

# Supporting Information

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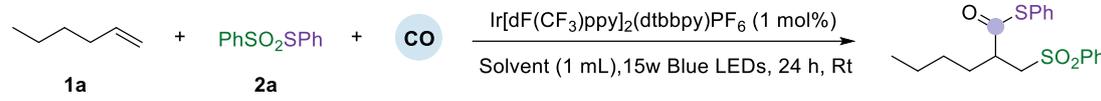
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## 1. General information

Unless otherwise noted, all reactions were carried out under N<sub>2</sub>. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) as eluent. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on 400 MHz or 700 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as the internal standard and CDCl<sub>3</sub> (<sup>1</sup>H NMR  $\delta$  7.26, <sup>13</sup>C NMR  $\delta$  77.16) as solvent. All coupling constants (*J*) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by GC-FID or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI-TOF) or Agilent 6540 Accurate-MS spectrometer (Q-TOF). Because of the high toxicity of carbon monoxide, all the reactions should be performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.

## 2. Optimization of the reaction conditions

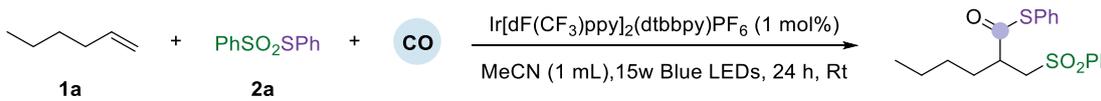
Table S1. Optimization of solvents



Entry	Solvent	Yield (%)
1	MeCN	31
2	DCM	trace
3	Acetone	20
4	EA	12
5	THF	9
6	1,4-dioxane	10
7	DMF	18
8	Toluene	9
9	DME	10

Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (1 mol%), MeCN (1 mL), CO (60 bar), Rt, 24 h, 15w Blue LEDs. Isolated yields.

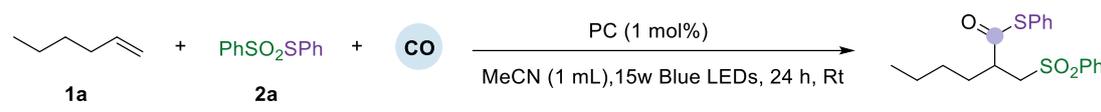
Table S2. Optimization of substrate ratio



Entry	<b>1a : 2a (mmol)</b>	Yield (%)
1	1.5 : 1	22
2	2.5 : 1	25
3	3 : 1	26
4	3.5 : 1	30
5	1 : 2	28

Reaction conditions: **1a**, **2a**, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (1 mol%), MeCN (1 mL), CO (60 bar), Rt, 24 h, 15w Blue LEDs. Isolated yields.

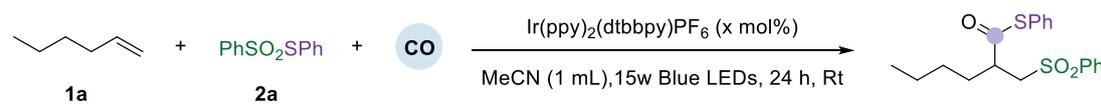
Table S3. Optimization of photocatalysts



Entry	PC	Yield (%)
1	<i>fac</i> -(Irppy) <sub>3</sub>	40
2	4-CzIPN	45
3	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> ·6H <sub>2</sub> O	trace
4	Eosin Y	trace
5	Ir(ppy) <sub>2</sub> (dtbbpy)PF <sub>6</sub>	48

Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), photocatalysts (1 mol%), MeCN (1 mL), CO (60 bar), Rt, 24 h, 15w Blue LEDs. Isolated yields.

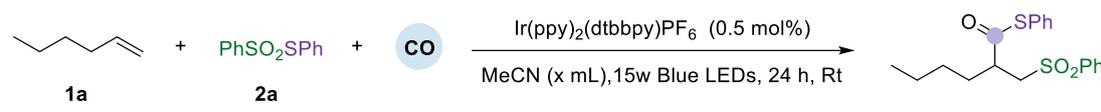
Table S4. Optimization of photocatalysts dosage



Entry	PC (x mol%)	Yield (%)
1	0.5	57
2	1.5	52
3	2	52
4	3	55
5 <sup>b</sup>	0.5	50.

Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (x mol%), MeCN (1 mL), CO (60 bar), Rt, 24 h, 15w Blue LEDs. <sup>b</sup>40w Blue LEDs. Isolated yields.

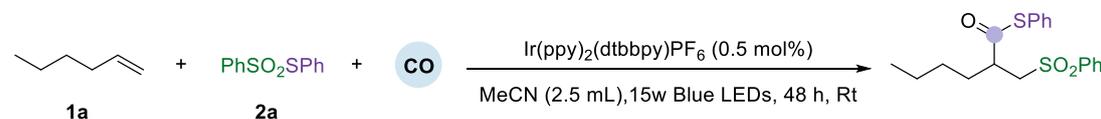
Table S5. Optimization of solvent dosage



Entry	MeCN (x mL)	Yield (%)
1	0.5	53
2	1.5	55
3	2	50
4	2.5	60
5 <sup>b</sup>	2.5	31
6 <sup>c</sup>	2.5	65

Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (0.5 mol%), MeCN (2.5 mL), CO (60 bar), Rt, 24 h, 15w Blue LEDs. <sup>b</sup>CO (40 bar). <sup>c</sup>48h. Isolated yields.

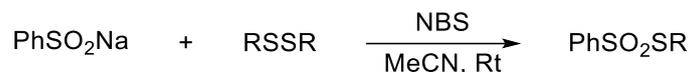
Table S6. Without photocatalysts or in dark



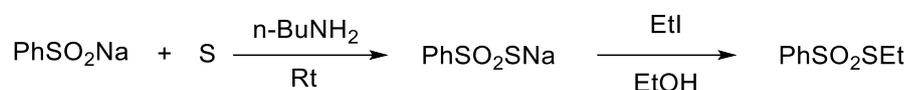
Entry	Without PC	Yield (%)
1	15w Blue LED	7
2 <sup>b</sup>	In dark	N.D.

Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), MeCN (2.5 mL), CO (60 bar), Rt, 48 h, 15w Blue LEDs. <sup>b</sup>Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (0.5 mol%) and in dark. Isolated yields.

### 3. General procedure for preparation of benzenesulfonylthioates



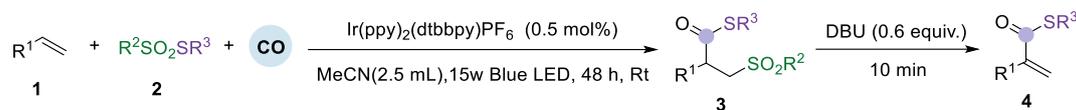
A mixture of sodium sulfinate (4.0 mmol), disulfide (1.0 mmol) and *N*-bromosuccinimide (2.0 mmol) in acetonitrile (15.0 mL) was stirred at room temperature for 15 h. Subsequently, the solvent was evaporated, the residue was redissolved in EtOAc, washed with water and extracted with EtOAc (3x15 mL). The combined organic phases were dried over MgSO<sub>4</sub>. After filtration and concentration, the residue was purified by flash chromatography.



A mixture of PhSO<sub>2</sub>Na (1.0 equiv.) and S (1.0 equiv.) in *n*-BuNH<sub>2</sub> (1.0 mmol/mL) was stirred at room temperature for 0.5 h. After removal of the solvent under reduced pressure, the residue was washed by Et<sub>2</sub>O to obtain a white solid PhSO<sub>2</sub>SNa. Then PhSO<sub>2</sub>SNa was dissolved in EtOH (1.0 mmol/mL), then C<sub>2</sub>H<sub>5</sub>I (2.0 equiv.) was added to the solution. The reaction mixture was stirred at 40-45 °C for 24 h. After removal of the solvent under reduced pressure, the reaction mixture was poured on a solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>. The precipitate was filtered and dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>, the residue was purified through column chromatography afforded the desired product as a yellow oil.

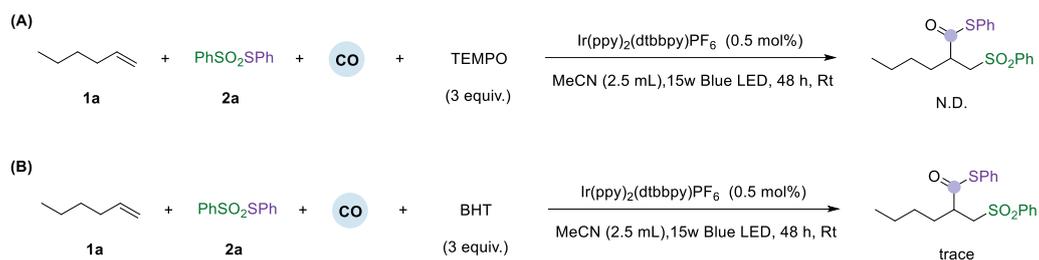
In general, benzenesulfonylthioate substrates were obtained in quantitative yields, all are known compounds.

#### 4. General procedure for the synthesis of $\alpha,\beta$ -unsaturated thioesters



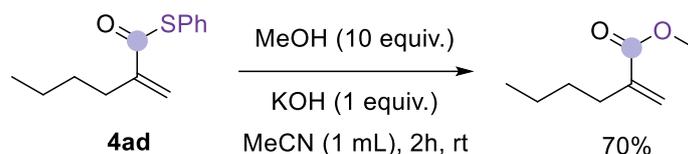
A 4 mL screw-cap vial was charged with **1** (0.2 mmol), **2** (0.1 mmol), Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (0.5 mol%) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. Then MeCN (2.5 mL) was added with a syringe under N<sub>2</sub> atmosphere. The closed autoclave was flushed two times with nitrogen (~ 10 bar), and a pressure of 60 bar CO were charged. The reaction mixture was stirred at room temperature under 15w Blue LEDs (450 - 460 nm) for 48 hours. After the reaction, the pressure was released carefully. Add DBU (0.6 equiv.) to the reaction solution and stir at room temperature under air atmosphere for ten minutes. The mixture was concentrated under vacuum. The crude product was purified by column chromatography (PE/EA = 50/1) on silica gel to afford the corresponding products. It is worth noting that  $\alpha,\beta$ -unsaturated thioesters is easily decomposed in DBU, so the product should be quickly processed after the reaction is completed.

## 5. Control experiments



A 4 mL screw-cap vial was charged with **1a** (0.2 mmol), **2a** (0.1 mmol), Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (0.5 mol%), radical scavenger (3 equiv.) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. Then MeCN (2.5 mL) was added with a syringe under N<sub>2</sub> atmosphere. The closed autoclave was flushed two times with nitrogen (~ 10 bar), and a pressure of 60 bar CO were charged. The reaction mixture was stirred at room temperature under 15w Blue LEDs (450 - 460 nm) for 48 hours.

## 6. Synthetic applications



A 4 mL screw-cap vial was charged with **4ad** (0.1 mmol), KOH (1 equiv.), MeOH (10 equiv.), MeCN (2.5 mL) and an oven-dried stirring bar. At room temperature under air atmosphere for 2 hours. The product was confirmed by GC-MS, and the yield was 70% by NMR.

## 7. Polymerization of $\alpha,\beta$ -unsaturated thioesters



In a glove box,  $\alpha,\beta$ -unsaturated thioester (1 mmol), AIBN (1 mol%), and a drying stirring bar were added to a 4 mL screw-cap vial and stirred at 60 °C overnight under  $N_2$ .

## 8. Characterization data of the corresponding product



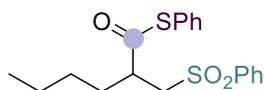
### **S-phenyl 2-((phenylsulfonyl)methyl)pentanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3aa** as a yellow solid (19.1 mg, 55%). Melting point: 77.4-79.3 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.95 (d, J = 7.5 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.7 Hz, 2H), 7.45 – 7.30 (m, 5H), 3.74 (dd, J = 14.3, 8.4 Hz, 1H), 3.34 – 3.23 (m, 1H), 3.13 (dd, J = 14.3, 3.9 Hz, 1H), 1.85 – 1.72 (m, 1H), 1.69 – 1.59 (m, 1H), 1.46 – 1.36 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.2, 139.3, 134.5, 134.1, 129.7, 129.5, 129.3, 128.4, 127.1, 57.3, 47.4, 35.4, 19.9, 13.8.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>18</sub>H<sub>21</sub>O<sub>3</sub>S<sub>2</sub> 349.0927, found: 349.0917.



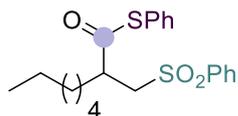
### **S-phenyl 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3ab** as a yellow oil (23.5 mg, 65%). Melting point: 63.0-65.0 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.01 – 7.91 (m, 2H), 7.67 (dd, J = 8.4, 6.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.43 – 7.28 (m, 5H), 3.74 (dd, J = 14.3, 8.4 Hz, 1H), 3.33 – 3.21 (m, 1H), 3.14 (dd, J = 14.3, 3.9 Hz, 1H), 1.88 – 1.74 (m, 1H), 1.71 – 1.61 (m, 1H), 1.37 – 1.28 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.2, 139.2, 134.5, 134.1, 129.7, 129.5, 129.3, 128.4, 127.1, 57.3, 47.5, 33.1, 28.6, 22.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>23</sub>O<sub>3</sub>S<sub>2</sub> 363.1083, found: 363.1078.



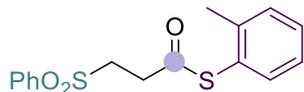
### ***S*-phenyl 2-((phenylsulfonyl)methyl)octanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3ac** as a yellow liquid (19.5 mg, 50%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.01 – 7.92 (m, 2H), 7.72 – 7.64 (m, 1H), 7.57 (dd, *J* = 10.5, 4.7 Hz, 2H), 7.39 (dt, *J* = 3.9, 2.8 Hz, 3H), 7.36 – 7.31 (m, 2H), 3.74 (dd, *J* = 14.3, 8.4 Hz, 1H), 3.34 – 3.21 (m, 1H), 3.13 (dd, *J* = 14.3, 3.9 Hz, 1H), 1.87 – 1.73 (m, 1H), 1.72 – 1.58 (m, 1H), 1.38 – 1.23 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.2, 139.3, 134.5, 134.1, 129.7, 129.5, 129.3, 128.4, 127.1, 57.3, 47.5, 33.4, 31.6, 29.0, 26.5, 22.6, 14.2.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>21</sub>H<sub>27</sub>O<sub>3</sub>S<sub>2</sub> 391.1396, found: 397.1397.



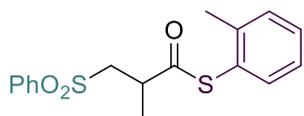
### ***S*-(*o*-tolyl) 3-(phenylsulfonyl)propanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3ad** as a yellow liquid (16.3 mg, 51%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.92 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.72 – 7.65 (m, 1H), 7.63 – 7.55 (m, 2H), 7.37 – 7.28 (m, 3H), 7.25 – 7.17 (m, 1H), 3.70 – 3.25 (m, 2H), 3.24 – 2.86 (m, 2H), 2.30 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.5, 142.2, 138.7, 136.0, 134.2, 131.0, 130.6, 129.6, 128.2, 126.8, 126.2, 51.4, 36.2, 20.8.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>17</sub>O<sub>3</sub>S<sub>2</sub> 321.0614, found: 321.0621.



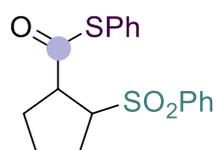
### ***S*-(*o*-tolyl) 2-methyl-3-(phenylsulfonyl)propanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3ae** as a yellow liquid (18.4 mg, 55%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.94 (dd, J = 7.4, 6.0 Hz, 2H), 7.72 – 7.62 (m, 1H), 7.58 (dd, J = 10.5, 4.8 Hz, 2H), 7.31 (dd, J = 10.5, 7.0 Hz, 3H), 7.24 – 7.15 (m, 1H), 3.74 (dd, J = 14.2, 6.9 Hz, 1H), 3.58 – 3.29 (m, 1H), 3.10 (dd, J = 14.2, 5.6 Hz, 1H), 2.32 (s, 3H), 1.45 (d, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.2, 142.3, 139.4, 136.0, 134.1, 131.0, 130.5, 129.6, 128.2, 126.8, 126.4, 58.4, 42.4, 20.8, 19.1.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>19</sub>O<sub>3</sub>S<sub>2</sub> 335.0770, found: 335.0777.



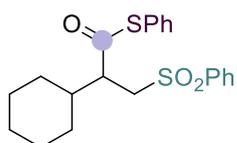
### **S-phenyl 2-(phenylsulfonyl)cyclopentane-1-carbothioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3af** as a yellow liquid (15.6 mg, 45%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.04 – 7.87 (m, 2H), 7.73 – 7.62 (m, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.44 – 7.32 (m, 3H), 7.25 – 7.18 (m, 2H), 4.21 – 3.91 (m, 1H), 3.72 – 3.44 (m, 1H), 2.40 – 2.17 (m, 2H), 2.14 – 1.95 (m, 1H), 1.94 – 1.70 (m, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.1, 138.5, 134.5, 133.9, 129.7, 129.5, 129.3, 128.8, 127.1, 65.8, 53.4, 33.5, 27.8, 26.1.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>18</sub>H<sub>19</sub>O<sub>3</sub>S<sub>2</sub> 347.0770, found: 347.0775.



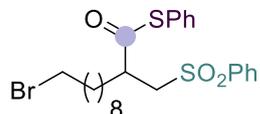
### **S-phenyl 2-cyclohexyl-3-(phenylsulfonyl)propanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3ah** as a yellow oil (16.3 mg, 42%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.94 (dd, J = 5.2, 3.4 Hz, 2H), 7.73 – 7.62 (m, 1H), 7.57 (dd, J = 10.5, 4.7 Hz, 2H), 7.40 (dd, J = 6.6, 3.6 Hz, 3H), 7.36 – 7.29 (m, 2H), 3.78 (dd, J = 14.4, 10.0 Hz, 1H), 3.22 – 3.04 (m, 2H), 1.82 – 1.59 (m, 6H), 1.32 – 0.81 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.5, 139.2, 134.5, 134.0, 129.6, 129.5, 129.3, 128.4, 127.4, 55.3, 52.9, 41.4, 30.6, 29.6, 26.3, 26.3, 26.0.

HRMS (ESI-TOF): calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{21}\text{H}_{25}\text{O}_3\text{S}_2$  389.1240, found: 389.1245.



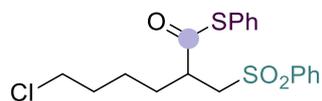
### S-phenyl 11-bromo-2-((phenylsulfonyl)methyl)undecanethioate

The reaction solution was processed as general experimental procedure to afford the corresponding product **3ai** as a yellow liquid (35.7 mg, 70%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.5$  Hz, 2H), 7.67 (t,  $J = 7.4$  Hz, 1H), 7.58 (t,  $J = 7.7$  Hz, 2H), 7.39 (dd,  $J = 9.4, 5.7$  Hz, 3H), 7.35 – 7.29 (m, 2H), 3.74 (dd,  $J = 14.3, 8.3$  Hz, 1H), 3.40 (t,  $J = 6.8$  Hz, 2H), 3.33 – 3.20 (m, 1H), 3.13 (dd,  $J = 14.3, 3.9$  Hz, 1H), 1.89 – 1.74 (m, 3H), 1.65 (td,  $J = 14.1, 6.9$  Hz, 1H), 1.41 (dd,  $J = 15.5, 5.6$  Hz, 3H), 1.31 (d,  $J = 27.8$  Hz, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.2, 139.2, 134.5, 134.1, 129.7, 129.5, 129.3, 128.4, 127.1, 57.3, 47.5, 34.2, 33.3, 32.9, 29.4, 29.2, 29.2, 28.8, 28.2, 26.5.

HRMS (ESI-TOF): calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{24}\text{H}_{32}\text{BrO}_3\text{S}_2$  511.0971, found: 511.0967.



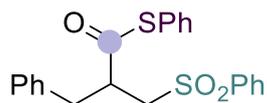
### S-phenyl 6-chloro-2-((phenylsulfonyl)methyl)hexanethioate

The reaction solution was processed as general experimental procedure to afford the corresponding product **3aj** as a yellow liquid (22.6 mg, 57%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 5.2, 3.3$  Hz, 2H), 7.74 – 7.61 (m, 1H), 7.58 (dd,  $J = 10.5, 4.8$  Hz, 2H), 7.43 – 7.37 (m, 3H), 7.36 – 7.31 (m, 2H), 3.72 (dd,  $J = 14.3, 7.9$  Hz, 1H), 3.52 (t,  $J = 6.5$  Hz, 2H), 3.43 – 3.24 (m, 1H), 3.15 (dd,  $J = 14.3, 4.4$  Hz, 1H), 1.96 – 1.66 (m, 4H), 1.62 – 1.44 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.0, 139.2, 134.5, 134.2, 129.8, 129.6, 129.4, 128.3, 126.9, 57.2, 47.3, 44.5, 32.4, 32.1, 23.8.

HRMS (ESI-TOF): calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{19}\text{H}_{22}\text{ClO}_3\text{S}_2$  397.0693, found: 397.0694.



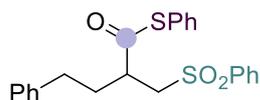
### S-phenyl 2-cyclohexyl-4,4,4-trifluorobutanethioate

The reaction solution was processed as general experimental procedure to afford the corresponding product **3ak** as a yellow solid (25.3 mg, 45%). Melting point: 108.1-110.0 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.92 – 7.83 (m, 2H), 7.70 – 7.59 (m, 1H), 7.59 – 7.49 (m, 2H), 7.44 – 7.34 (m, 3H), 7.33 – 7.22 (m, 5H), 7.15 – 7.03 (m, 2H), 3.72 (dd, J = 14.3, 8.7 Hz, 1H), 3.58 – 3.36 (m, 1H), 3.21 – 3.05 (m, 2H), 2.88 (dd, J = 13.8, 8.0 Hz, 1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.8, 139.1, 136.3, 134.5, 134.0, 129.8, 129.5, 129.4, 129.3, 129.0, 128.3, 127.4, 126.9, 56.4, 49.1, 39.2.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>S<sub>2</sub> 397.0927, found: 397.0927.



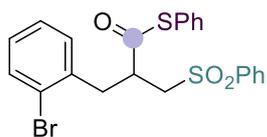
### S-phenyl 4-phenyl-2-((phenylsulfonyl)methyl)butanethioate

The reaction solution was processed as general experimental procedure to afford the corresponding product **3al** as a yellow liquid (23.8 mg, 58%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.86 (d, J = 7.6 Hz, 2H), 7.61 (q, J = 7.2 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.42 – 7.27 (m, 5H), 7.25 – 7.14 (m, 3H), 7.10 (d, J = 7.2 Hz, 2H), 3.70 (dd, J = 14.3, 7.9 Hz, 1H), 3.32 – 3.21 (m, 1H), 3.14 (dd, J = 14.3, 4.4 Hz, 1H), 2.63 (t, J = 7.6 Hz, 2H), 2.19 – 2.03 (m, 1H), 2.01 – 1.87 (m, 1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.9, 140.3, 139.1, 134.5, 134.1, 129.8, 129.6, 129.4, 128.7, 128.5, 128.4, 126.9, 126.5, 57.3, 47.2, 34.7, 32.8.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>23</sub>H<sub>23</sub>O<sub>3</sub>S<sub>2</sub> 411.1083, found: 411.1089



### S-phenyl 2-(2-bromobenzyl)-3-(phenylsulfonyl)propanethioate

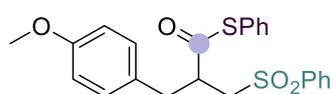
The reaction solution was processed as general experimental procedure to afford the

corresponding product **3am** as a yellow liquid (28.2 mg, 41%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.00 – 7.82 (m, 2H), 7.75 – 7.59 (m, 1H), 7.54 (dd, J = 7.7, 6.4 Hz, 3H), 7.43 – 7.32 (m, 3H), 7.26 – 7.18 (m, 3H), 7.17 – 7.11 (m, 1H), 7.08 (dd, J = 7.5, 1.6 Hz, 1H), 3.84 (dd, J = 14.3, 9.4 Hz, 1H), 3.74 – 3.53 (m, 1H), 3.23 – 3.04 (m, 2H), 2.96 (dd, J = 13.6, 8.1 Hz, 1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.7, 138.8, 135.9, 134.5, 134.0, 133.5, 131.8, 129.8, 129.5, 129.3, 129.2, 128.4, 127.8, 126.9, 124.9, 56.6, 47.2, 39.7.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>22</sub>H<sub>20</sub>BrO<sub>3</sub>S<sub>2</sub> 475.0032, found: 475.0038



### **S-phenyl 2-(4-methoxybenzyl)-3-(phenylsulfonyl)propanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3an** as a yellow solid (18.3 mg, 43%). Melting point: 80.7-82.5 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.88 (d, J = 7.7 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.43 – 7.21 (m, 5H), 7.00 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H), 3.70 (dd, J = 14.3, 8.7 Hz, 1H), 3.53 – 3.35 (m, 1H), 3.16 – 2.99 (m, 2H), 2.81 (dd, J = 13.9, 7.9 Hz, 1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.9, 158.9, 139.1, 134.5, 134.0, 130.3, 129.8, 129.5, 129.4, 128.3, 128.2, 127.0, 114.3, 56.3, 55.4, 49.3, 38.4.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>23</sub>H<sub>23</sub>O<sub>4</sub>S<sub>2</sub> 427.1032, found: 427.1042.



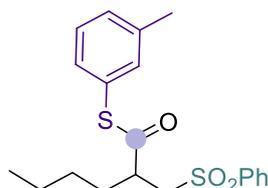
### **S-(p-tolyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3ba** as a yellow solid (19.2 mg, 51%). Melting point: 83.2-85.2 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.97 – 7.90 (m, 2H), 7.70 – 7.63 (m, 1H), 7.57 (dd, J = 10.5, 4.7 Hz, 2H), 7.20 (s, 4H), 3.74 (dd, J = 14.3, 8.2 Hz, 1H), 3.32 – 3.17 (m, 1H), 3.13 (dd, J = 14.3, 4.0 Hz, 1H), 2.36 (s, 3H), 1.86 – 1.73 (m, 1H), 1.72 – 1.59 (m, 1H), 1.30 (dd, J = 8.7, 5.1 Hz, 4H), 0.89 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.7, 140.1, 139.3, 134.5, 134.0, 130.2, 129.5, 128.4, 123.6, 57.3, 47.4, 33.1, 28.6, 22.5, 21.5, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>20</sub>H<sub>25</sub>O<sub>3</sub>S<sub>2</sub> 377.1240, found: 377.1236.



### ***S*-(*m*-tolyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bb** as a yellow liquid (21.8 mg, 58%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.01 – 7.85 (m, 2H), 7.74 – 7.63 (m, 1H), 7.58 (dd, J = 10.5, 4.7 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.13 (d, J = 6.9 Hz, 2H), 3.75 (dd, J = 14.3, 8.3 Hz, 1H), 3.34 – 3.20 (m, 1H), 3.18 – 3.06 (m, 1H), 2.36 (s, 3H), 1.81 (dq, J = 14.6, 7.2 Hz, 1H), 1.73 – 1.60 (m, 1H), 1.32 (dd, J = 7.7, 3.5 Hz, 4H), 0.89 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.4, 139.3, 139.2, 135.0, 134.0, 131.5, 130.6, 129.5, 129.2, 128.4, 126.7, 57.3, 47.5, 33.1, 28.6, 22.4, 21.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>20</sub>H<sub>25</sub>O<sub>3</sub>S<sub>2</sub> 377.1240, found: 377.1237.



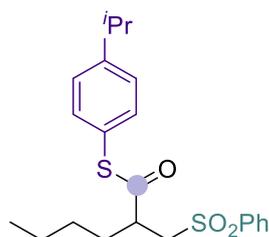
### ***S*-(*o*-tolyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bc** as a yellow solid (29.7 mg, 79%). Melting point: 71.3-73.3 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.95 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.24 – 7.17 (m, 1H), 3.73 (dd, J = 14.3, 8.2 Hz, 1H), 3.37 – 3.23 (m, 1H), 3.13 (dd, J = 14.3, 3.9 Hz, 1H), 2.33 (s, 3H), 1.90 – 1.75 (m, 1H), 1.73 – 1.62 (m, 1H), 1.40 – 1.28 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.7, 142.2, 139.3, 136.0, 134.0, 130.9, 130.4, 129.5, 128.3, 126.7, 126.6, 57.2, 47.3, 33.1, 28.6, 22.4, 20.8, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>20</sub>H<sub>25</sub>O<sub>3</sub>S<sub>2</sub> 377.1240, found: 377.1237.



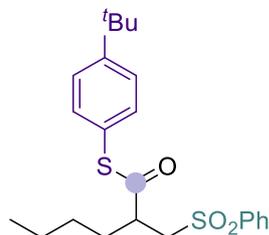
**S-(4-isopropylphenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bd** as a yellow liquid (21.9 mg, 41%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.01 – 7.88 (m, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.36 – 7.07 (m, 4H), 3.74 (dd, J = 14.3, 8.2 Hz, 1H), 3.32 – 3.18 (m, 1H), 3.13 (dd, J = 14.3, 3.9 Hz, 1H), 2.96 – 2.85 (m, 1H), 1.87 – 1.73 (m, 1H), 1.71 – 1.60 (m, 1H), 1.32 – 1.10 (m, 10H), 0.89 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.7, 150.8, 139.3, 134.5, 134.0, 129.5, 128.4, 127.6, 123.9, 57.3, 47.4, 34.1, 33.1, 28.6, 23.9, 22.5, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>22</sub>H<sub>29</sub>O<sub>3</sub>S<sub>2</sub> 405.1553, found: 405.1559.



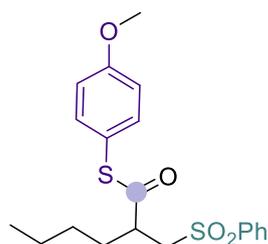
**S-(4-(tert-butyl)phenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3be** as a yellow solid (19.2 mg, 46%). Melting point: 69.5-71.5 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.01 – 7.87 (m, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.58 (dd, J = 10.5, 4.8 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.29 – 7.18 (m, 2H), 3.74 (dd, J = 14.3, 8.2 Hz, 1H), 3.31 – 3.20 (m, 1H), 3.13 (dd, J = 14.3, 3.9 Hz, 1H), 1.87 – 1.74 (m, 1H), 1.72 – 1.59 (m, 1H), 1.36 – 1.26 (m, 13H), 0.89 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.7, 153.0, 139.3, 134.2, 134.0, 129.5, 128.4, 126.5, 123.6, 57.3, 47.4, 34.9, 33.1, 31.3, 28.6, 22.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>23</sub>H<sub>31</sub>O<sub>3</sub>S<sub>2</sub> 419.1709, found: 419.1710.



***S*-(4-methoxyphenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bf** as a white solid (19.6 mg, 50%). Melting point: 83.9-85.8 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.98 – 7.87 (m, 2H), 7.71 – 7.63 (m, 1H), 7.57 (dd, J = 10.5, 4.7 Hz, 2H), 7.25 – 7.14 (m, 2H), 7.01 – 6.83 (m, 2H), 3.82 (s, 3H), 3.73 (dd, J = 14.3, 8.3 Hz, 1H), 3.31 – 3.19 (m, 1H), 3.12 (dd, J = 14.3, 3.9 Hz, 1H), 1.86 – 1.71 (m, 1H), 1.69 – 1.60 (m, 1H), 1.37 – 1.27 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 199.2, 160.9, 139.3, 136.1, 134.0, 129.5, 128.4, 117.8, 115.0, 57.3, 55.5, 47.2, 33.1, 28.6, 22.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>20</sub>H<sub>25</sub>O<sub>4</sub>S<sub>2</sub> 393.1189, found: 393.1189.



***S*-(2-methoxyphenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

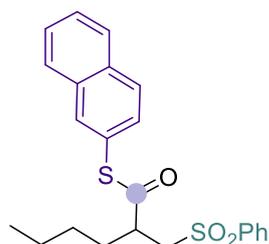
The reaction solution was processed as general experimental procedure to afford the corresponding product **3bg** as a yellow liquid (16.5 mg, 42%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.00 – 7.81 (m, 2H), 7.74 – 7.61 (m, 1H), 7.57 (t, J =

7.6 Hz, 2H), 7.44 – 7.33 (m, 1H), 7.30 (dd, J = 7.6, 1.7 Hz, 1H), 7.02 – 6.82 (m, 2H), 3.81 (s, 3H), 3.70 (dd, J = 14.3, 7.4 Hz, 1H), 3.33 – 3.24 (m, 1H), 3.14 (dd, J = 14.3, 4.8 Hz, 1H), 1.89 – 1.77 (m, 1H), 1.77 – 1.65 (m, 1H), 1.41 – 1.29 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.4, 159.2, 139.4, 136.7, 134.0, 132.0, 129.5, 128.3, 121.2, 115.4, 111.7, 57.2, 56.0, 47.4, 33.0, 28.4, 22.5, 14.0.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>20</sub>H<sub>25</sub>O<sub>4</sub>S<sub>2</sub> 393.1189, found: 393.1187.



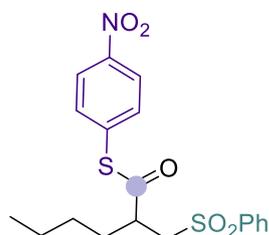
**S-(naphthalen-2-yl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bh** as a yellow liquid (17.3 mg, 42%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.97 (d, J = 7.5 Hz, 2H), 7.89 – 7.78 (m, 4H), 7.68 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 2H), 7.56 – 7.47 (m, 2H), 7.36 (dd, J = 8.5, 1.5 Hz, 1H), 3.77 (dt, J = 16.2, 8.1 Hz, 1H), 3.44 – 3.22 (m, 1H), 3.16 (dd, J = 14.3, 3.8 Hz, 1H), 1.92 – 1.77 (m, 1H), 1.68 (dt, J = 15.2, 7.0 Hz, 1H), 1.43 – 1.28 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.4, 139.3, 134.4, 134.1, 133.6, 133.6, 130.8, 129.6, 129.0, 128.4, 128.1, 127.9, 127.4, 126.8, 124.4, 57.3, 47.6, 33.1, 28.7, 22.5, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>23</sub>H<sub>25</sub>O<sub>3</sub>S<sub>2</sub> 413.1240, found: 413.1235.



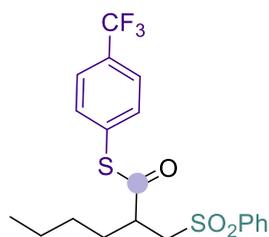
**S-(4-nitrophenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bi** as a yellow liquid (13.4 mg, 33%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.24 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.63 – 7.54 (m, 4H), 3.80 – 3.66 (m, 1H), 3.35 – 3.26 (m, 1H), 3.15 (dd, J = 14.2, 3.3 Hz, 1H), 1.88 – 1.74 (m, 1H), 1.70 – 1.60 (m, 1H), 1.39 – 1.29 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)** δ 196.4, 139.1, 135.6, 134.9, 134.2, 129.6, 128.3, 124.6, 124.1, 57.4, 48.0, 33.0, 28.6, 22.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>22</sub>NO<sub>5</sub>S<sub>2</sub> 408.0934, found: 408.0933.



