

Supporting Information For  
**Vinylene-linked Diketopyrrolopyrrole Covalent Organic Framework for  
Photocatalytic Oxidation Reactions**

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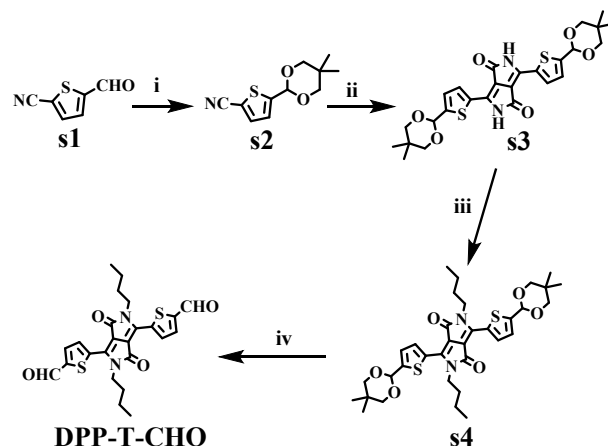
## 1. Materials and Measurements

All the solvents, intermediate chemicals and catalysts are commercially available from local chemical distributors, and used without further purification.

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of intermedia products, monomers and photocatalytic products were individually recorded at 400/100 MHz 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  $K\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). Transform Infrared (FT-IR) spectra in the region of 400-4000  $\text{cm}^{-1}$  were obtained with a Perkin-Elmer 1600 FT-IR spectrometer. Solid state  $^{13}\text{C}$  CP-MAS spectrum was acquired at BRUKER AVANCE NEO 400WB.  $\text{N}_2$  adsorption-desorption isotherm was obtained using an ASAP 2020/TriStar 3000 (Micromeritics) apparatus measured at 77 K, the sample was degassed at 100  $^\circ\text{C}$  for 12 h under high vacuum before analysis. High resolution transmission electron microscopy (TEM) images and HAADF-STEM images were obtained using TEM (Talos F200X). The corresponding elemental mapping images were obtained by using Talos F200i. Ultraviolet-visible (UV-vis) absorption spectra was recorded on a Shimadzu UV-2600 Double Beam UV-vis Spectrophotometer. Mott-Schottky measurement was performed in  $\text{Na}_2\text{SO}_4$  solution (0.5M) on a CHI660E electrochemical workstation in a three-electrode system. The working electrode was prepared by dropcasting an 5% Nafion (50  $\mu\text{L}$ ) 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/AgCl, Mott-Schottky plots were measured at alternating current frequencies of 2000 Hz, 2500 Hz and 3000 Hz. Chenhua electrochemical workstation (CHI660D Instruments, Shanghai Chenhua Instrument Co., Ltd., Shanghai, China) was used to measure the photocurrent. Thermogravimetric analysis (TGA) was performed on a TGA/DSC 3+ in the temperature range of 30-800  $^\circ\text{C}$  under a nitrogen atmosphere and a heating rate of 10  $^\circ\text{C}/\text{min}$ . Electron paramagnetic resonance (EPR) spectra was measured by Bruker A300 EPR Spectroscopy. The apparent quantum yields (AQY) were calculated according to the formula:  $\text{AQY (100\%)} = (M_{(\text{product})} * N_A * h * c) / (P * S * t * \lambda) * 100\%$ , where the  $M_{(\text{product})}$  is the mole number of

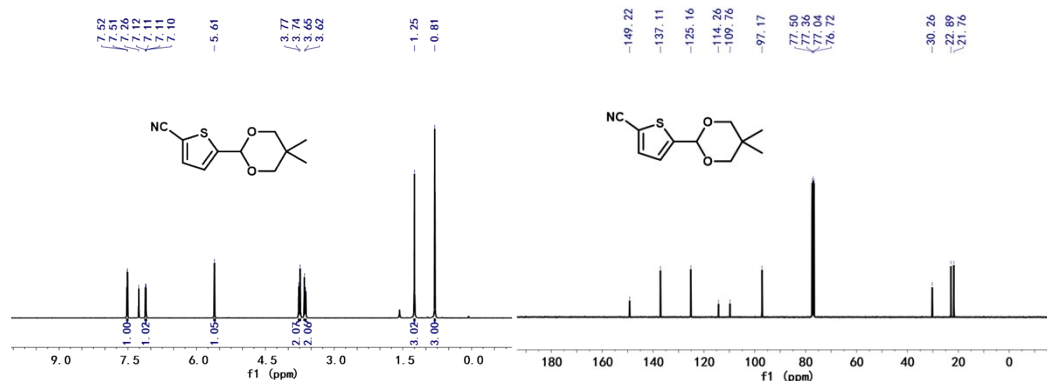
product,  $N_A$  is Avogadro constant,  $h$  is Planck constant,  $c$  is speed of light,  $P$  (the light power intensity) is 633 W/m<sup>2</sup>,  $S$  (irradiation area) is 1.5 cm<sup>2</sup>,  $t$  is irradiation time,  $\lambda$  is 460 nm.

## 2. Synthesis of Intermediate Products and Monomer



**Scheme S1** Synthesis procedure of monomer DPP-T-CHO. i: Neopentyl glycol, *p*-Toluenesulfonic acid monohydrate, toluene, 113 °C; ii: Diethyl succinate, *t*-BuONa, tert-Amyl alcohol, 100 °C; iii: 1-Bromobutane, K<sub>2</sub>CO<sub>3</sub>, 18-crown-6, DMF, 110 °C; iv: 1M HCl, THF, 75 °C.

**s2:** To a 100 mL pressure tube was charged with 5-formylthiophene-2-carbonitrile (s1, 6.0 g, 43.7 mmol), Neopentyl glycol (5.5 g, 52.5 mmol), *p*-Toluenesulfonic acid monohydrate (249.6 mg, 1.3 mmol) and 25 mL toluene. Then the reaction was executed in nitrogen atmosphere overnight at 113 °C. After cooling to room temperature, the solution was poured into water and extracted three times with ethyl acetate to collect the organic phase. Subsequently, the organic phase was dried and the solvent was removed in vacuo. The crude product was purified by silica gel chromatography (Petroleum ether as eluent) to obtain 9.2 g s2 as a white powder with 94.5% of yield. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ (ppm) 7.52-7.51 (d,  $J$  = 4.0 Hz, 1H), 7.12-7.10 (d,  $J$  = 8.0Hz, 1H), 5.61 (s, 1H), 3.77-3.74 (d,  $J$  = 12.0 Hz, 2H), 3.65-3.62 (d,  $J$  = 12.0 Hz, 2H), 1.25 (s, 3H), 0.81 (s, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ (ppm): 149.22, 137.11, 125.16, 114.26, 109.76, 97.17, 30.26, 22.89, 21.76. HR-MS:  $m/z$  [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>14</sub>NO<sub>2</sub>S: 224.0745, found: 224.0743.

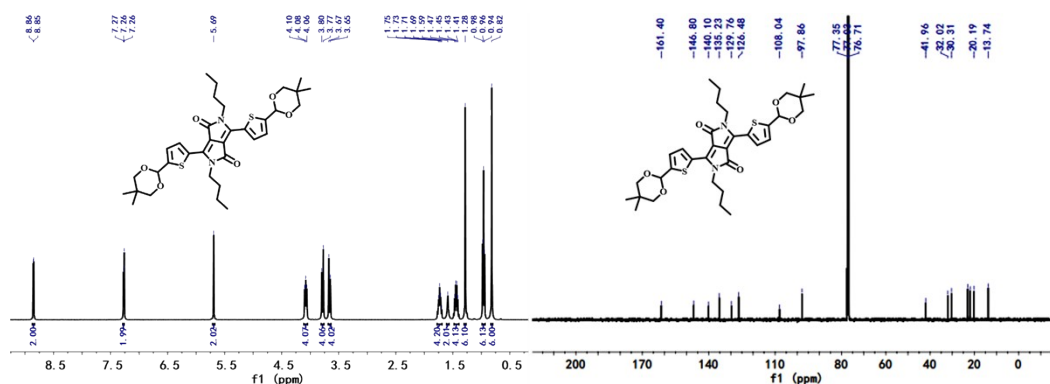


**Fig. S1** The  $^1\text{H}$ -NMR (left) and  $^{13}\text{C}$ -NMR spectra of **s2**.

**s3:** In  $\text{N}_2$  atmosphere, Sodium tert-butoxide (6.5g, 68.0 mmol) was dissolved in 40 mL tert-Amyl alcohol and stirred at  $100^\circ\text{C}$  for 1h. After that, 5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophene-2-carbonitrile (**s2**, 9.5 g, 42.5 mmol) was added. Then Diethyl succinate (2.96g, 17.0 mmol) was dissolved in 20 mL tert-Amyl alcohol and dropwised into the reaction solution with a constant pressure dropping funnel. Subsequently, the resulting suspension was strongly stirred at  $100^\circ\text{C}$  for 24 hours. After cooling to room temperature, glacial acetic acid (30 mL) and methanol (300 mL) were added into the reaction system, and the mixture was stirred at  $55^\circ\text{C}$  for another 2 h. Then the mixture was filtered, washed several times with methanol and water, and dried in vacuo to give 2.2 g crude **s3** as black-red solid without any purification.

