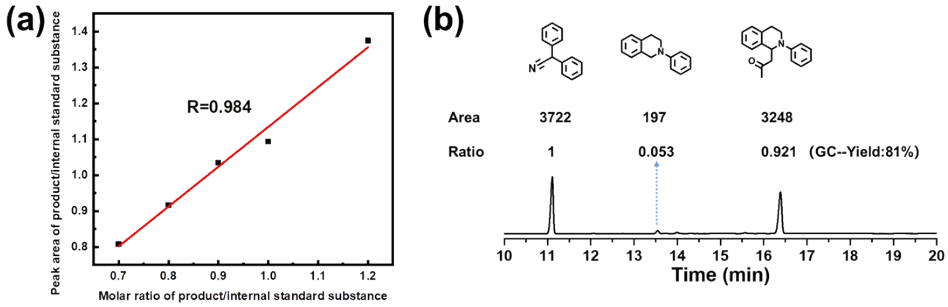


Fig. S21 Yield of **3a** determined by GC with DPAT as internal standard (**with sunlight**).

5.4. Photograph of photocatalytic device under the irradiation of natural sunlight

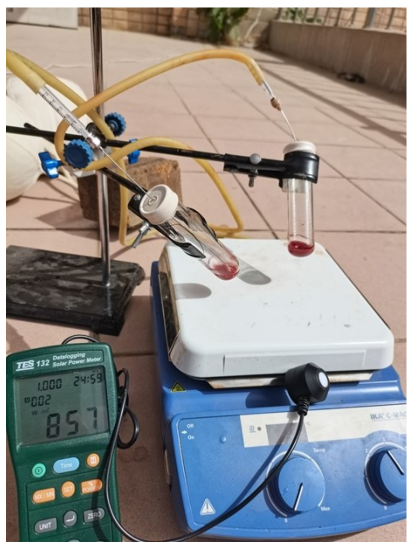


Fig. S22 photocatalytic devices under the irradiation of natural sunlight.

6. Control experiments

Table S1. The control experiment determined by ^{1}H-NMR analysis.

Reactant	Solvent	Light	COF	O_2	L-proline (mol%)	Time (h)	T.M.	Yield (%)
1a	CH_3CN	√	√	√	30	9	3a	72
1a	Toluene	√	√	√	30	9	3a	51
1a	CH_3OH	√	√	√	30	9	3a	84
1a	CH_3OH	√	√	-	30	9	3a	0
1a	CH_3OH	√	-	√	30	9	3a	27
1a	CH_3OH	-	√	√	30	9	3a	0
1a	CH_3OH	√	√	√	0	9	3a	5
[b]1a	CH_3OH	√	-	√	30	9	3a	44

[b] The monomer **TPPy** (5 mg) was used as catalyst instead of **TPPy-PBT-COF** (5 mg).

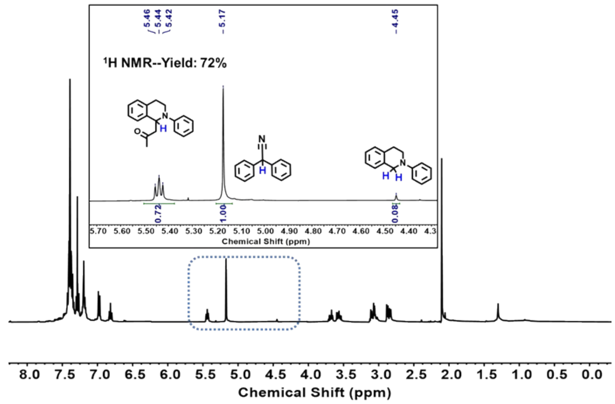


Fig. S23 Yield of **3a** with CH_3CN as solvent.

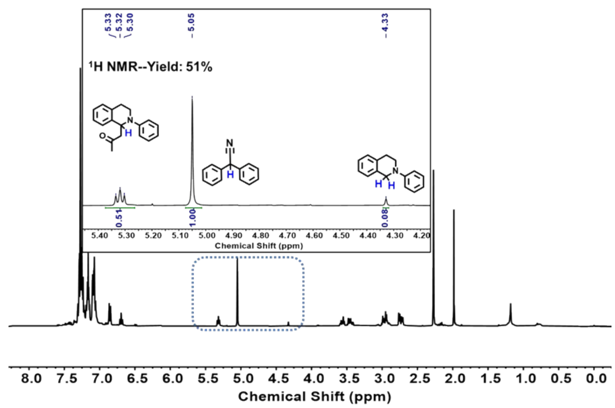


Fig. S24 Yield of **3a** with toluene as solvent.

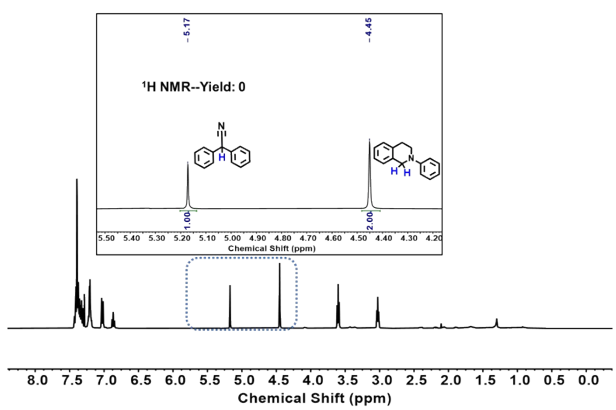


Fig. S25 Yield of **3a** in the absence of O_2.

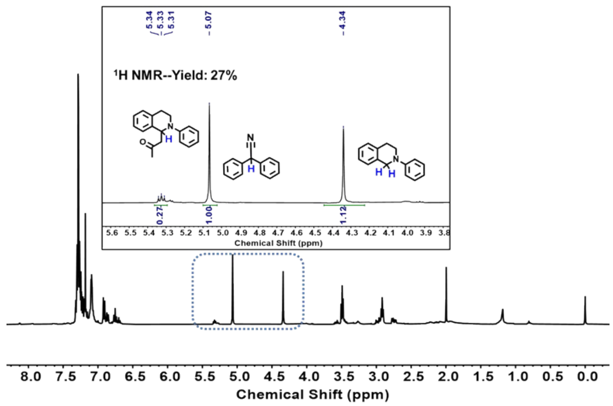


Fig. S26 Yield of **3a** in the absence of **TPPy-PBT-COF**.

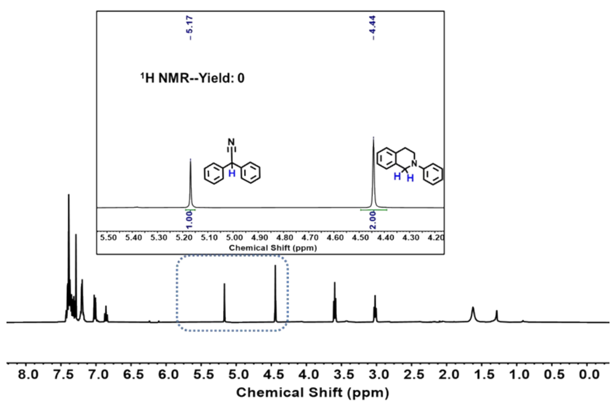


Fig. S27 Yield of **3a** in the absence of light.

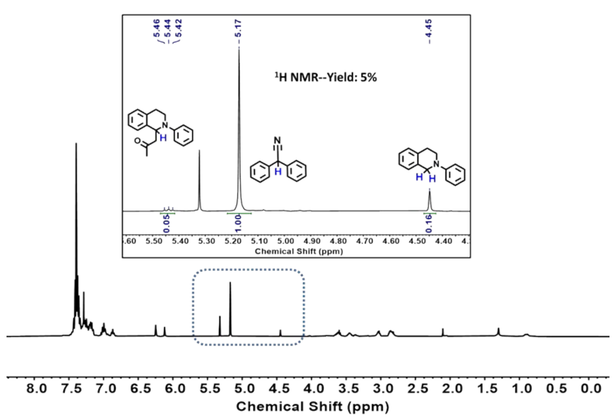


Fig. S28 Yield of **3a** in the absence of L-proline.

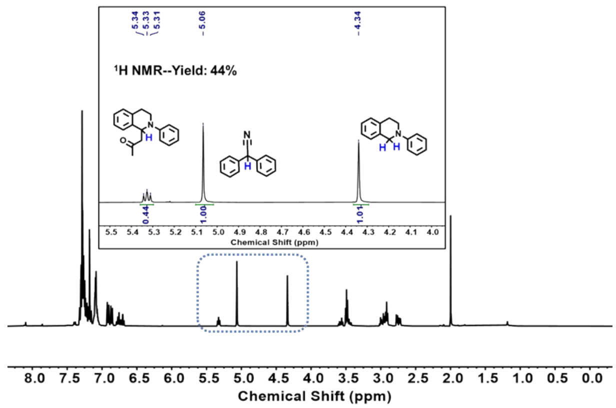


Fig. S29 Yield of **3a** with **TPPy** as catalyst.

7. Subatrate scope and categories of nucleophile

7.1. The synthetic procedures for substrates 1b-1h.

The compounds **1b-1h** used in the photocatalysis were synthesized according to the literature.[1]

1b: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.13-7.01 (m, 6H), 6.87-6.83 (m, 2H), 4.28 (s, 2H), 3.45-3.42 (t, J = 5.9 Hz, 2H), 2.92-2.90 (t, J = 5.9 Hz, 2H), 2.21 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 148.61, 134.75, 134.56, 129.75, 128.63, 128.49, 126.56, 126.29, 125.97, 115.91, 51.53, 47.33, 29.08, 20.44.

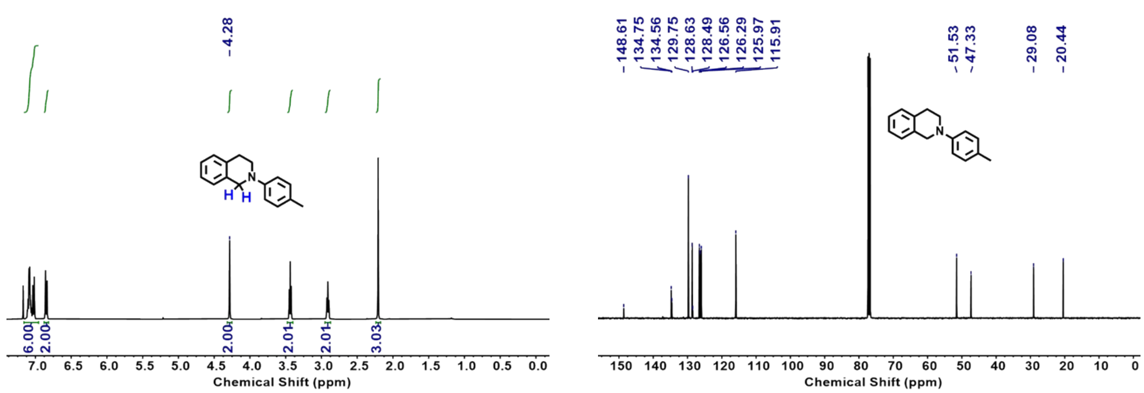


Fig. S30 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **1b**.

1c: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.22-7.12 (m, 4H), 7.01-6.89 (m, 4H), 4.33 (s, 2H), 3.49-3.46 (t, J = 5.9 Hz, 2H), 2.99-2.97 (t, J = 5.9 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 157.96, 155.60, 147.39, 134.54, 134.28, 128.66, 126.53, 126.42, 126.07, 117.24, 117.16, 115.72, 115.50, 51.93, 47.82, 29.03.