**S-(4-(trifluoromethyl)phenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

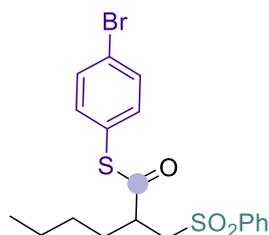
The reaction solution was processed as general experimental procedure to afford the corresponding product **3bj** as a yellow solid (25.8mg, 60%). Melting point: 70.1-72.0 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.04 – 7.83 (m, 2H), 7.67 (dd, J = 17.0, 8.0 Hz, 3H), 7.59 (t, J = 7.6 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 3.74 (dd, J = 14.2, 8.9 Hz, 1H), 3.35 – 3.23 (m, 1H), 3.14 (dd, J = 14.2, 3.5 Hz, 1H), 1.89 – 1.73 (m, 1H), 1.72 – 1.58 (m, 1H), 1.38 – 1.27 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)** δ 197.2, 139.2, 134.6, 134.2, 131.8, 131.6 (q, *J*<sub>C-F</sub> = 32.8 Hz), 129.6, 128.3, 126.1 (q, *J*<sub>C-F</sub> = 3.6 Hz), 123.9 (q, *J*<sub>C-F</sub> = 272.4 Hz), 57.4, 47.8, 33.0, 28.6, 22.4, 13.9.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -62.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>20</sub>H<sub>22</sub>F<sub>3</sub>O<sub>3</sub>S<sub>2</sub> 431.0957, found: 431.0960.



**S-(4-bromophenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

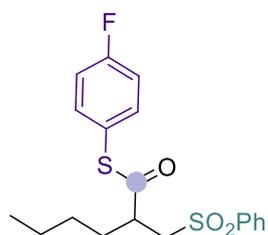
The reaction solution was processed as general experimental procedure to afford the

corresponding product **3bk** as a yellow solid (22.0 mg, 50%). Melting point: 69.8-71.7 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.03 – 7.90 (m, 2H), 7.71 – 7.64 (m, 1H), 7.58 (dd, J = 10.5, 4.7 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.23 – 7.15 (m, 2H), 3.73 (dd, J = 14.2, 8.7 Hz, 1H), 3.32 – 3.20 (m, 1H), 3.13 (dd, J = 14.3, 3.7 Hz, 1H), 1.86 – 1.73 (m, 1H), 1.69 – 1.59 (m, 1H), 1.37 – 1.27 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.7, 139.2, 136.0, 134.1, 132.6, 129.6, 128.3, 126.2, 124.4, 57.3, 47.6, 33.0, 28.6, 22.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>22</sub>BrO<sub>3</sub>S<sub>2</sub> 441.0188, found: 441.0192.



#### **S-(4-fluorophenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

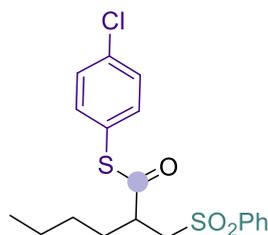
The reaction solution was processed as general experimental procedure to afford the corresponding product **3bl** as a yellow liquid (26.6 mg, 70%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.95 (d, J = 7.6 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.43 – 7.28 (m, 2H), 7.09 (t, J = 8.6 Hz, 2H), 3.82 – 3.66 (m, 1H), 3.34 – 3.22 (m, 1H), 3.18 – 3.07 (m, 1H), 1.87 – 1.70 (m, 1H), 1.69 – 1.53 (m, 1H), 1.30 (dd, J = 8.8, 5.1 Hz, 4H), 0.89 (t, J = 6.9 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.3, 163.7 (d,  $J_{C-F}$  = 250.4 Hz), 139.2, 136.6 (d,  $J_{C-F}$  = 8.6 Hz), 134.1, 129.5, 128.3, 122.4 (d,  $J_{C-F}$  = 3.4 Hz), 116.6 (d,  $J_{C-F}$  = 22.2 Hz), 57.3, 47.4, 33.0, 28.6, 22.4, 13.9

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -110.7

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>22</sub>FO<sub>3</sub>S<sub>2</sub> 381.0889, found: 381.0993.



#### **S-(4-chlorophenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bm** as a yellow liquid (24.6 mg, 62%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.98 – 7.90 (m, 2H), 7.63 (dt, J = 15.2, 7.4 Hz, 3H), 7.37 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 3.73 (dd, J = 14.2, 8.7 Hz, 1H), 3.34 – 3.21 (m, 1H), 3.13 (dd, J = 14.3, 3.7 Hz, 1H), 1.88 – 1.70 (m, 1H), 1.69 – 1.57 (m, 1H), 1.40 – 1.27 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.8, 139.2, 136.2, 135.8, 134.1, 129.6, 129.6, 128.4, 125.6, 57.3, 47.5, 33.0, 28.6, 22.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>22</sub>ClO<sub>3</sub>S<sub>2</sub> 397.0693, found: 397.0697.



#### **S-(3-chlorophenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bn** as a yellow liquid (24.2 mg, 61%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.96 – 7.91 (m, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.7 Hz, 2H), 7.41 – 7.28 (m, 3H), 7.25 – 7.20 (m, 1H), 3.75 (dd, J = 14.3, 8.7 Hz, 1H), 3.42 – 3.20 (m, 1H), 3.14 (dd, J = 14.3, 3.6 Hz, 1H), 1.93 – 1.73 (m, 1H), 1.70 – 1.57 (m, 1H), 1.43 – 1.28 (m, 4H), 0.90 (dd, J = 9.2, 4.8 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.4, 139.2, 134.9, 134.2, 132.6, 130.3, 129.9, 129.6, 128.8, 128.4, 57.2, 47.7, 33.1, 28.6, 22.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>22</sub>ClO<sub>3</sub>S<sub>2</sub> 397.0693, found: 397.0692.



#### **S-(2-chlorophenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bo** as a yellow solid (17.4 mg, 44%). Melting point: 110.0-112.0 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.03 – 7.82 (m, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.53 – 7.41 (m, 2H), 7.41 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 3.72 (dd, J = 14.3, 7.9 Hz, 1H), 3.38 – 3.24 (m, 1H), 3.15 (dd, J = 14.3, 4.3 Hz, 1H), 1.93 – 1.79 (m, 1H), 1.79 – 1.65 (m, 1H), 1.41 – 1.27 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.3, 139.2, 138.5, 137.3, 134.1, 131.5, 130.4, 129.6, 128.3, 127.5, 126.6, 57.1, 47.6, 32.9, 28.5, 22.5, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>22</sub>ClO<sub>3</sub>S<sub>2</sub> 397.0693, found: 397.0692.



### **S-(2-fluorophenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bp** as a yellow oil (24.3 mg, 64%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.01 – 7.89 (m, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.43 – 7.30 (m, 1H), 7.16 – 7.00 (m, 3H), 3.74 (dd, J = 14.3, 8.6 Hz, 1H), 3.32 – 3.21 (m, 1H), 3.14 (dd, J = 14.3, 3.6 Hz, 1H), 1.87 – 1.74 (m, 1H), 1.72 – 1.58 (m, 1H), 1.38 – 1.27 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)** δ 197.5, 162.6 (d, J = 249.4 Hz), 139.2, 134.2, 130.6 (d, J = 8.2 Hz), 130.1 (d, J = 3.2 Hz), 129.6, 128.9 (d, J = 8.2 Hz), 128.4, 121.4 (d, J = 22.7 Hz), 116.9 (d, J = 21.1 Hz), 57.3, 47.6, 33.1, 28.6, 22.4, 13.9.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -106.3.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>22</sub>FO<sub>3</sub>S<sub>2</sub> 381.0889, found: 381.0993.



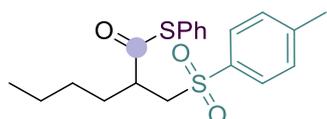
### **S-(3,5-dichlorophenyl) 2-((phenylsulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bq** as a yellow solid (21.5 mg, 50%). Melting point: 59.5-61.5 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.98 – 7.90 (m, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 2H), 7.39 (t, J = 1.8 Hz, 1H), 7.26 – 7.18 (m, 2H), 3.75 (dd, J = 14.3, 8.9 Hz, 1H), 3.38 – 3.21 (m, 1H), 3.14 (dd, J = 14.3, 3.4 Hz, 1H), 1.88 – 1.74 (m, 1H), 1.69 – 1.58 (m, 1H), 1.38 – 1.28 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.7, 139.1, 135.4, 134.3, 132.4, 123.0, 123.0, 129.6, 128.4, 57.2, 47.8, 33.1, 28.6, 22.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>21</sub>Cl<sub>2</sub>O<sub>3</sub>S<sub>2</sub> 431.0304, found: 431.0311.



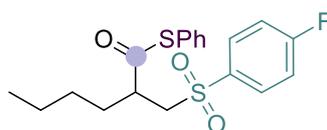
### S-phenyl 2-(tosylmethyl)hexanethioate

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bv** as a yellow liquid (19.9mg, 53%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.82 (d, J = 8.3 Hz, 2H), 7.44 – 7.35 (m, 4H), 7.34 – 7.29 (m, 2H), 7.19 (s, 1H), 3.73 (dd, J = 14.3, 8.4 Hz, 1H), 3.38 – 3.17 (m, 1H), 3.17 – 2.98 (m, 1H), 2.45 (s, 3H), 1.94 – 1.72 (m, 1H), 1.70 – 1.59 (m, 1H), 1.43 – 1.27 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.2, 145.1, 136.2, 134.5, 130.1, 129.7, 129.3, 128.4, 127.2, 57.4, 47.6, 33.1, 28.6, 22.4, 21.8, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>20</sub>H<sub>25</sub>O<sub>3</sub>S<sub>2</sub> 377.1240, found: 377.1242.



### S-phenyl 2-(((4-fluorophenyl)sulfonyl)methyl)hexanethioate

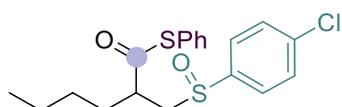
The reaction solution was processed as general experimental procedure to afford the corresponding product **3bw** as a yellow liquid (19.4 mg, 51%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.00 – 7.88 (m, 2H), 7.44 – 7.36 (m, 3H), 7.35 – 7.29 (m, 2H), 7.23 (dd, J = 6.7, 4.7 Hz, 2H), 3.75 (dd, J = 14.3, 8.6 Hz, 1H), 3.31 – 3.18 (m, 1H), 3.13 (dd, J = 14.3, 3.6 Hz, 1H), 1.91 – 1.76 (m, 1H), 1.74 – 1.59 (m, 1H), 1.42 – 1.28 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.2, 166.1 (d,  $J_{C-F}$  = 256.8 Hz), 135.3 (d,  $J_{C-F}$  = 3.1 Hz), 134.4, 131.3 (d,  $J_{C-F}$  = 9.7 Hz), 129.8, 129.4, 127.0, 116.8 (d,  $J_{C-F}$  = 22.7 Hz), 57.4, 47.6, 33.2, 28.6, 22.4, 13.9.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -103.0.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>22</sub>FO<sub>3</sub>S<sub>2</sub> 391.0989, found: 391.0993.



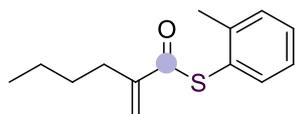
### **S-phenyl 2-(((4-chlorophenyl)sulfonyl)methyl)hexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **3bx** as a yellow liquid (17.0 mg, 43%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.91 – 7.81 (m, 2H), 7.57 – 7.51 (m, 2H), 7.43 – 7.38 (m, 3H), 7.32 – 7.27 (m, 2H), 3.77 (dd,  $J$  = 14.4, 8.8 Hz, 1H), 3.34 – 3.18 (m, 1H), 3.12 (dd,  $J$  = 14.4, 3.5 Hz, 1H), 1.88 – 1.75 (m, 1H), 1.71 – 1.59 (m, 1H), 1.34 (dd,  $J$  = 9.1, 5.5 Hz, 4H), 0.90 (t,  $J$  = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 198.1, 141.0, 137.6, 134.4, 130.0, 129.8, 129.8, 129.4, 126.9, 57.3, 47.6, 33.2, 28.6, 22.4, 13.9.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>19</sub>H<sub>22</sub>ClO<sub>3</sub>S<sub>2</sub> 397.0693, found: 397.0684.



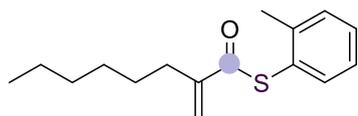
### **S-(o-tolyl) 2-methylenehexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **4aa** as a yellow liquid (11.7 mg, 50%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.41 (d,  $J$  = 7.5 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.26 – 7.20 (m, 1H), 6.24 (s, 1H), 5.66 (t,  $J$  = 1.2 Hz, 1H), 2.67 – 2.10 (m, 5H), 1.53 – 1.43 (m, 2H), 1.36 (dd,  $J$  = 15.0, 7.3 Hz, 2H), 0.92 (t,  $J$  = 7.3 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 191.6, 148.7, 142.6, 136.4, 130.9, 130.2, 127.4, 126.7, 122.7, 31.9, 30.5, 22.4, 20.9, 14.0.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>14</sub>H<sub>19</sub>OS 235.1151, found: 235.1152.



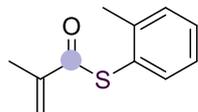
#### **S-(*o*-tolyl) 2-methyleneoctanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **4ab** as a yellow liquid (12.1 mg, 46%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.25 – 7.19 (m, 1H), 6.24 (s, 1H), 5.66 (s, 1H), 2.64 – 2.01 (m, 5H), 1.52 – 1.43 (m, 2H), 1.32 (dd, *J* = 15.9, 4.5 Hz, 6H), 0.89 (t, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 191.6, 148.7, 142.6, 136.4, 130.9, 130.2, 127.4, 126.7, 122.7, 32.2, 31.7, 29.0, 28.4, 22.7, 20.8, 14.2.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>23</sub>OS 263.1465, found: 263.1464.



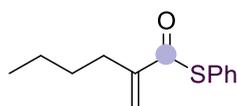
#### **S-(*o*-tolyl) 2-methylprop-2-enethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **4ac** as a yellow liquid (8.6 mg, 45%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.41 (d, *J* = 7.4 Hz, 1H), 7.33 (dt, *J* = 6.2, 3.2 Hz, 2H), 7.25 – 7.13 (m, 1H), 6.24 (d, *J* = 0.7 Hz, 1H), 5.70 (dd, *J* = 2.9, 1.4 Hz, 1H), 2.35 (s, 4H), 2.21 – 1.84 (m, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 191.3, 143.8, 142.6, 136.4, 130.9, 130.2, 127.2, 126.7, 123.9, 20.9, 18.4.

**HRMS (ESI-TOF):** calcd for [M+H]<sup>+</sup> C<sub>11</sub>H<sub>13</sub>OS 193.0682, found: 193.0678.



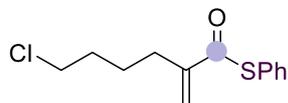
#### **S-phenyl 2-methylenehexanethioate**

The reaction solution was processed as general experimental procedure to afford the corresponding product **4ad** as a yellow liquid (12.1 mg, 55%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.50 – 7.39 (m, 5H), 6.23 (s, 1H), 5.68 (t, *J* = 1.3 Hz, 1H), 2.40 – 2.34 (m, 2H), 1.53 – 1.43 (m, 2H), 1.42 – 1.32 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.9, 148.5, 135.1, 129.4, 129.3, 128.0, 122.9, 31.8, 30.5, 22.4, 14.0.

HRMS (ESI-TOF): calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{13}\text{H}_{17}\text{OS}$  221.0995, found: 221.0997.



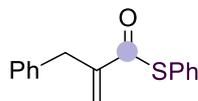
#### S-phenyl 6-chloro-2-methylenehexanethioate

The reaction solution was processed as general experimental procedure to afford the corresponding product **4ae** as a yellow liquid (11.9 mg, 47%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.36 (m, 5H), 6.27 (s, 1H), 5.72 (t,  $J = 1.2$  Hz, 1H), 3.55 (t,  $J = 6.6$  Hz, 2H), 2.39 (t,  $J = 7.6$  Hz, 2H), 1.87 – 1.73 (m, 2H), 1.70 – 1.54 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.8, 147.8, 135.1, 129.6, 129.3, 127.7, 123.6, 44.8, 32.2, 31.4, 25.7.

HRMS (ESI-TOF): calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{13}\text{H}_{16}\text{ClOS}$  255.0605, found: 255.0606.



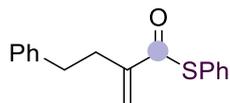
#### S-phenyl 2-benzylprop-2-enethioate

The reaction solution was processed as general experimental procedure to afford the corresponding product **4af** as a yellow liquid (10.2 mg, 40%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (s, 5H), 7.31 (t,  $J = 7.3$  Hz, 2H), 7.25 – 7.18 (m, 3H), 6.35 (s, 1H), 5.59 (s, 1H), 3.69 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.4, 147.7, 138.1, 135.1, 129.6, 129.3, 128.7, 127.7, 126.7, 124.9, 38.0.

HRMS (ESI-TOF): calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{16}\text{H}_{15}\text{OS}$  255.0838, found: 255.0835.



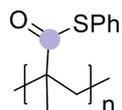
#### S-phenyl 2-methylene-4-phenylbutanethioate

The reaction solution was processed as general experimental procedure to afford the corresponding product **4ag** as a yellow liquid (13.4 mg, 50%).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.49 – 7.39 (m, 5H), 7.33 – 7.26 (m, 2H), 7.20 (dd,  $J = 7.1, 5.2$  Hz, 3H), 6.25 (s, 1H), 5.65 (s, 1H), 2.82 (dd,  $J = 9.2, 6.4$  Hz, 2H), 2.74 – 2.63 (m, 2H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  191.8, 147.4, 141.2, 135.1, 129.6, 129.3, 128.7, 128.5, 127.8, 126.2, 124.0, 34.8, 34.2.

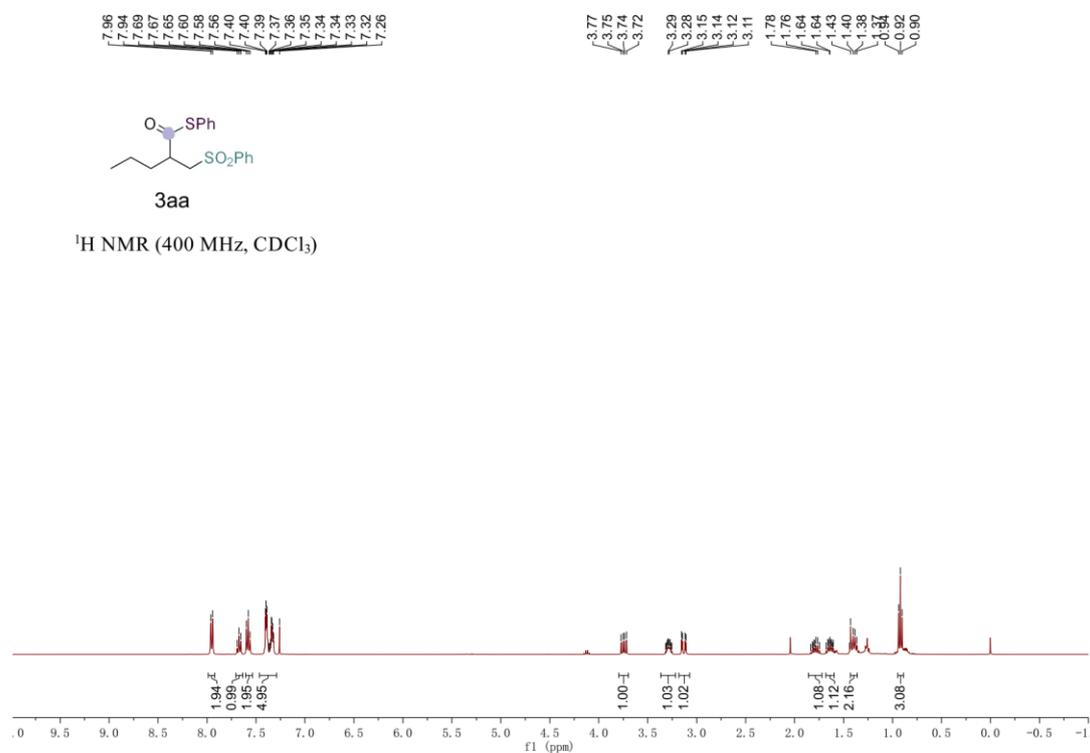
**HRMS (ESI-TOF):** calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{17}\text{H}_{18}\text{OS}$  269.0995, found: 269.0994.



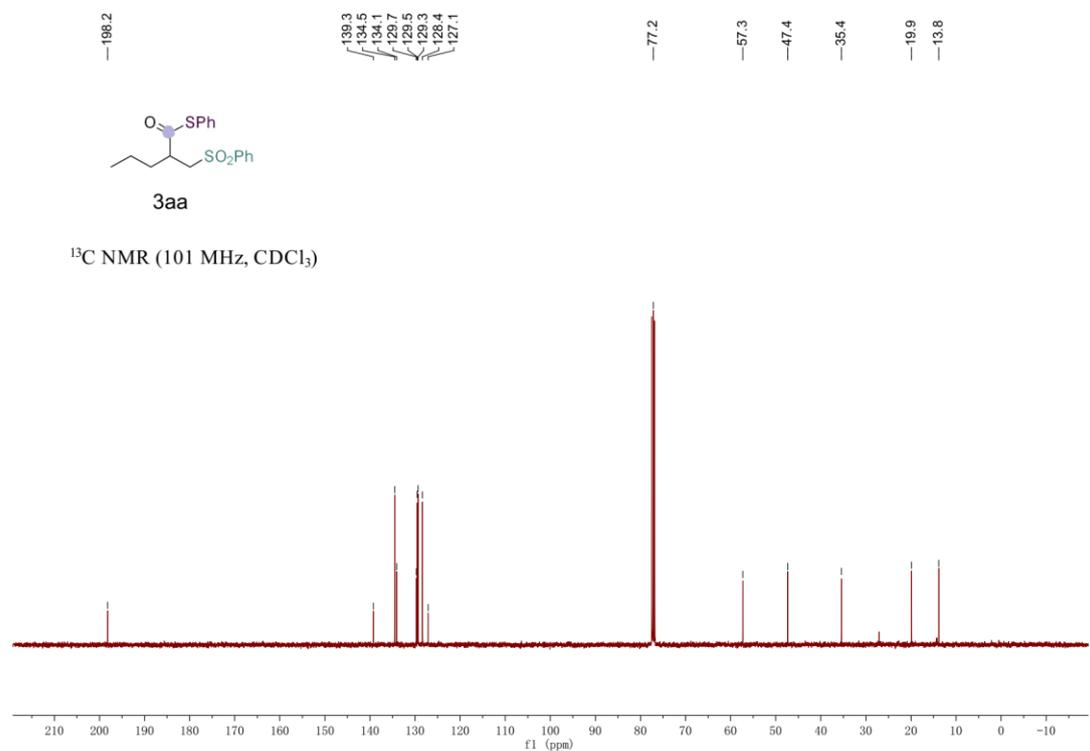
product **5aa** as a colorless solid ( $M_n$ :198485,  $D$ : 2.07)

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.36 (s, 5H), 2.51 – 1.97 (m, 2H), 1.73 – 1.42 (m, 3H).

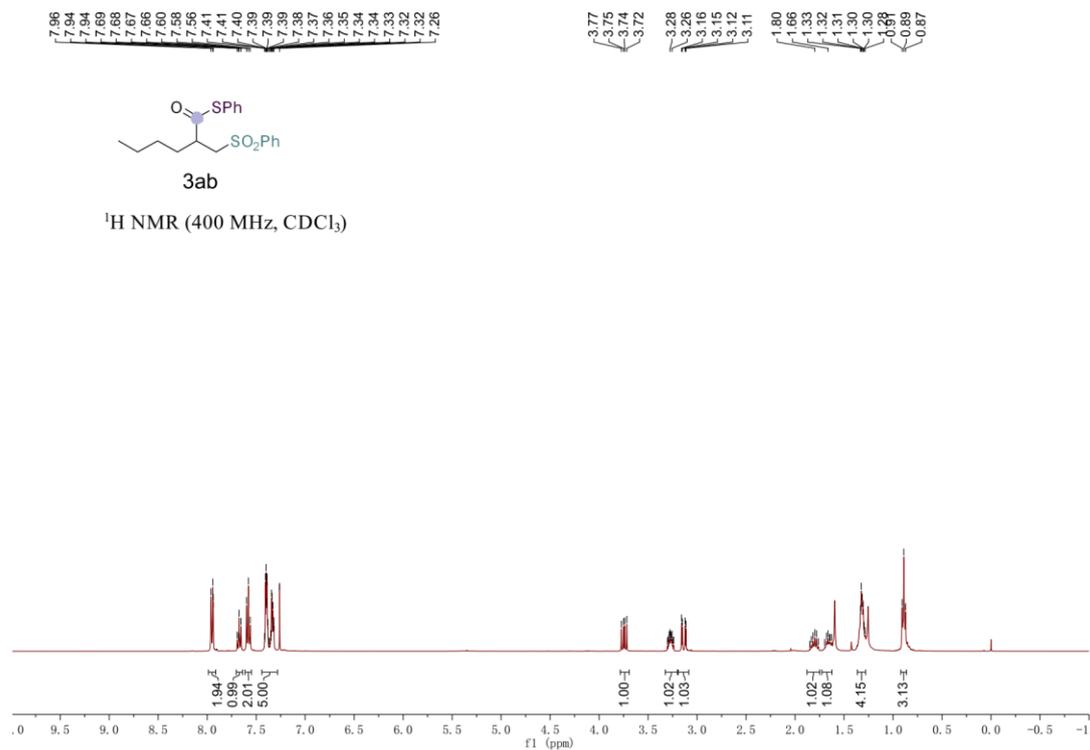
## 9. The NMR spectrum



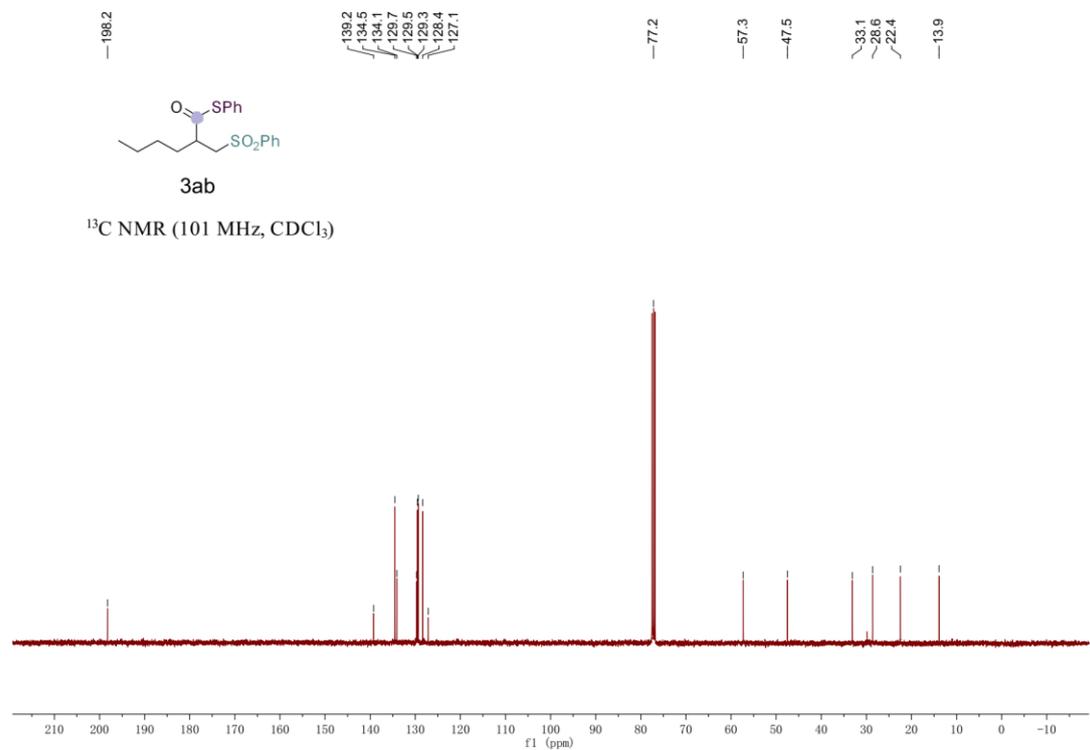
Supplementary Figure 1. <sup>1</sup>H NMR spectrum of **3aa** in CDCl<sub>3</sub> (400 MHz)



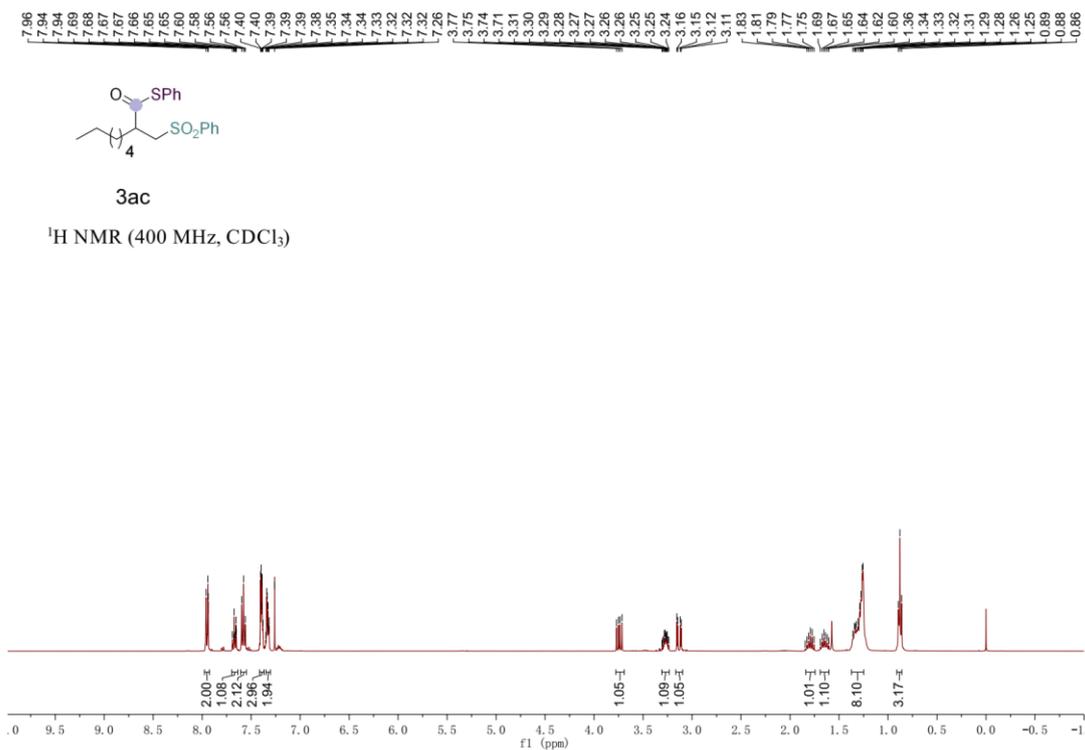
Supplementary Figure 2. <sup>13</sup>C NMR spectrum of **3aa** in CDCl<sub>3</sub> (101 MHz)



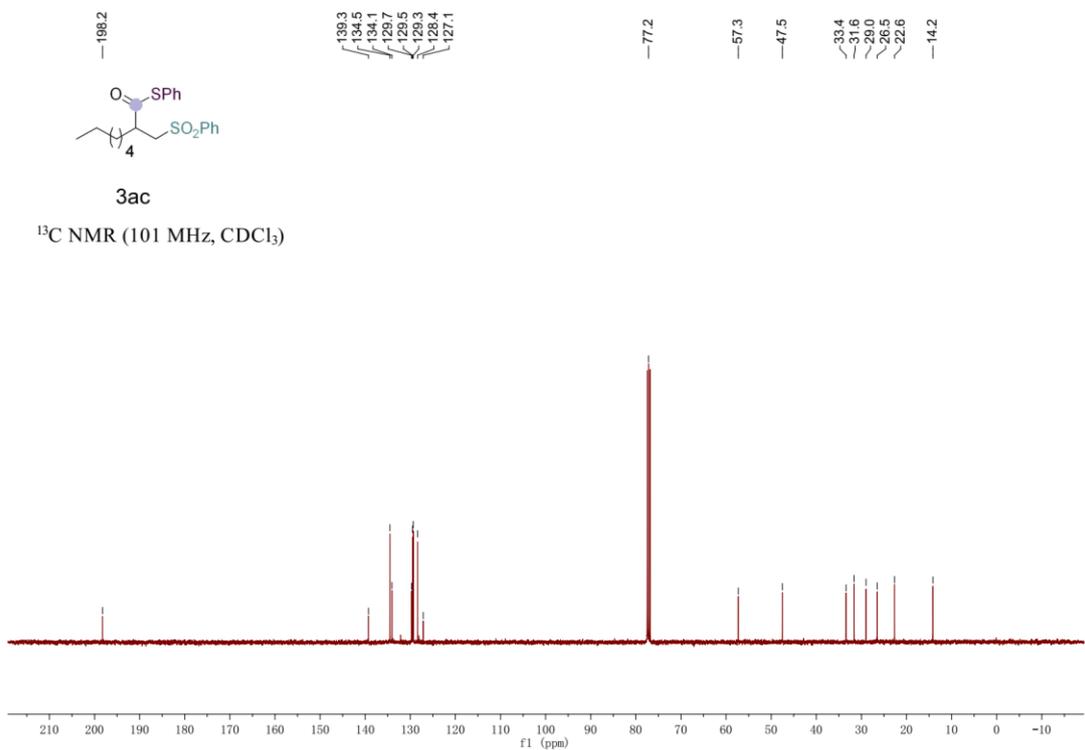
Supplementary Figure 3. <sup>1</sup>H NMR spectrum of **3ab** in CDCl<sub>3</sub> (400 MHz)



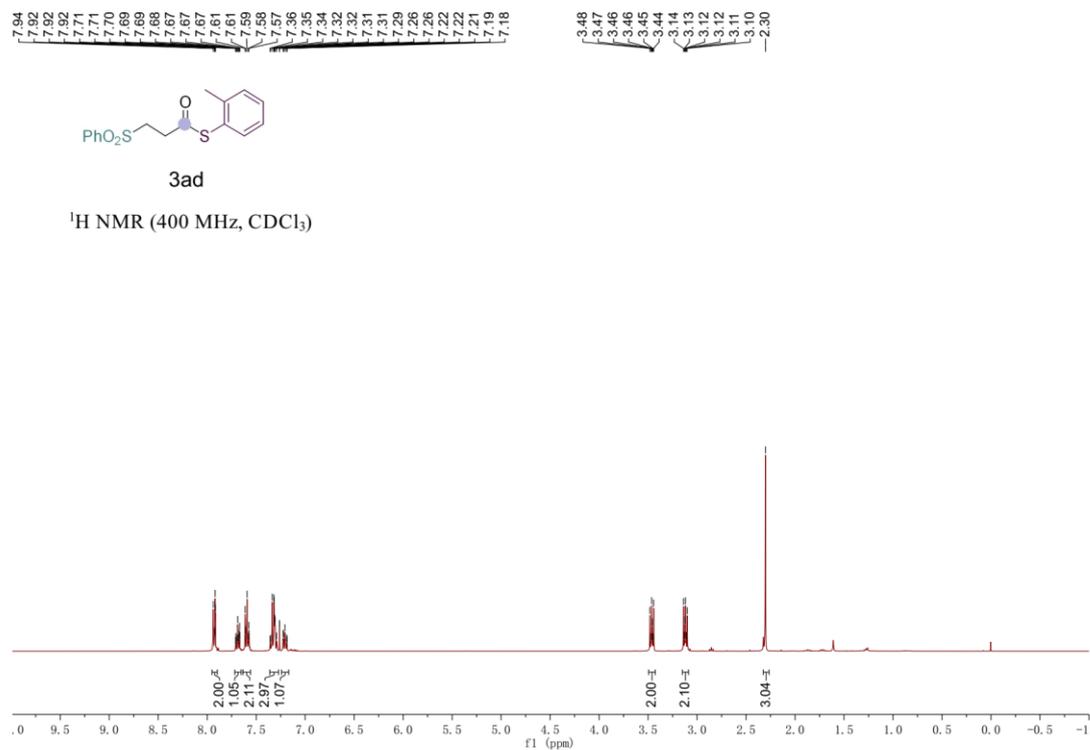
Supplementary Figure 4. <sup>13</sup>C NMR spectrum of **3ab** in CDCl<sub>3</sub> (101 MHz)