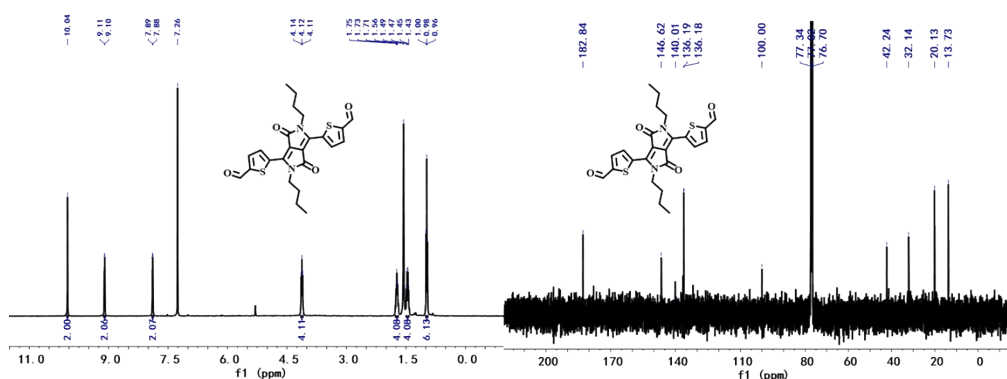
**s4:** To a 100 mL pressure tube was added **s3** (600.0 mg, 1.1 mmol), 1-Bromobutane (388.8 mg, 2.9 mmol),  $\text{K}_2\text{CO}_3$  (470.6mg, 3.4 mmol), catalyst 18-crown-6 (45.0 mg, 0.17 mmol) and 25 mL DMF. The reaction system was degassed-inflated with  $\text{N}_2$  5 times and reacted at  $110^\circ\text{C}$  overnight. After that, the solution was poured into water and extracted three times with dichloromethane to obtain organic phase. The organic phase was dried, condensed and purified via silica gel chromatography (dichloromethane as eluent) to obtain 377.0 mg **s4** as dark red solid, and the total yield from **s2** to **s4** is 12.7%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$ (ppm) 8.86-8.85 (d,  $J = 4.0$  Hz, 2H), 7.27-7.26 (d,  $J = 4.0$  Hz, 2H), 5.69 (s, 2H), 4.10-4.06 (t,  $J = 16.0$  Hz, 4H), 3.80-3.77 (d,  $J = 12.0$  Hz, 4H), 3.67-3.65 (d,  $J = 8.0$  Hz, 4H), 1.73-1.69 (m,  $J = 24.0$  Hz, 4H), 1.59(s, 2H), 1.47-1.41 (m, 4H), 1.28 (s, 6H), 0.98-0.94 (t,  $J=16.0\text{Hz}$ , 6H), 082 (s, 6H).  $^{13}\text{C}$ NMR

(CDCl<sub>3</sub>, 100 MHz):  $\delta$ (ppm) 161.40, 146.80, 135.23, 129.76, 126.48, 108.04, 97.86, 41.96, 30.31, 20.19, 13.74. HR-MS:  $m/z$  [M+Na]<sup>+</sup> calcd for C<sub>34</sub>H<sub>44</sub>N<sub>2</sub>NaO<sub>6</sub>S<sub>2</sub>: 663.2538, found: 663.2531.



**Fig. S2** The <sup>1</sup>H-NMR (left) and <sup>13</sup>C-NMR spectra of **s4**.

**DPP-T-CHO:** To a 250 mL round-bottom flask was added 300.0 mg **s4**, 80 mL THF and 3 mL HCl aqueous solution (1 M). The solution was refluxed for 3 hours and then poured into water. Purple solid was collected by filtration, and pure DPP-T-CHO was obtained via silica gel chromatography with dichloromethane as eluent (200.0 mg, 91% of yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ (ppm) 10.04 (s, 2H), 9.11-9.10 (d,  $J$  = 4.0 Hz, 2H), 7.89-7.88 (d,  $J$  = 4.0 Hz, 2H), 4.14-4.11 (t,  $J$  = 12.0 Hz, 4H), 1.75-1.71(m, 4H), 1.49-1.43 (m, 4H), 1.00-0.96 (t,  $J$ =16.0Hz, 6H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ (ppm) 182.84, 146.62, 140.01, 136.19, 136.18, 100.00, 42.24, 32.14, 20.13, 13.73. HR-MS:  $m/z$  [M+H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: 469.1256, found: 469.1255.

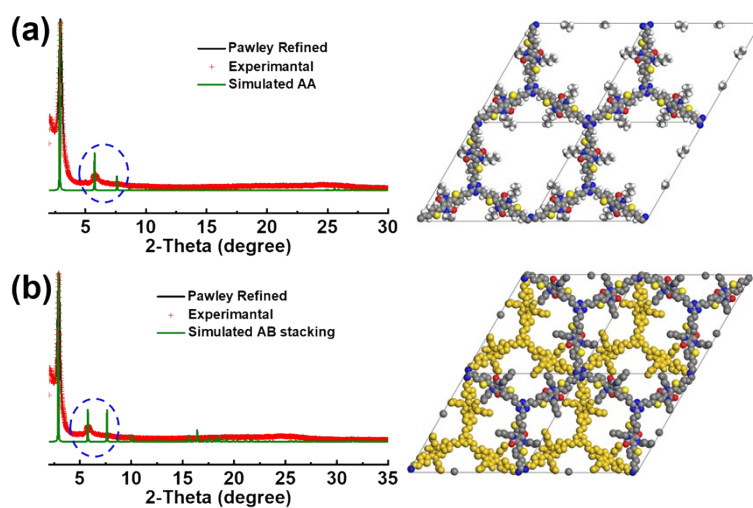


**Fig. S3** The <sup>1</sup>H-NMR (left) and <sup>13</sup>C-NMR spectra of **DPP-T-CHO**.

**DPP-COF:** To a 10 mL Pyrex tube was added DPP-T-CHO (52.7mg, 0.1125 mmol), 2,4,6-trimethyl-1,3,5-triazine (TMT, 9.2 mg, 0.075 mmol), benzoic anhydride (67.87 mg, 0.3 mmol)

and benzoic acid (36.6 mg, 0.3 mmol). Then, the tube was sealed and heated at 190 °C for 3 days. After reaction, a dark black powder was collected by sucking filtration and thoroughly washed with acetone, anhydrous ethanol, tetrahydrofuran, and dichloromethane, respectively. The collected sample was dried under vacuum at 120 °C for 24 h to give a dark black powder (55.3 mg, 95.5 % of yield).

### 3. Simulated and Experimental Structure of DPP-COF



**Fig. S4** The simulated and experimental PXRD pattern of (a) AA and (b) AB stacking model with corresponding stacking structures.

## 4. TGA Curve

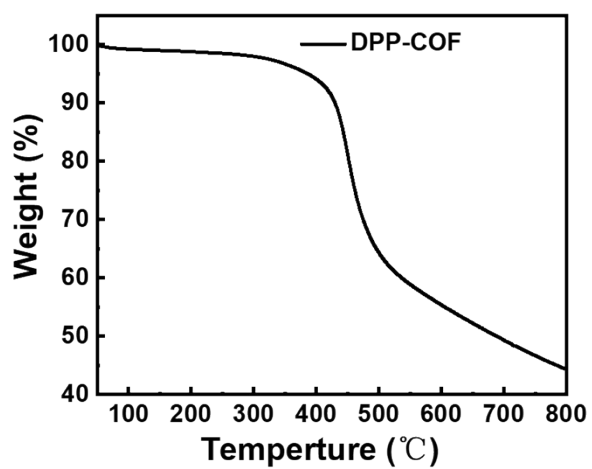


Fig. S5 TGA curve of DPP-COF.

