

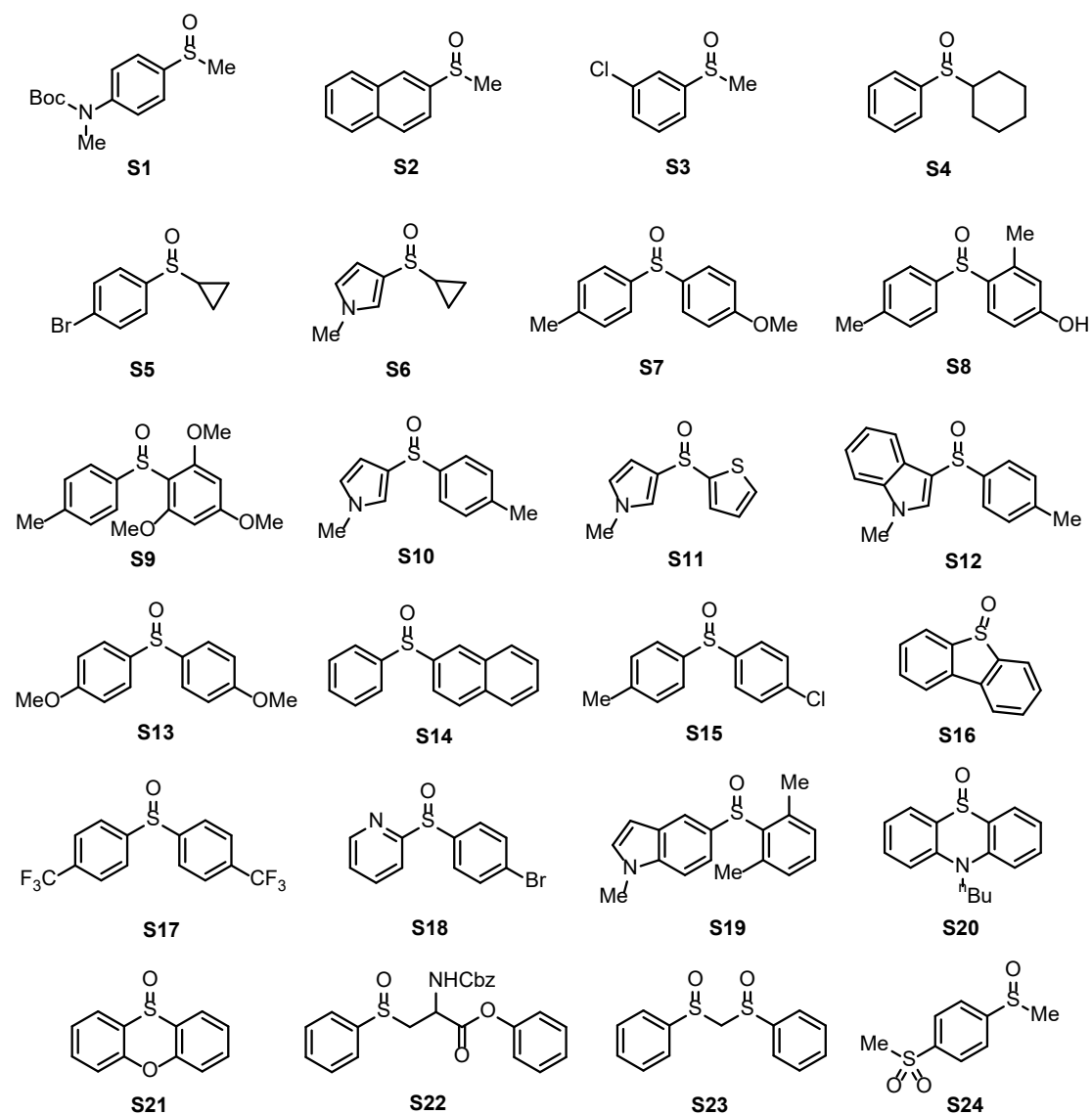
## Table of Contents

<b>1. General information</b>	<b>S2</b>
<b>2. Synthesis of sulfoxides</b>	<b>S3</b>
<b>3. General procedure</b>	<b>S4</b>
<b>4. Gram-scale reaction</b>	<b>S5</b>
<b>5. Decagram-scale reaction</b>	<b>S7</b>
<b>6. Control experiments</b>	<b>S8</b>
<b>7. Characterization data of sulfide</b>	<b>S10</b>
<b>8. References</b>	<b>S20</b>
<b>9. NMR Spectra</b>	<b>S21</b>

## 1. General information

All the reactions were carried out under N<sub>2</sub> atmosphere using glassware without being predried. Dichloroethane (DCE), aluminum trichloride (AlCl<sub>3</sub>), tetrabutylammonium chloride (<sup>n</sup>Bu<sub>4</sub>NCl), aluminum sheet, graphite felt are all obtained from commercial sources. The electrochemical instrument is HONGSHENGFENG DPS-305BM. Column chromatography was performed on silica gel (200-300 mesh). NMR spectra were recorded in CDCl<sub>3</sub> on 500 MHz spectrometers. <sup>1</sup>H NMR chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (0 ppm). The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and dt = doublet of triplets, m = multiplet. HRMS were obtained on an Ultima Global spectrometer with an ESI source. Melting points are uncorrected.

## 2. Synthesis of sulfoxides



The starting materials sulfoxides **S1-S2**<sup>1</sup>, **S3**<sup>2</sup>, **S4-S5**<sup>3</sup>, **S6-S12**<sup>4</sup>, **S13-S16**<sup>5</sup>, **S17**<sup>6</sup>, **S18**<sup>7</sup>, **S19**<sup>8</sup>, **S20**<sup>9</sup>, **S21**<sup>10</sup>, **S22-S23**<sup>11</sup>, **S24**<sup>12</sup> were prepared according to literature procedure.

### 3. General procedure

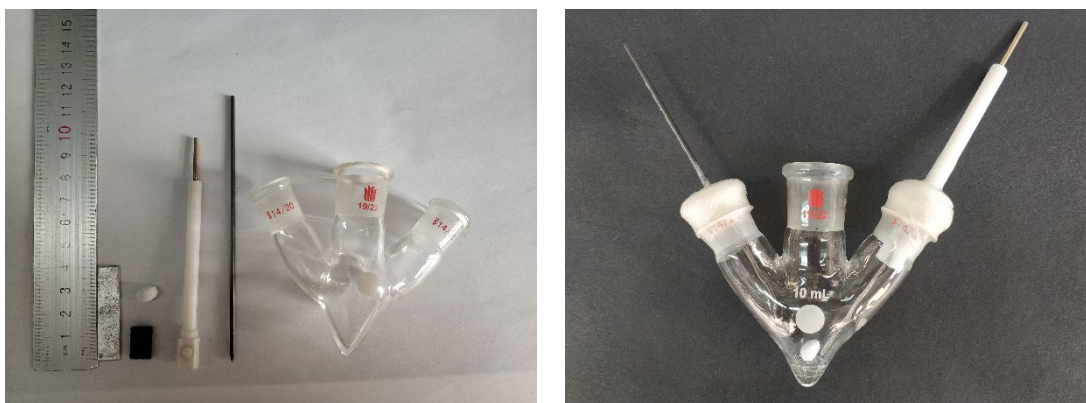


Figure S1. Components required for the reaction

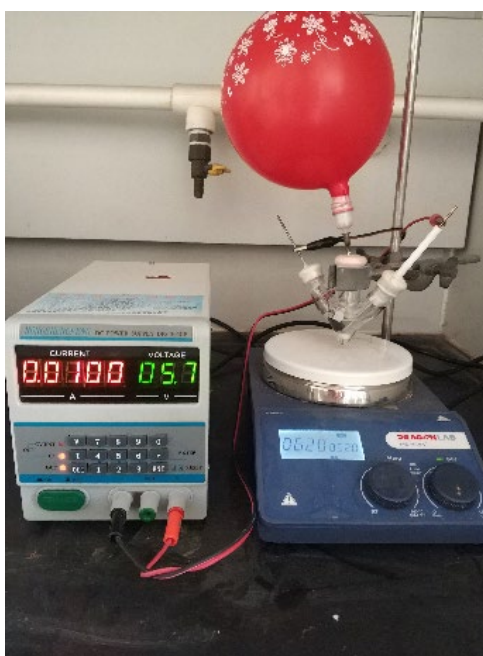
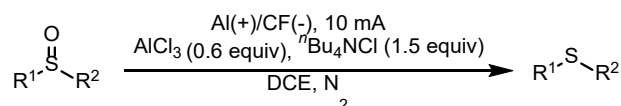


Figure S2. Typical reaction set up



To a solution of sulfoxide (0.4 mmol), AlCl<sub>3</sub> (0.24 mmol, 0.6 equiv), <sup>n</sup>Bu<sub>4</sub>NCl (0.6 mmol, 1.5 equiv), and DCE (5 mL) was equipped with an aluminum sheet (20 × 8 × 2 mm) as the anode and a graphite felt (12 × 8 × 2 mm) as the cathode. The whole cell was undivided cell. The reaction mixture was stirred at a constant current of 10 mA under N<sub>2</sub> at room temperature for 2-6 h. After completion of the reaction (monitored by TLC), 0.5 M HCl (10 mL) was added to quench the reaction and the mixture was

extracted with DCM ( $3 \times 10$  mL). The combined organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give the corresponding product.

#### 4. Gram-scale reaction

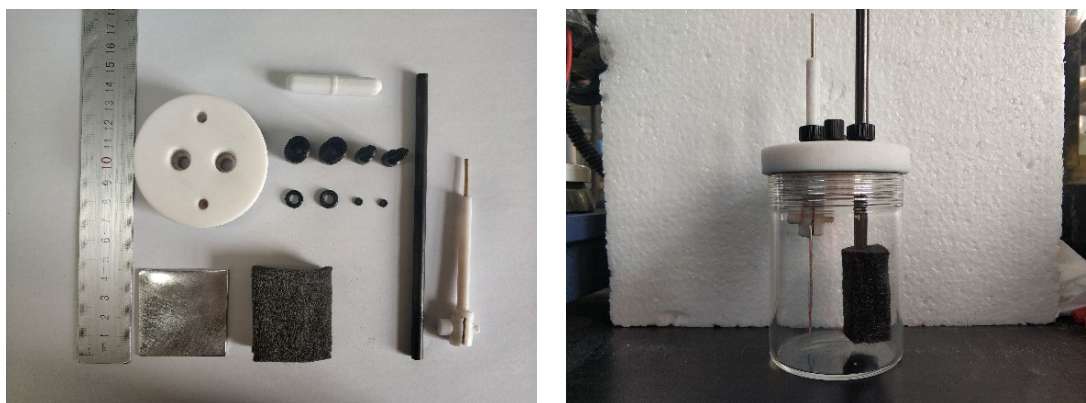
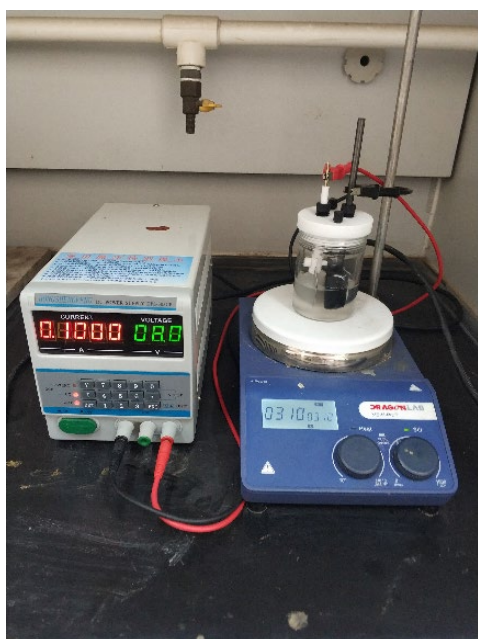


Figure S3. Components required for gram-scale reaction

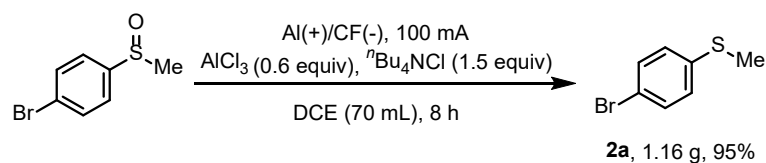


At the beginning of the reaction

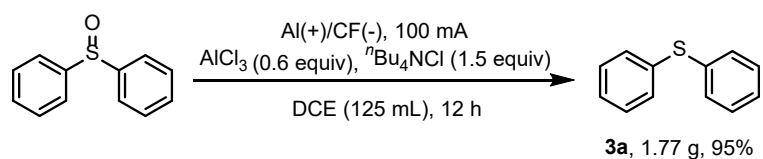


At the end of the reaction

Figure S4. Typical reaction set up for gram-scale reaction



To a solution of 1-bromo-4-(methylsulfinyl)benzene (1.31 g, 6 mmol),  $\text{AlCl}_3$  (0.48 g, 3.6 mmol),  $n\text{Bu}_4\text{NCl}$  (2.5 g, 9 mmol), and DCE (70 mL) was equipped with an aluminum sheet ( $45 \times 30 \times 1$  mm) as the anode and a graphite felt ( $45 \times 30 \times 10$  mm) as the cathode. The reaction was conducted in a 150 mL beaker-type cell (Figures S3 and S4). The reaction mixture was stirred at a constant current of 100 mA under  $\text{N}_2$  at room temperature for 8 h. After completion of the reaction (monitored by TLC), 0.5 M HCl (20 mL) was added to quench the reaction and the mixture was extracted with DCM ( $3 \times 20$  mL). The combined organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give product **2a** in 95% yield (1.15 g) as a light yellow oil.



To a solution of diphenyl sulfoxide (2.02 g, 10 mmol),  $\text{AlCl}_3$  (0.8 g, 6 mmol),  $n\text{Bu}_4\text{NCl}$  (4.17 g, 15 mmol), and DCE (125 mL) was equipped with an aluminum sheet ( $45 \times 30 \times 1$  mm) as the anode and a graphite felt ( $45 \times 30 \times 10$  mm) as the cathode. The reaction was conducted in a 150 mL beaker-type cell. The reaction mixture was stirred at a constant current of 100 mA under  $\text{N}_2$  at room temperature for 12 h. After completion of the reaction (monitored by TLC), 0.5 M HCl (20 mL) was added to quench the reaction and the mixture was extracted with DCM ( $3 \times 20$  mL). The combined organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give product **2a** in 95% yield (1.77 g) as a light yellow oil.

## 5. Decagram-scale reaction

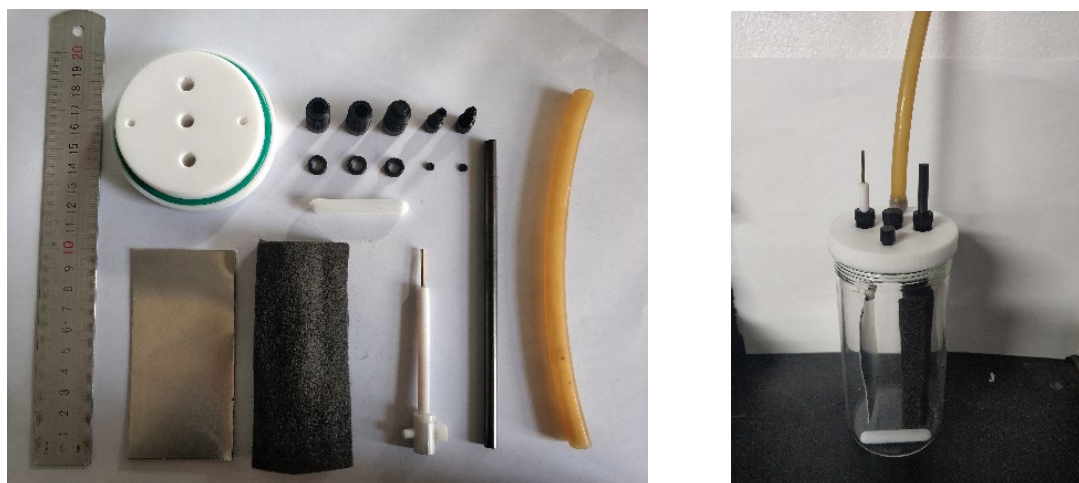


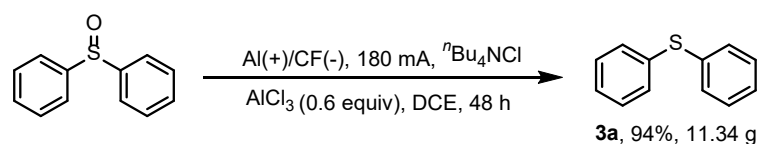
Figure S5. Components required for the decagram-scale reaction



At the beginning of the reaction

At the end of the reaction

Figure S6. Typical reaction set up for the decagram-scale reaction



To a solution of diphenyl sulfoxide (13.15 g, 65 mmol),  $\text{AlCl}_3$  (5.2 g, 39 mmol),  ${}^n\text{Bu}_4\text{NCl}$  (27.1 g, 97.5 mmol), and DCE (400 mL) was equipped with an aluminum sheet (50 × 100 × 1 mm) as the anode and a graphite felt (50 × 100 × 10 mm)

as the cathode. The reaction was conducted in a 500 mL beaker-type cell (Figures S5 and S6). The reaction mixture was stirred at a constant current of 180 mA under N<sub>2</sub> at room temperature for 48 h. After completion of the reaction (monitored by TLC), 0.5 M HCl (50 mL) was added to quench the reaction and the mixture was extracted with DCM (3 × 50 mL). The combined organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give product **2a** in 94% yield (11.34 g, Figure S7) as a light yellow oil.

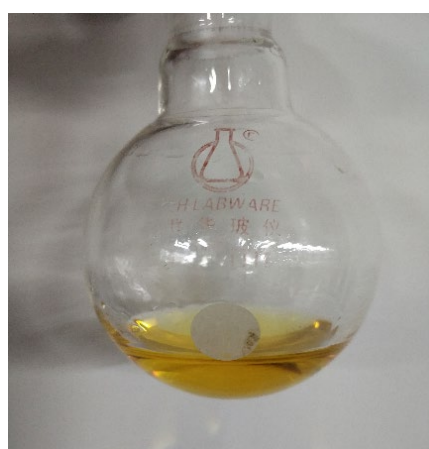
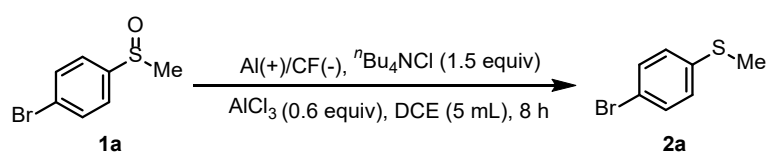


Figure S7. Pure product of **2a**

## 6. Control experiments

### Constant potential electrolysis

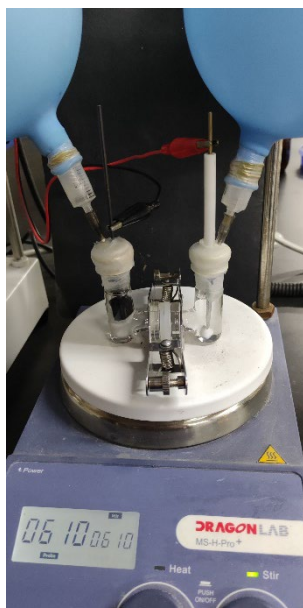


entry	constant potential	yield (%)
1	$E_{\text{cathode}} = -2.0 \text{ V vs Ag/AgCl}$	trace
2	$E_{\text{cathode}} = -2.8 \text{ V vs Ag/AgCl}$	76

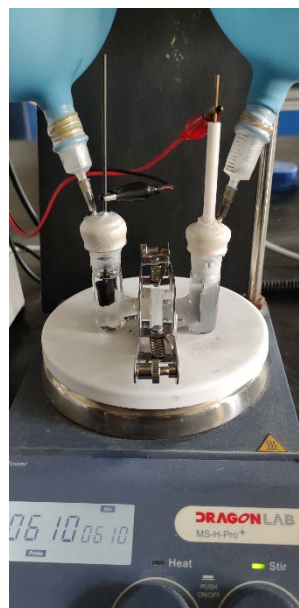
The reaction was proceeded under standard conditions with Ag/AgCl as a reference electrode. Cathodic potential was controlled by the electrochemical workstation (Corrtest CS300H). Compound **2a** was obtained by flash column chromatography.



## Divided cell electrolysis

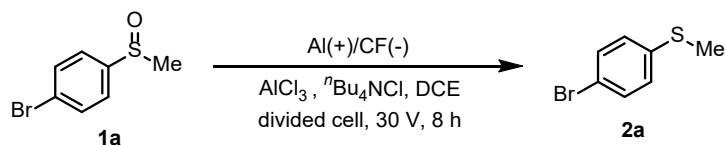


At the beginning of the reaction



At the end of the reaction

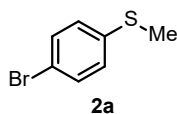
Figure S8. Typical reaction set up of divided cell electrolysis



entry	AlCl <sub>3</sub> in the cathode chamber	yield (%)
1	-	0
2	0.6 equiv	38

The model reaction was carried out in a divided cell equipped with a proton exchange membrane (DuPont). Substrate **1a** (0.4 mmol), AlCl<sub>3</sub> (0.24 mmol, 0.6 equiv), <sup>t</sup>Bu<sub>4</sub>NCl (5 mmol) and DCE (5 mL) were added to the cathode chamber while the anode chamber was added <sup>t</sup>Bu<sub>4</sub>NCl (5 mmol) and DCE (5 mL). The reaction mixture was stirred at a constant cell potential of 30 V at room temperature until the current dropped to 1 mA (8 h). Compound **2a** was obtained by flash column chromatography.

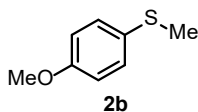
## 7. Characterization data of sulfide



76 mg, 94% yield. Yellow oil. The spectra matched with the previous report.<sup>13</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 2.46 (s, 3H).

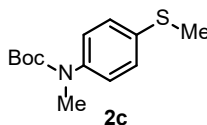
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 137.8, 131.9, 128.2, 118.7, 16.0.



57 mg, 92% yield. Light yellow oil. The spectra matched with the previous report.<sup>14</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.29 – 7.25 (m, 2H), 6.90 – 6.82 (m, 2H), 3.79 (s, 3H), 2.45 (s, 3H).

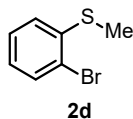
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.3, 130.3, 128.9, 114.7, 55.5, 18.2.



52 mg, 51% yield. Yellow oil. The spectra matched with the previous report.<sup>15</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.21 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 3.22 (s, 3H), 2.46 (s, 3H), 1.44 (s, 9H).

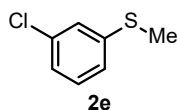
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.8, 141.3, 135.1, 127.2, 126.0, 80.4, 37.4, 28.4, 16.4.



65 mg, 80% yield. Colorless oil. The spectra matched with the previous report.<sup>16</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.52 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.13 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.03 – 6.97 (m, 1H), 2.47 (s, 3H).

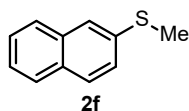
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.8, 132.8, 127.9, 125.8, 125.5, 121.9, 15.8.



54 mg, 85% yield. Colorless oil. The spectra matched with the previous report.<sup>17</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.22 – 7.17 (m, 2H), 7.14 – 7.08 (m, 2H), 2.48 (s, 3H).

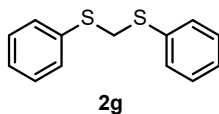
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 140.8, 134.9, 129.9, 126.0, 125.1, 124.6, 15.7.



67 mg, 96% yield. White solid. M.p = 124 – 126 °C. The spectra matched with the previous report.<sup>18</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.46 – 7.38 (m, 2H), 2.61 (s, 3H).

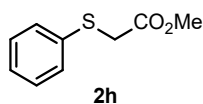
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 136.2, 134.0, 131.4, 128.3, 127.8, 126.9, 126.7, 125.8, 125.3, 123.5, 15.9.



68 mg, 73% yield. White solid. M.p = 39 – 41 °C. The spectra matched with the previous report.<sup>19</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.39 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.26 – 7.23 (m, 2H), 4.34 (s, 2H).

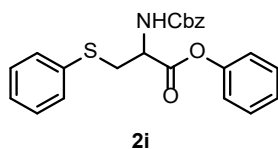
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 135.1, 130.8, 129.1, 127.3, 40.7.



39 mg, 54% yield. Colorless oil. The spectra matched with the previous report.<sup>13</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.30 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.25 – 7.20 (m, 1H), 3.71 (s, 3H), 3.65 (s, 2H).

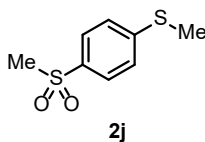
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.3, 135.0, 130.0, 129.2, 127.1, 52.6, 36.6.



110 mg, 67% yield. White solid. M.p = 71 – 73 °C. The spectra matched with the previous report.<sup>11</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.36 – 7.31 (m, 7H), 7.27 (dd, *J* = 8.3, 6.4 Hz, 2H), 7.24 – 7.20 (m, 2H), 6.94 (d, *J* = 7.9 Hz, 2H), 5.64 (d, *J* = 7.9 Hz, 1H), 5.13 – 5.05 (m, 2H), 4.90 – 4.84 (m, 1H), 3.62 – 3.50 (m, 2H).

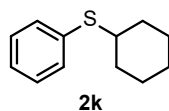
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 169.2, 155.6, 150.3, 136.1, 134.6, 131.2, 129.6, 129.4, 128.7, 128.4, 128.2, 127.4, 126.4, 121.4, 67.3, 54.3, 37.2.



70 mg, 86% yield. White solid. M.p = 97 – 99 °C. The spectra matched with the previous report.<sup>20</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 3.02 (s, 3H), 2.51 (s, 3H).

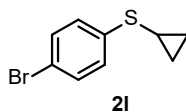
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 147.3, 136.3, 127.7, 125.5, 44.8, 14.8.



74 mg, 94% yield. Colorless oil. The spectra matched with the previous report.<sup>21</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.40 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 3.16 – 3.07 (m, 1H), 1.99 (d, *J* = 12.2 Hz, 2H), 1.78 (dd, *J* = 8.7, 3.8 Hz, 2H), 1.66 – 1.57 (m, 1H), 1.41 – 1.25 (m, 5H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 135.3, 132.0, 128.9, 126.7, 46.7, 33.5, 26.2, 25.9.

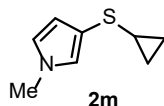


65 mg, 70% yield. Light yellow oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 2.20 – 2.13 (m, 1H), 1.12 – 1.03 (m, 2H), 0.72 – 0.66 (m, 2H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 138.3, 131.8, 128.1, 118.6, 12.2, 8.7.

**HRMS** (ESI-TOF, [M + H<sup>+</sup>]): calcd for C<sub>9</sub>H<sub>9</sub>BrS, 228.9687, found 228.9692.

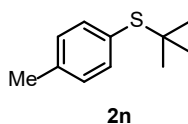


33 mg, 54% yield. Yellow oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 6.68 (t, *J* = 2.0 Hz, 1H), 6.58 (t, *J* = 2.5 Hz, 1H), 6.24 – 6.19 (m, 1H), 3.63 (s, 3H), 2.13 – 2.06 (m, 1H), 0.86 – 0.77 (m, 2H), 0.67 – 0.61 (m, 2H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 124.6, 122.5, 113.3, 112.8, 36.5, 17.1, 8.4.

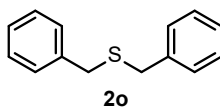
**HRMS** (ESI-TOF, [M + H<sup>+</sup>]): calcd for C<sub>8</sub>H<sub>11</sub>NS, 154.0690, found 154.0689.