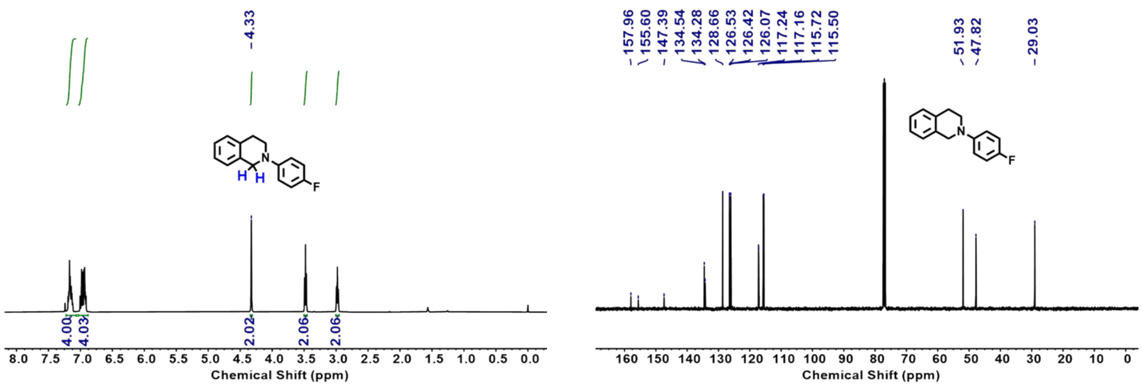


Fig. S31 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **1c**.

1d: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.23-7.15 (m, 5H), 6.72-6.69 (dd, J = 8.0, 4.0 Hz, 1H), 6.64-6.60 (m, 1H), 6.51-6.46 (m, 1H), 4.41 (s, 2H), 3.57-3.54 (t, J = 5.6 Hz, 2H), 3.00-2.97 (t, J = 6.6 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 165.28, 162.87, 152.02, 151.92, 134.87, 134.04, 130.27, 130.17, 128.46, 126.56, 126.24, 109.92, 104.68, 104.46, 101.50, 101.25, 50.12, 45.90, 29.02.

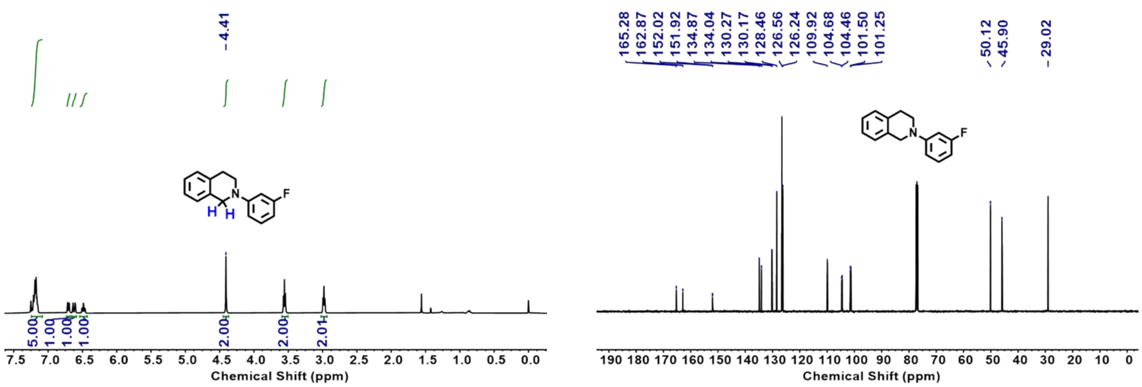


Fig. S32 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **1d**.

1e: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.24-7.13 (m, 6H), 6.90-6.86 (m, 2H), 4.38 (s, 2H), 3.54-3.52 (t, J = 4.0 Hz, 2H), 2.99-2.96 (t, J = 6.0 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 149.07, 134.70, 134.09, 129.03, 128.54, 126.54, 126.51, 126.17, 123.34, 116.16, 50.65, 46.54, 28.97.

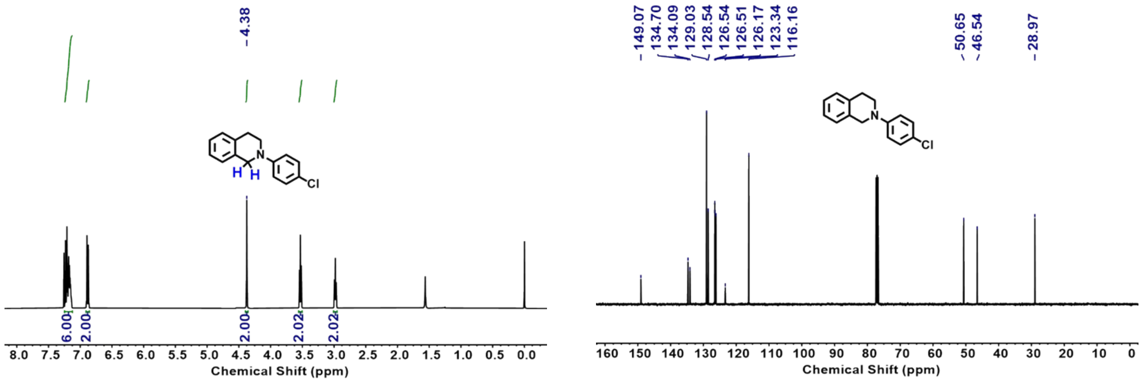


Fig. S33 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **1e**.

1f: ^{1}H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.23-7.16 (m, 5H), 6.92-6.91 (t, J = 2.3 Hz, 1H), 6.84-6.81 (m, 1H), 6.78-6.75 (m, 1H), 4.41 (s, 2H), 3.57-3.54 (t, J = 5.8 Hz, 2H), 3.00-2.97 (t, J = 6.1 Hz, 2H). ^{13}C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 151.39, 135.10, 134.83, 134.01, 130.15, 128.47, 126.58, 126.56, 126.25, 118.00, 114.39, 112.62, 50.09, 45.92, 29.06.

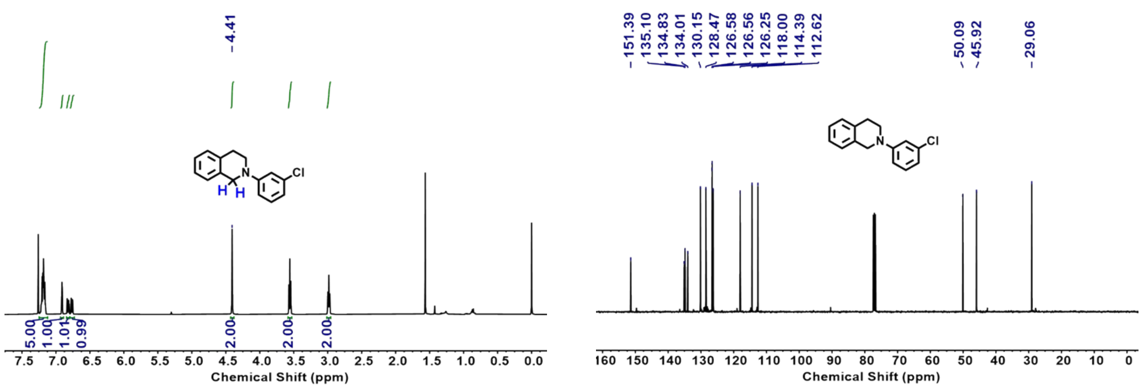


Fig. S34 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **1f**.

1g: ^{1}H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.28-7.24 (d, J = 9.0 Hz, 2H), 7.14-7.05 (m, 4H), 6.75-6.73 (d, J = 9.0 Hz, 2H), 4.28 (s, 2H), 3.45-3.42 (t, J = 5.9 Hz, 2H), 2.90-2.87 (t, J = 5.9 Hz, 2H). ^{13}C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 149.40, 134.71, 134.03, 131.92, 128.52, 126.53, 126.19, 116.50, 110.49, 50.45, 46.34, 28.45.

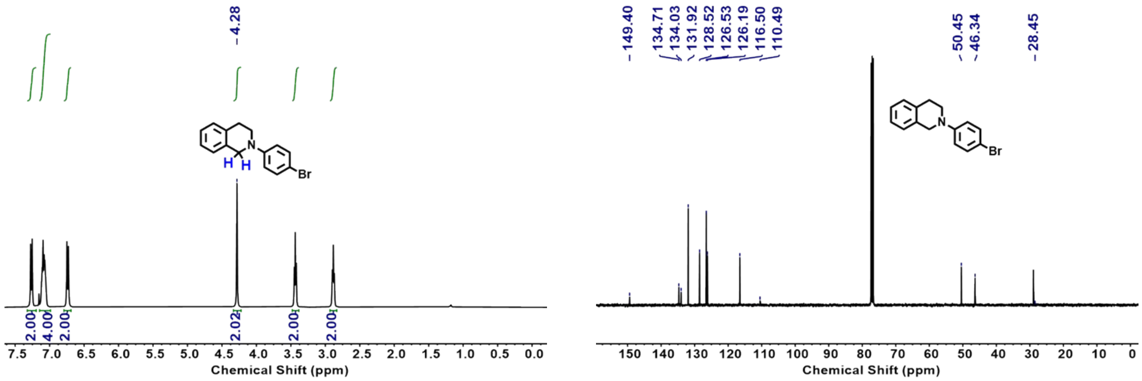


Fig. S35^{1}H-NMR (left) and ^{13}C-NMR (right) of **1g**.

1h: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.57-7.53 (m, 2H), 7.25-7.17 (m, 4H), 6.78-6.75 (d, *J* = 8.8 Hz, 2H), 4.41 (s, 2H), 3.58-3.55 (t, *J* = 5.8 Hz, 2H), 3.02-2.99 (t, *J* = 6.0 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 150.26, 137.81, 134.73, 134.00, 128.49, 126.55, 126.53, 126.20, 116.93, 50.17, 46.06, 28.90.

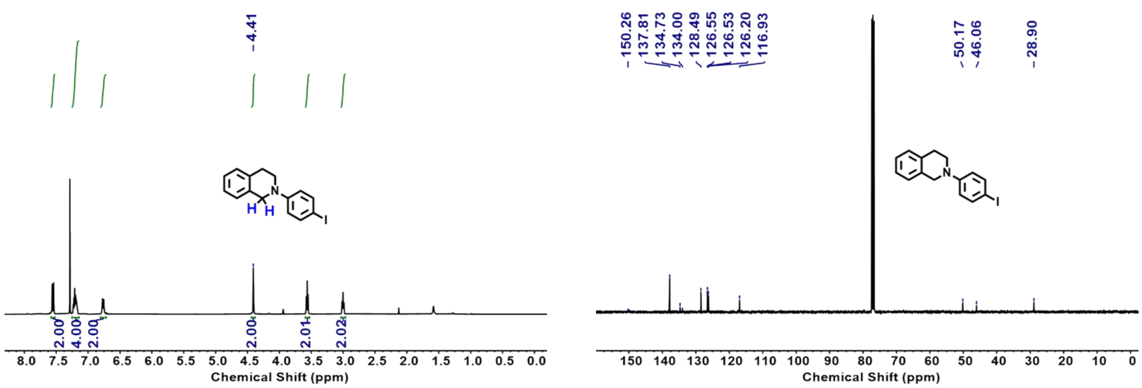


Fig. S36 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **1h**.

7.2. Synthetic procedures for 3b-3h (Mannich reaction).

3b-3h: Same procedures as for **3a** under irradiation of natural sunlight, but now **1b**-**1h** were used as the substrates.

3b: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.21-7.13 (m, 4H), 7.09-7.07 (d, *J* = 8.7 Hz, 2H), 6.90-6.88 (d, *J* = 8.7 Hz, 2H), 5.39-5.35 (t, *J* = 6.5 Hz, 1H), 3.69-3.63 (m, 1H), 3.56-3.49 (m, 1H), 3.10-3.02 (m, 2H), 2.86-2.77 (m, 2H), 2.28 (s, 3H), 2.10 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100

MHz) δ (ppm): 207.43, 146.90, 138.30, 134.41, 129.86, 128.82, 128.00, 126.87, 126.73, 126.23, 115.70, 55.20, 50.08, 42.21, 31.04, 26.99, 20.36.