## 5. TEM Images

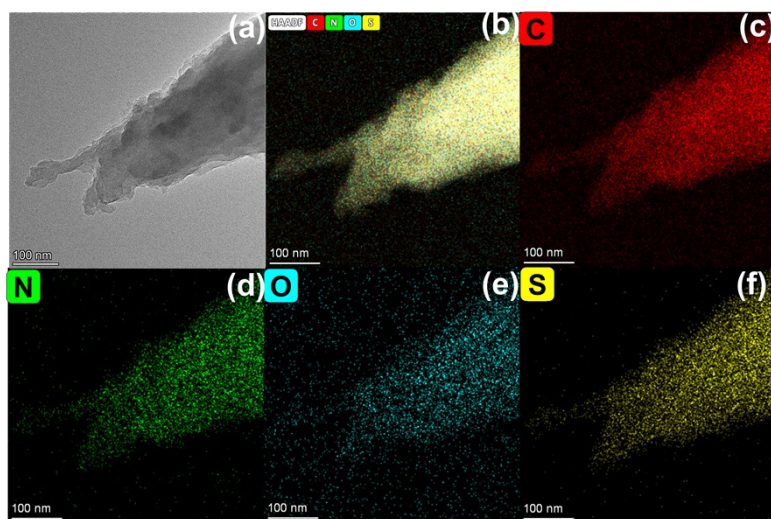
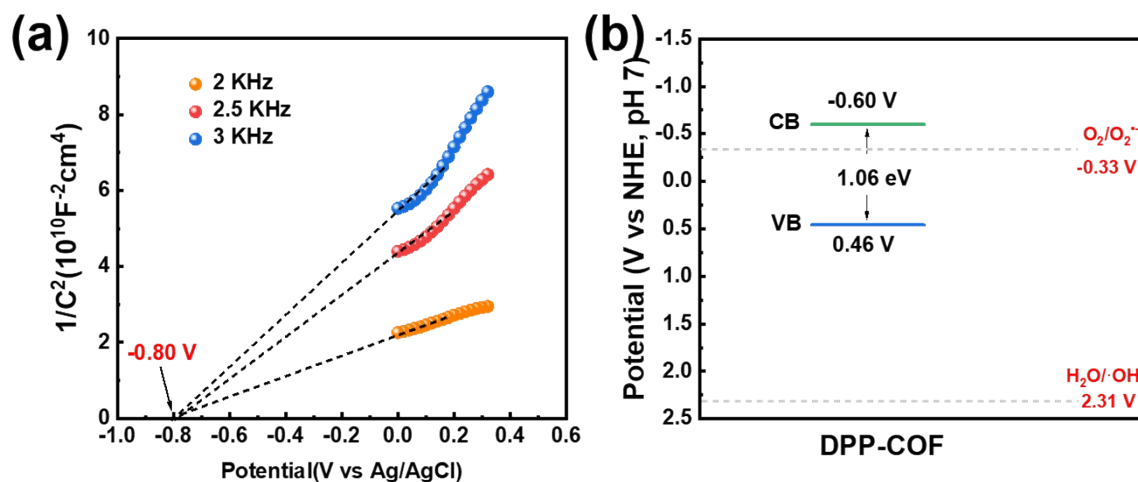


Fig. S6 HAADF-STEM image and corresponding elemental mapping images of DPP-COF.

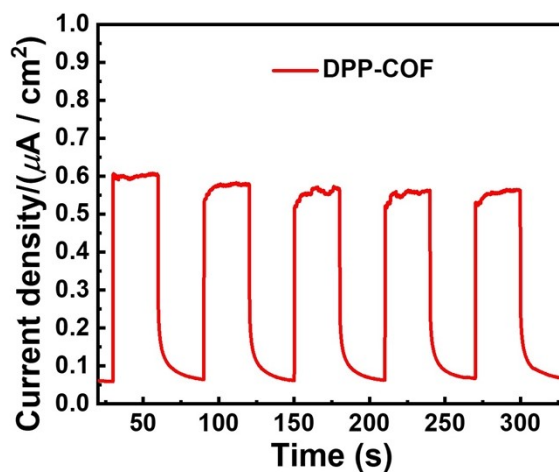


## 6. Mott-Schottky Plots and Band Potentials



**Fig. S7** (a) Mott-Schottky plots of DPP-COF, and the band potential was calculated according to the formula:  $E(NHE) = E(Ag/AgCl) + 0.197$ . (b) The bands potentials.

## 7. Photocurrent Response Curve



**Fig. S8** Photocurrent response curve of DPP-COF.

## 8. Photocatalytic Experiments

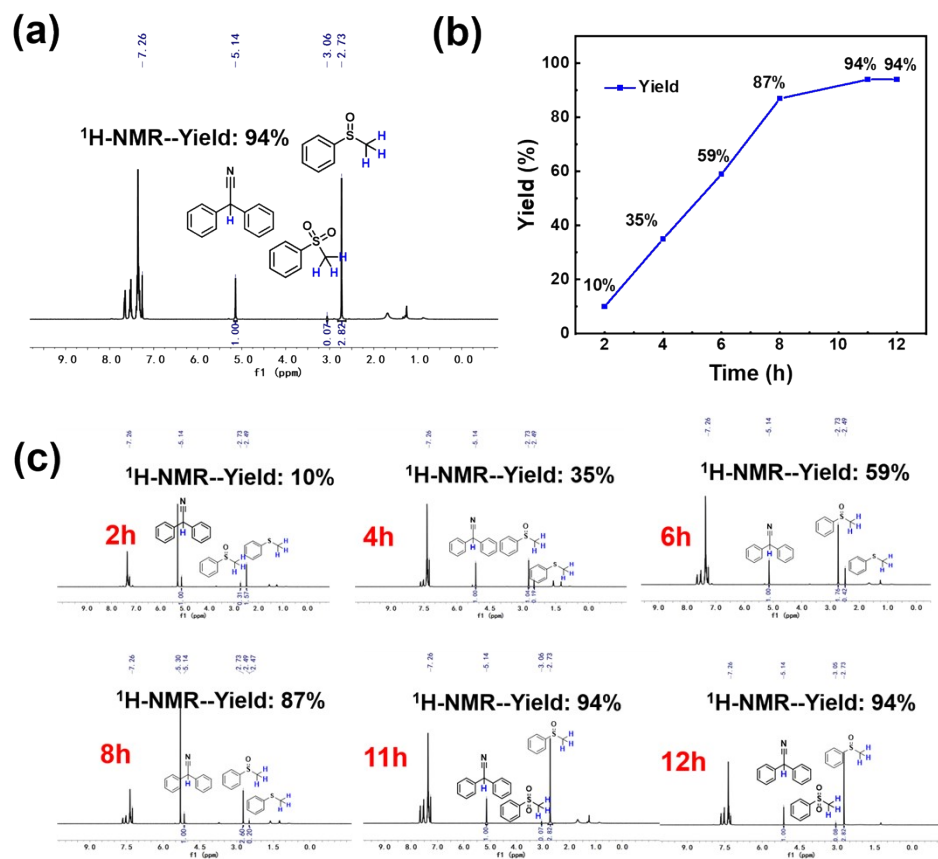
### 8.1 General Procedure for Photocatalytic Oxidation Reaction

**Photooxidation of sulfides:** A 10 mL quartz tube was charged with reaction substrate (0.3 mmol), COF photocatalyst (10 mg), solvent (3 mL). The mixture was bubbled with oxygen and stirred, then the tube was irradiated with a 10 W blue LED lamp (460 nm) in room temperature. After reaction, the solution was centrifuged and the solvent was removed by rotary evaporation. Yields were determined by <sup>1</sup>H-NMR spectroscopy with 0.3 mmol diphenylacetonitrile (DPAT) as internal standard. The isolated yield was obtained by purifying the solution by silica gel flash chromatography (Petroleum ether : ethyl acetate, v/v = 1 : 1 as eluent).