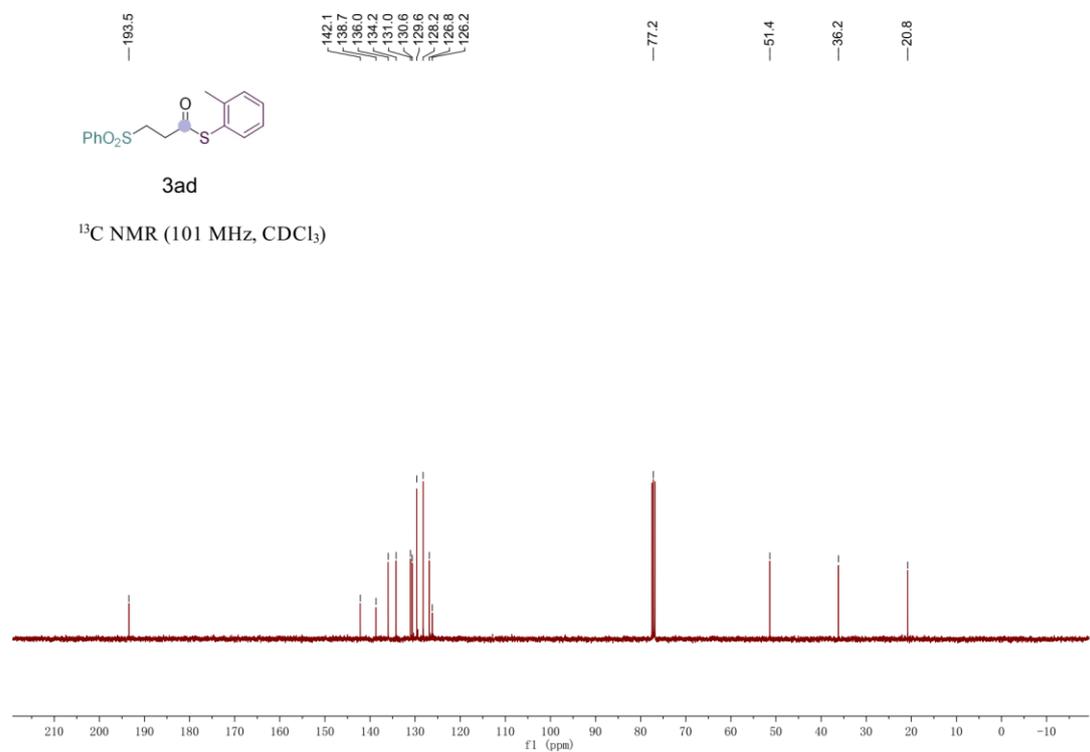
Supplementary Figure 5.  $^1\text{H NMR}$  spectrum of **3ac** in  $\text{CDCl}_3$  (400 MHz)



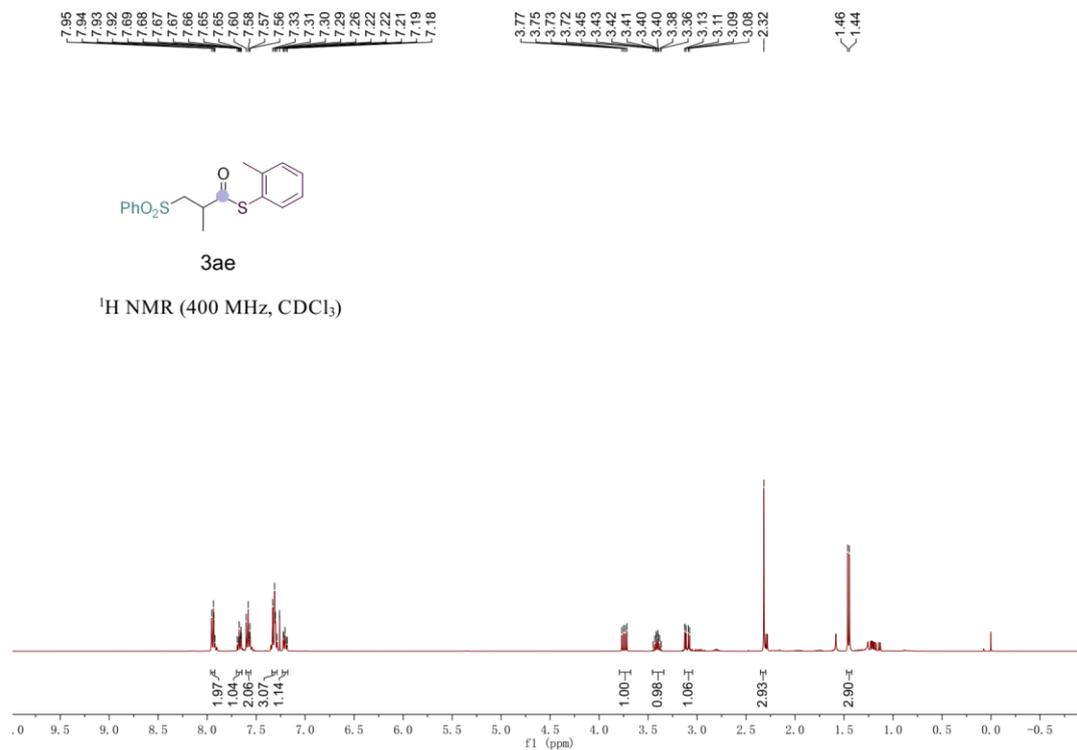
Supplementary Figure 6.  $^{13}\text{C NMR}$  spectrum of **3ac** in  $\text{CDCl}_3$  (101 MHz)



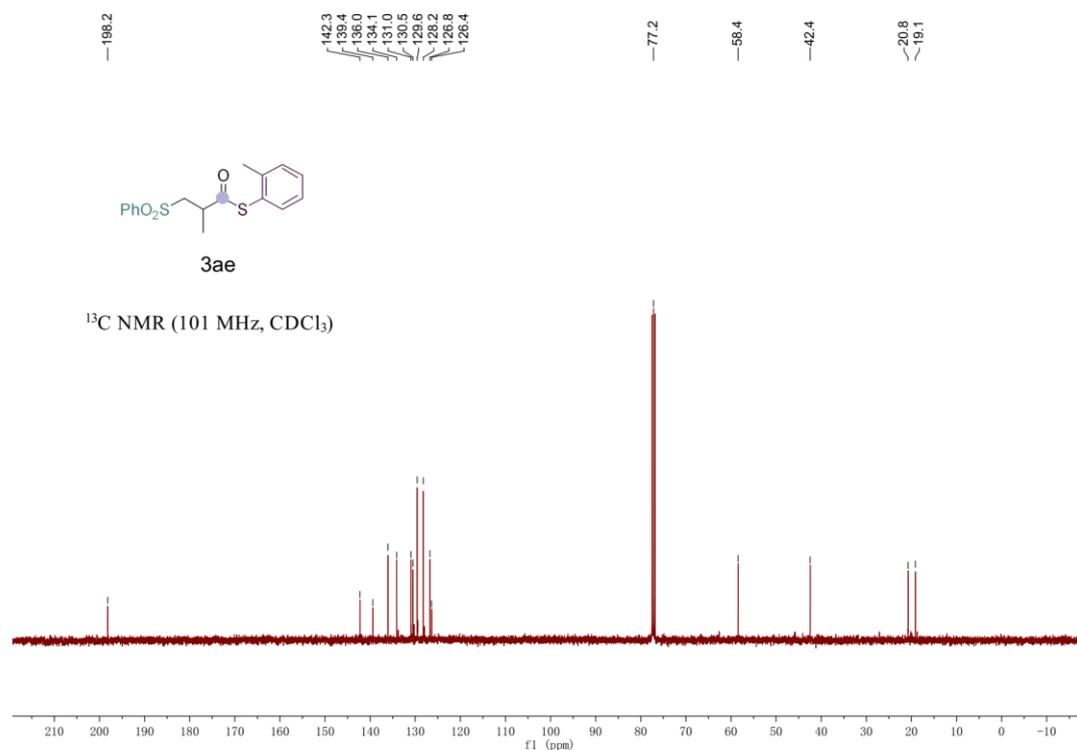
Supplementary Figure 7.  $^1\text{H NMR}$  spectrum of **3ad** in  $\text{CDCl}_3$  (400 MHz)



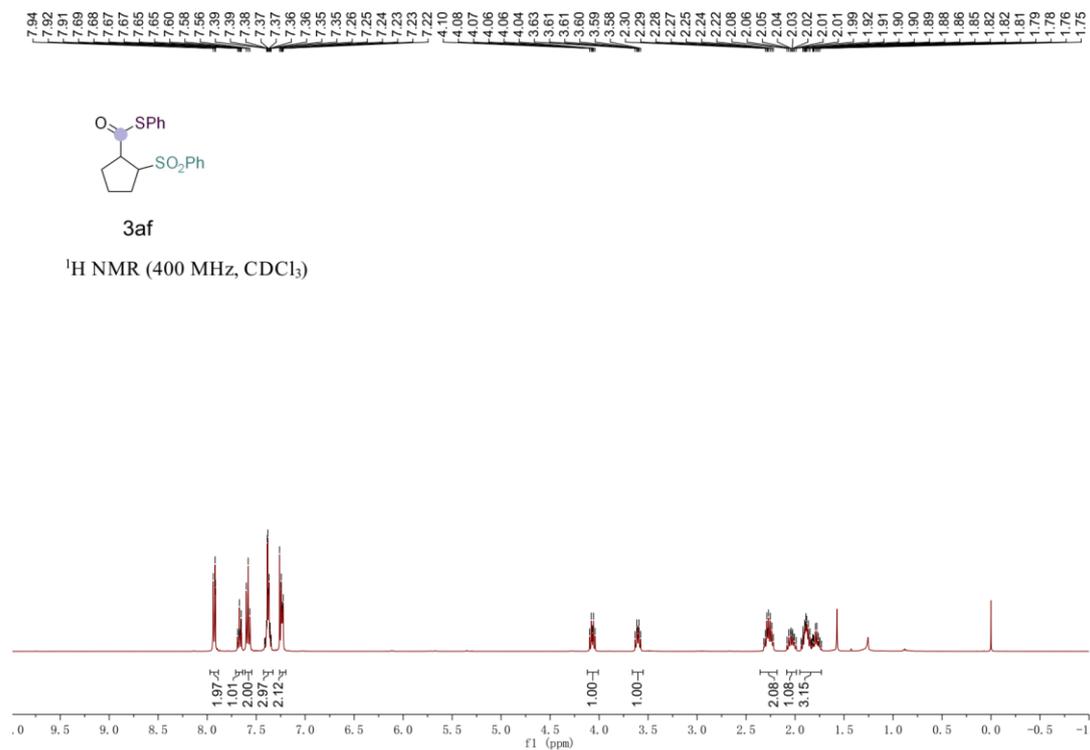
Supplementary Figure 8.  $^{13}\text{C NMR}$  spectrum of **3ad** in  $\text{CDCl}_3$  (101 MHz)



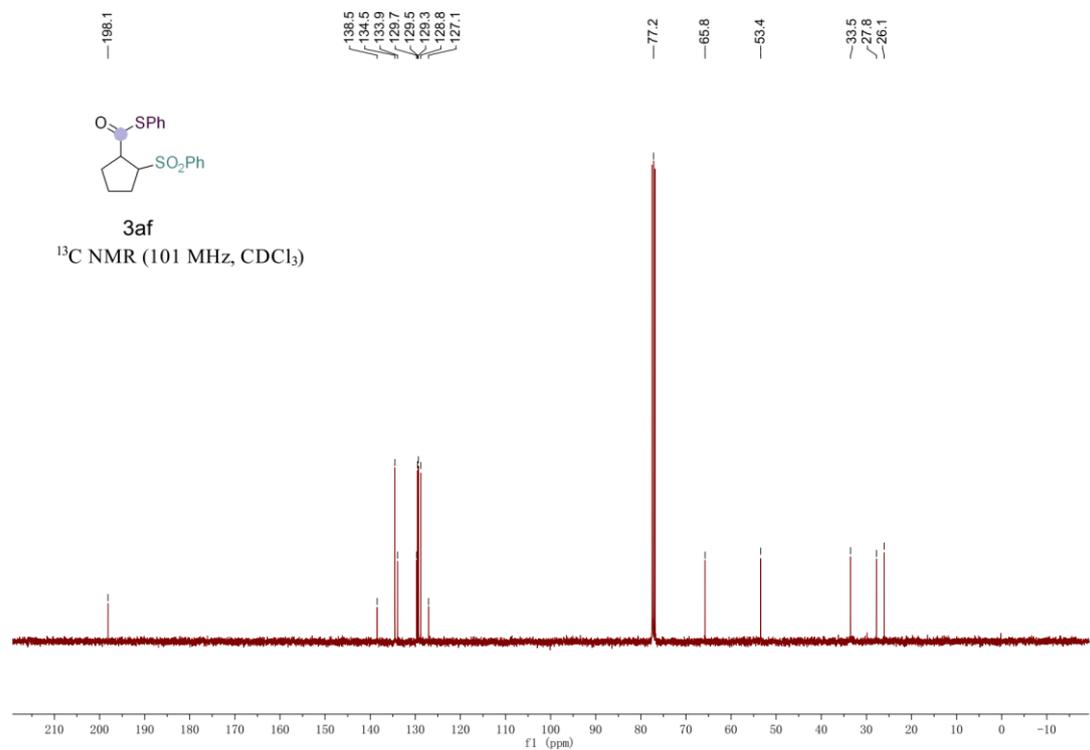
Supplementary Figure 9. <sup>1</sup>H NMR spectrum of **3ae** in CDCl<sub>3</sub> (400 MHz)



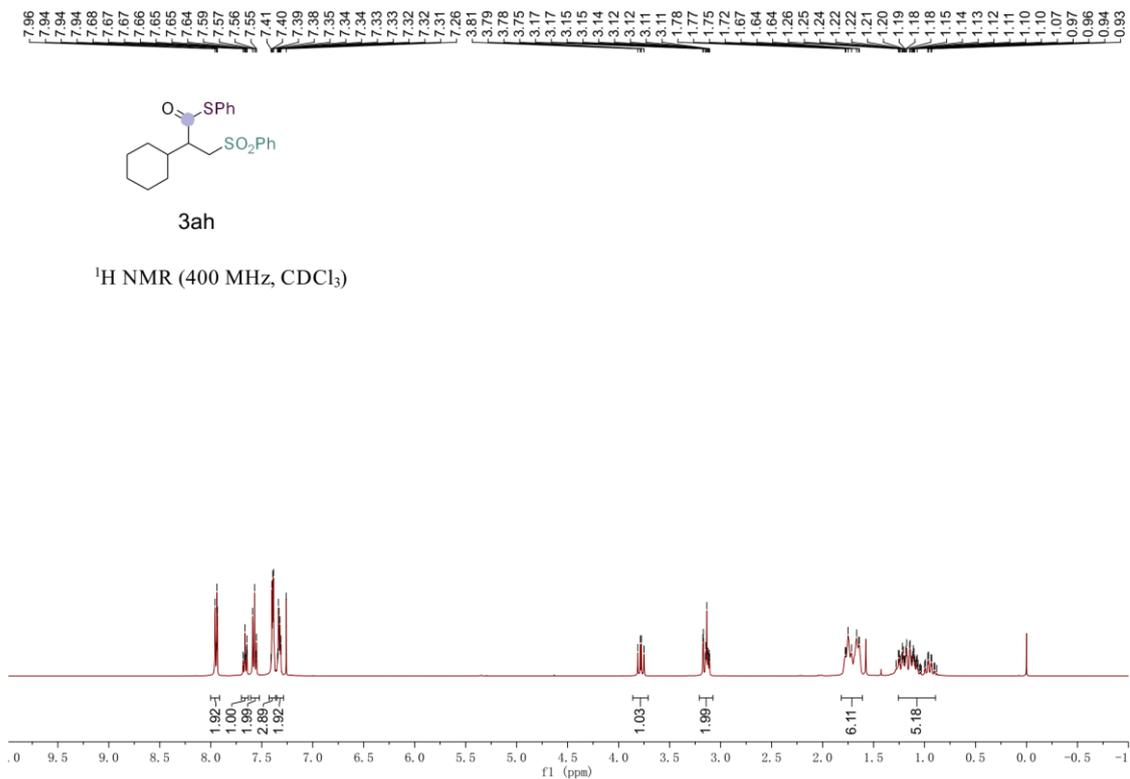
Supplementary Figure 10. <sup>13</sup>C NMR spectrum of **3ae** in CDCl<sub>3</sub> (101 MHz)



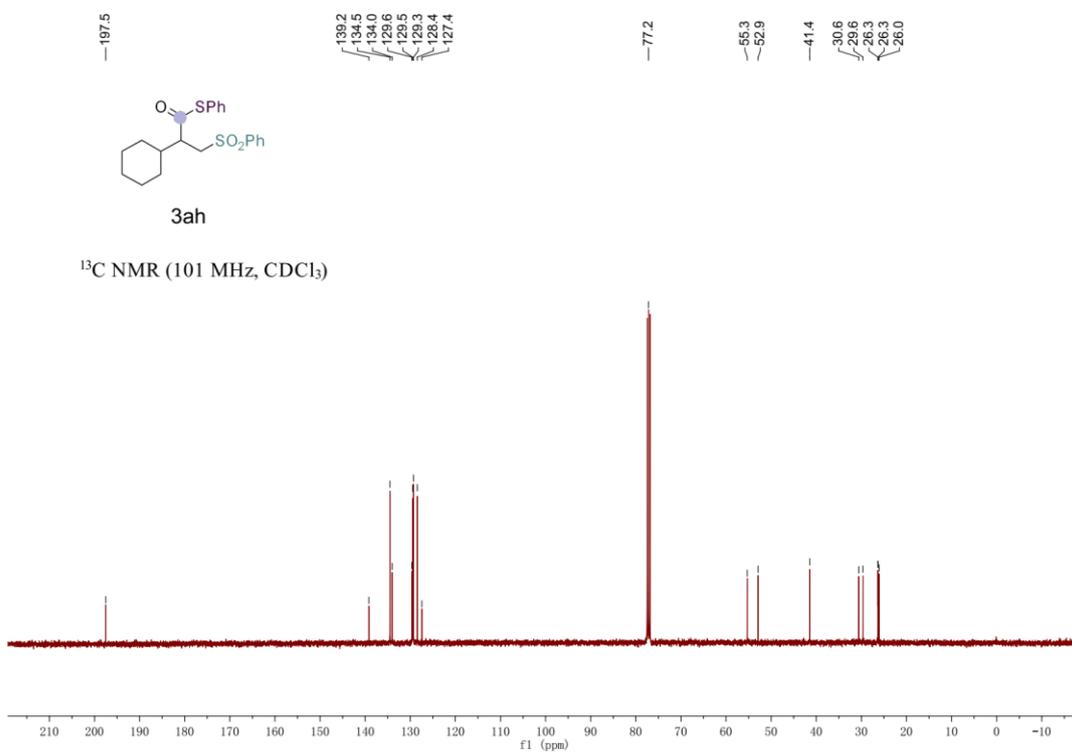
Supplementary Figure 11.  $^1\text{H NMR}$  spectrum of **3af** in  $\text{CDCl}_3$  (400 MHz)



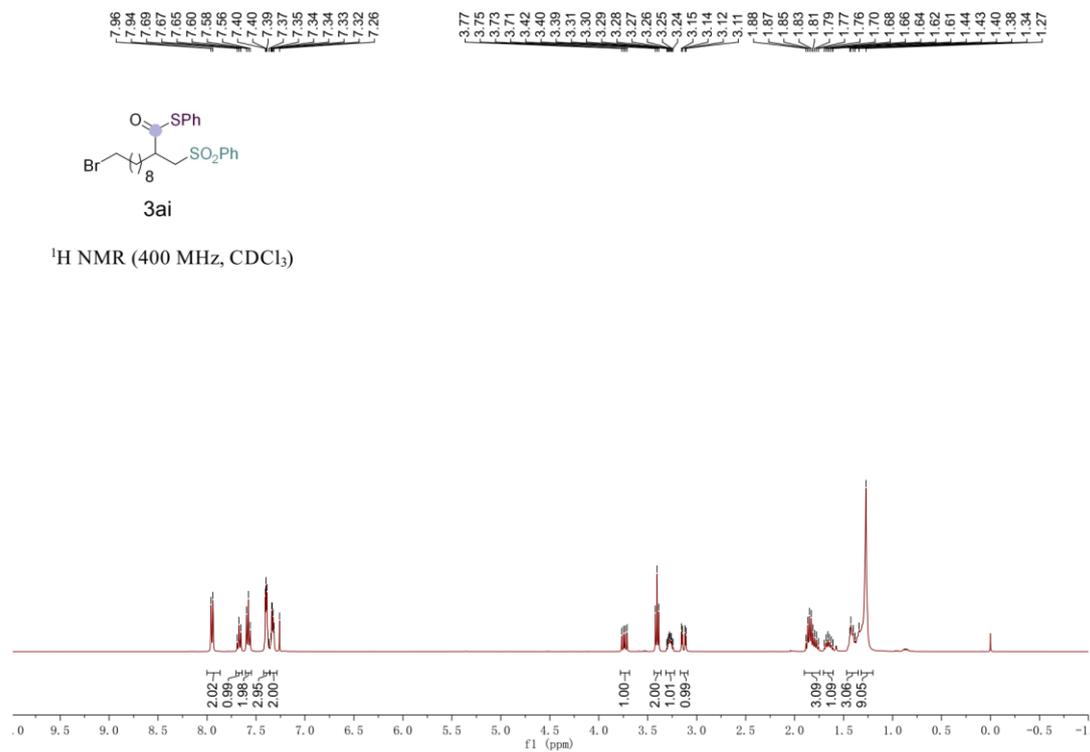
Supplementary Figure 12.  $^{13}\text{C NMR}$  spectrum of **3af** in  $\text{CDCl}_3$  (101 MHz)



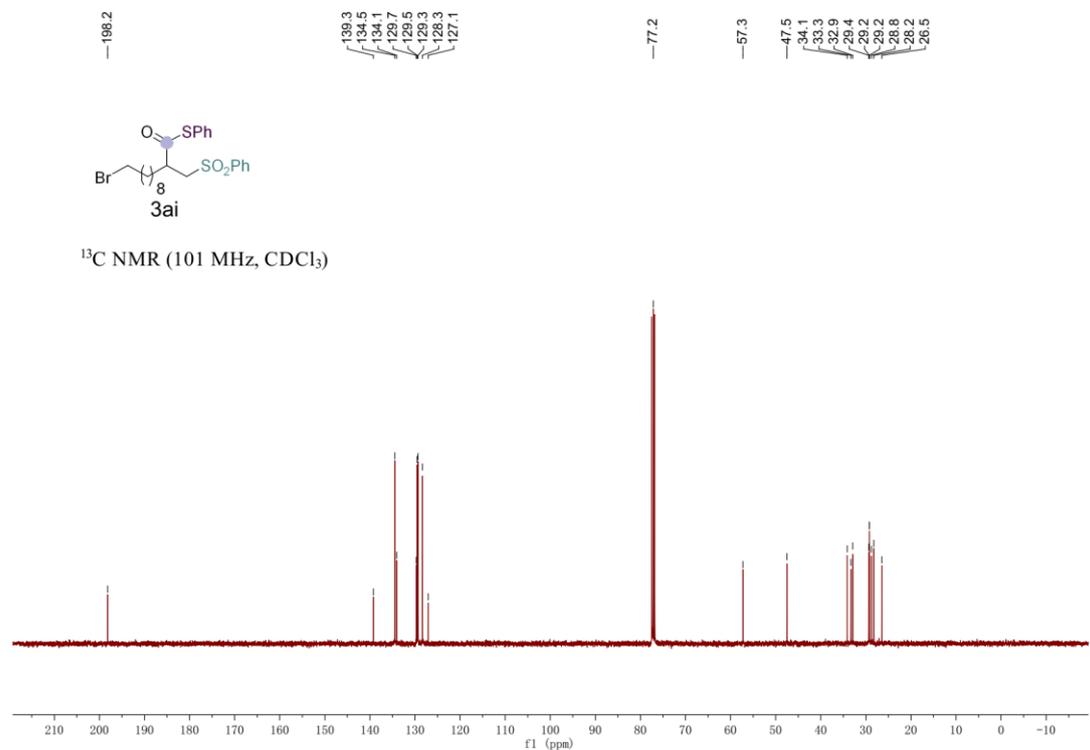
Supplementary Figure 13.  $^1\text{H NMR}$  spectrum of **3ah** in  $\text{CDCl}_3$  (400 MHz)



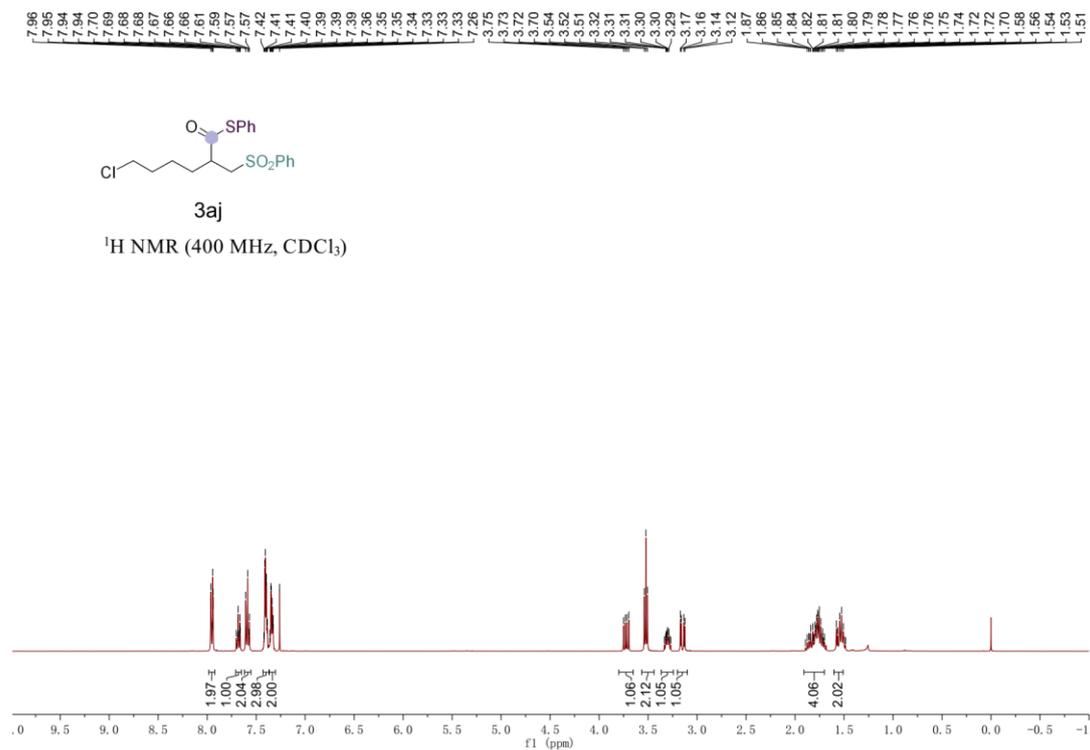
Supplementary Figure 14.  $^{13}\text{C NMR}$  spectrum of **3ah** in  $\text{CDCl}_3$  (101 MHz)



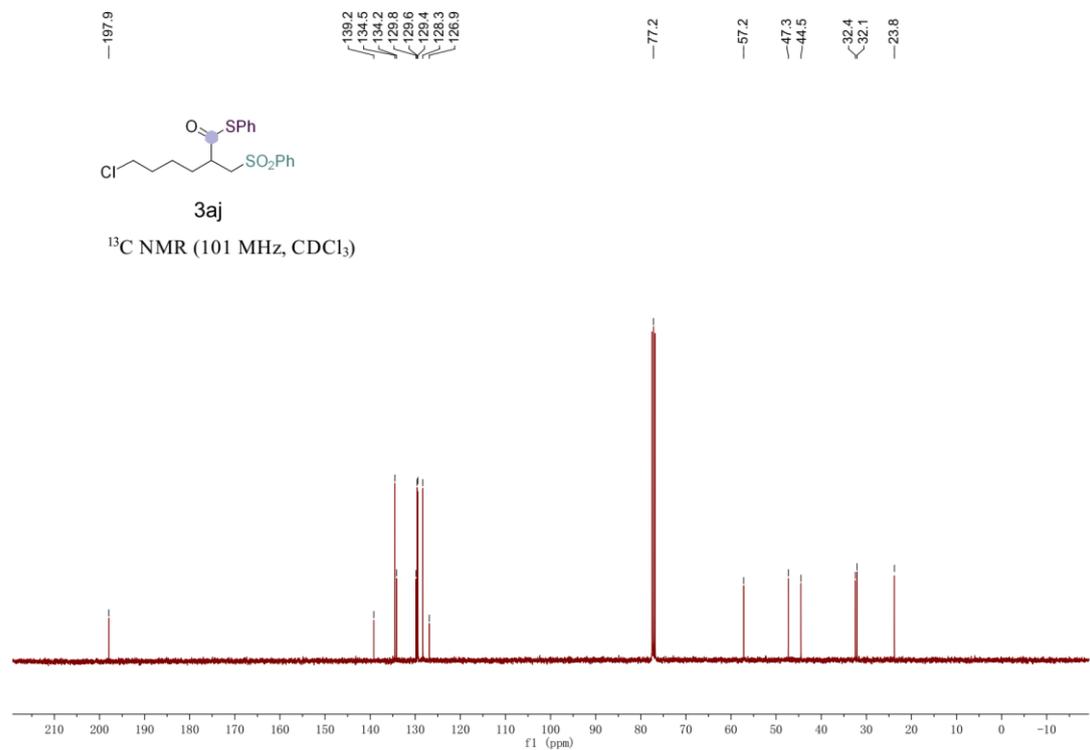
Supplementary Figure 15.  $^1\text{H}$  NMR spectrum of **3ai** in CDCl<sub>3</sub> (400 MHz)



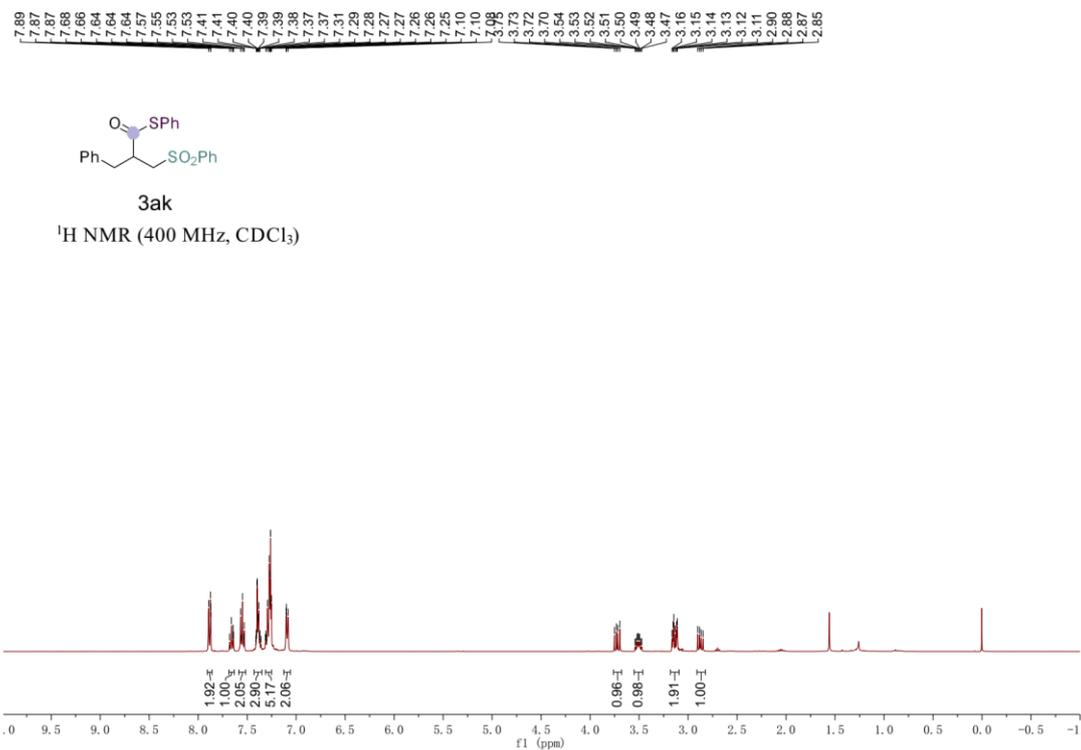
Supplementary Figure 16.  $^{13}\text{C}$  NMR spectrum of **3ai** in CDCl<sub>3</sub> (101 MHz)



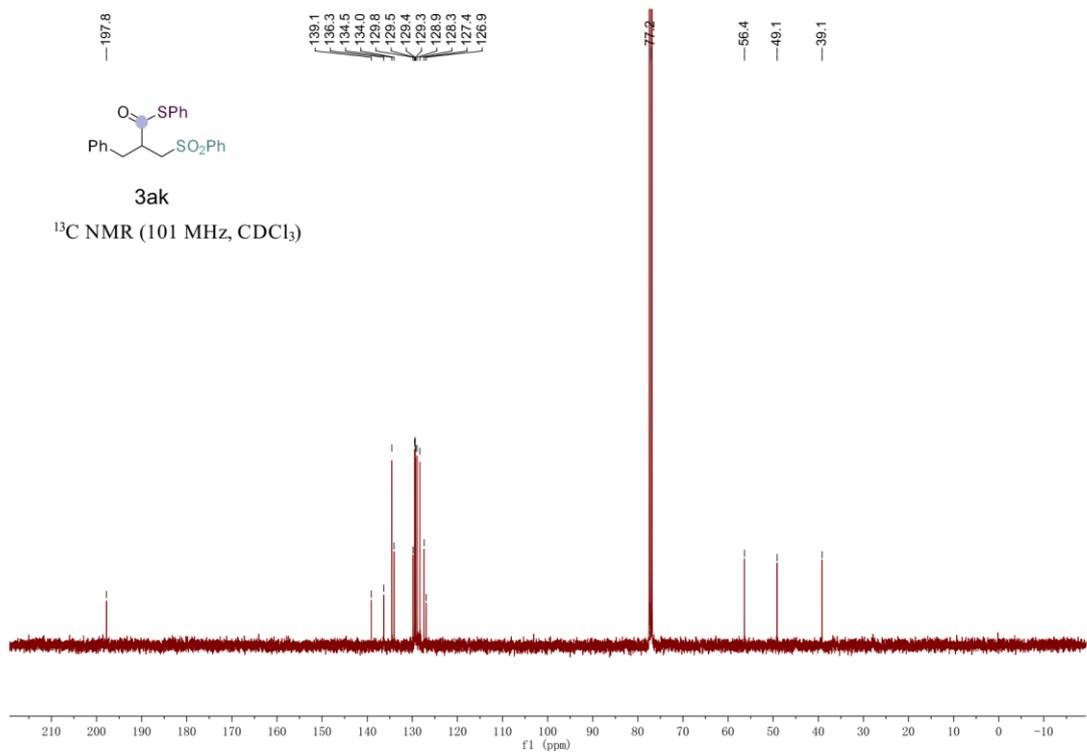
Supplementary Figure 17. <sup>1</sup>H NMR spectrum of **3aj** in CDCl<sub>3</sub> (400 MHz)



