

## Supporting Information

### Visible-light heterogeneous photocatalysis with an ionic porous organic polymer (IPOP): synthesis of $\beta$ -keto sulfoxides and benzothiophene diesters by tandem radical addition-oxidations

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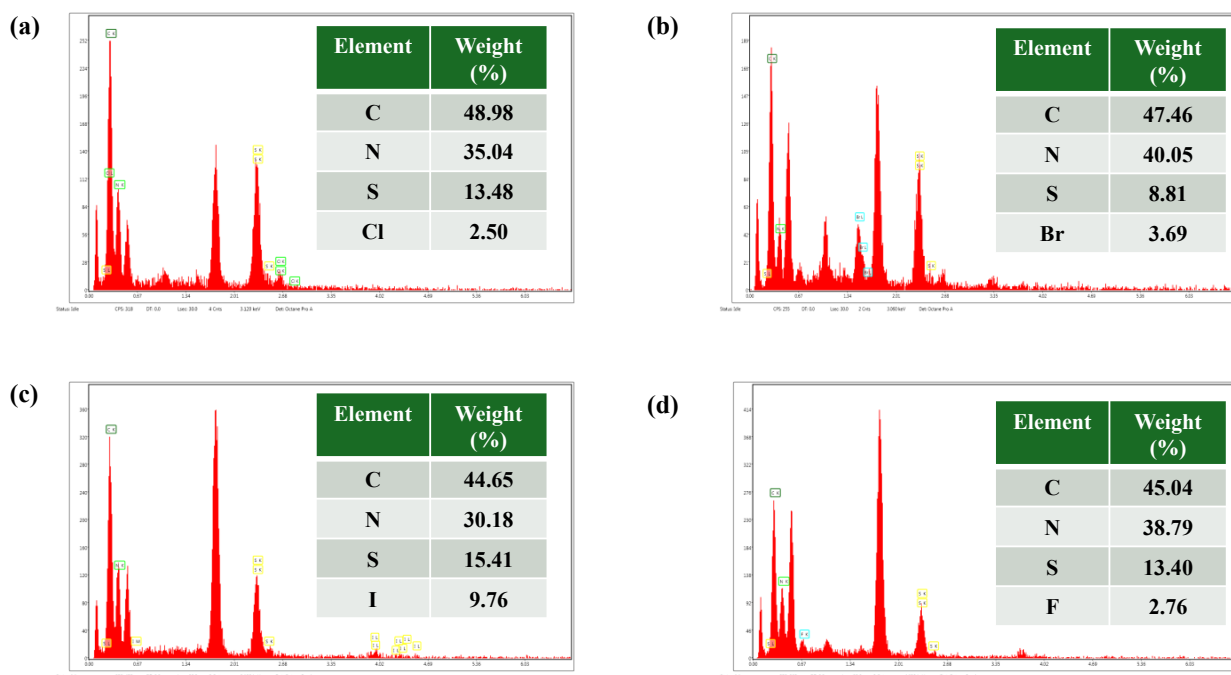
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## General aspects

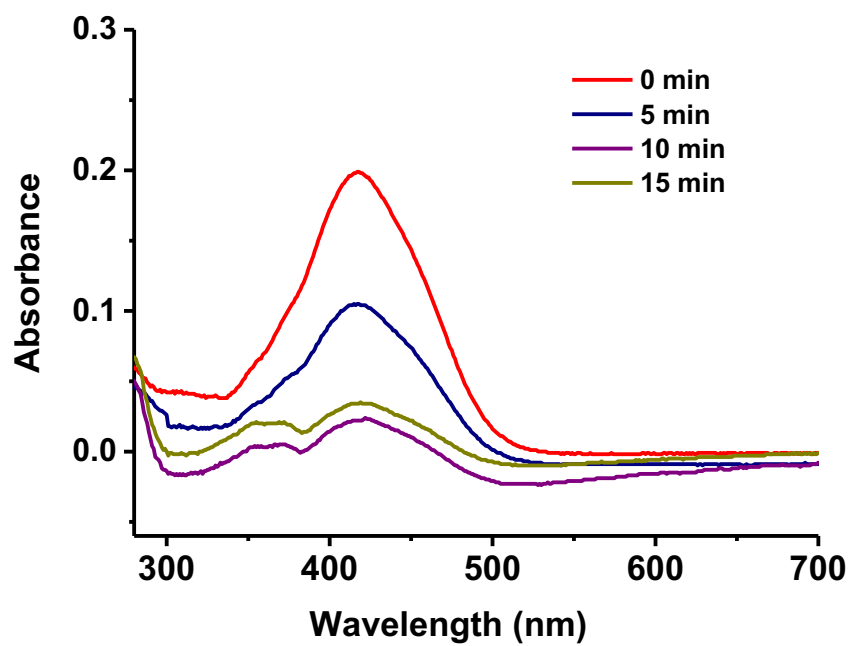
All the reagents employed were available from commercial sources and were used without further purification. Freshly distilled solvents were used for the synthesis. Column chromatography was performed using silica gel of 100-200  $\mu$  mesh.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on JEOL-Lambda spectrometers. Solid-state  $^{13}\text{C}$  NMR spectra were recorded on Bruker AVANCE III 500 spectrometer. IR spectra were recorded using a Bruker Vector 22 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on Agilent 6546 LC/QTOF machine. Thermogravimetric analyses were carried out with a Mettler Toledo TGA apparatus under  $\text{N}_2$  atmosphere with a heating rate of 10  $^\circ\text{C}/\text{min}$ . SEM images were recorded on a Nova Nano SEM 450 scanning electron microscope. TEM images were recorded using a carbon coated Cu grid on a FEI Titan G2 60-300 with HRTEM operating at a voltage of 300 kV. XPS analyses were carried out on an X-ray photoelectron spectroscopy module (PHI 5000 Versa Prob II, FEI Inc.) and Omicron Nano tech. XPS. The gas adsorption and desorption studies were performed using Quantachrome AutosorbIQ automated gas sorption analyzer. The electron paramagnetic resonance analyses (EPR) were recorded using Bruker EMX EPR.

## Description of ion exchange experiment of CyNTzTz-IPOP with KX

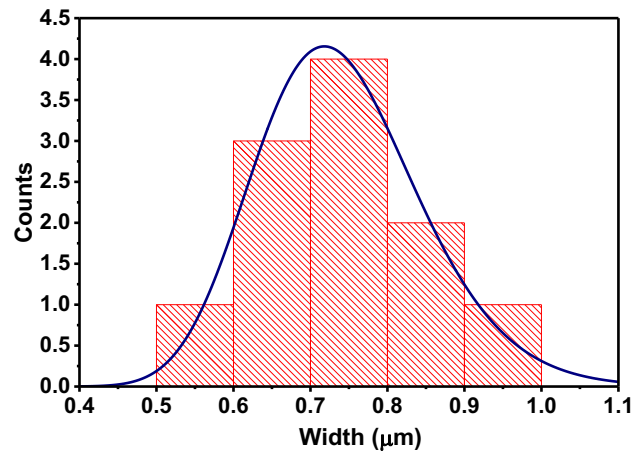
CyNTzTz-IPOP (30 mg) was taken in a round bottom flask in MeCN (5 mL) and a saturated solution of the KX 5 mL (X= F, Br, and I) was added to it. The resulting mixture was heated at 60 °C for 3 h. Afterwards, the solid polymer was filtered out from the reaction and repeated the process 5 times. Then, the polymer was thoroughly washed with water and dried at 70 °C for 10h. The exchange of Cl<sup>-</sup> ions by I<sup>-</sup>, Br<sup>-</sup>, and F<sup>-</sup> was analysed by EDS analyses.



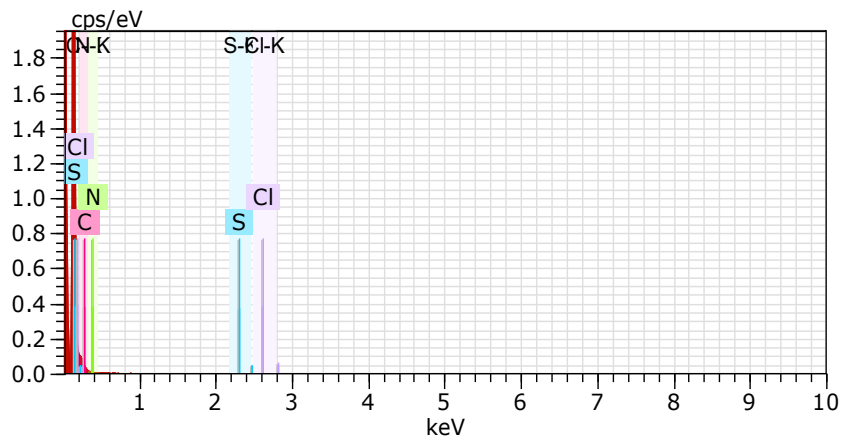
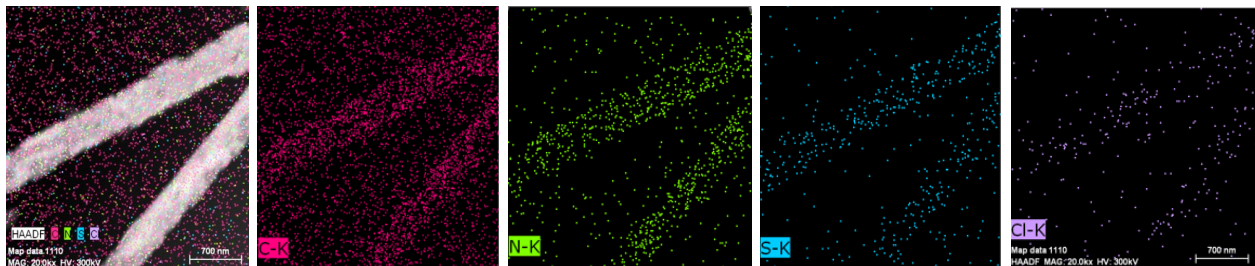
**Fig. S1** EDS analyses of (a) CyNTzTz-IPOP (parent polymer); (b) CyNTzTz-IPOP exchanged with Br<sup>-</sup>; (c) CyNTzTz-IPOP exchanged with I<sup>-</sup>; (d) CyNTzTz-IPOP exchanged with F<sup>-</sup>.



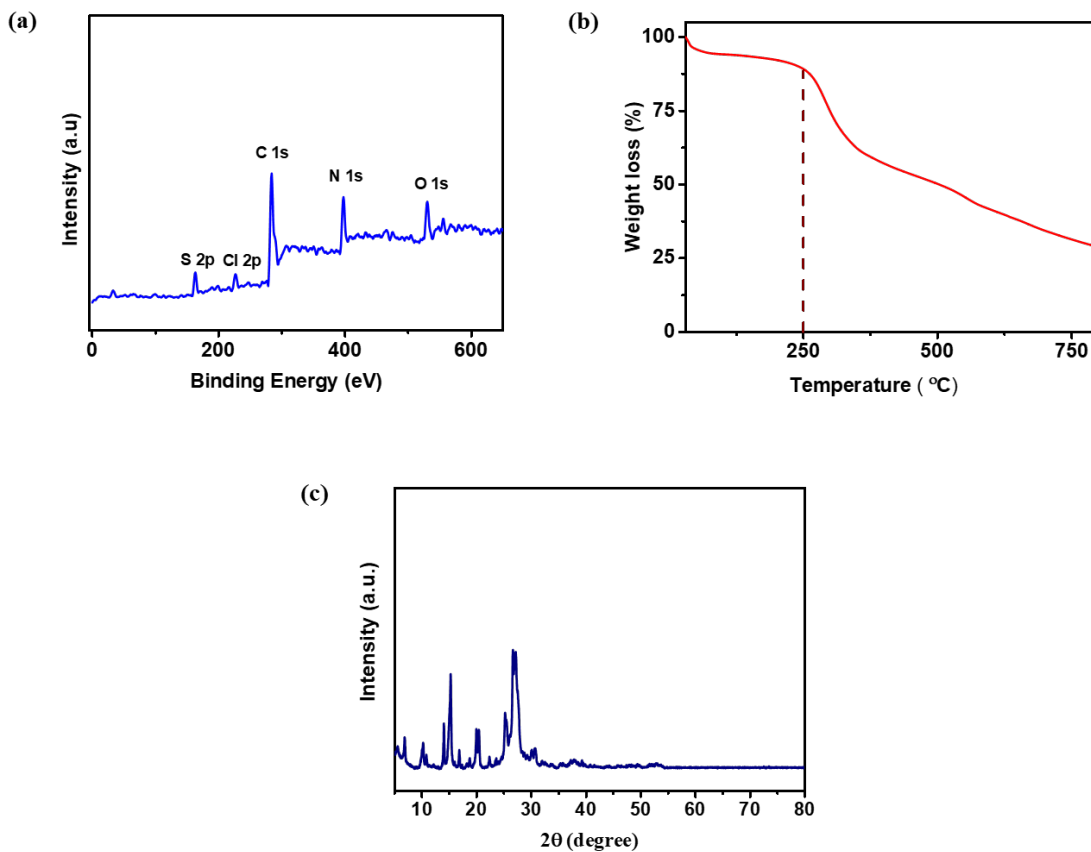
**Fig. S2** Anion exchange of CyNTzTz-IPOP with methyl orange (MO) at a concentration of 5 ppm



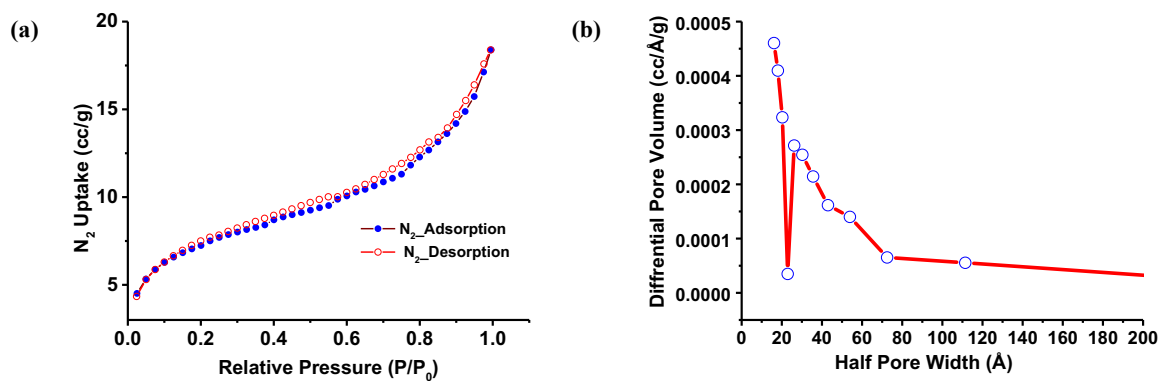
**Fig. S3** Particle size distribution histogram for CyNTzTz-IPOP based on SEM analysis.



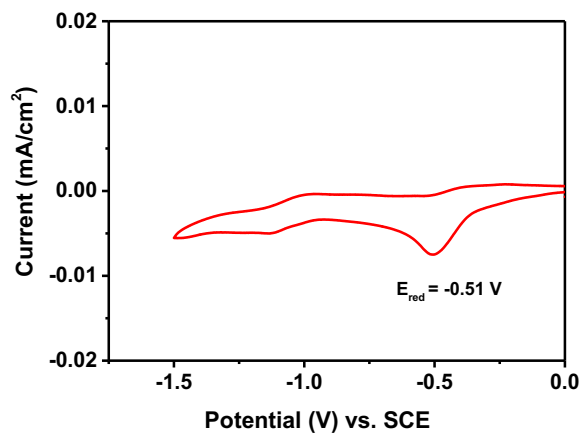
**Fig. S4** HR-TEM elemental mapping for CyNTzTz-IPOP.