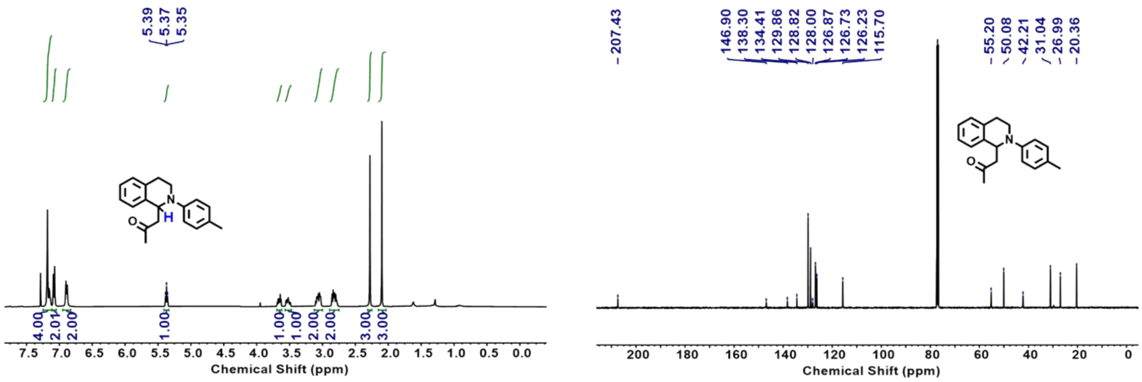


Fig. S37 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3b**.

3c: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.20-7.11 (m, 4H), 6.97-6.86 (m, 4H), 5.30-5.27 (t, *J* = 6.5 Hz, 1H), 3.61-3.55 (m, 1H), 3.52-3.46 (m, 1H), 3.06-2.98 (m, 2H), 2.82-2.73 (m, 2H), 2.08 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 207.21, 157.72, 155.36, 145.77, 138.05, 134.24, 128.90, 126.83, 126.35, 117.22, 117.14, 115.80, 115.58, 55.58, 50.12, 42.66, 31.05, 26.74.

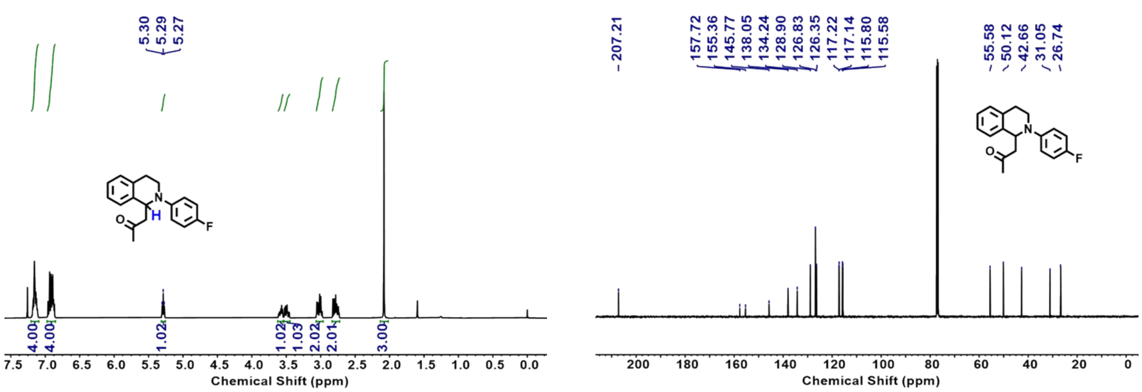


Fig. S38 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3c**.

3d: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.21-7.13 (m, 5H), 6.70-6.67 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.62-6.58 (dt, *J* = 12.7, 2.6 Hz, 1H), 6.48-6.42 (td, *J* = 8.2, 2.4 Hz, 1H), 5.39-5.35 (t, *J* = 5.2 Hz, 1H), 3.62-3.50 (m, 2H), 3.09-3.02 (m, 2H), 2.89-2.81 (m, 2H), 2.09 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 207.03, 165.34, 162.93, 150.44, 150.33, 137.95, 134.33, 130.47, 130.36, 128.62, 127.06, 126.91, 126.48, 109.45, 109.42, 104.34, 104.13, 101.02, 100.76, 54.56, 50.24, 42.25, 31.23, 27.25.

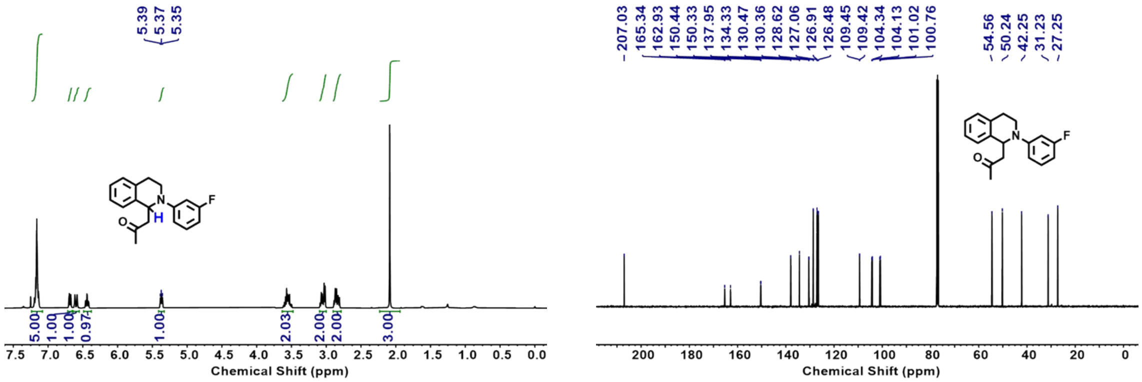


Fig. S39 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3d**.

3e: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.20-7.12 (m, 6H), 6.87-6.83 (m, 2H), 5.36-5.32 (t, J = 6.7 Hz, 1H), 3.62-3.47 (m, 2H), 3.07-3.00 (m, 2H), 2.85-2.78 (m, 2H), 2.08 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 207.07, 147.48, 137.95, 134.23, 129.16, 128.74, 126.98, 126.84, 126.43, 122.99, 115.82, 54.78, 50.16, 42.22, 31.16, 27.03.

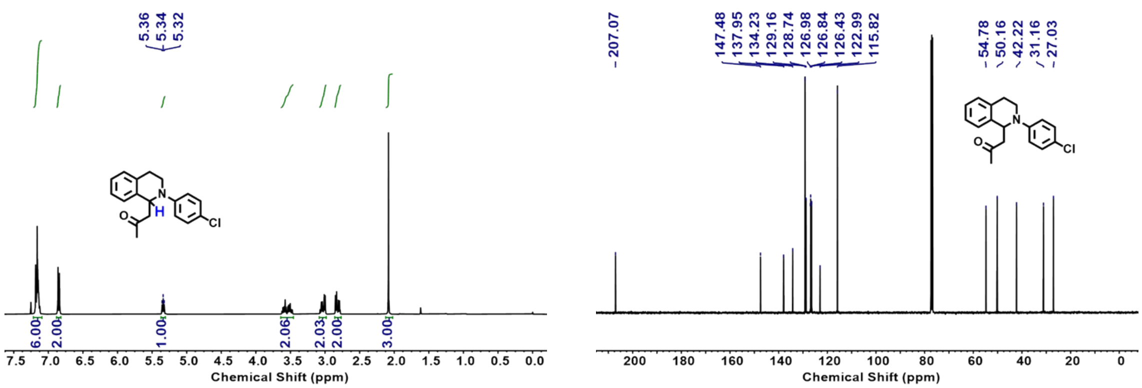


Fig. S40 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3e**.

3f: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.21-7.13 (m, 5H), 6.88-6.87 (t, J = 2.3 Hz, 1H), 6.83-6.80 (dd, J = 8.3, 2.6 Hz, 1H), 6.74-6.71 (dd, J = 7.8, 2.2 Hz, 1H), 5.39-5.35 (t, J = 5.4 Hz, 1H), 3.63-3.50 (m, 2H), 3.08-3.02 (m, 2H), 2.88-2.81 (m, 2H), 2.09 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 206.99, 149.81, 137.87, 135.19, 134.27, 130.32, 128.65, 127.06, 126.90, 126.48, 117.75, 113.93, 112.28, 54.52, 50.22, 42.14, 31.23, 27.16.

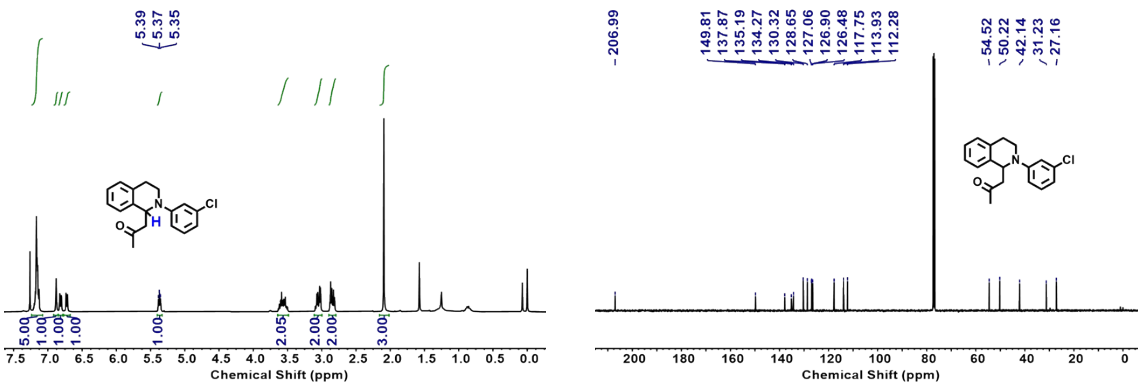


Fig. S41 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3f**.

3g: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.36-7.32 (m, 2H), 7.22-7.15 (m, 4H), 6.86-6.82 (m, 2H), 5.39-5.35 (t, J = 8.0 Hz， 1H), 3.65-3.59 (m, 1H), 3.57-3.50 (m, 1H), 3.10-3.03 (m, 2H), 2.89-2.83 (m, 2H), 2.11 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 207.75, 147.79, 137.89, 134.20, 132.06, 128.70, 127.01, 126.83, 126.45, 116.16, 54.67, 50.14, 42.19, 31.17, 27.04.

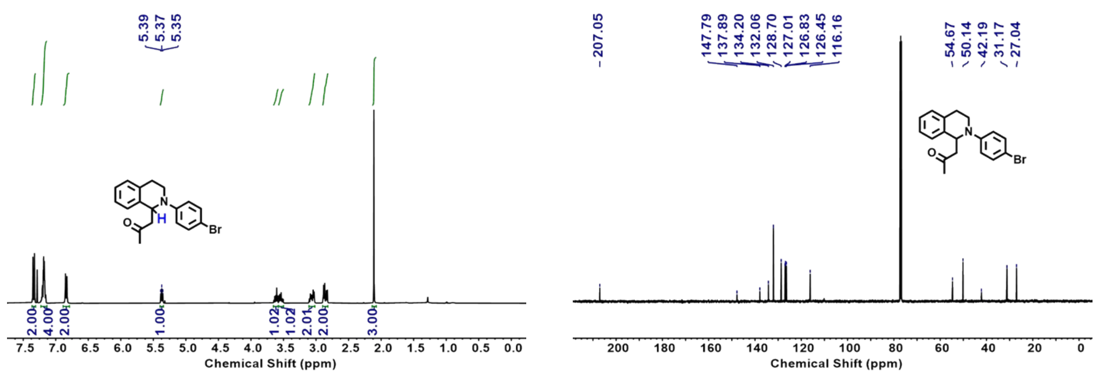


Fig. S42 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3g**.