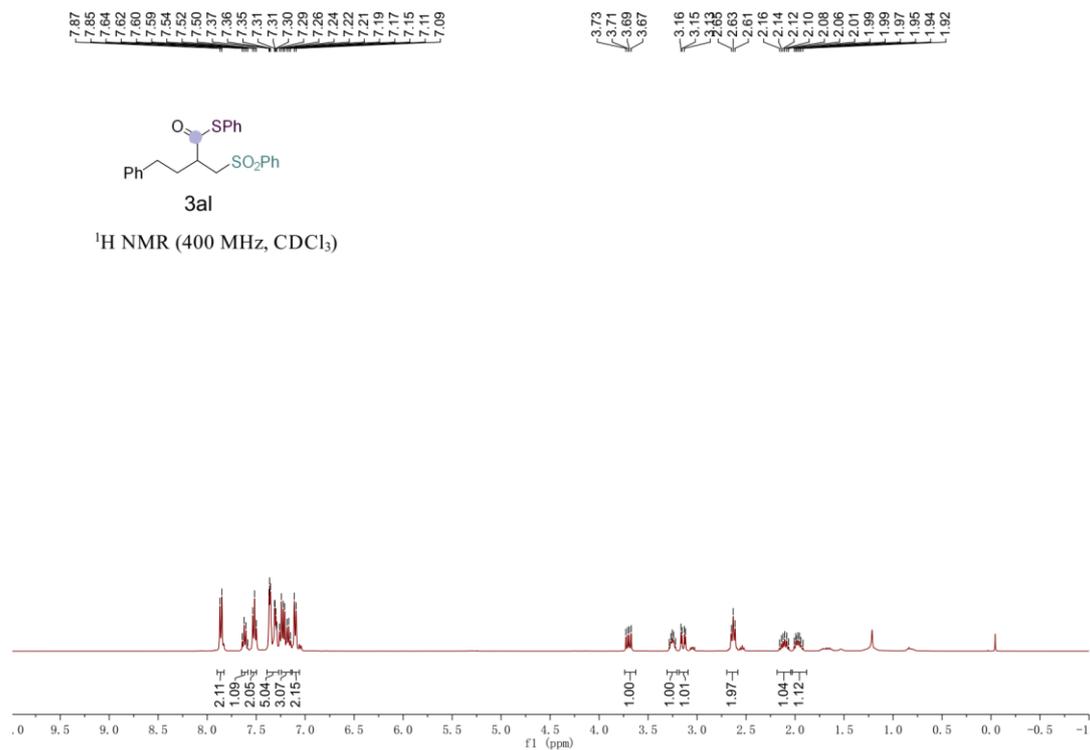
Supplementary Figure 18. <sup>13</sup>C NMR spectrum of **3aj** in CDCl<sub>3</sub> (101 MHz)



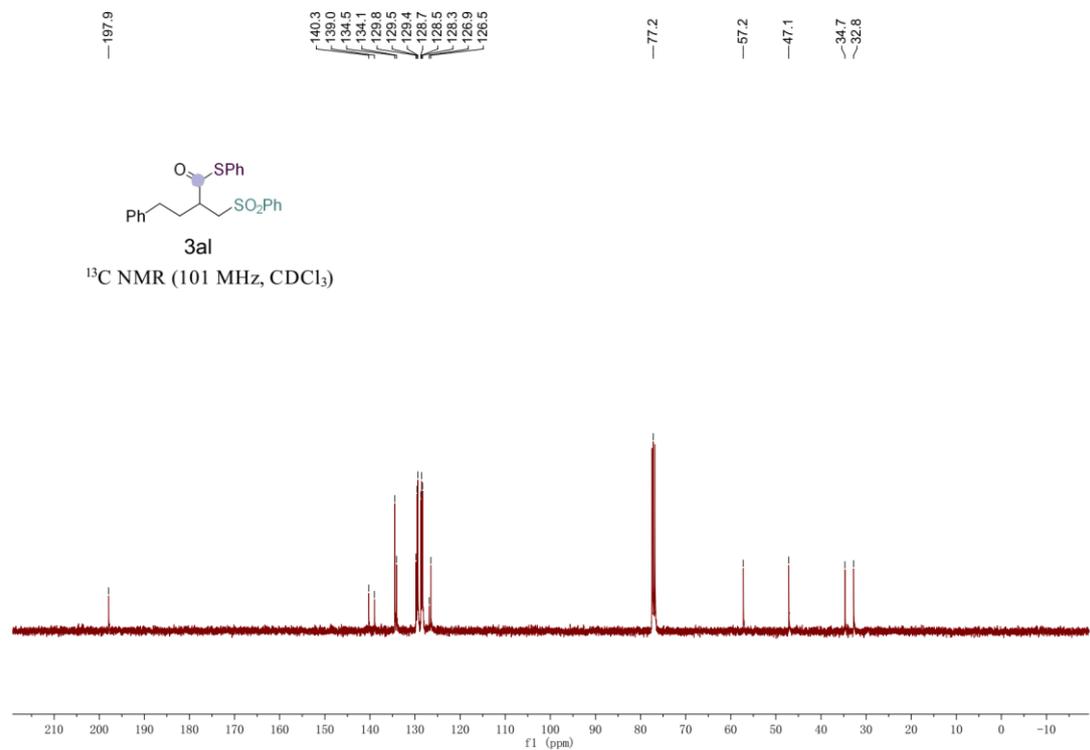
Supplementary Figure 19. <sup>1</sup>H NMR spectrum of **3ak** in CDCl<sub>3</sub> (400 MHz)



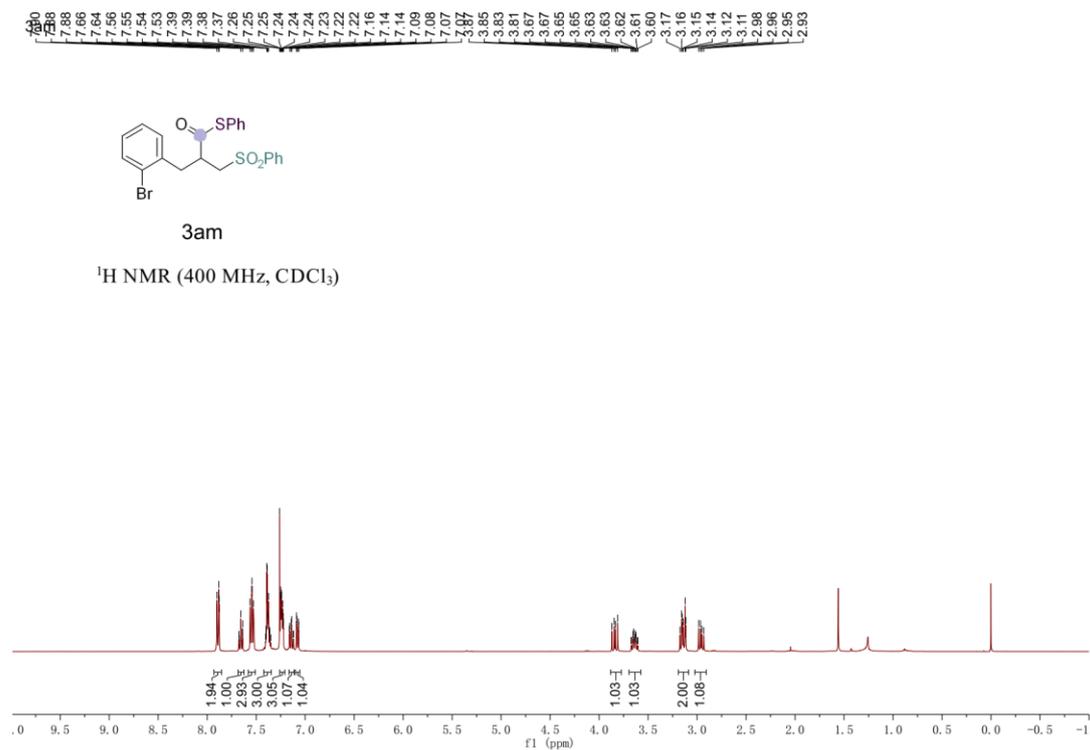
Supplementary Figure 20. <sup>13</sup>C NMR spectrum of **3ak** in CDCl<sub>3</sub> (101 MHz)



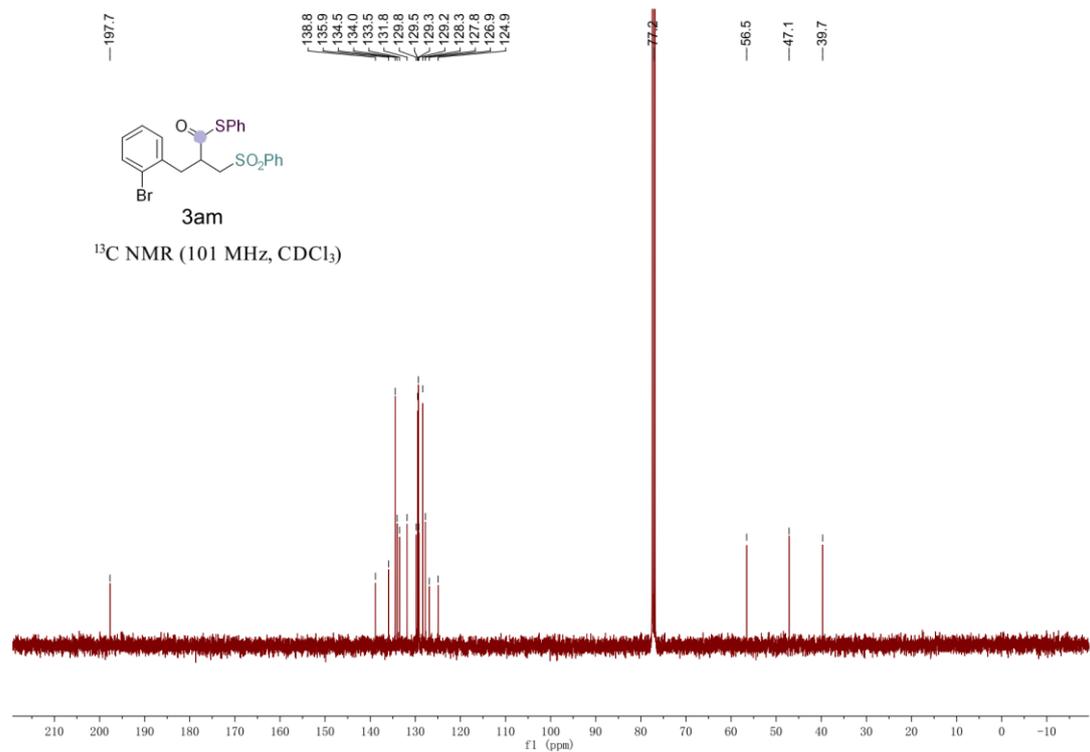
Supplementary Figure 21. <sup>1</sup>H NMR spectrum of **3al** in CDCl<sub>3</sub> (400 MHz)



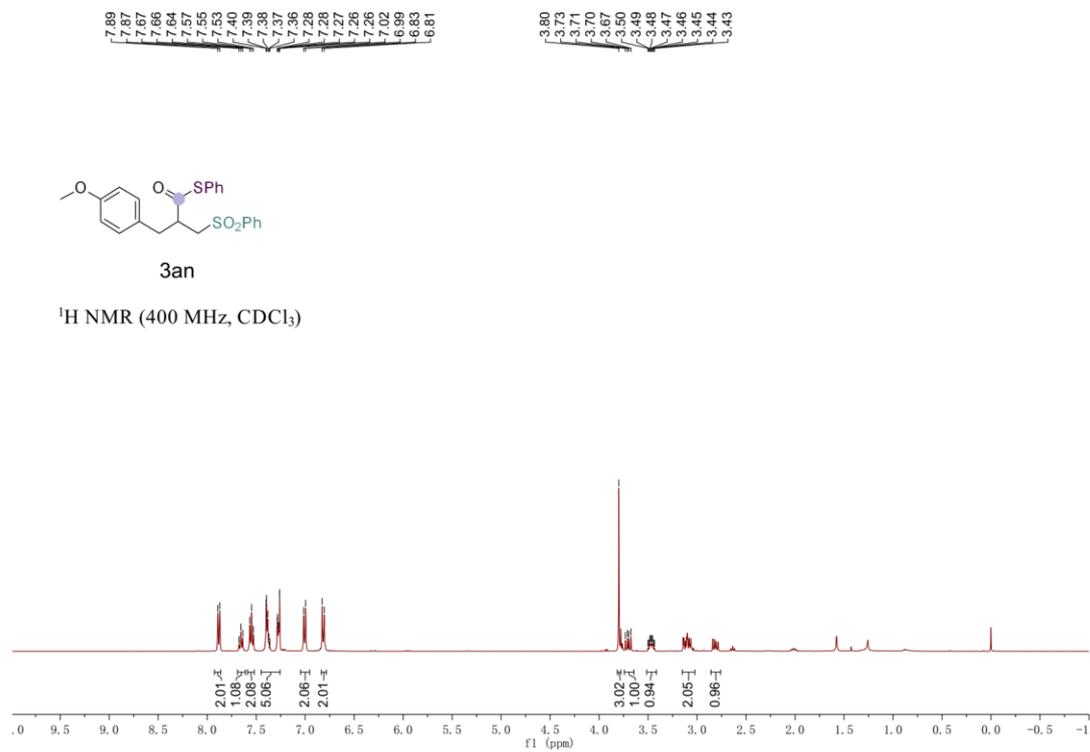
Supplementary Figure 22. <sup>13</sup>C NMR spectrum of **3ak** in CDCl<sub>3</sub> (101 MHz)



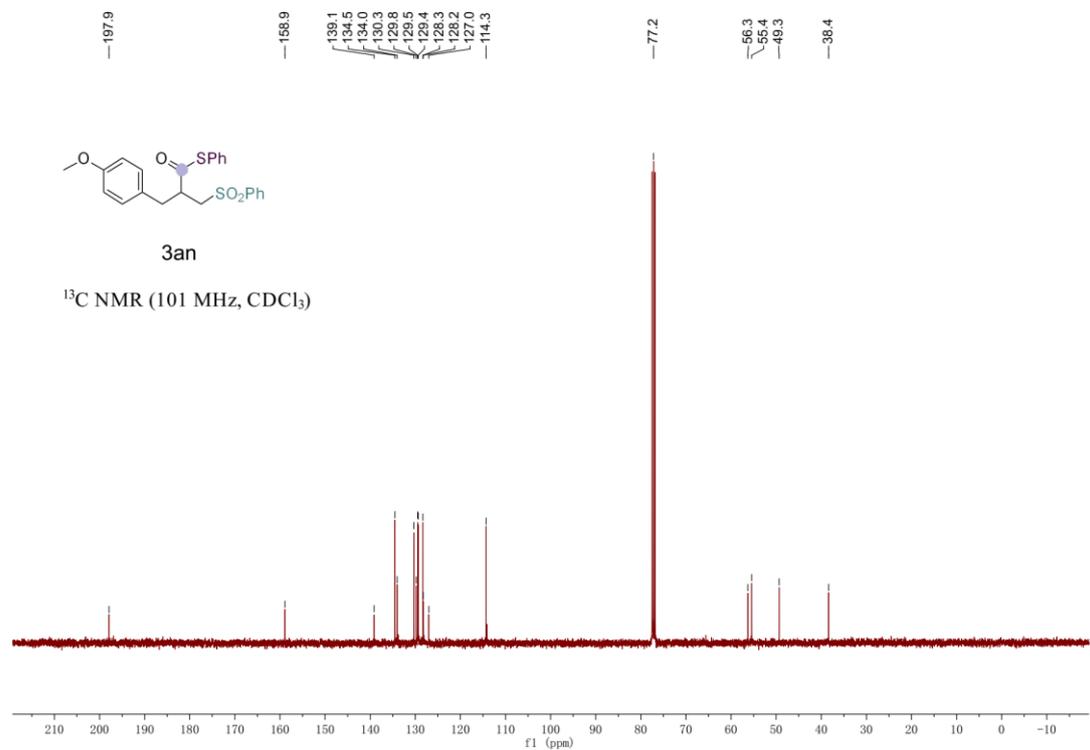
Supplementary Figure 23.  $^1\text{H NMR}$  spectrum of **3am** in  $\text{CDCl}_3$  (400 MHz)



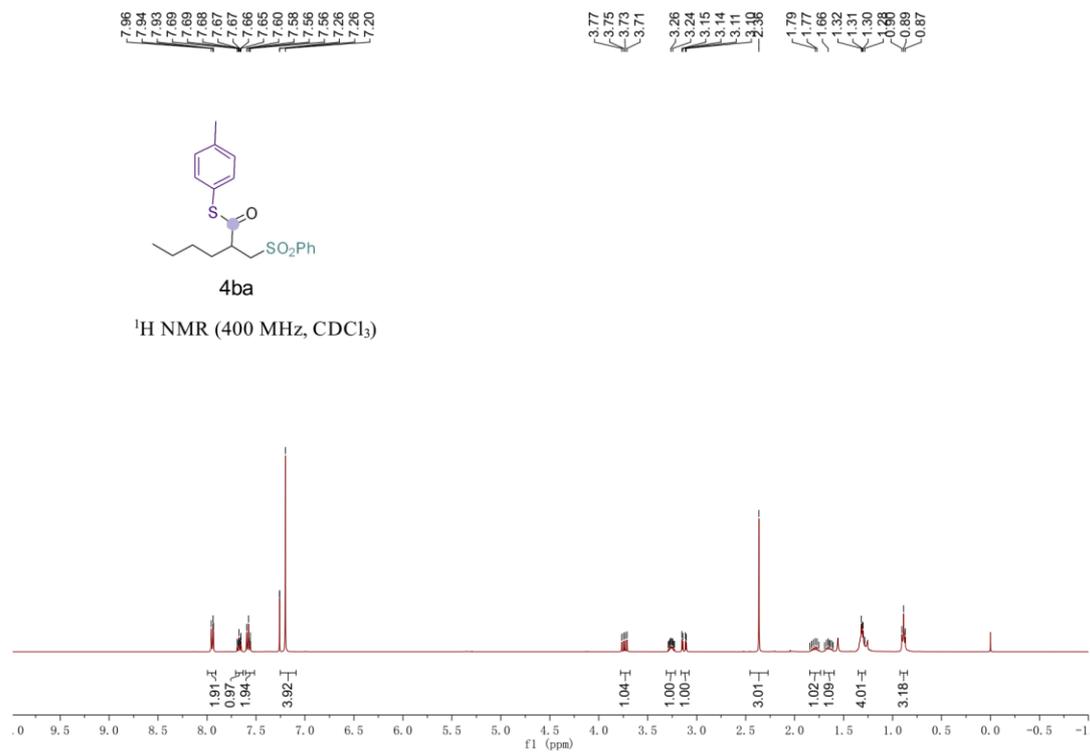
Supplementary Figure 24.  $^{13}\text{C NMR}$  spectrum of **3am** in  $\text{CDCl}_3$  (101 MHz)



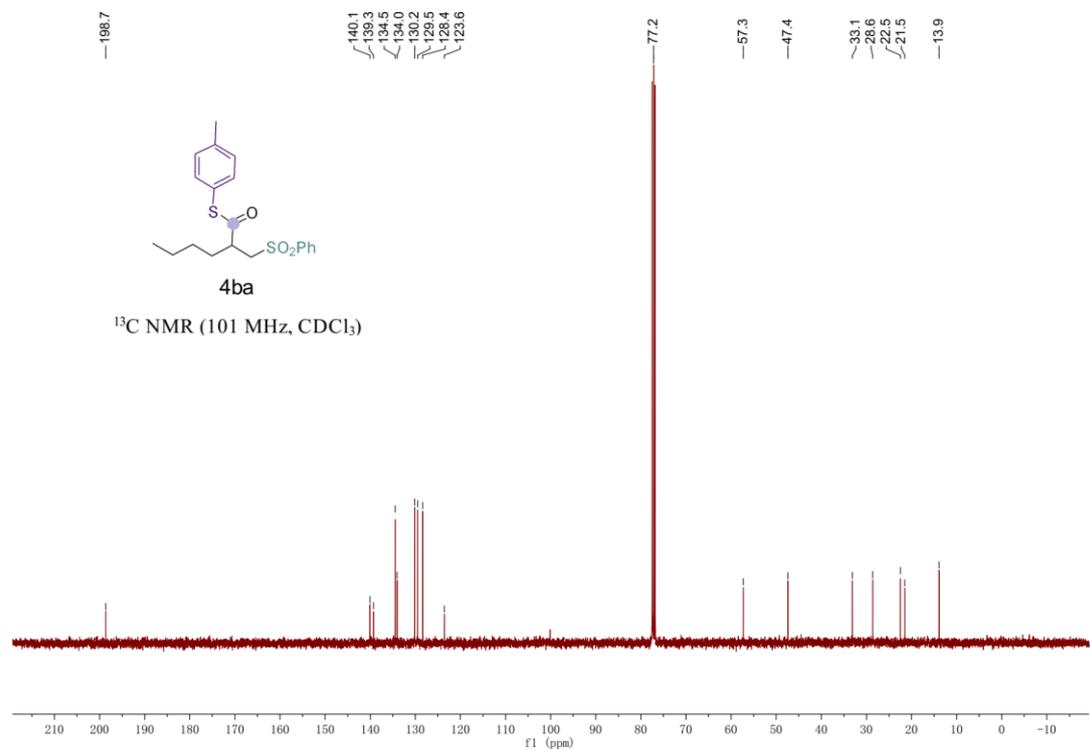
Supplementary Figure 25. <sup>1</sup>H NMR spectrum of **3an** in CDCl<sub>3</sub> (400 MHz)



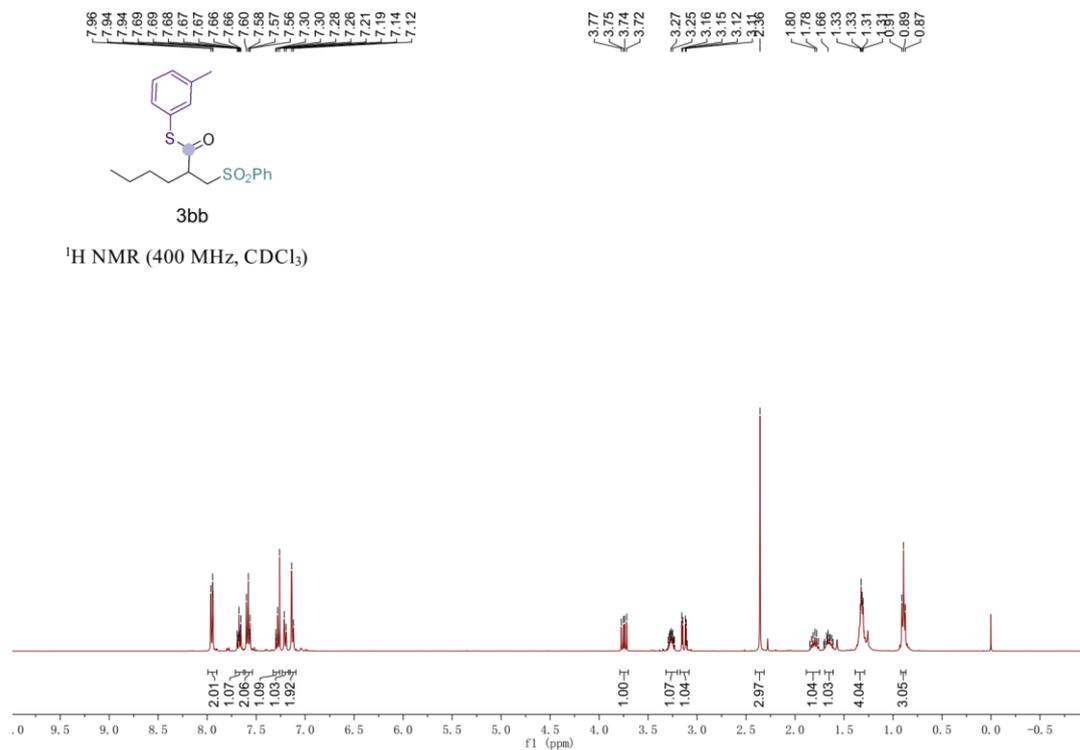
Supplementary Figure 26. <sup>13</sup>C NMR spectrum of **3an** in CDCl<sub>3</sub> (101 MHz)



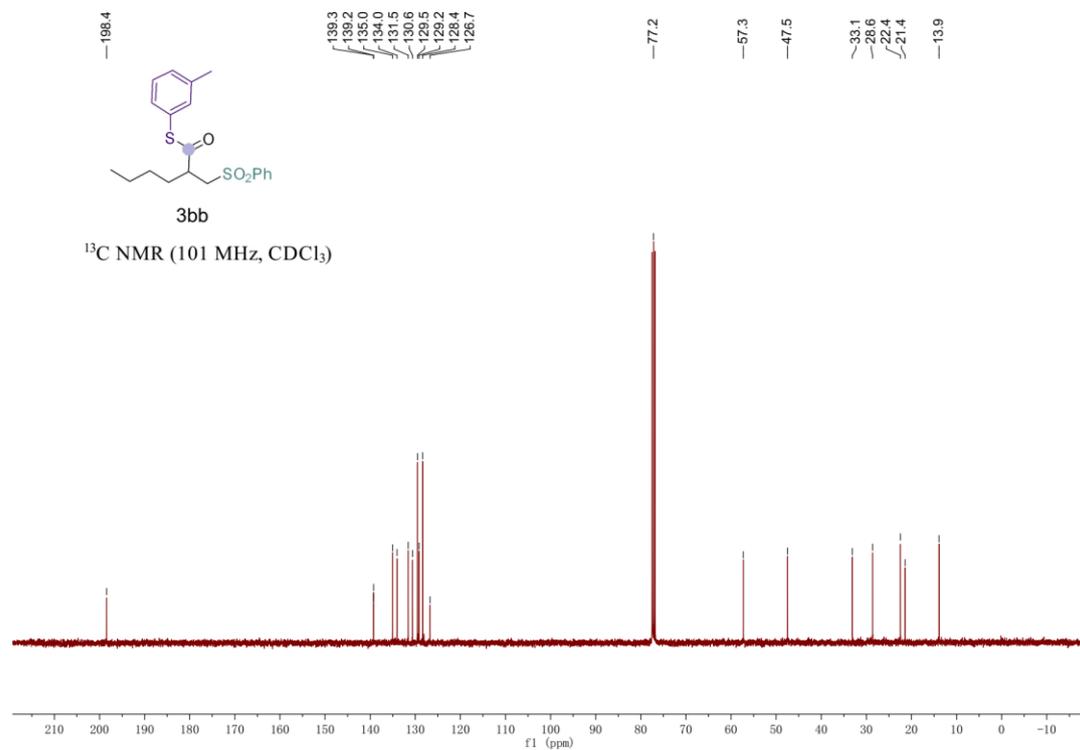
Supplementary Figure 27. <sup>1</sup>H NMR spectrum of **3ba** in CDCl<sub>3</sub> (400 MHz)



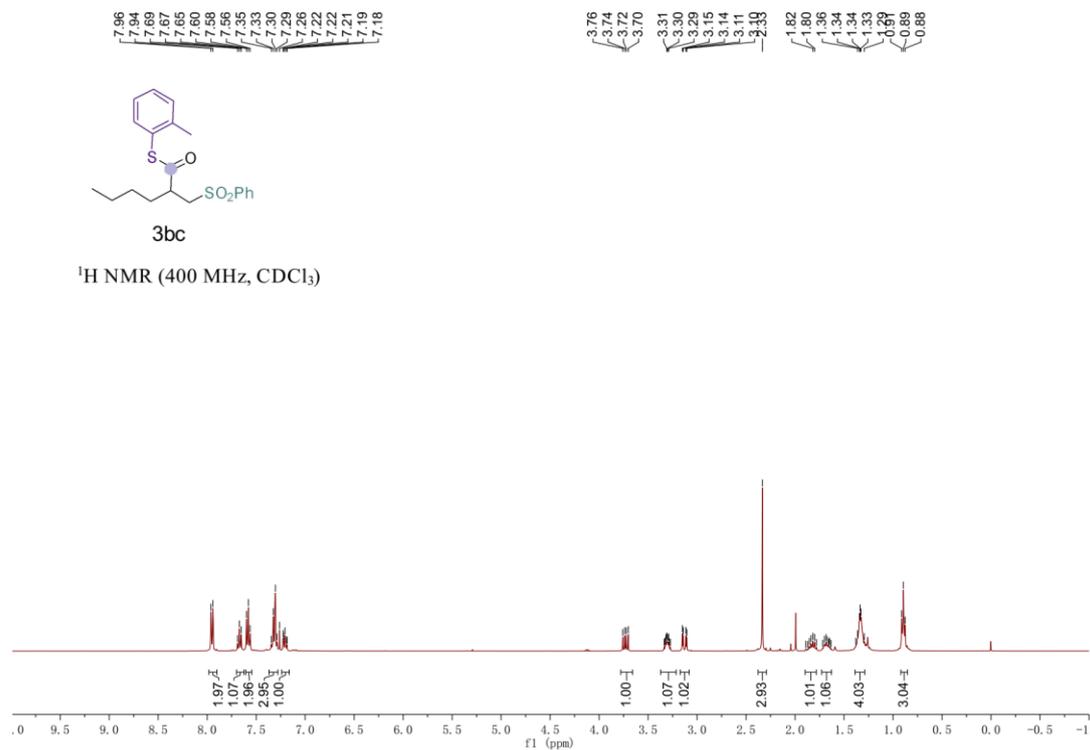
Supplementary Figure 28. <sup>13</sup>C NMR spectrum of **3ba** in CDCl<sub>3</sub> (101 MHz)



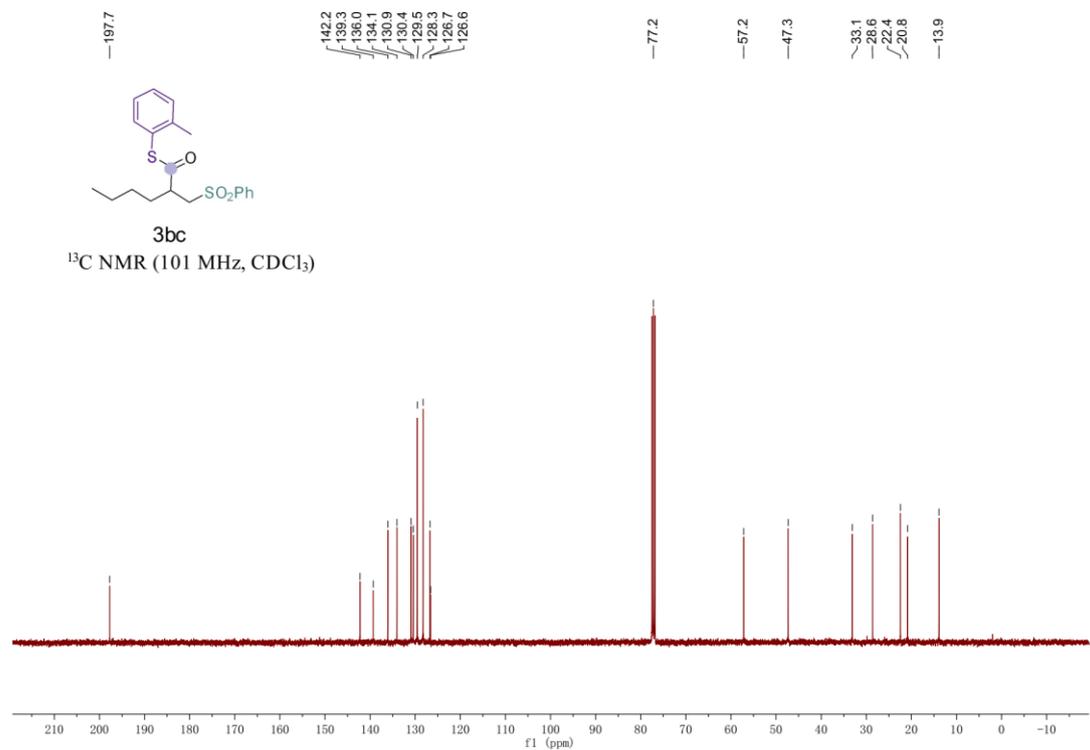
Supplementary Figure 29. <sup>1</sup>H NMR spectrum of **3bb** in CDCl<sub>3</sub> (400 MHz)



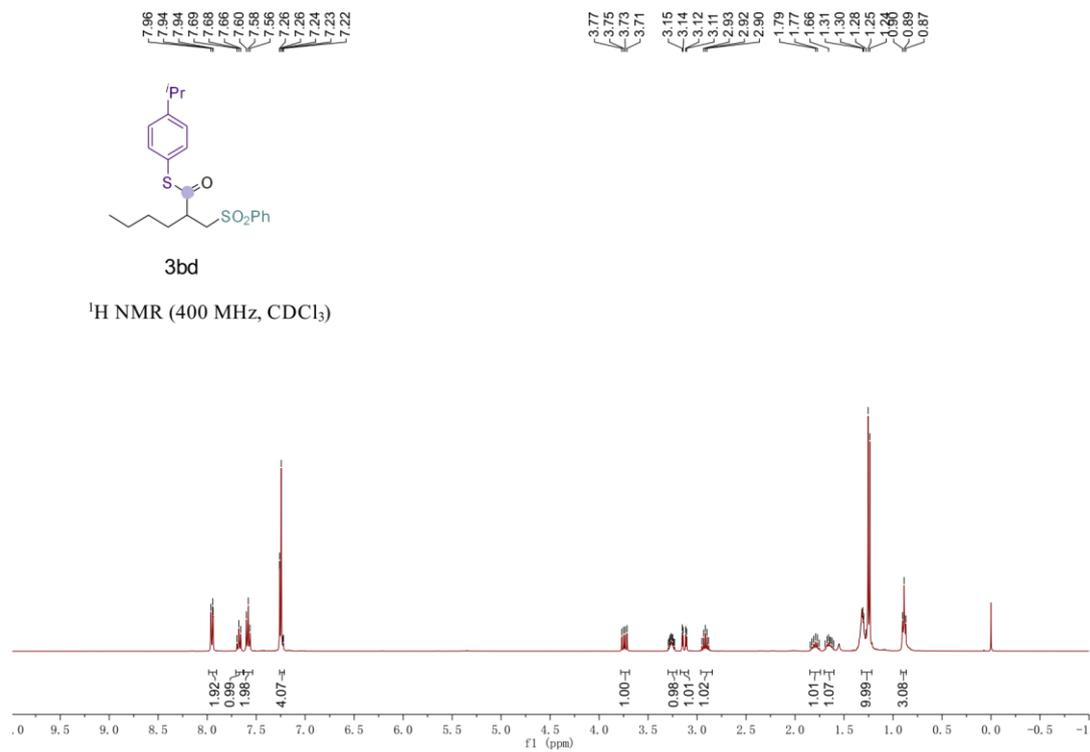
Supplementary Figure 30. <sup>13</sup>C NMR spectrum of **3bb** in CDCl<sub>3</sub> (101 MHz)