33 mg, 46% yield. Colorless oil. The spectra matched with the previous report.<sup>22</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 2.36 (s, 3H), 1.27 (s, 9H).

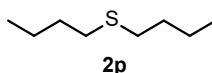
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 138.9, 137.5, 129.4, 129.3, 45.7, 31.0, 21.4.



55 mg, 64% yield. Colorless oil. The spectra matched with the previous report.<sup>14</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.55 – 6.65 (m, 10H), 3.62 (s, 4H).

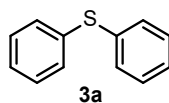
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 138.3, 129.1, 128.6, 127.1, 35.7.



52 mg, 88% yield. Colorless oil. The spectra matched with the previous report.<sup>14</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 2.50 (dd, *J* = 8.1, 6.8 Hz, 4H), 1.59 – 1.53 (m, 4H), 1.44 – 1.36 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H).

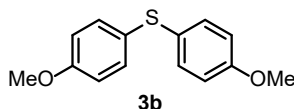
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  32.0, 22.2, 13.9.



67 mg, 90% yield. Light yellow oil. The spectra matched with the previous report.<sup>13</sup>

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J = 7.2$  Hz, 4H), 7.29 (t,  $J = 7.5$  Hz, 4H), 7.25 – 7.22 (m, 2H).

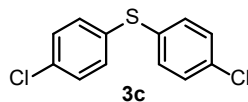
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  135.9, 131.2, 129.3, 127.2.



99 mg, 94% yield. Light yellow oil. The spectra matched with the previous report.<sup>21</sup>

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J = 8.7$  Hz, 4H), 6.84 (d,  $J = 8.7$  Hz, 4H), 3.79 (s, 6H).

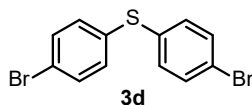
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 132.8, 127.6, 114.9, 55.5.



53 mg, 52% yield. White solid. M.p = 87 – 89 °C. The spectra matched with the previous report.<sup>23</sup>

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.23 (m, 8H).

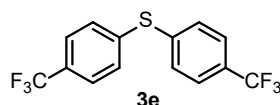
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  134.1, 133.6, 132.4, 129.6.



77 mg, 56% yield. White solid. M.p = 112 – 114 °C. The spectra matched with the previous report.<sup>23</sup>

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.38 (m, 4H), 7.22 – 7.15 (m, 4H).

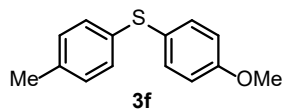
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  134.6, 132.7, 132.6, 121.6.



52 mg, 40% yield. Colorless oil. The spectra matched with the previous report.<sup>16</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.6 (d, *J* = 8.2 Hz, 4H), 7.5 (d, *J* = 8.3 Hz, 4H).

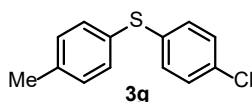
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 139.7, 131.2, 129.8 (q, *J* = 32.8 Hz), 126.4 (d, *J* = 3.7 Hz), 124.0 (q, *J* = 272.1 Hz).



90 mg, 98% yield. Yellow oil. The spectra matched with the previous report.<sup>24</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.39 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 2.32 (s, 3H).

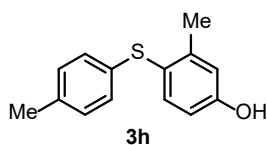
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 159.5, 136.2, 134.5, 129.9, 129.5, 125.7, 115.0, 55.4, 21.1.



84 mg, 90% yield. White solid. M.p = 110 – 112 °C. The spectra matched with the previous report.<sup>23</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.29 (m, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.17 (dd, *J* = 10.9, 8.3 Hz, 4H), 2.36 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 138.2, 136.1, 132.6, 132.4, 130.9, 130.8, 130.3, 129.3, 21.3.

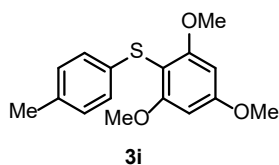


28 mg, 30% yield. Light red oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 8.3 Hz, 1H), 7.08 – 6.98 (m, 4H), 6.78 (d, *J* = 2.8 Hz, 1H), 6.70 – 6.64 (m, 1H), 5.27 – 5.10 (m, 1H), 2.33 (s, 3H), 2.30 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 156.1, 143.6, 136.8, 135.5, 134.4, 129.9, 128.0, 124.1, 117.8, 114.0, 21.0.

**HRMS** (ESI-TOF, [M - H<sup>+</sup>]): calcd for C<sub>14</sub>H<sub>14</sub>OS, 229.0693, found 229.0702.

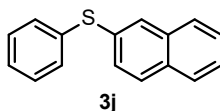


71 mg, 84% yield. Yellow solid. M.p = 90 – 92 °C

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.00 – 6.90 (m, 4H), 6.21 (s, 2H), 3.86 (s, 3H), 3.81 (s, 6H), 2.25 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 162.9, 162.6, 135.1, 134.2, 129.4, 126.1, 99.4, 91.3, 56.4, 55.5, 21.0.

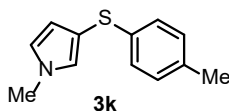
**HRMS** (ESI-TOF, [M + Na<sup>+</sup>]): calcd for C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>S, 313.0874, found 313.0872.



91 mg, 96% yield. Yellow oil. The spectra matched with the previous report.<sup>18</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.86 (s, 1H), 7.84 – 7.80 (m, 1H), 7.77 (dd, *J* = 16.2, 8.93 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 136.0, 133.9, 133.2, 132.4, 131.1, 130.0, 129.4, 129.0, 128.9, 127.9, 127.6, 127.2, 126.7, 126.3.

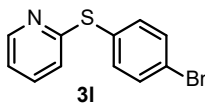


59 mg, 73% yield. Yellow oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.08 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 6.25 (dd, *J* = 2.9, 1.5 Hz, 1H), 3.68 (s, 3H), 2.29 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 137.2, 134.5, 129.5, 127.5, 126.3, 123.2, 114.8, 109.1, 36.6, 21.0.

**HRMS** (ESI-TOF, [M + H<sup>+</sup>]): calcd for C<sub>12</sub>H<sub>13</sub>NS, 204.0847, found 204.0845.

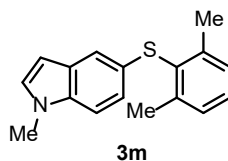




46 mg, 42% yield. Yellow oil. The spectra matched with the previous report.<sup>25</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.42 (d, *J* = 7.0 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.02 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 160.5, 149.9, 137.0, 136.3, 132.9, 130.5, 123.6, 121.9, 120.4.

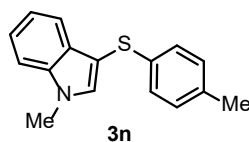


74 mg, 69% yield. Yellow solid. M.p = 82 – 84 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.24 – 7.20 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 3H), 7.01 – 6.94 (m, 2H), 6.33 (d, *J* = 3.1 Hz, 1H), 3.74 (s, 3H), 2.48 (s, 6H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 143.7, 135.2, 132.8, 129.4, 129.4, 128.8, 128.4, 127.4, 121.5, 119.1, 109.9, 100.5, 33.0, 22.2.

**HRMS** (ESI-TOF, [M + H<sup>+</sup>]): calcd for C<sub>17</sub>H<sub>17</sub>NS, 268.1160, found 268.1157.

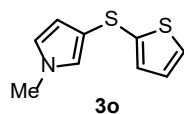


60 mg, 63% yield. White solid. M.p = 74 – 76 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.05 – 6.86 (m, 4H), 3.80 (s, 3H), 2.29 – 2.13 (m, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 137.6, 136.1, 135.0, 134.6, 130.0, 129.6, 126.3, 122.6, 120.5, 119.9, 109.8, 101.4, 33.2, 21.0.

**HRMS** (ESI-TOF, [M + H<sup>+</sup>]): calcd for C<sub>16</sub>H<sub>15</sub>NS, 254.1003, found 254.1007.

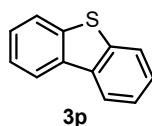


43 mg, 56% yield. Yellow oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.21 (dd, *J* = 5.3, 1.4 Hz, 1H), 7.05 (dd, *J* = 3.6, 1.4 Hz, 1H), 6.90 (dd, *J* = 5.3, 3.6 Hz, 1H), 6.79 (t, *J* = 2.1 Hz, 1H), 6.57 (t, *J* = 2.5 Hz, 1H), 6.25 (dd, *J* = 2.8, 1.7 Hz, 1H), 3.63 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 139.4, 129.5, 127.4, 125.8, 122.8, 113.3, 112.9, 36.6.

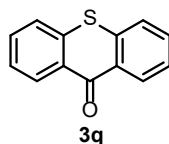
**HRMS** (ESI-TOF, [M + H<sup>+</sup>]): calcd for C<sub>9</sub>H<sub>9</sub>NS<sub>2</sub>, 196.0255, found 196.0253.



43 mg, 58% yield. White solid. M.p = 87 – 89 °C. The spectra matched with the previous report.<sup>26</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.20 – 8.14 (m, 2H), 7.90 – 7.85 (m, 2H), 7.50 – 7.45 (m, 4H).

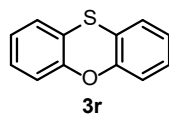
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 139.4, 135.6, 126.7, 124.4, 122.8, 121.6.



71 mg, 84% yield. Yellow solid. M.p = 207 – 209 °C. The spectra matched with the previous report.<sup>27</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.64 – 8.56 (m, 2H), 7.63 – 7.58 (m, 2H), 7.58 – 7.53 (m, 2H), 7.49 – 7.44 (m, 2H).

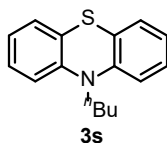
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 180.1, 137.4, 132.4, 130.0, 129.4, 126.4, 126.1.



69 mg, 86% yield. White solid. M.p = 54 – 56 °C. The spectra matched with the previous report.<sup>18</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.16 – 7.12 (m, 2H), 7.10 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.05 – 6.98 (m, 4H).

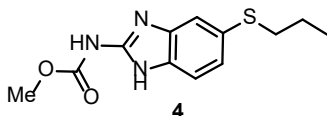
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 152.3, 127.8, 126.9, 124.6, 120.2, 117.9.



96 mg, 94% yield. Light yellow oil. The spectra matched with the previous report.<sup>28</sup>

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.15 (d, *J* = 7.3 Hz, 4H), 6.89 (d, *J* = 9.2 Hz, 4H), 3.86 (s, 2H), 1.84 – 1.77 (m, 2H), 1.51 – 1.43 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 145.4, 127.5, 127.3, 125.1, 122.4, 115.6, 47.3, 29.2, 20.3, 14.0.



80 mg, 74% yield. Yellow solid. The spectra matched with the previous report.<sup>29</sup>

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 11.78 (s, 2H), 7.45 (s, 1H), 7.35 (s, 1H), 7.10 (s, 1H), 3.77 (s, 3H), 2.85 (t, *J* = 7.1 Hz, 2H), 1.53 (m, 2H), 0.96 (s, 3H).

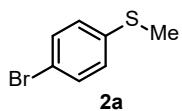
**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>) δ 154.7, 147.8, 136.7, 135.3, 126.9, 124.1, 115.9, 114.2, 52.5, 36.7, 22.1, 13.1.

**HRMS** (ESI-TOF, [M + H<sup>+</sup>]): calcd for C<sub>12</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>S, 266.0963, found 266.0967.

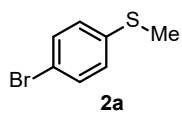
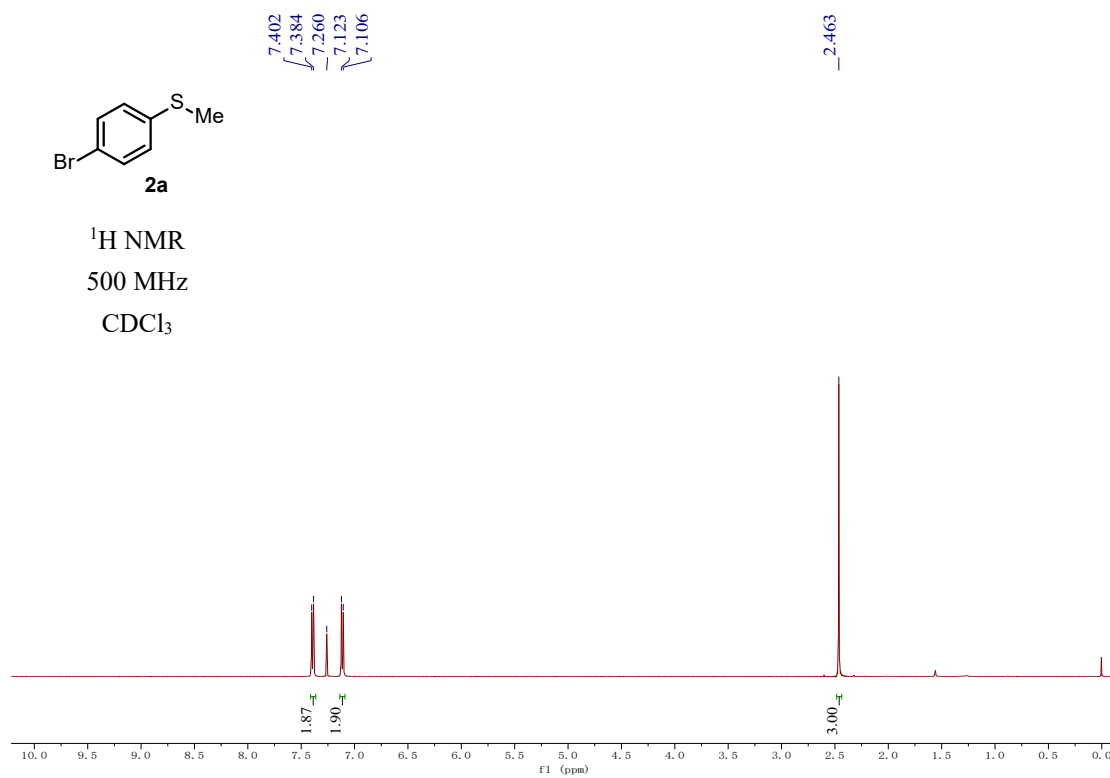
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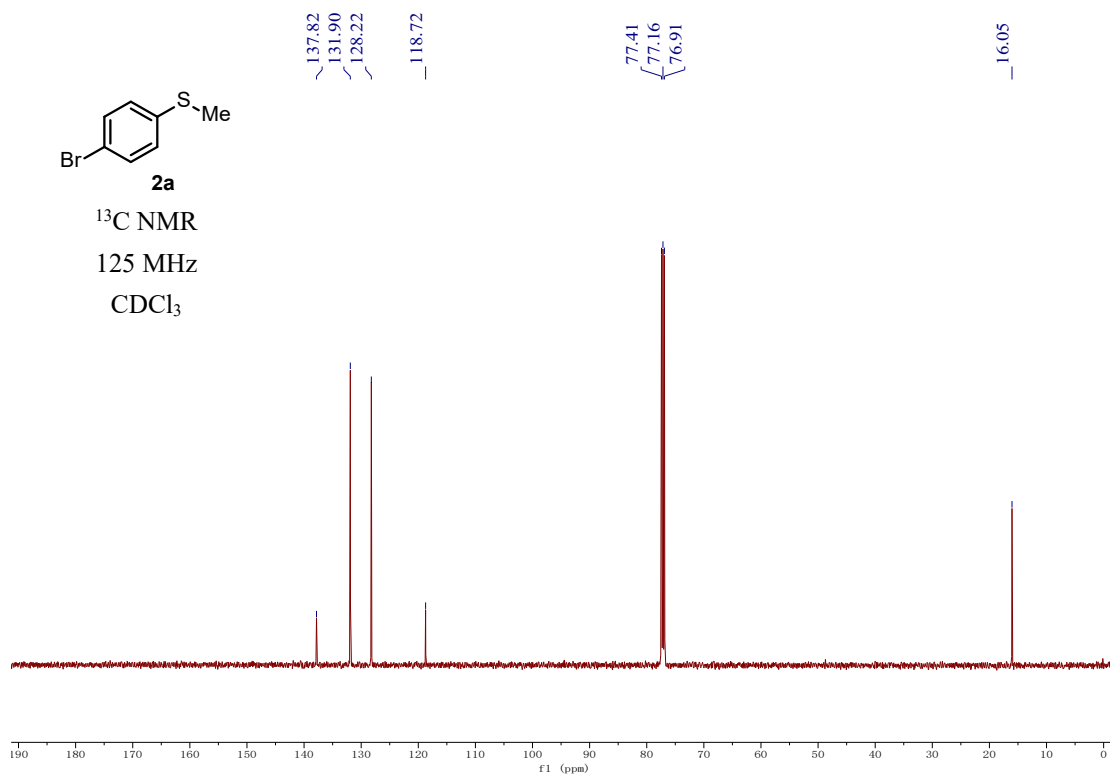
## 9. NMR Spectra

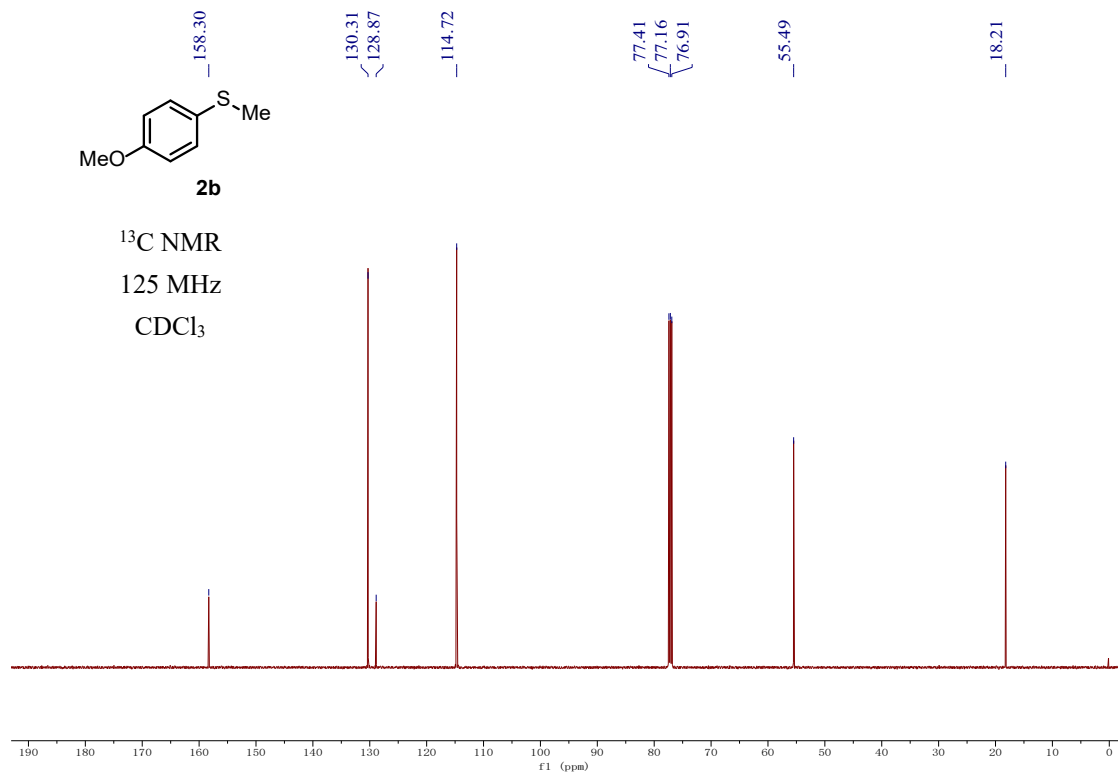
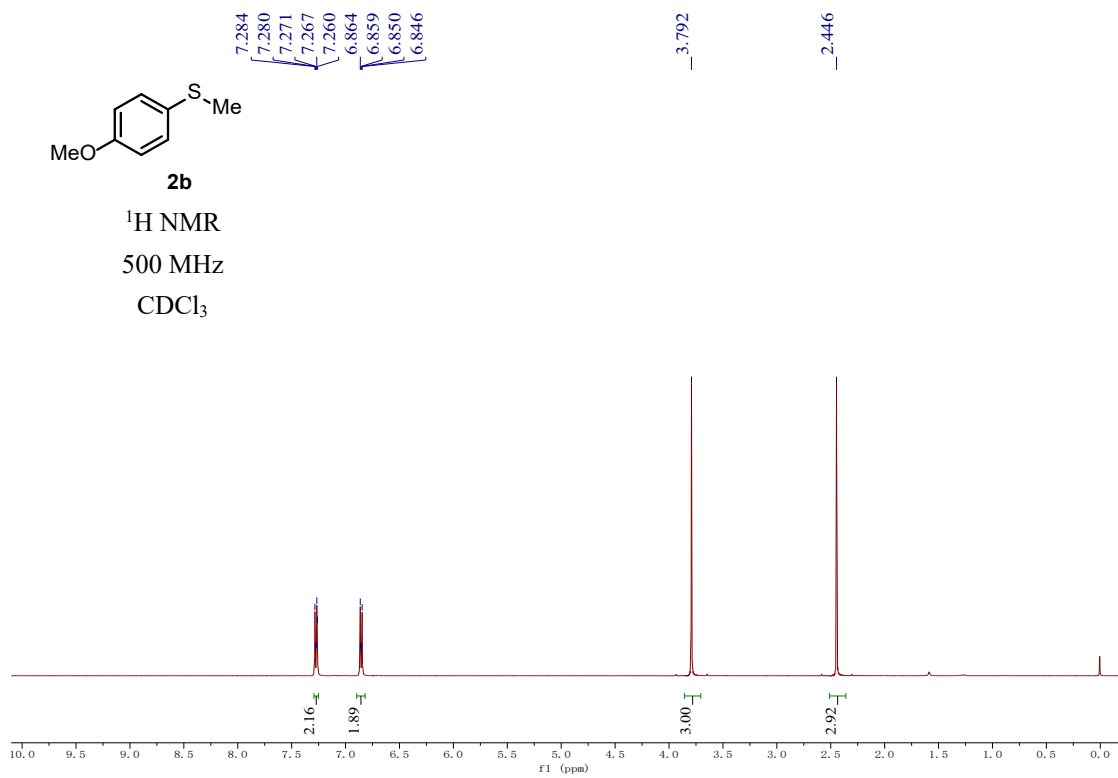


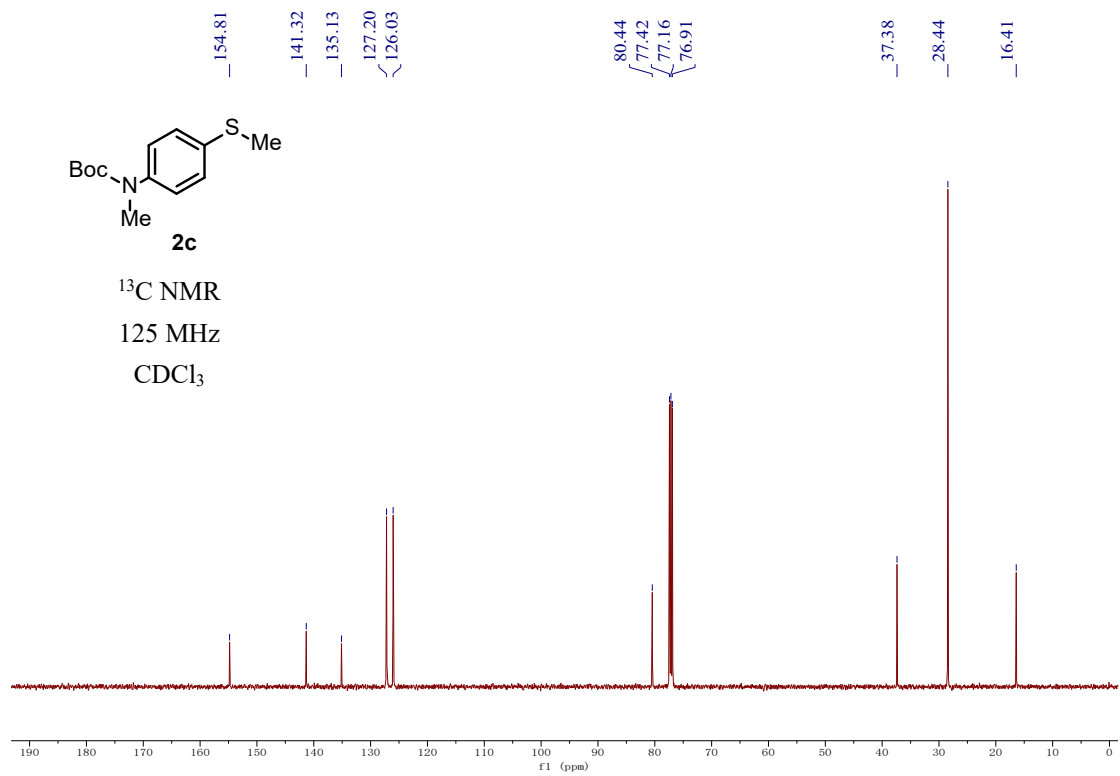
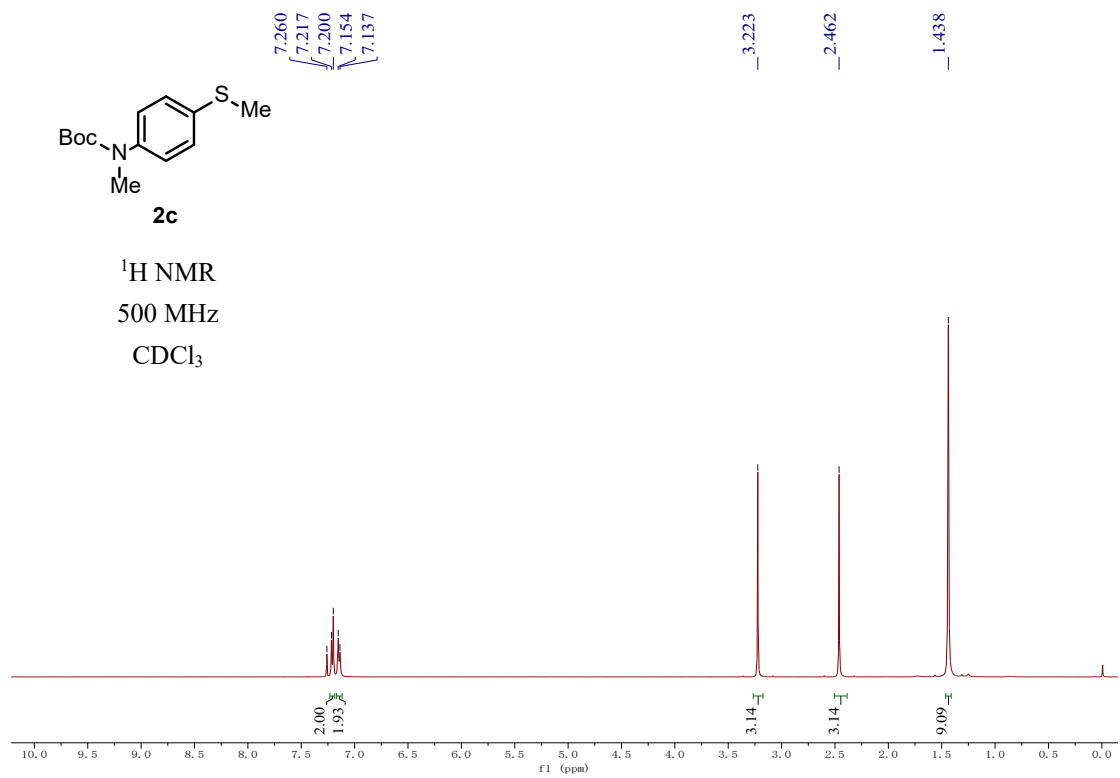
$^1\text{H}$  NMR  
500 MHz  
 $\text{CDCl}_3$