**Photooxidation of THIQs:** A 10 mL quartz tube was charged with reaction substrate (0.3 mmol), COF photocatalyst (10 mg), CH<sub>3</sub>CN (3 mL). The mixture was placed in air atmosphere and stirred, then the tube was irradiated with a 10 W blue LED lamp (460 nm) in room temperature. After reaction, the solution was centrifuged and the solvent was removed by rotary evaporation. Yields were determined by <sup>1</sup>H-NMR spectroscopy with 0.3 mmol diphenylacetonitrile (DPAT) as internal standard. The isolated yield was obtained by purifying the solution by silica gel flash chromatography (Petroleum ether : dichloromethane, v/v = 1 : 1 as eluent).

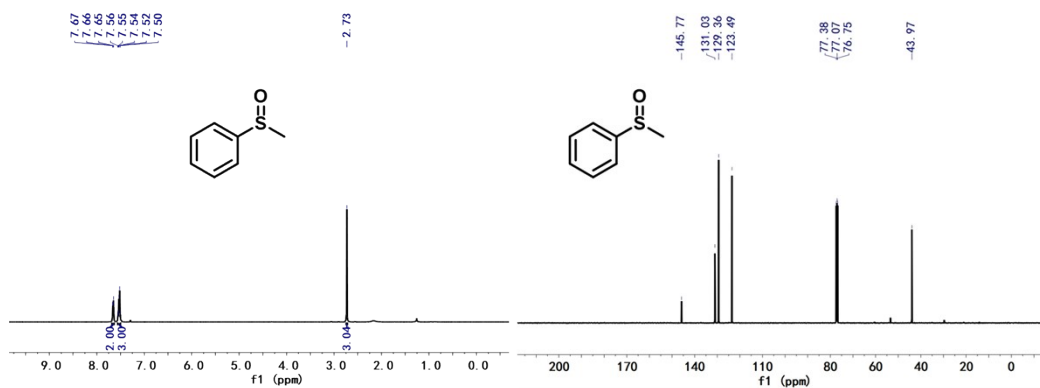
### 8.2 Photocatalytic oxidation of sulfides

#### 8.2.1 Yield of 2a Determined by <sup>1</sup>H-NMR Analysis



**Fig. S9** (a) Yield of model oxidation reaction determined by  $^1\text{H-NMR}$  spectra. (b, c) Reaction time examination of **2a** based on DPP-COF as photocatalyst with corresponding  $^1\text{H-NMR}$  spectra.

**2a**:  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 7.67-7.65 (t,  $J = 8.0$  Hz, 2H), 7.56-7.50 (m, 3H), 2.73 (s, 3H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 145.77, 131.03, 129.36, 123.49, 43.97.



**Fig. S10**  $^1\text{H-NMR}$  (left) and  $^{13}\text{C-NMR}$  (right) spectra of **2a**.

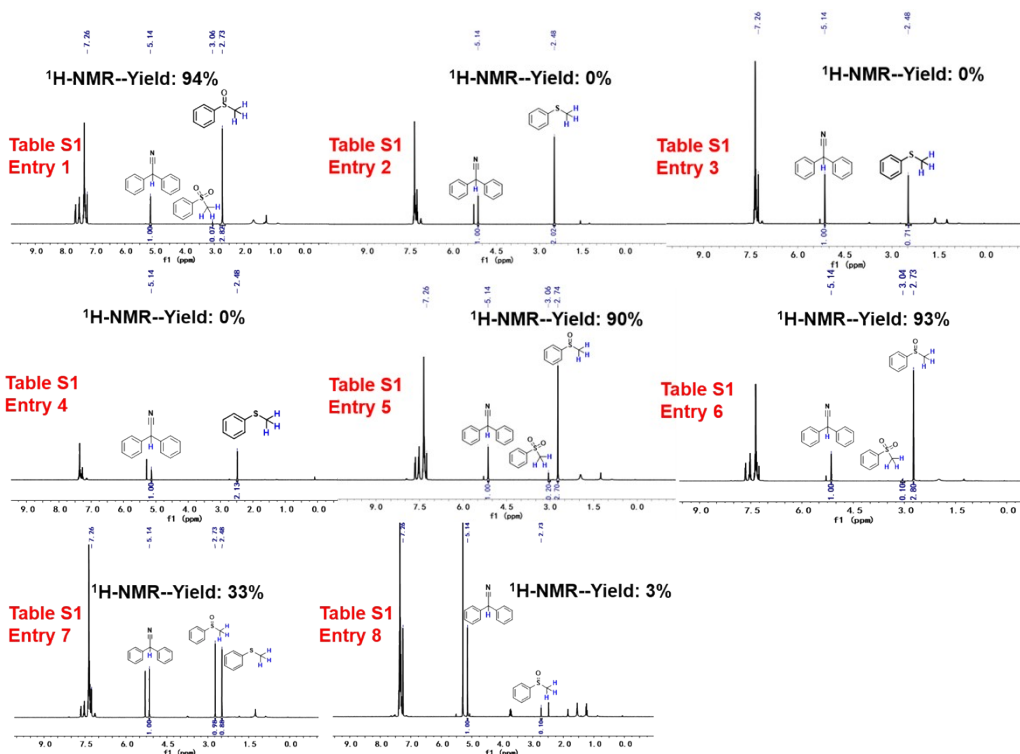
## 8.2.2 Control Experiments and Generality Discussion

**Table S1** The control experiments (photooxidation of **1a**).

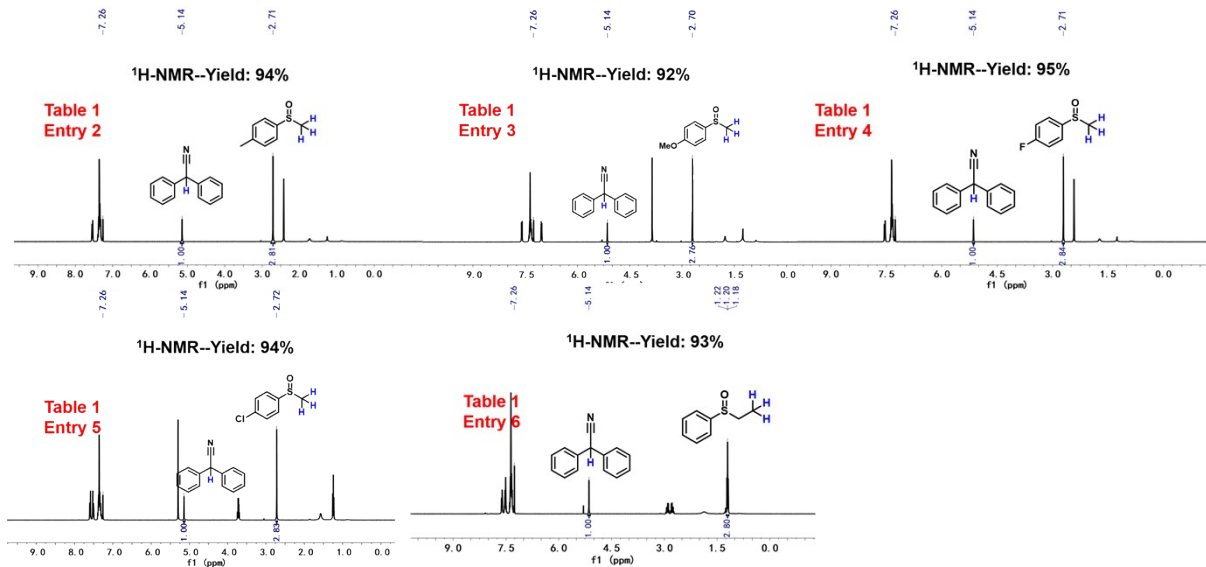
**1a** + O<sub>2</sub>  $\xrightarrow[\text{Blue LED lamp (460 nm)}]{\text{COF, Solvent, RT}}$  **2a**

Entry	Solvent	Light	Catalyst	O <sub>2</sub>	Time (h)	Yield (%)
1	EtOH	460 nm	DPP- COF	√	11	94 <sup>[a]</sup> 90 <sup>[b]</sup>
2	EtOH	460 nm	DPP- COF	-	11	0 <sup>[a]</sup>
3	EtOH	-	DPP- COF	√	11	0 <sup>[a]</sup>
4	EtOH	460 nm	-	√	11	0 <sup>[a]</sup>
5	MeCN	460 nm	DPP- COF	√	11	90 <sup>[a]</sup>
6	MeOH	460 nm	DPP- COF	√	11	93 <sup>[a]</sup>
7	EtOH	White LED	DPP- COF	√	11	33 <sup>[a]</sup>
8	EtOH	520 nm	DPP- COF	√	11	3 <sup>[a]</sup>