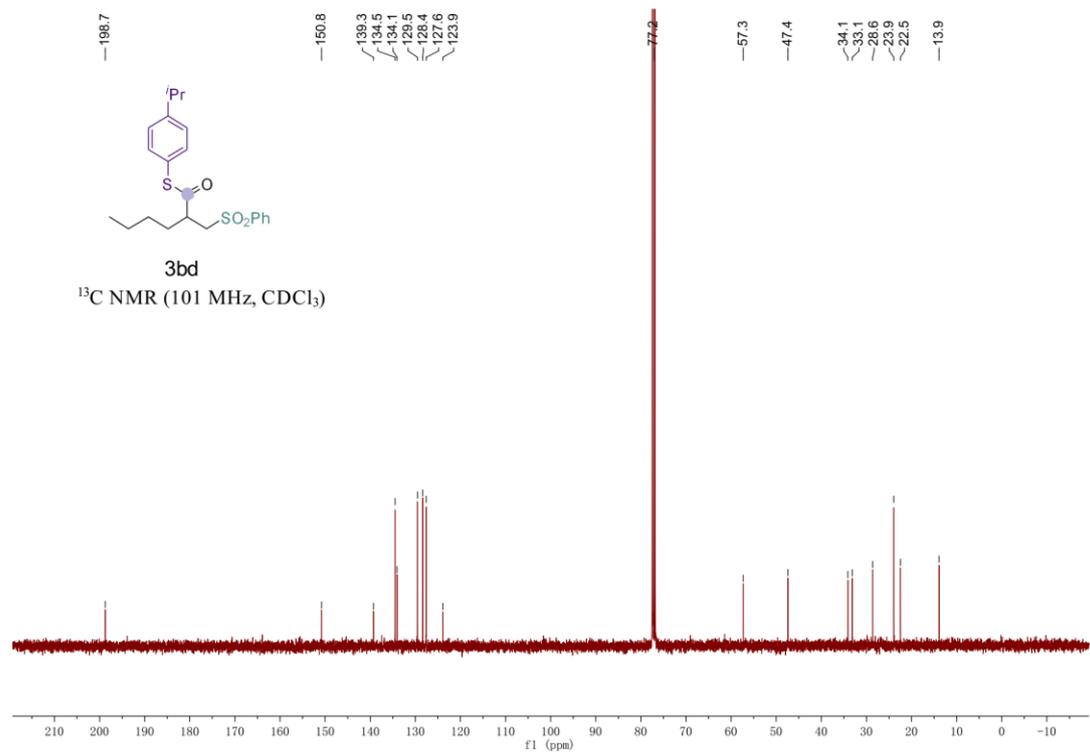
Supplementary Figure 31.  $^1\text{H}$  NMR spectrum of **3bc** in  $\text{CDCl}_3$  (400 MHz)



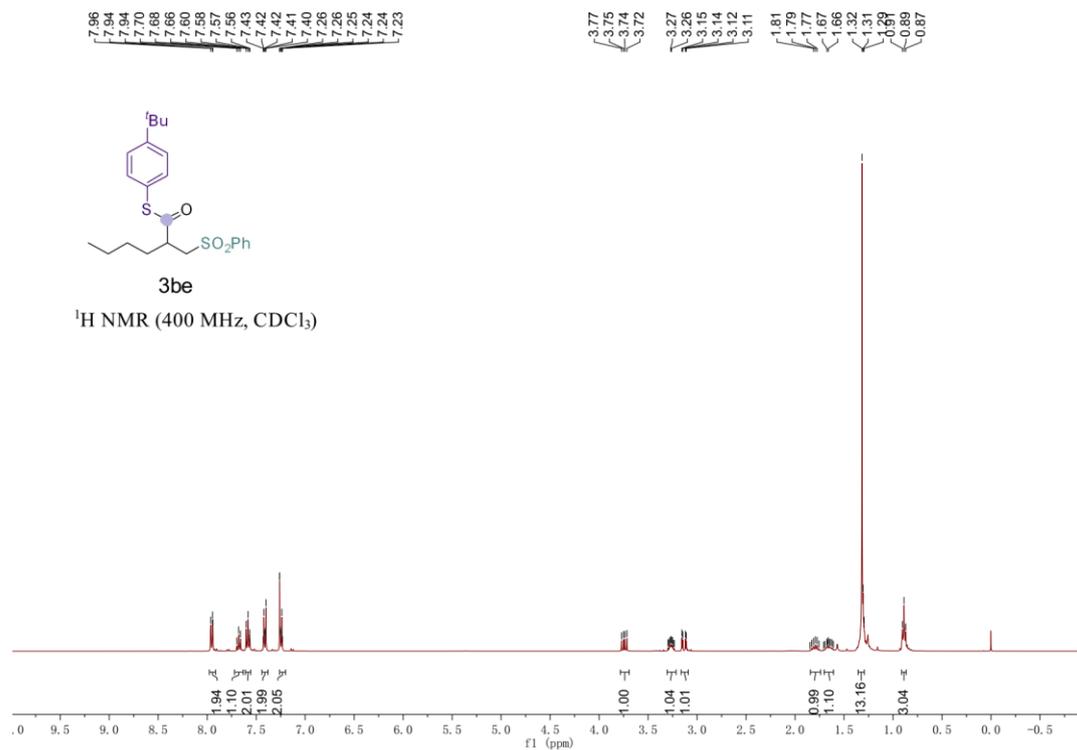
Supplementary Figure 32.  $^{13}\text{C}$  NMR spectrum of **3bc** in  $\text{CDCl}_3$  (101 MHz)



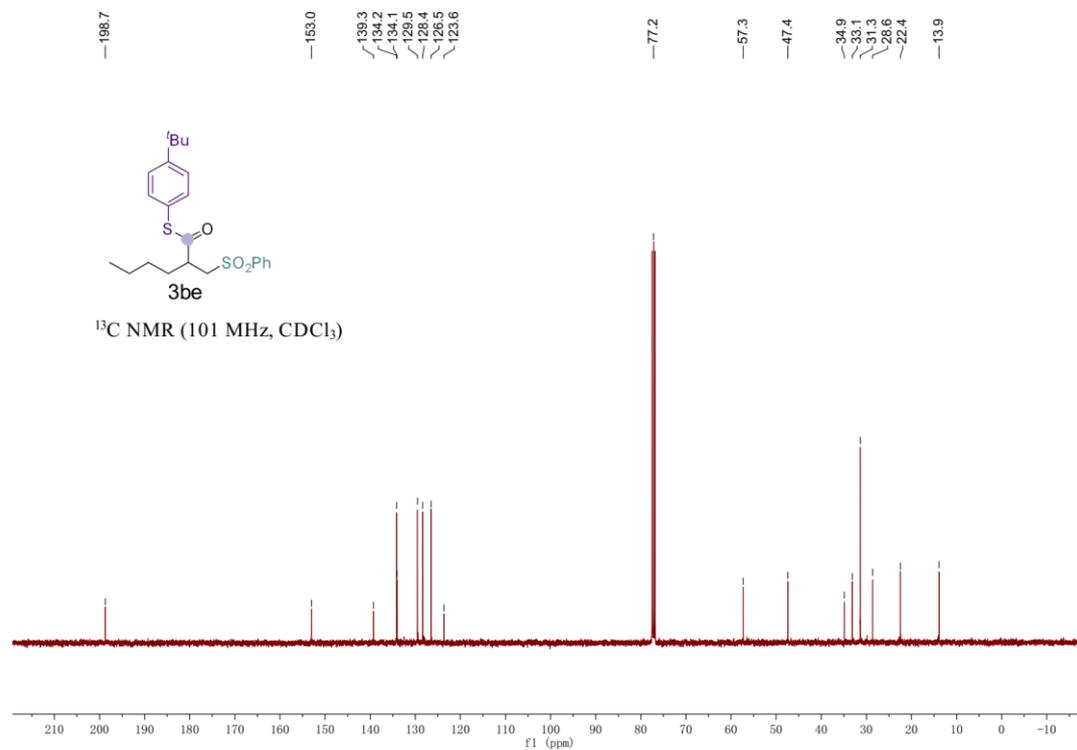
Supplementary Figure 33. <sup>1</sup>H NMR spectrum of **3bd** in CDCl<sub>3</sub> (400 MHz)



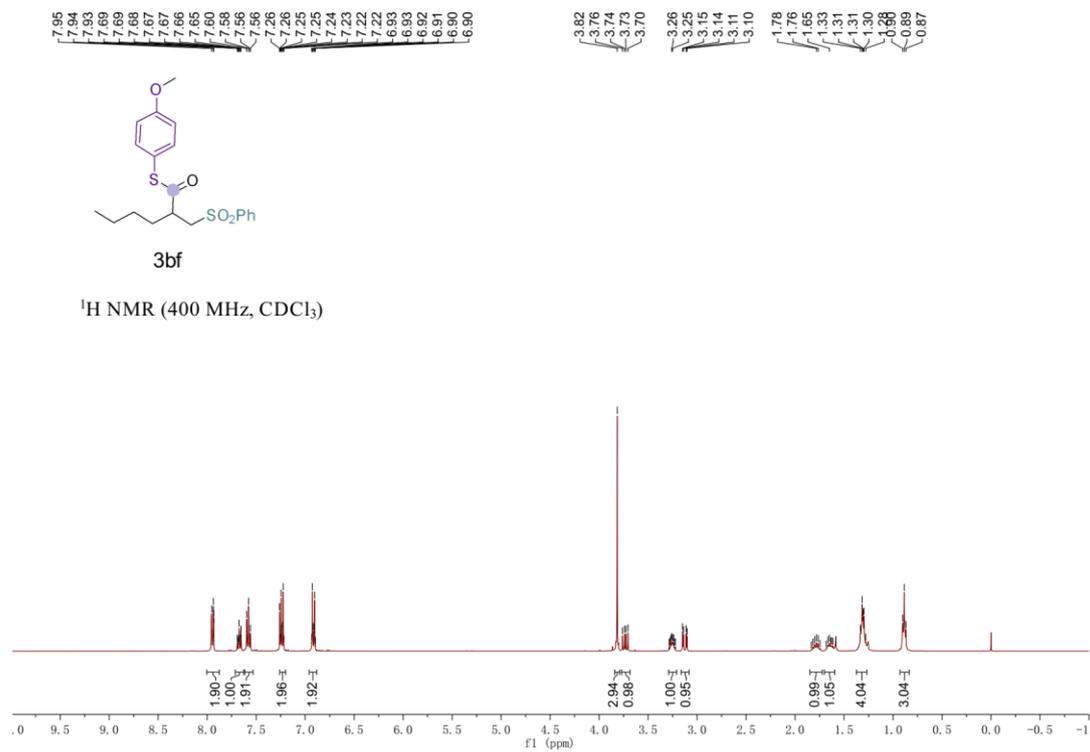
Supplementary Figure 34. <sup>13</sup>C NMR spectrum of **3bd** in CDCl<sub>3</sub> (101 MHz)



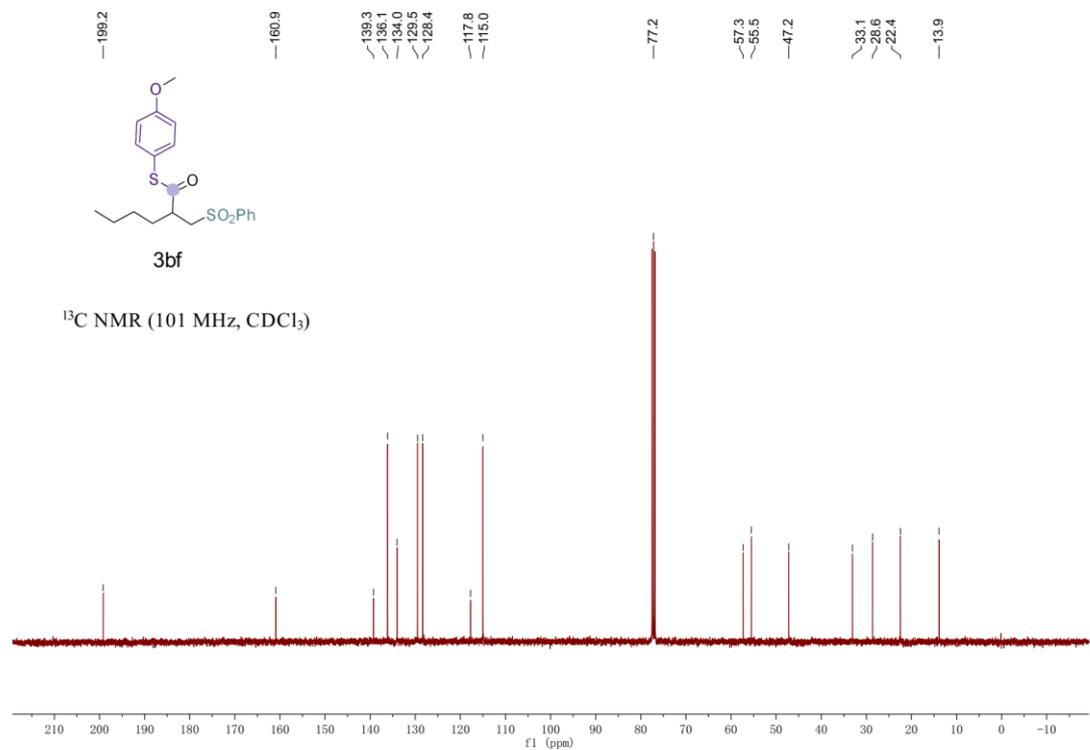
Supplementary Figure 35. <sup>1</sup>H NMR spectrum of **3be** in CDCl<sub>3</sub> (400 MHz)



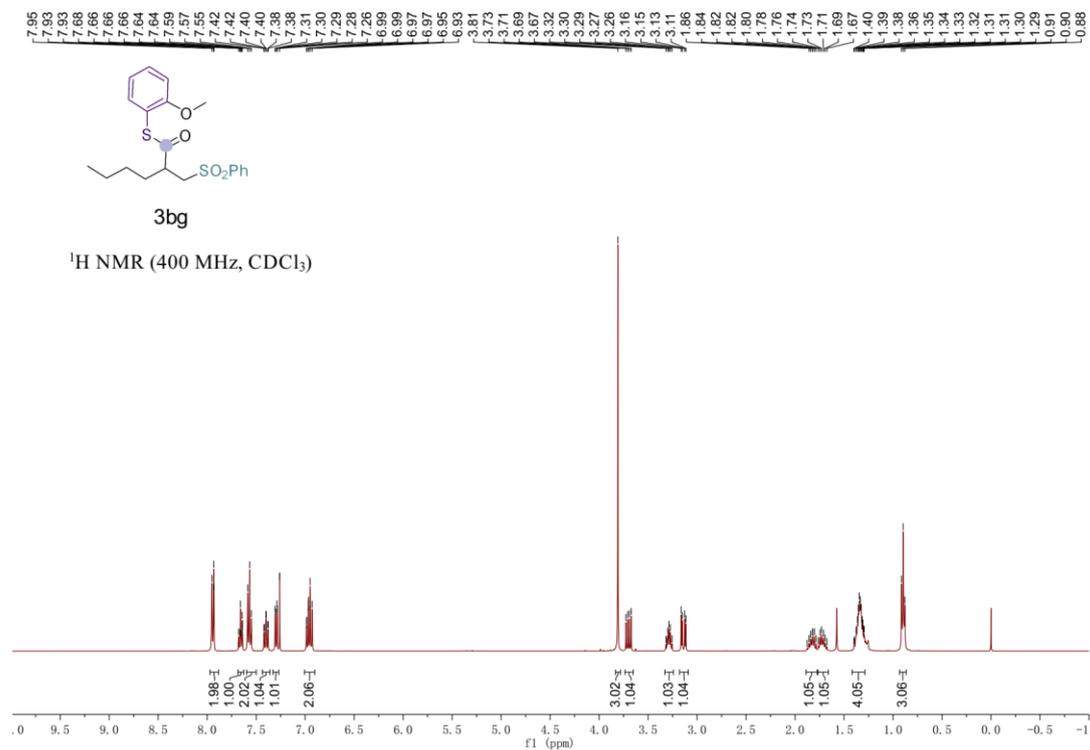
Supplementary Figure 36. <sup>13</sup>C NMR spectrum of **3be** in CDCl<sub>3</sub> (101 MHz)



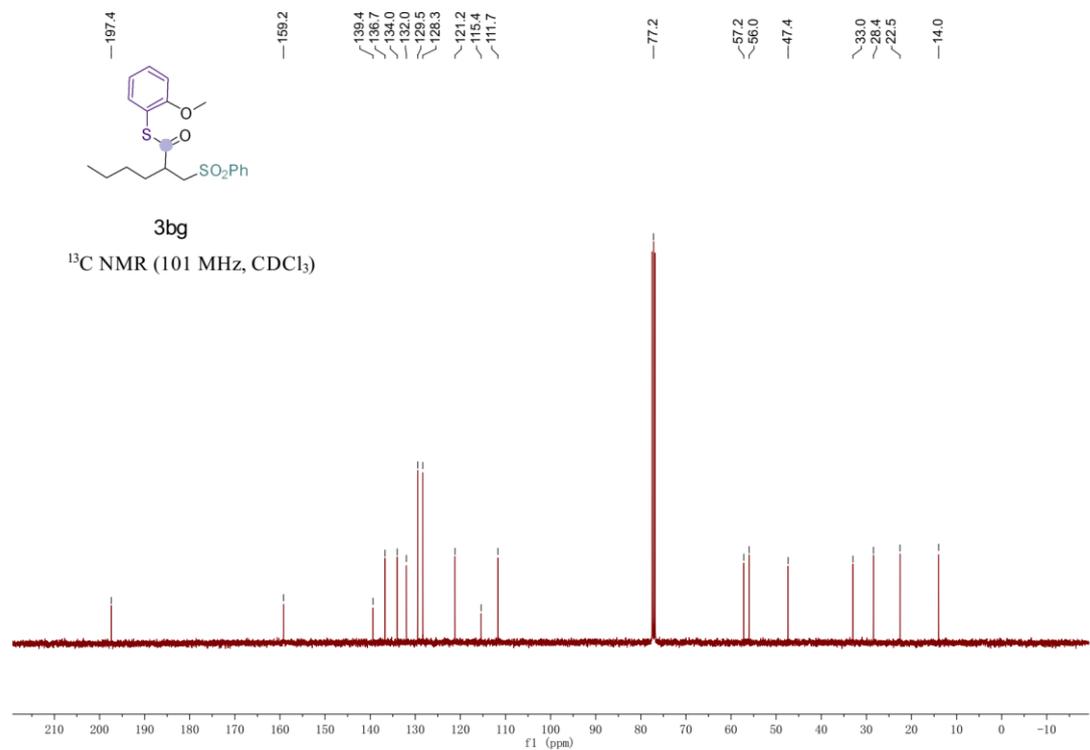
Supplementary Figure 37. <sup>1</sup>H NMR spectrum of **3bf** in CDCl<sub>3</sub> (400 MHz)



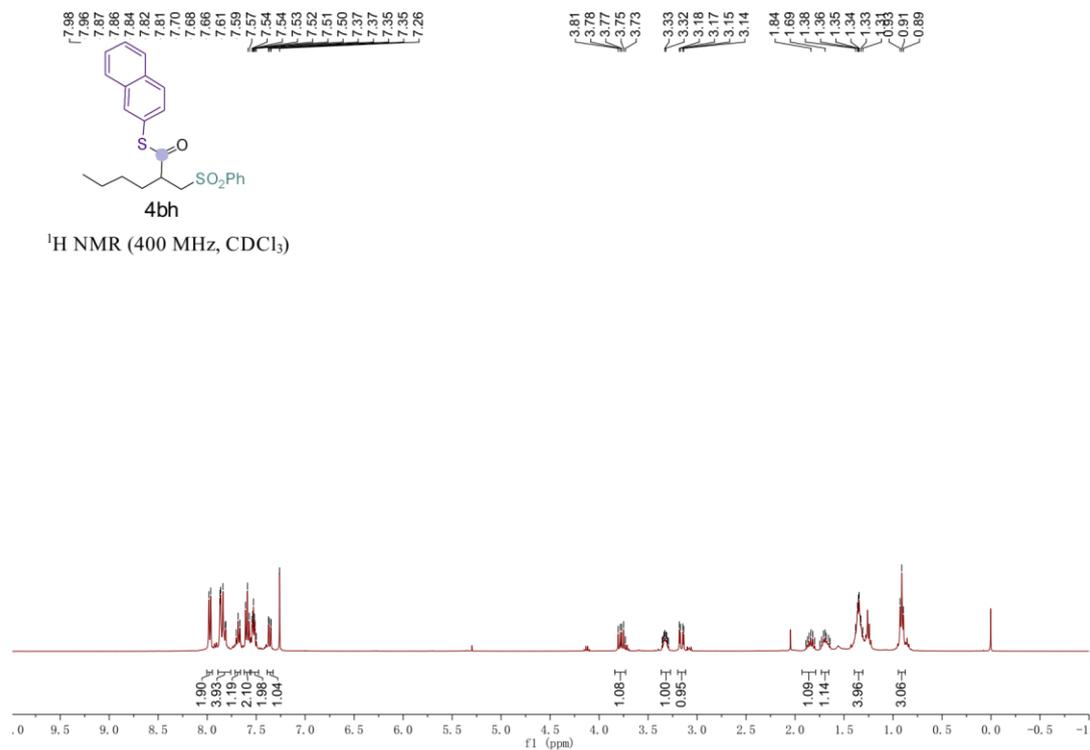
Supplementary Figure 38. <sup>13</sup>C NMR spectrum of **3bf** in CDCl<sub>3</sub> (101 MHz)



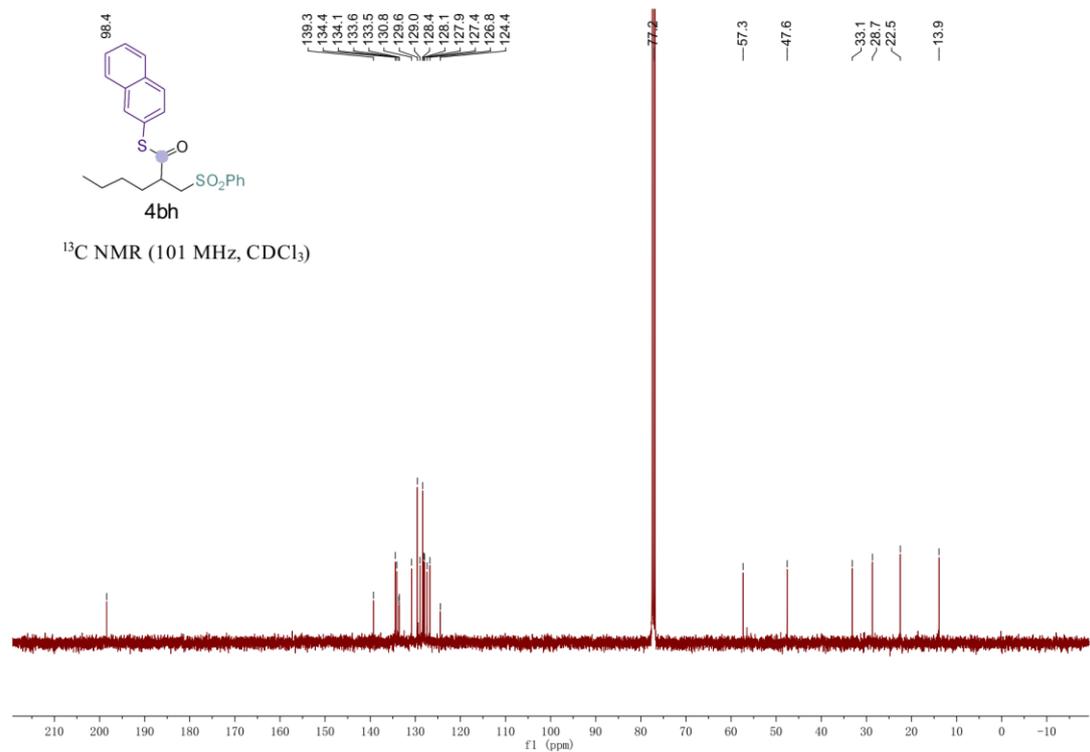
Supplementary Figure 39.  $^1\text{H NMR}$  spectrum of **3bg** in  $\text{CDCl}_3$  (400 MHz)



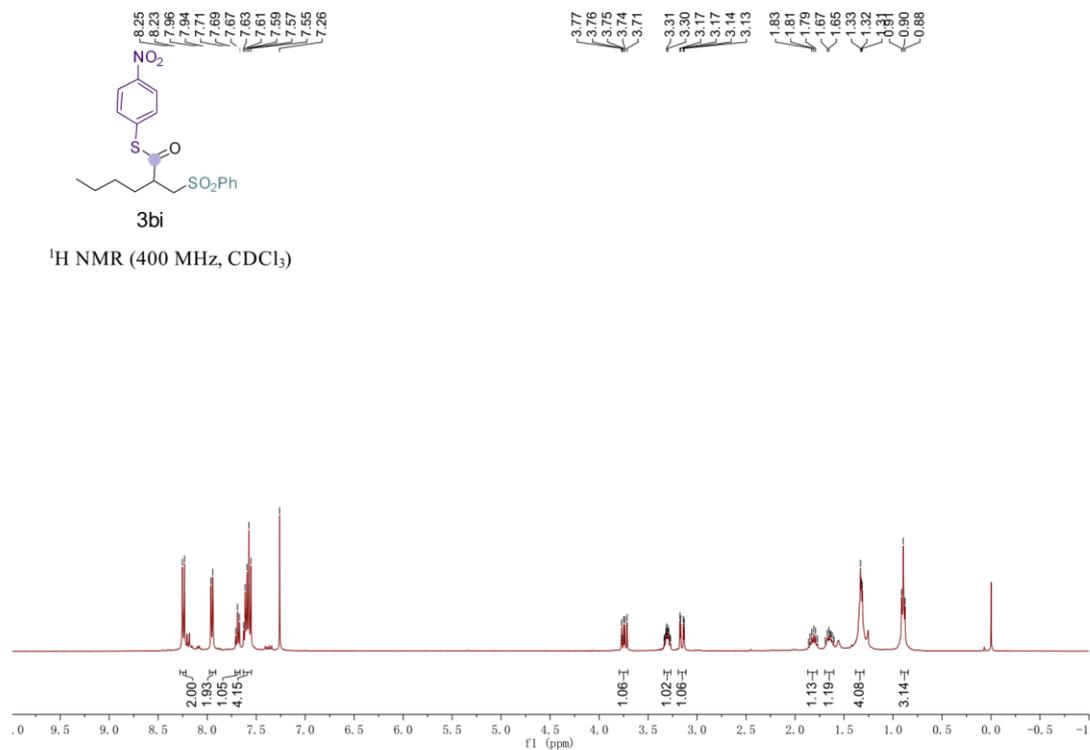
Supplementary Figure 40.  $^{13}\text{C NMR}$  spectrum of **3bf** in  $\text{CDCl}_3$  (101 MHz)



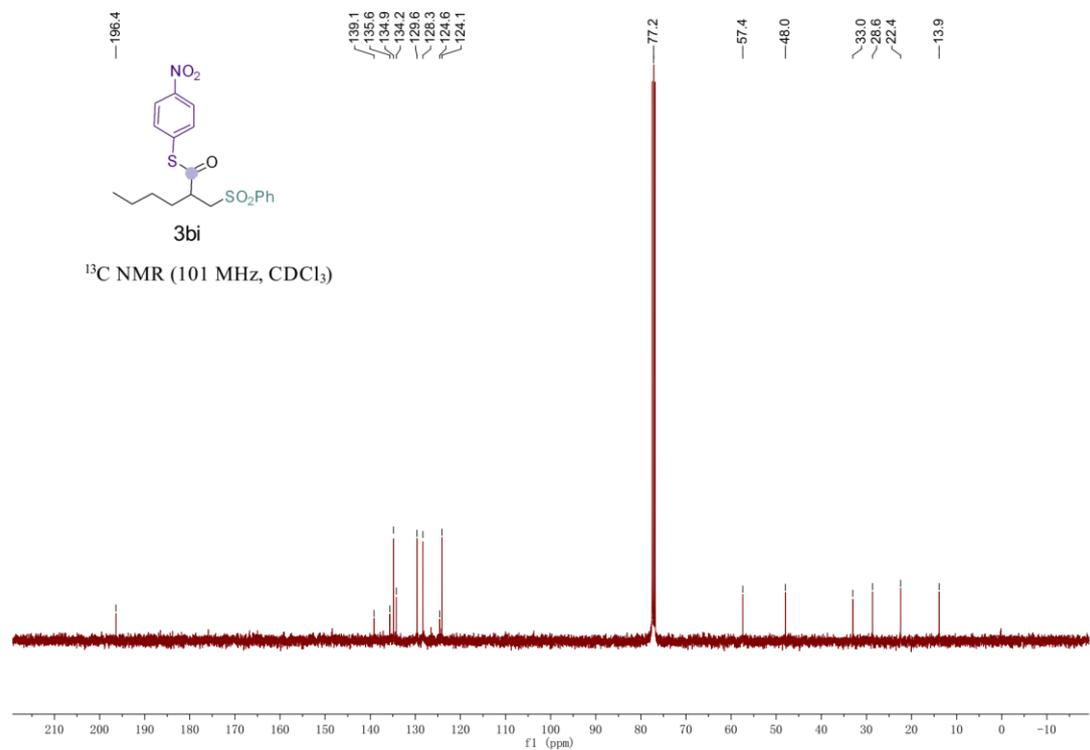
Supplementary Figure 41. <sup>1</sup>H NMR spectrum of **3bh** in CDCl<sub>3</sub> (400 MHz)



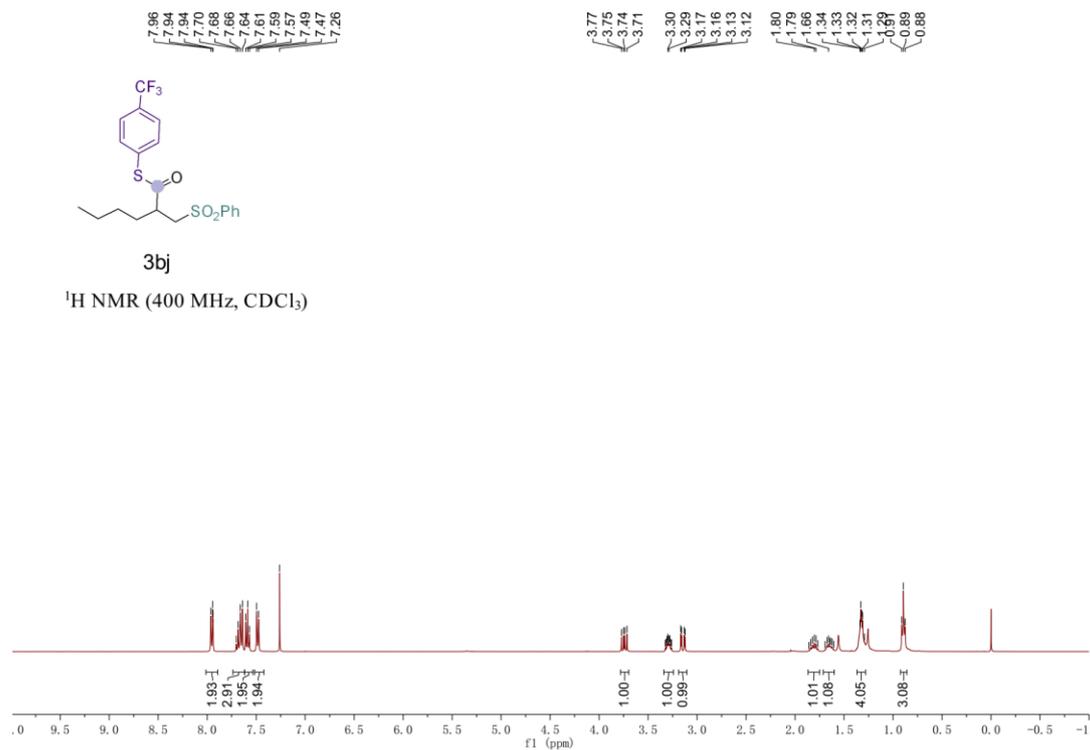
Supplementary Figure 42. <sup>13</sup>C NMR spectrum of **3bh** in CDCl<sub>3</sub> (101 MHz)



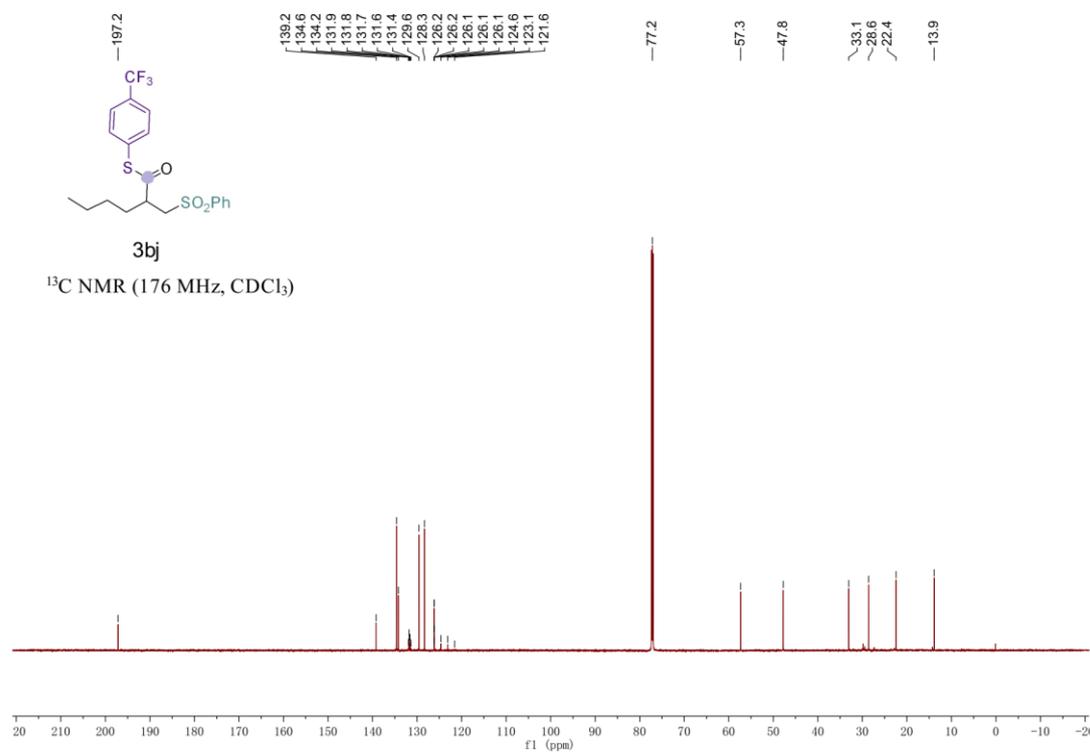
Supplementary Figure 43. <sup>1</sup>H NMR spectrum of **3bi** in CDCl<sub>3</sub> (400 MHz)



