

## Supplementary Information

# Visible-light-promoted sulfonylation of thiols with aryldiazonium and sodium metabisulphite leading to unsymmetrical thiosulfonates

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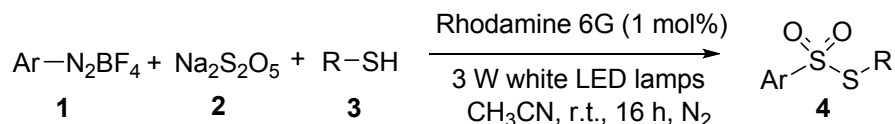
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## 1. General information

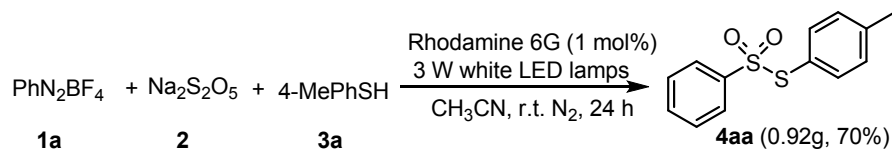
All commercially available reagent grade chemicals were purchased from Adamas, Strem, MERYER, Alfa Aesar and Energy Chemical Company and used as received without further purification unless otherwise stated.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded in  $\text{CDCl}_3$  on a Bruker Avance III 500MHz or 400 MHz spectrometer with TMS as internal standard at room temperature, the chemical shifts ( $\delta$ ) were expressed in ppm and  $J$  values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). High-resolution mass spectra (HRMS) were obtained on an LTQ Orbitrap XL mass spectrometry equipped with an ESI source. Column chromatography was performed on silica gel (200-300 mesh).

**2. General procedure for visible-light-promoted sulfonylation of thiols with aryldiazonium and sodium metabisulphite leading to unsymmetrical thiosulfonates.**



In a tube (25 mL), aryldiazonium tetrafluoroborate **1** (0.4 mmol), Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> **2** (0.4 mmol), thiols **3** (0.2 mmol), Rhodamine 6G (1 mol%), and CH<sub>3</sub>CN (2 mL) were added. The reaction mixture was stirred and irradiated by 3 W white LEDs at room temperature under nitrogen atmosphere for 16h. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **4**.