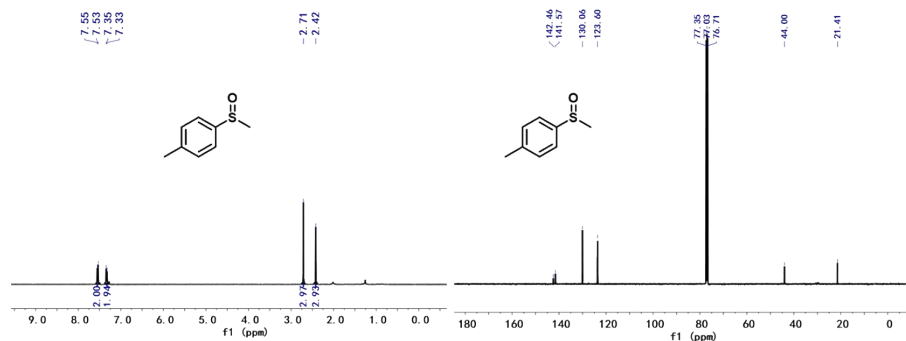
<sup>[a]</sup> Yields were determined by <sup>1</sup>H-NMR spectra. <sup>[b]</sup> Isolated yield.



**Fig. S11** Corresponding <sup>1</sup>H-NMR spectra of the control experiments (Table S1) with DPAT as internal standard.

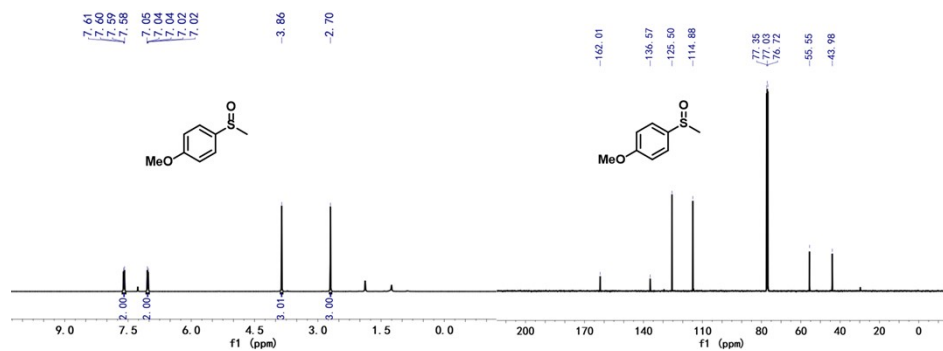


**Fig. S12** Yield of **2b-2f** catalyzed by DPP-COF determined by  $^1\text{H-NMR}$  with DPAT as internal standard.



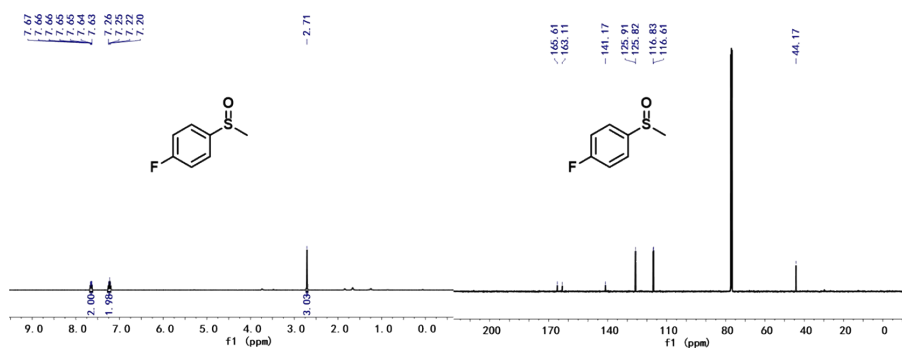
**Fig. S13**  $^1\text{H-NMR}$  (left) and  $^{13}\text{C-NMR}$  (right) spectra of **2b**.

**Isolated 2b:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 7.55-7.53 (d,  $J = 8.0$  Hz, 2H), 7.35-7.33 (d,  $J = 8.0$  Hz, 2H), 2.71 (s, 3H), 2.42 (s, 3H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 142.46, 141.57, 130.06, 123.60, 44.00, 21.41.



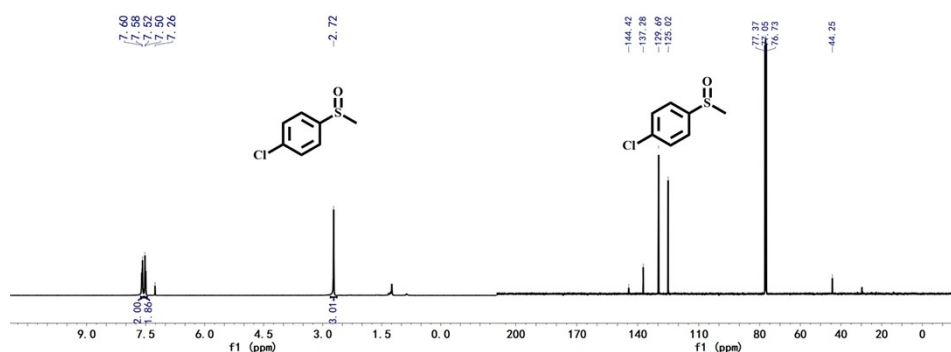
**Fig. S14**  $^1\text{H}$ -NMR (left) and  $^{13}\text{C}$ -NMR (right) spectra of **2c**.

**Isolated 2c** :  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 7.61-7.58 (m, 2H), 7.05-7.02 (m, 2H), 3.86 (s, 3H), 2.70 (s, 3H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 162.01, 136.57, 125.50, 114.88, 55.55, 43.98.



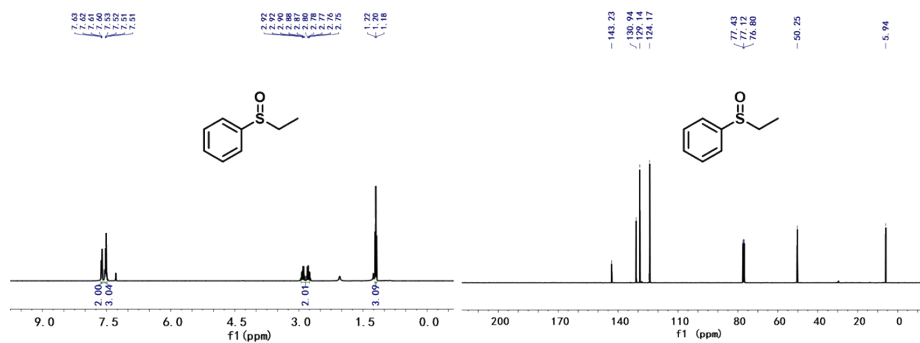
**Fig. S15**  $^1\text{H}$ -NMR (left) and  $^{13}\text{C}$ -NMR (right) spectra of **2d**.

**Isolated 2d** :  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 7.67-7.63 (m, 2H), 7.26-7.20 (m, 2H), 2.71 (s, 3H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 165.61, 163.11, 141.17, 125.91, 125.82, 116.83, 116.61, 44.17.