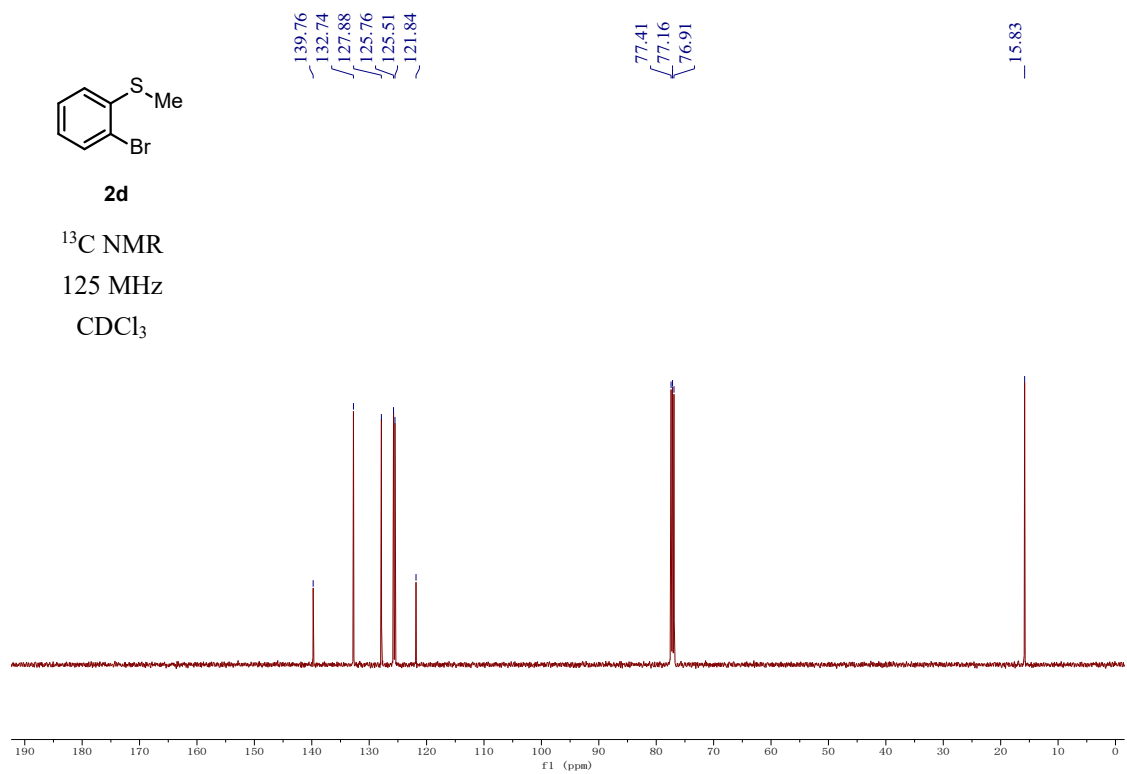
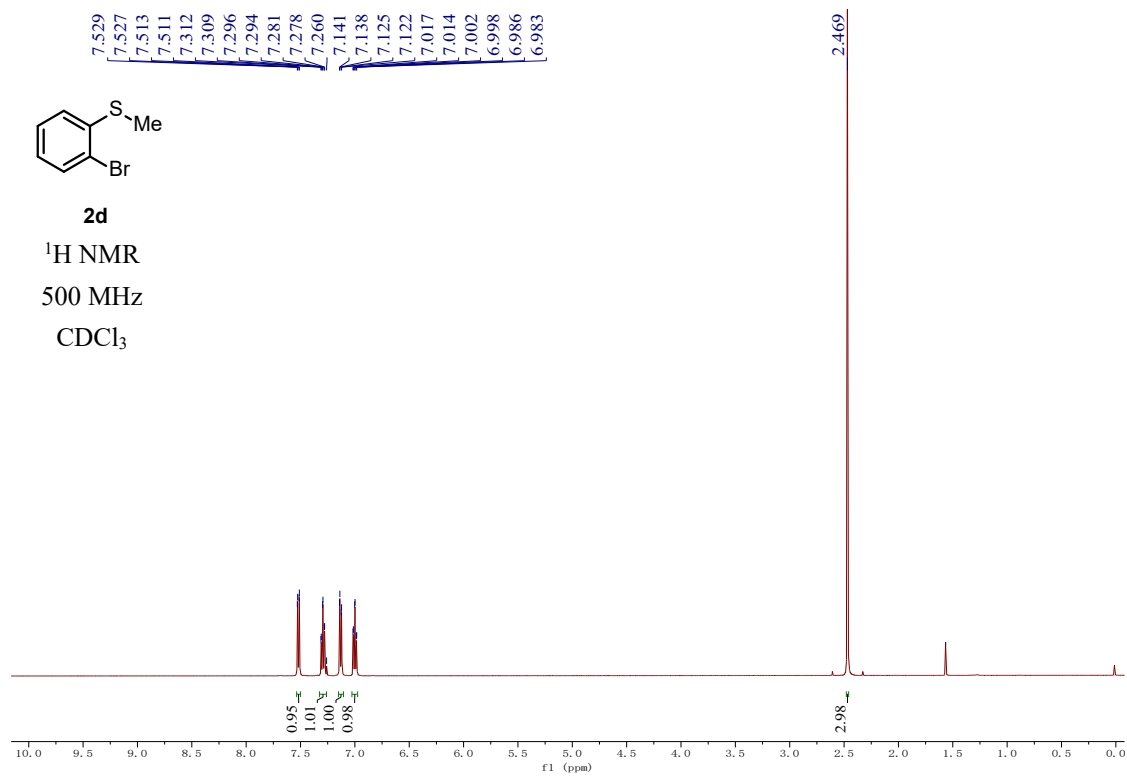


$^{13}\text{C}$  NMR  
125 MHz  
 $\text{CDCl}_3$

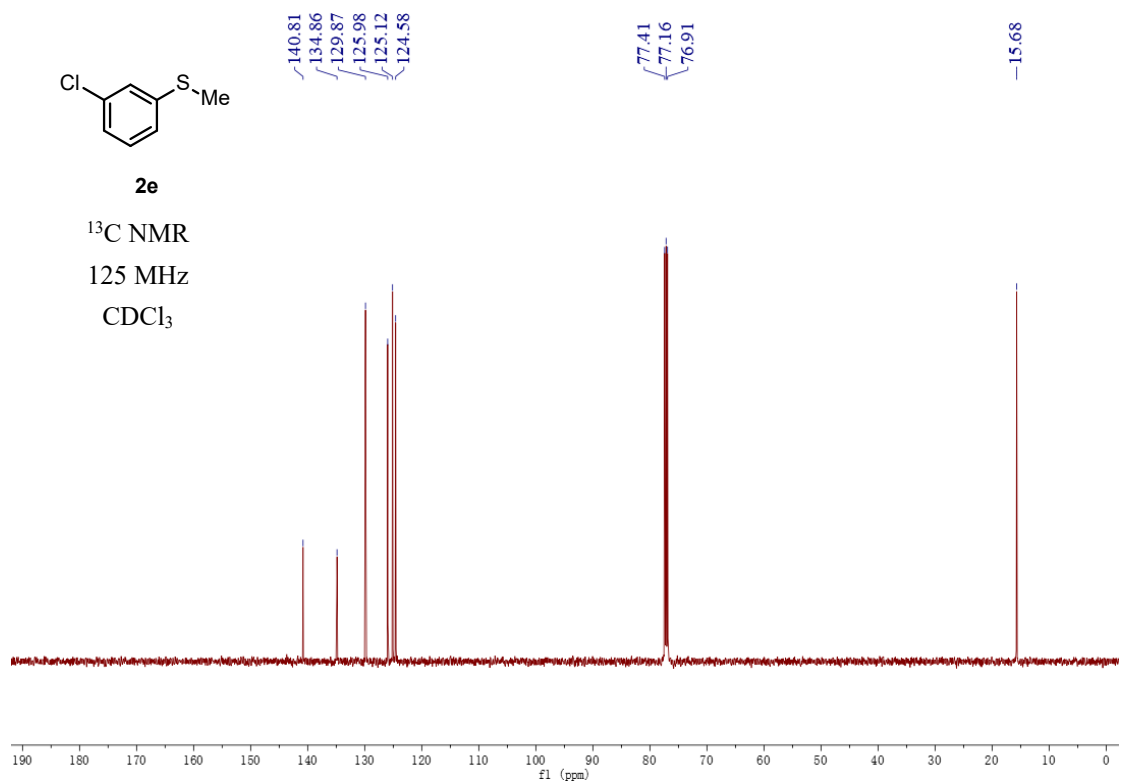
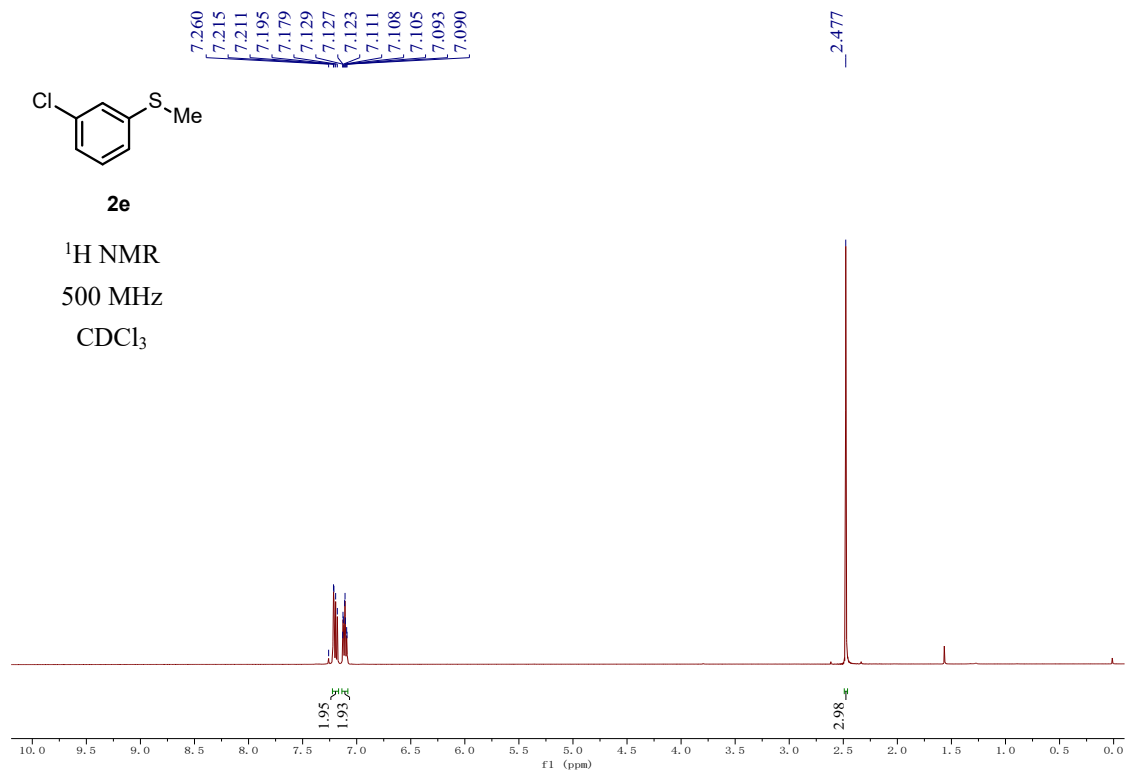


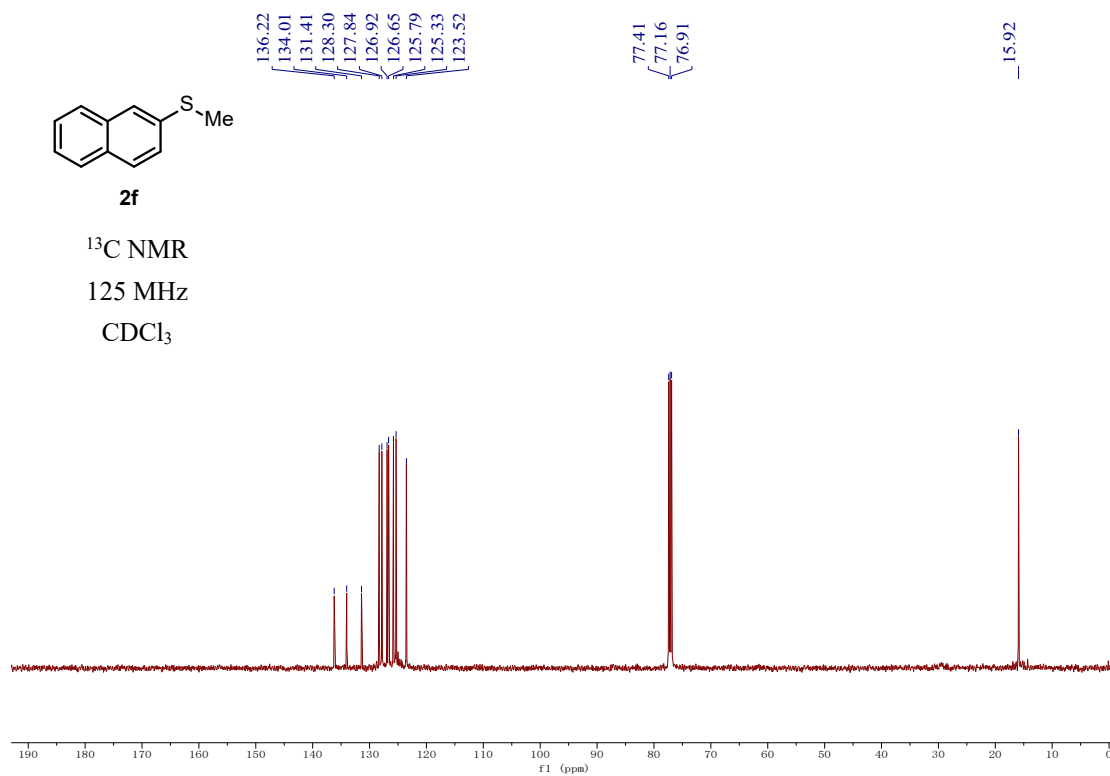
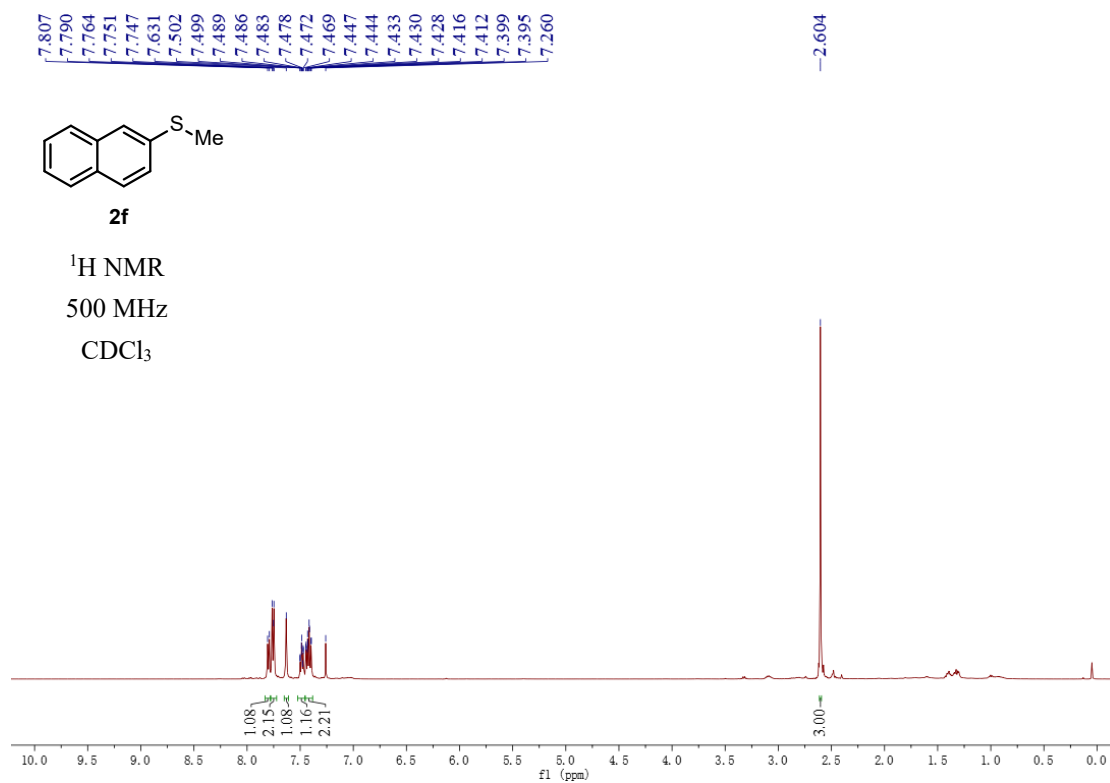


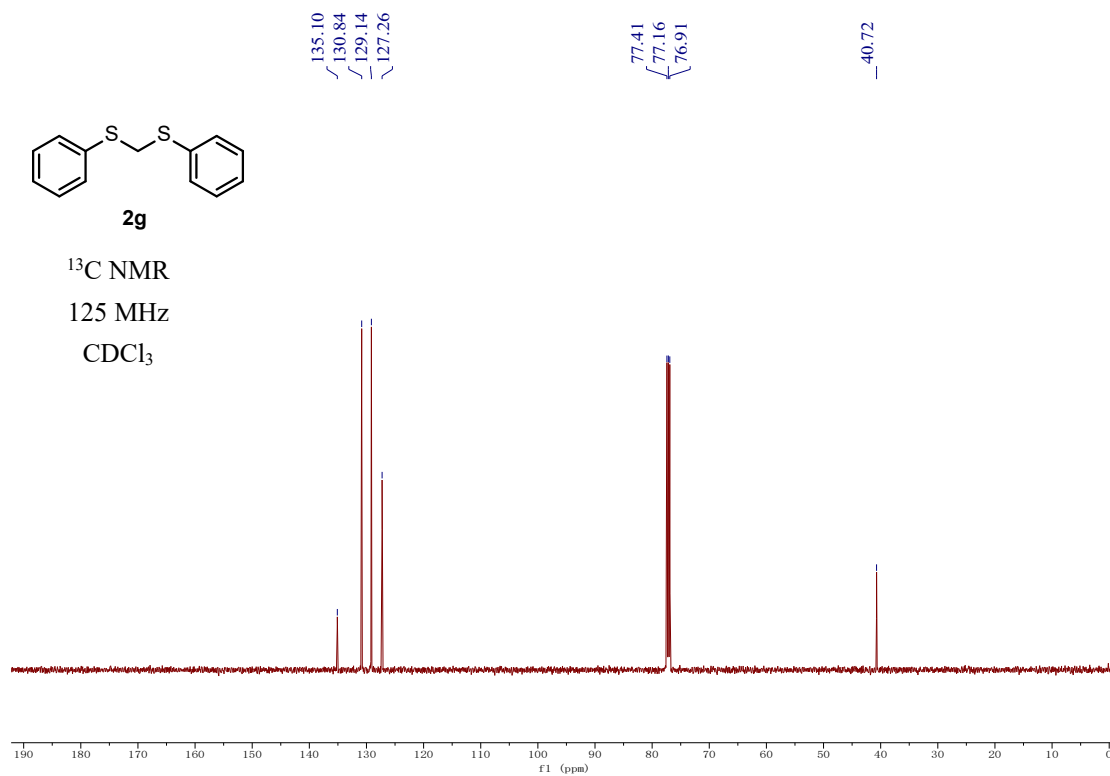
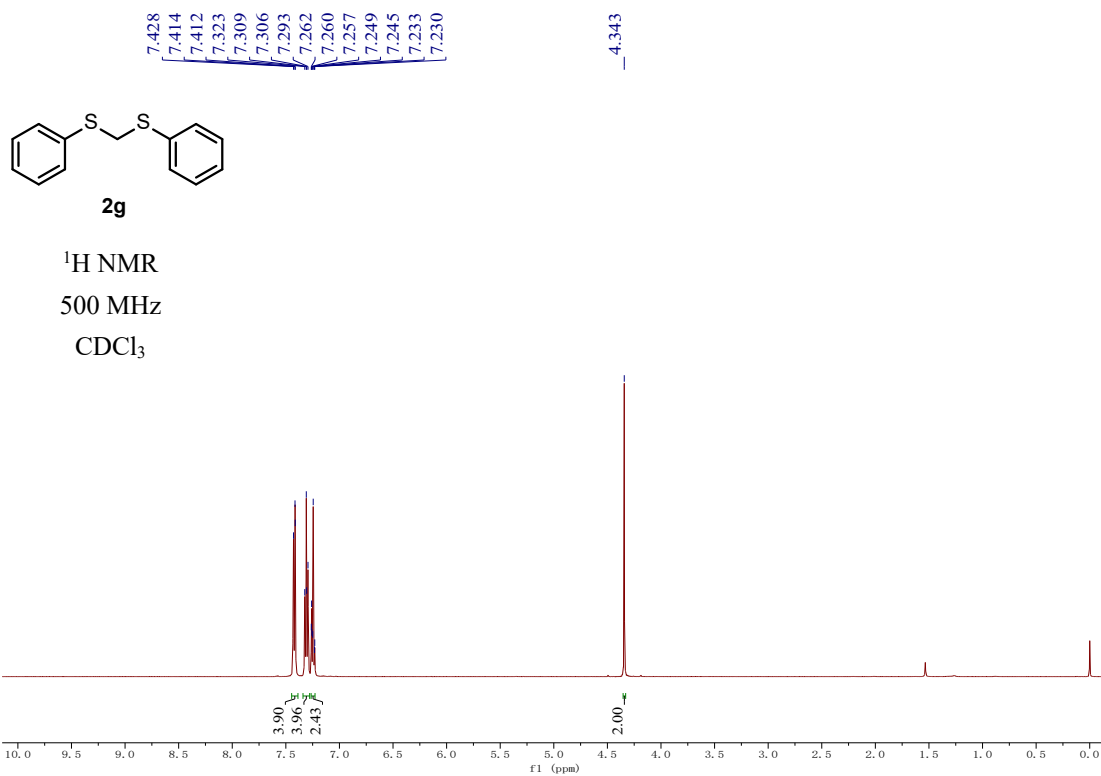


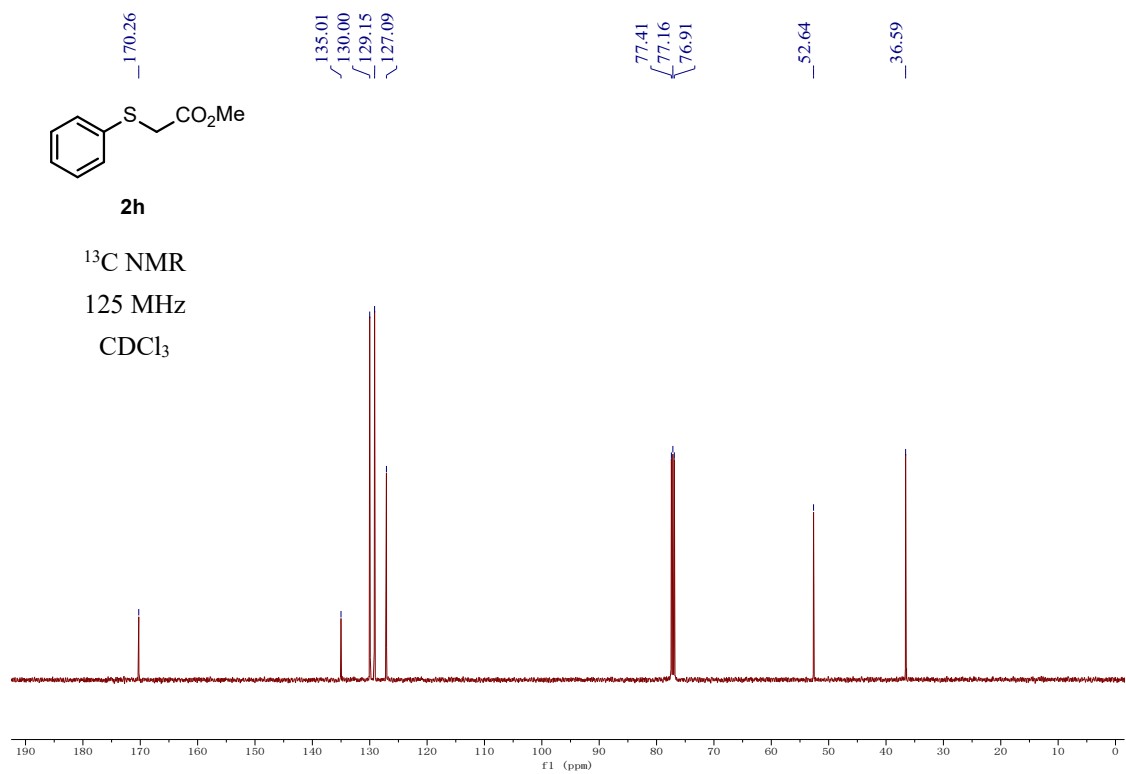
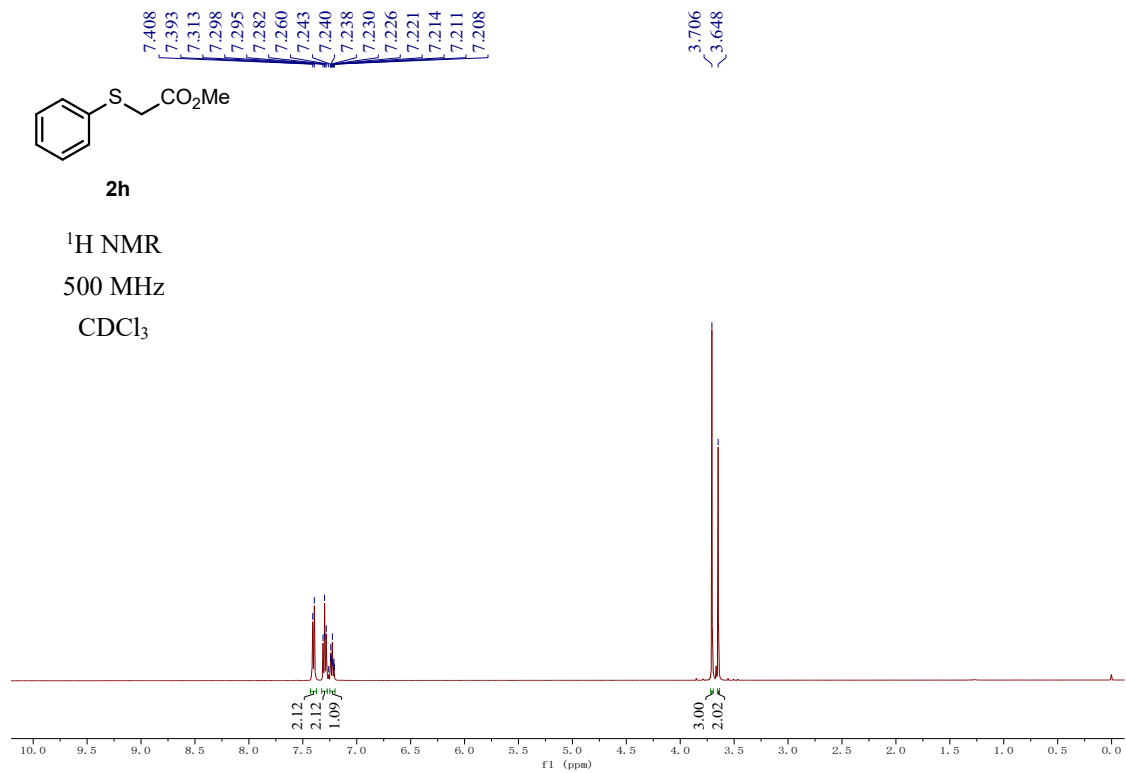