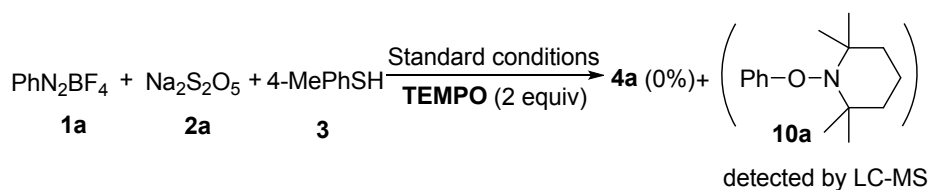
**Gram-scale experiment**



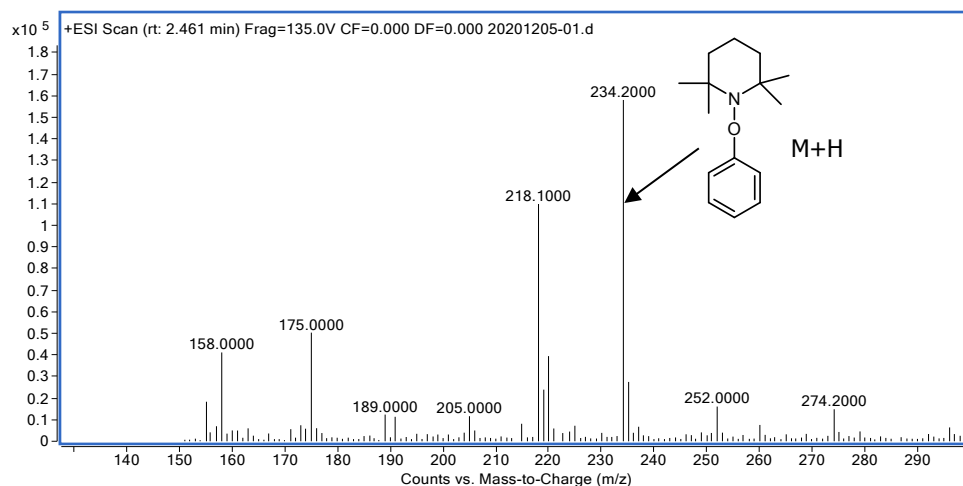
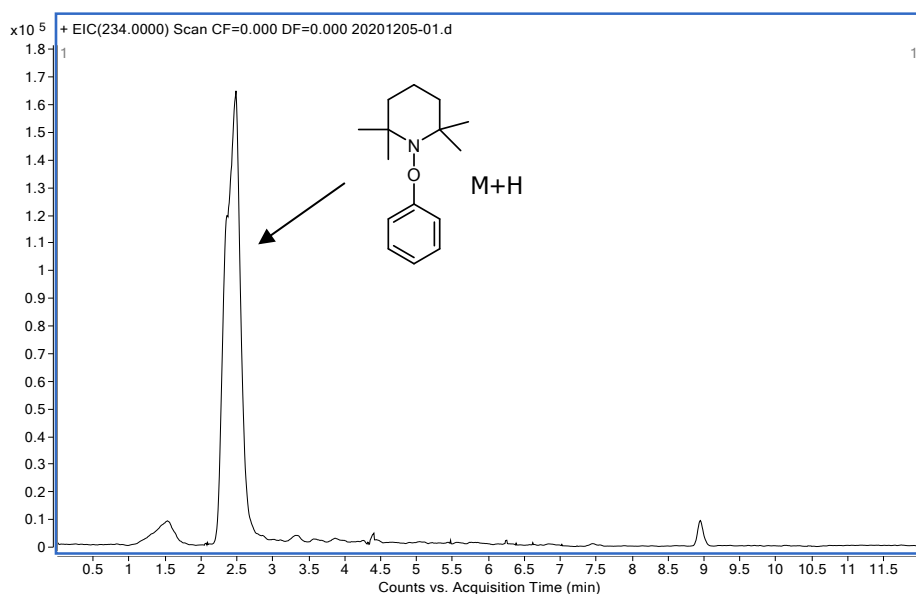
In a tube (25 mL), phenyldiazonium tetrafluoroborate **1a** (10 mmol), Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> **2** (10 mmol), 4-methylbenzenethiol **3a** (5 mmol), Rhodamine 6G (1 mol%), and CH<sub>3</sub>CN (5 mL) were added. The reaction mixture was stirred and irradiated by 3 W white LEDs at room temperature under nitrogen atmosphere for 24h. After completion of the reaction, 5 mL water was added. The mixture was extracted by ethyl acetate. The extracting solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **4aa** in 0.92g (70%).

### 3. Preliminary mechanistic studies

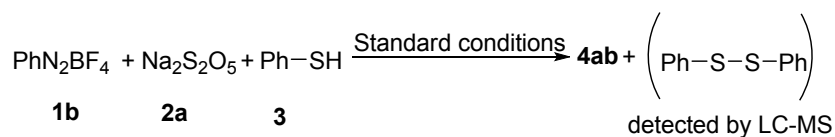
#### 3.1 The addition of TEMPO in the model reaction system.