**Fig. S5** (a) XPS full survey spectrum of CyNTzTz-IPOP, (b) TGA plot of CyNTzTz-IPOP, and (c) PXRD of CyNTzTz-IPOP.



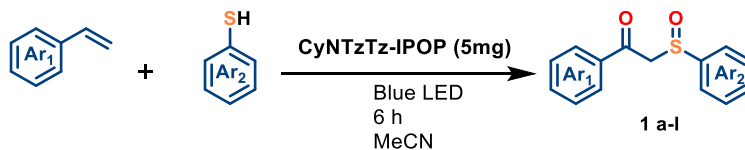
**Fig. S6** (a) N<sub>2</sub> sorption isotherm of CyNTzTz-IPOP and (b) pore size distribution plot of CyNTzTz-IPOP at 77 K by NLDFT method.



**Fig. S7** Cyclic voltammogram of CyNTzTz-IPOP.



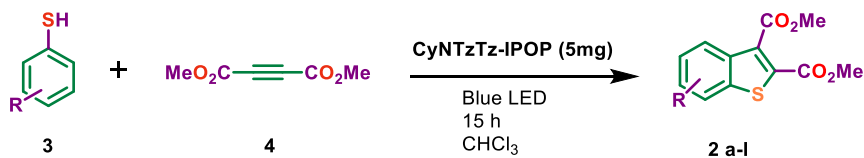
**Table S1** Optimization of the reaction conditions for the synthesis of  $\beta$ -keto sulfoxide catalyzed by **CyNTzTz-IPOP**.<sup>a-i</sup>



Entry	Conditions	Time (h)	Isolated yield (%)
1	MeCN/O <sub>2</sub> /Blue LED	4	60
2	CHCl <sub>3</sub> /O <sub>2</sub> /Blue LED	6	20
3	EtOAc/O <sub>2</sub> /Blue LED	6	30
4	MeOH/O <sub>2</sub> /Blue LED	6	50
5	EtOH/O <sub>2</sub> /Blue LED	6	45
<b>6</b>	<b>MeCN/O<sub>2</sub>/Blue LED</b>	<b>6</b>	<b>83</b>
7	MeCN/O <sub>2</sub> /Blue LED	8	80
7 <sup>b</sup>	MeCN/O <sub>2</sub> /White LED	6	60
8 <sup>c</sup>	MeCN/O <sub>2</sub> /Blue LED	6	74
9 <sup>d</sup>	MeCN/O <sub>2</sub> /Blue LED	6	80
11 <sup>e</sup>	MeCN/N <sub>2</sub> /Blue LED	6	0
12 <sup>f</sup>	MeCN/Air/Blue LED	6	70
10 <sup>g</sup>	MeCN/O <sub>2</sub> /dark	6	0
13 <sup>h</sup>	MeCN/O <sub>2</sub> /Blue LED	6	0
14 <sup>i</sup>	MeCN/O <sub>2</sub> /Blue LED	6	25

<sup>a</sup>Reaction conditions: styrene (0.5 mmol), thiophenol (1.0 mmol), **CyNTzTz-IPOP** (5 mg), blue-LED (10 W, 427 nm) and under oxygen atmosphere. <sup>b</sup>White LED. <sup>c</sup>Thiophenol (0.75 mmol). <sup>d</sup>Thiophenol (1.25 mmol). <sup>e</sup>Under N<sub>2</sub> atmosphere. <sup>f</sup>Air as oxidant. <sup>g</sup>Dark. <sup>h</sup>In the absence of catalyst. <sup>i</sup>In presence of the catalyst **BpyTzTz** (5 mg).

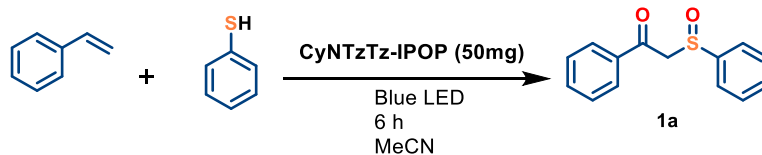
**Table S2** Optimization of the reaction conditions for the synthesis of benzothiophene dicarboxylate catalyzed by **CyNTzTz-IPOP**.<sup>a-h</sup>



Entry	Conditions	Time (h)	Isolated yield (%)
1	4 (2eq)/CHCl <sub>3</sub> /N <sub>2</sub> /Blue LED	10	70
2	4 (2eq)/EtOH/N <sub>2</sub> /Blue LED	24	45
3	4 (2eq)/MeCN/N <sub>2</sub> /Blue LED	20	77
3	4 (2eq)/DCM/N <sub>2</sub> /Blue LED	20	60
4	4 (2eq)/EtOAc/N <sub>2</sub> /Blue LED	20	30
<b>5</b>	<b>4 (2eq)/CHCl<sub>3</sub>/ N<sub>2</sub>/Blue LED</b>	<b>15</b>	<b>88</b>
6 <sup>b</sup>	4 (2eq)/CHCl <sub>3</sub> /N <sub>2</sub> /White LED	20	60
6 <sup>c</sup>	4 (1.5eq)/CHCl <sub>3</sub> / N <sub>2</sub> /Blue LED	15	55
7d <sup>d</sup>	4 (3eq)/CHCl <sub>3</sub> / N <sub>2</sub> /Blue LED	15	87
8 <sup>e</sup>	4 (2eq)/CHCl <sub>3</sub> /N <sub>2</sub> /dark	20	0
10 <sup>f</sup>	4b (2eq)/CHCl <sub>3</sub> /O <sub>2</sub> /Blue LED	20	75
12 <sup>g</sup>	4 (2eq)/CHCl <sub>3</sub> /N <sub>2</sub> /Blue LED	20	0
13 <sup>h</sup>	4 (2eq)/CHCl <sub>3</sub> /N <sub>2</sub> /Blue LED	15	30

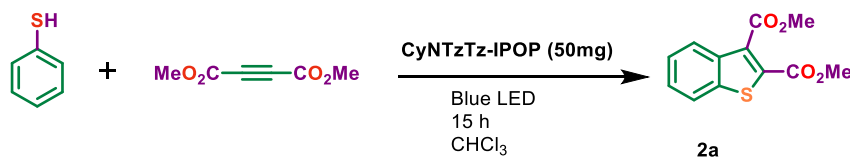
<sup>a</sup>Reaction conditions: thiophenol (0.5 mmol), diethyl but-2-ynedioate (1.0 mmol), **CyNTzTz-IPOP** (5 mg), and blue -LED (10W, 427 nm) under N<sub>2</sub> atmosphere. <sup>b</sup>White LED. <sup>c</sup>Dimethyl acetylenedicarboxylate (0.75 mmol). <sup>d</sup>Dimethyl acetylenedicarboxylate (1.5 mmol). <sup>e</sup>Under dark. <sup>f</sup>Oxygen atmosphere. <sup>g</sup>In the absence of catalyst. <sup>h</sup>In presence of the catalyst **BpyTzTz** (5 mg).

### Scheme S1 Gram-scale synthesis of 1-phenyl-2-(phenylsulfinyl)ethenone (1a).



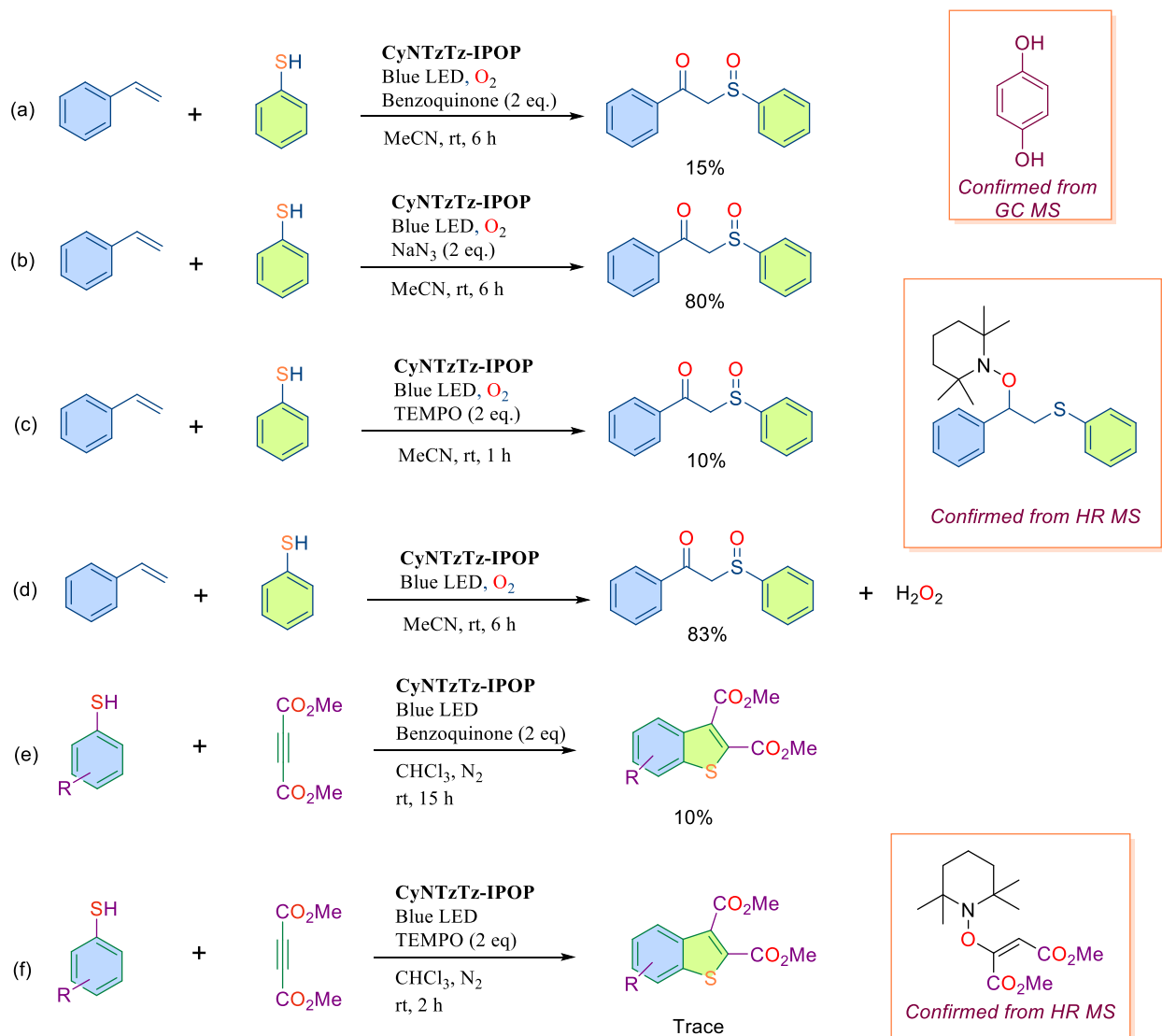
A round bottom flask was charged with styrene (1.04 g, 10.0 mmol), thiophenol (2.2 g, 20.0 mmol), **CyNTzTz-IPOP** (50 mg) and MeCN (20 mL). The mixture was exposed to blue-LED light (427 nm, 10 W) under an O<sub>2</sub> atmosphere at room temperature. After 6 h, the catalyst was separated from the reaction mixture by filtration and washed thoroughly with EtOAc (20 mL  $\times$  2) followed by DCM (20 mL  $\times$  2). The solvent was then evaporated from the filtrate, and the resulting crude mixture was purified by silica-gel column chromatography using 60:40 hexane/EtOAc eluent, yielding 1.80 g of the product (74% yield).

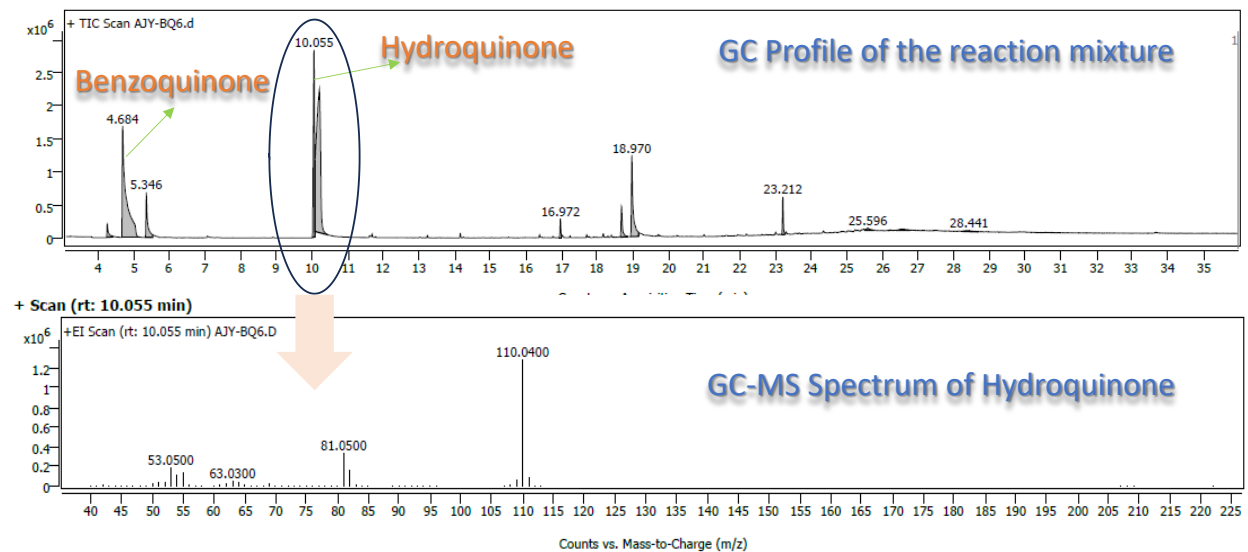
### Scheme S2 Gram-scale synthesis of dimethyl benzo[*b*]thiophene-2,3-dicarboxylate (2a).



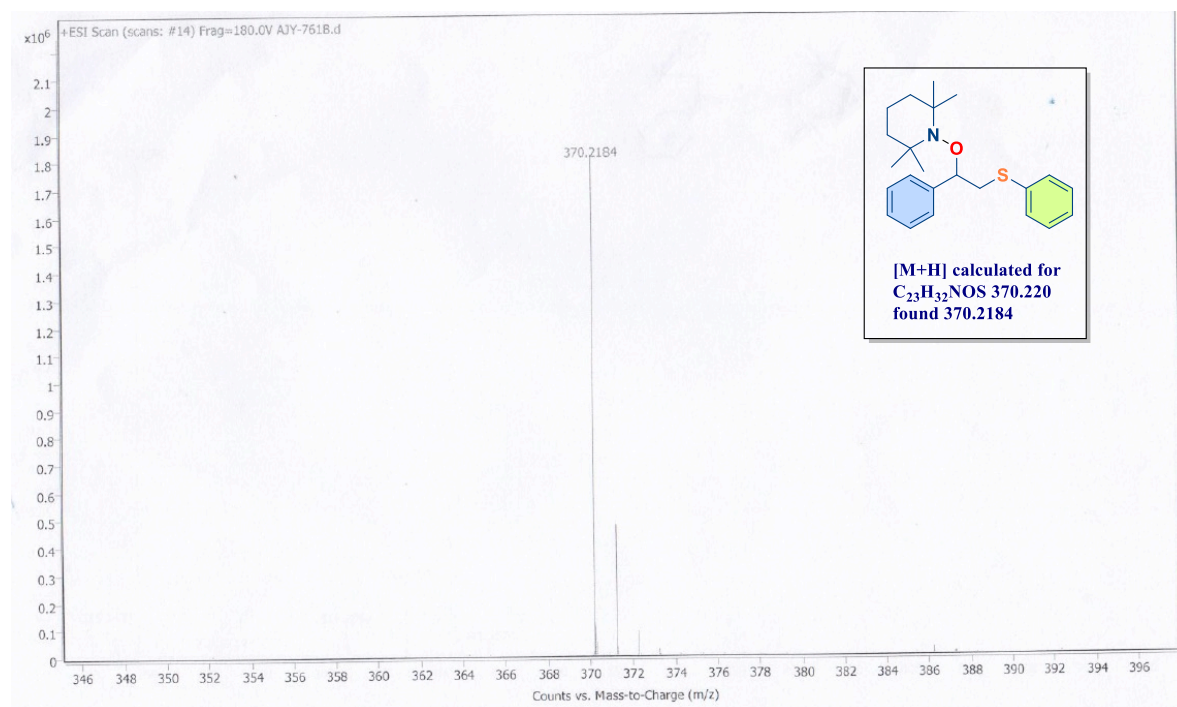
A round bottom flask was loaded with thiophenol (1.10 g, 10.0 mmol), dimethyl acetylenedicarboxylate (2.8 g, 20.0 mmol), **CyNTzTz-IPOP** (50 mg), and CHCl<sub>3</sub> (20 mL). The reaction mixture was irradiated with blue-LED light (427 nm, 10 W) under nitrogen atmosphere at room temperature. After 15h, the catalyst was separated by filtration from the reaction mixture and washed thoroughly with EtOAc (20 mL  $\times$  2) and DCM (20 mL  $\times$  2). The filtrate was evaporated in a rotary evaporator to yield a residue, which upon short-pad silica-gel column chromatography using 80:20 hexane/EtOAc solvent as an eluent led to the product in 2.12 g (85% yield).