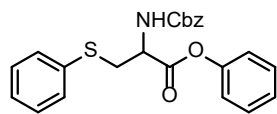








7.454  
7.439  
7.351  
7.341  
7.334  
7.323  
7.320  
7.287  
7.284  
7.270  
7.266  
7.258  
7.255  
7.243  
7.236  
7.222  
7.207  
6.950  
6.934  
5.649  
5.634  
5.111  
5.086  
5.076  
5.052  
4.893  
4.883  
4.877  
4.873  
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3.519  
3.508

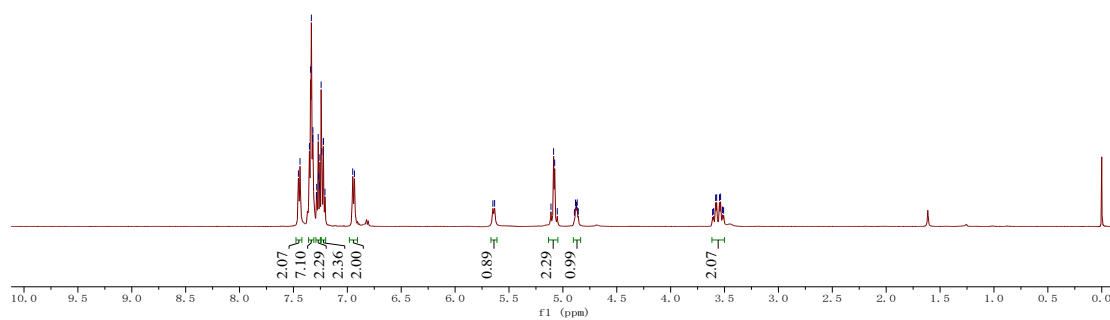


**2i**

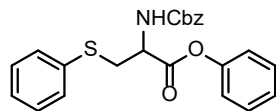
<sup>1</sup>H NMR

500 MHz

CDCl<sub>3</sub>



169.16  
155.65  
150.35  
136.13  
134.56  
131.23  
129.57  
129.36  
128.67  
128.37  
128.23  
127.40  
126.37  
121.36  
77.42  
77.16  
76.91  
67.30  
54.28  
37.19

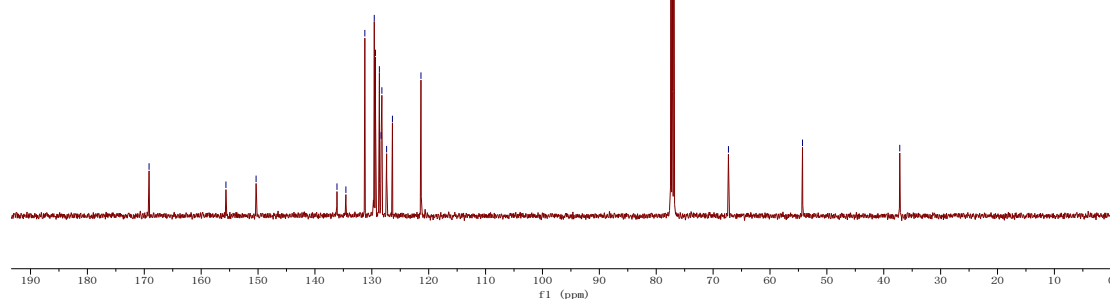


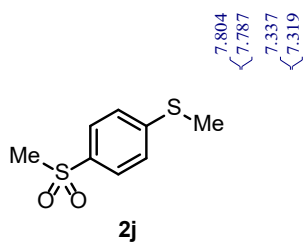
**2i**

<sup>13</sup>C NMR

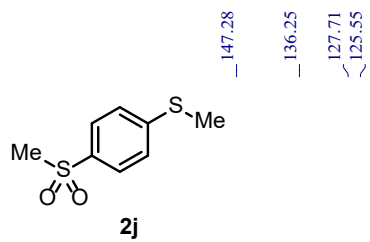
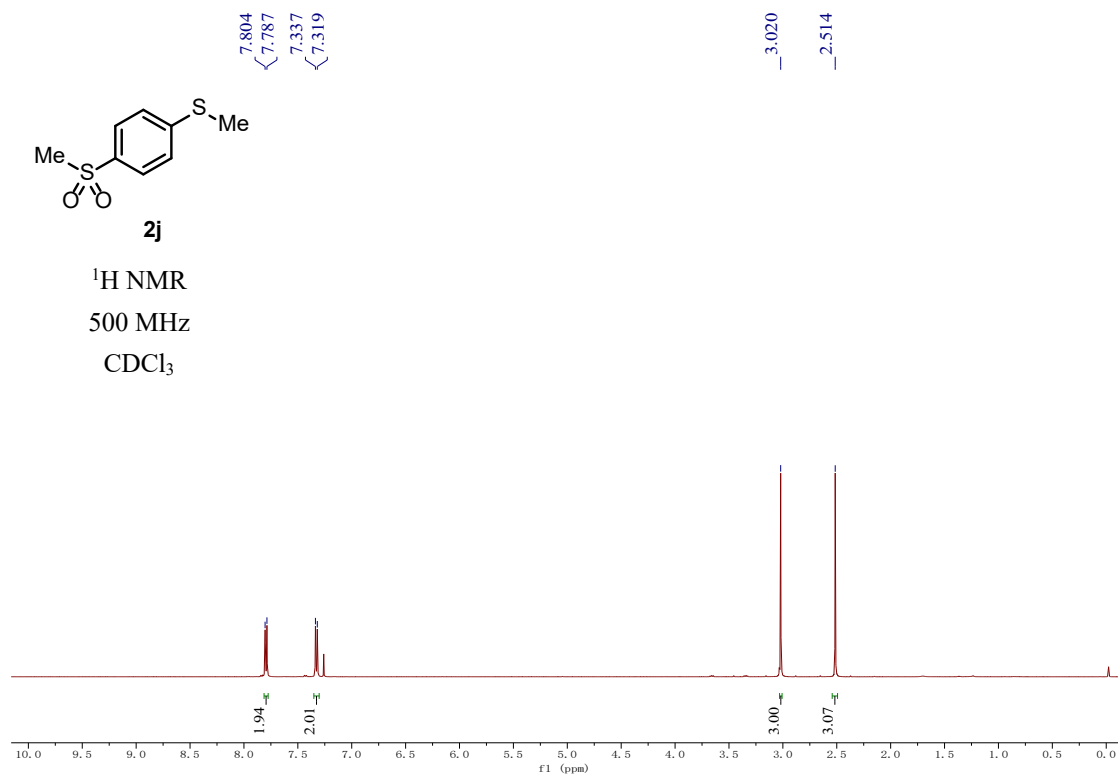
125 MHz

CDCl<sub>3</sub>

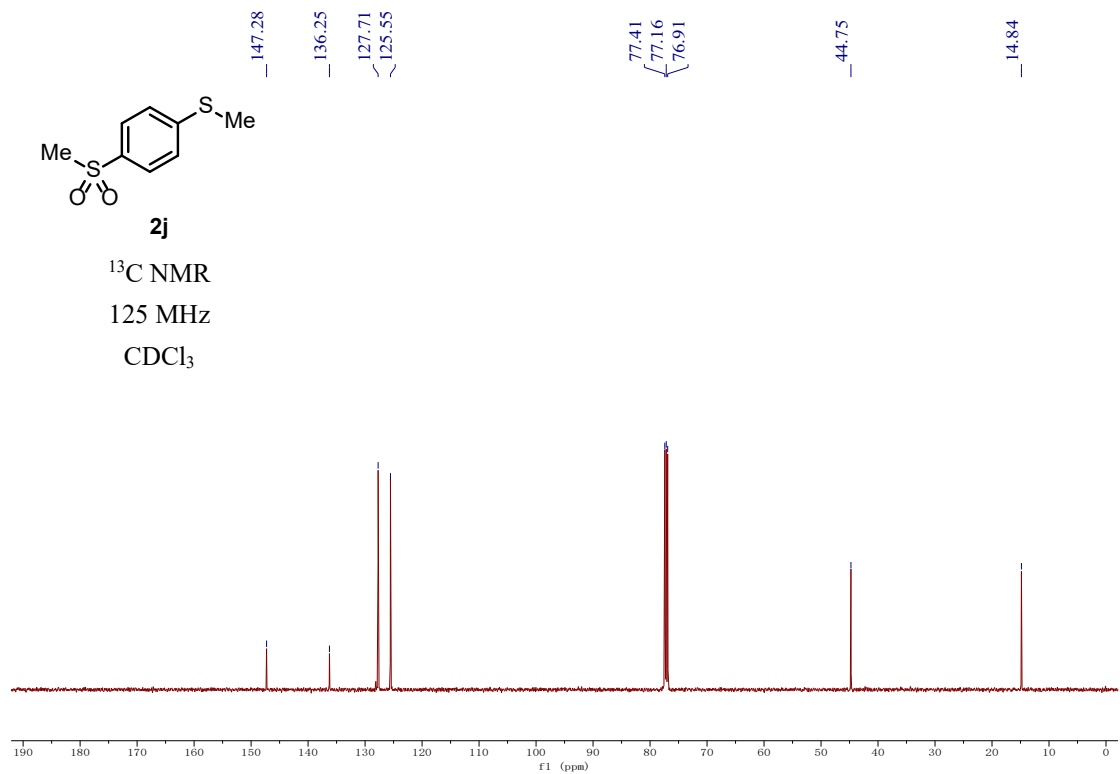


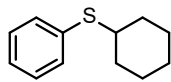


<sup>1</sup>H NMR  
 500 MHz  
 CDCl<sub>3</sub>



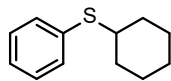
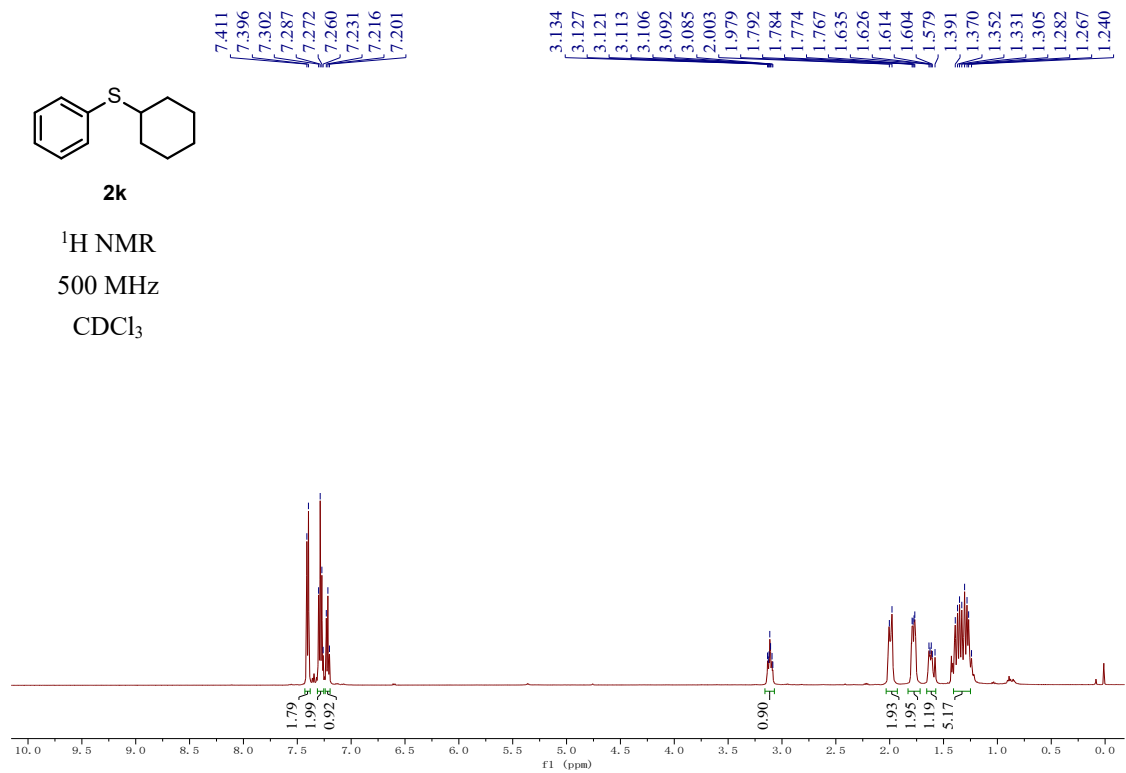
<sup>13</sup>C NMR  
 125 MHz  
 CDCl<sub>3</sub>





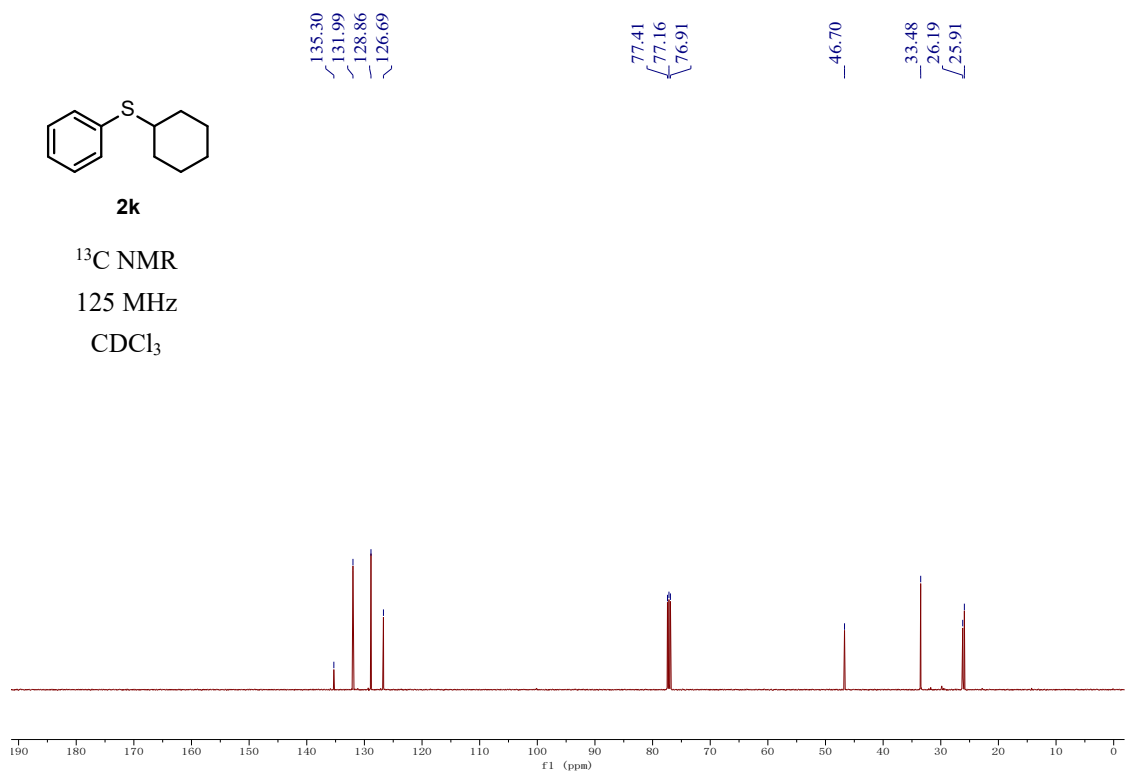
**2k**

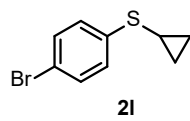
<sup>1</sup>H NMR  
500 MHz  
CDCl<sub>3</sub>



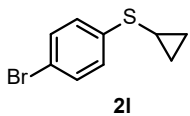
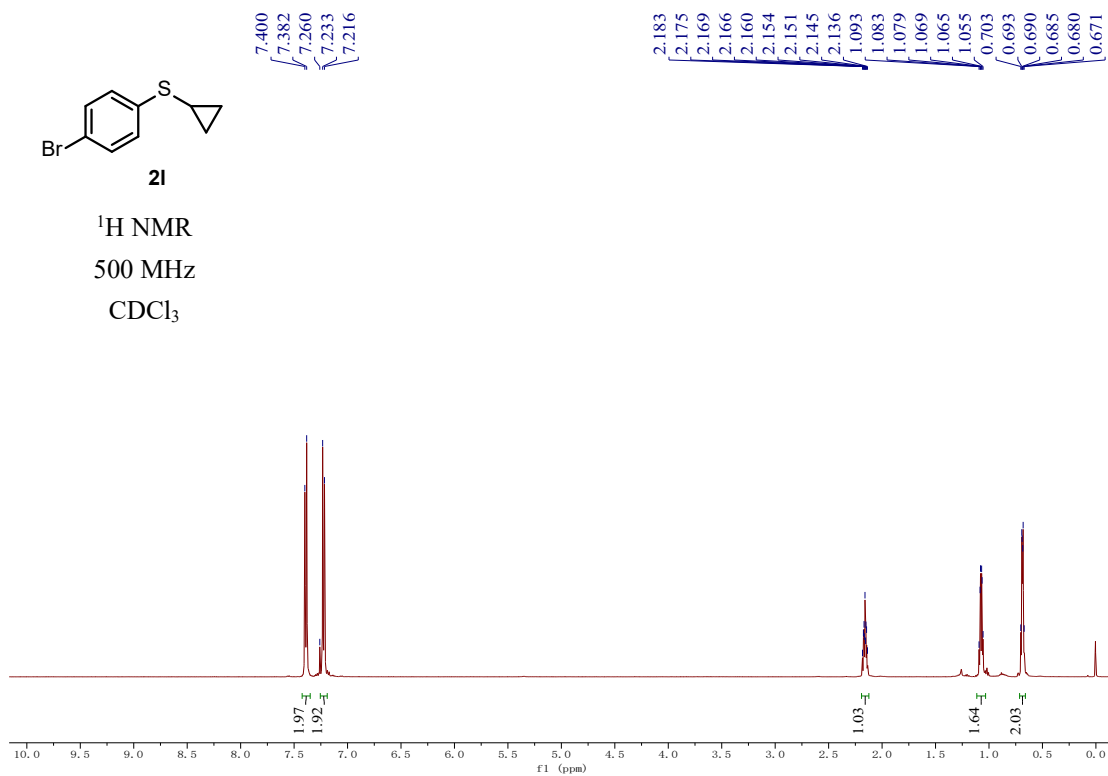
**2k**

<sup>13</sup>C NMR  
125 MHz  
CDCl<sub>3</sub>

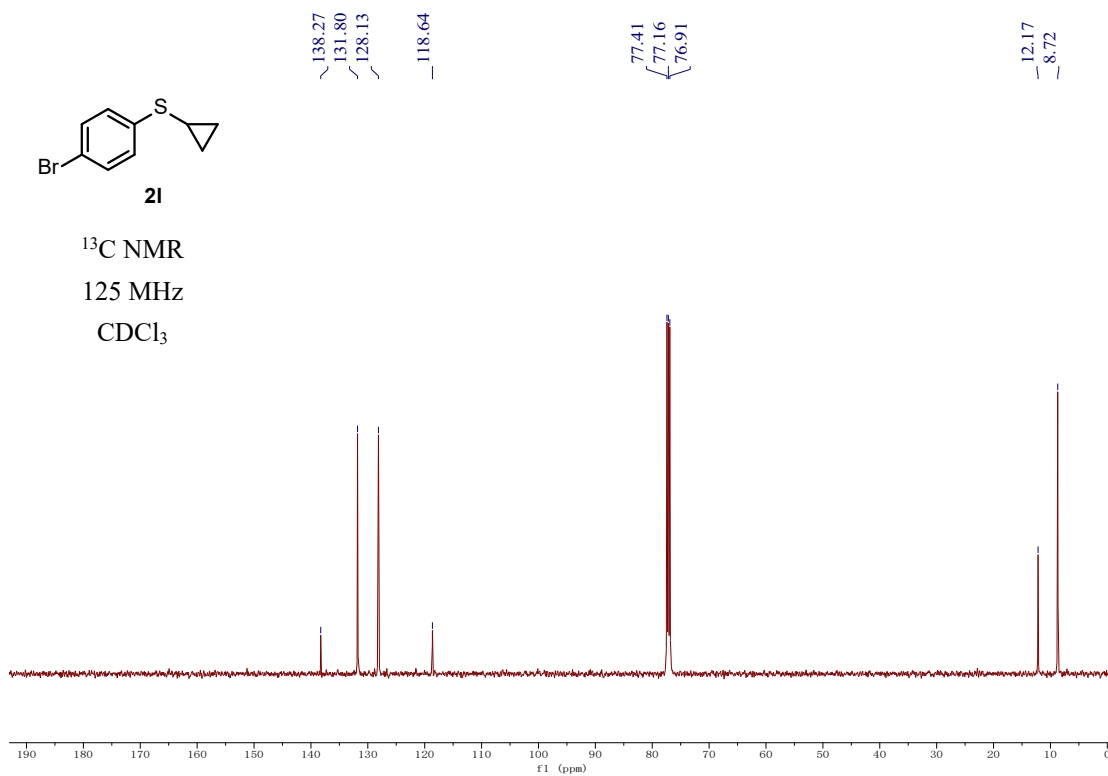




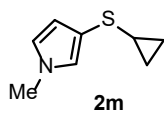
<sup>1</sup>H NMR  
500 MHz  
CDCl<sub>3</sub>



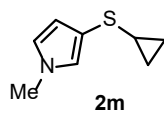
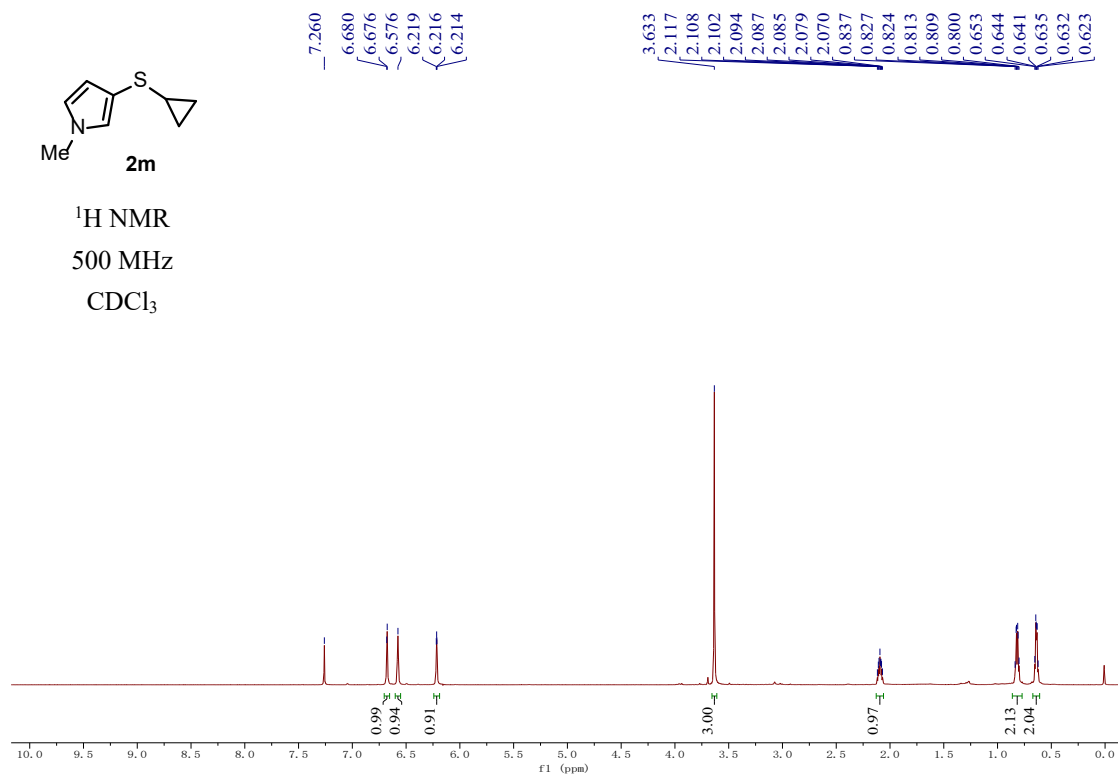
<sup>13</sup>C NMR  
125 MHz  
CDCl<sub>3</sub>