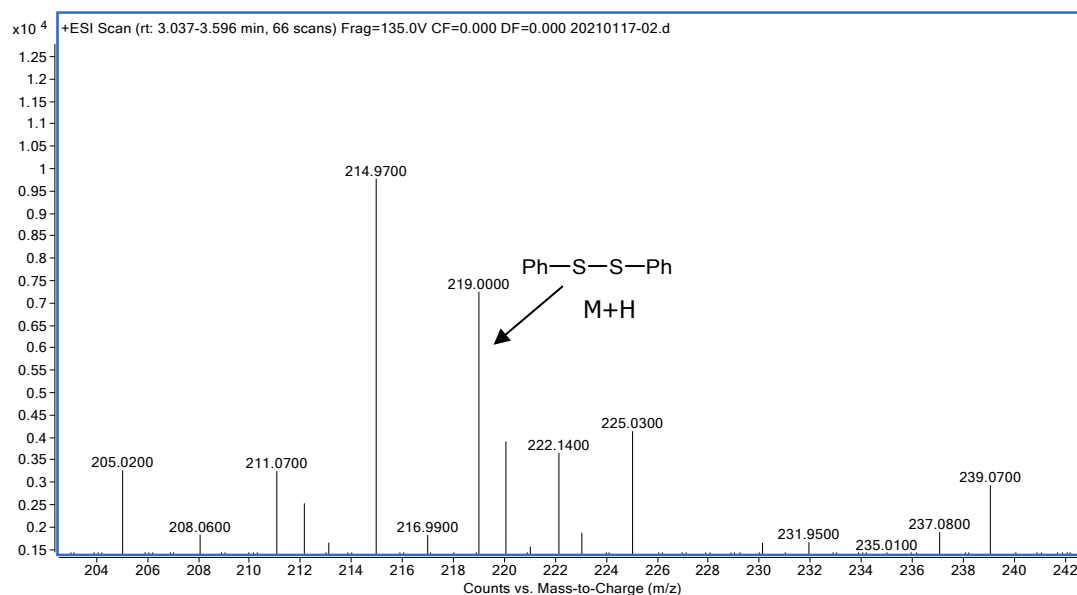
In a tube (25 mL), phenyldiazonium tetrafluoroborate **1a** (0.4 mmol), Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> **2a** (0.4 mmol), 4-methylbenzenethiol **3a** (0.2 mmol), Rhodamine 6G (1 mol%), TEMPO (0.4 mmol), and CH<sub>3</sub>CN (2 mL) were added. The reaction mixture was stirred and irradiated by 3 W white LEDs at room temperature under nitrogen atmosphere for 16h. After completion of the reaction, the reaction mixture was concentrated in vacuum. None of the desired product **4aa** was detected and aryl-TEMPO adduct was detected by LC-MS.



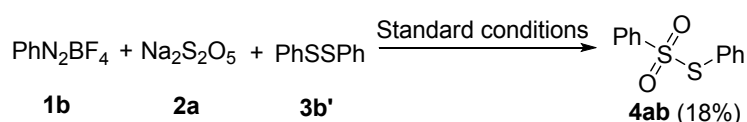
### 3.2 The detection of disulfide in the reaction system



In a tube (25 mL), phenyldiazonium tetrafluoroborate **1a** (0.4 mmol), Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> **2a** (0.4 mmol), 4-methylbenzenethiol **3a** (0.2 mmol) and CH<sub>3</sub>CN (2 mL) were added. The reaction mixture was stirred and irradiated by 3 W white LEDs at room temperature under nitrogen atmosphere for 16h. After completion of the reaction, the reaction mixture was concentrated in vacuum. In addition to product **4ab**, 1,2-diphenyldisulfide **3b'** was detected.



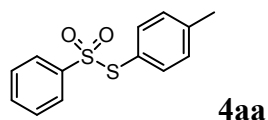
### 3.2 The reaction of phenyldiazonium tetrafluoroborate, Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, 1,2-diphenyldisulfide under the standard conditions



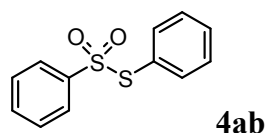
In a tube (25 mL), phenyldiazonium tetrafluoroborate **1a** (0.4 mmol), Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> **2a** (0.4 mmol), 1,2-diphenyldisulfide **3b'** (0.2 mmol) and CH<sub>3</sub>CN (2 mL) were added. The reaction mixture was stirred and irradiated by 3 W white LEDs at room temperature under nitrogen atmosphere for 16h. After completion of the reaction, the

reaction mixture was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **4ab** in 18% yield.