**Scheme S3** Control experiments for the synthesis of  $\beta$ -keto sulfoxides (a-d) and benzothiophene dicarboxylates (e,f).

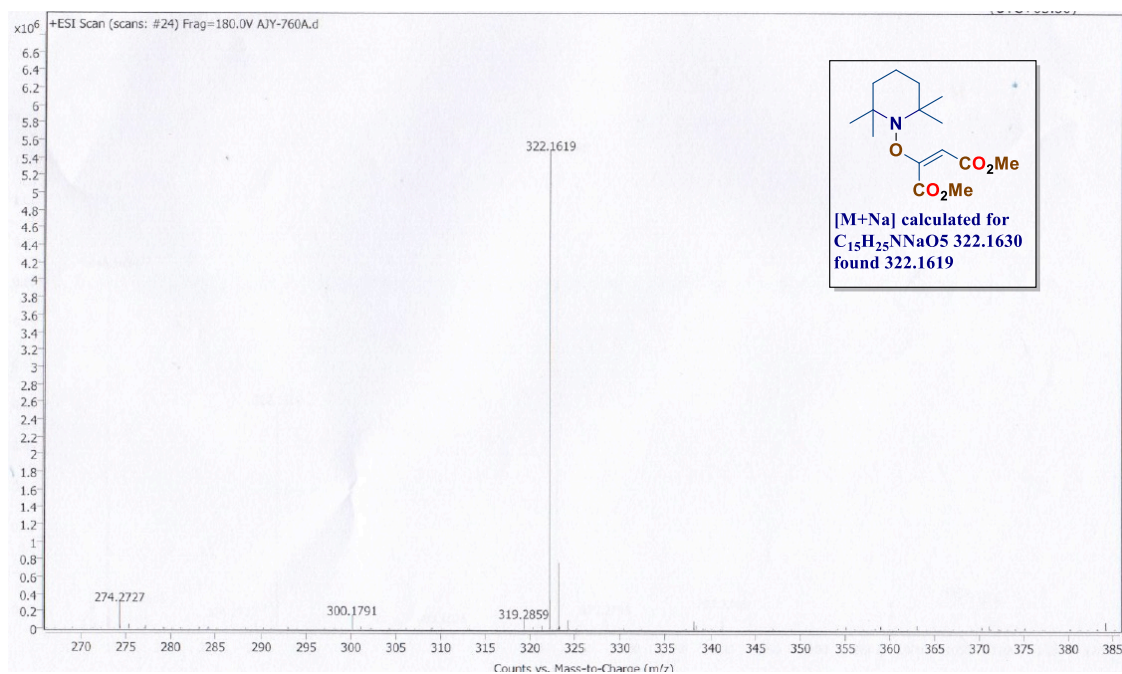




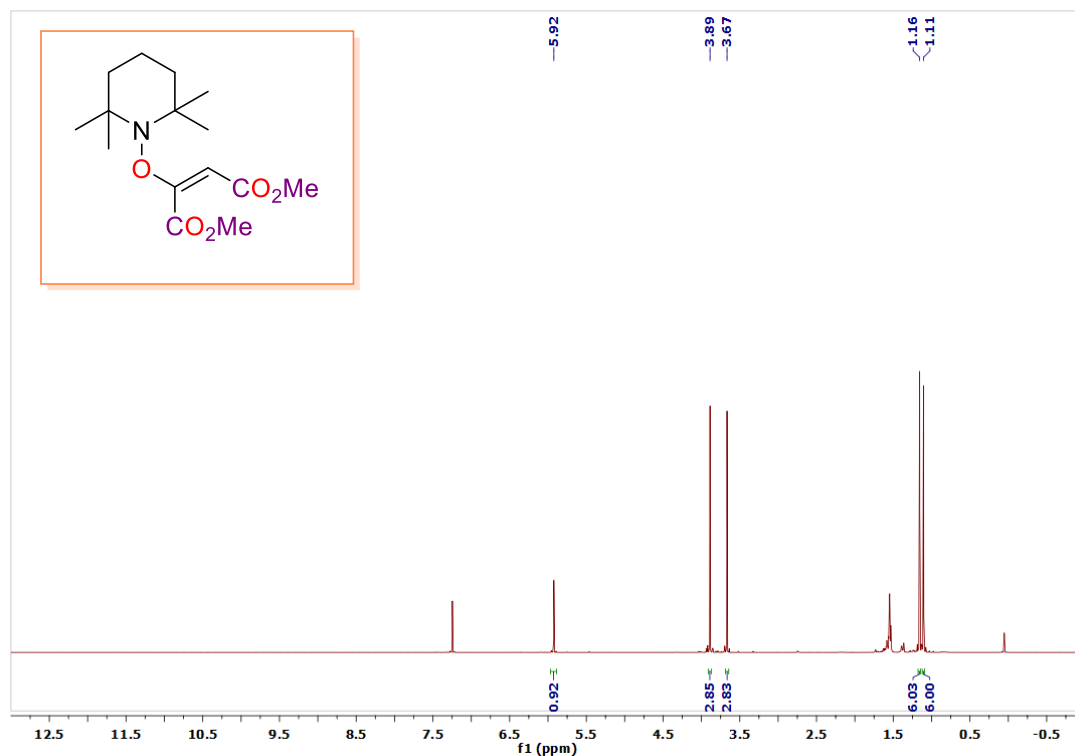
**Fig. S8** GC-MS spectrum of the reduction product of benzoquinone, i.e., hydroquinone, in the quenching experiment, formed in the synthesis of  $\beta$ -keto sulfoxide by blue-LED irradiation of CyNTzTz-IPOP in the presence of oxygen.



**Fig. S9** ESI-MS spectrum of the adduct formed with TEMPO in the synthesis of  $\beta$ -keto sulfoxide.



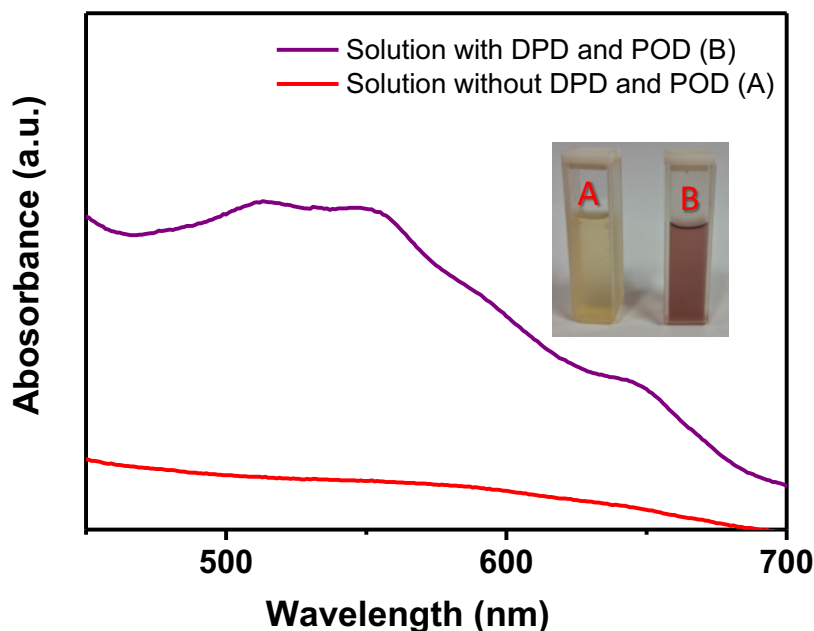
**Fig. S10** ESI-MS spectrum of the adduct formed between dimethyl acetylenedicarboxylate and TEMPO.



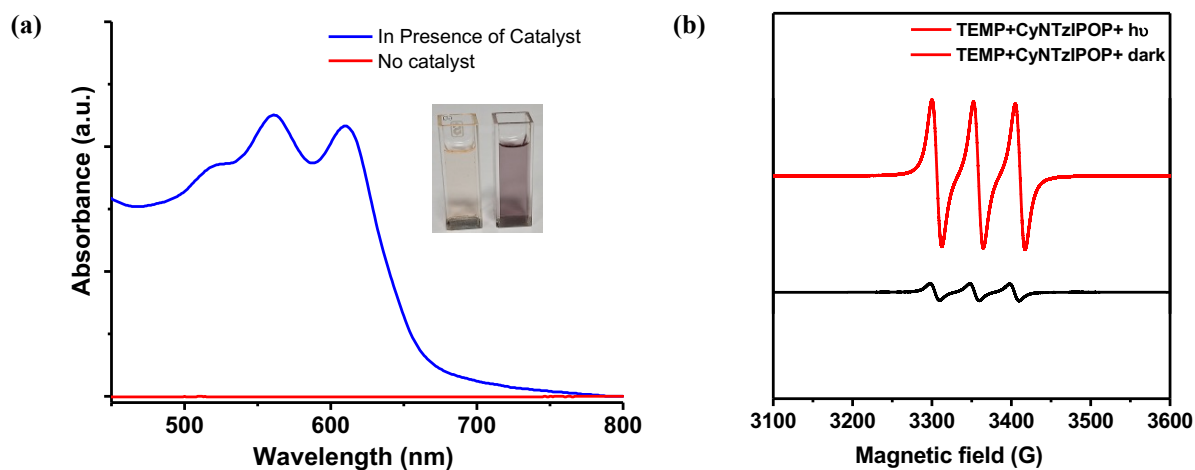
**Fig. S11**  $^1H$  NMR spectrum of the adduct formed between dimethyl acetylenedicarboxylate and TEMPO.

### Detection of H<sub>2</sub>O<sub>2</sub> by DPD/POD method:

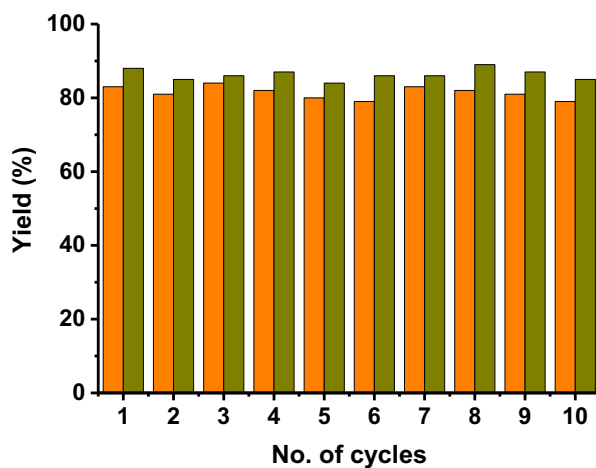
During the reaction of thiol-ene addition and oxidation reaction, the formation of H<sub>2</sub>O<sub>2</sub> was confirmed by the DPD (*N,N*-diethyl-*p*-phenylenediamine)/POD (horseradish peroxidase) method. A solution of POD (1.0 mg) was prepared by dissolving it in distilled water (1 mL). In the same manner, a solution of DPD (10.0 mg) was prepared by dissolving it in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution (1 mL). The catalyst **CyNTzTz-IPOP** was filtered out from the reaction mixture obtained by irradiation of the solution of styrene and thiophenol in the presence of the catalyst **CyNTzTz-IPOP** for 6 h. To this reaction mixture (1 mL) in a glass vial was added 0.4 mL of 0.5 M (pH = 6) phosphate buffer followed by 10 μL of DPD and 10 μL POD solutions. The color of the reaction mixture changed to pink due to the presence of H<sub>2</sub>O<sub>2</sub> in the reaction mixture; POD evidently undergoes oxidation with H<sub>2</sub>O<sub>2</sub>. The oxidized POD subsequently oxidizes DPD into DPD cation radical. The pink colour of the solution is attributed to the DPD cation radical, which shows two characteristic peaks at 510 nm and 551 nm in UV-vis spectrum.



**Fig. S12** UV-visible absorption spectrum of the irradiated reaction mixture of thiophenol and styrene in the presence of the catalyst with (purple) and without DPD and POD (red); the absorption in the visible region (purple) is attributed to the cation radical of DPD.

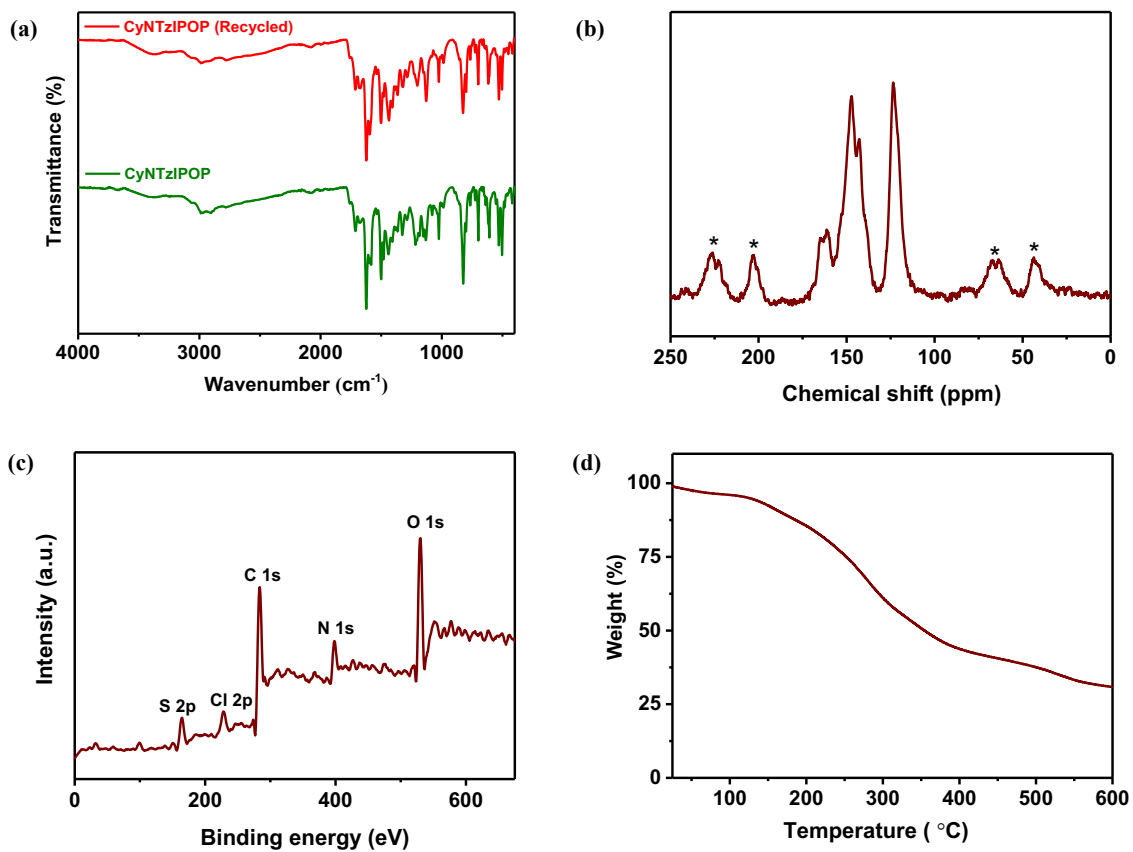


**Fig. S13** (a) UV-visible absorption spectra for evidence in favor of the formation of TMPD cationic radical upon irradiation of CyNTzTz-IPOP in the presence of oxygen, and (b) EPR spectra of the mixture of CyNTzTz-IPOP and TEMP in MeCN in dark and upon irradiation with light under oxygen atmosphere.