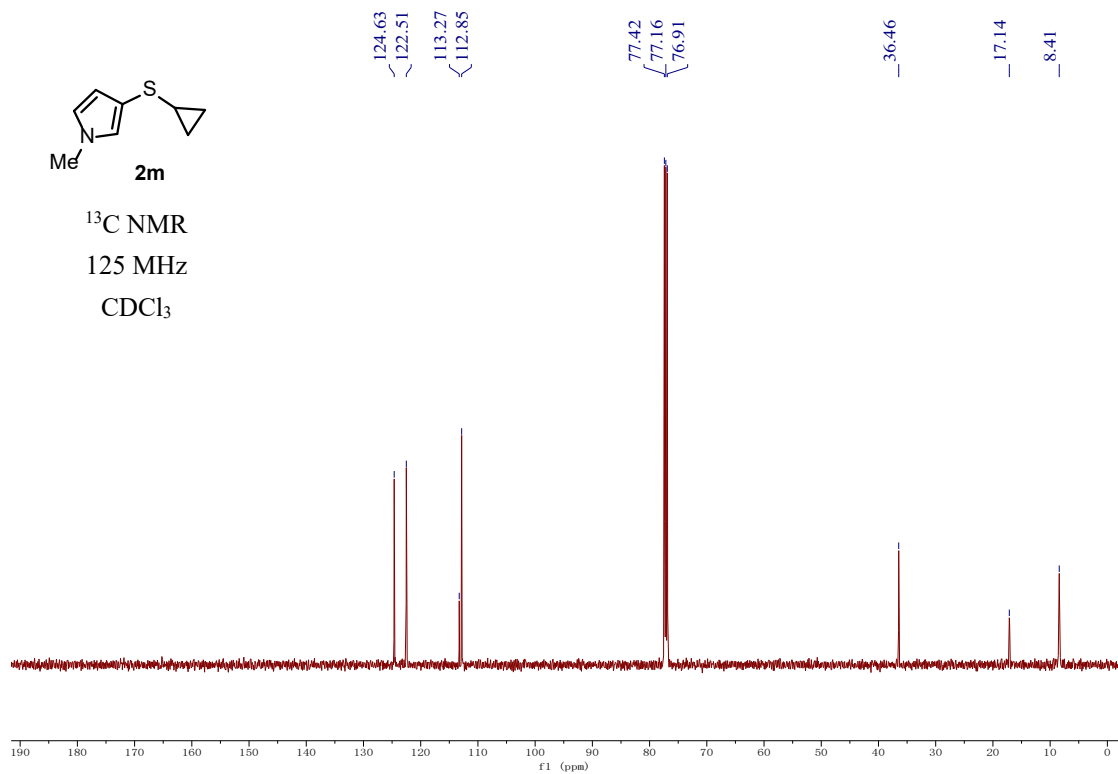


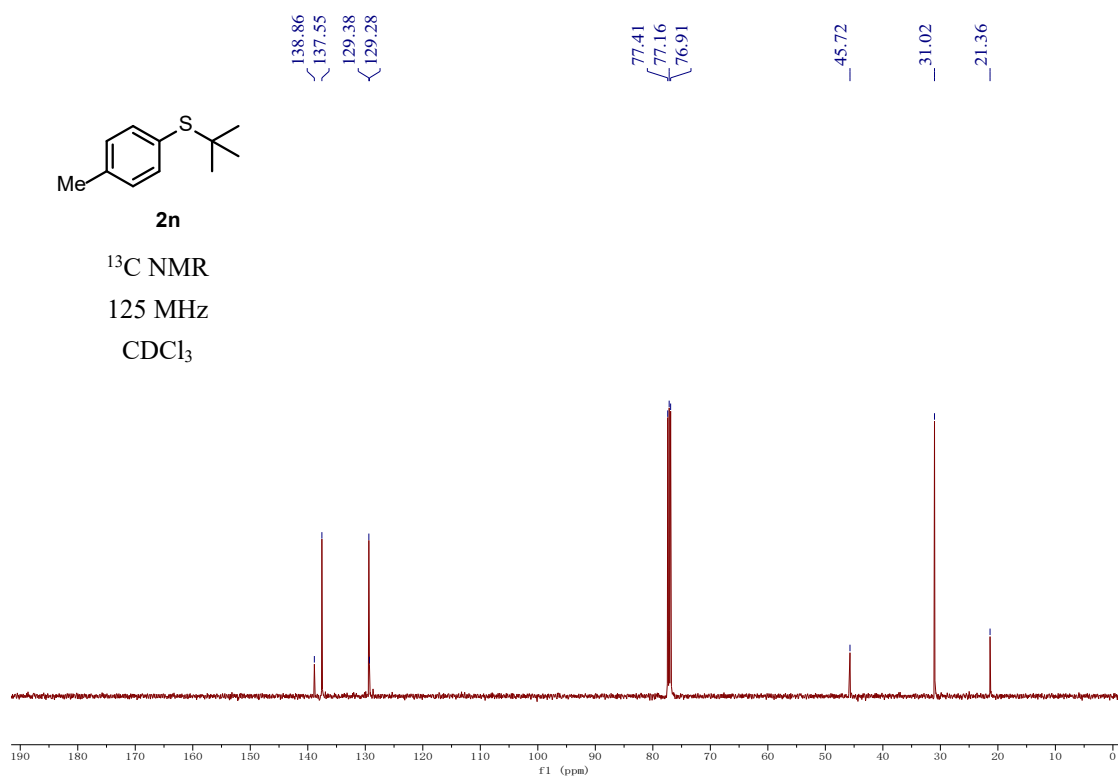
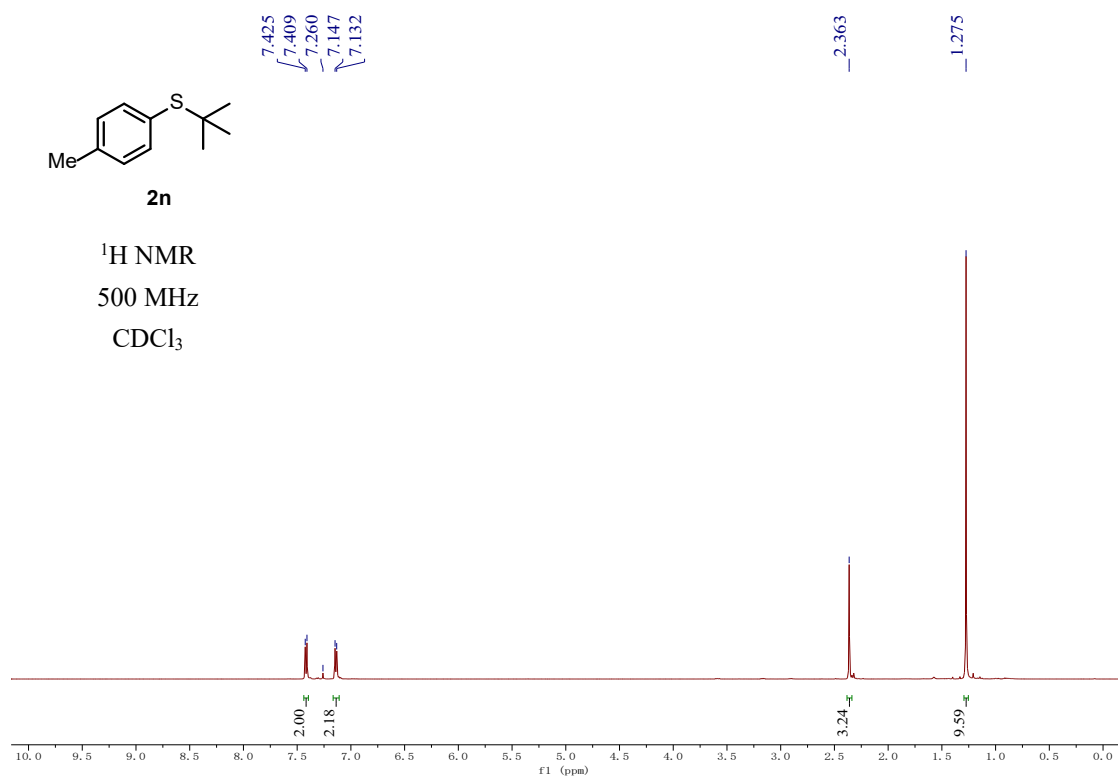


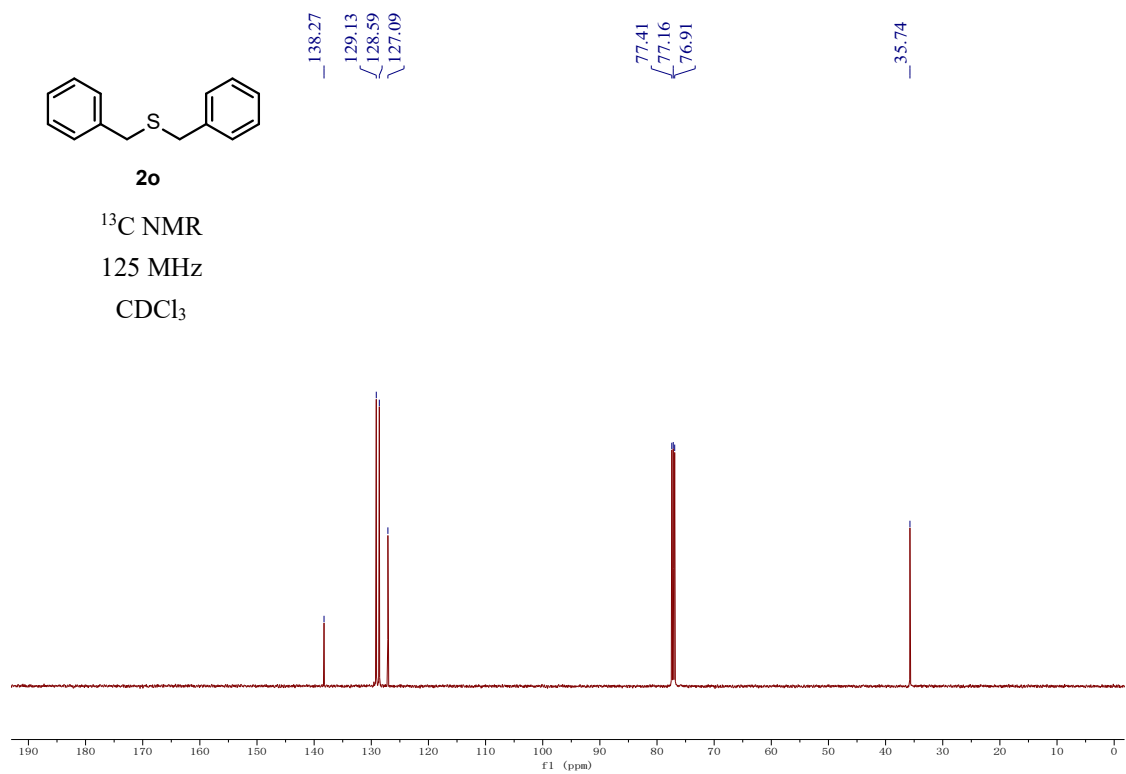
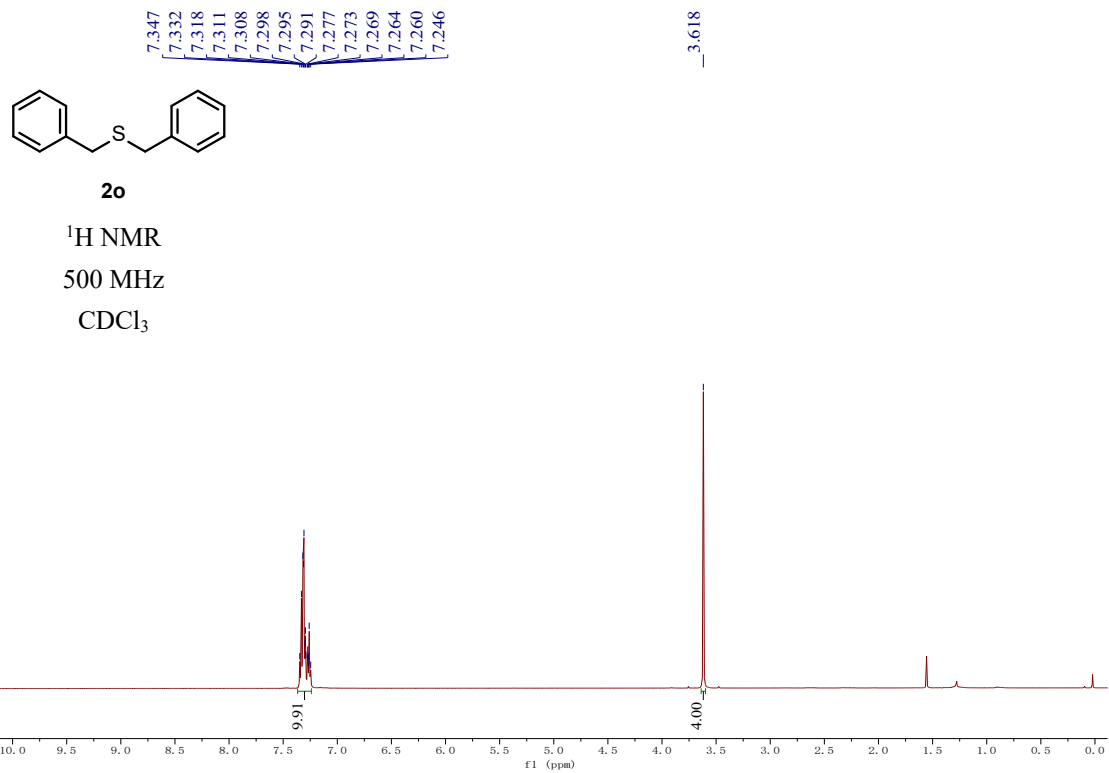
<sup>1</sup>H NMR  
 500 MHz  
 CDCl<sub>3</sub>

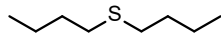


<sup>13</sup>C NMR  
 125 MHz  
 CDCl<sub>3</sub>







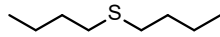
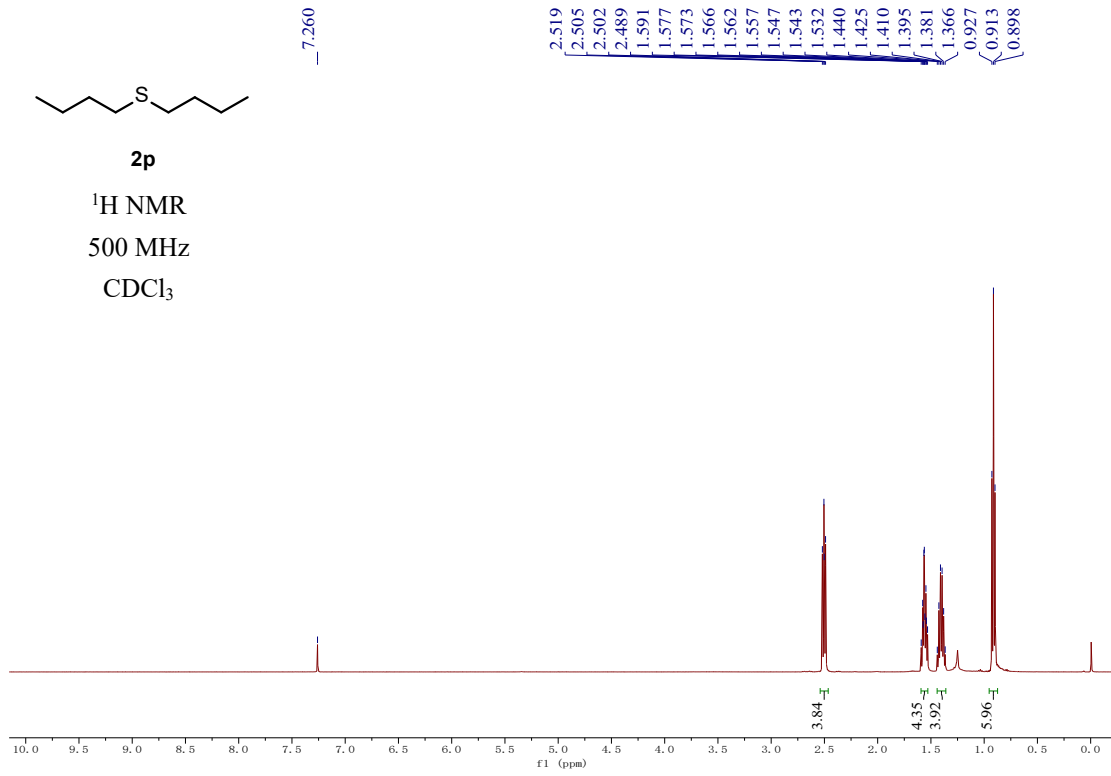


**2p**

<sup>1</sup>H NMR

500 MHz

CDCl<sub>3</sub>

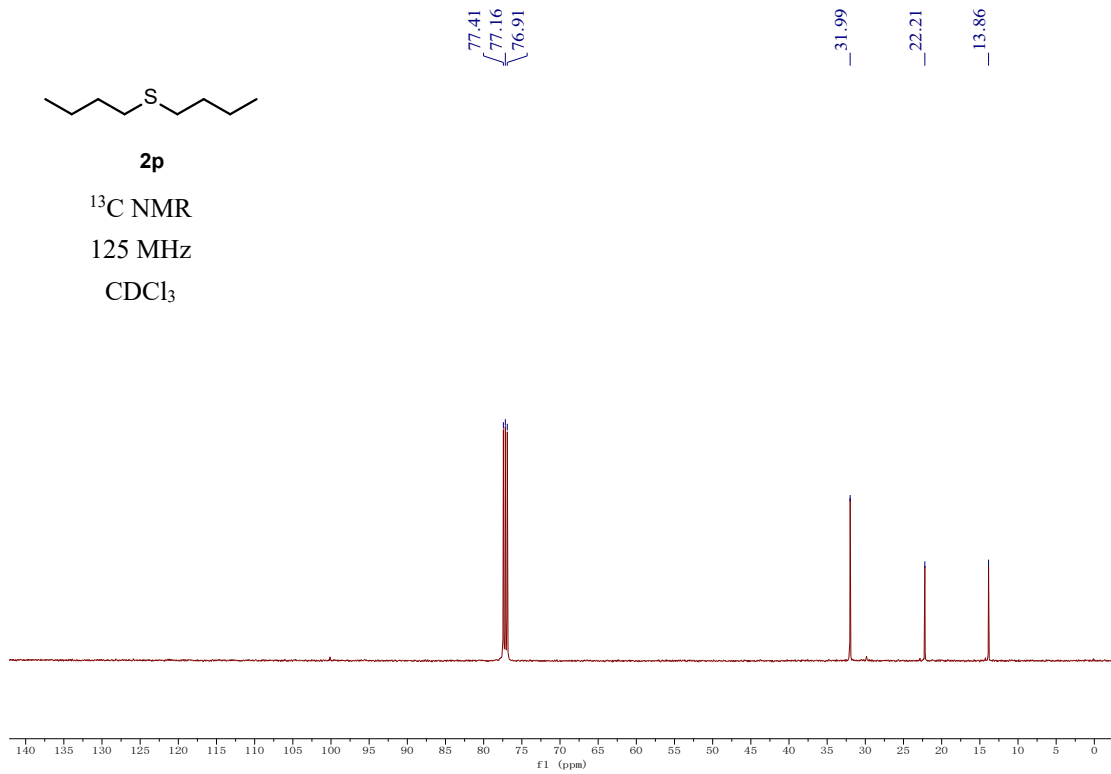


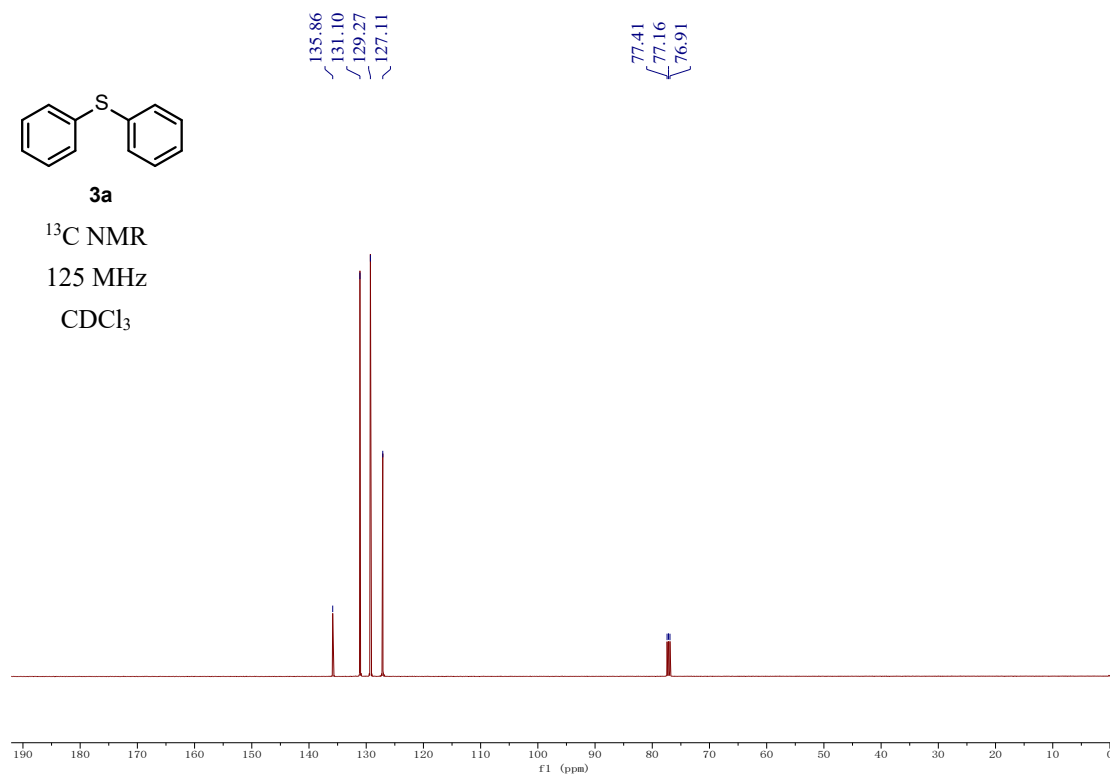
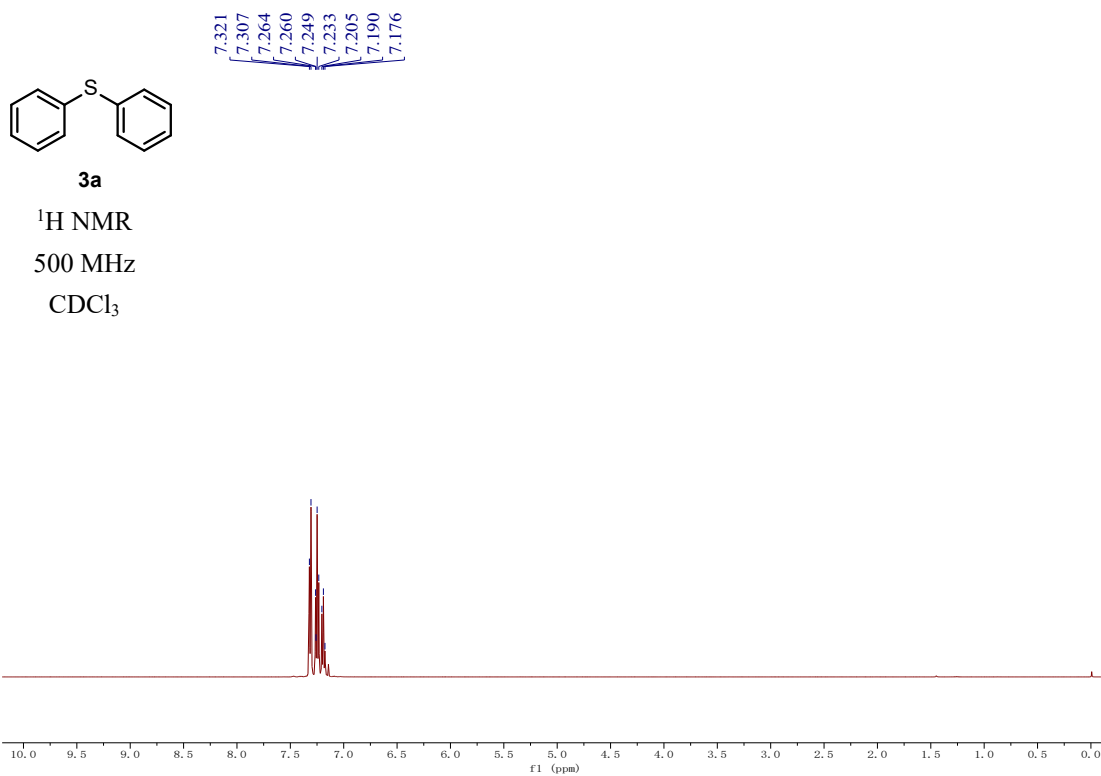
**2p**

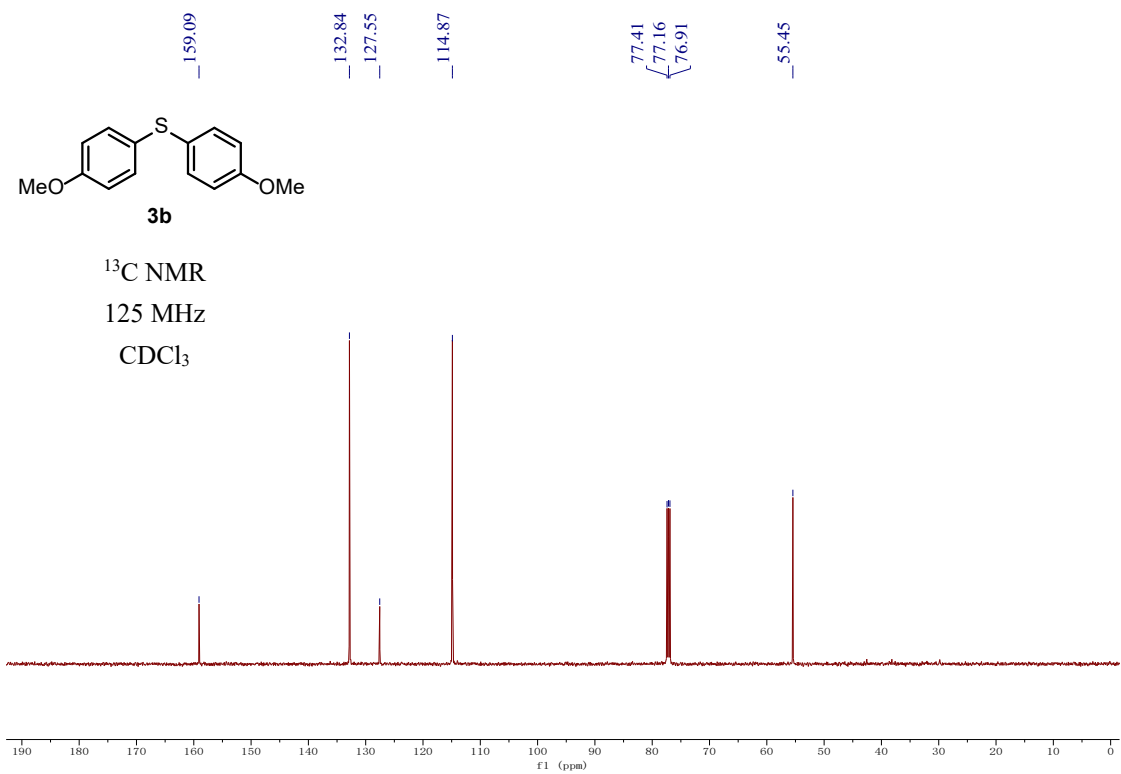
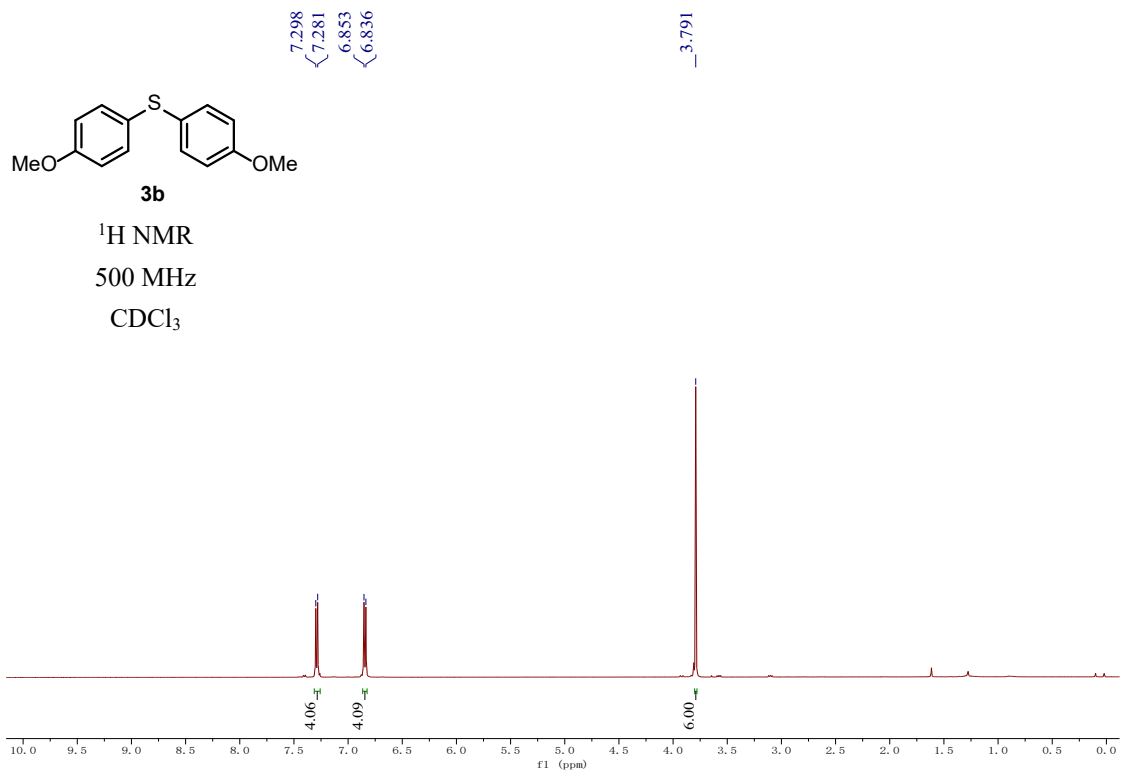
<sup>13</sup>C NMR