3h: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm)： 7.49-7.45 (m, 2H), 7.19-7.11 (m, 4H), 6,71-6.67 (m, 2H), 5.35-5.32 (t, J = 5.4 Hz, 1H), 3.60-3.46 (m, 2H), 3.06-2.98 (m, 2H), 2.85-2.79 (m, 2H), 2.07 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm) 207.01, 148.35, 137.96, 137.92, 134.24, 128.69, 127.05, 126.85, 126.47, 116.52, 79.26, 54.45, 50.15, 42.03, 31.21, 27.14.

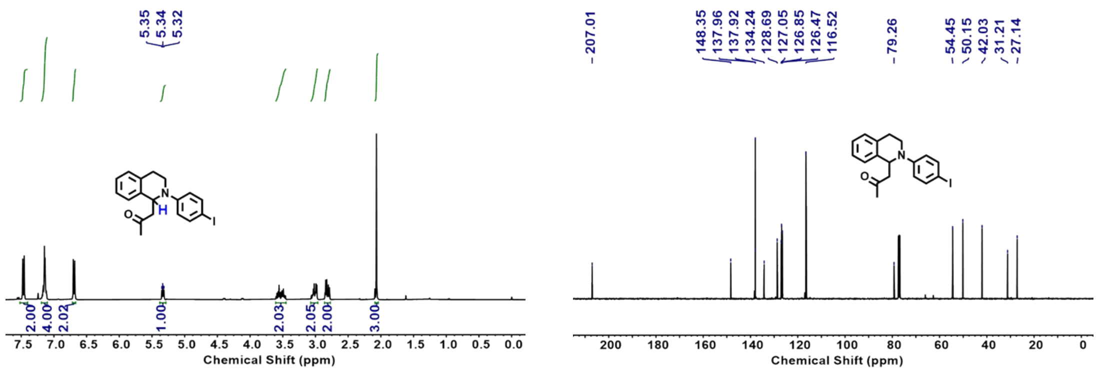


Fig. S43 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3h**.

7.3. Yields of 3b-3h determined by ^{1}H-NMR and GC analysis

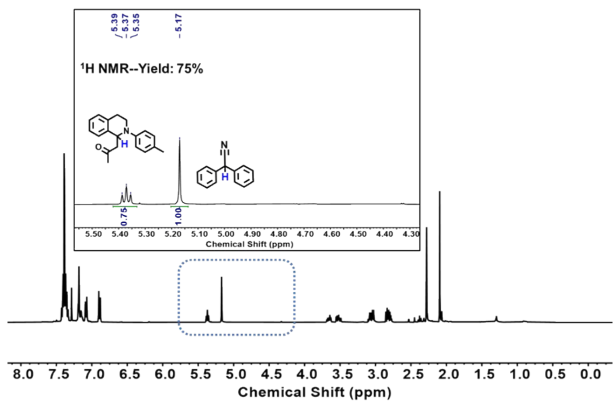


Fig. S44 Yield of **3b** determined by ^{1}H-NMR with DPAT as internal standard.

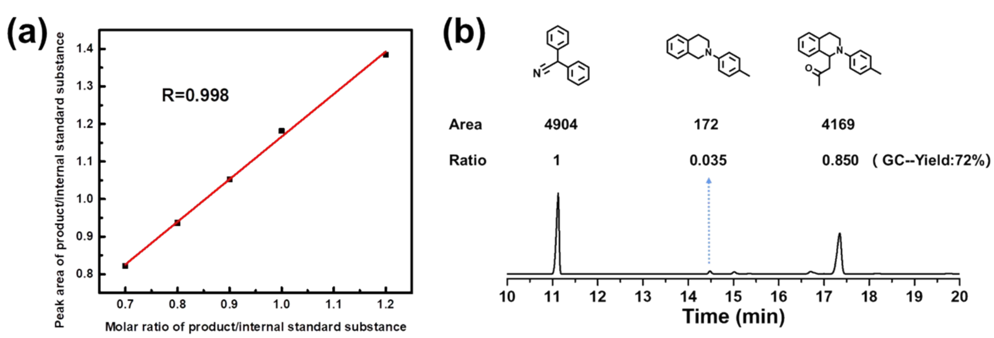


Fig. S45 Yield of **3b** determined by GC with DPAT as internal standard.

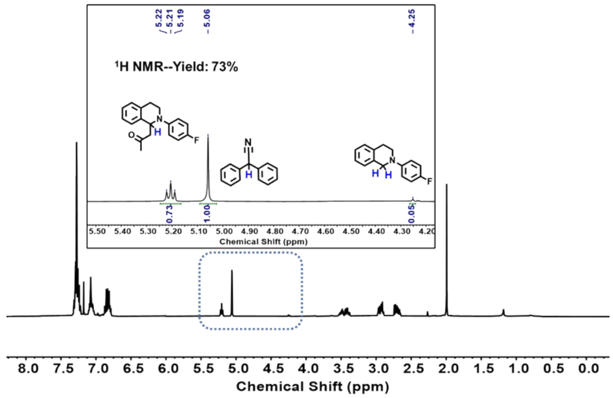


Fig. S46 Yield of **3c** determined by ^{1}H-NMR with DPAT as internal standard.

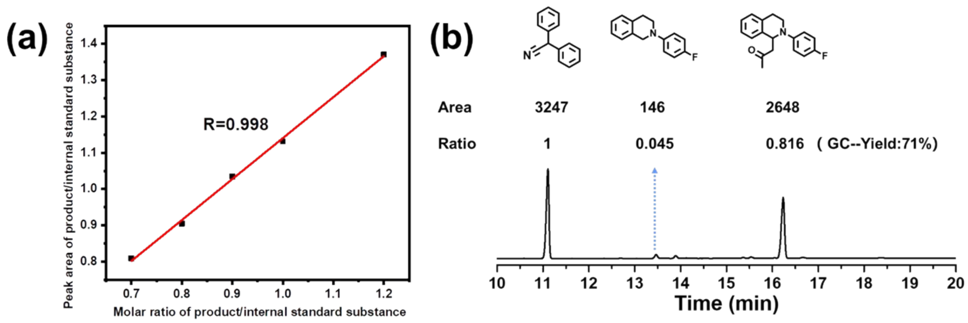


Fig. S47 Yield of **3c** determined by GC with DPAT as internal standard.

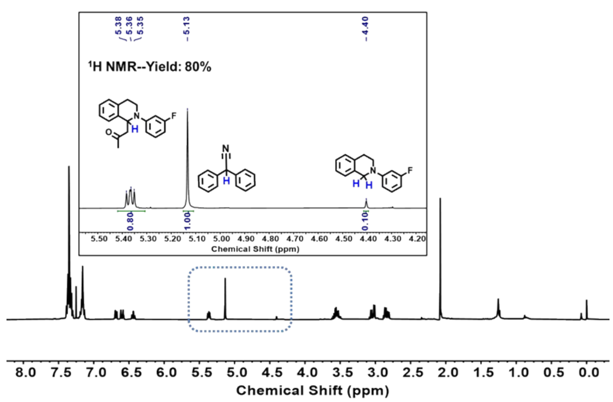


Fig. S48 Yield of **3d** determined by ^{1}H-NMR with DPAT as internal standard.

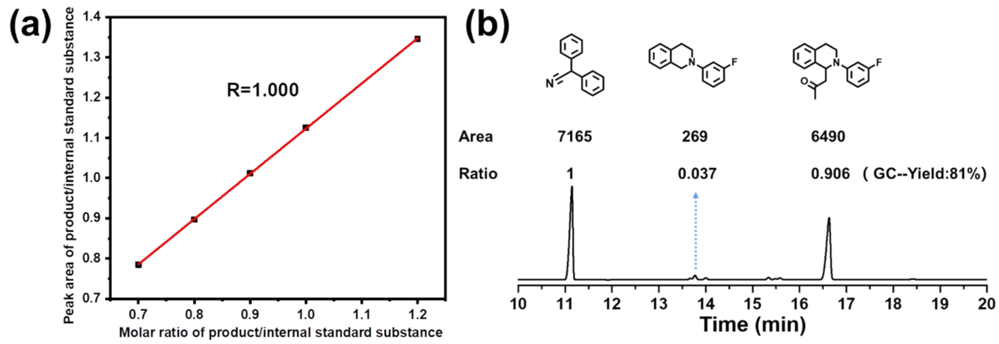


Fig. S49 Yield of **3d** determined by GC with DPAT as internal standard.

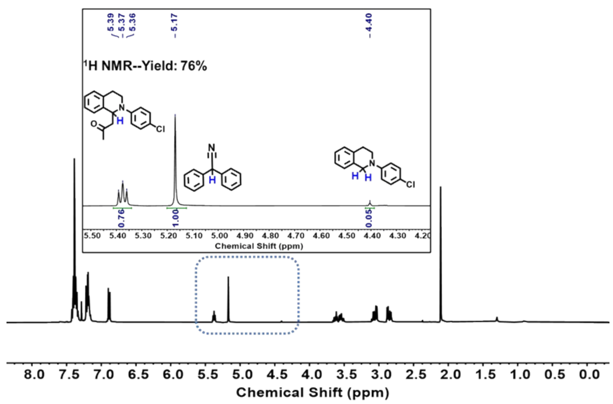


Fig. S50 Yield of **3e** determined by [1]H-NMR with DPAT as internal standard.

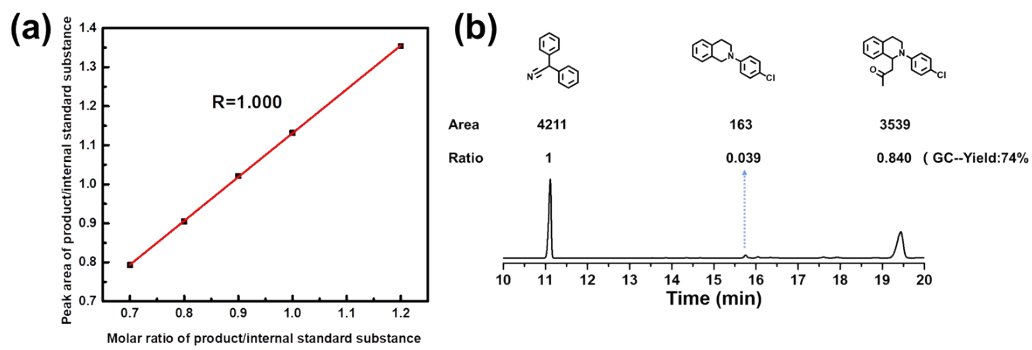


Fig.51 Yield of **3e** determined by GC with DPAT as internal standard.

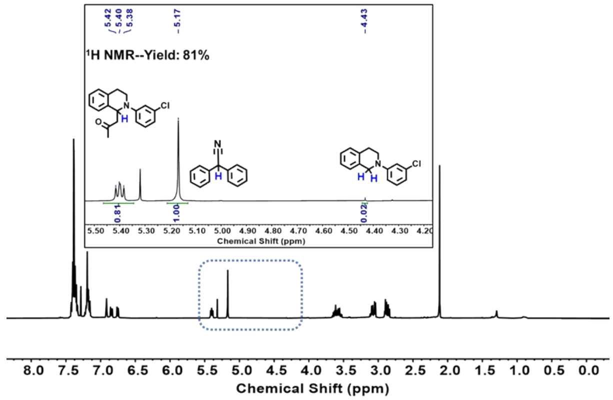


Fig. S52 Yield of **3f** determined by ^{1}H-NMR with DPAT as internal standard.