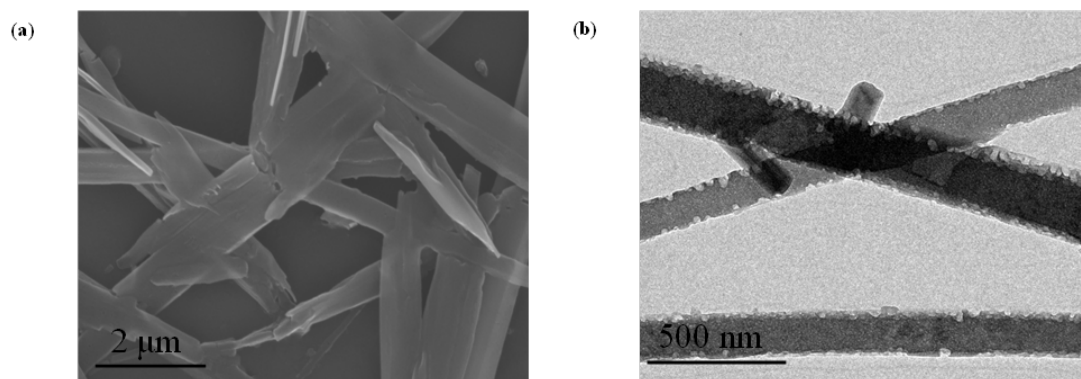


**Fig. S14** Recyclability of CyNTzTz-IPOP for the synthesis of  $\beta$ -keto sulfoxide (orange) and benzothiophene dicarboxylate (olive).





**Fig. S15** (a) FT-IR spectra of CyNTzTz-IPOP (green) and recycled CyNTzTz-IPOP (red), (b)  $^{13}\text{C}$  CP-MAS solid-state NMR of recycled CyNTzTzIPOP, (c) XPS spectrum of the recycled CyNTzTz-IPOP, and (d) TGA plot of the recycled CyNTzTz-IPOP.



**Fig. S16** (a) FESEM and (b) HR-TEM images of the recycled CyNTzTz-IPOP.

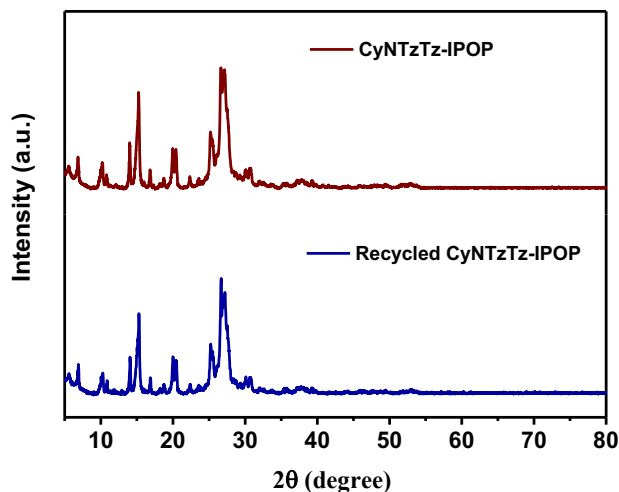


Fig. S17 PXRD of recycled polymer **CyNTzTz-IPOP** (blue) and fresh polymer **CyNTzTz-IPOP** (brown).

#### Characterizations of the products:

**1-Phenyl-2-(phenylsulfinyl)ethenone (1a)<sup>1</sup>:** Yield 83%; yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.68 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.40 (m, 5H), 4.55 (d, *J* = 14.1 Hz, 1H), 4.28 (d, *J* = 14.1 Hz, 1H).

**1-Phenyl-2-(p-tolylsulfinyl)ethenone (1b)<sup>2</sup>:** Yield 80%; yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 3.6 Hz, 2H), 7.48 (d, *J* = 3.6 Hz, 3H), 7.24 (d, *J* = 8.8, 2H), 4.53 (d, *J* = 14.1 Hz, 1H), 4.24 (d, *J* = 14.1 Hz, 1H), 2.39 (s, 3H).

**2-((2,4-dimethylphenyl)sulfinyl)-1-phenylethan-1-one (1c):** Yield 72%; yellow solid; mp 95-105 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 4.41 (d, *J* = 13.8 Hz, 1H), 4.25 (d, *J* = 13.8 Hz, 1H), 2.34 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 191.39, 141.80, 138.32, 136.30, 134.88, 134.05, 131.60, 128.96, 128.78, 128.16, 124.14, 64.23, 21.27, 18.21. ESI-MS<sup>+</sup> *m/z* calcd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>SNa 295.0768 [M+Na]<sup>+</sup>, found 295.0788.

**2-((4-Methoxyphenyl)sulfinyl)-1-phenylethan-1-one (1d)<sup>3</sup>:** Yield 78%; yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 7.8 Hz, 2H), 7.62-7.56 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 4.56 (d, *J* = 13.9 Hz, 1H), 4.26 (d, *J* = 14.0 Hz, 1H), 3.82 (s, 3H).

**2-((4-Bromophenyl)sulfinyl)-1-phenylethan-1-one (1e)<sup>3</sup>:** Yield 77%; pale yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 9.1 Hz, 3H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.55 (d, *J* = 14.4 Hz, 1H), 4.30 (d, *J* = 14.4 Hz, 1H).

**2-((4-Chlorophenyl)sulfinyl)-1-phenylethan-1-one (1f)<sup>3</sup>:** Yield 74%; yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.63-7.58 (m, 3H), 7.45 (t, *J* = 8.1 Hz, 4H), 4.55 (d, *J* = 14.4 Hz, 1H), 4.30 (d, *J* = 14.6 Hz, 1H).

**2-(3,5-Dichlorophenylsulfinyl)-1-phenylethanone (1g):** Yield 67%; white solid; mp 102-110 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.57 (s, 2H), 7.47 (m, 3H), 4.57 (d, *J* = 14.6 Hz, 1H), 4.33 (d, *J* = 14.6 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 190.94, 147.17, 136.38, 135.77, 134.53, 131.62, 128.98, 128.77, 122.80, 66.06. ESI-MS<sup>+</sup> *m/z* calcd for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>2</sub>SNa 334.9676 [M+Na]<sup>+</sup>, found 334.9698.

**2-(Naphthalen-2-ylsulfinyl)-1-phenylethan-1-one (1h)<sup>3</sup>:** Yield 88%; yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.23 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 4H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.57 (dt, *J* = 15.0, 7.4 Hz, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 4.62 (d, *J* = 14.3 Hz, 1H), 4.37 (d, *J* = 14.3 Hz, 1H).

**1-(4-(Tert-butyl)phenyl)-2-(phenylsulfinyl)ethan-1-one (1i)<sup>4</sup>:** Yield 80%; yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.65 (m, 2H), 7.48-7.47 (m, 3H), 7.44 (d, *J* = 8.2 Hz, 2H), 4.54 (d, *J* = 14.1 Hz, 1H), 4.25 (d, *J* = 14.1 Hz, 1H), 1.31 (s, 9H).

**1-(4-Fluorophenyl)-2-(phenylsulfinyl)ethan-1-one (1j)<sup>4</sup>:** Yield 79%; colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.94 – 7.85 (m, 2H), 7.69 – 7.62 (m, 2H), 7.48 (s, 3H), 7.10 (t, *J* = 8.5 Hz, 2H), 4.48 (d, *J* = 14.0 Hz, 1H), 4.24 (d, *J* = 14.0 Hz, 1H).

**4-(2-(Phenylsulfinyl)acetyl)benzotrile (1k):** Yield 86%; yellow solid; mp 90-95 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.50 (d, *J* = 2.0 Hz, 3H), 4.44 (d, *J* = 13.8 Hz, 1H), 4.30 (d, *J* = 13.8 Hz, 1H). <sup>13</sup>C NMR (125 MHz,

CDCl<sub>3</sub>)  $\delta$  190.34, 189.92, 142.59, 139.05, 132.60, 131.93, 129.55, 129.34, 124.16, 117.64, 117.30, 65.32. ESI-MS<sup>+</sup> m/z calcd for C<sub>15</sub>H<sub>11</sub>NO<sub>2</sub>SNa 292.0408 [M+Na]<sup>+</sup>, found 292.0455.

**1-(Naphthalen-2-yl)-2-(phenylsulfinyl)ethan-1-one (1k)**<sup>5</sup>: Yield 84%; yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (s, 1H), 7.89 (m, 4H), 7.70 (d, *J* = 6.4 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 6.5 Hz, 3H), 4.69 (d, *J* = 14.1 Hz, 1H), 4.40 (d, *J* = 14.1 Hz, 1H).

**Dimethyl benzo[*b*]thiophene-2,3-dicarboxylate (2a)**<sup>6</sup>: Yield 88%; light yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.43 (m, 2H), 4.00 (s, 3H), 3.93 (s, 3H).

**Dimethyl 5-methylbenzo[*b*]thiophene-2,3-dicarboxylate (2b)**<sup>6</sup>: Yield 85%; colorless solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 (d, *J* = 12 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 4.01 (s, 3H), 3.92 (s, 3H), 2.46 (s, 3H).

**Dimethyl 7-methylbenzo[*b*]thiophene-2,3-dicarboxylate (2c)**<sup>6</sup>: Yield 82%; colorless solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (d, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 4.01 (s, 3H), 3.94 (s, 3H), 2.55 (s, 3H).

**Dimethyl 5,7-dimethylbenzo[*b*]thiophene-2,3-dicarboxylate (2d)**<sup>7</sup>: Yield 80%; light yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (s, 1H), 7.00 (s, 1H), 4.01 (s, 3H), 3.90 (s, 3H), 2.48 (s, 3H), 2.41 (s, 3H).

**Dimethyl 5-isopropylbenzo[*b*]thiophene-2,3-dicarboxylate (2e)**<sup>7</sup>: Yield 85%; light yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (d, *J* = 8.5 Hz, 1H), 7.71 (s, 1H), 7.39 (d, *J* = 9.8 Hz, 1H), 4.02 (s, 3H), 3.92 (s, 3H), 3.11 – 2.91 (m, 1H), 1.29 (d, *J* = 6.9 Hz, 6H).

**Dimethyl 5-methoxybenzo[*b*]thiophene-2,3-dicarboxylate (2f)**<sup>7</sup>: Yield 81%; colorless solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, *J* = 8.9 Hz, 1H), 7.33 (d, *J* = 2.2 Hz, 1H), 7.13 (dd, *J* = 9.1, 2.3 Hz, 1H), 4.00 (s, 3H), 3.92 (s, 3H), 3.86 (s, 3H).

**Dimethyl 7-methoxybenzo[*b*]thiophene-2,3-dicarboxylate (2g)<sup>6</sup>:** Yield 80%; Colorless solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.00 (s, 3H), 3.99 (s, 3H), 3.93 (s, 3H).

**Dimethyl 5-bromobenzo[*b*]thiophene-2,3-dicarboxylate (2h)<sup>6</sup>:** Yield 81%; light yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 1.4 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.58 (dd, *J*<sub>1</sub> = 8.7, *J*<sub>2</sub> = 1.9 Hz, 1H), 4.01 (s, 3H), 3.94 (s, 3H).

**Dimethyl 5-chlorobenzo[*b*]thiophene-2,3-dicarboxylate (2i)<sup>7</sup>:** Yield 78%; colorless solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 1.9 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.45 (dd, *J*<sub>1</sub> = 8.7, *J*<sub>2</sub> = 2.0 Hz, 1H), 4.01 (s, 3H), 3.94 (s, 3H).

**Dimethyl 5,7-dichlorobenzo[*b*]thiophene-2,3-dicarboxylate (2j)<sup>7</sup>:** Yield 71%; colorless solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (s, 1H), 7.49 (s, 1H), 4.00 (s, 2H), 3.95 (s, 2H).

**Dimethyl naphtho[2,1-*b*]thiophene-1,2-dicarboxylate (2k)<sup>6</sup>:** Yield 87%; light yellow; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.95 – 7.93 (m, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.65 – 7.52 (m, 2H), 4.16 (s, 3H), 3.95 (s, 3H).

**Dimethyl 5-nitrobenzo[*b*]thiophene-2,3-dicarboxylate (2l):** Yield 82%; pale yellow solid; mp 108-116 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.87 (d, *J* = 2.2 Hz, 1H), 8.32 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 4.05 (s, 3H), 3.97 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 162.43, 160.34, 145.37, 144.07, 136.57, 135.58, 131.98, 122.45, 120.44, 119.68, 52.4, 52.24. ESI-MS<sup>+</sup> *m/z* calcd for C<sub>12</sub>H<sub>9</sub>NO<sub>6</sub>SNa 318.0048 [M+Na]<sup>+</sup>, found 318.0029.

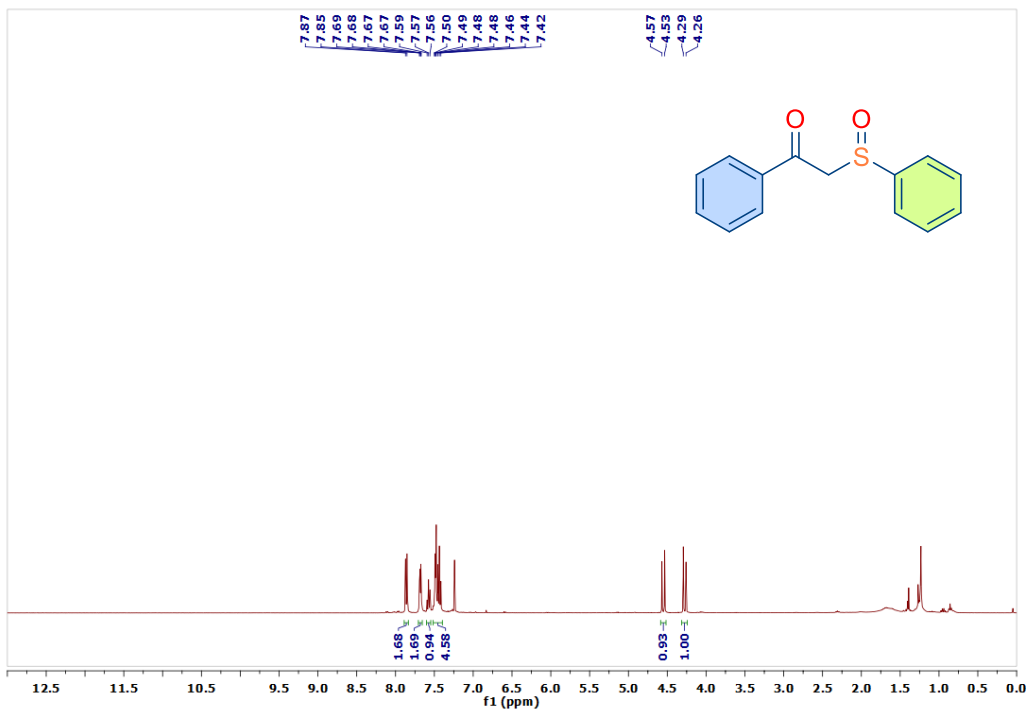


Fig. S18  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 1a.