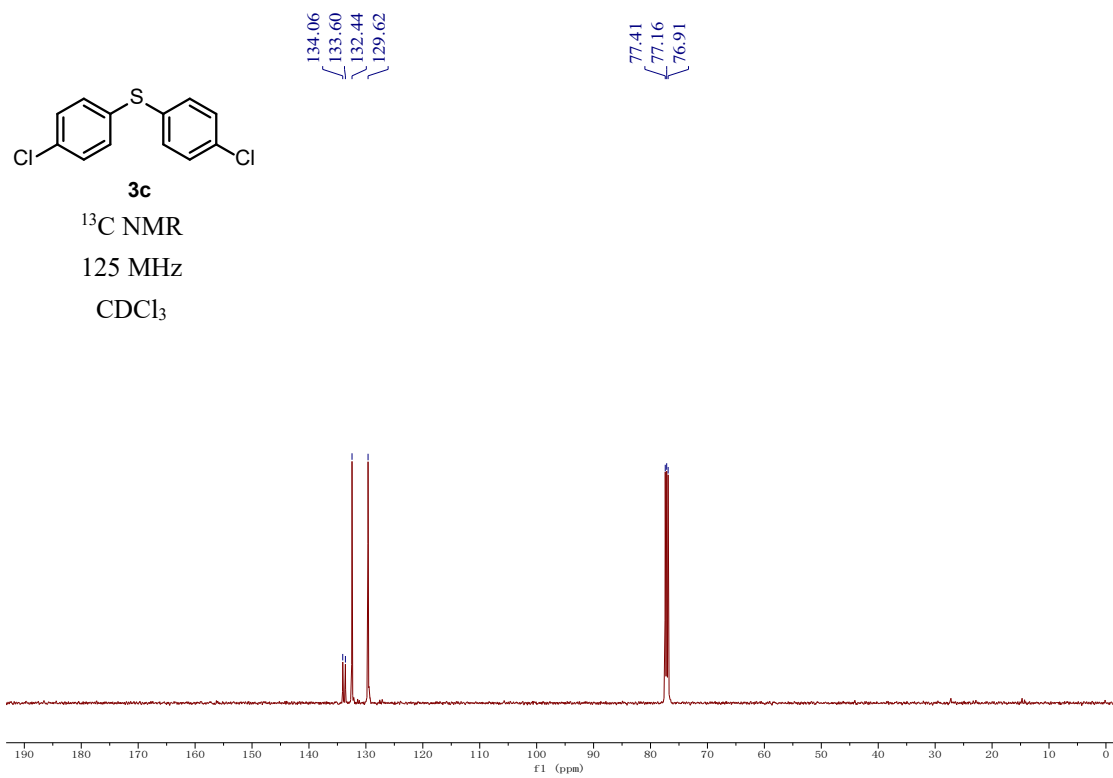
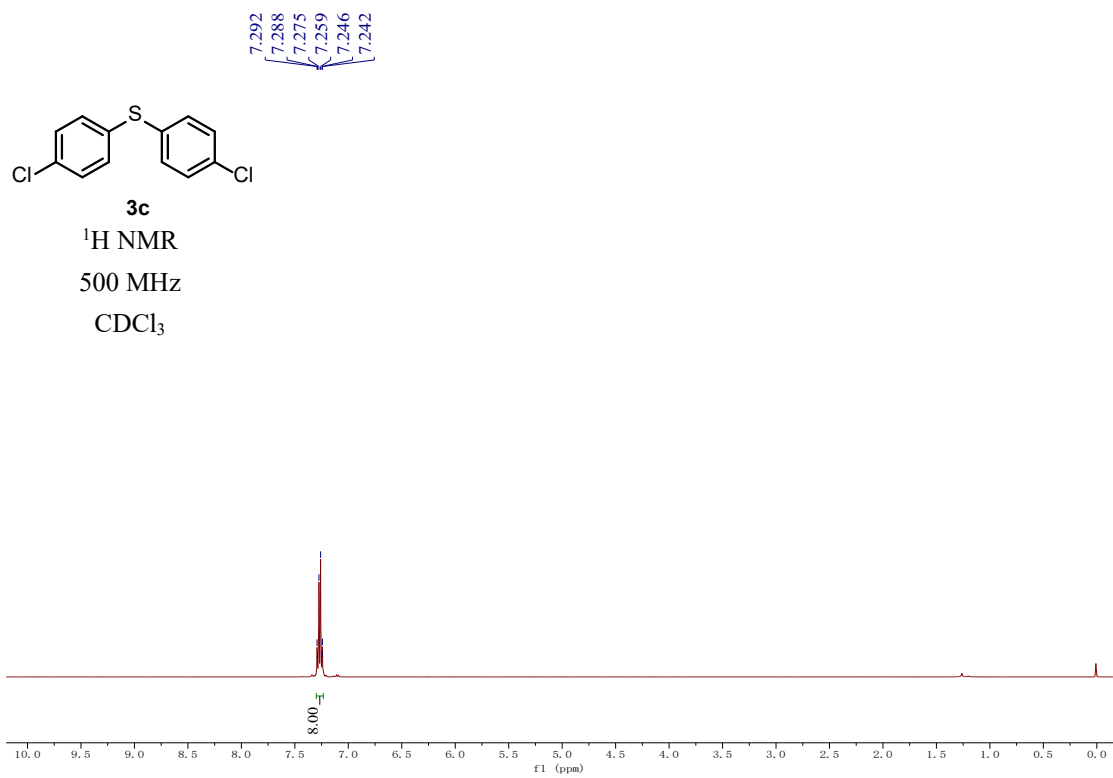
125 MHz

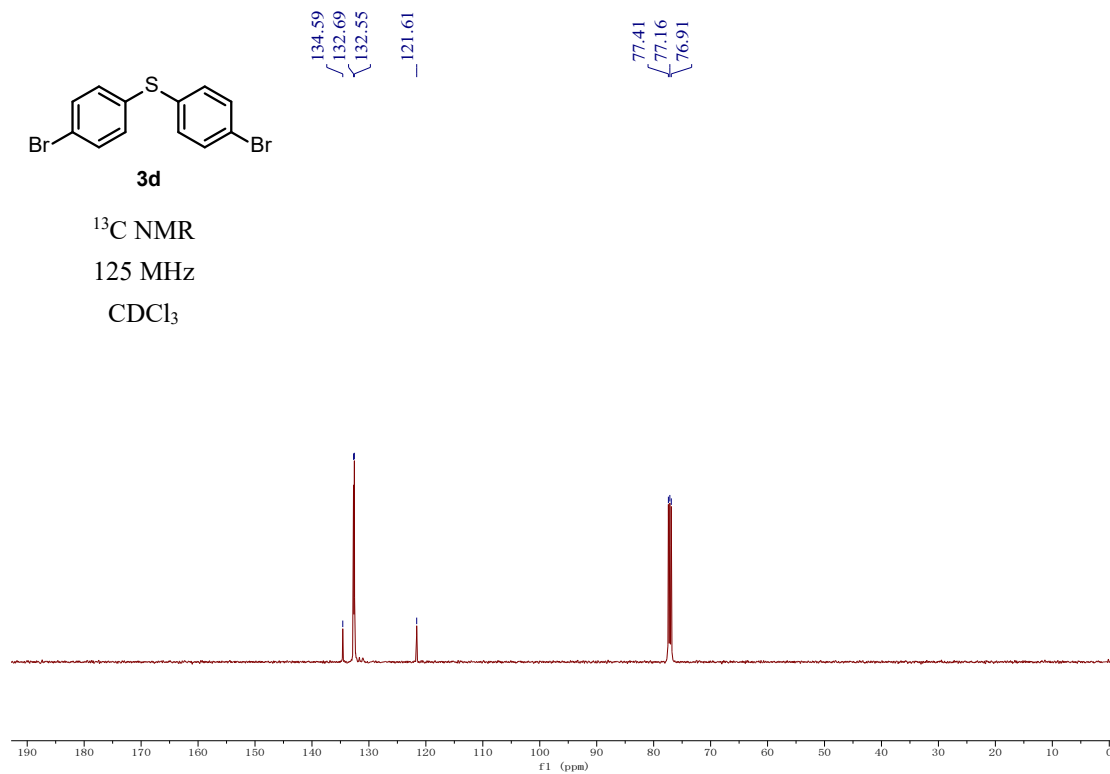
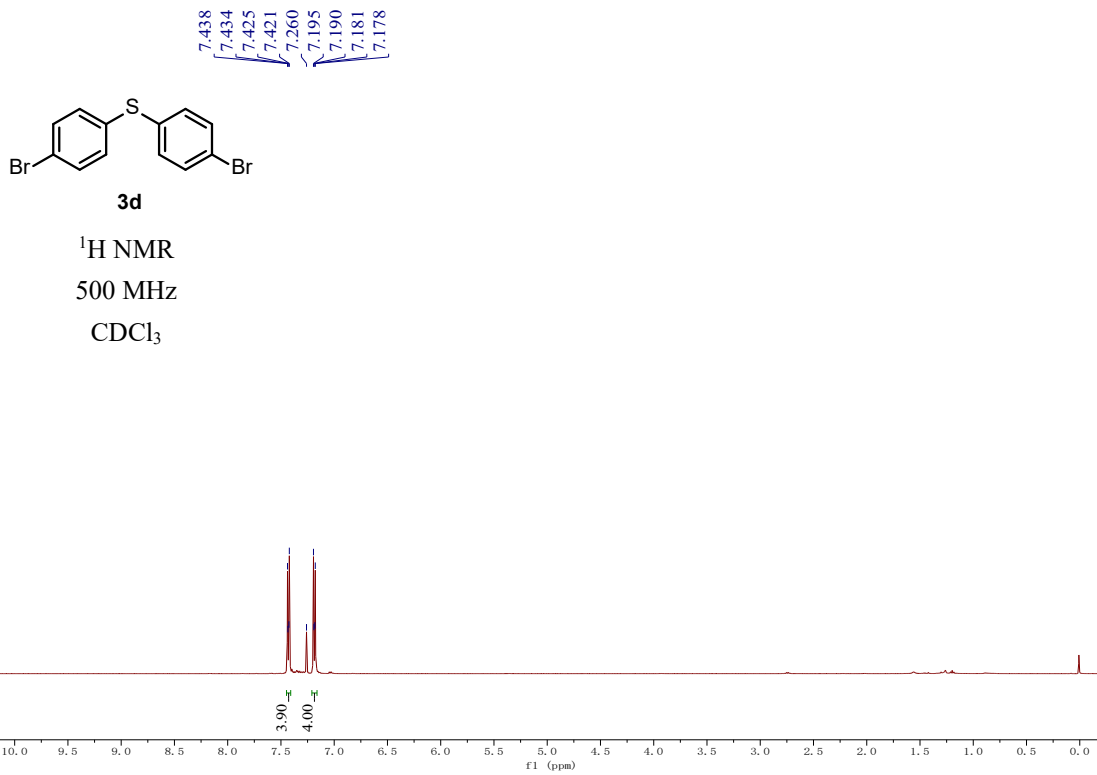
CDCl<sub>3</sub>



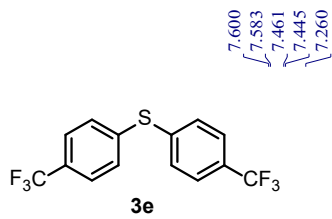




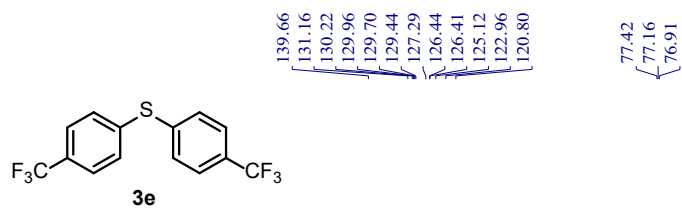
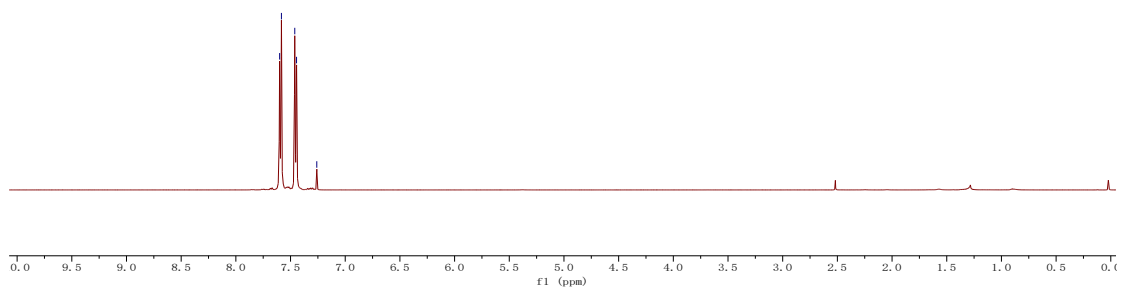




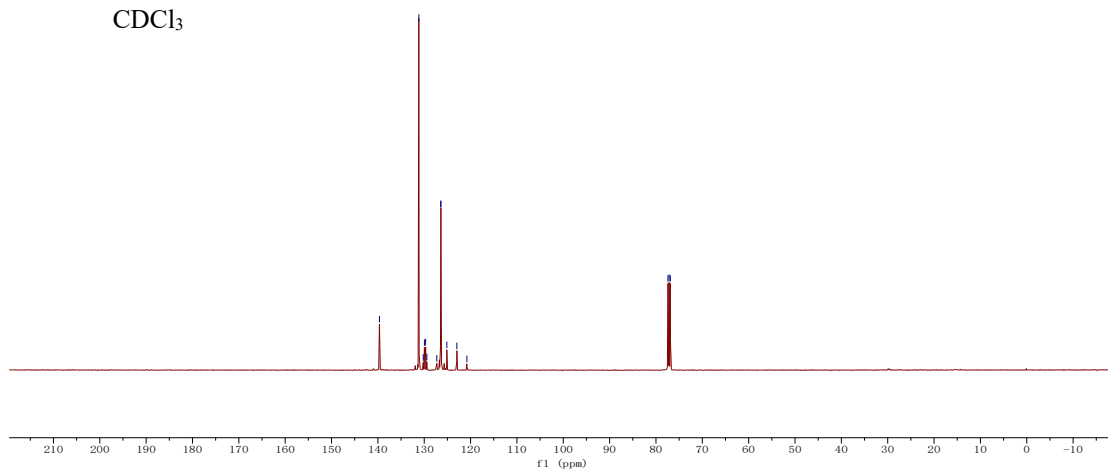


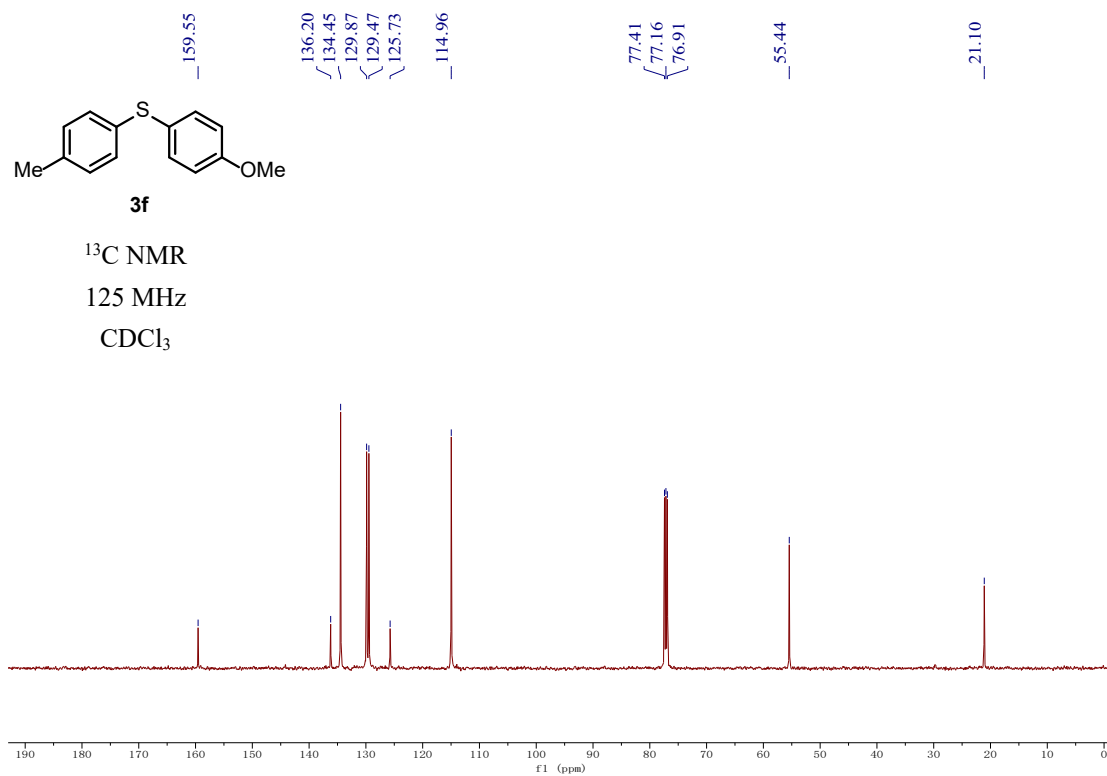
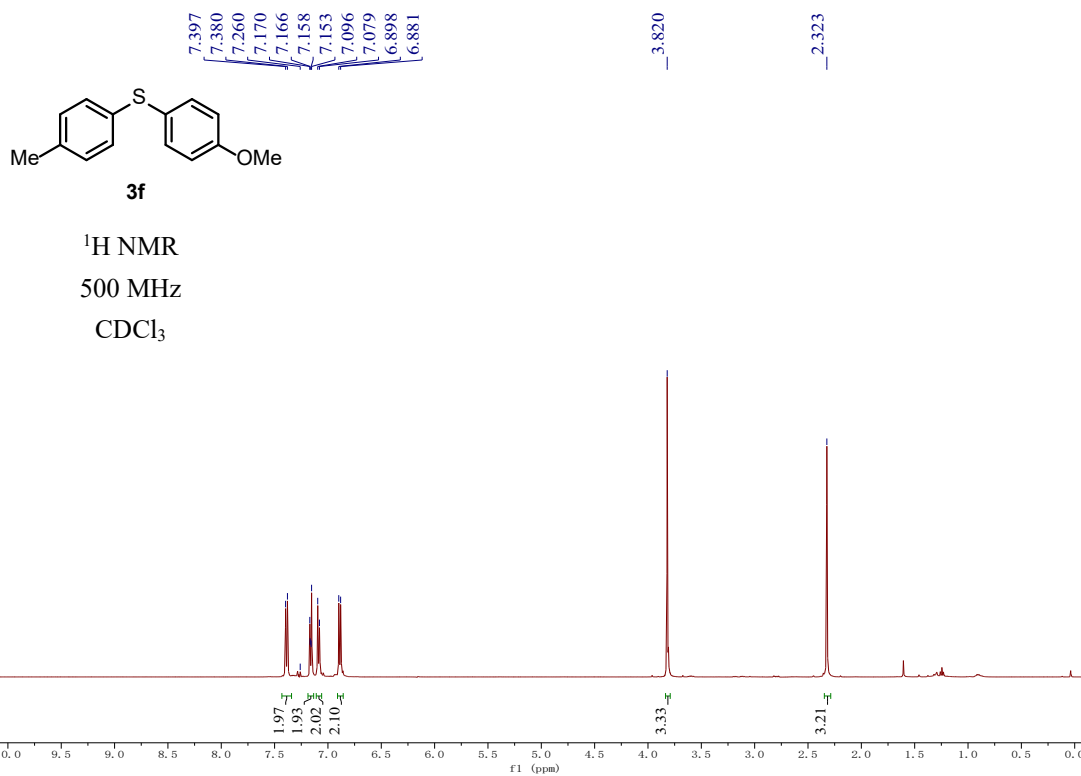


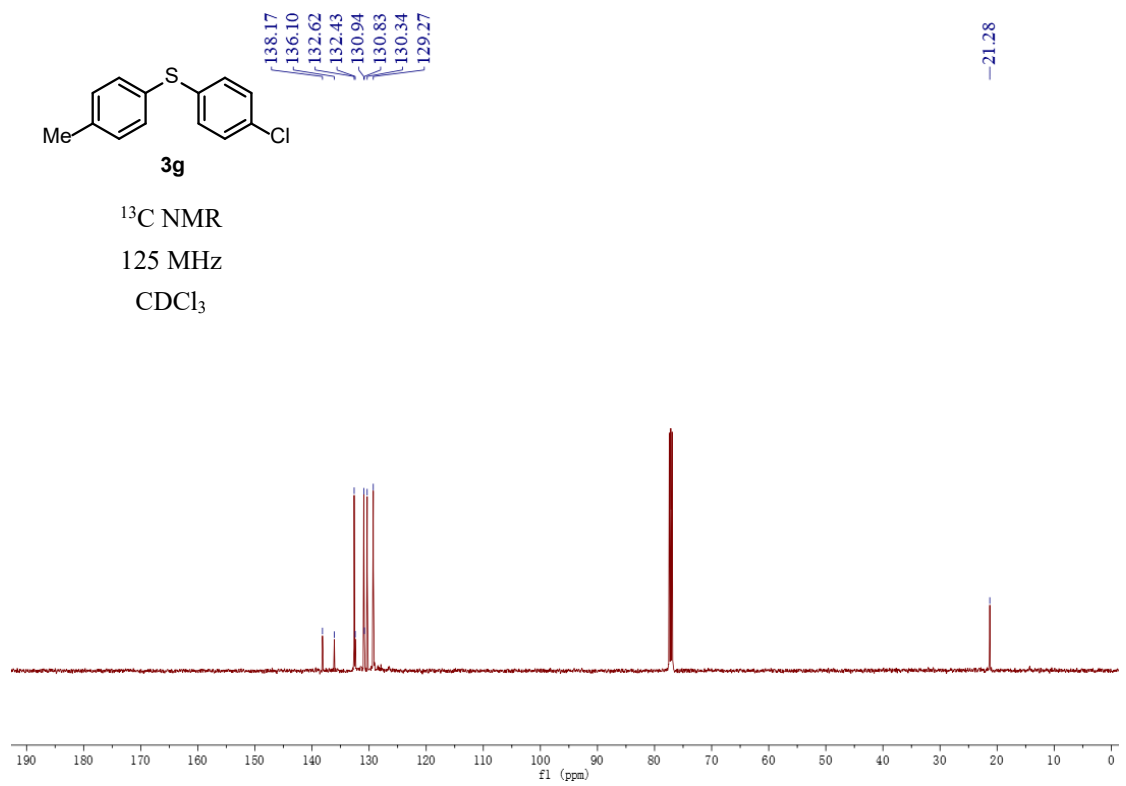
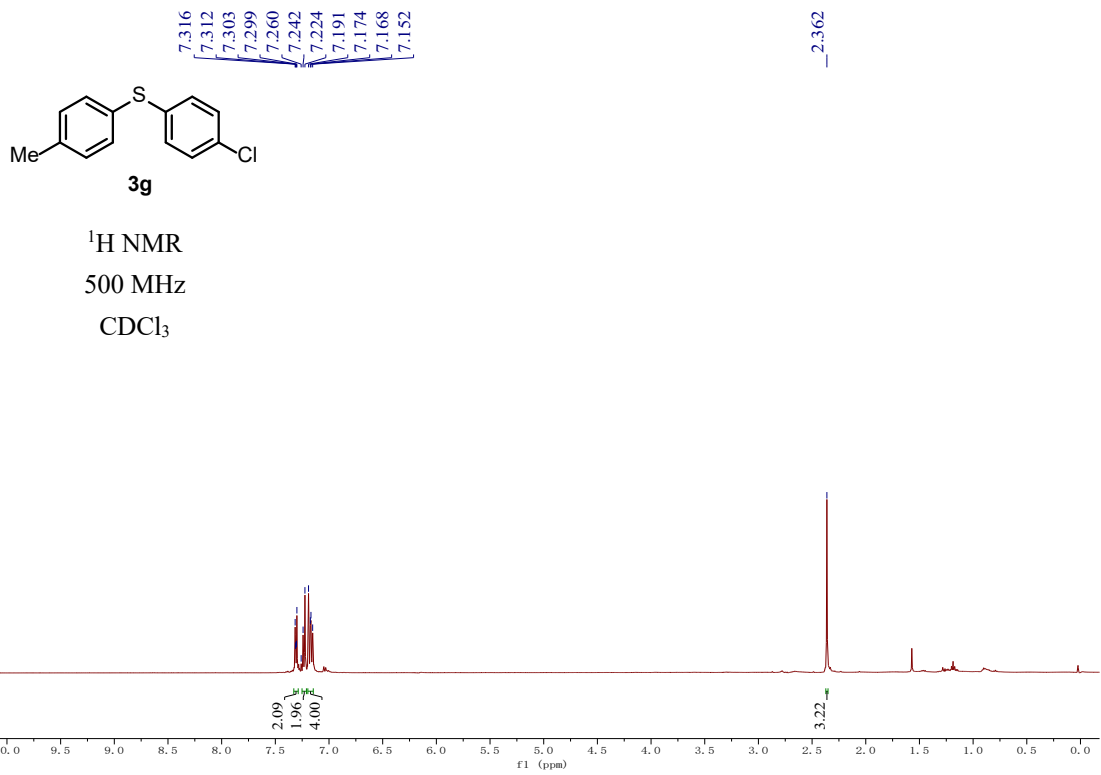
<sup>1</sup>H NMR  
500 MHz  
CDCl<sub>3</sub>

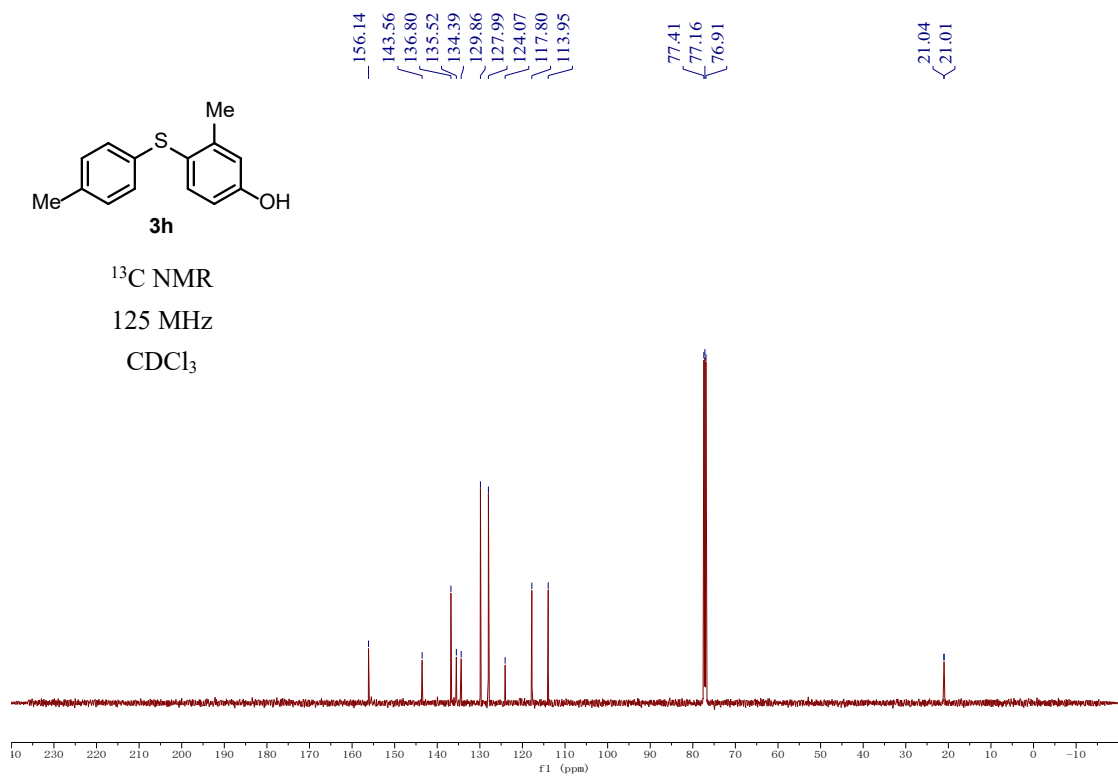
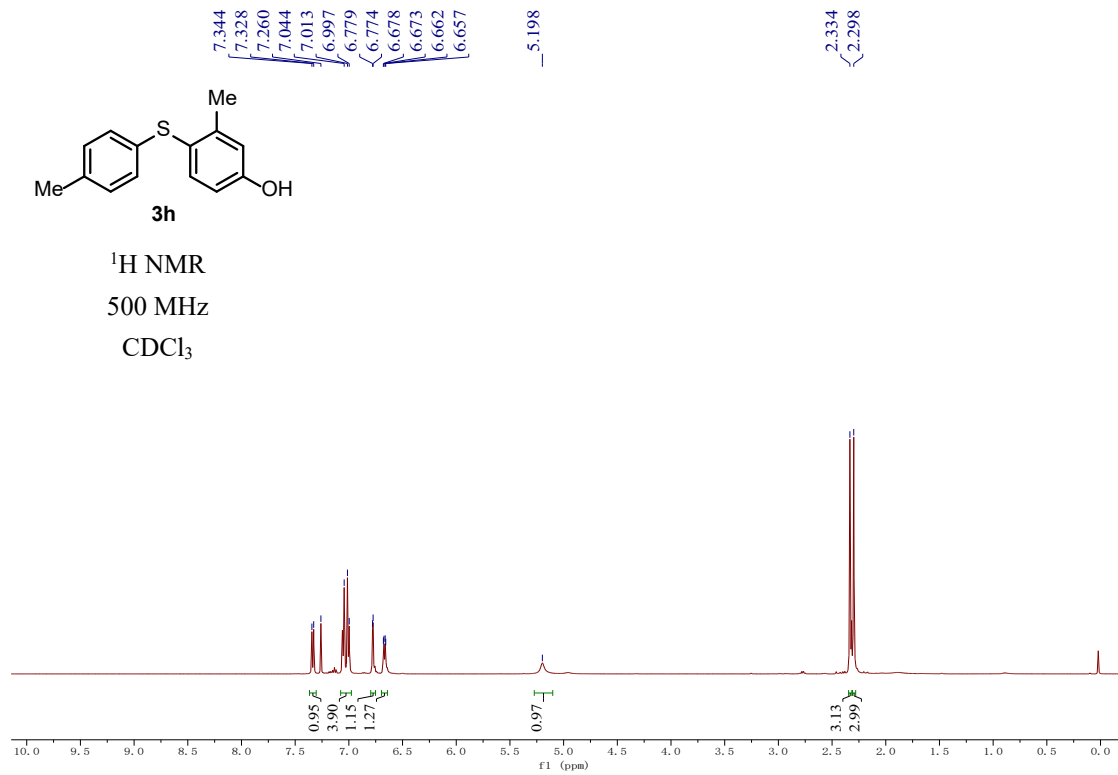