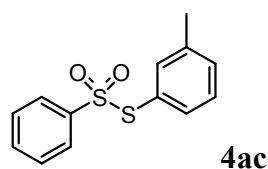
#### 4. Characterization data of products



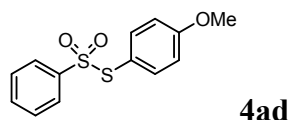
**S-p-tolyl benzenesulfonothioate** Yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58-7.56 (m, 3H), 7.42 (t,  $J = 7.3$  Hz, 2H), 7.22 (d,  $J = 7.7$  Hz, 2H), 7.13(d,  $J = 7.8$  Hz, 2H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm)  $\delta$  143.1, 142.2, 136.5, 133.6, 130.2, 128.8, 127.6, 124.4, 21.5. ESI HRMS: calculated for  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  265.0357, found 265.0353.



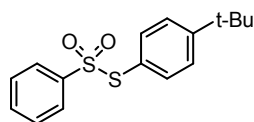
**S-phenyl benzenesulfonothioate** Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 - 7.55 (m, 3H), 7.48 - 7.45 (m, 1H), 7.43-7.40 (m, 2H), 7.34-7.31 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.9, 136.6, 133.7, 131.5, 129.5, 128.8, 127.8, 127.6. ESI HRMS: calculated for  $\text{C}_{12}\text{H}_{11}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  251.0200, found 251.0217.



**S-m-tolyl benzenesulfonothioate** Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58-7.54 (m, 3H), 7.40 (d,  $J = 7.2$  Hz, 2H), 7.24 (s, 1H), 7.19 (t,  $J = 7.5$  Hz, 1H), 7.12 - 7.10 (m, 2H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.9, 139.5, 137.2, 133.6, 133.6, 132.2, 129.2, 128.7, 127.7, 127.4, 21.2. ESI HRMS: calculated for  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  265.0357, found 265.0369.

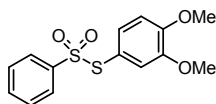


**S-4-methoxyphenyl benzenesulfonothioate** Yellow solid, mp 56 - 57  $^\circ\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59-7.56 (m, 3H), 7.43 (t,  $J = 7.4$  Hz, 2H), 7.24 (d,  $J = 8.6$  Hz, 2H), 6.83 (d,  $J = 8.6$  Hz, 2H), 3.82 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.4, 143.0, 138.4, 133.6, 128.8, 127.6, 118.5, 115.0, 55.5. ESI HRMS: calculated for  $\text{C}_{13}\text{H}_{13}\text{O}_3\text{S}_2$   $[\text{M}+\text{H}]^+$  281.0306, found 281.0301.



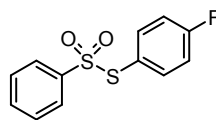
**4ae**

**S-4-tert-butylphenyl benzenesulfonothioate** White solid, mp 60 - 61 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.59 - 7.55 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 8.4 Hz, 2H), 1.31 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.3, 143.1, 136.3, 133.6, 128.8, 127.6, 126.6, 124.4, 35.0, 31.2. ESI HRMS: calculated for C<sub>16</sub>H<sub>19</sub>O<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup> 307.0826, found 307.0811.



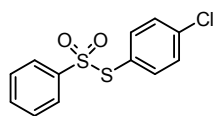
**4af**

**S-3,4-dimethoxyphenyl benzenesulfonothioate** Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.61 - 7.57 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 6.96 (dd, *J*<sub>1</sub> = 1.8 Hz, *J*<sub>2</sub> = 8.4 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 1.8 Hz, 1H), 3.90 (s, 3H), 3.71 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 152.0, 149.1, 142.9, 133.5, 130.4, 128.8, 127.8, 118.7, 118.6, 111.4, 56.0, 55.9. ESI HRMS: calculated for C<sub>14</sub>H<sub>15</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup> 311.0412, found 311.0408.



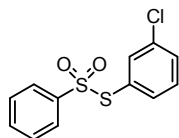
**4ag**

**S-4-fluorophenyl benzenesulfonothioate** Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.62 - 7.57 (m, 3H), 7.47 - 7.42 (m, 2H), 7.36 - 7.32 (m, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 3.98 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.8 (t, *J* = 252.5 Hz), 142.7, 138.9 (d, *J* = 9.1 Hz), 133.8, 128.9, 127.6, 123.4 (d, *J* = 3.3 Hz), 116.8 (d, *J* = 22.1 Hz). ESI HRMS: calculated for C<sub>12</sub>H<sub>9</sub>FN<sub>2</sub>O<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup> 290.9926, found 290.9944.