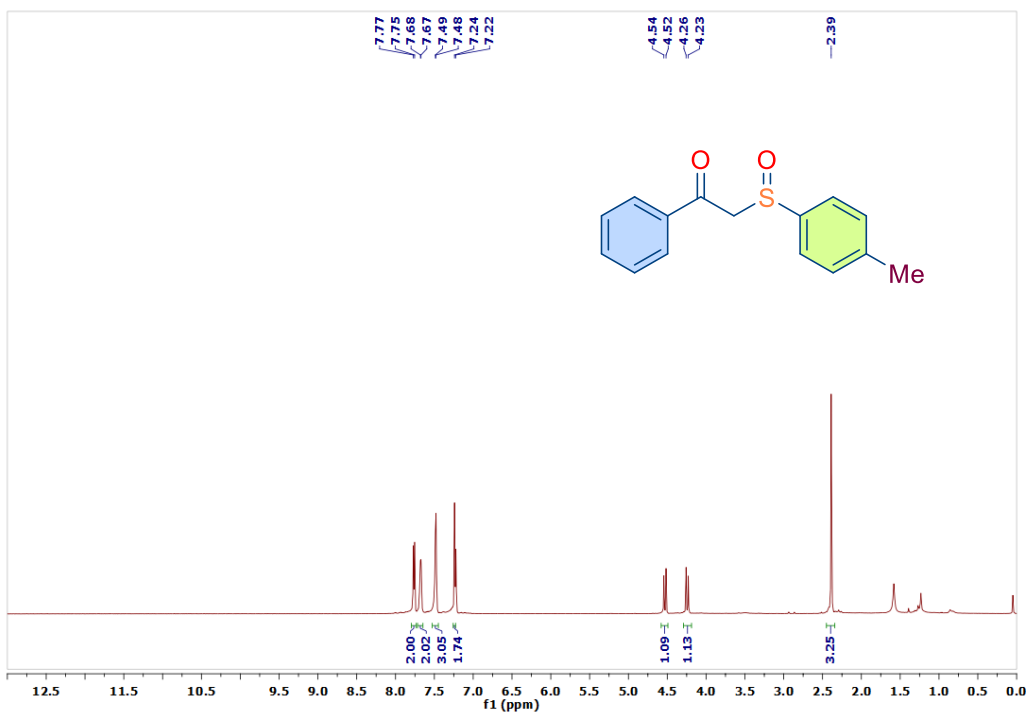


Fig. S19  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 1b.

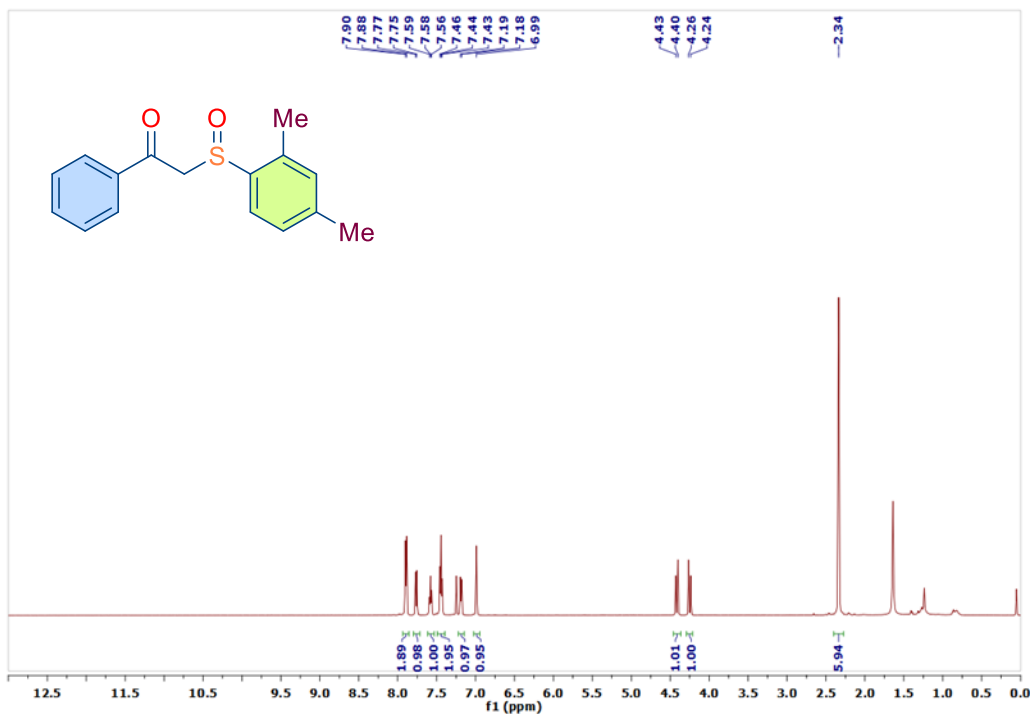


Fig. S20 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **1c**.

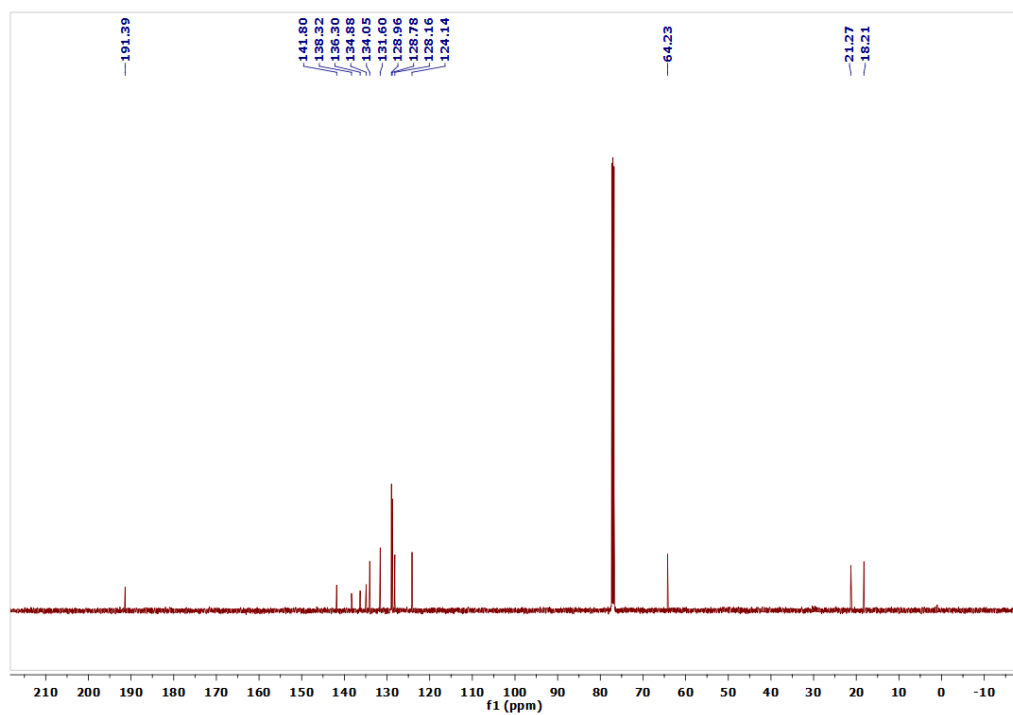
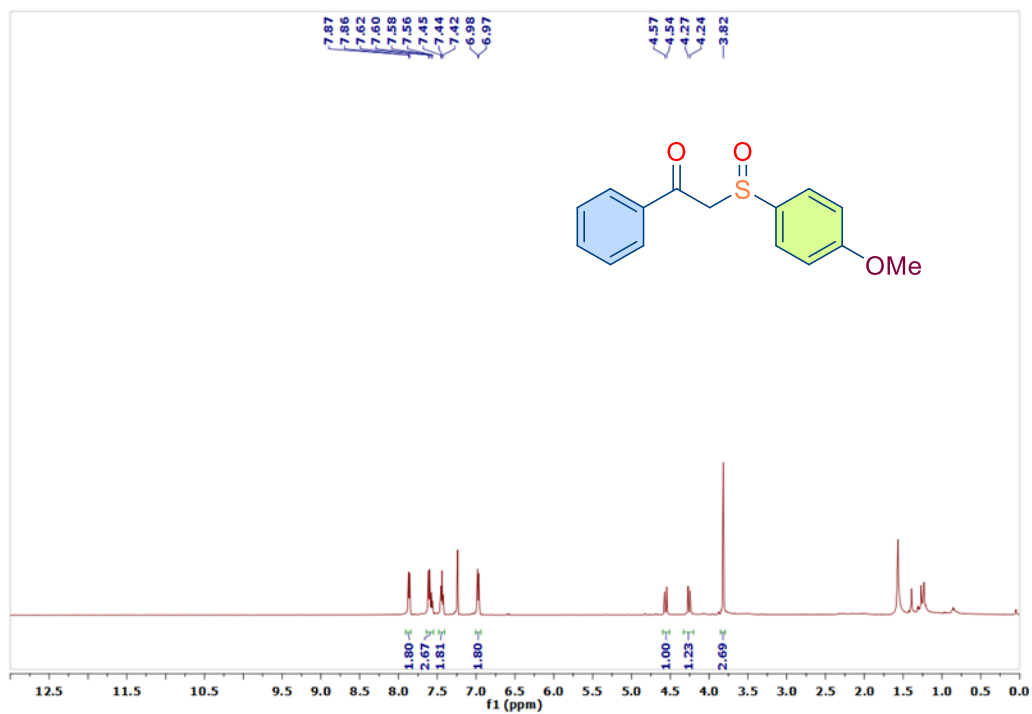
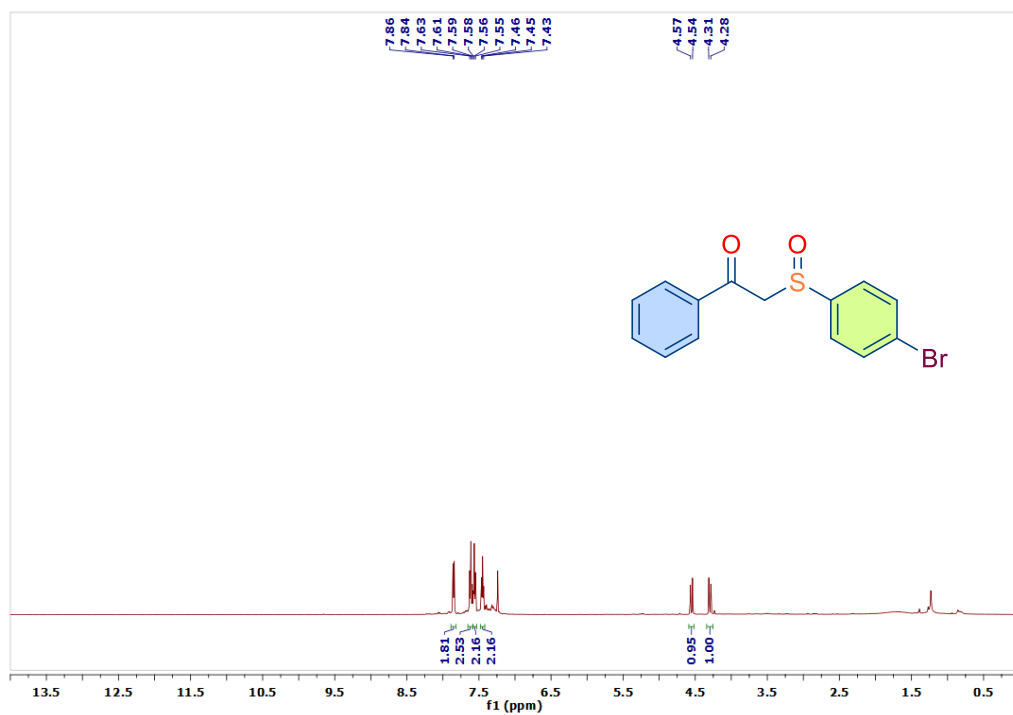


Fig. S21 <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **1c**.