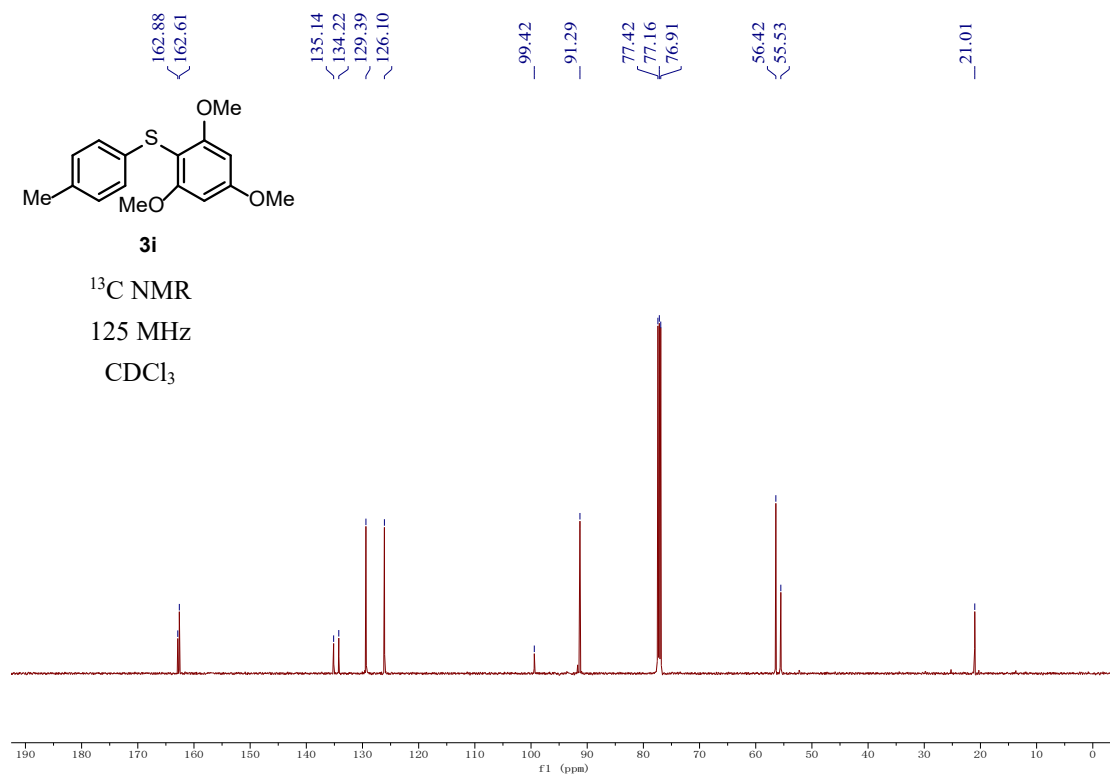
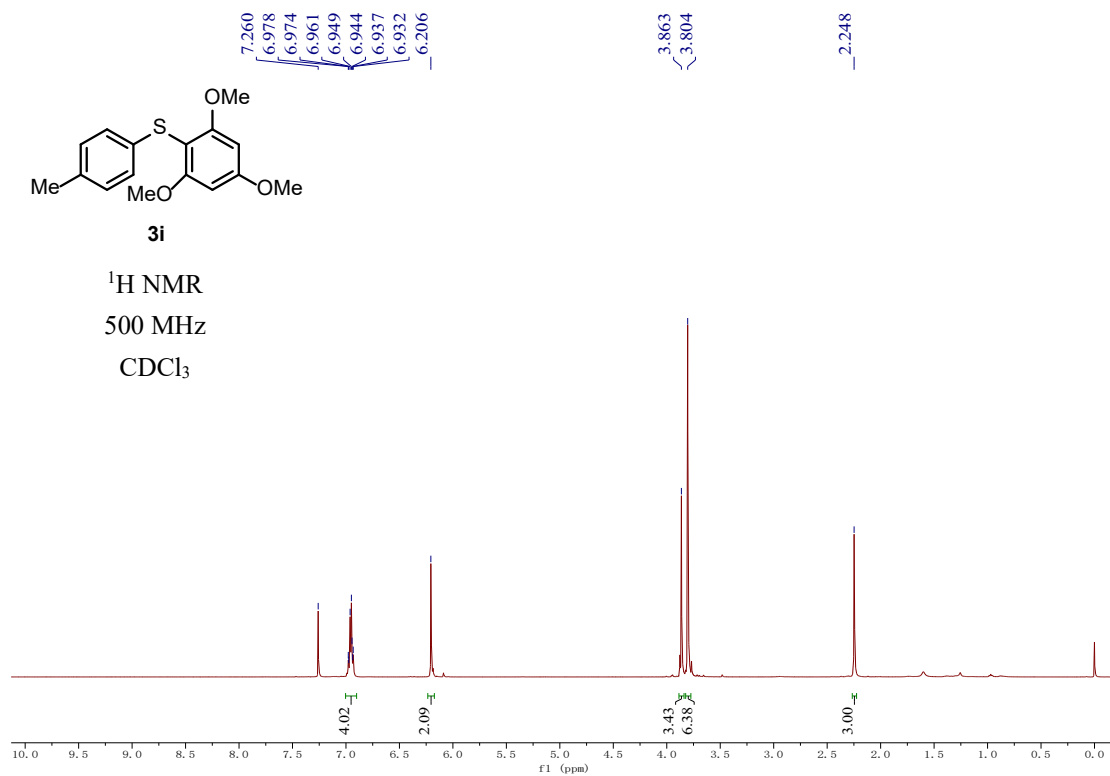
<sup>13</sup>C NMR  
125 MHz  
CDCl<sub>3</sub>



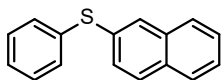








7.802  
7.828  
7.816  
7.809  
7.791  
7.774  
7.759  
7.753  
7.741  
7.507  
7.497  
7.493  
7.486  
7.478  
7.475  
7.465  
7.441  
7.437  
7.424  
7.420  
7.413  
7.409  
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7.314  
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7.273  
7.260

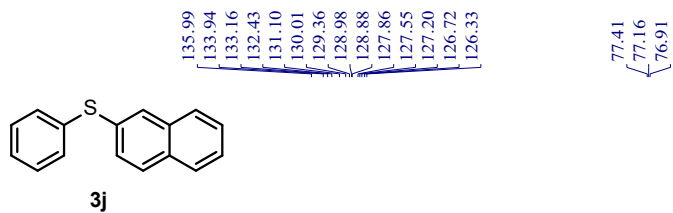
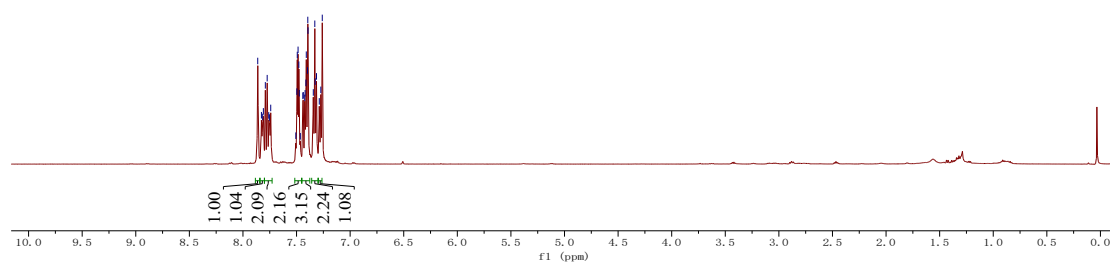


**3j**

<sup>1</sup>H NMR

500 MHz

CDCl<sub>3</sub>

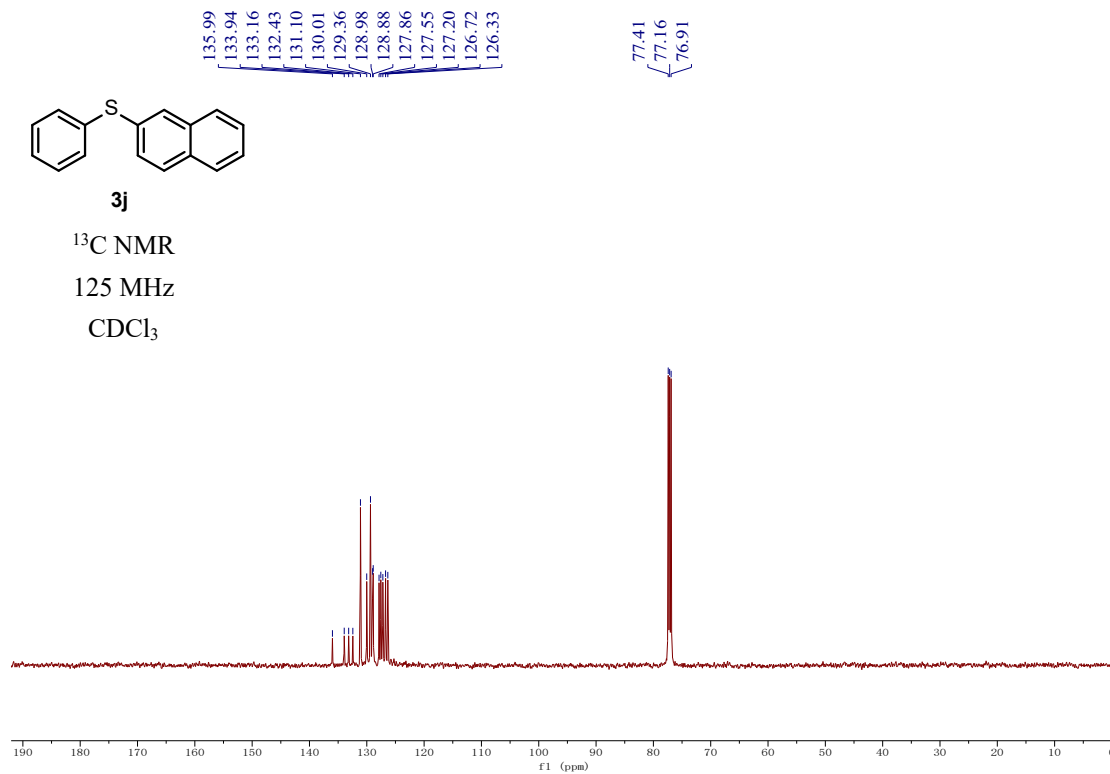


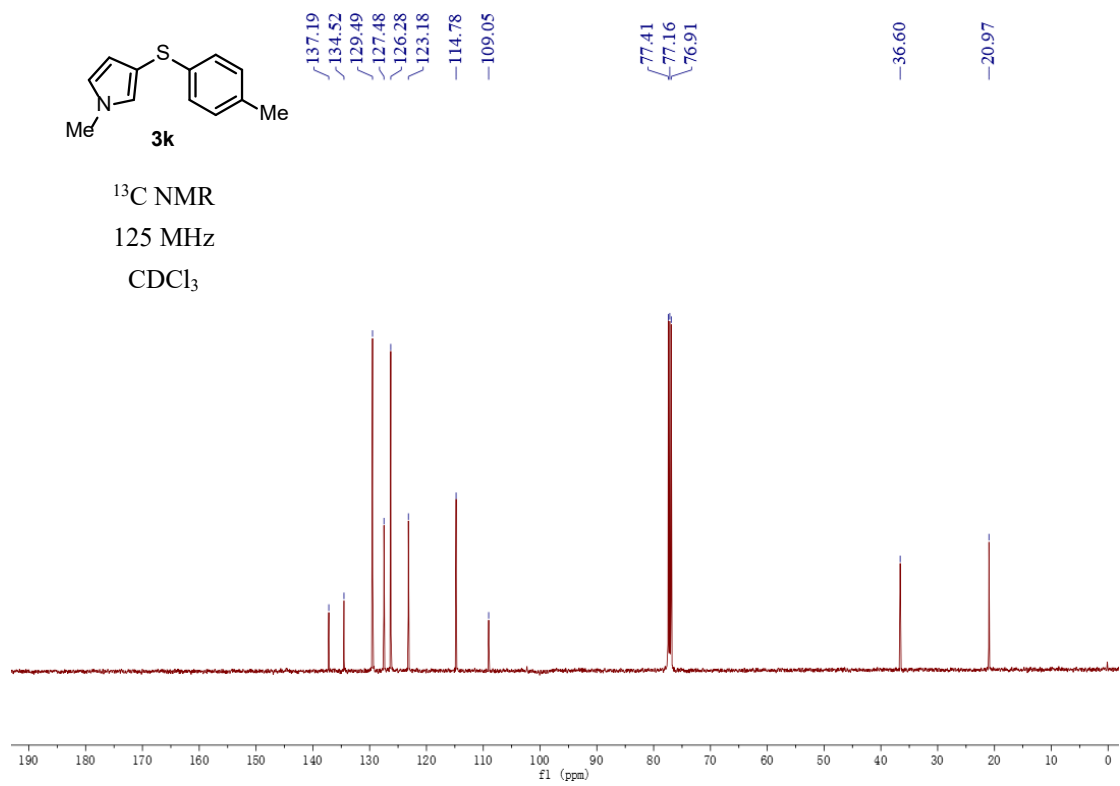
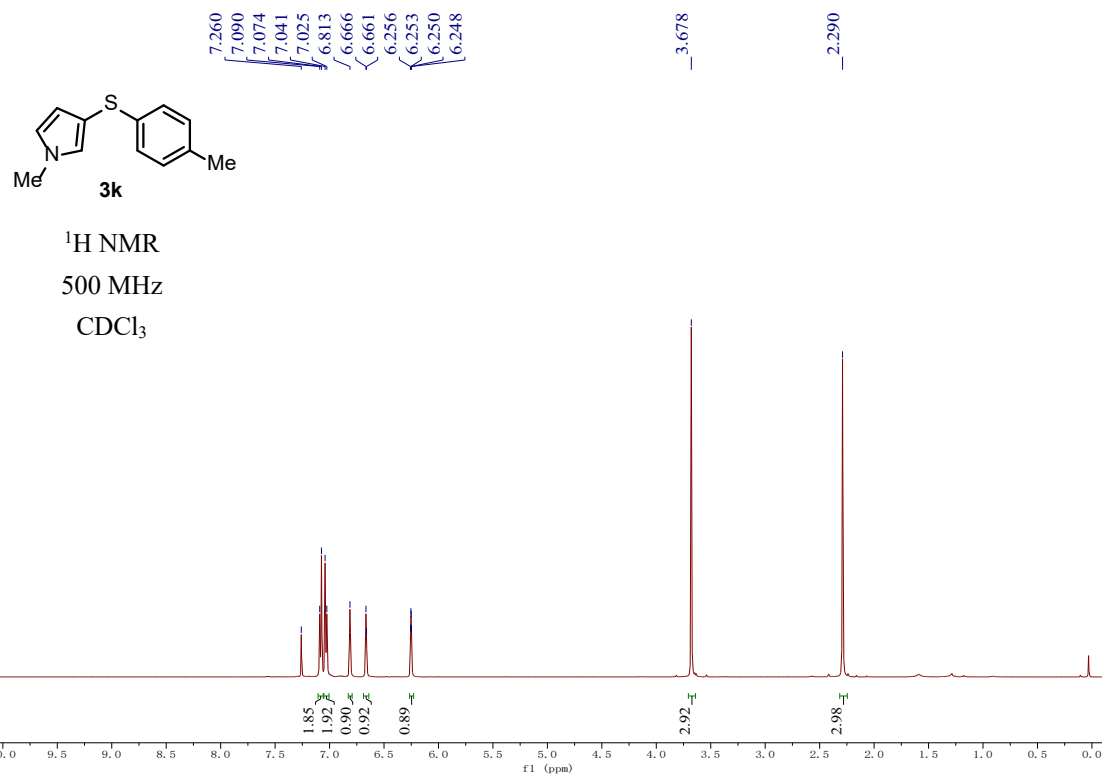
**3j**

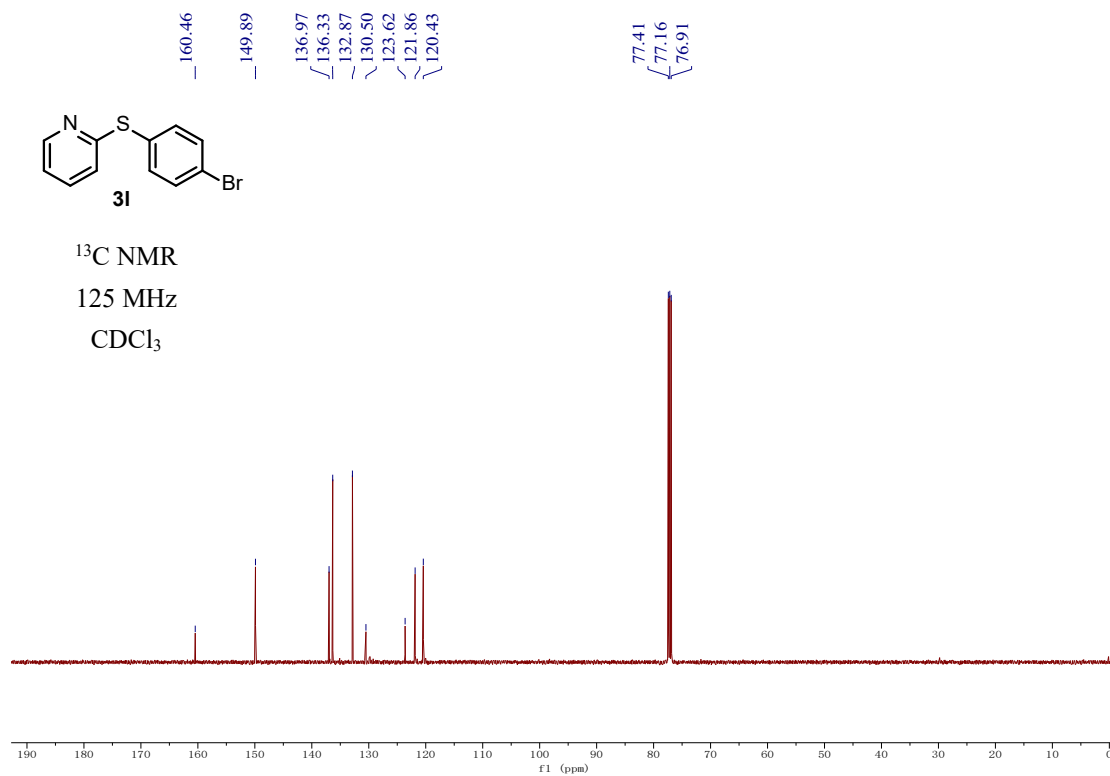
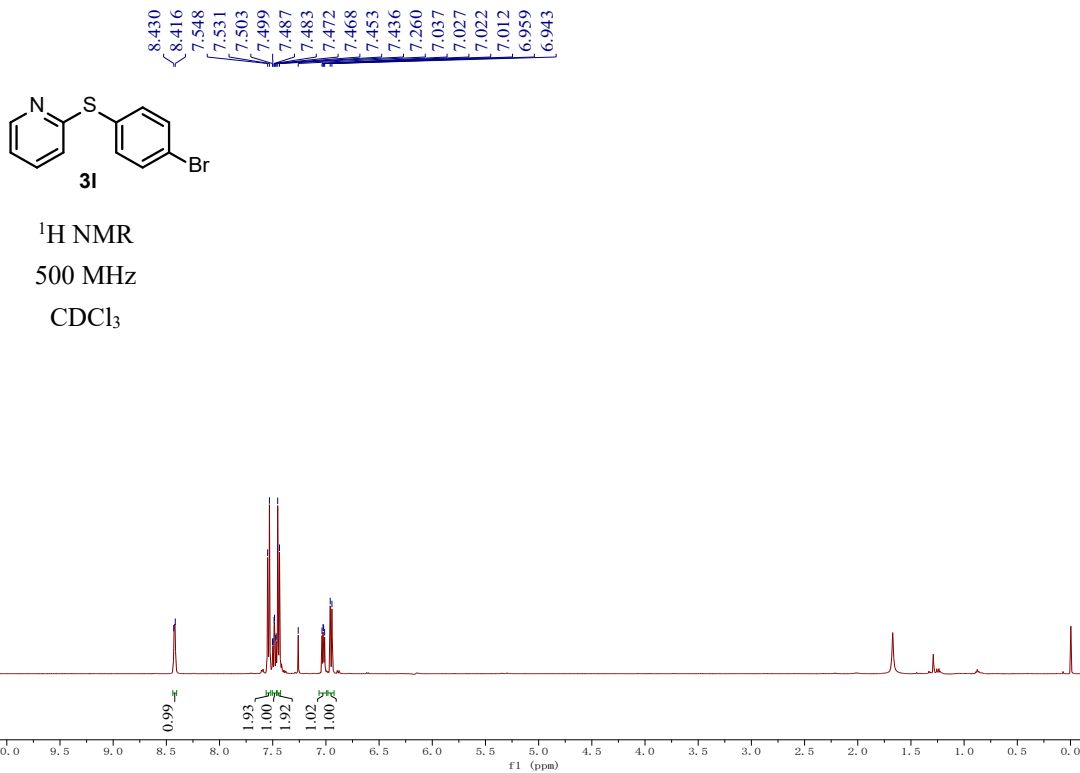
<sup>13</sup>C NMR

125 MHz

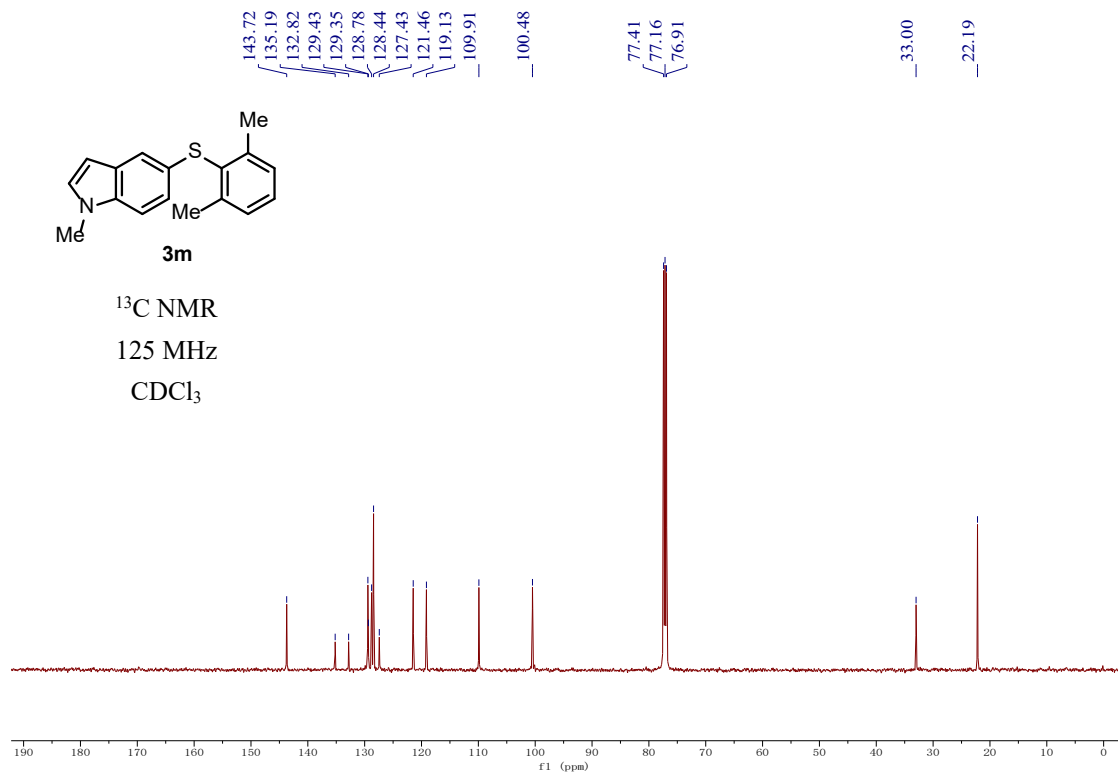
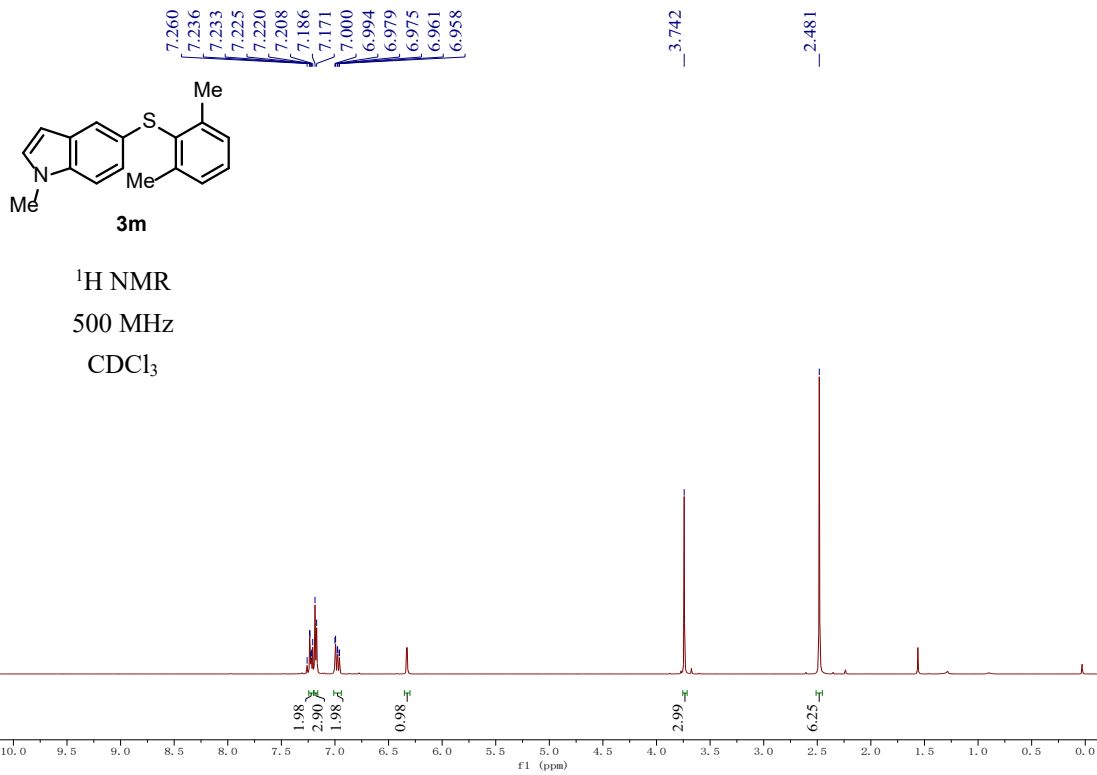
CDCl<sub>3</sub>