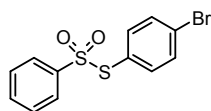
**4ah**

**S-4-chlorophenyl benzenesulfonothioate** White solid, mp, 66 - 67 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.62 - 7.58 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.33-7.27 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.8, 138.3, 137.8, 133.9, 129.8, 129.0, 127.6, 126.3. ESI HRMS: calculated for C<sub>12</sub>H<sub>10</sub>ClO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup> 284.9811, found 284.9815.



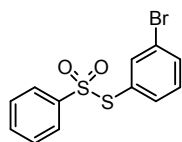
**4ai**

**S-3-chlorophenyl benzenesulfonothioate** Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.64 - 7.60 (m, 3H), 7.50 - 7.46 (m, 3H), 7.32 - 7.29 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.7, 136.1, 134.9, 134.7, 134.0, 131.6, 130.5, 129.5, 129.0, 127.6. ESI HRMS: calculated for C<sub>12</sub>H<sub>10</sub>ClO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup> 284.9811, found 284.9822.



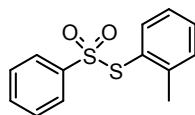
**4aj**

**S-4-bromophenyl benzenesulfonothioate** White solid, mp, 72 - 73 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.62-7.58 (m, 3H), 7.49-7.44 (m, 4H), 7.20 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm) δ 142.8, 137.9, 133.9, 132.8, 129.0, 127.6, 126.9, 126.8. ESI HRMS: calculated for C<sub>12</sub>H<sub>9</sub>BrNaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup> 350.9125, found 350.9087.



**4ak**

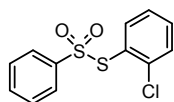
**S-3-bromophenyl benzenesulfonothioate** Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.64 - 7.58 (m, 4H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 1.8 Hz, 1H), 7.35-7.33 (m, 1H), 7.23 (t, *J* = 7.9 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.6, 138.9, 135.1, 134.5, 134.0, 130.7, 129.7, 129.0, 127.7, 122.7. ESI HRMS: calculated for C<sub>12</sub>H<sub>9</sub>BrNaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup> 350.9125, found 350.9125.



**4al**

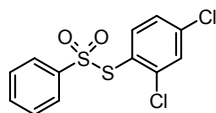
#### **S-o-tolyl benzenesulfonothioate**

Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.61-7.54 (m, 3H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.38-7.32 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 2.12 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 144.2, 143.3, 138.3, 133.7, 131.9, 131.0, 128.9, 127.5, 127.1, 126.9, 20.6. ESI HRMS: calculated for C<sub>13</sub>H<sub>13</sub>O<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup> 265.0357, found 265.0336.



**4am**

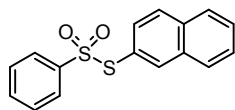
**S-2-chlorophenyl benzenesulfonothioate** White solid, mp, 63 - 64 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.68 (dd, *J*<sub>1</sub> = 1.6 Hz, *J*<sub>2</sub> = 7.8 Hz, 1H), 7.62 - 7.51 (m, 3H), 7.45 - 7.39 (m, 3H), 7.38-7.36 (m, 1H), 7.31 (t, *J*<sub>1</sub> = 1.7 Hz, *J*<sub>2</sub> = 7.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.4, 140.3, 139.6, 134.0, 133.0, 130.3, 129.1, 127.8, 127.5, 127.0. ESI HRMS: calculated for C<sub>12</sub>H<sub>10</sub>ClO<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup> 284.9811, found 284.9826.



**4an**

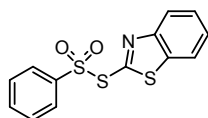
**S-2,4-dichlorophenyl benzenesulfonothioate** Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.64 - 7.60 (m, 4H), 7.48 - 7.44 (m, 2H), 7.39 (d, *J* = 2.2 Hz, 1H), 7.31 (dd, *J*<sub>1</sub> = 2.2 Hz, *J*<sub>2</sub> = 8.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.4, 141.1, 140.2, 138.9, 134.1, 130.2, 129.2, 128.2, 127.5, 125.7. ESI HRMS: calculated for C<sub>12</sub>H<sub>9</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup> 318.9421, found 318.9435.