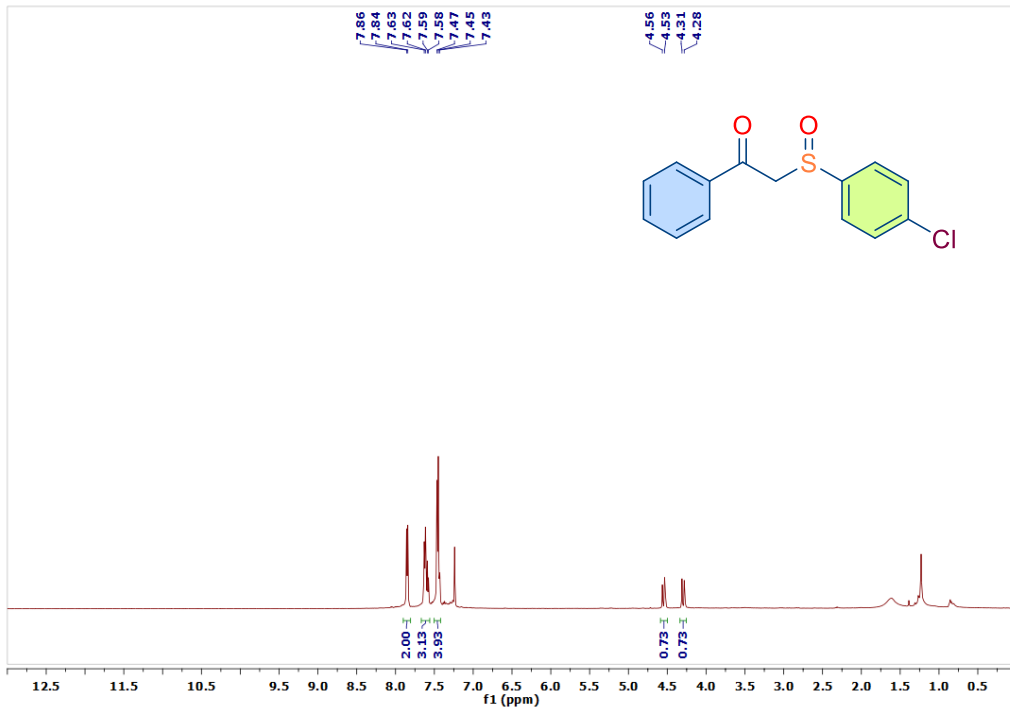


**Fig. S22**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **1d**.

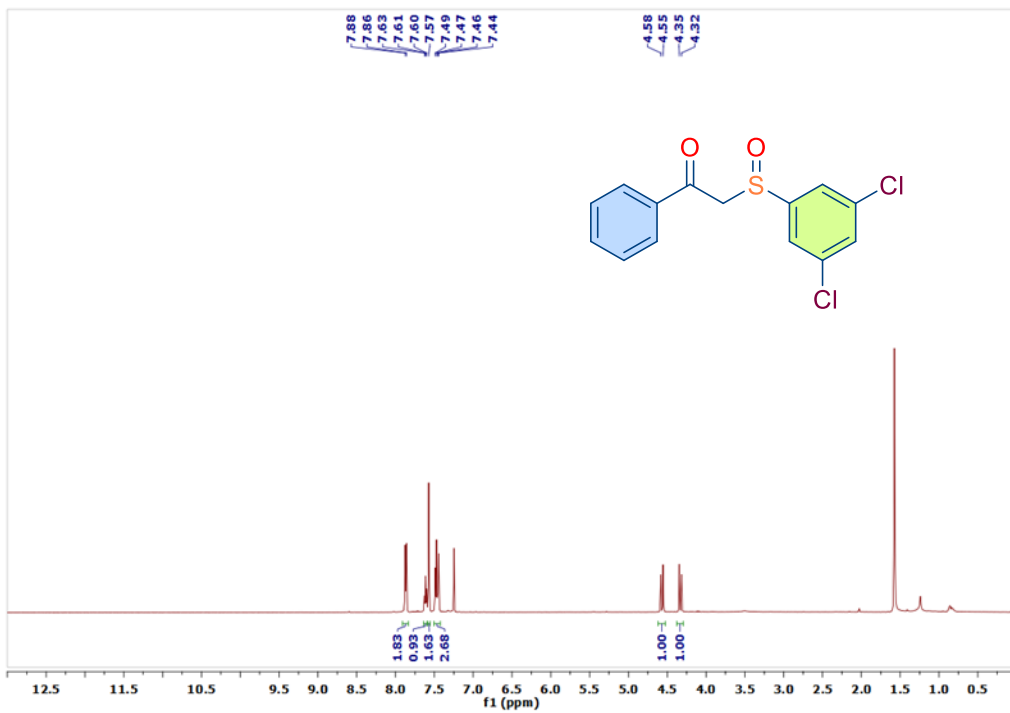


**Fig. S23**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **1e**.





**Fig. S24**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **1f**.



**Fig. S25**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **1g**.

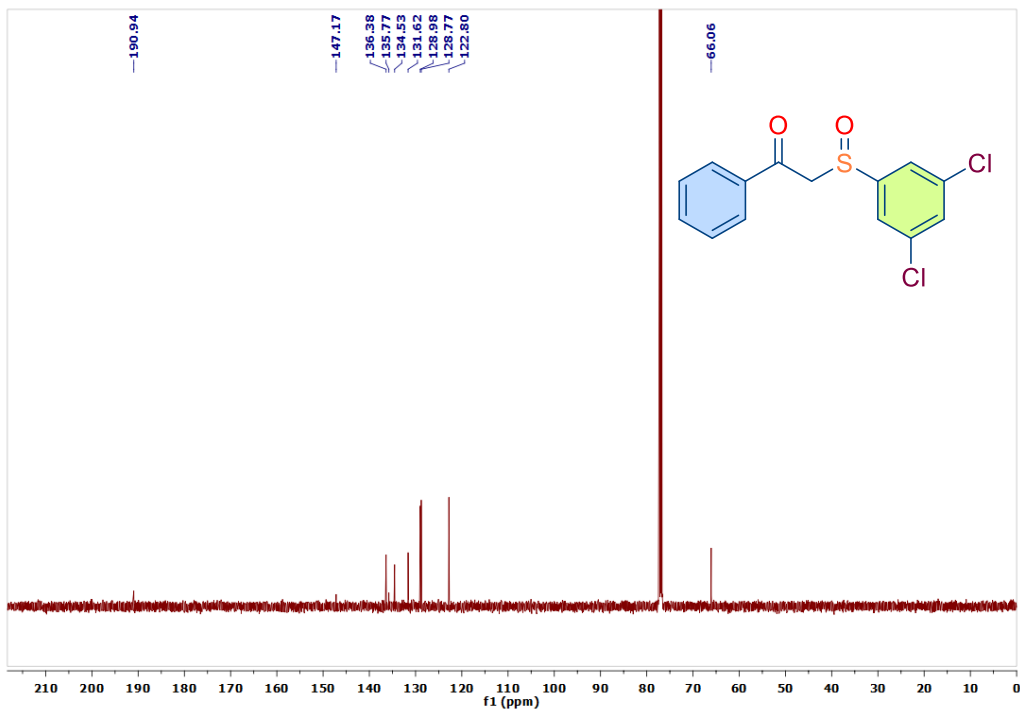


Fig. S26 <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **1g**.

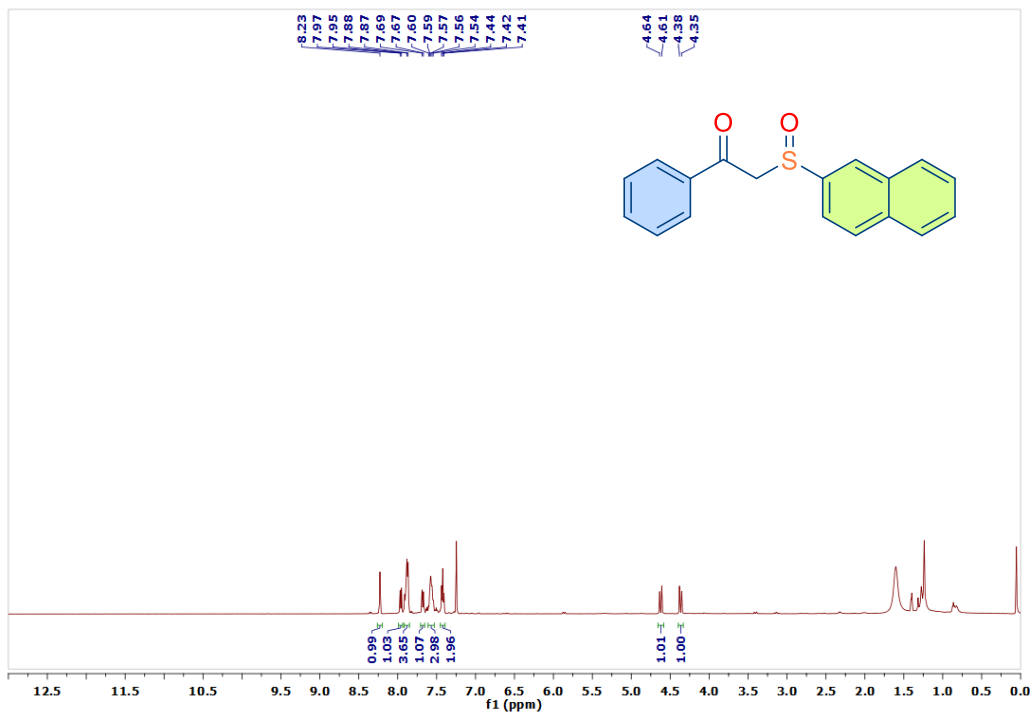
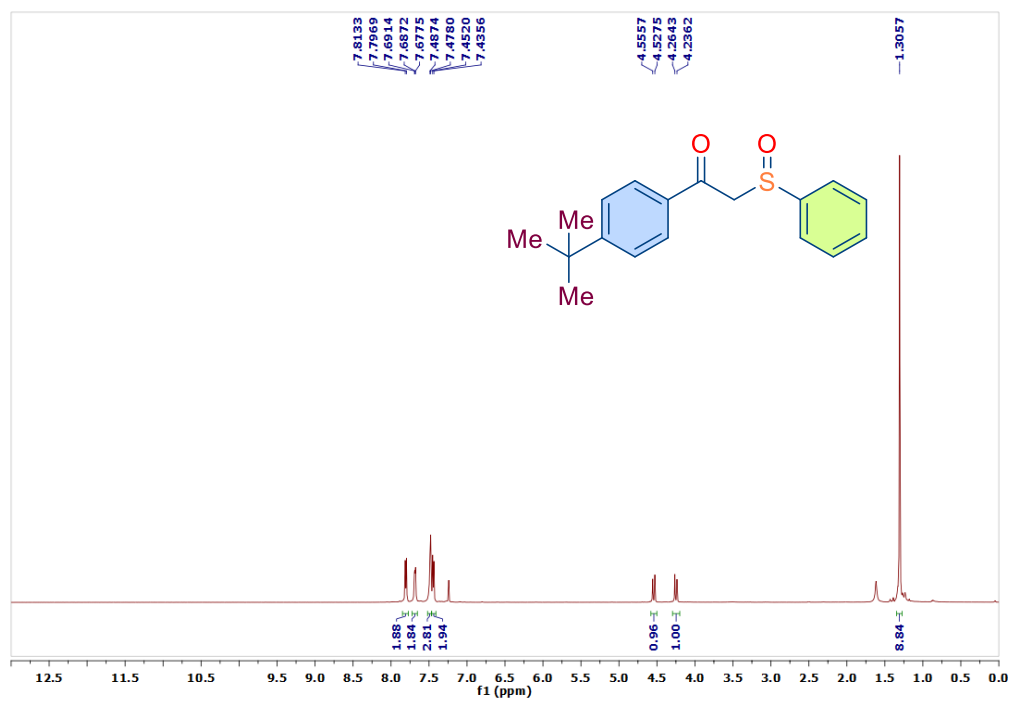
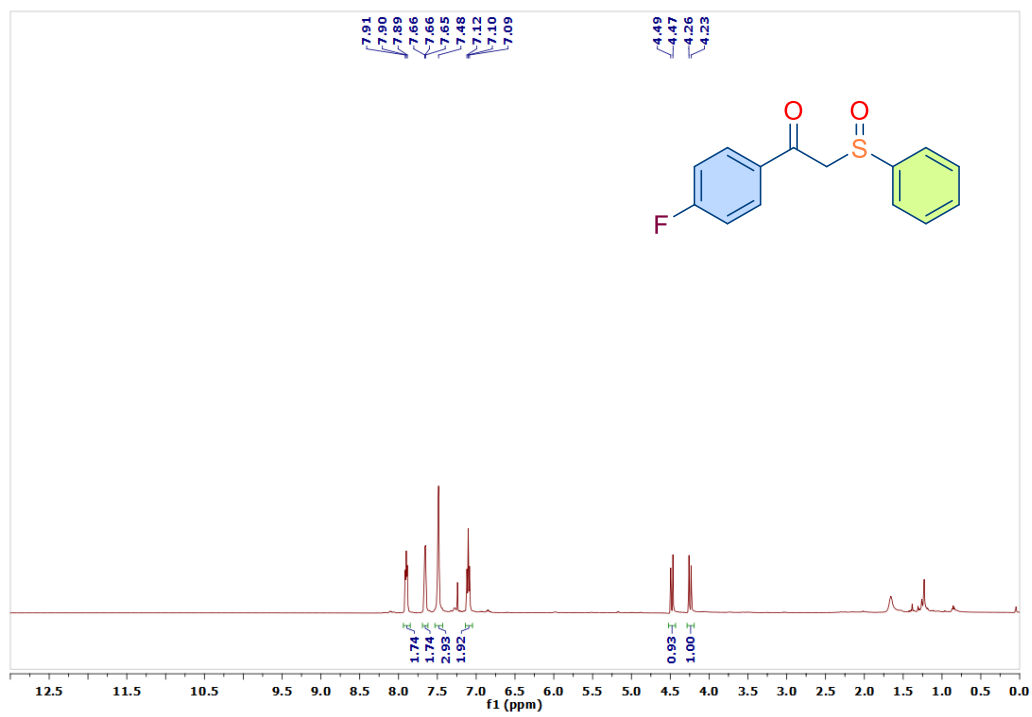


Fig. S27 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **1h**.



**Fig. S28** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **1i**.



**Fig. S29** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **1j**.

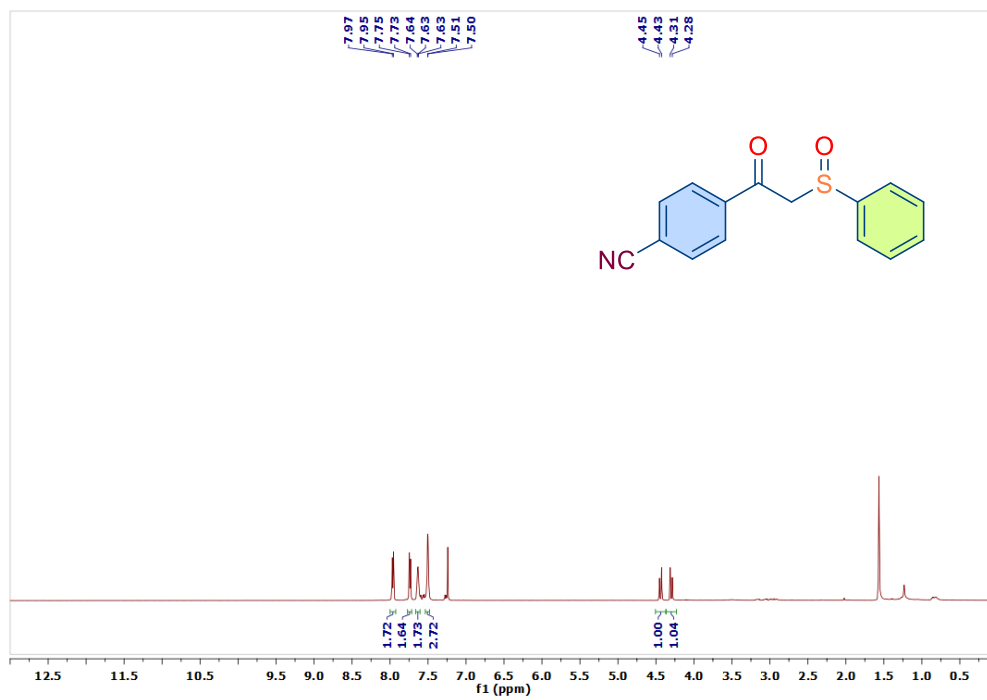


Fig. S30  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **1k**.

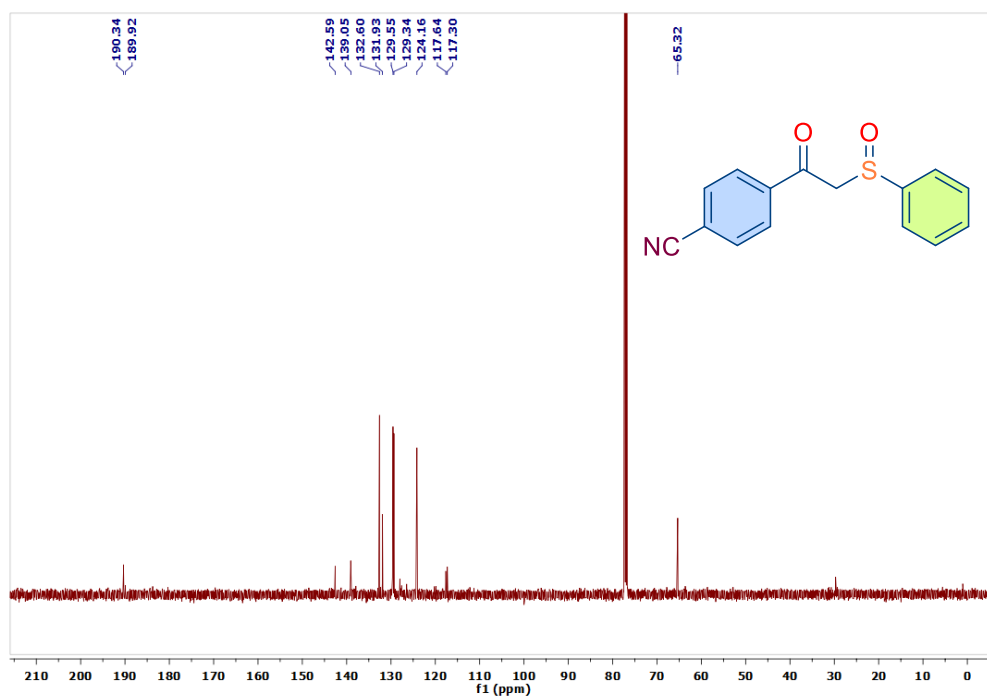


Fig. S31  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **1k**.

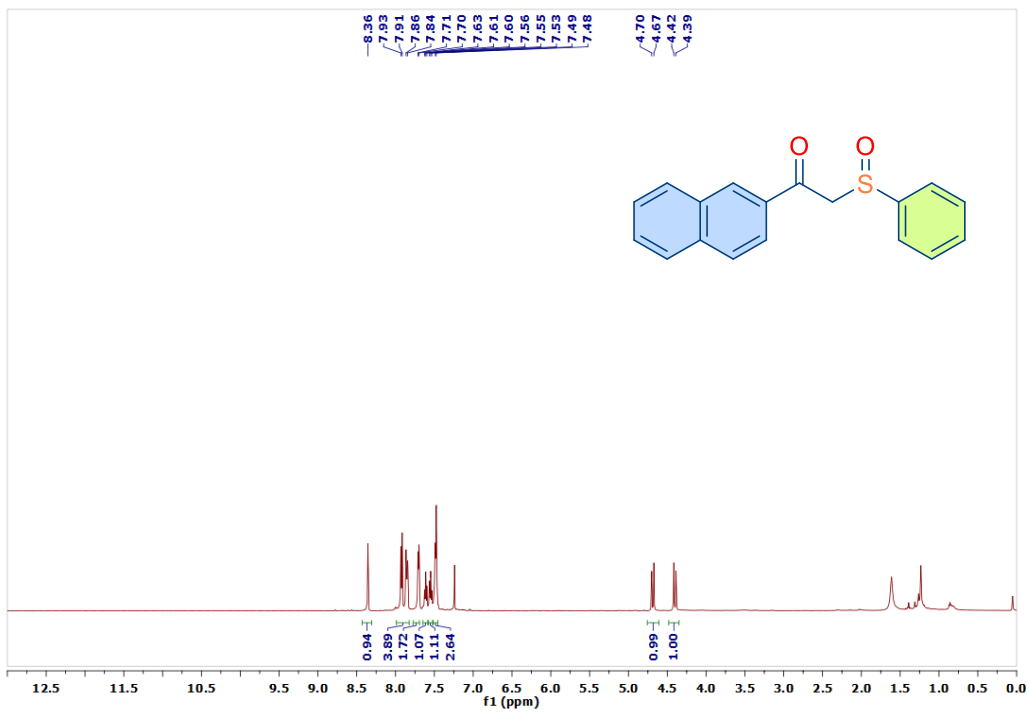


Fig. S32  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **1l**.