**Fig. S16**  $^1\text{H}$ -NMR (left) and  $^{13}\text{C}$ -NMR (right) spectra of **2e**.

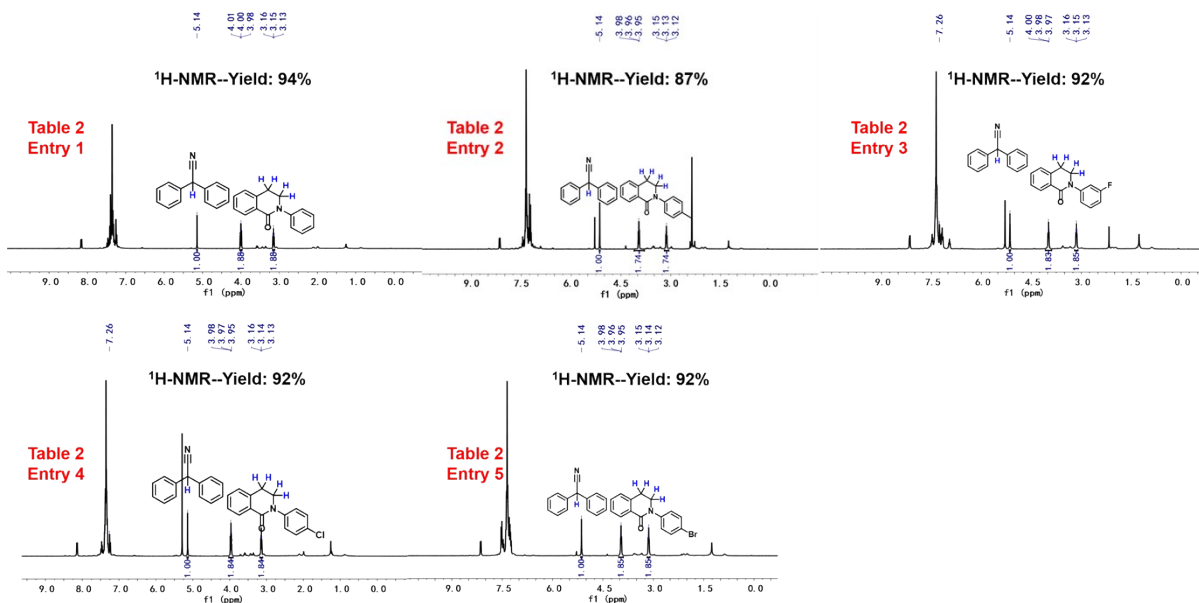
**Isolated 2e:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 7.60-7.58 (d,  $J = 8.0$  Hz, 2H), 7.52-7.50 (d,  $J = 8.0$  Hz, 2H), 2.72 (s, 3H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 144.42, 137.28, 129.69, 125.02, 44.25.



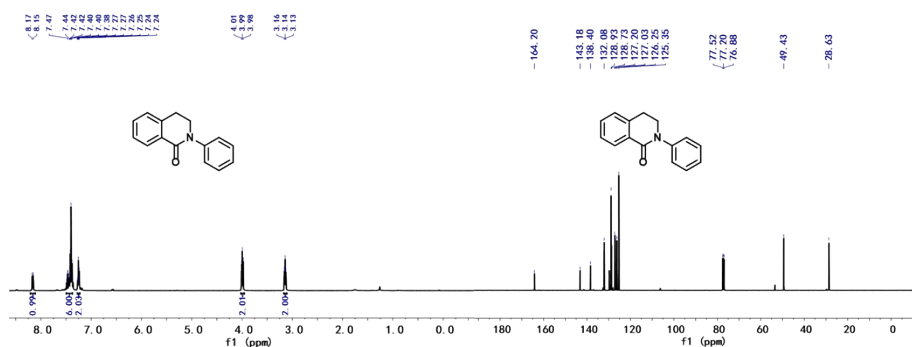
**Fig. S17**  $^1\text{H-NMR}$  (left) and  $^{13}\text{C-NMR}$  (right) spectra of **2f**.

**Isolated 2f:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 7.63-7.60 (m, 2H), 7.53-7.51 (m, 3H), 2.92-2.75 (m, 2H), 1.22-1.18 (t,  $J = 16.0$  Hz, 3H).  $^{13}\text{C-NMR}$ ( $\text{CDCl}_3$ ,100MHz):  $\delta$  (ppm) 143.23, 130.94, 129.14, 124.17, 50.25, 5.94.

### 8.3 Photocatalytic oxidation of THIQs



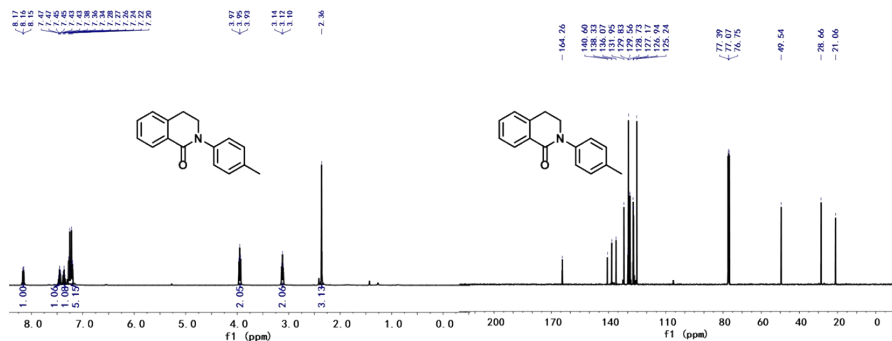
**Fig. S18** Yield of **4a-4e** catalyzed by DPP-COF determined by <sup>1</sup>H-NMR with DPAT as internal standard.



**Fig. S19** <sup>1</sup>H-NMR (left) and <sup>13</sup>C-NMR (right) spectra of **4a**.

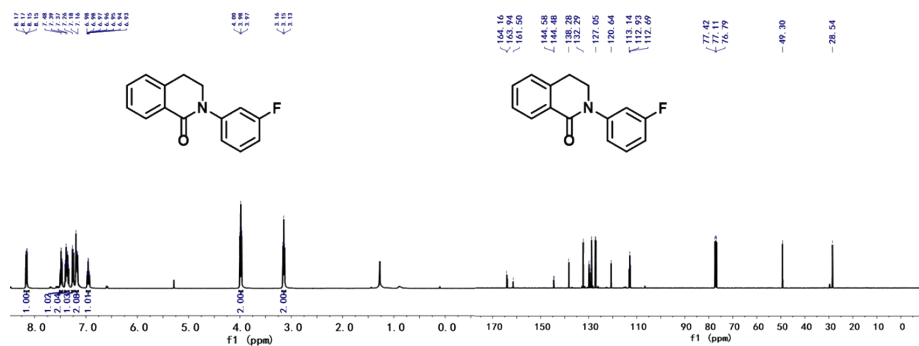
**Isolated 4a** : <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) 8.17-8.15 (dd,  $J$  = 8.0 Hz, 1H), 7.47-7.38 (m, 6H), 7.27-7.24 (d,  $J$  = 12.0 Hz, 2H), 4.01-3.98 (t,  $J$  = 12.0 Hz, 2H), 3.16-3.13 (t,  $J$  = 12.0 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  (ppm) 164.20, 143.18, 138.40, 132.08, 128.93, 128.73, 127.20, 127.03, 126.25, 125.35, 49.43, 28.63.





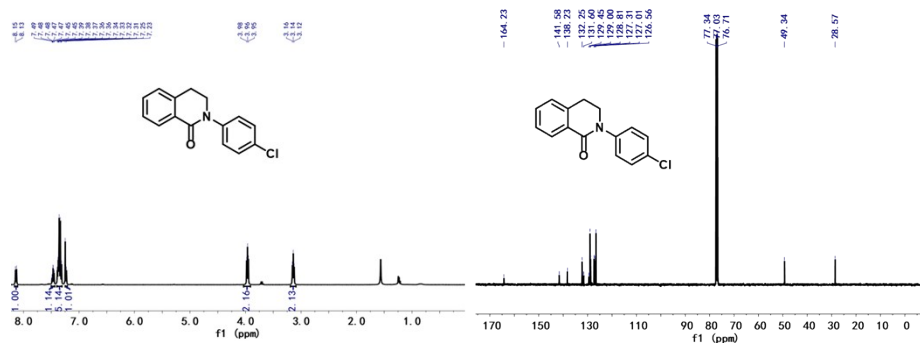
**Fig. S20**  $^1\text{H}$ -NMR (left) and  $^{13}\text{C}$ -NMR (right) spectra of **4b**.

**Isolated 4b** :  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.17-8.15 (d,  $J = 8.0$  Hz, 1H), 7.47-7.43 (t,  $J = 16.0$  Hz, 1H), 7.38-7.34 (t,  $J = 12.0$  Hz, 1H), 7.28-7.20 (m, 5H), 3.97-3.93 (m,  $J = 16.0$  Hz, 2H), 3.14-3.10 (t,  $J = 16.0$  Hz, 2H), 2.36 (s, 3H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100MHz):  $\delta$  (ppm) 164.26, 140.60, 138.33, 136.07, 131.95, 129.83, 129.56, 128.73, 127.17, 126.94, 125.24, 49.54, 28.66, 21.06.