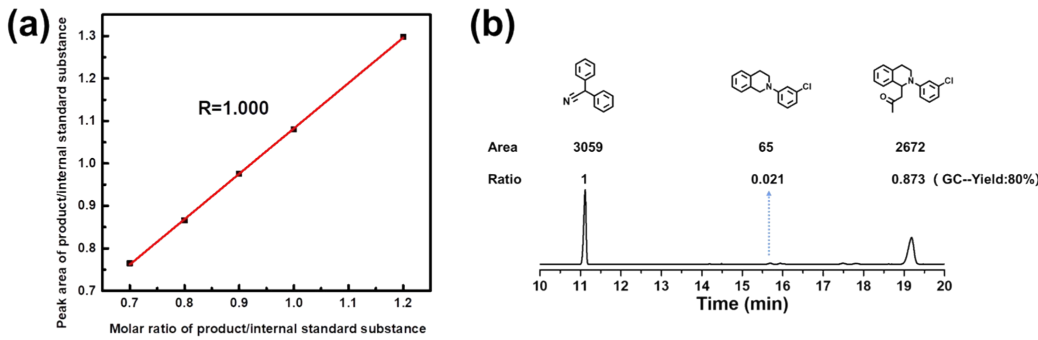


Fig. S53 Yield of **3f** determined by GC with DPAT as internal standard.

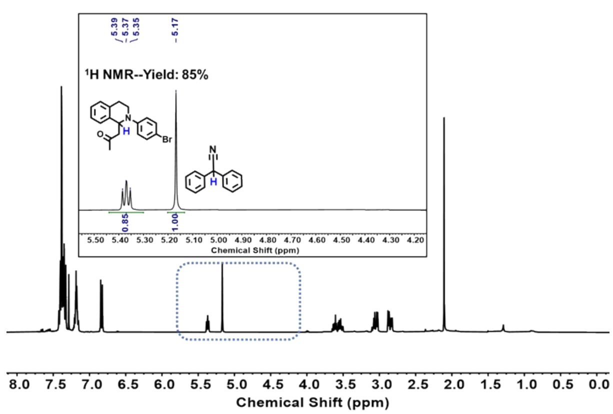


Fig. S54 Yield of **3g** determined by ^{1}H-NMR with DPAT as internal standard.

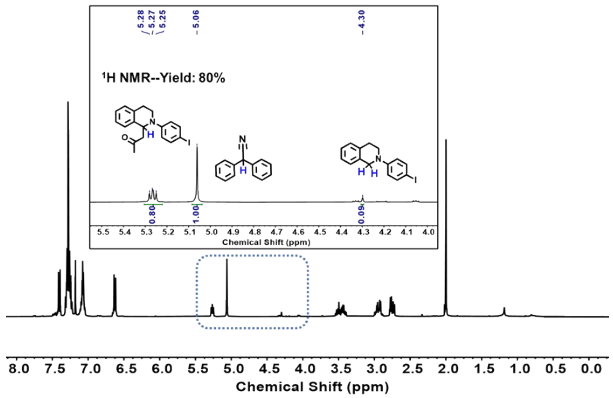


Fig. S55 Yield of **3h** determined by ^{1}H-NMR with DPAT as internal standard.

7.4. Synthetic procedures for 3i-3j (Aza-Henry reaction).

A 10 mL quartz tube was charged with **1a** (0.2 mmol), **TPPy-PBT-COF** (5 mg), nitroalkanes (0.5 mL) and methanol (2 mL). The mixture was bubbled with oxygen and stirred, then the tube was irradiated with natural sunlight in room temperature. After reaction, the solution was centrifuged and the supernatant was removed by rotary evaporation. Yields were determined by ^{1}H NMR spectroscopy with 0.2 mmol DPAT as internal standard.

3i: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.23-7.05 (m, 6H), 6.91-6.89 (d, J = 8.0 Hz, 2H), 6.79-6.76 (t, J = 7.3 Hz, 1H), 5.49-5.46 (t, J = 7.2 Hz, 1H), 4.82-4.77 (dd, J = 11.9, 7.8 Hz, 1H), 4.51-4.46 (dd, J = 11.7, 6.6 Hz, 1H), 3.62-3.51 (m, 2H), 3.05-2.98 (m, 1H), 2.75-2.68 (m, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 148.44, 135.31, 132.94, 129.54, 129.23, 128.16, 127.03, 126.74, 119.45, 115.11, 78.81, 58.23, 42.09, 26.47.

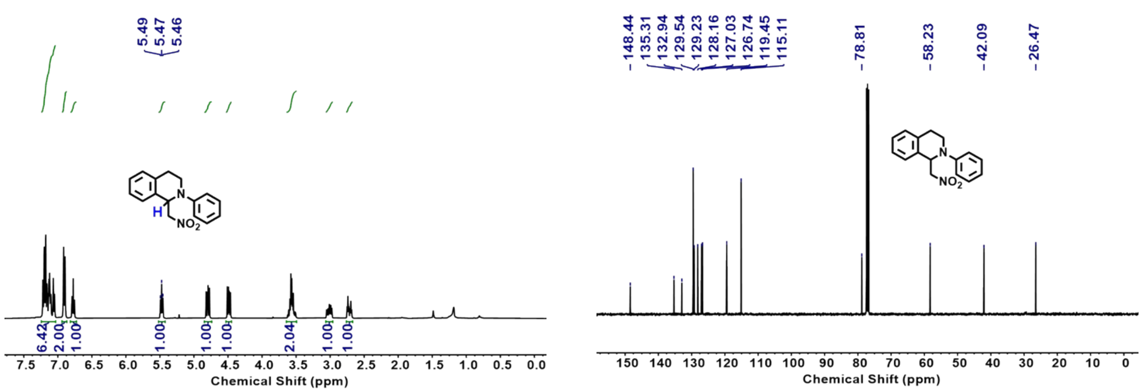


Fig. S56 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3i**.

3j: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.22-7.02 (m, 6H), 6.94-6.89 (m, 2H), 6.77-6.72 (m, 1H), 5.19-5.14 (t, *J* = 9.4 Hz, 1H), 5.01-4.77 (m, 1H), 3.79-3.47 (m, 2H), 3.02-2.81 (m, 2H), 1.63-1.62 (d, *J* = 6.9 Hz, 1H), 1.47-1.46 (d, *J* = 6.7 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 149.17, 148.89, 135.64, 134.80, 133.83, 132.04, 129.46, 129.34, 129.14, 128.74, 128.39, 128.24, 127.28, 126.64, 126.16, 119.35, 118.80, 115.43, 114.49, 88.99, 85.46, 62.77, 61.17, 43.58, 42.68, 26.78, 26.41, 17.47, 16.42.

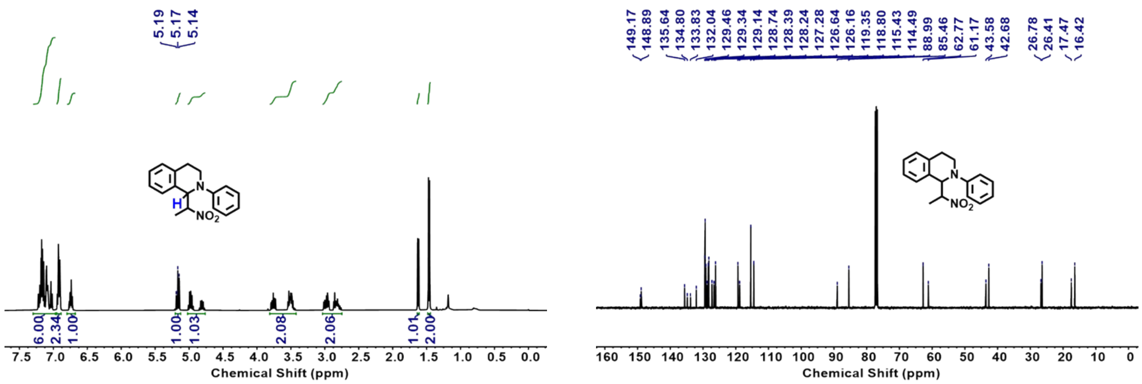


Fig. S57 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3j**.

7.5. Yields of 3i-3j determined by ^{1}H-NMR analysis

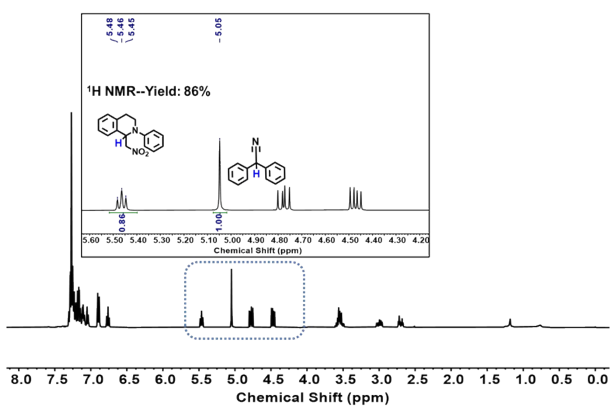


Fig. S58 Yield of **3i** determined by ^{1}H-NMR with DPAT as internal standard.

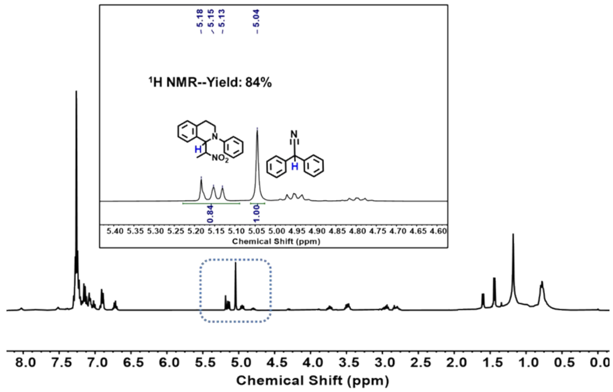


Fig. S59 Yield of **3j** determined by ^{1}H-NMR with DPAT as internal standard.

7.6. Synthetic procedures for 3k-3l (CDC reaction with dialkyl malonates).

A 10 mL quartz tube was charged with **1a** (0.2 mmol), **TPPy-PBT-COF** (5 mg), dialkyl malonates (0.2 mL) and methanol (2 mL). The mixture was bubbled with oxygen and stirred, then the tube was irradiated with natural sunlight in room temperature. After reaction, the solution was centrifuged and the supernatant was removed by rotary evaporation. Yields were determined by ^{1}H-NMR spectroscopy with 0.2 mmol DPAT as internal standard.

3k: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.27-7.20 (m, 4H), 7.17-7.13 (m, 2H), 7.04-7.02 (d, *J* = 8.0 Hz, 2H), 6.82-6.78 (t, *J* = 7.2 Hz, 1H), 5.76-5.74 (d, *J* = 8.0 Hz, 1H), 4.01-3.98 (d, *J* = 9.4 Hz, 1H), 3.75-3.55 (m, 8H), 3.15-3.07 (m, 1H), 2.94-2.88 (m, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm) 168.33, 167.44, 148.80, 135.69, 134.81, 129.15, 129.03, 127.67, 127.08, 126.08, 118.65, 115.22, 59.14, 58.21, 52.60, 52.59, 42.19, 26.06.