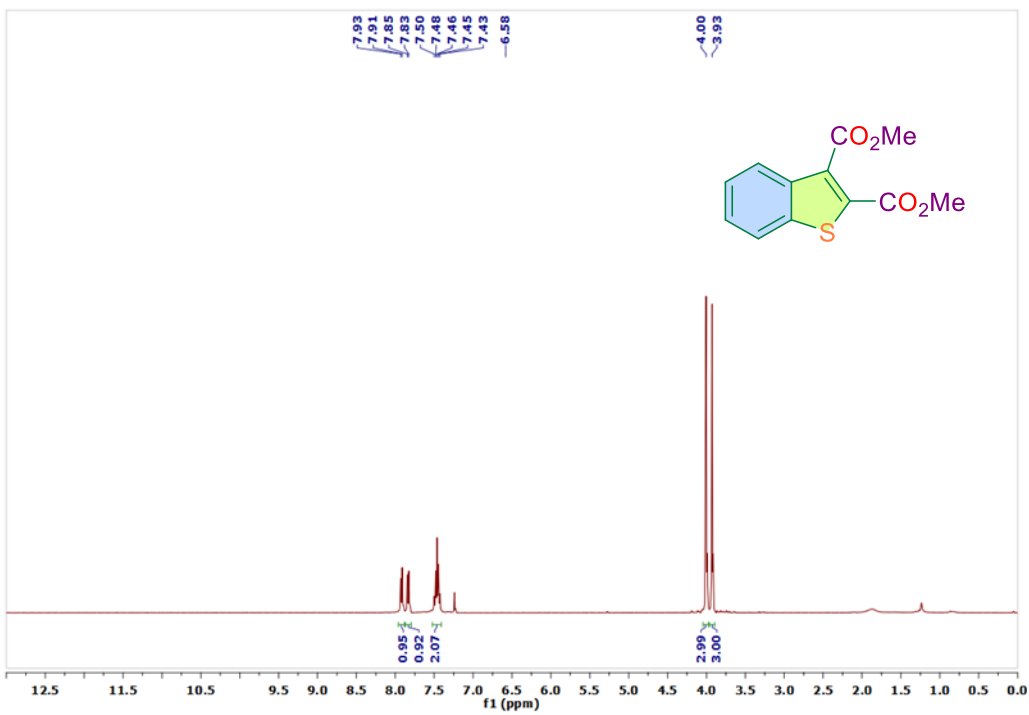
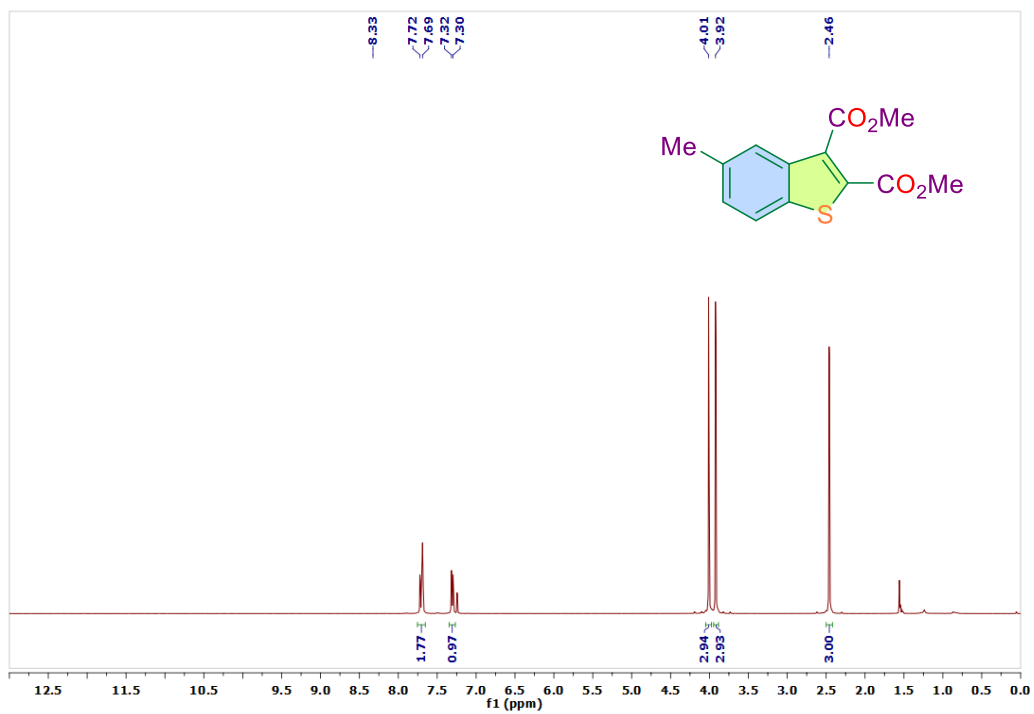
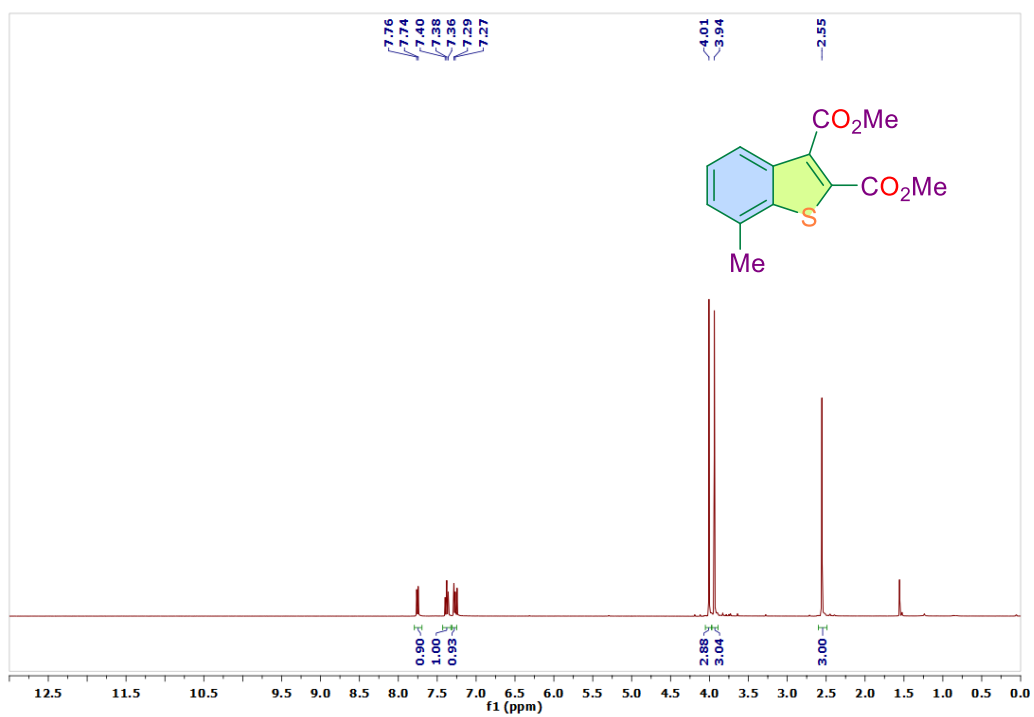


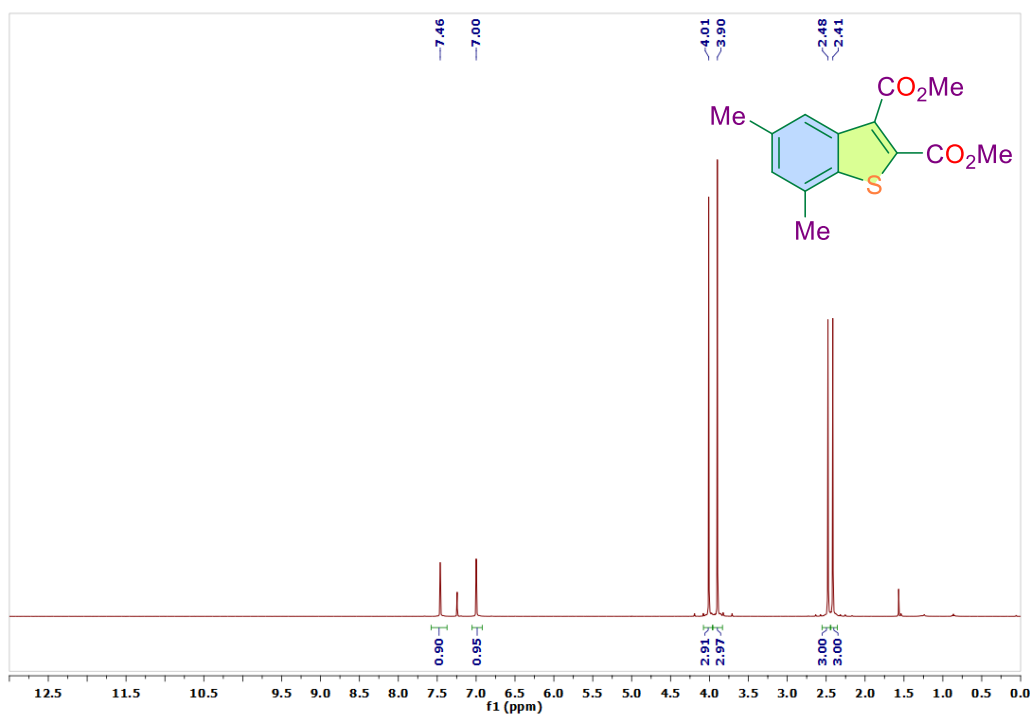
Fig. S33  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2a**.



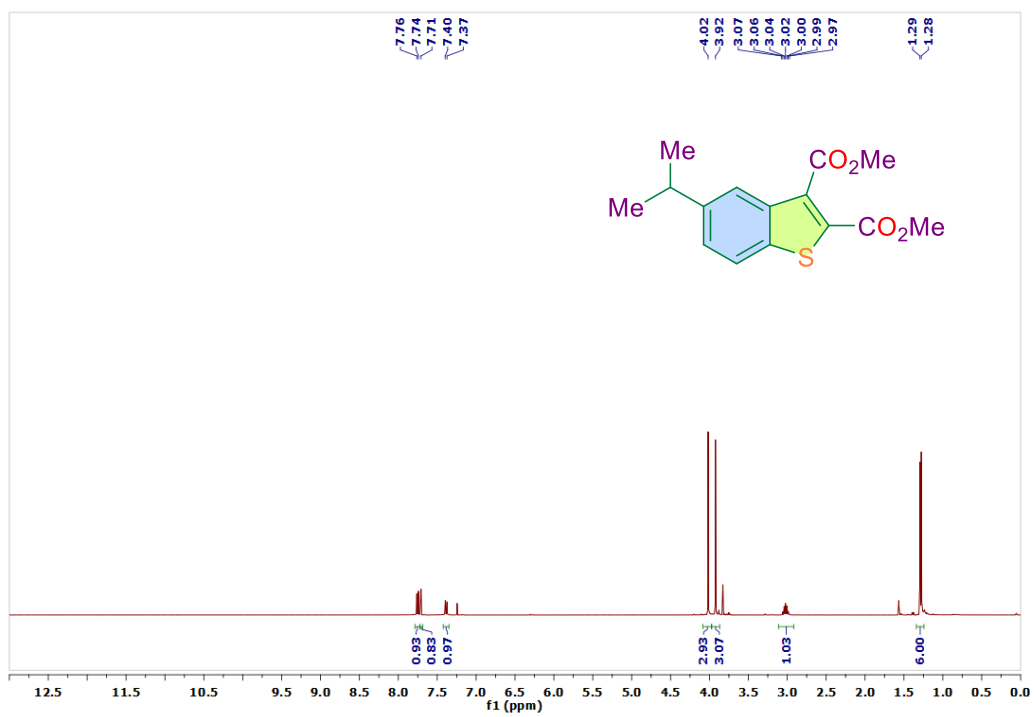
**Fig. S34**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2b**.



**Fig. S35**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2c**.



**Fig. S36**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2d**.



**Fig. S37**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2e**.

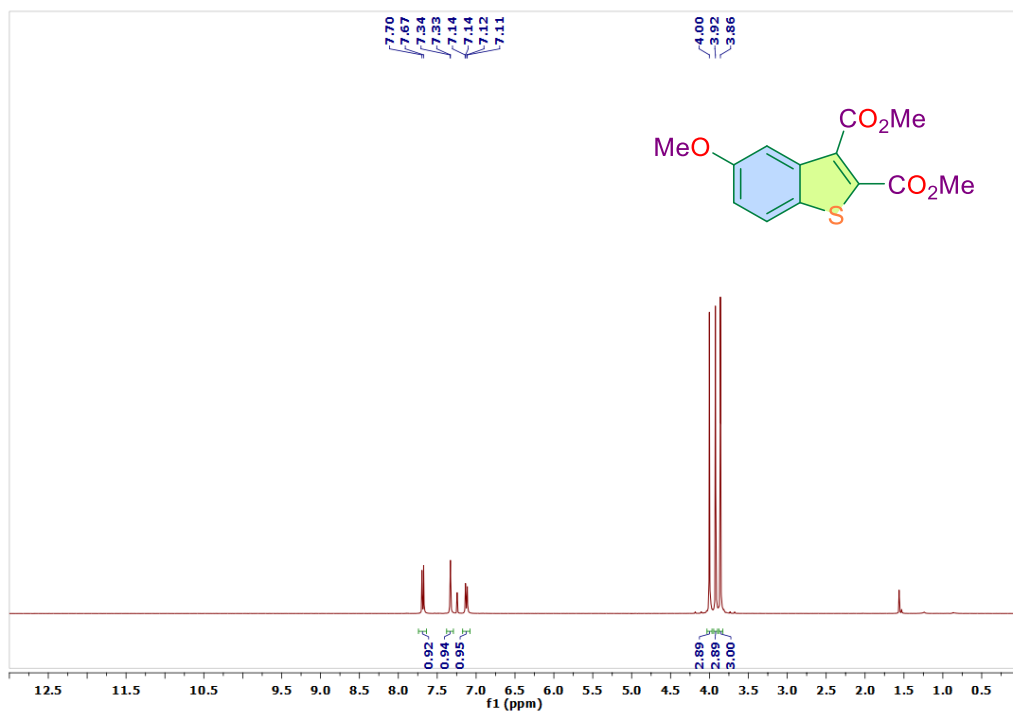


Fig. S38  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2f**.