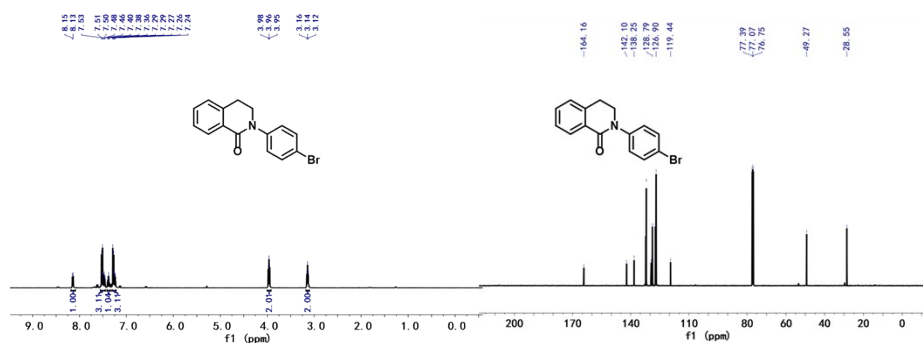
**Fig. S21**  $^1\text{H}$ -NMR (left) and  $^{13}\text{C}$ -NMR (right) spectra of **4c**.

**Isolated 4c** :  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.17-8.15 (dd,  $J = 8.0$  Hz, 1H), 7.50-7.46 (m, 1H), 7.40-7.34 (m, 2H), 7.26-7.24 (m, 1H), 7.19-7.16 (m, 2H), 6.98-6.13 (m, 1H), 4.00-3.97 (t,  $J = 12.0$  Hz, 2H), 3.16-3.13 (t,  $J = 12.0$  Hz, 2H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100MHz):  $\delta$  (ppm) 164.16, 163.94, 161.50, 144.58, 144.48, 138.28, 132.29, 127.05, 120.64, 113.14, 112.93, 112.69, 49.30, 28.54.



**Fig. S22**  $^1\text{H-NMR}$  (left) and  $^{13}\text{C-NMR}$  (right) spectra of **4d**.

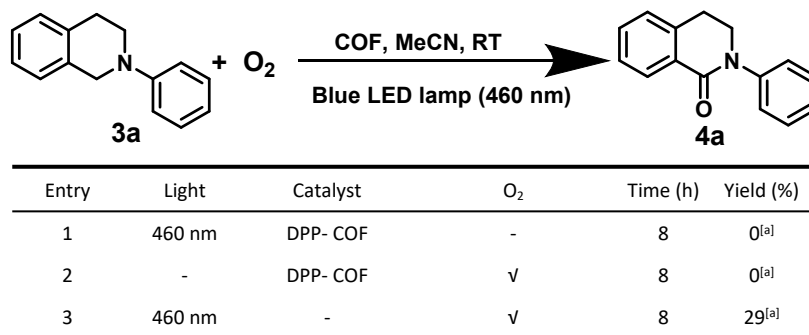
**Isolated 4d:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.15-8.13 (d,  $J = 8.0$  Hz, 1H), 7.49-7.45 (m, 1H), 7.39-7.31 (m, 5H), 7.25-7.23 (d,  $J = 8.0$  Hz, 1H), 3.98-3.95 (t,  $J = 12.0$  Hz, 2H), 3.16-3.12 (t,  $J = 16.0$  Hz, 2H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 164.23, 141.58, 138.23, 132.25, 131.60, 129.45, 129.00, 128.81, 127.31, 127.01, 126.56, 49.34, 28.57.



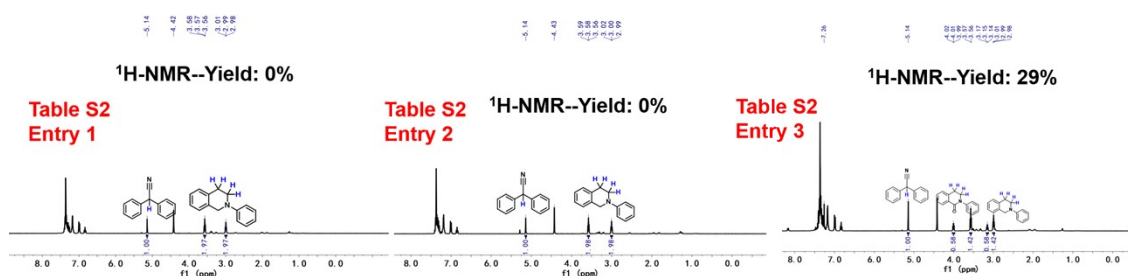
**Fig. S23**  $^1\text{H-NMR}$  (left) and  $^{13}\text{C-NMR}$  (right) spectra of **4e**.

**Isolated 4e:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 8.15-8.13 (d,  $J = 8.0$  Hz, 1H), 7.53-7.46 (m, 3H), 7.40-7.36 (m, 1H), 7.29-7.24 (m, 3H), 3.98-3.95 (t,  $J = 12.0$  Hz, 2H), 3.16-3.12 (t,  $J = 16.0$  Hz, 2H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 164.16, 142.10, 138.25, 128.79, 126.90, 119.44, 49.27, 28.55.

**Table S2 The control experiments (Photooxidation of 3a).**



<sup>[a]</sup> Yields were determined by <sup>1</sup>H-NMR spectra.



**Fig. S24** Yield of **4a** in the control experiments determined by <sup>1</sup>H-NMR.

## 8.4 Comparison of DPP-COF and Reported High-performing COFs

**Table S3 The performance of different COFs in the photooxidation of sulfides.<sup>1-12</sup>**

Entry	Substrates (1a)	COF	Light Source / Time	Yield	Conv.	Sel.	Ref.
				(%)	(%)	(%)	
1	0.3 mmol	DPP-COF (10 mg)	10 W blue LED/11 h	94			<b>This Work</b>
2	0.3 mmol	BI-COF-1 (8 mg)	300 W Xe lamp/8 h		100	92	1
3	0.1 mmol	En-COF-P (5 mg)	30 W blue LED/9 h		99	99	2
4	0.1 mmol	TpBpy-COF (5 mg)	Blue LED/6 h		99.9	99.9	3
5	0.11 mol	PDI-PDA (6 mg)	410-420 nm LED/4 h	90.4			4
6	0.3 mmol	BSe-COF (10 mg)	9 W blue LED/8 h	95			5
7	0.1 mmol	COF-NUST-1 (4 mg)	30 W blue LED/4 h		99	98	6
8	0.15 mmol	TPDH-PTBA (5 mg)	Blue LED/12 h		99		7

9	0.5 mmol	TBPA-COF (5 mg)	Blue LED/1.2 h	91	98	8
10	0.3 mmol	R-DTP-COF-QA (12 mg)	Red LED/16 h	94		9
11	0.2 mmol	PyPor-COF (1 mg)	5W red LED/24 h	99		10
12	0.05 mmol	CuPor-Dha (10 mg)	Blue LED /10 h	82		11
13	0.05 mmol	DhaTph-Zn (10 mg)	300 W Xe lamp/10 h	82	99	12

**Table S4 The performance of different COFs in the photooxidation of THIQs.<sup>13-17</sup>**

Entry	Substrates	COF	Light Source / Time	Yield (%)	Ref.
1	3a (0.3 mmol)	DPP-COF (10 mg)	10 W blue LED/8 h	94	<b>This Work</b>
2	3b (0.3 mmol)	DPP-COF (10 mg)	10 W blue LED/8 h	87	<b>This Work</b>
3	3a (0.2 mmol)	2D-COF-1 (8 mg)	40 W blue LED/12 h	90	13
4	3a (0.1 mmol)	COF-TCZ-O (3 mg)	30 W blue LED/16 h	83	14
5	3b (0.1 mmol)	TRO-OMe (2.5 mg)	White LED/5 h	90	15
6	3a (0.1 mmol)	OZBT-COF (5 mg)	30 W blue LED/10 h	85	16
7	3a (0.1 mmol)	TEP-27FO (2.5 mg)	40 W red LED/2 h	91	17

## 8.5 Recycling Experiments

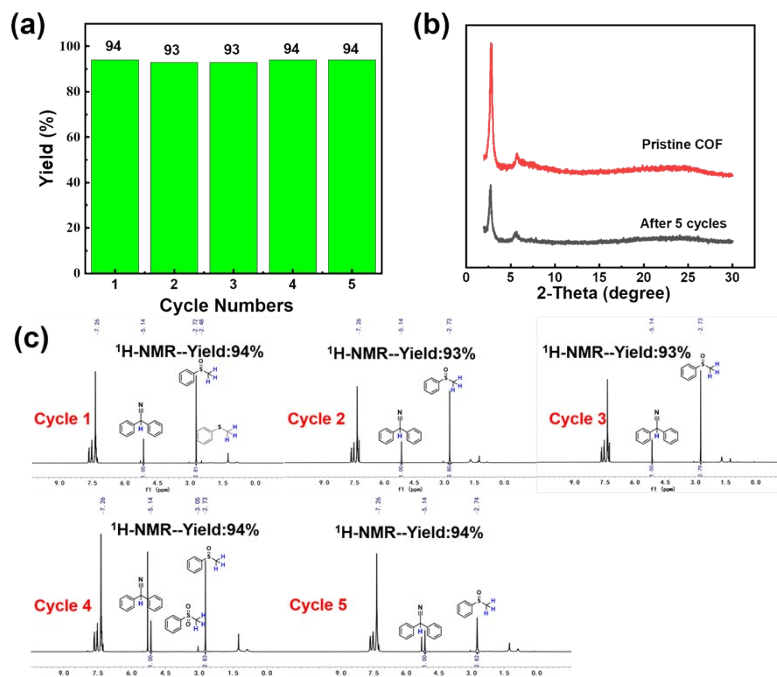


Fig. S25 (a, c) The recycle yields of 2a. (b) PXRD patterns after 5 cycles.