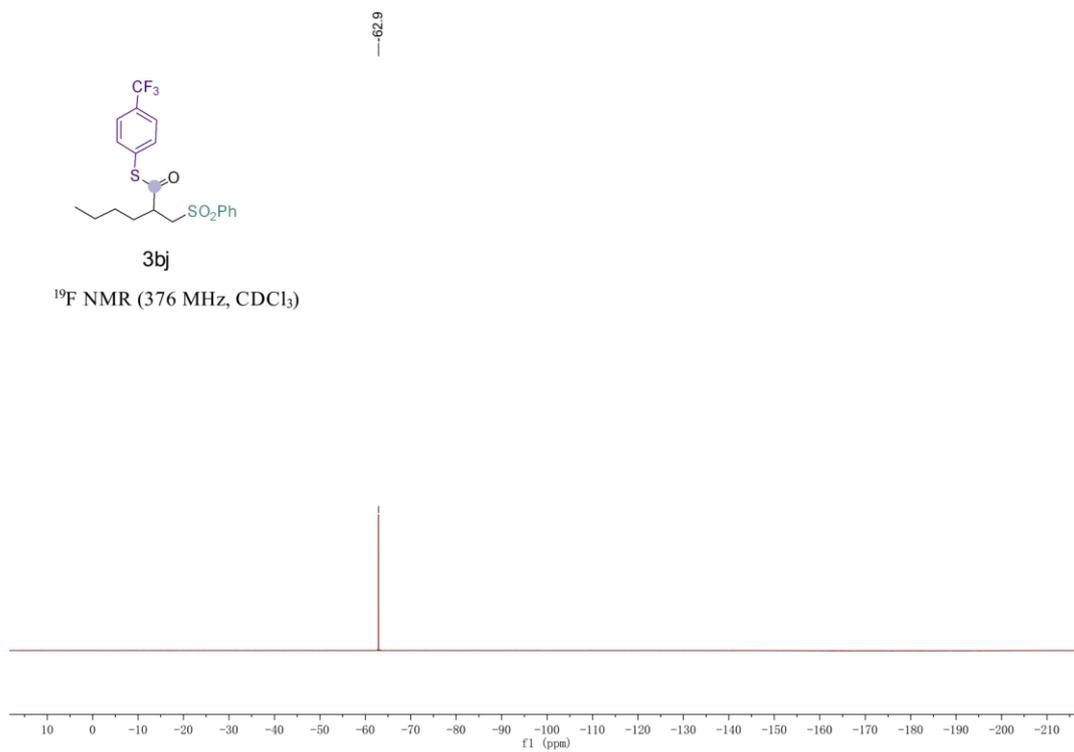
Supplementary Figure 44. <sup>13</sup>C NMR spectrum of **3bi** in CDCl<sub>3</sub> (101 MHz)



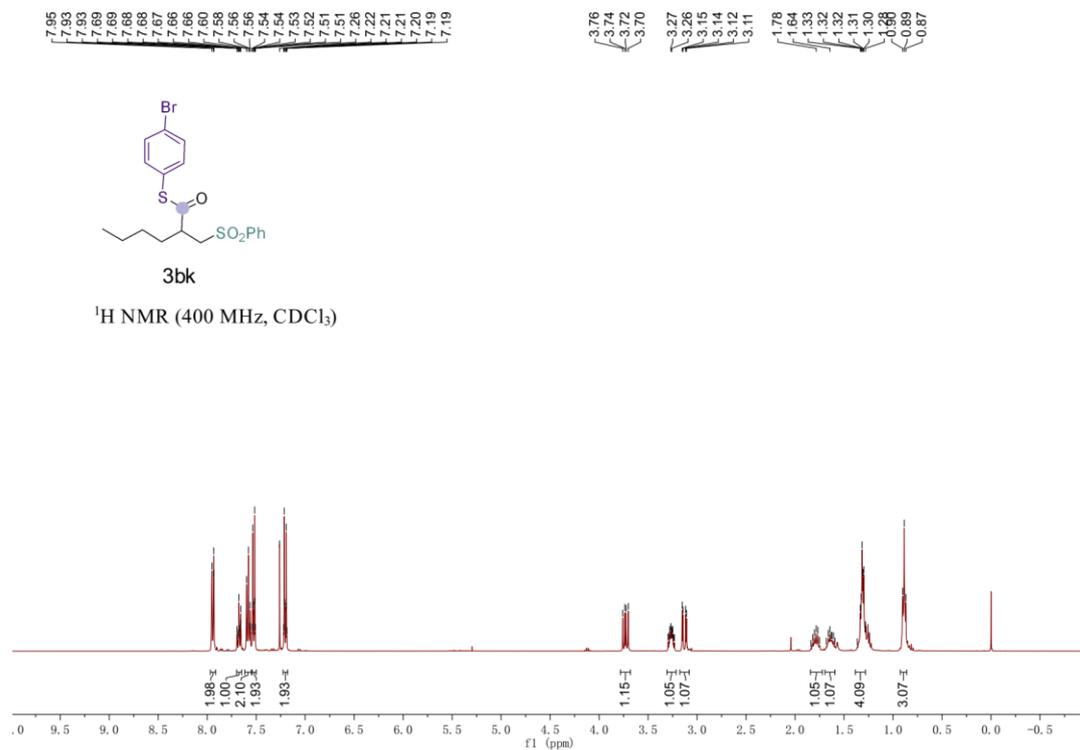
Supplementary Figure 45. <sup>1</sup>H NMR spectrum of **3bj** in CDCl<sub>3</sub> (400 MHz)



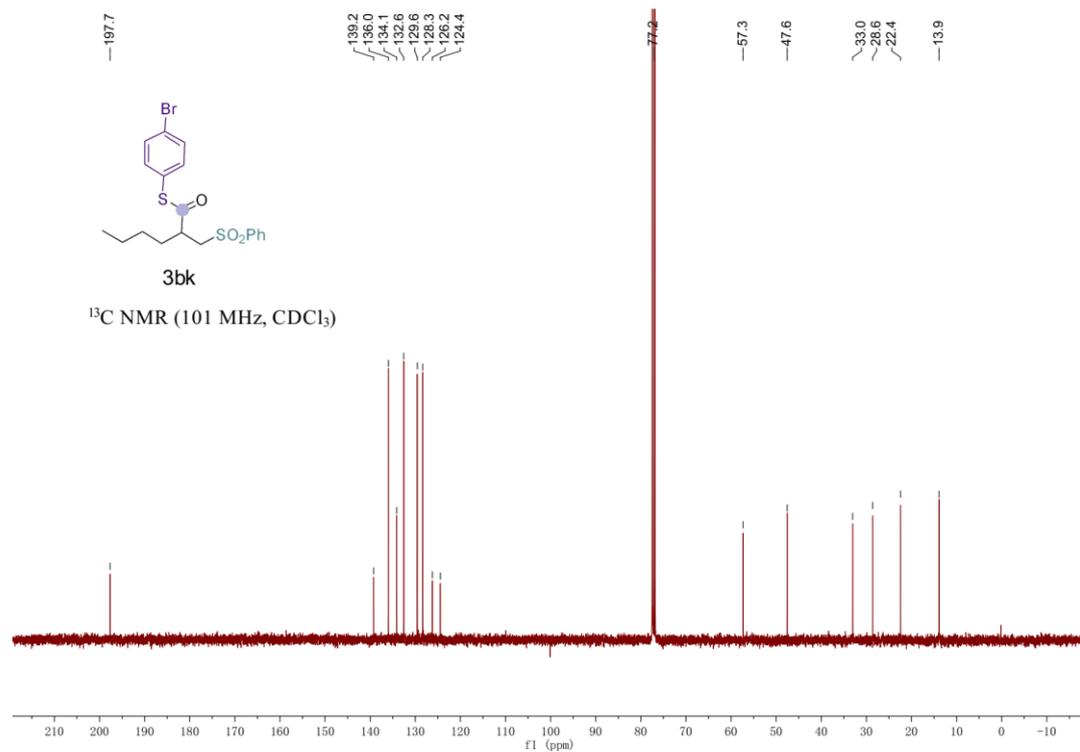
Supplementary Figure 46. <sup>13</sup>C NMR spectrum of **3bj** in CDCl<sub>3</sub> (176 MHz)



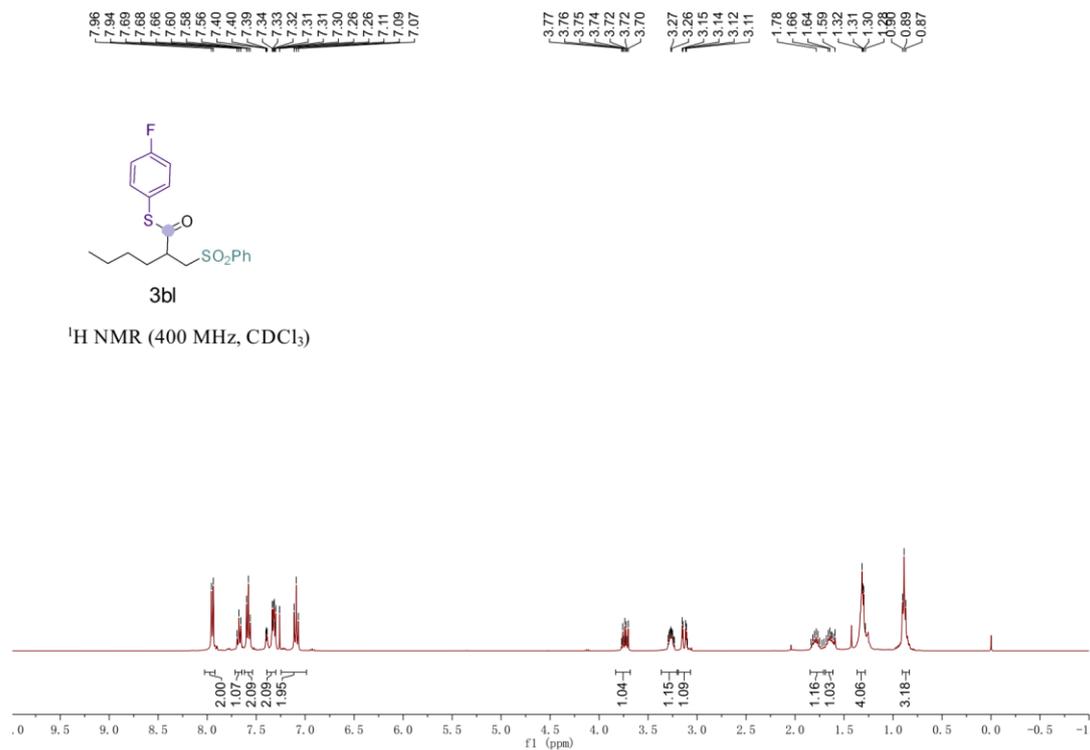
Supplementary Figure 47. <sup>19</sup>F NMR spectrum of **3bj** in CDCl<sub>3</sub> (376 MHz)



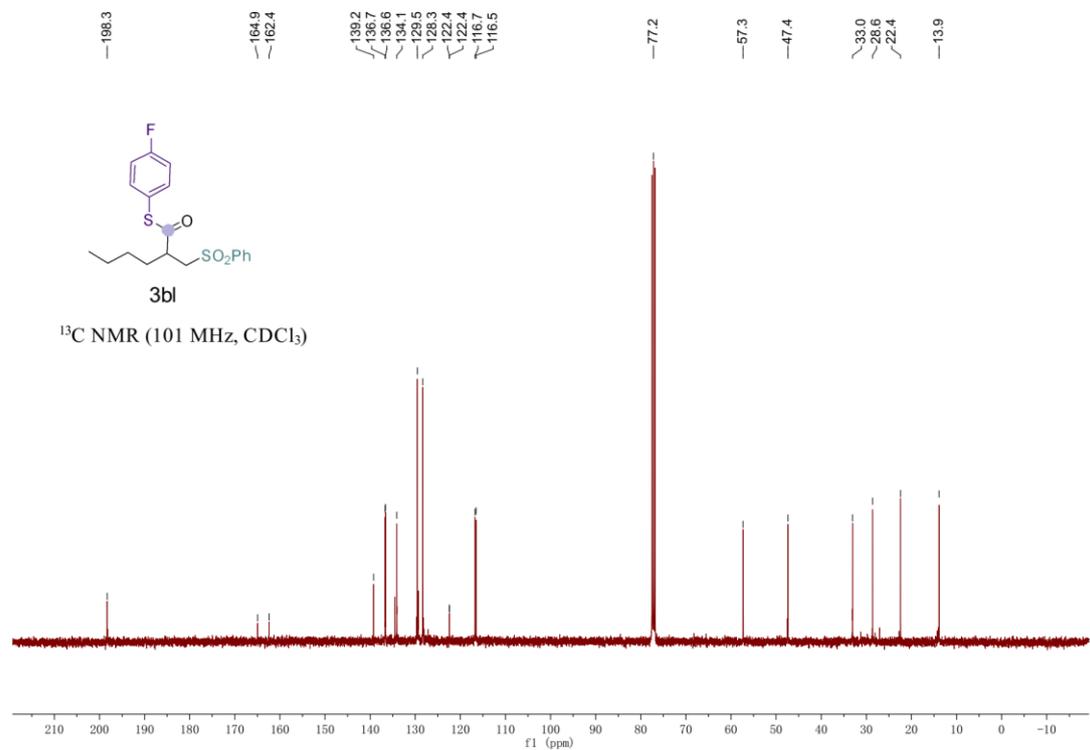
Supplementary Figure 48. <sup>1</sup>H NMR spectrum of **3bk** in CDCl<sub>3</sub> (400 MHz)



Supplementary Figure 49. <sup>13</sup>C NMR spectrum of **3bk** in CDCl<sub>3</sub> (101 MHz)



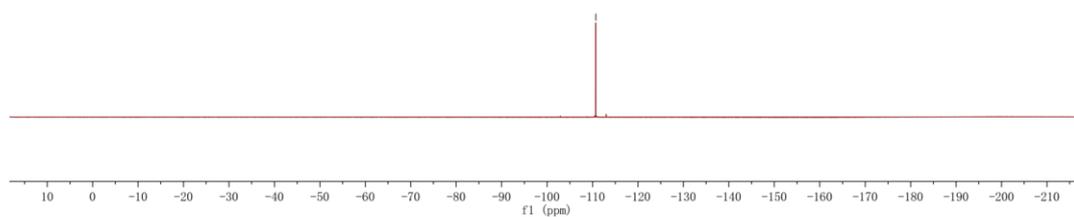
Supplementary Figure 50. <sup>1</sup>H NMR spectrum of **3bl** in CDCl<sub>3</sub> (400 MHz)



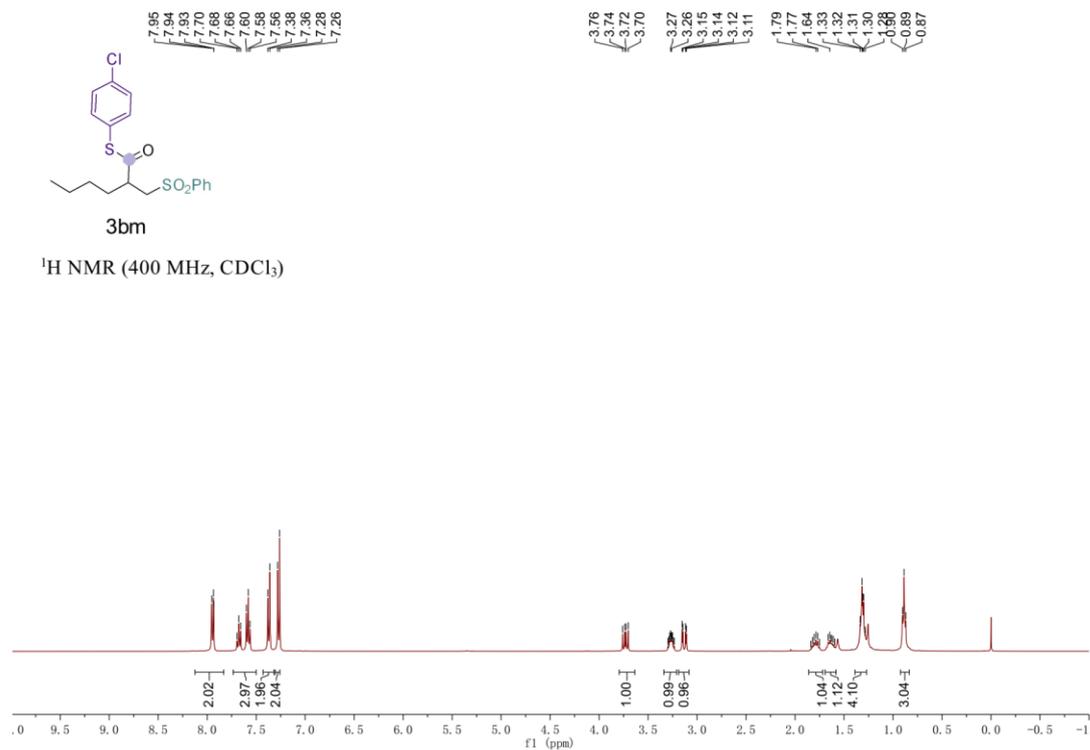
Supplementary Figure 51. <sup>13</sup>C NMR spectrum of **3bl** in CDCl<sub>3</sub> (101 MHz)



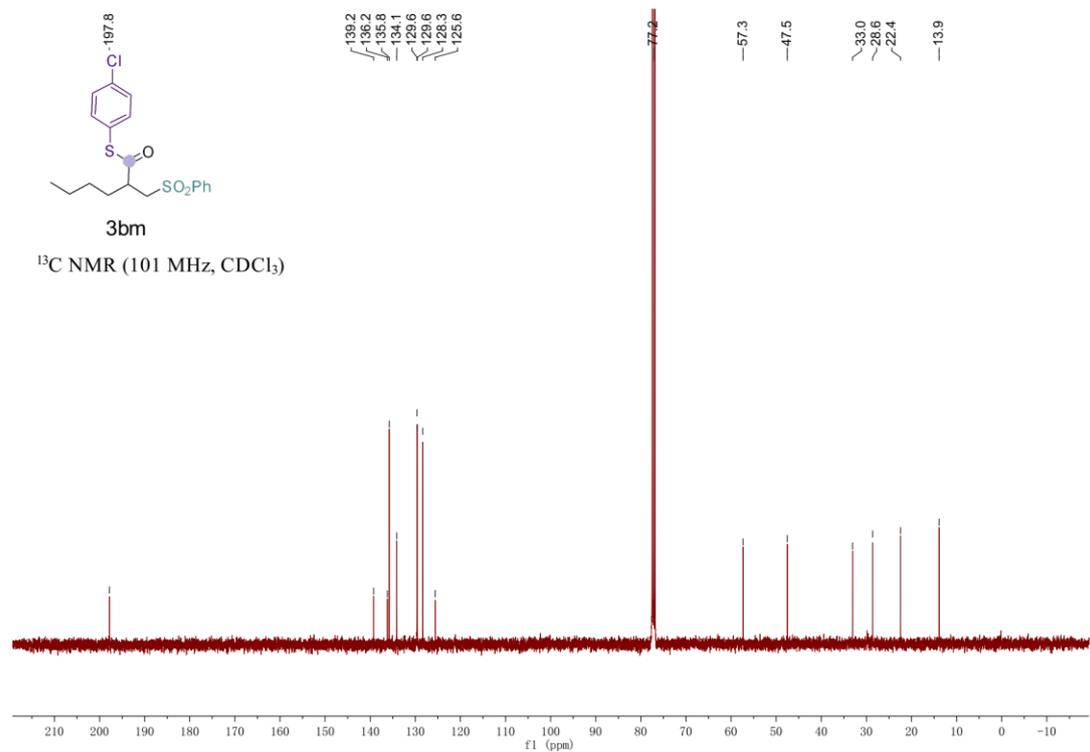
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



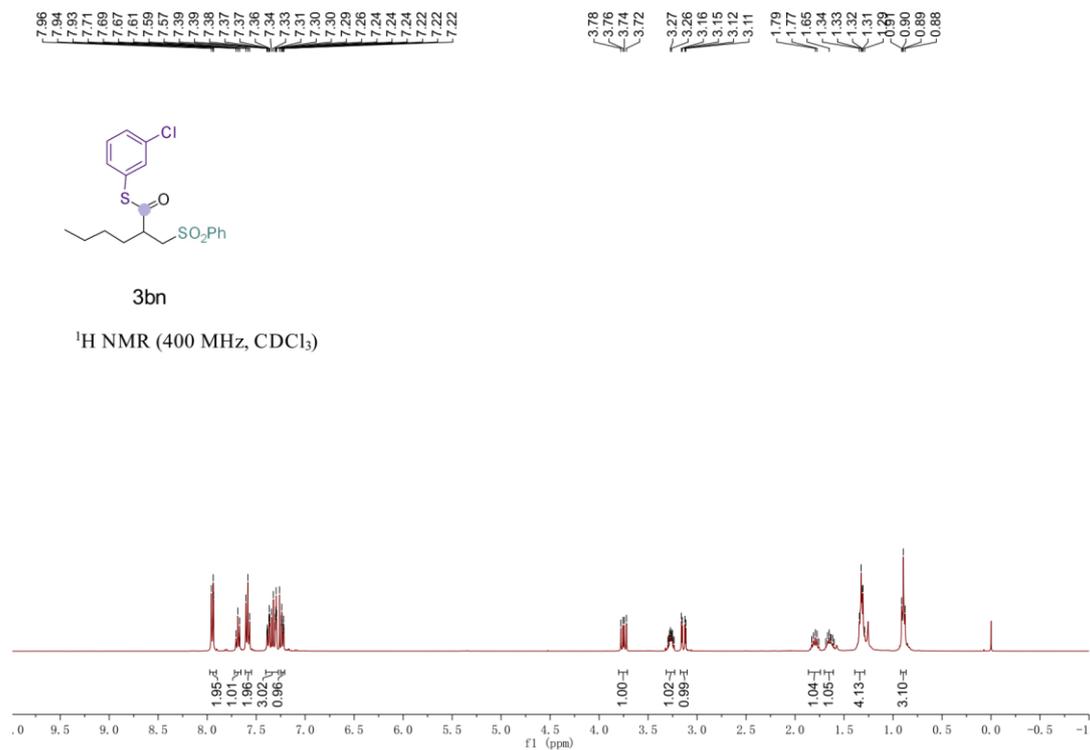
Supplementary Figure 52. <sup>19</sup>F NMR spectrum of **3bl** in CDCl<sub>3</sub> (376 MHz)



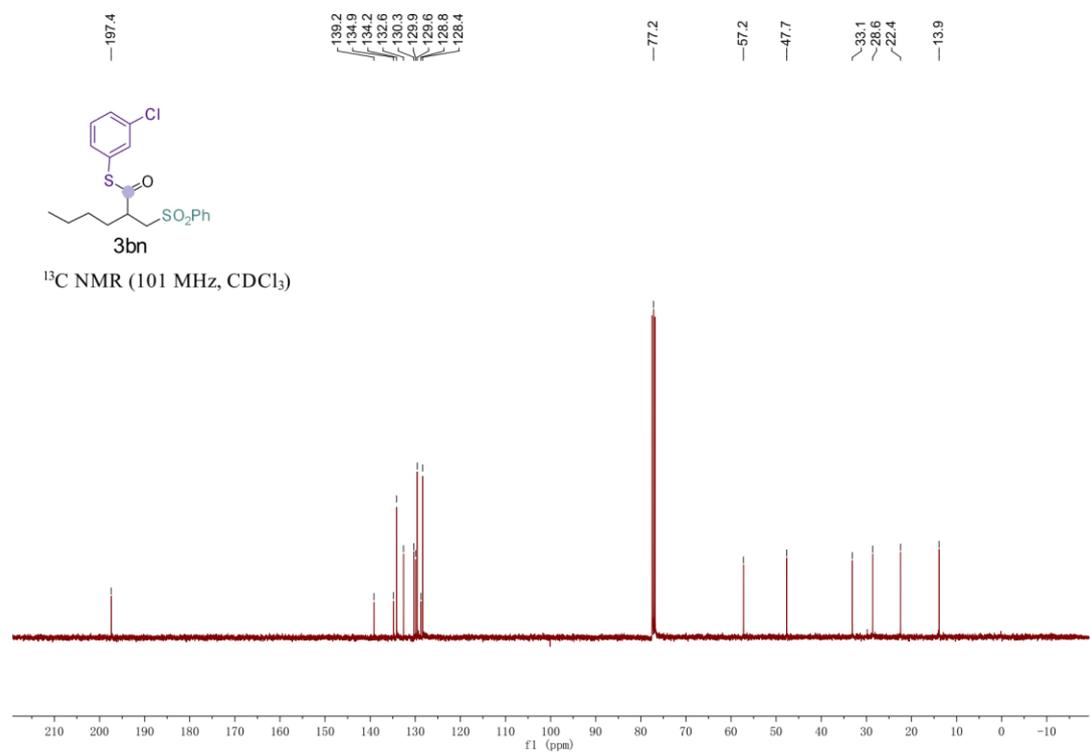
Supplementary Figure 53. <sup>1</sup>H NMR spectrum of **3bm** in CDCl<sub>3</sub> (400 MHz)



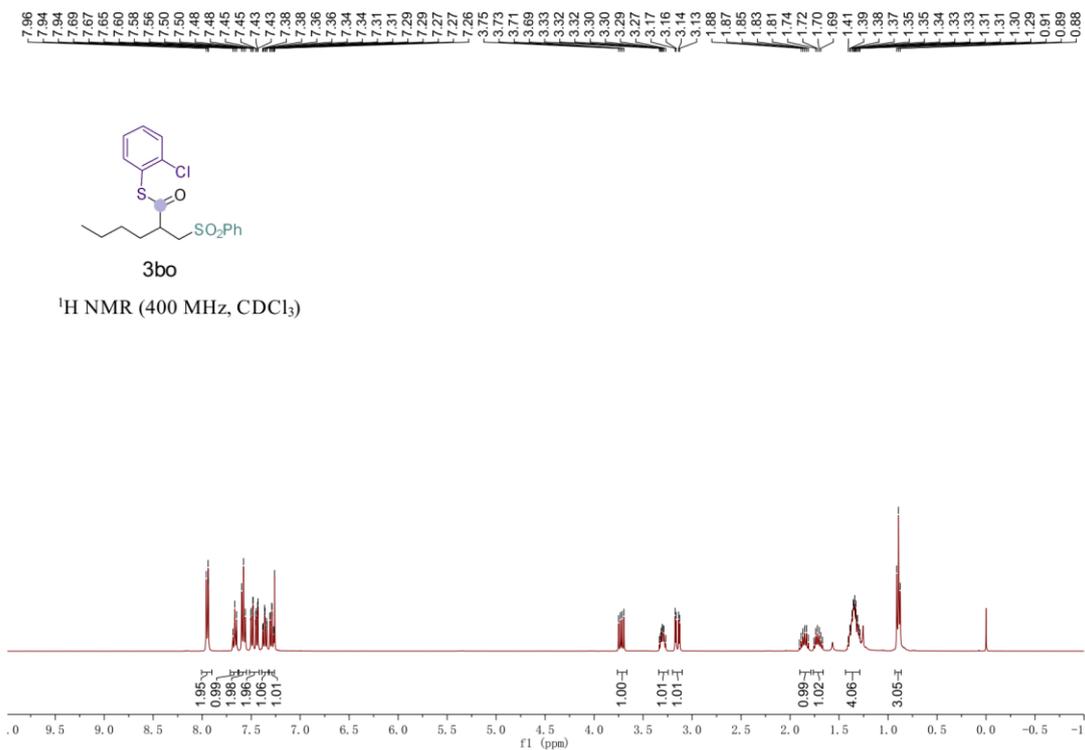
Supplementary Figure 54. <sup>13</sup>C NMR spectrum of **3bm** in CDCl<sub>3</sub> (101 MHz)



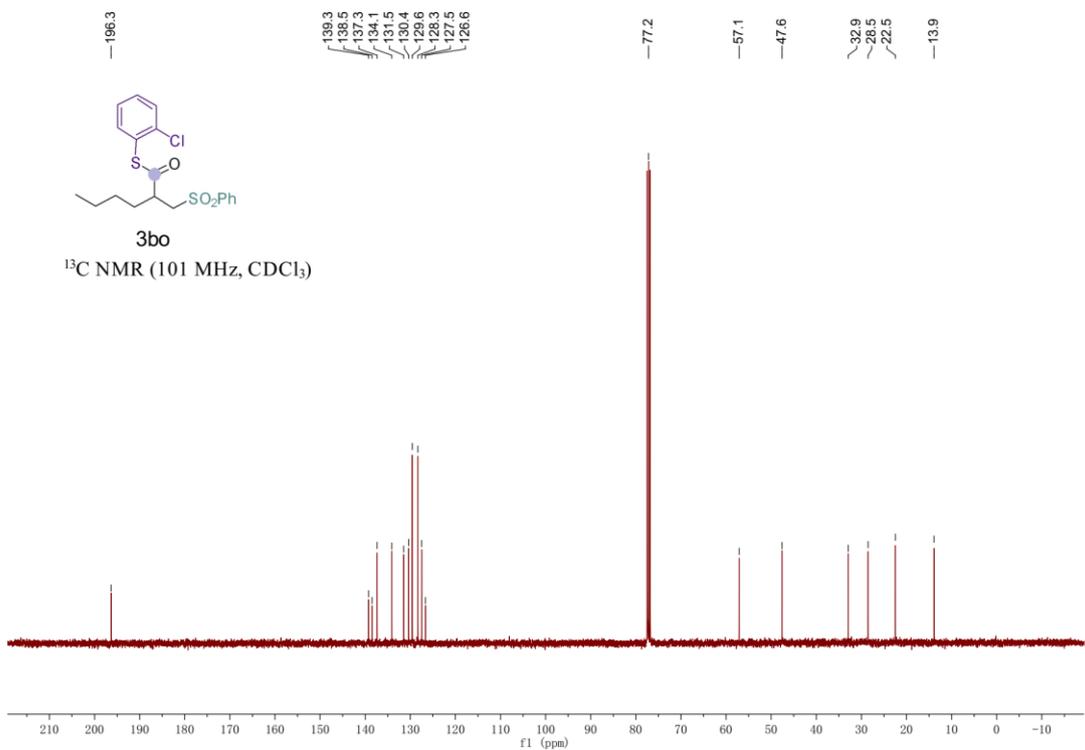
Supplementary Figure 55. <sup>1</sup>H NMR spectrum of **3bn** in CDCl<sub>3</sub> (400 MHz)



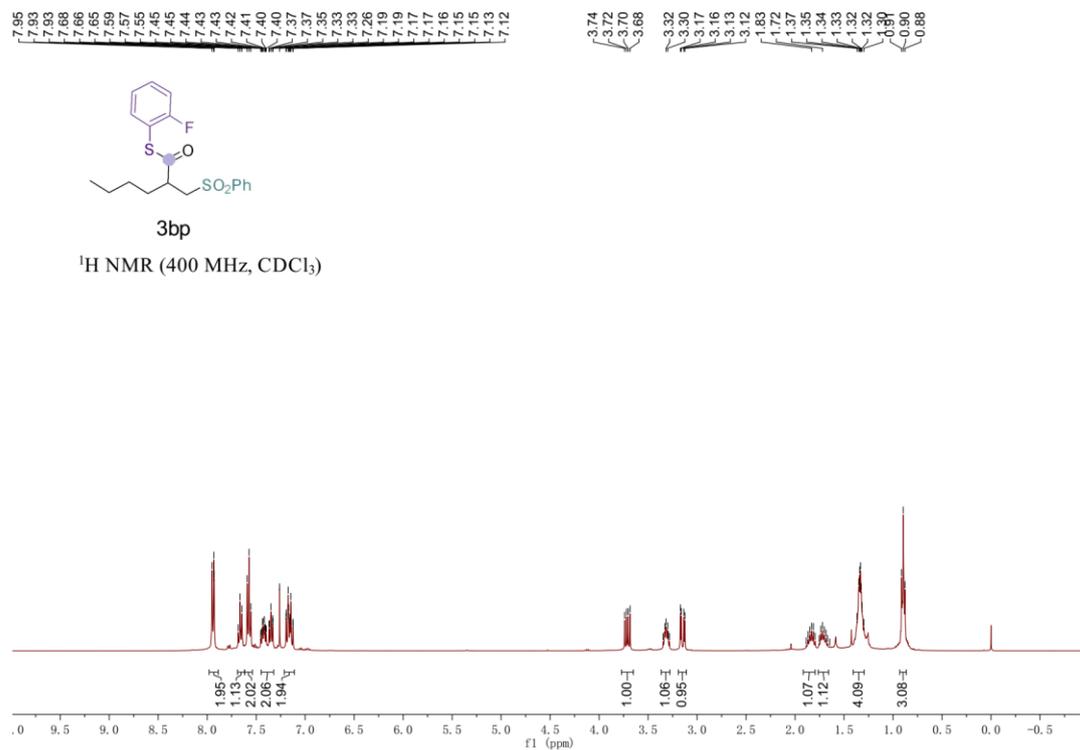
Supplementary Figure 56. <sup>13</sup>C NMR spectrum of **3bn** in CDCl<sub>3</sub> (101 MHz)



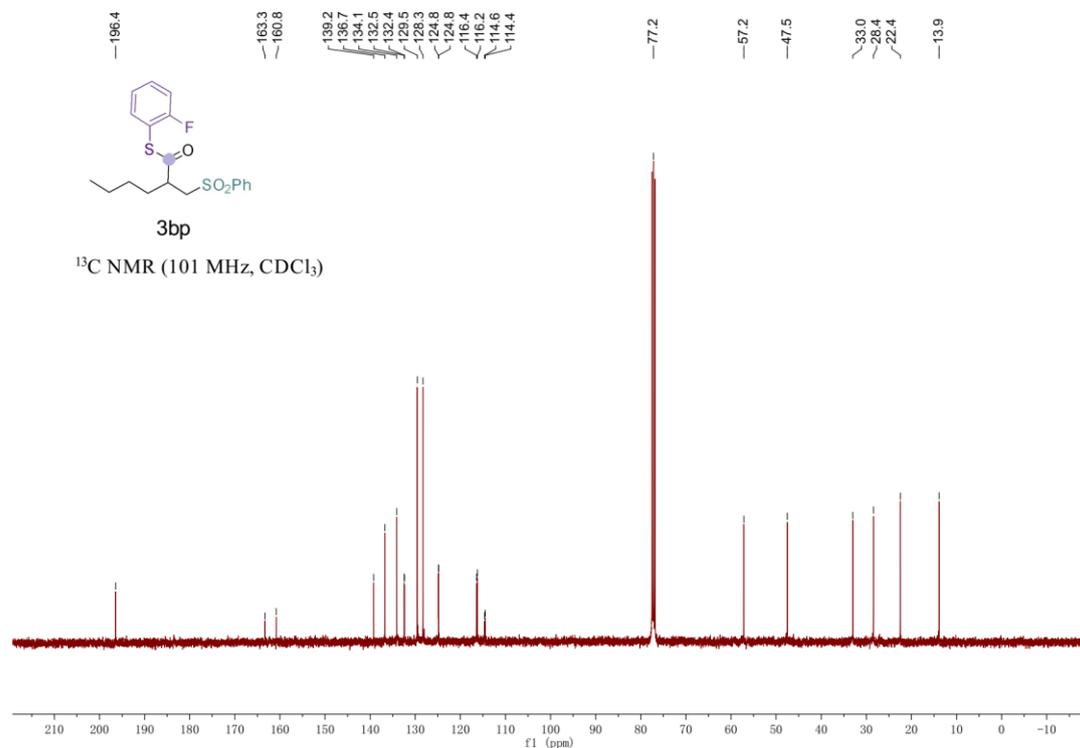
Supplementary Figure 57.  $^1\text{H NMR}$  spectrum of **3bo** in  $\text{CDCl}_3$  (400 MHz)