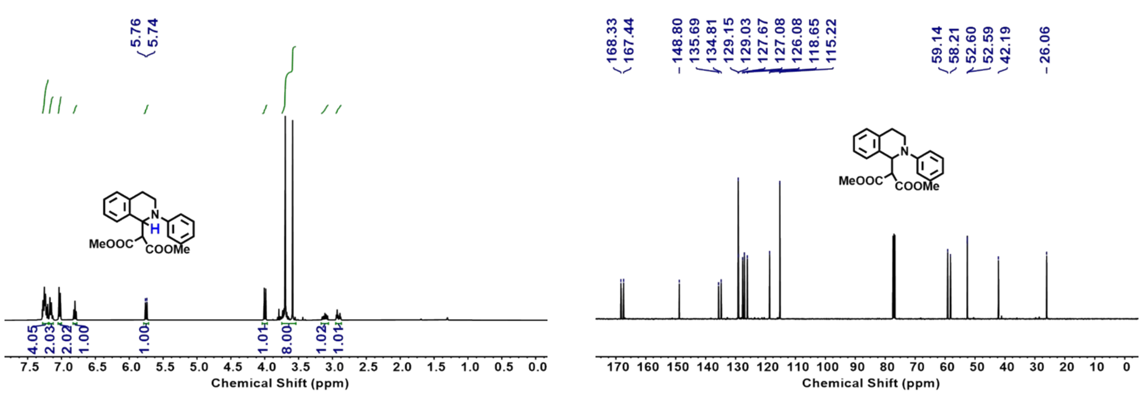


Fig. S60 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3k**.

3l: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.17-7.01 (m, 6H), 6.92-6.90 (d, *J* = 7.8 Hz, 2H), 6.69-6.66 (t, *J* = 7.3 Hz, 1H), 5.66-5.64 (d, *J* = 8.0 Hz, 1H), 4.10-3.86 (m, 4H), 3.84-3.81 (d, *J* = 9.3 Hz, 1H), 3.67-3.53 (m, 2H), 3.04-2.96 (m, 1H), 2.84-2.77 (m, 1H), 1.11-1.08 (t, *J* = 7.1 Hz, 3H), 1.03-0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm) 167.99, 167.16, 148.87, 135.98, 134.83, 129.08, 128.91, 127.53, 127.19, 126.02, 118.45, 115.09, 61.60, 59.56, 57.89, 42.28, 26.13, 13.96, 13.90.

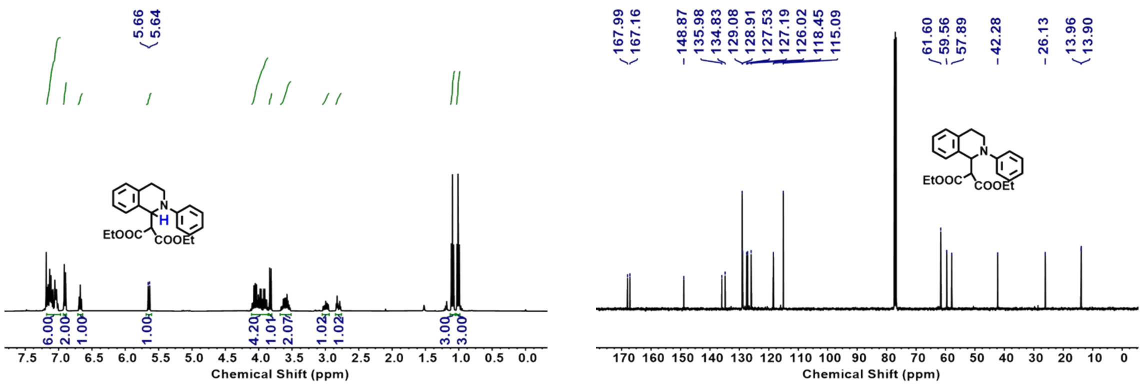


Fig. S61 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3l**.

7.7. Yields of 3k-3l determined by ^{1}H-NMR analysis

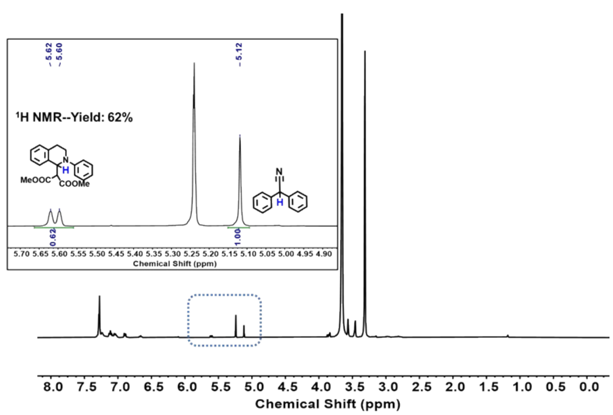


Fig. S62 Yield of **3k** determined by ^{1}H-NMR with DPAT as internal standard.

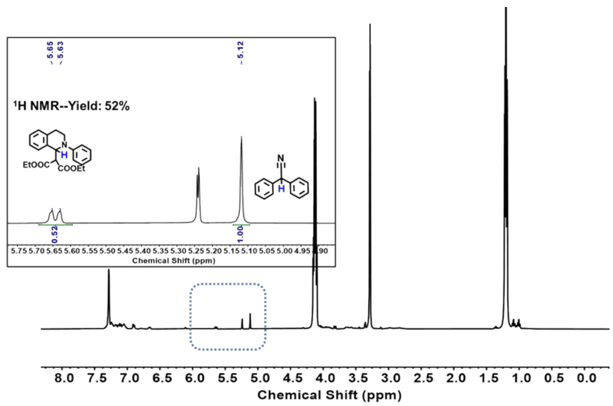
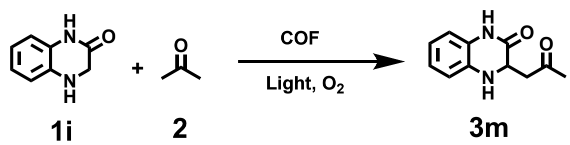


Fig. S63 Yield of **3l** determined by ^{1}H-NMR with DPAT as internal standard.

7.8. Mannich reaction with 3,4-dihydroquinoxalin-2-one as subatrate



Scheme S2 Chemical structure and synthetic route of **3m**.

Synthesis procesure for **3m**: A 10 mL quartz tube was charged with **1i** (0.2 mmol), **TPPy-PBT-COF** (5 mg), DMF (1 mL). The mixture was bubbled with oxygen and stirred, then the tube was irradiated with natural sunlight at room temperature. After 7 hours, 0.06mmol L-Proline and 0.5 mL aceton were added, the reaction was performed for additional 21 hours in dark. After reaction, the solution was centrifuged and the supernatant was removed by rotary evaporation. Yield was determined by ^{1}H-NMR spectroscopy with 0.2 mmol DPAT as internal standard. ^{1}H-NMR (DMSO-d_6, 400 MHz) δ (ppm): 10.28 (s, 1H), 6.79-6.68 (m, 3H), 6.63-6.59 (m, 1H), 5.86 (s, 1H), 4.16-4.12 (m, 1H), 3.00-2.94 (dd, J = 17.0, 5.1 Hz, 1H), 2.74-2.68 (dd, J = 17.0, 7.1 Hz, 1H), 2.16 (s, 3H). ^{13}C-NMR (DMSO-d_6, 100 MHz) δ (ppm): 206.41, 167.48, 134.58, 126.47, 123.23, 118.52, 115.30, 114.12, 52.31, 45.30, 30.82.

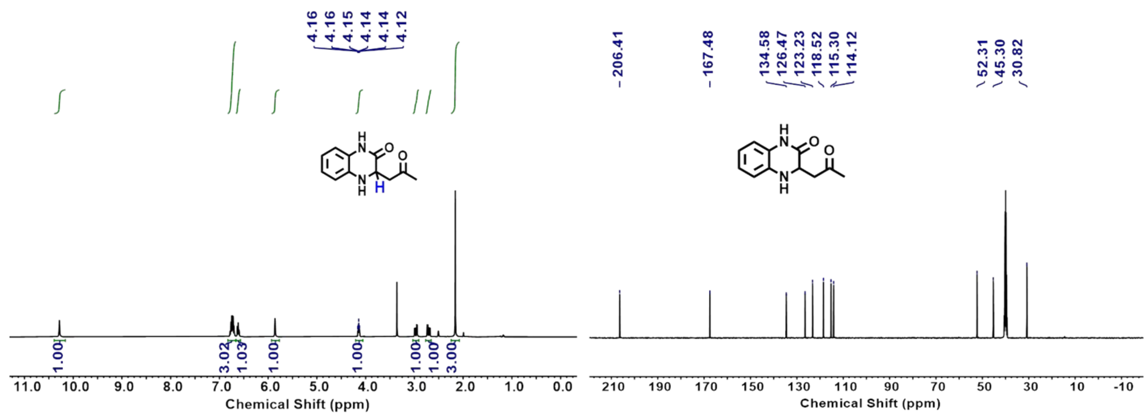


Fig. S64 ^{1}H-NMR (left) and ^{13}C-NMR (right) of **3m**.

7.9. Yield of 3m determined by ^{1}H-NMR analysis

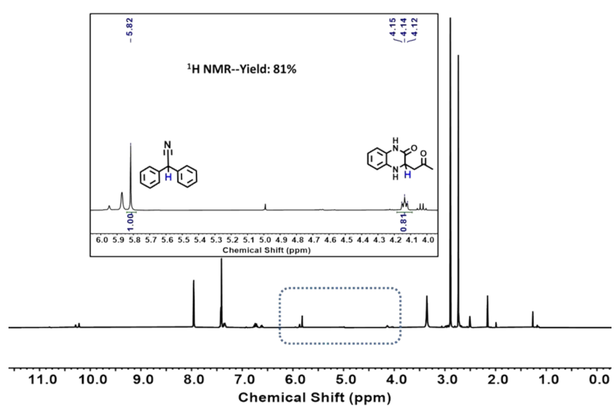


Fig. S65 Yield of **3m** determined by ^{1}H-NMR with DPAT as internal standard.

7.10. Synthetic procedures for large-scale experiment

A 100 mL quartz tube was charged with **1g** (3.47 mmol，1 g), L-proline (1.04 mmol, 0.12 g), TPPy-PBT-COF (50 mg), acetone (8 mL) and methanol (30 mL). The mixture was bubbled with oxygen and stirred, then the tube was irradiated with natural light (0.04 w/cm^{2}-0.10 w/cm^{2}) for 20 h in room temperature. After reaction, the solution was centrifuged and the supernatant was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1) as eluent. An excellent yield (0.9142 g, 77%) was afforded in the scaled-up reaction.

8. Recycling experiments

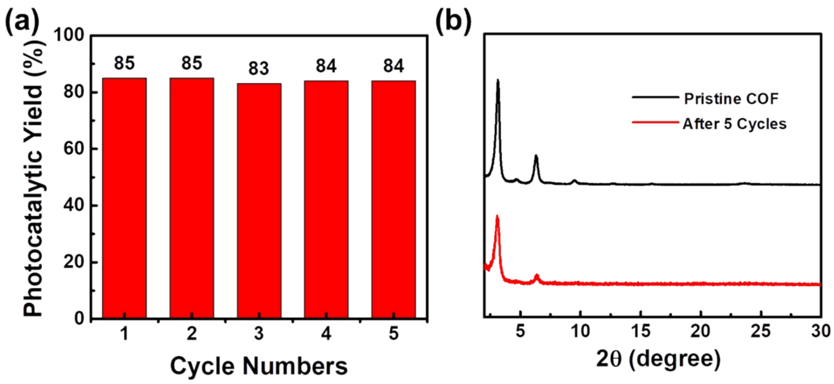


Fig. S66 (a) Recycling experiments of **3g** irradiated by natural sunlight. (b) PXRD patterns of pristine COF (black) and recycled **TPPy-PBT-COF** after 5 cycles (red).