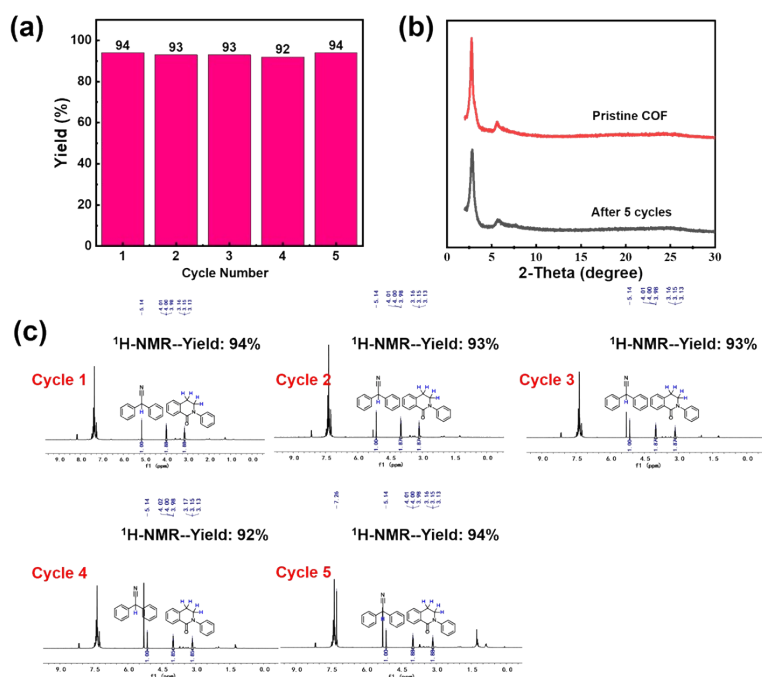
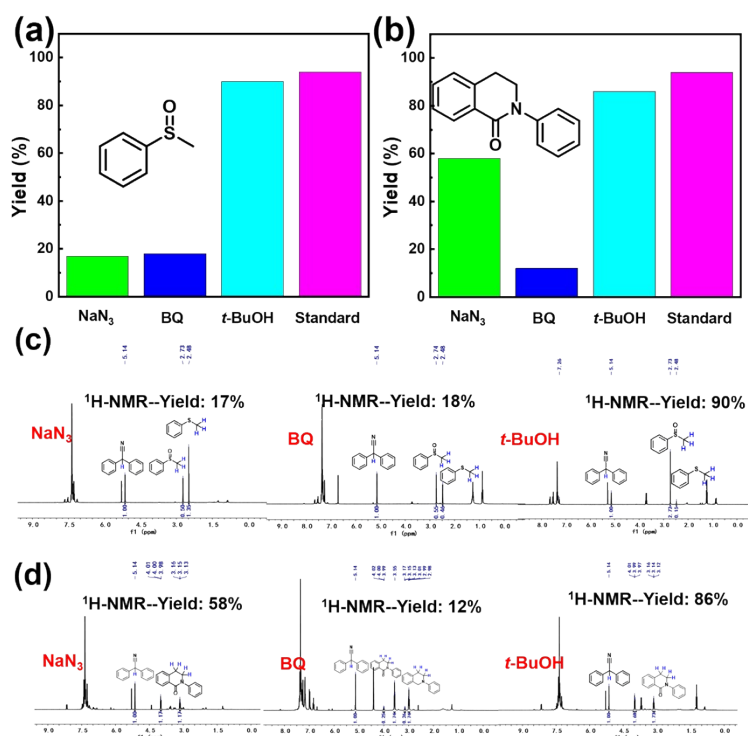


Fig. S26 (a, c) The recycle yields of 4a. (b) PXRD patterns after 5 cycles.

## 8.6 Quenching Experiments



**Fig. S27** Quenching experiments and corresponding <sup>1</sup>H-NMR Yields of (a, c) 2a and (b, d) 4a in the presence of quenching agents. NaN<sub>3</sub>/BQ/*t*-BuOH = 0.3/0.3/0.3 equivalent of substrates, respectively.

## 9. Crystallographic Parameters

DPP-COF    Space group: <i>P3</i>			
$a = 35.51 \text{ \AA}, b = 35.51 \text{ \AA}, c = 3.65 \text{ \AA}$			
$\alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ$			
Atom	x	y	z
N1	0.04312	-0.97092	1.07869
C2	0.01401	-0.95679	1.07913
C3	0.02841	-0.91058	1.04128
C4	0.06881	-0.88216	0.934
C5	0.08363	-0.83638	0.85551
S6	0.13458	-0.8033	0.68798
C7	0.12433	-0.7611	0.69497
C8	0.08312	-0.77301	0.81869

C9	0.05981	-0.81589	0.91057
C10	0.15676	-0.71625	0.5845
N11	0.20371	-0.69705	0.60678
C12	0.22082	-0.65465	0.49355
C13	0.18573	-0.64695	0.39508
C14	0.1476	-0.68639	0.46222
C15	0.17657	-0.61708	0.27279
N16	0.12962	-0.63628	0.25051
C17	0.11251	-0.67868	0.36374
C18	0.20901	-0.57224	0.16232
C19	0.25022	-0.56032	0.0386
C20	0.27352	-0.51744	-0.05328
C21	0.2497	-0.49696	0.00179
S22	0.19875	-0.53004	0.16931
C23	0.26452	-0.45117	-0.07671
C24	0.30493	-0.42276	-0.18399
C25	0.31932	-0.37655	-0.22184
N26	0.36241	-0.34738	-0.2214
C27	0.22662	-0.71921	0.7463
C28	0.27587	-0.68999	0.80077
C29	0.29667	-0.7164	0.93608
C30	0.34507	-0.68742	1.01832
C31	0.10672	-0.61413	0.11099
C32	0.05746	-0.64335	0.05652
C33	0.03666	-0.61693	-0.07879
C34	-0.01174	-0.64591	-0.16102
O35	0.07397	-0.70552	0.36925
O36	0.25937	-0.62781	0.48804
H37	0.00429	-0.90082	1.07761
H38	0.09198	-0.89305	0.88709
H39	0.0704	-0.75149	0.85361
H40	0.02722	-0.83073	1.02003
H41	0.26294	-0.58185	0.00368
H42	0.30611	-0.5026	-0.16274
H43	0.24135	-0.44028	-0.0298
H44	0.32904	-0.43251	-0.22032
H45	0.22097	-0.74628	0.56321
H46	0.21172	-0.73429	1.00891
H47	0.282	-0.66351	0.99212
H48	0.292	-0.67403	0.54559

H49	0.29287	-0.7414	0.73573
H50	0.27924	-0.73488	1.18056
H51	0.36402	-0.67514	0.76281
H52	0.35719	-0.70658	1.16623
H53	0.3511	-0.65887	1.1853
H54	0.12161	-0.59905	-0.15162
H55	0.11236	-0.58705	0.29408
H56	0.04134	-0.65931	0.3117
H57	0.05134	-0.66983	-0.13483
H58	0.05409	-0.59845	-0.32327
H59	0.04046	-0.59194	0.12156
H60	-0.03068	-0.6582	0.09449
H61	-0.01777	-0.67446	-0.328
H62	-0.02385	-0.62676	-0.30894

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