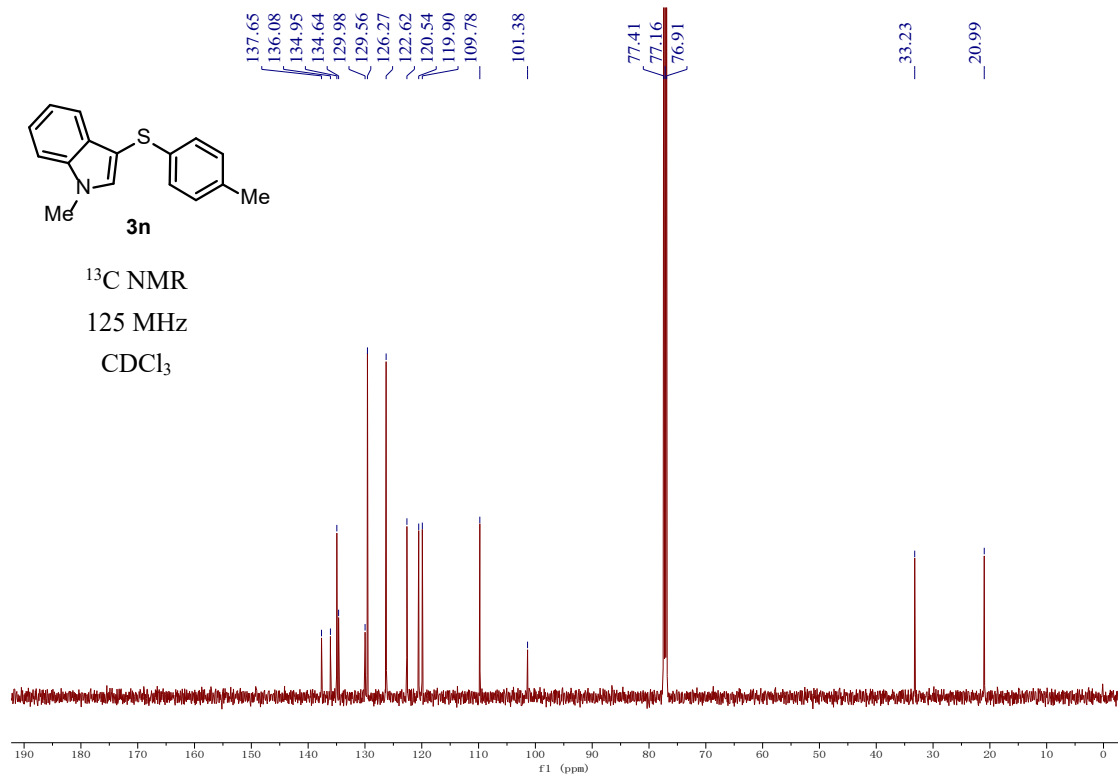
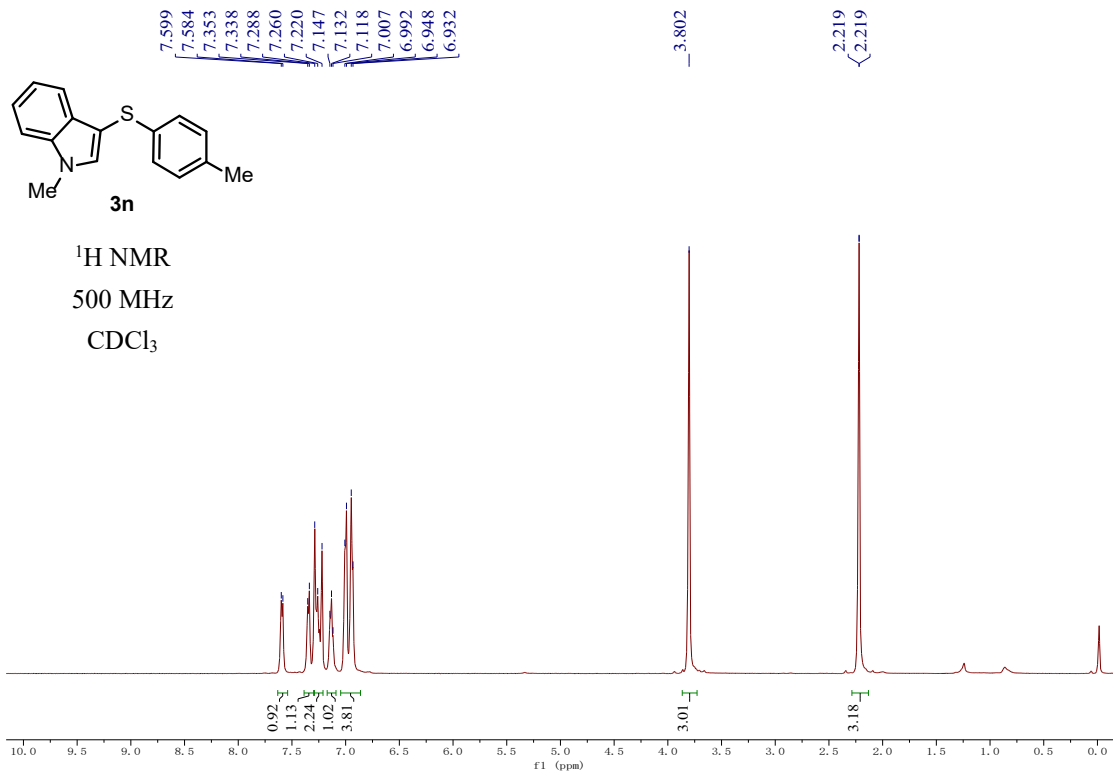


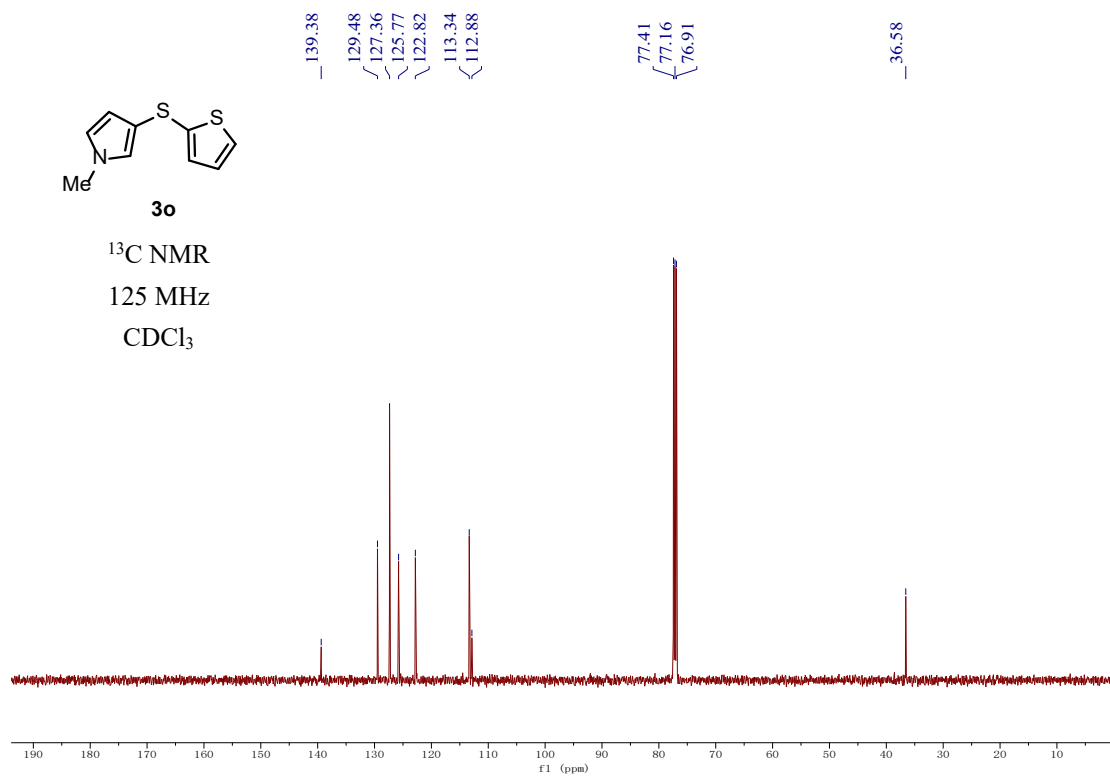
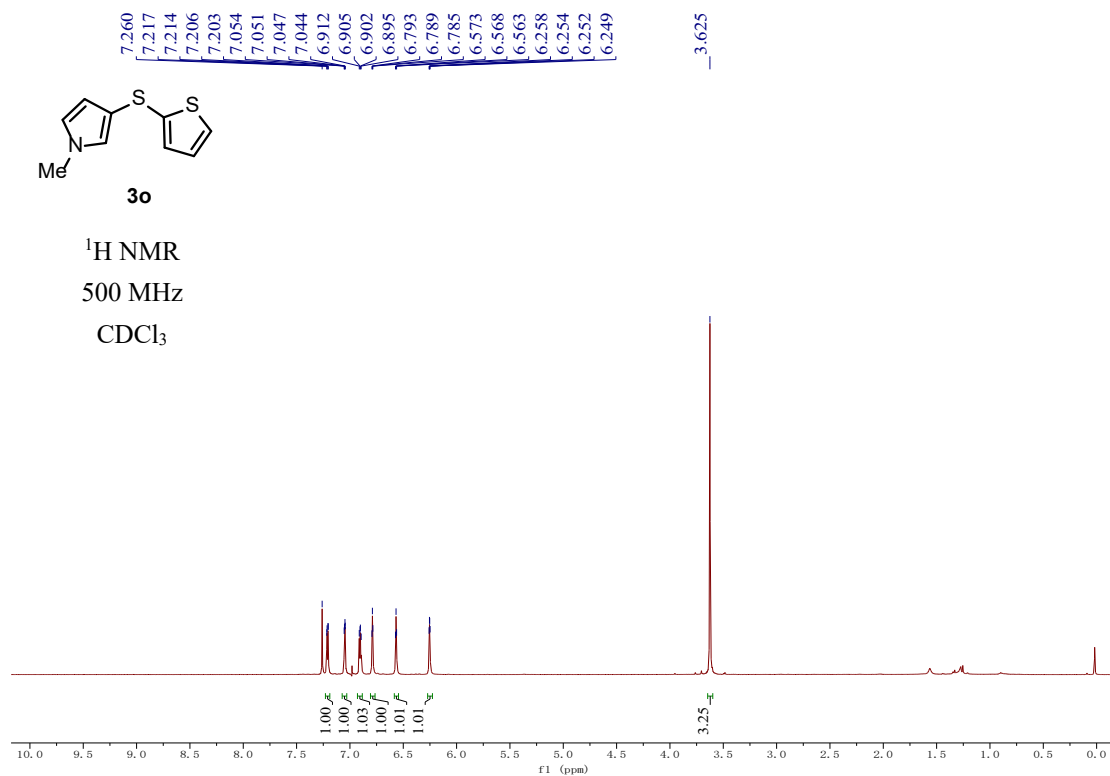




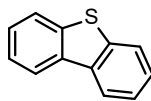








8.193  
8.186  
8.179  
8.174  
8.167  
8.159  
8.157  
7.897  
7.889  
7.883  
7.879  
7.877  
7.871  
7.863  
7.496  
7.488  
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7.482  
7.476  
7.473  
7.470  
7.467  
7.462  
7.459  
7.260

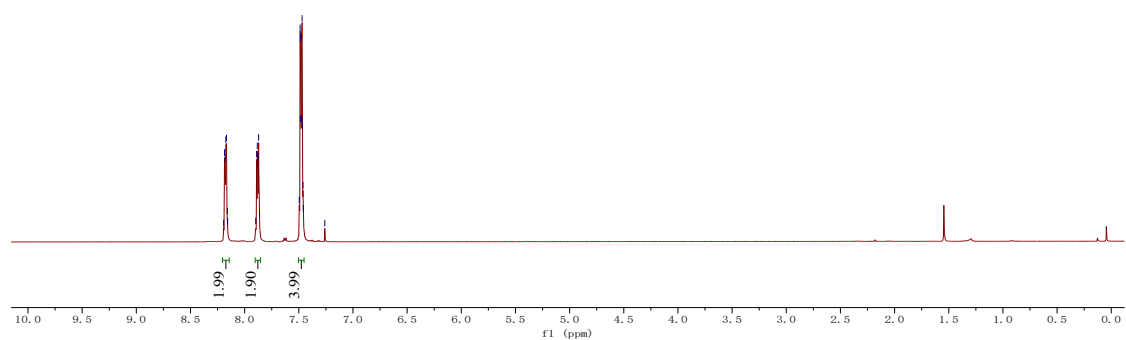


**3p**

<sup>1</sup>H NMR

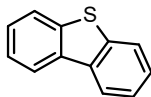
500 MHz

CDCl<sub>3</sub>



139.44  
135.55  
126.70  
124.35  
122.81  
121.58

77.30  
77.05  
76.80

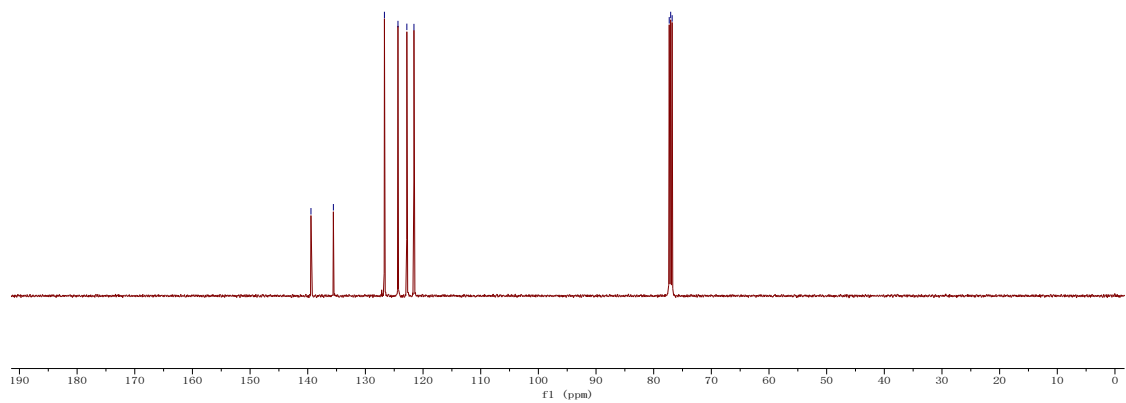


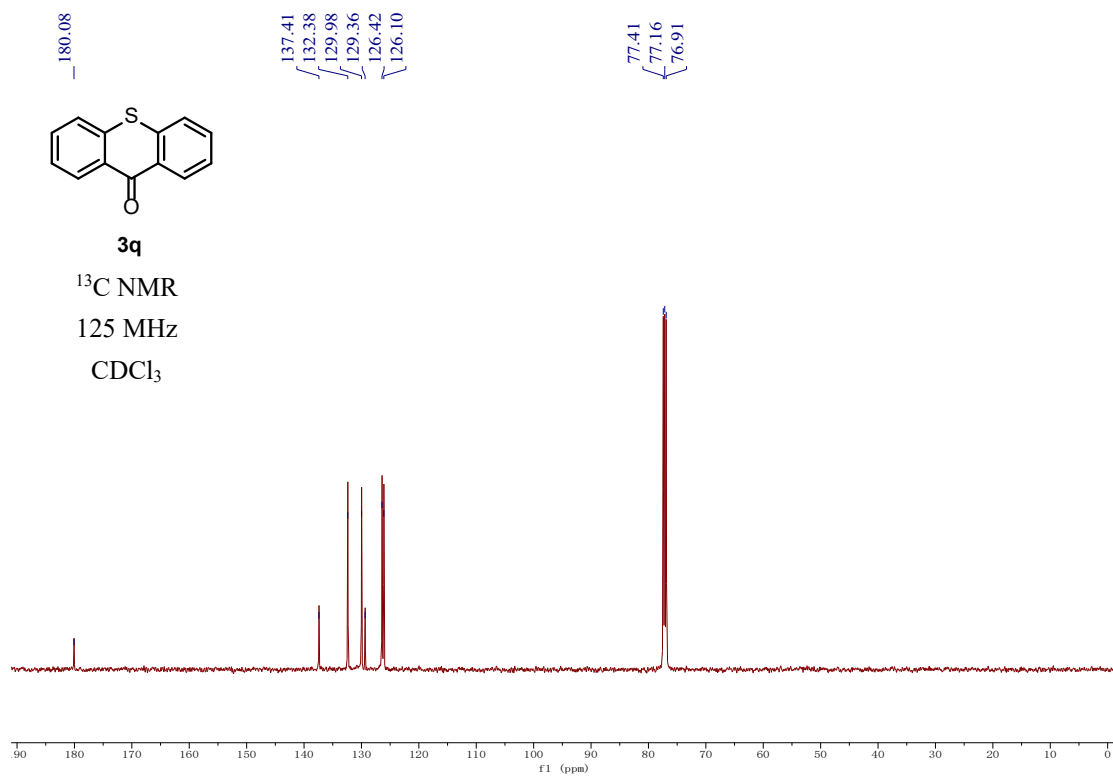
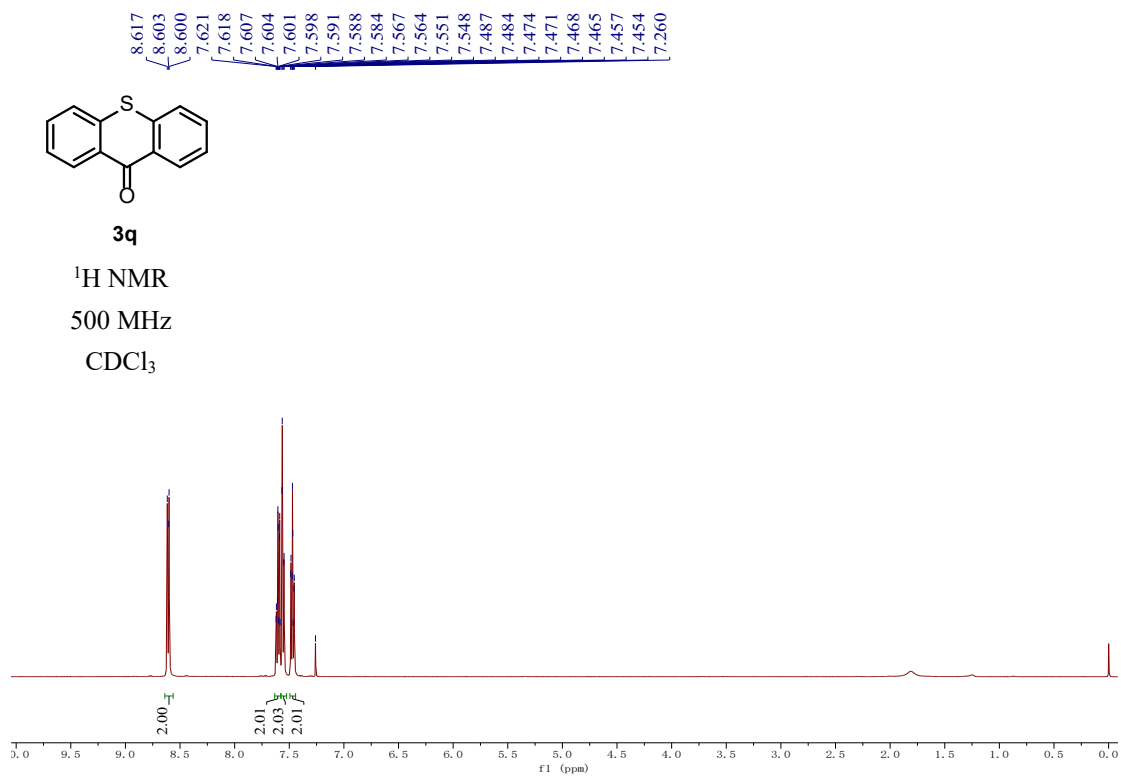
**3p**

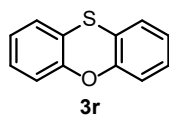
<sup>13</sup>C NMR

125 MHz

CDCl<sub>3</sub>

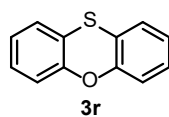
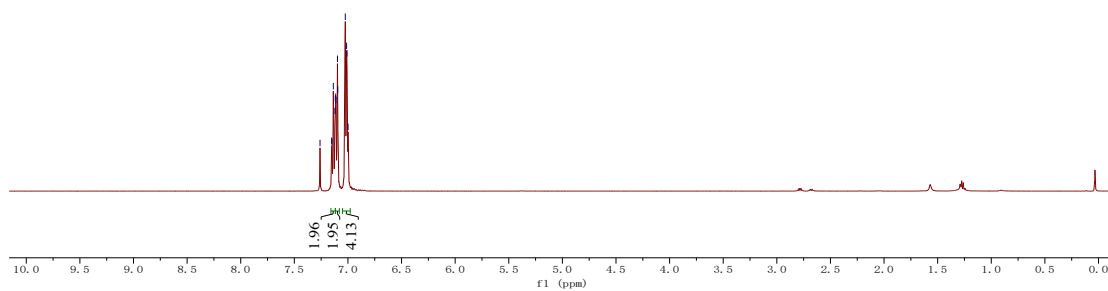






7.260  
7.152  
7.149  
7.136  
7.121  
7.118  
7.114  
7.111  
7.098  
7.095  
7.025  
7.012  
7.009  
6.999

<sup>1</sup>H NMR  
500 MHz  
CDCl<sub>3</sub>

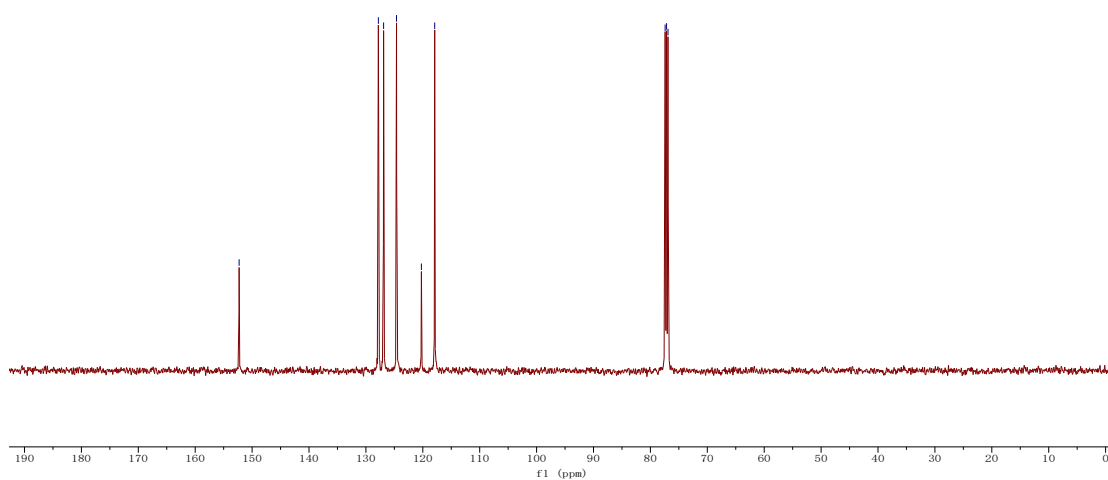


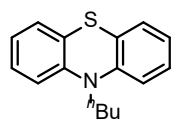
152.28

127.81  
126.89  
124.62  
120.25  
117.91

77.41  
77.16  
76.91

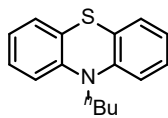
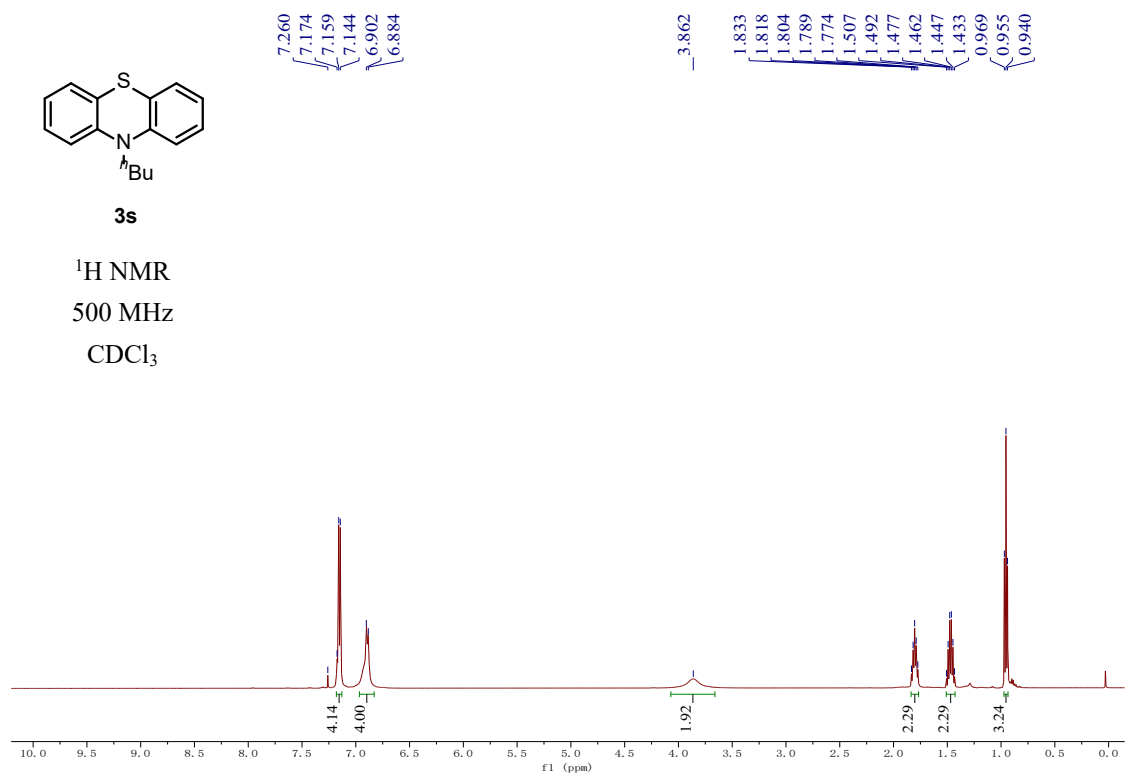
<sup>13</sup>C NMR  
125 MHz  
CDCl<sub>3</sub>





**3s**

$^1\text{H}$  NMR  
500 MHz  
 $\text{CDCl}_3$



**3s**

$^{13}\text{C}$  NMR  
125 MHz  
 $\text{CDCl}_3$