9. Detection of H_2O_2

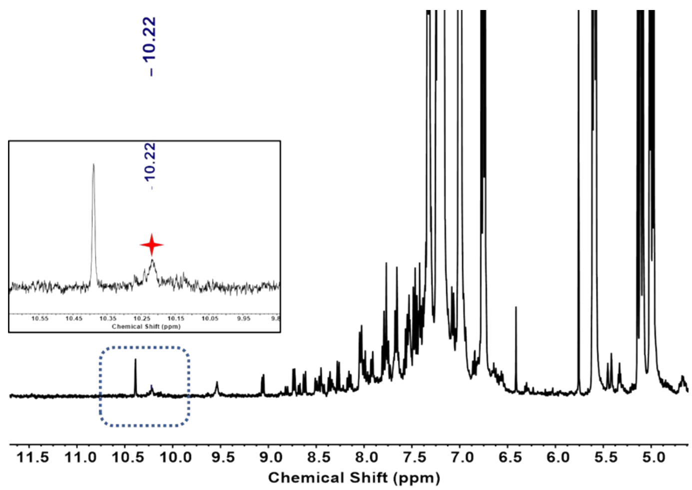


Fig. S67 ^{1}H-NMR detection of the H_2O_2 generated in the photocatalytic reaction. The peak at 10.22 ppm is H_2O_2 (DMSO-d_6, 400 MHz).

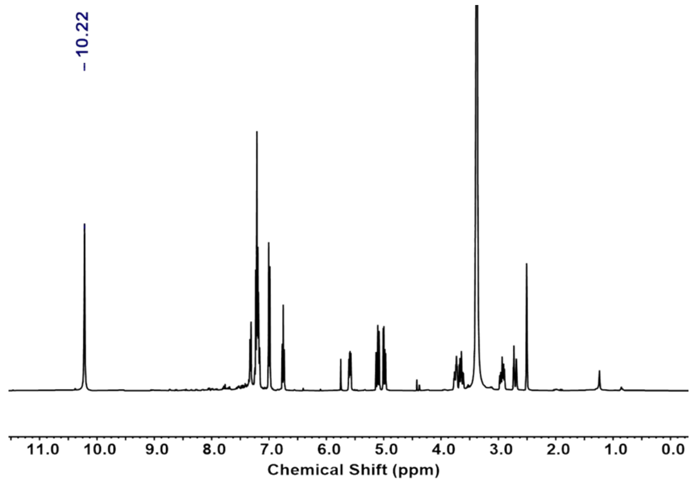


Fig. S68 Comparison ^{1}H-NMR spectrum: one drop of H_2O_2 was added in the photocatalytic reaction, which confirmed the peak at 10.22 ppm is H_2O_2 (DMSO-d_6, 400 MHz).

10. Crystallographic parameters

TPPY-PBT-COF Space group: *P1* a = 42.31Å, b = 38.50 Å, c = 7.77 Å α = 81.94°, β = 99.65°, γ = 91.05°			
Atom	x	y	z
C1	0.25877	0.47437	0.94364
C2	0.28784	0.45595	0.97841
C3	0.28871	0.41928	0.97736
C4	0.25946	0.3972	0.97068
C5	0.23967	0.39731	1.09873
C6	0.21254	0.37602	1.09548
C7	0.20517	0.35354	0.96765
C8	0.22513	0.3531	0.84007
C9	0.2521	0.37471	0.84214
C10	-0.16089	0.03546	0.87947
C11	-0.16321	0.07235	0.85482
C12	-0.13368	0.01869	0.84895
C13	-0.1347	0.09456	0.84179
C14	-0.1246	0.10533	0.67996
C15	-0.09701	0.12587	0.67394
C16	-0.07969	0.13628	0.82858
C17	-0.08983	0.12487	0.99067
C18	-0.11716	0.10433	0.99663
N19	-0.05124	0.15699	0.81876
C20	-0.00852	0.19552	0.92357
C21	0.00852	0.19325	0.78511
C22	0.03773	0.21069	0.7805

C23	0.05053	0.23042	0.91482
C24	0.03333	0.23274	1.05249
C25	0.00411	0.21547	1.05667
C26	0.0815	0.24902	0.91082
C27	0.10854	0.23271	0.87366
C28	0.1372	0.2502	0.87056
C29	0.14072	0.28495	0.90604
C30	0.11385	0.3017	0.94386
C31	0.08462	0.28395	0.94617
N32	0.17658	0.33285	0.96676
C33	-0.03903	0.17688	0.93485
C34	0.17167	0.30333	0.9034
H35	0.23613	0.46141	0.90969
H36	0.24522	0.414	1.20095
H37	0.19733	0.37673	1.19403
H38	0.2196	0.33675	0.73665
H39	0.26711	0.37416	0.74253
H40	-0.11412	0.03335	0.80095
H41	-0.13787	0.09758	0.5597
H42	-0.08923	0.13387	0.54858
H43	-0.0764	0.13094	1.1137
H44	-0.12454	0.09572	1.12269
H45	-0.00067	0.17806	0.68058
H46	0.05016	0.209	0.67098
H47	-0.05107	0.18017	1.04397
H48	0.19059	0.29126	0.85395
C49	-0.18603	0.01485	0.9364
C50	-0.19139	0.08887	0.87063
H51	-0.19251	0.11571	0.84765
C52	0.37471	0.47597	1.07196
C53	0.34661	0.45704	1.02948
C54	0.34732	0.42065	1.01348
C55	0.31816	0.40259	0.98827
C56	0.37745	0.40032	1.01877
C57	0.40174	0.41398	0.92612
C58	0.42905	0.39414	0.9257
C59	0.43244	0.35978	1.01339
C60	0.40794	0.34564	1.10396
C61	0.38092	0.36571	1.10641
C62	0.7843	0.03185	0.96616
C63	0.7812	0.06885	0.92873
C64	0.76126	0.01047	1.03723
C65	0.75267	0.08941	0.94893
C66	0.72111	0.07865	0.89332

C67	0.69495	0.09932	0.90455
C68	0.69965	0.1317	0.96643
C69	0.73103	0.14257	1.02453
C70	0.75716	0.12176	1.01451
N71	0.67199	0.15232	0.97077
C72	0.64156	0.20381	0.98747
C73	0.6116	0.18708	0.96938
C74	0.58406	0.20447	0.98156
C75	0.58473	0.23959	1.01223
C76	0.61438	0.25708	1.02315
C77	0.6425	0.2393	1.01249
C78	0.55521	0.2579	1.03135
C79	0.53351	0.24089	1.13319
C80	0.50552	0.2578	1.14979
C81	0.49861	0.29208	1.06535
C82	0.52048	0.30944	0.96566
C83	0.54859	0.29251	0.94945
N84	0.46084	0.34044	1.00548
C85	0.67165	0.18572	0.98013
C86	0.46866	0.30903	1.08486
H87	0.39787	0.46334	1.10967
H88	0.39962	0.44006	0.85326
H89	0.44759	0.40552	0.85521
H90	0.40909	0.31926	1.17295
H91	0.36264	0.35396	1.17773
H92	0.74124	0.0213	1.08179
H93	0.71642	0.05468	0.83678
H94	0.67089	0.09064	0.85884
H95	0.7356	0.16658	1.08158
H96	0.78097	0.13062	1.06349
H97	0.61597	0.28436	1.04282
H98	0.66503	0.2533	1.02479
H99	0.51588	0.336	0.89989
H100	0.56488	0.30625	0.87027
H101	0.69339	0.201	0.98177
H102	0.45362	0.29454	1.16873
C103	-0.18218	0.9759	0.9773
C104	0.37385	0.51391	1.07316
C105	0.34472	0.53222	1.04664
C106	0.34386	0.56881	1.04841
C107	0.31445	0.586	1.02506
C108	0.37314	0.59065	1.06729
C109	0.39598	0.58578	1.22176
C110	0.42442	0.60501	1.23334

C111	0.42952	0.63071	1.09458
C112	0.40589	0.63696	0.94342
C113	0.37796	0.61692	0.92961
C114	0.79063	0.95467	1.03252
C115	0.79257	0.91777	1.05174
C116	0.76333	0.9721	1.05807
C117	0.76462	0.89478	1.07463
C118	0.74956	0.89355	1.22321
C119	0.72198	0.87338	1.23536
C120	0.7101	0.85281	1.10404
C121	0.72598	0.85283	0.95913
C122	0.75292	0.8738	0.94424
N123	0.68096	0.83362	1.11477
C124	0.6452	0.78487	1.07606
C125	0.61648	0.80418	1.03763
C126	0.58705	0.78698	1.03404
C127	0.58575	0.7502	1.07348
C128	0.61475	0.73114	1.117
C129	0.64411	0.74827	1.11455
C130	0.55426	0.73208	1.07078
C131	0.52865	0.74783	1.1276
C132	0.49859	0.73159	1.12068
C133	0.49367	0.69872	1.06283
C134	0.51921	0.68305	1.00768
C135	0.54849	0.69943	1.00924
N136	0.45951	0.64879	1.10481
C137	0.67631	0.80237	1.071
C138	0.46197	0.68219	1.05533
H139	0.3967	0.52692	1.09502
H140	0.39193	0.56659	1.33118
H141	0.44236	0.60015	1.35101
H142	0.40958	0.65648	0.83411
H143	0.36028	0.62152	0.81053
H144	0.74391	0.95865	1.09384
H145	0.75861	0.90895	1.32696
H146	0.70992	0.87362	1.34751
H147	0.71693	0.83756	0.85477
H148	0.76433	0.87423	0.82907
H149	0.61674	0.83248	1.00542
H150	0.56527	0.80252	0.99764
H151	0.69572	0.78822	1.03633
H152	0.4407	0.69858	1.01689
C153	0.25803	0.51262	0.9338
C154	0.28579	0.53184	0.98066

C155	0.28495	0.56873	0.98906
C156	0.25475	0.59047	0.9708
C157	0.22652	0.57669	1.02796
C158	0.19967	0.5979	1.01774
C159	0.20118	0.63405	0.96936
C160	0.22927	0.64856	0.91744
C161	0.25513	0.62694	0.91206
C162	-0.15382	0.95939	0.95419
C163	-0.15031	0.92225	0.99517
C164	-0.1311	0.98037	0.87646
C165	-0.12107	0.90377	1.00212
C166	-0.09078	0.9182	1.05933
C167	-0.06241	0.89981	1.06343
C168	-0.0634	0.86589	1.01864
C169	-0.09327	0.85078	0.96605
C170	-0.12158	0.86935	0.95855
N171	-0.03388	0.84766	1.02347
C172	-0.00037	0.79621	1.04978
C173	0.02466	0.81417	0.97783
C174	0.05261	0.79628	0.96507
C175	0.0567	0.76013	1.02827
C176	0.03165	0.743	1.10523
C177	0.00397	0.7605	1.11377
C178	0.08671	0.74149	1.01511
C179	0.11629	0.75918	1.02647
C180	0.14441	0.74184	1.01487
C181	0.14369	0.70641	0.99188
C182	0.11429	0.68869	0.9778
C183	0.08612	0.70611	0.98742
N184	0.17372	0.65491	0.9746
C185	-0.03083	0.81374	1.05472
C186	0.1737	0.68831	0.98425
H187	0.23542	0.52516	0.87728
H188	0.22535	0.55003	1.09155
H189	0.17807	0.58639	1.0577
H190	0.23109	0.67637	0.8748
H191	0.27541	0.63925	0.86054
H192	-0.1116	0.96918	0.82844
H193	-0.08874	0.94346	1.1057
H194	-0.03956	0.91168	1.10622
H195	-0.0949	0.825	0.92508
H196	-0.14375	0.85706	0.90837
H197	0.02246	0.84186	0.92844
H198	0.07075	0.81086	0.90292