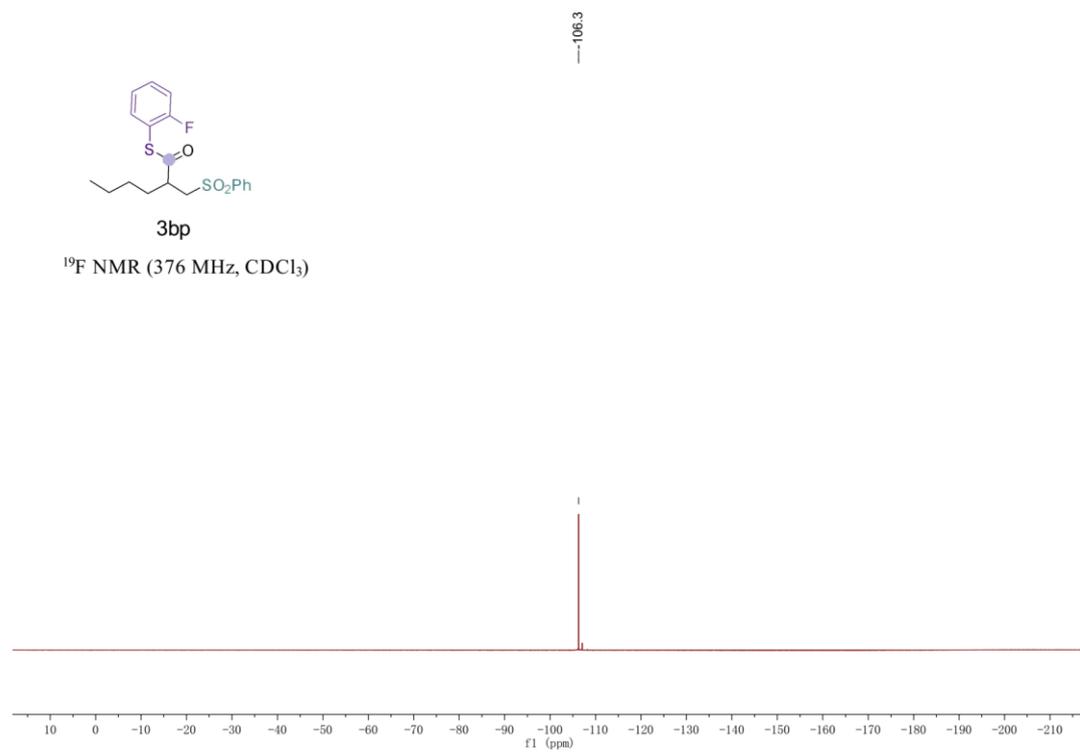
Supplementary Figure 58.  $^{13}\text{C NMR}$  spectrum of **3bo** in  $\text{CDCl}_3$  (101 MHz)



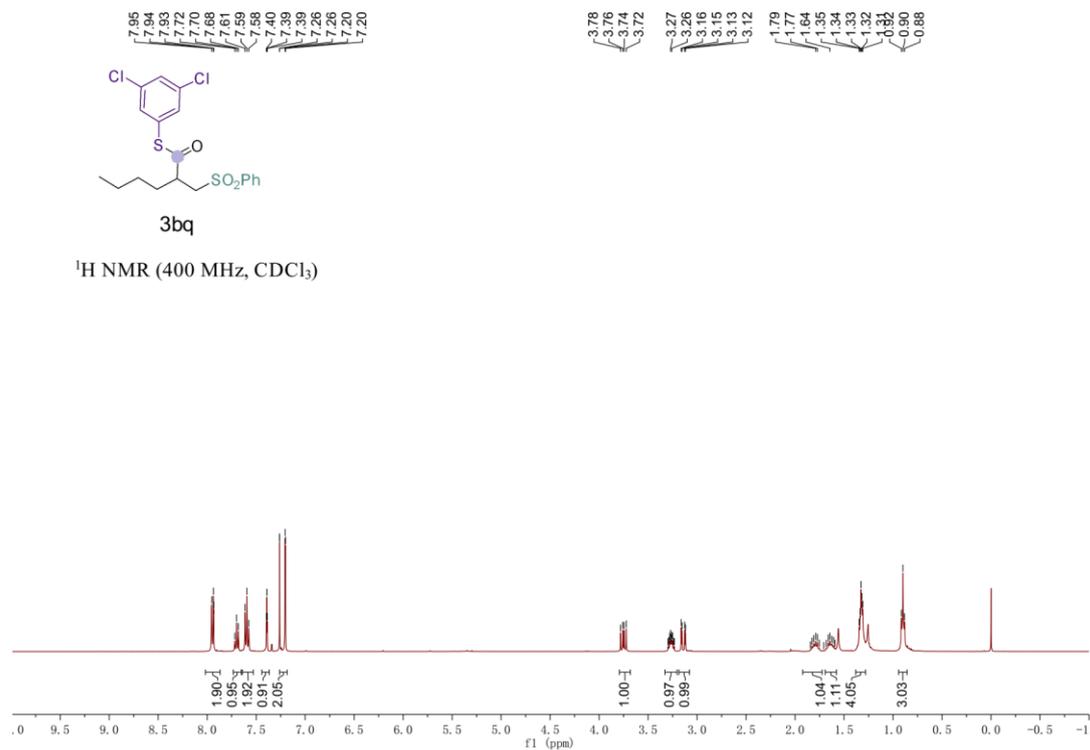
Supplementary Figure 59. <sup>1</sup>H NMR spectrum of **3bp** in CDCl<sub>3</sub> (400 MHz)



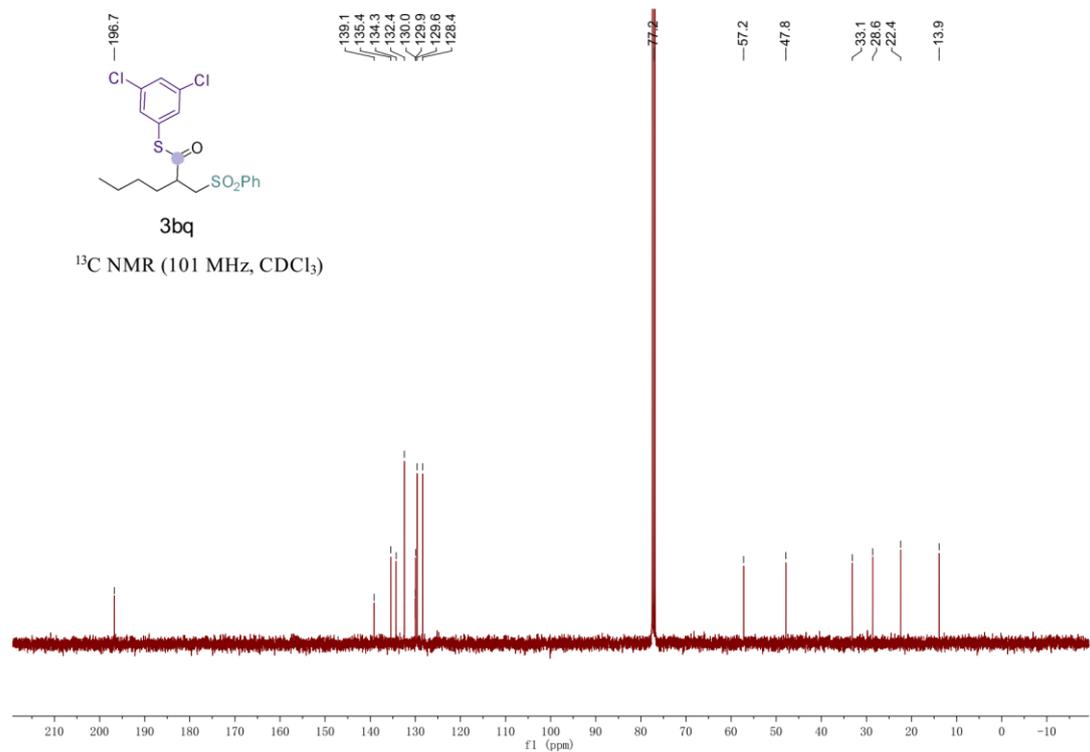
Supplementary Figure 60. <sup>13</sup>C NMR spectrum of **3bp** in CDCl<sub>3</sub> (101 MHz)



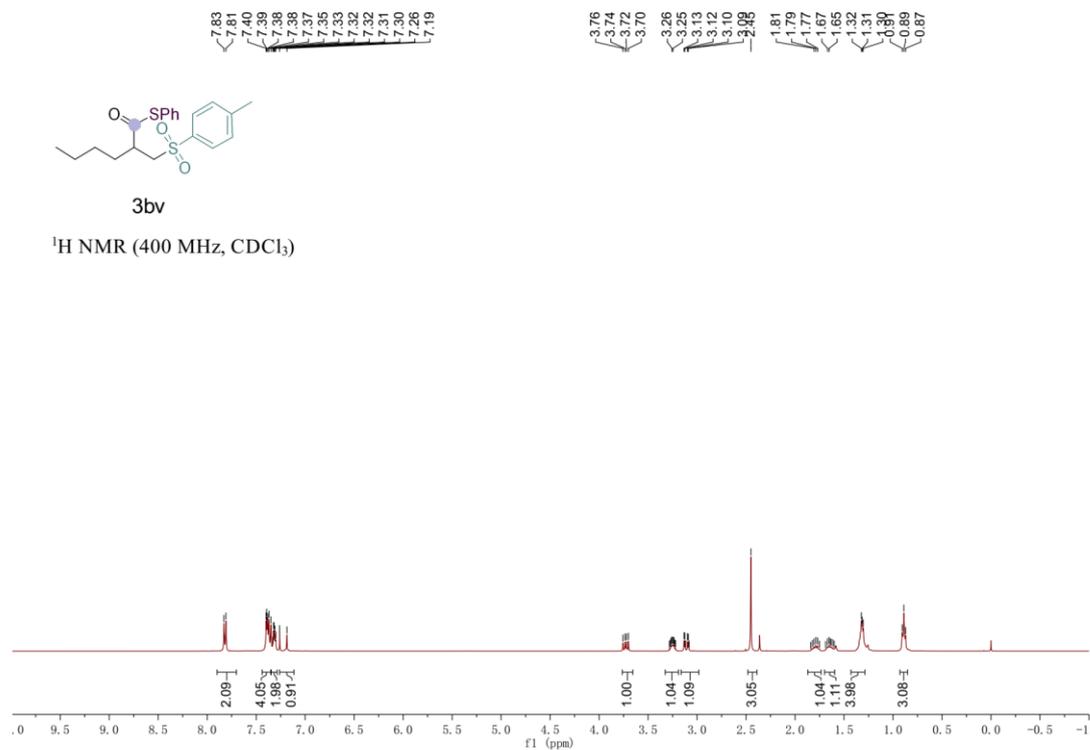
Supplementary Figure 61.  $^{19}\text{F}$  NMR spectrum of **3bp** in  $\text{CDCl}_3$  (376 MHz)



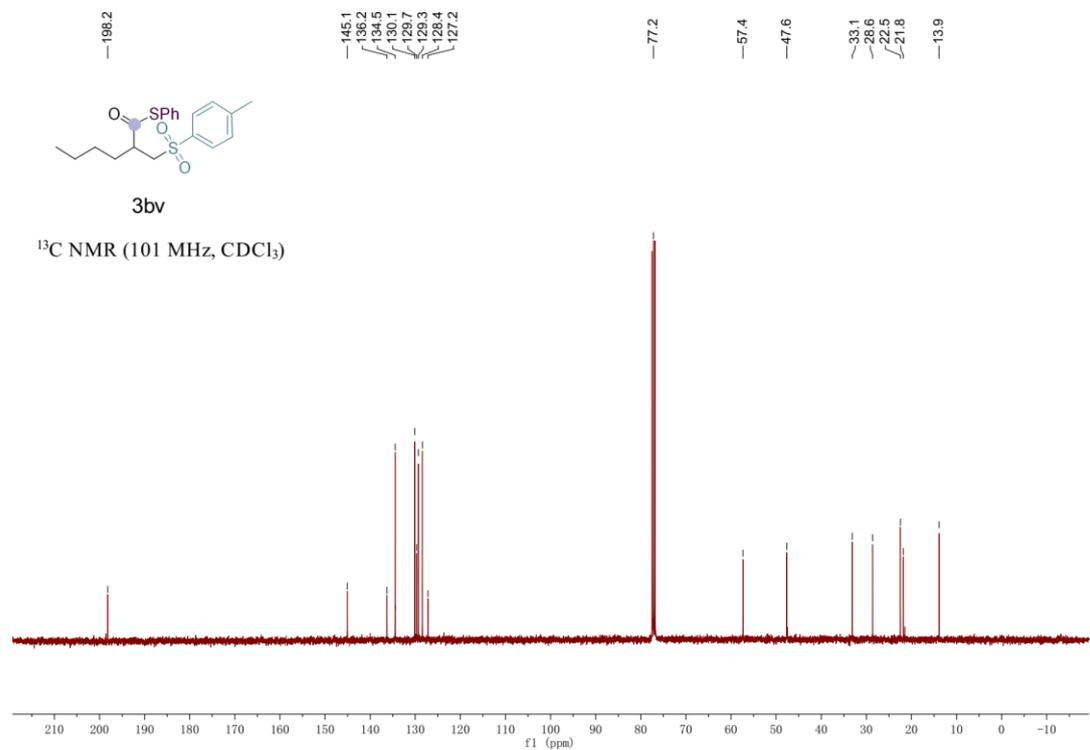
Supplementary Figure 62. <sup>1</sup>H NMR spectrum of **3bq** in CDCl<sub>3</sub> (400 MHz)



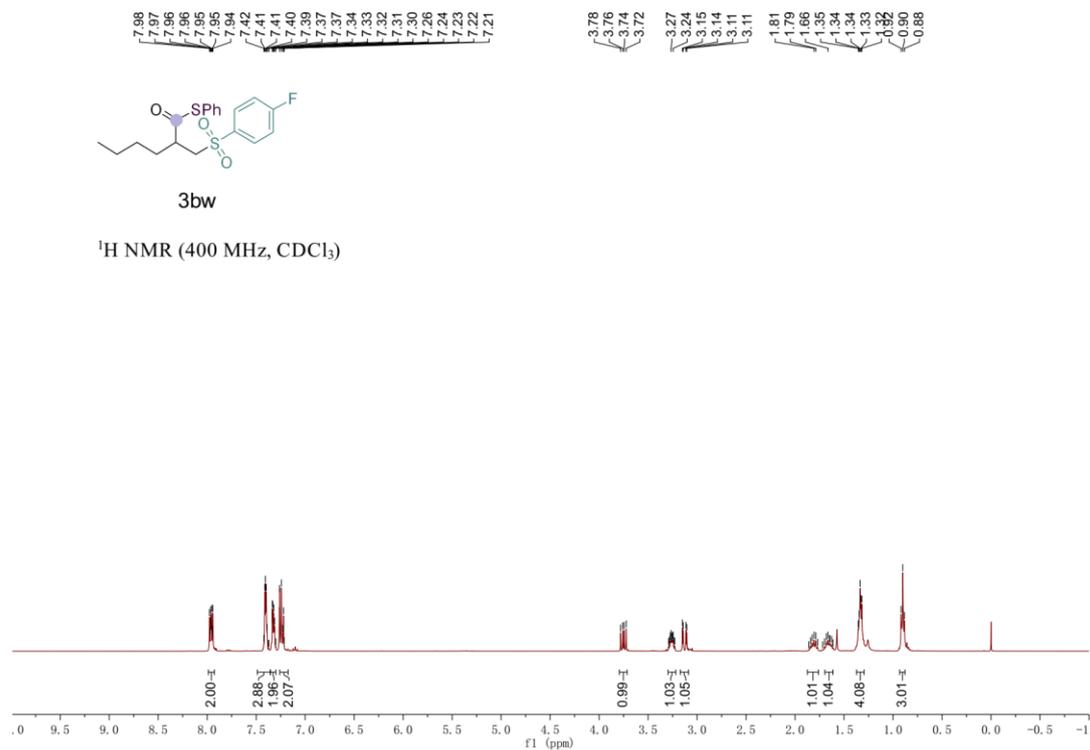
Supplementary Figure 63. <sup>13</sup>C NMR spectrum of **3bq** in CDCl<sub>3</sub> (101 MHz)



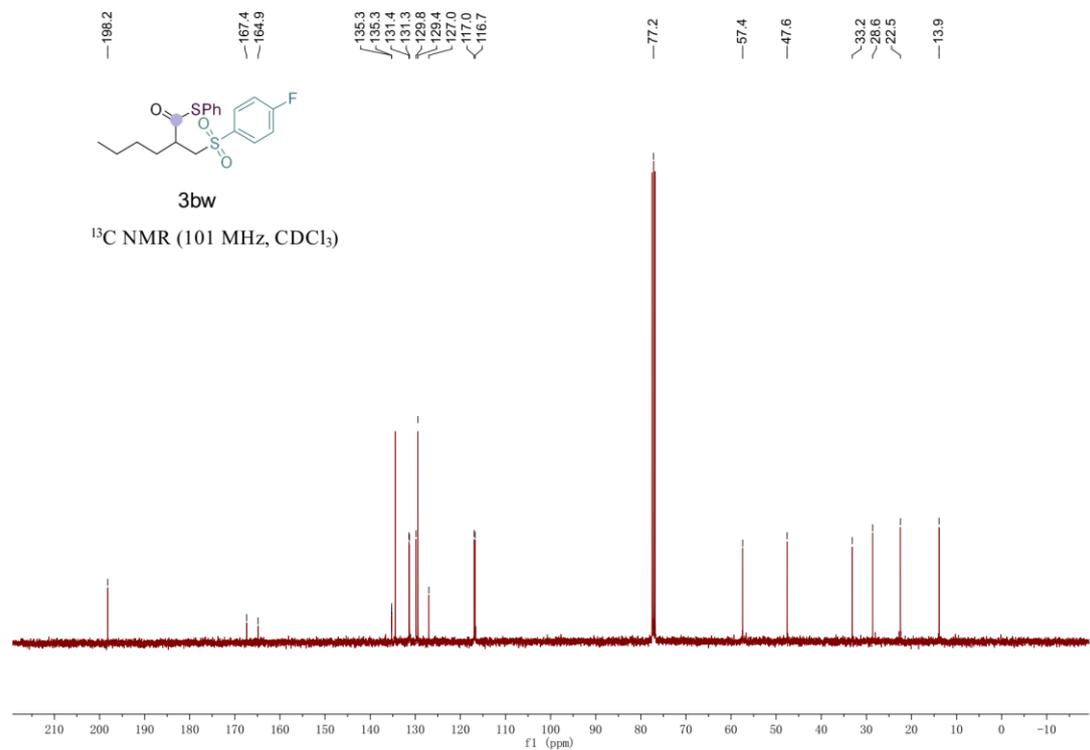
Supplementary Figure 64.  $^1\text{H}$  NMR spectrum of **3bv** in  $\text{CDCl}_3$  (400 MHz)



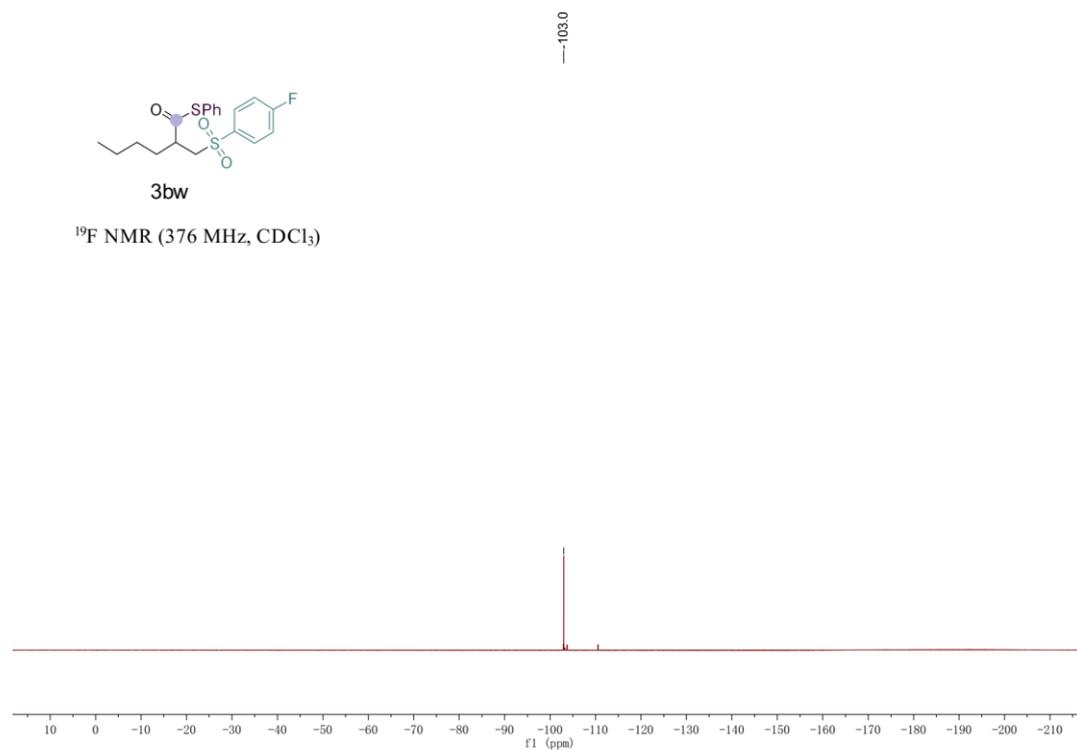
Supplementary Figure 65.  $^{13}\text{C}$  NMR spectrum of **3bv** in  $\text{CDCl}_3$  (101 MHz)



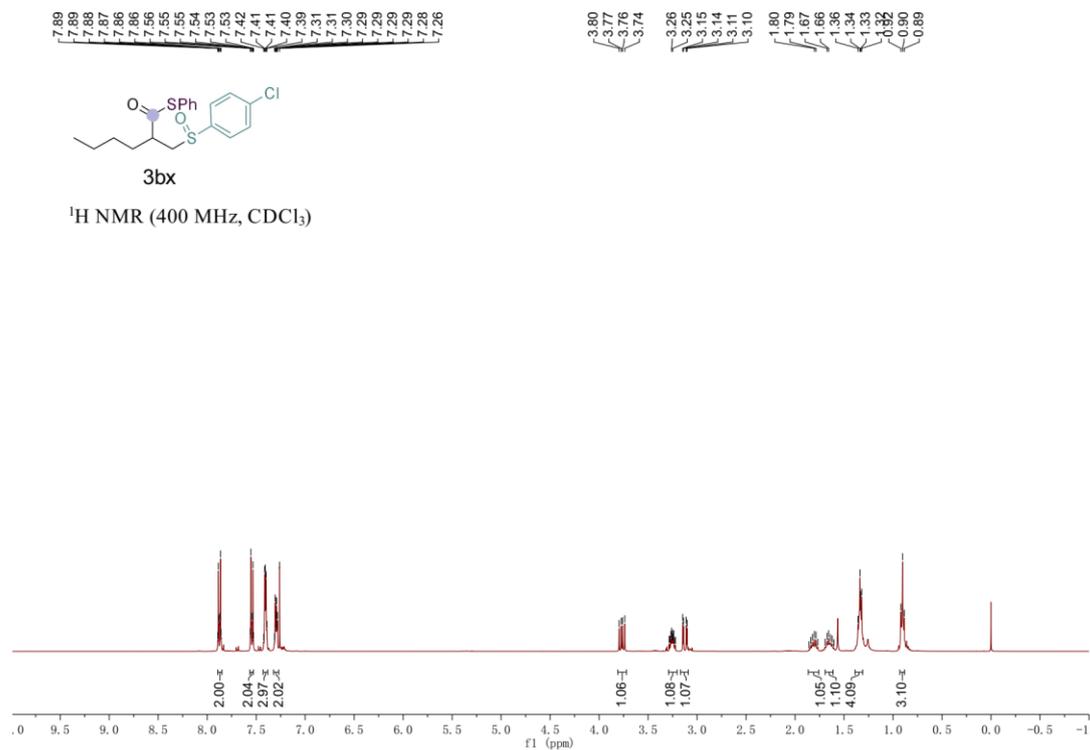
Supplementary Figure 66. <sup>1</sup>H NMR spectrum of **3bw** in CDCl<sub>3</sub> (400 MHz)



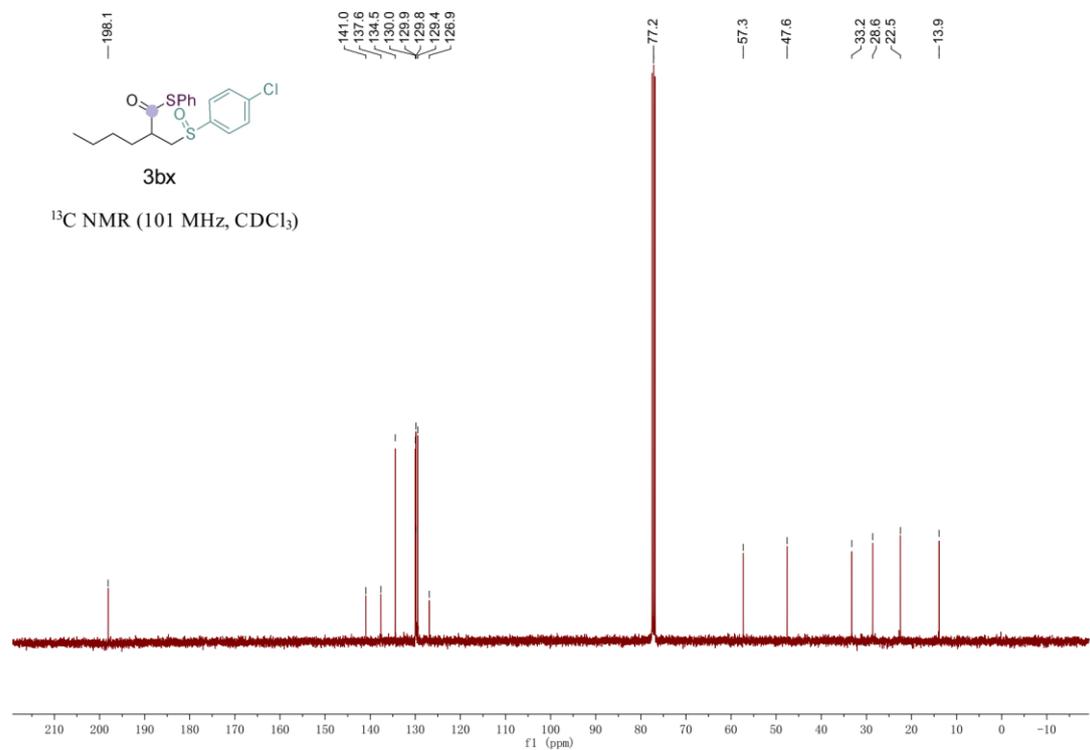
Supplementary Figure 67. <sup>13</sup>C NMR spectrum of **3bw** in CDCl<sub>3</sub> (101 MHz)



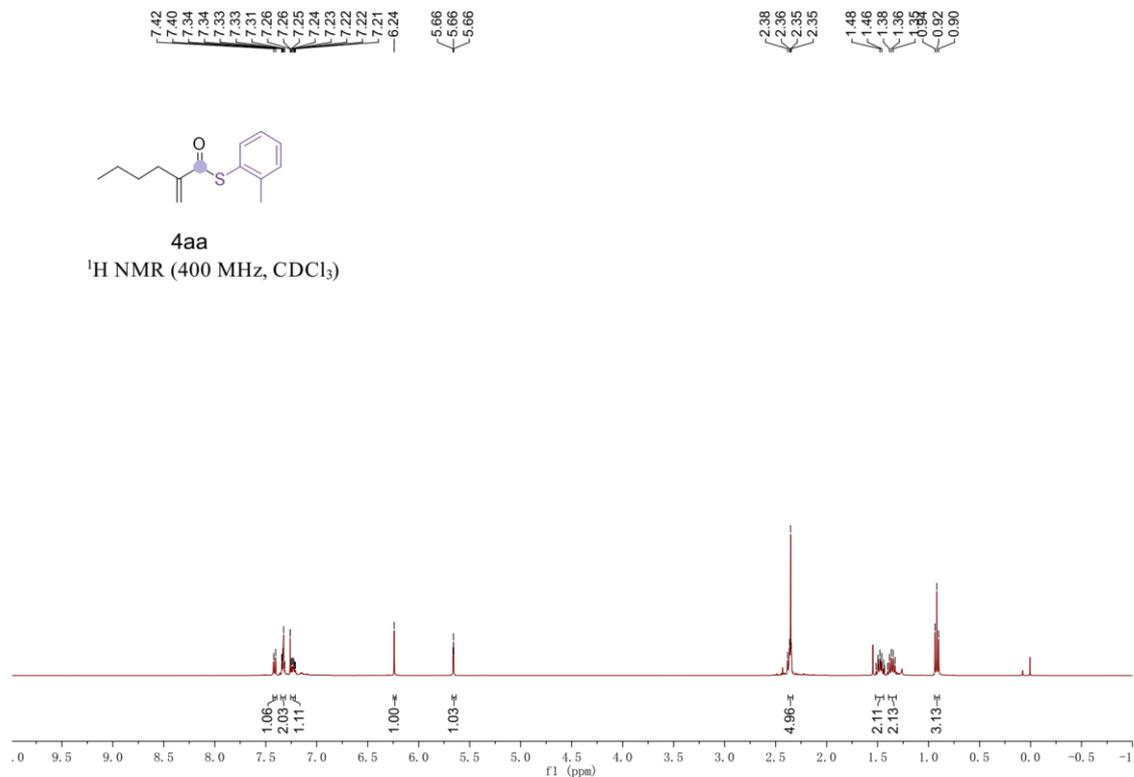
Supplementary Figure 68.  $^{19}\text{F}$  NMR spectrum of **3bw** in  $\text{CDCl}_3$  (376 MHz)



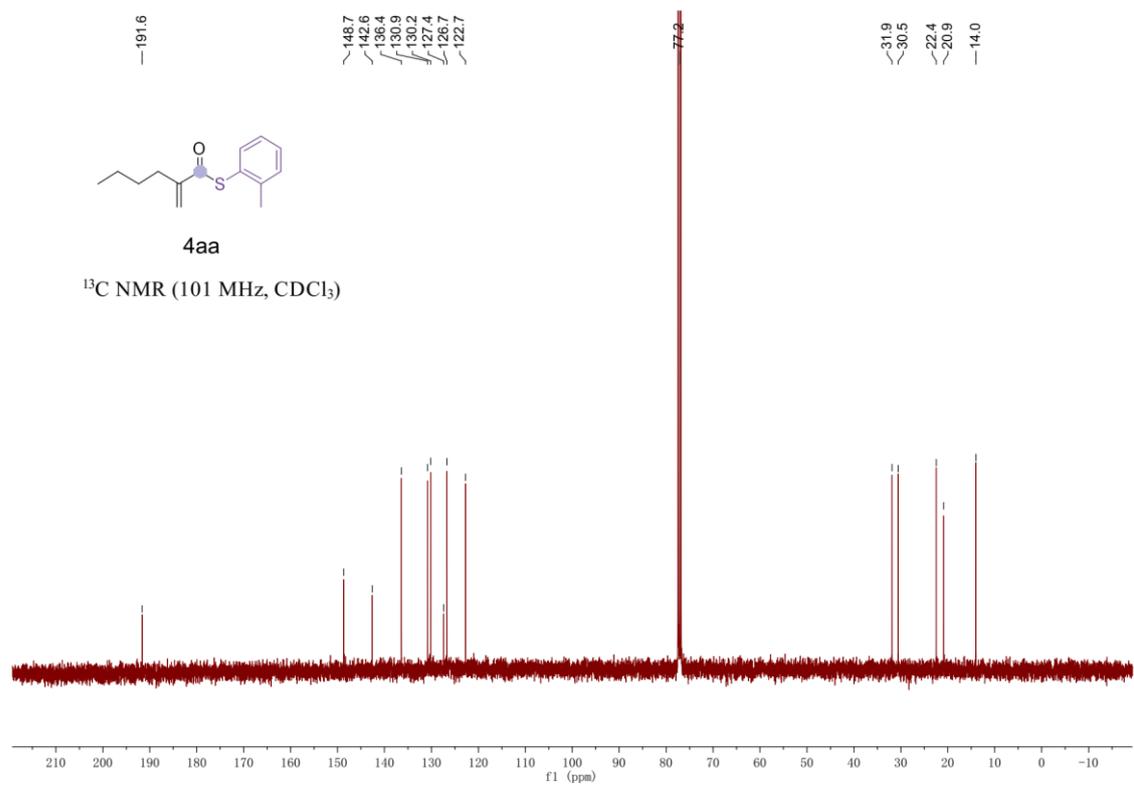
Supplementary Figure 69.  $^1\text{H NMR}$  spectrum of **3bx** in  $\text{CDCl}_3$  (400 MHz)



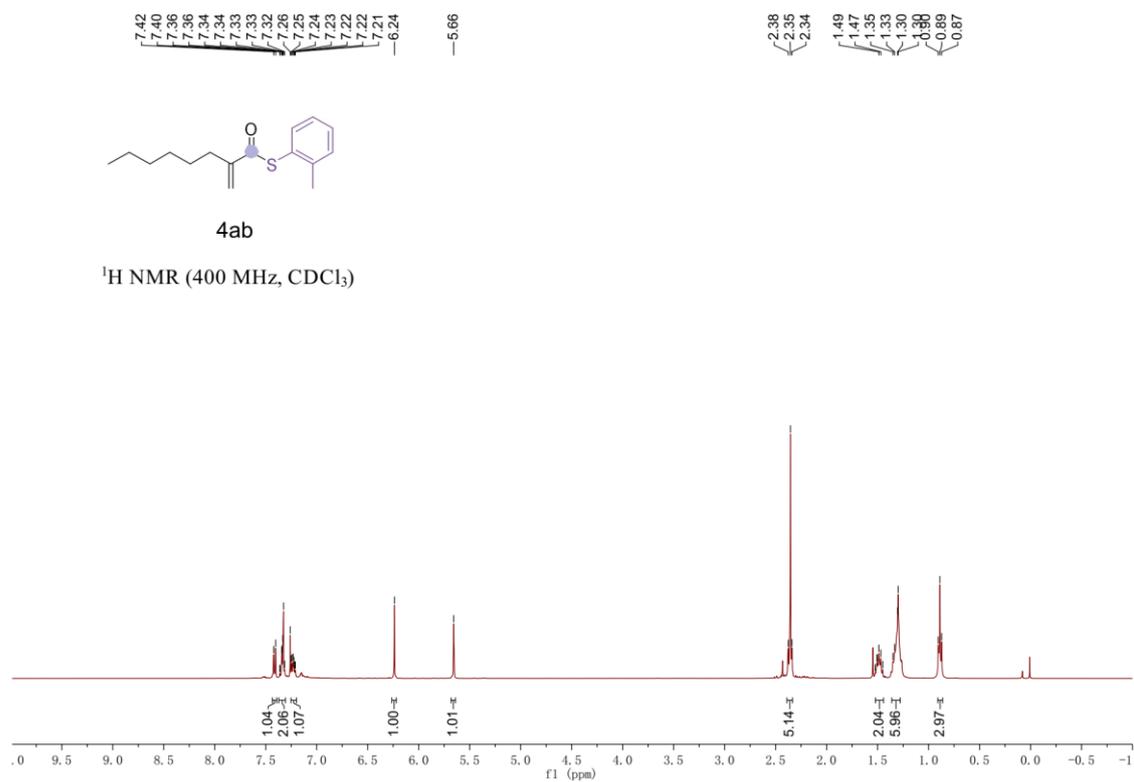
Supplementary Figure 70.  $^{13}\text{C NMR}$  spectrum of **3bx** in  $\text{CDCl}_3$  (101 MHz)