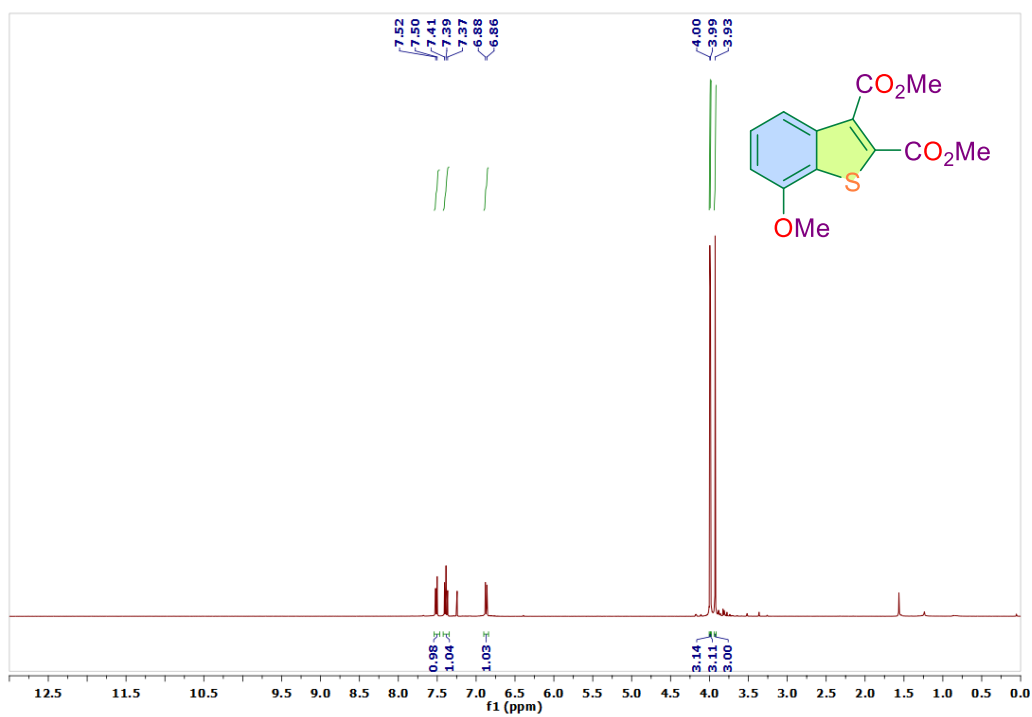
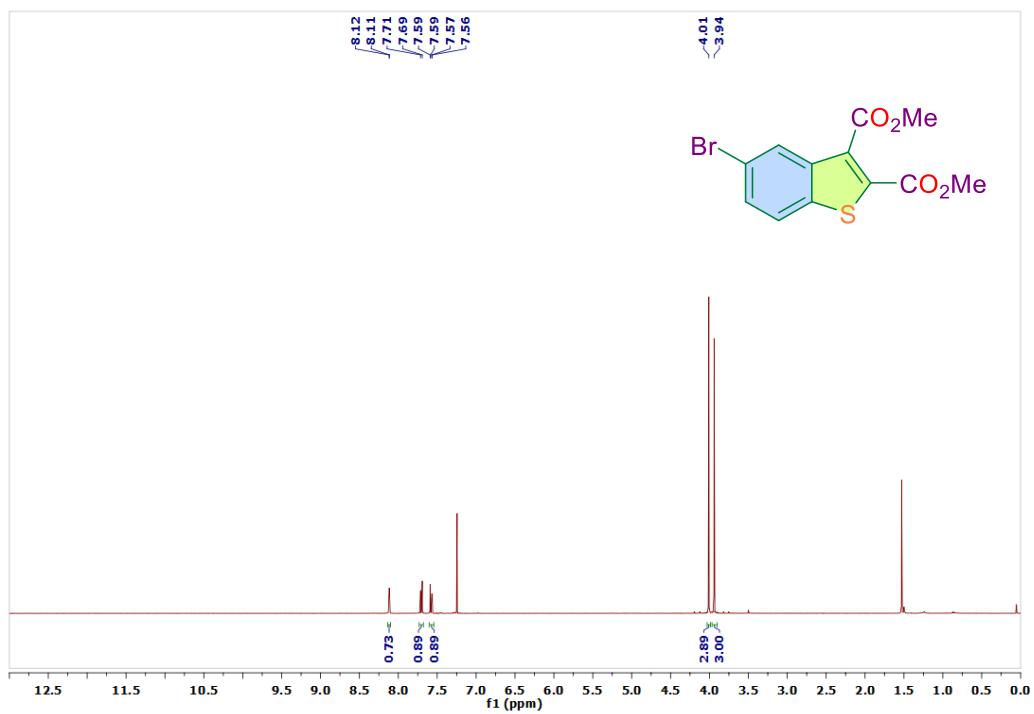
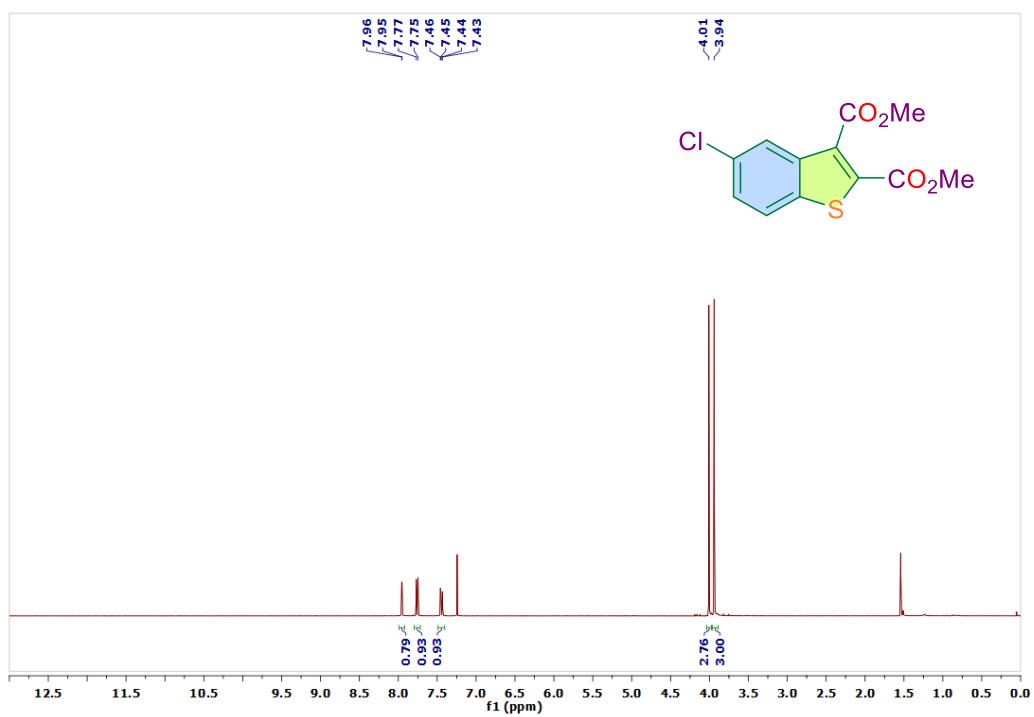


Fig.S39  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2g**.





**Fig. S40**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2h**.



**Fig. S41**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2i**.

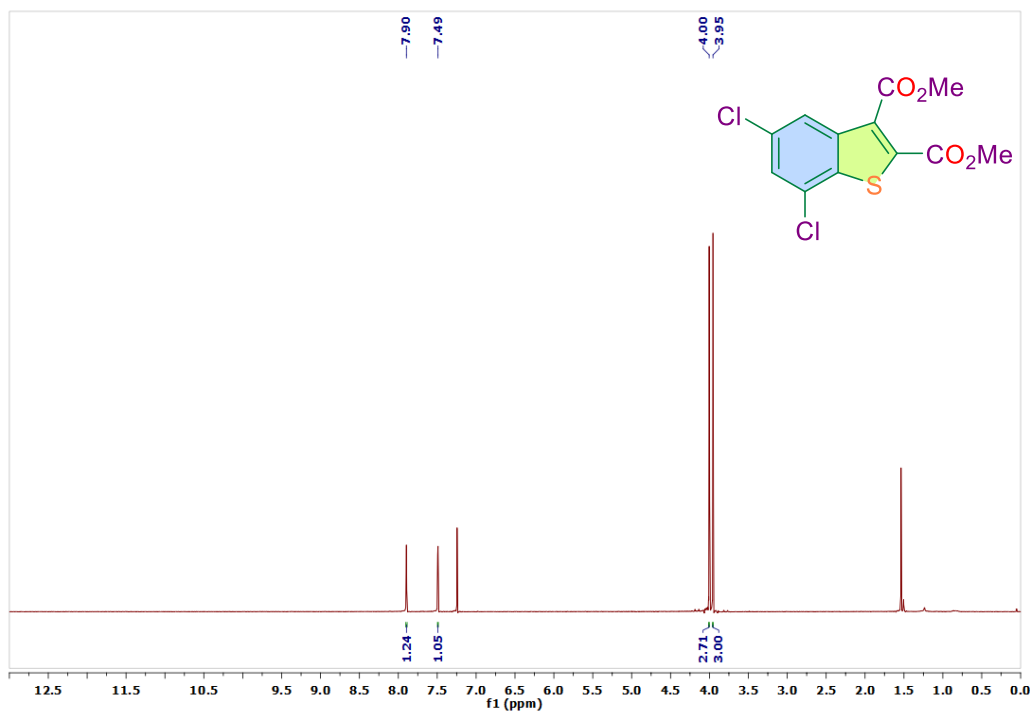


Fig. S42  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2j**.

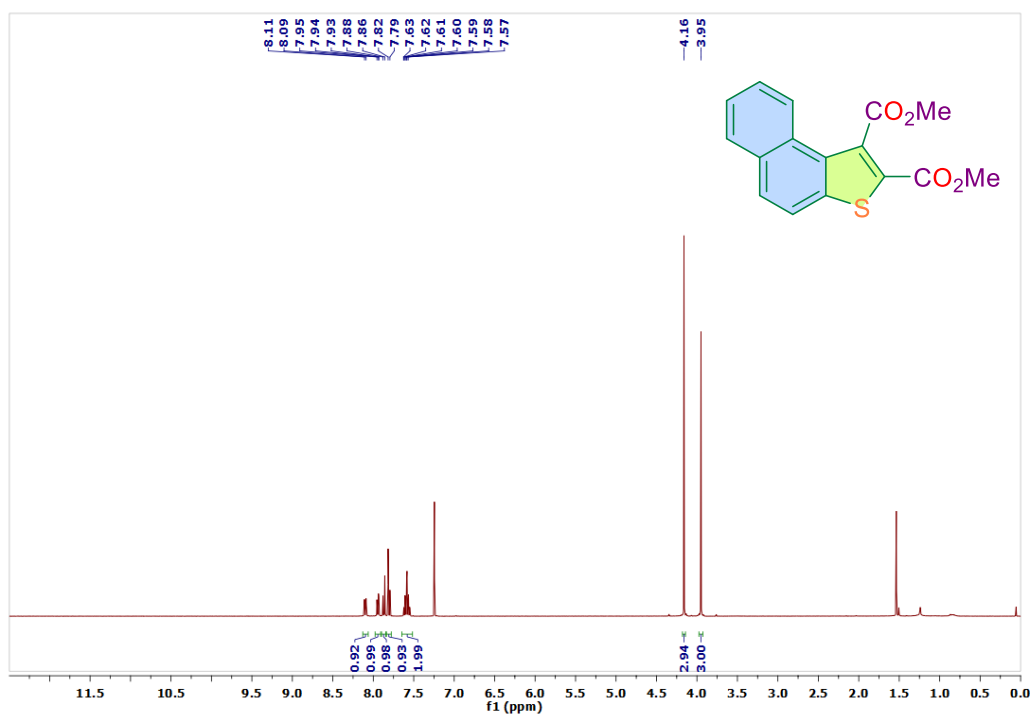


Fig. S43  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2k**.

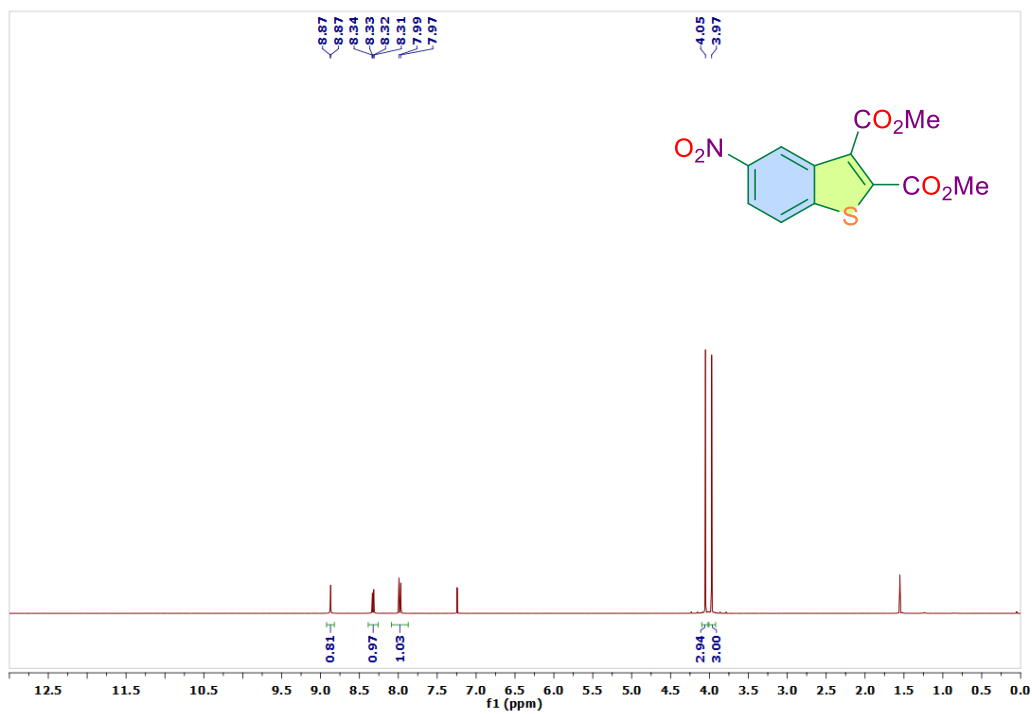


Fig. S44  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **21**.

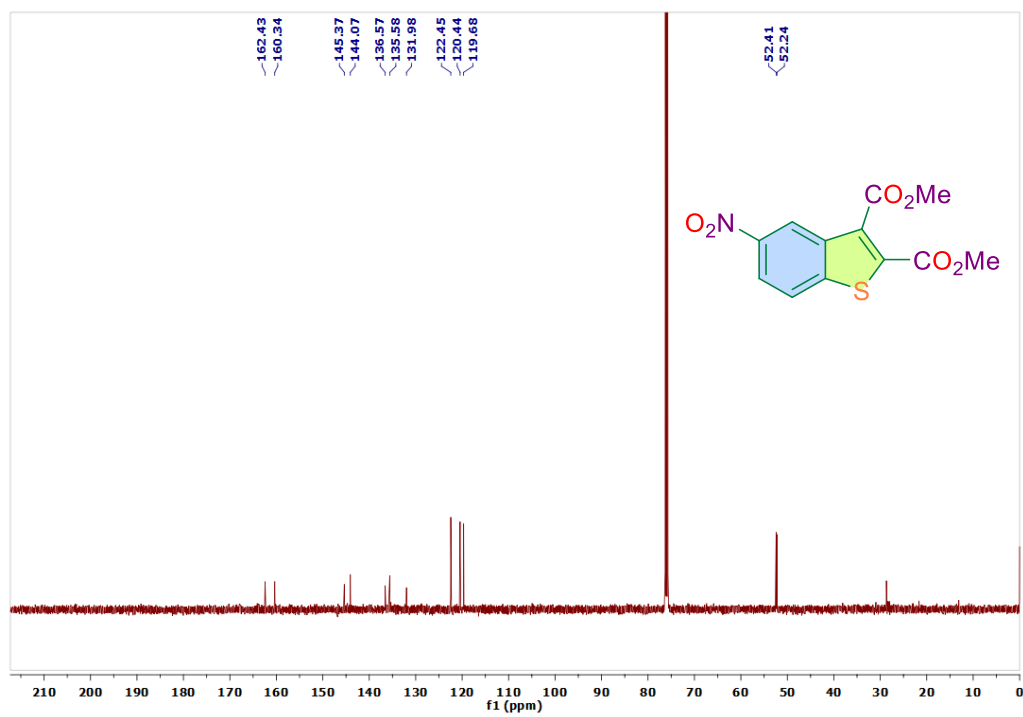


Fig. S45  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **21**.

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