H199	0.11292	0.66139	0.95773
H200	0.06383	0.69192	0.9678
H201	-0.05071	0.79764	1.089
H202	0.1958	0.70306	0.99466
C203	0.82107	0.90176	1.03625
H204	0.82226	0.87342	1.06316
C205	0.31676	0.4748	1.00667
C206	0.31569	0.51367	1.01413
C207	0.22639	0.67497	0.50905
C208	0.19688	0.69215	0.48878
C209	0.19525	0.72819	0.50326
C210	0.1657	0.74348	0.50652
C211	0.2238	0.75104	0.50356
C212	0.24041	0.75394	0.36047
C213	0.26786	0.7745	0.36019
C214	0.27878	0.79319	0.5002
C215	0.26197	0.79069	0.64344
C216	0.23451	0.76982	0.64436
C217	0.64027	1.11537	0.43006
C218	0.64022	1.07847	0.43131
C219	0.61174	1.13429	0.41848
C220	0.61236	1.05754	0.42128
C221	0.58544	1.06566	0.28904
C222	0.55807	1.04466	0.28424
C223	0.55731	1.01464	0.40798
C224	0.58448	1.00579	0.53713
C225	0.61181	1.02664	0.54155
N226	0.52814	0.99491	0.40535
C227	0.49501	0.94458	0.47518
C228	0.46547	0.9624	0.42204
C229	0.43691	0.94548	0.43796
C230	0.43612	0.9098	0.5059
C231	0.46536	0.8914	0.55588
C232	0.4945	0.90867	0.54168
C233	0.40556	0.89169	0.525
C234	0.38408	0.90479	0.61998
C235	0.35532	0.88737	0.63915
C236	0.34744	0.85685	0.5619
C237	0.36901	0.84378	0.46677
C238	0.39793	0.86093	0.44977
N239	0.30766	0.81312	0.4944
C240	0.52627	0.9621	0.47013
C241	0.31678	0.83902	0.58111
H242	0.24879	0.68841	0.54228

H243	0.23228	0.73986	0.25
H244	0.2807	0.77595	0.25007
H245	0.27032	0.80395	0.7562
H246	0.22199	0.76776	0.75608
H247	0.58874	1.12173	0.41719
H248	0.58571	1.08801	0.18811
H249	0.53739	1.05173	0.18346
H250	0.58445	0.98346	0.63841
H251	0.63214	1.0194	0.64475
H252	0.36363	0.82028	0.40577
H253	0.41421	0.85041	0.3761
H254	0.54784	0.94686	0.52327
H255	0.3016	0.84867	0.66336
C256	-0.32892	1.0599	0.45097
H257	-0.33003	1.03245	0.43302
C258	0.66985	1.13329	0.45493
C259	0.11057	0.67012	0.39767
C260	0.13828	0.6892	0.44783
C261	0.13687	0.72471	0.47981
C262	0.10627	0.74341	0.48597
C263	0.08193	0.7267	0.56972
C264	0.05372	0.74452	0.57592
C265	0.04973	0.77991	0.50588
C266	0.07405	0.79708	0.42442
C267	0.1019	0.77906	0.41476
C268	-0.29918	1.11368	0.47755
C269	-0.29923	1.07685	0.47108
C270	-0.27111	1.13224	0.5247
C271	-0.27119	1.05602	0.48185
C272	-0.24486	1.06871	0.4028
C273	-0.21854	1.04727	0.40444
C274	-0.21804	1.01218	0.48071
C275	-0.24372	0.99921	0.56374
C276	-0.26983	1.02074	0.56381
N277	-0.19113	0.99081	0.47105
C278	-0.16021	0.93796	0.49274
C279	-0.13302	0.95609	0.44822
C280	-0.10458	0.93802	0.4528
C281	-0.10257	0.90143	0.50271
C282	-0.13044	0.8832	0.53717
C283	-0.15893	0.90133	0.53307
C284	-0.07158	0.88243	0.51844
C285	-0.042	0.89712	0.5845
C286	-0.01325	0.88031	0.58695

C287	-0.01242	0.8475	0.52878
C288	-0.04179	0.83159	0.47152
C289	-0.07096	0.84893	0.46506
N290	0.02047	0.79746	0.51407
N291	-0.03924	0.92646	0.64809
S292	0.00168	0.93668	0.71705
N293	0.01205	0.89672	0.64951
C294	-0.18965	0.95678	0.50295
C295	0.01856	0.83068	0.52552
H296	0.08724	0.68228	0.36444
H297	0.08461	0.69973	0.6312
H298	0.03518	0.7309	0.63908
H299	0.07125	0.82417	0.36397
H300	0.11987	0.79314	0.34929
H301	-0.24826	1.11935	0.57172
H302	-0.24497	1.09486	0.33319
H303	-0.19891	1.05774	0.34001
H304	-0.24382	0.9727	0.63104
H305	-0.28866	1.00972	0.63318
H306	-0.1335	0.98432	0.41269
H307	-0.08419	0.95284	0.41624
H308	-0.12997	0.85503	0.57459
H309	-0.17978	0.88679	0.56596
H310	-0.04224	0.80615	0.42701
H311	-0.09296	0.83647	0.41311
H312	-0.20984	0.94152	0.53839
H313	0.04009	0.8464	0.53943
C314	0.1122	0.63296	0.37809
C315	0.14172	0.61565	0.4005
C316	0.14321	0.57961	0.38888
C317	0.1146	0.55699	0.38578
C318	0.09521	0.5517	0.22691
C319	0.06848	0.52969	0.22862
C320	0.06106	0.51246	0.3883
C321	0.0805	0.51831	0.54745
C322	0.10707	0.54027	0.5456
C323	-0.2999	0.18946	0.50539
C324	-0.29956	0.22644	0.50796
C325	-0.2714	0.1703	0.52007
C326	-0.27109	0.24652	0.52908
C327	-0.24541	0.23719	0.66807
C328	-0.21751	0.25745	0.68421
C329	-0.21507	0.28807	0.5664
C330	-0.24098	0.29805	0.4307

C331	-0.26869	0.27778	0.41367
N332	-0.18551	0.30734	0.5808
C333	-0.15171	0.3581	0.5304
C334	-0.12281	0.33876	0.56949
C335	-0.09329	0.35574	0.56131
C336	-0.09203	0.39234	0.51233
C337	-0.121	0.41122	0.47681
C338	-0.1499	0.39462	0.4864
C339	-0.06085	0.41023	0.50544
C340	-0.03568	0.40367	0.6485
C341	-0.00679	0.42175	0.64766
C342	-0.00226	0.44637	0.50279
C343	-0.02705	0.45218	0.35663
C344	-0.05616	0.43432	0.35832
N345	0.03304	0.4906	0.38489
C346	-0.18323	0.34071	0.52718
C347	0.02811	0.46612	0.51085
H348	0.08979	0.61958	0.34407
H349	0.10075	0.56459	0.10251
H350	0.0536	0.52582	0.10524
H351	0.07508	0.50661	0.67384
H352	0.12177	0.54442	0.66922
H353	-0.24825	0.18262	0.52771
H354	-0.24704	0.21444	0.76549
H355	-0.19777	0.24939	0.78951
H356	-0.23963	0.32094	0.33421
H357	-0.28789	0.28588	0.30506
H358	-0.12298	0.31053	0.6044
H359	-0.07146	0.34024	0.59098
H360	-0.02406	0.47067	0.242
H361	-0.075	0.43925	0.24471
H362	-0.20462	0.35639	0.47671
H363	0.04627	0.45975	0.62639
C364	0.2281	0.6371	0.50667
C365	0.20061	0.61742	0.4605
C366	0.20205	0.58098	0.44258
C367	0.17284	0.56332	0.40295
C368	0.23259	0.55981	0.46211
C369	0.2608	0.57392	0.406
C370	0.28833	0.5533	0.42364
C371	0.28775	0.51736	0.48186
C372	0.25952	0.50254	0.53115
C373	0.23275	0.52359	0.52544
C374	0.6396	0.19086	0.457

C375	0.63978	0.22724	0.47019
C376	0.61143	0.17236	0.41197
C377	0.61212	0.24745	0.47647
C378	0.58652	0.23302	0.55786
C379	0.55976	0.2532	0.56432
C380	0.55782	0.28855	0.49252
C381	0.58371	0.30384	0.41817
C382	0.61032	0.28361	0.4101
N383	0.5295	0.30792	0.50047
C384	0.49139	0.35588	0.43209
C385	0.47001	0.33928	0.53718
C386	0.44207	0.35649	0.55337
C387	0.43502	0.39061	0.46527
C388	0.45612	0.40672	0.35689
C389	0.48405	0.38957	0.34108
C390	0.40543	0.4091	0.48264
C391	0.37623	0.39099	0.48461
C392	0.34794	0.40883	0.49107
C393	0.34825	0.44503	0.50047
C394	0.37785	0.46245	0.50826
C395	0.40555	0.44499	0.49883
N396	0.31618	0.497	0.48835
C397	0.52115	0.33855	0.41289
C398	0.31775	0.46305	0.50077
H399	0.25128	0.62523	0.55418
H400	0.26148	0.60044	0.33949
H401	0.3099	0.5651	0.38448
H402	0.25806	0.47497	0.57975
H403	0.21225	0.51112	0.57408
H404	0.58849	0.18527	0.36894
H405	0.58733	0.20628	0.62207
H406	0.54036	0.24117	0.62592
H407	0.58387	0.33137	0.36659
H408	0.62889	0.29649	0.34498
H409	0.47482	0.31303	0.60677
H410	0.4262	0.34324	0.63668
H411	0.45073	0.43234	0.2812
H412	0.49981	0.40256	0.25615
H413	0.53534	0.35167	0.32006
H414	0.29636	0.44726	0.50089
C415	-0.32946	0.17157	0.47602
C416	-0.32864	0.24477	0.48587
H417	-0.32749	0.27233	0.50034
C418	0.16844	0.6727	0.45925

C419	0.17034	0.63463	0.43661
H420	1.11531	1.32858	-0.02925
H421	1.06436	1.29765	-0.02562
H422	1.53179	0.77268	0.17808
H423	1.47927	0.74452	0.16288
H424	0.96133	1.38515	0.76301
H425	1.01193	1.41687	0.76188
N426	0.87638	1.44829	0.43551
S427	0.83562	1.46236	0.40667
N428	0.82337	1.41783	0.45142
H429	1.38978	0.92825	0.68105
H430	1.33918	0.89779	0.7139
H431	1.16533	1.77068	0.52755
H432	1.31512	1.61348	0.04079
H433	1.17265	1.53608	0.38249
H434	1.3182	1.37483	-0.02256
H435	1.04271	1.24756	0.15834
H436	0.99144	1.21747	0.1651
N437	1.10982	1.19723	-0.15624
S438	1.1487	1.18607	-0.19272
N439	1.16217	1.22947	-0.16452
H440	1.4657	0.86383	0.60901
H441	1.51668	0.89398	0.58408
N442	1.46166	0.99833	0.34914
S443	1.42033	1.01072	0.29766
N444	1.40939	0.96713	0.37687
H445	1.32573	1.39428	0.48739
H446	1.37505	1.36314	0.47734
N447	1.3829	1.4979	0.53674
S448	1.42436	1.50908	0.55584
N449	1.43357	1.46587	0.52104
H450	1.53836	1.21462	0.20224
H451	1.48925	1.24408	0.22946
N452	1.60603	1.15271	-0.07546
S453	1.56431	1.1426	-0.10716
N454	1.55566	1.18468	-0.05475
H455	1.11798	0.78639	0.04701
H456	1.16683	0.75606	0.02601
N457	1.0323	0.70751	0.186
S458	0.9964	0.69594	0.27184
N459	0.98154	0.73946	0.1981
H460	1.61489	0.70301	0.15461
H461	1.66608	0.73298	0.1456
N462	1.51709	0.65114	-0.06542

S463	1.55366	0.6417	-0.13586
N464	1.57056	0.6812	-0.06538

11. References

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