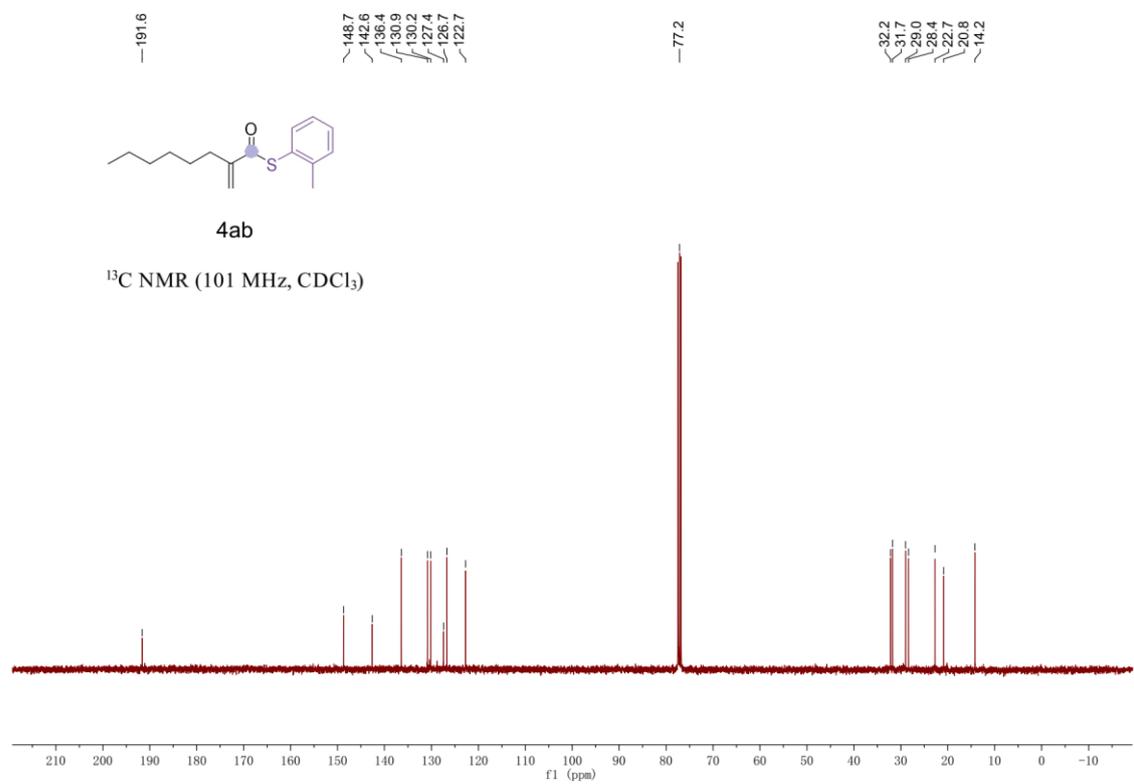
Supplementary Figure 71. <sup>1</sup>H NMR spectrum of **4aa** in CDCl<sub>3</sub> (400 MHz)



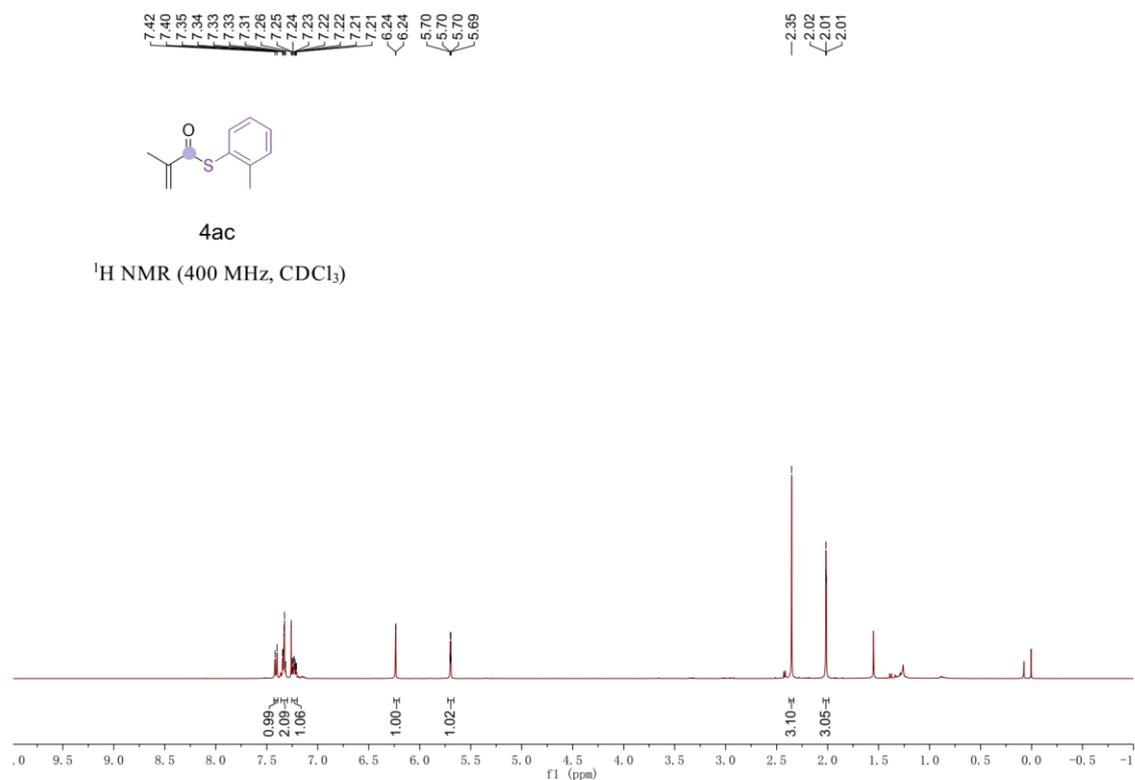
Supplementary Figure 72. <sup>13</sup>C NMR spectrum of **4aa** in CDCl<sub>3</sub> (101 MHz)



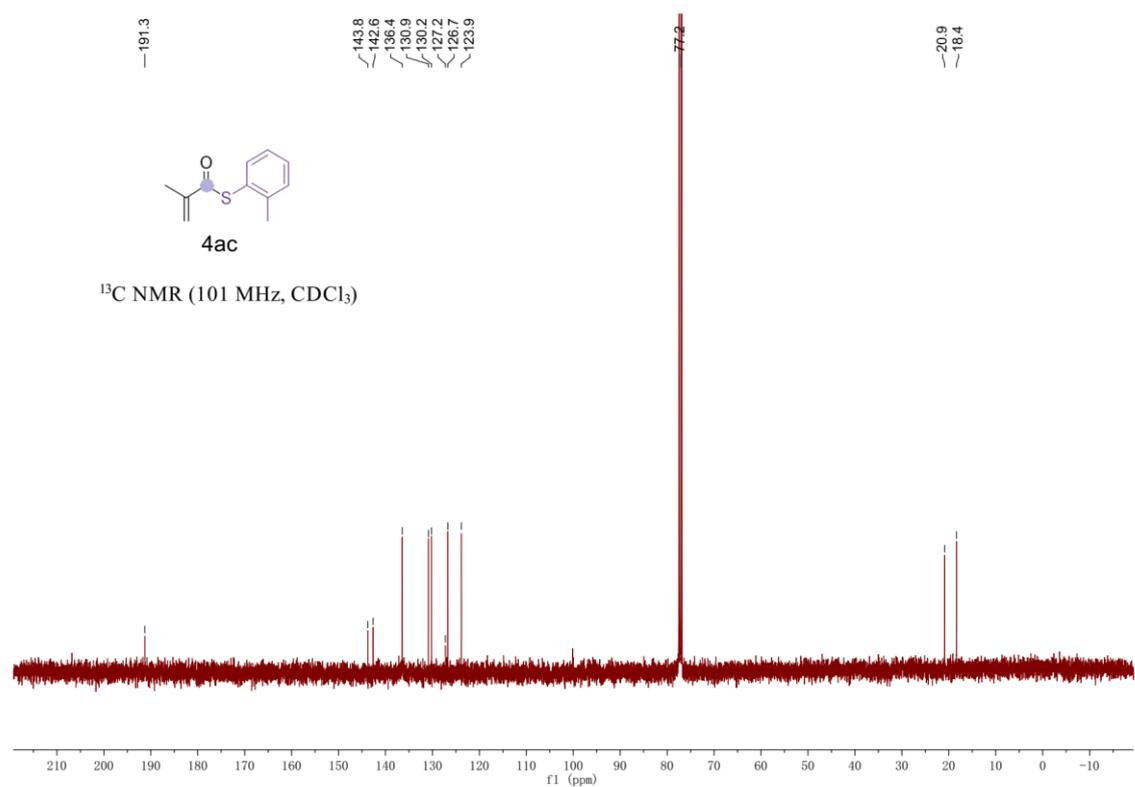
Supplementary Figure 73. <sup>1</sup>H NMR spectrum of **4ab** in CDCl<sub>3</sub> (400 MHz)



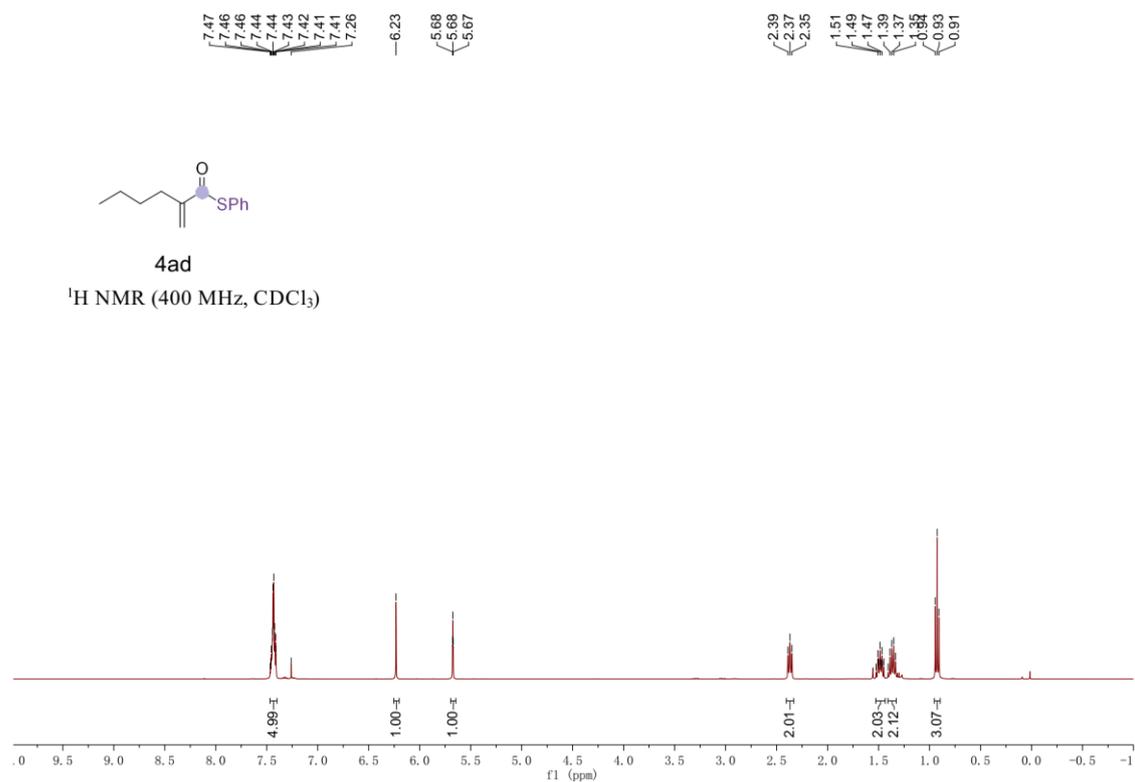
Supplementary Figure 74. <sup>13</sup>C NMR spectrum of **4ab** in CDCl<sub>3</sub> (101 MHz)



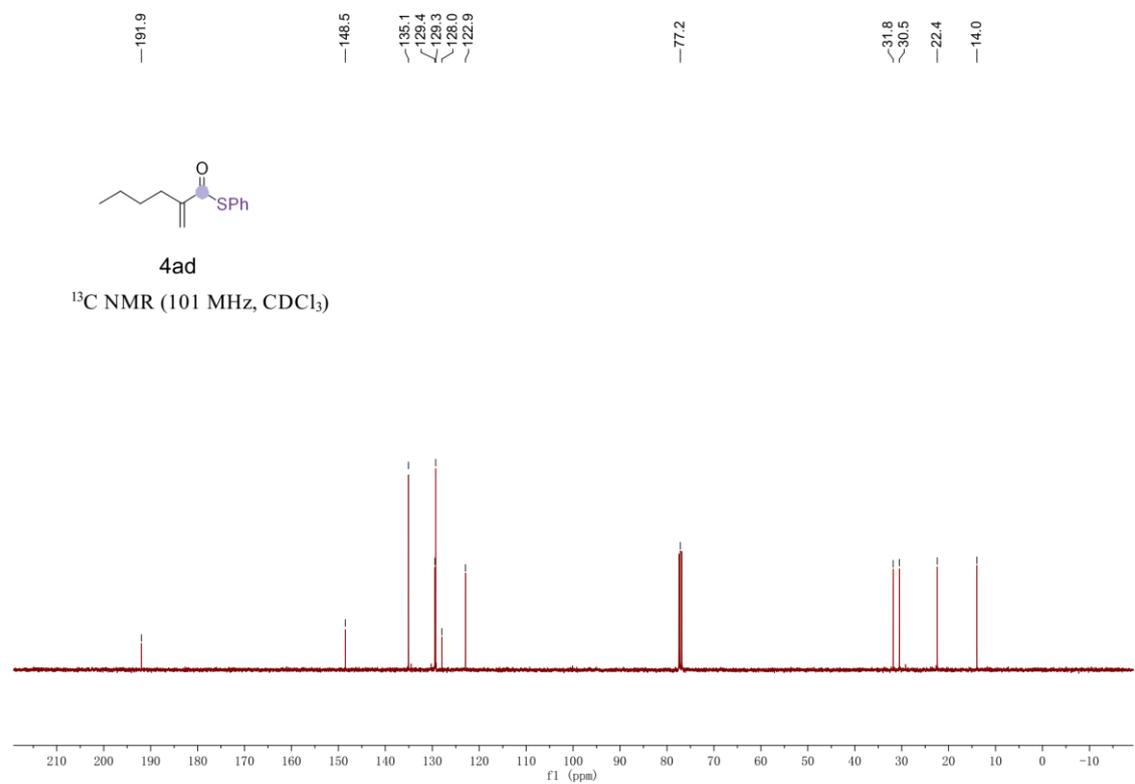
Supplementary Figure 75. <sup>1</sup>H NMR spectrum of **4ac** in CDCl<sub>3</sub> (400 MHz)



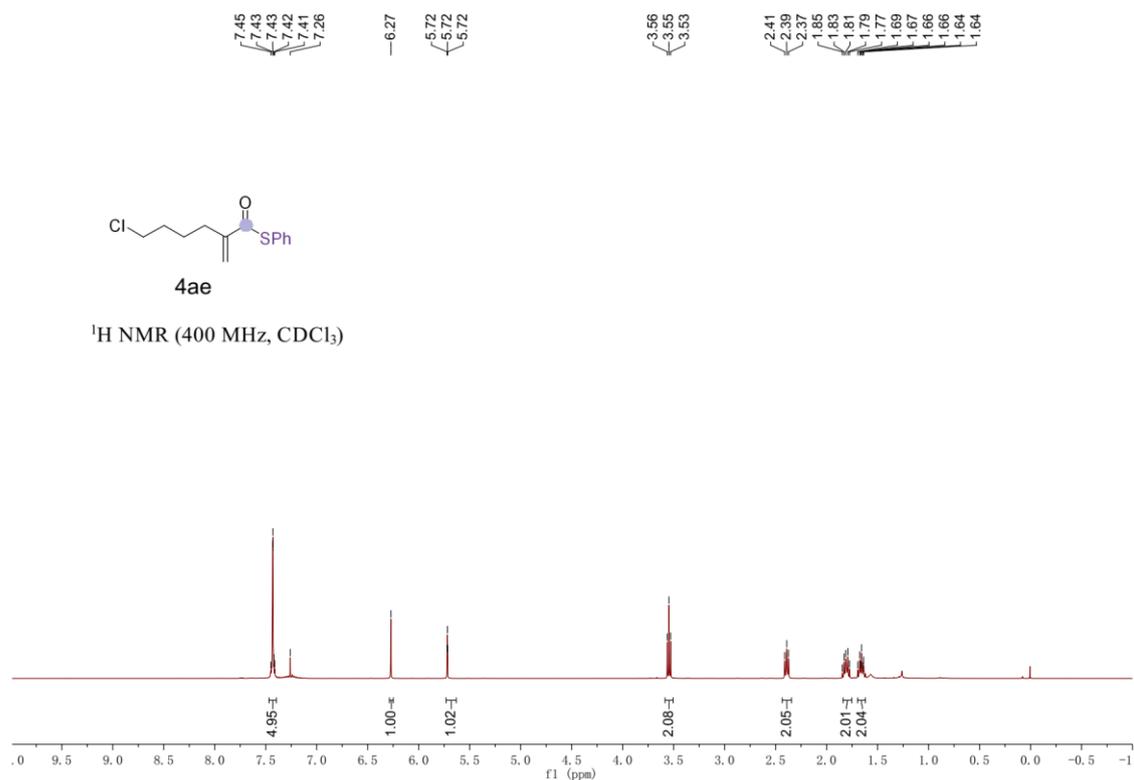
Supplementary Figure 76. <sup>13</sup>C NMR spectrum of **4ac** in CDCl<sub>3</sub> (101 MHz)



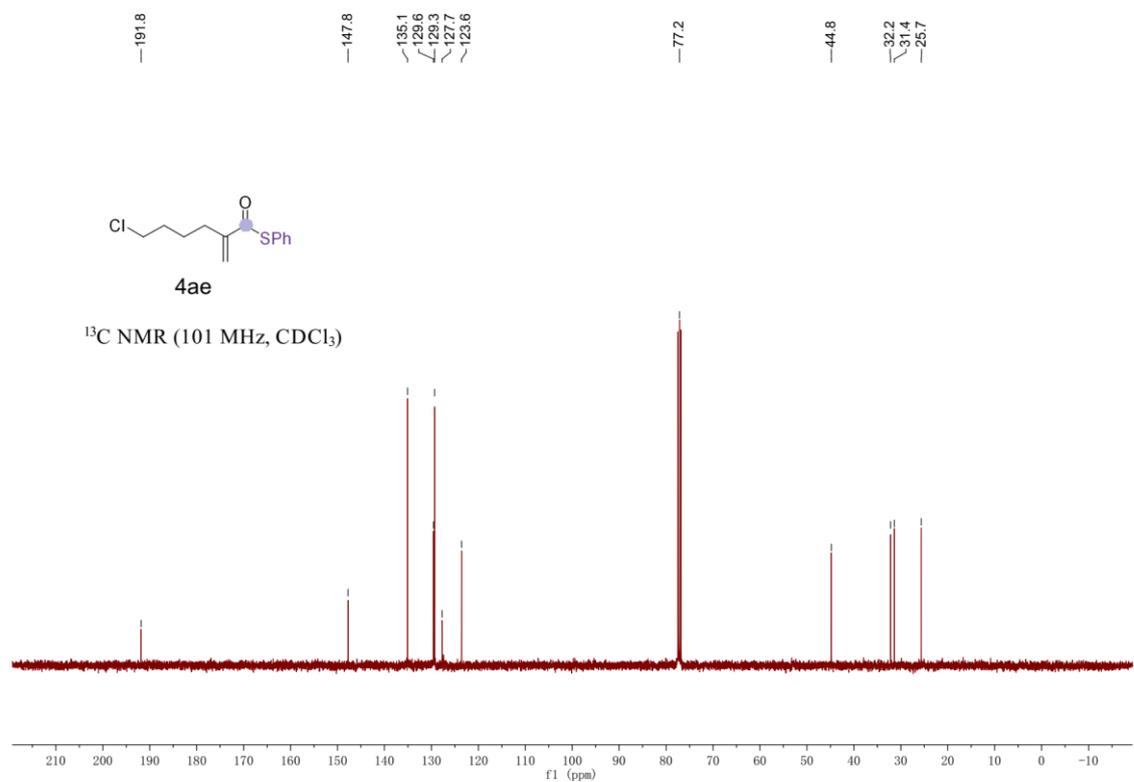
Supplementary Figure 77. <sup>1</sup>H NMR spectrum of **4ad** in CDCl<sub>3</sub> (400 MHz)



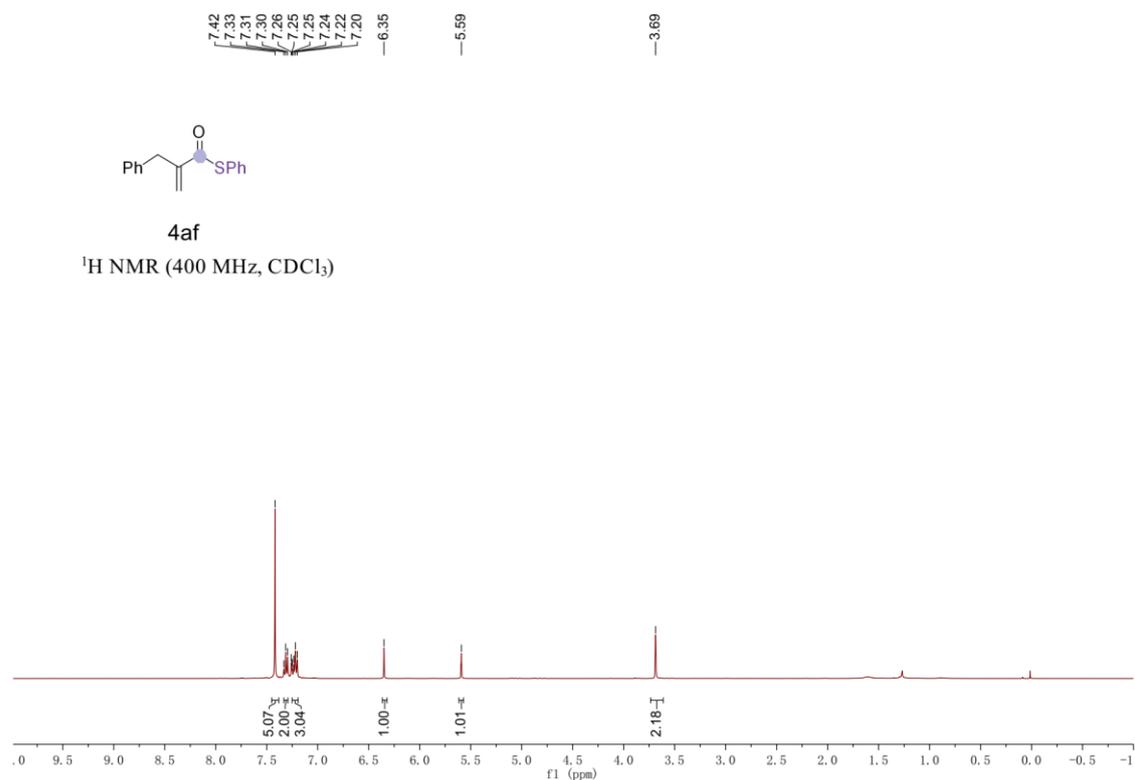
Supplementary Figure 78. <sup>13</sup>C NMR spectrum of **4ad** in CDCl<sub>3</sub> (101 MHz)



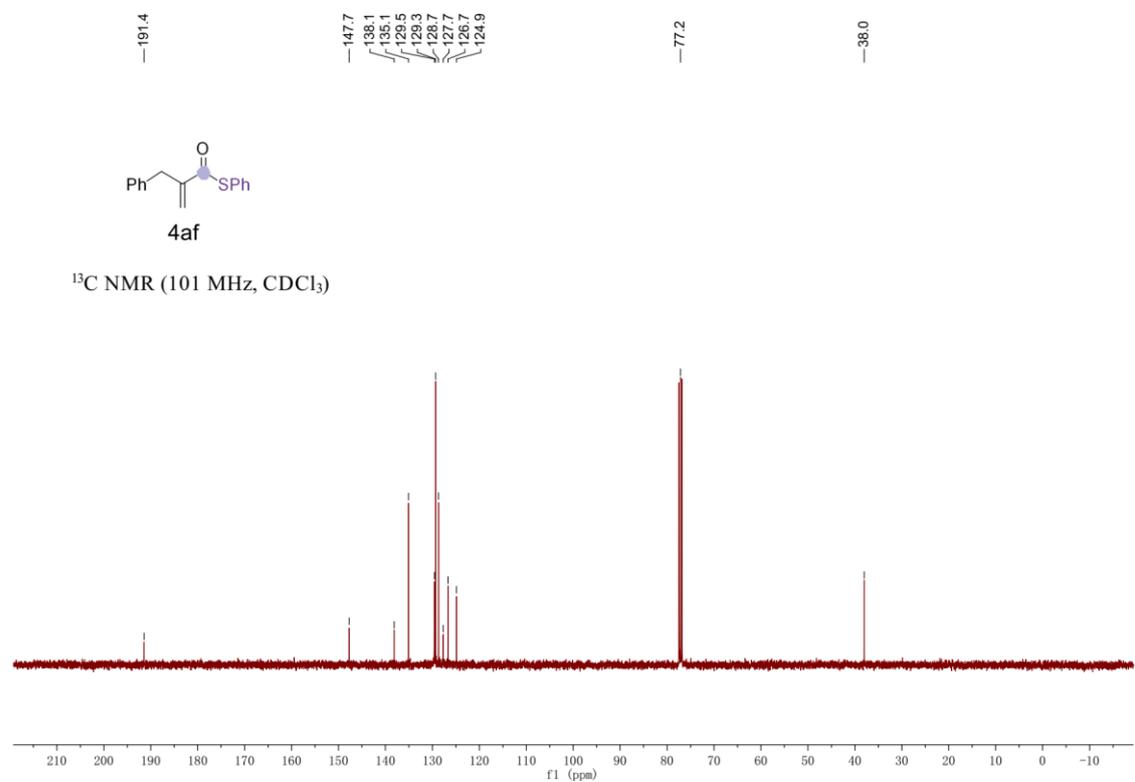
Supplementary Figure 79. <sup>1</sup>H NMR spectrum of **4ae** in CDCl<sub>3</sub> (400 MHz)



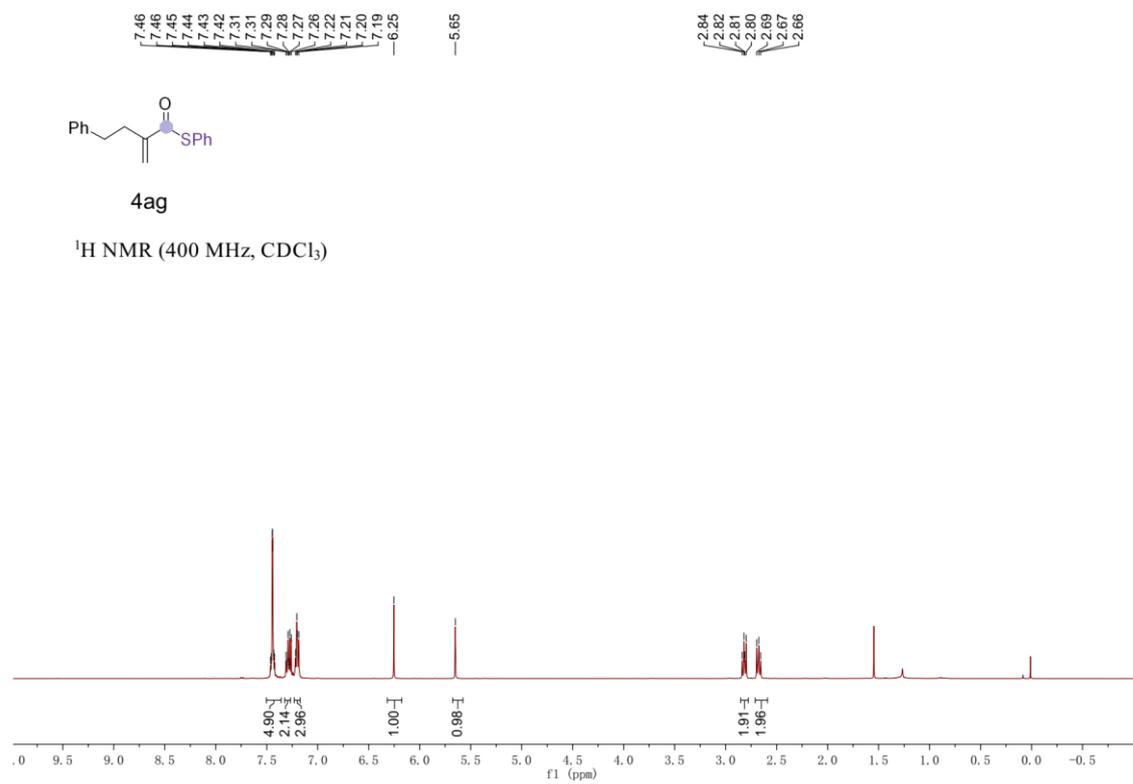
Supplementary Figure 80. <sup>13</sup>C NMR spectrum of **4ae** in CDCl<sub>3</sub> (101 MHz)



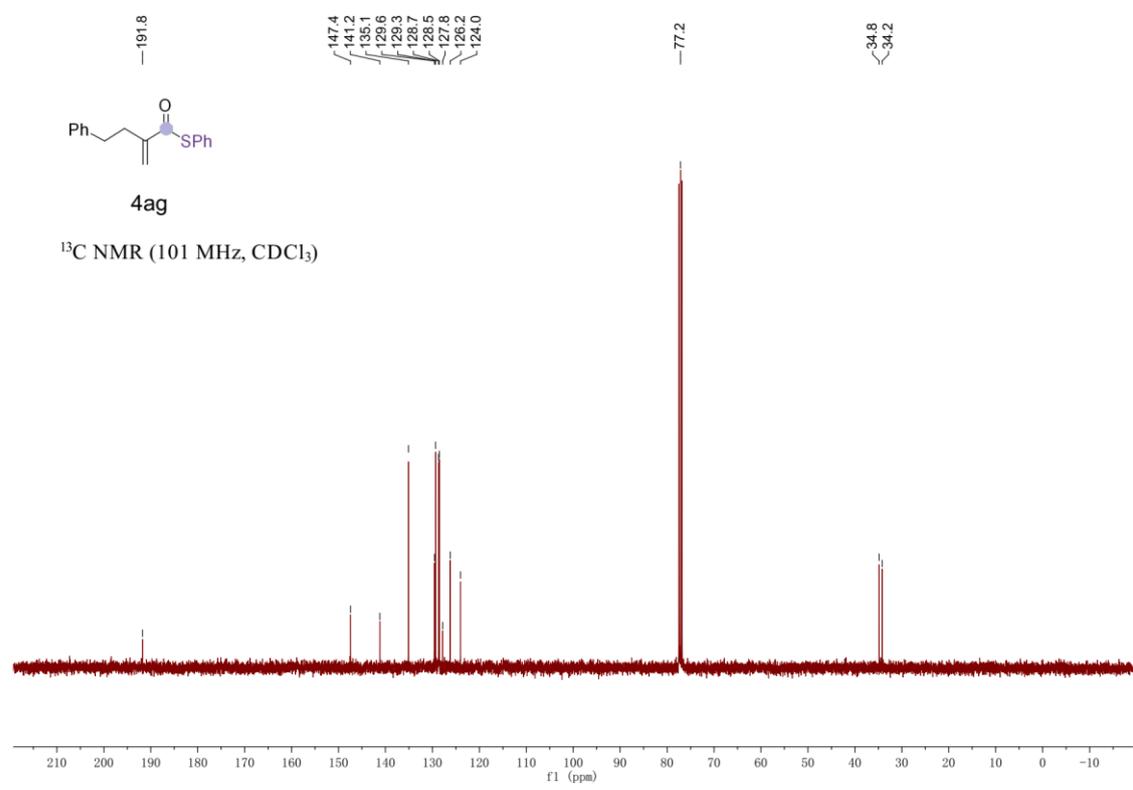
Supplementary Figure 81. <sup>1</sup>H NMR spectrum of **4af** in CDCl<sub>3</sub> (400 MHz)



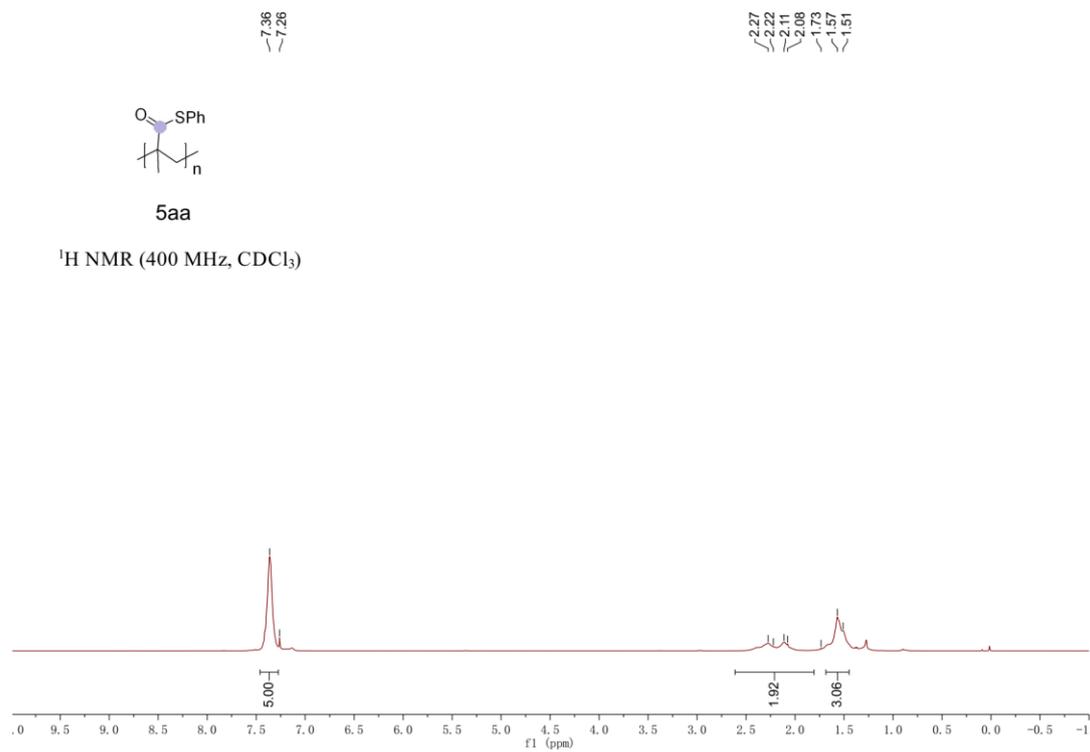
Supplementary Figure 82. <sup>13</sup>C NMR spectrum of **4af** in CDCl<sub>3</sub> (101 MHz)



Supplementary Figure 83. <sup>1</sup>H NMR spectrum of **4ag** in CDCl<sub>3</sub> (400 MHz)



Supplementary Figure 84. <sup>13</sup>C NMR spectrum of **4ag** in CDCl<sub>3</sub> (101 MHz)



Supplementary Figure 85. <sup>1</sup>H NMR spectrum of **5aa** in CDCl<sub>3</sub> (400 MHz)