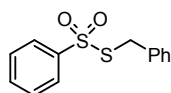
**4ao**

**naphthalen-2-yl benzenesulfonothioate** Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 (d,  $J = 7.8$  Hz, 2H), 7.79 (d,  $J = 8.6$  Hz, 1H), 7.74 (d,  $J = 7.9$  Hz, 1H), 7.62-7.51 (m, 5H), 7.40-7.36 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm)  $\delta$  142.9, 137.7, 134.1, 133.7, 133.3, 131.8, 129.2, 128.9, 128.5, 128.3, 127.8, 127.6, 127.0, 124.9. ESI HRMS: calculated for  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  301.0357, found 301.0333.



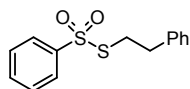
**4ap**

**S-benzo[d]thiazol-2-yl benzenesulfonothioate** Yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J = 8.2$  Hz, 1H), 7.74 (d,  $J = 7.0$  Hz, 2H), 7.65 (d,  $J = 8.0$  Hz, 1H), 7.53-7.46 (m, 3H), 7.42 (t,  $J = 8.6$  Hz, 1H), 7.28-7.25 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm)  $\delta$  169.8, 154.0, 135.6, 135.4, 130.5, 130.0, 126.2, 124.4, 122.0, 120.8. ESI HRMS: calculated for  $\text{C}_{13}\text{H}_{10}\text{NO}_2\text{S}_3$   $[\text{M}+\text{H}]^+$  307.9874, found 307.9883.



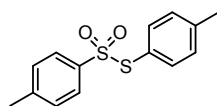
**4aq**

**S-benzyl benzenesulfonothioate** Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84-7.82 (m, 2H), 7.59 (t,  $J = 7.4$  Hz, 1H), 7.48 (t,  $J = 8.0$  Hz, 2H), 7.24-7.16 (m, 5H), 4.27 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.9, 133.6, 133.5, 129.2, 129.1, 128.8, 128.1, 126.9, 40.4. ESI HRMS: calculated for  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  265.0357, found 265.0369.



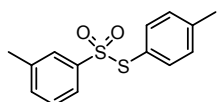
**4ar**

**S-phenethyl benzenesulfonothioate** Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (d,  $J = 7.4$  Hz, 2H), 7.74 (t,  $J = 7.4$  Hz, 1H), 7.66 (t,  $J = 7.9$  Hz, 2H), 7.40-7.30 (m, 3H), 7.19 (d,  $J = 7.0$  Hz, 2H), 3.34 (t,  $J = 7.4$  Hz, 2H), 3.00 (t,  $J = 7.4$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.9, 138.7, 133.8, 129.4, 128.7, 128.6, 127.0, 126.9, 37.2, 35.2. ESI HRMS: calculated for  $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  279.0513, found 279.0497.



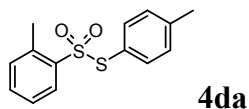
**4ba**

**S-p-tolyl 4-methylbenzenesulfonothioate** White solid, mp, 67 - 68 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 (d,  $J = 8.2$  Hz, 2H), 7.24 (d,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H), 7.14 (d,  $J = 7.9$  Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, ppm)  $\delta$  144.7, 142.1, 140.4, 136.5, 130.3, 129.4, 127.6, 124.6, 21.7, 21.5. ESI HRMS: calculated for  $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  279.0513, found 279.0533.

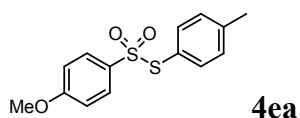


**4ca**

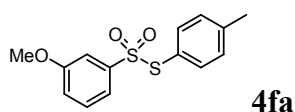
**S-p-tolyl 3-methylbenzenesulfonothioate** Yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.38-7.35 (m, 3H), 7.31-7.28 (m, 1H), 7.23 (d,  $J = 8.2$  Hz, 2H), 7.14 (d,  $J = 8.0$  Hz, 2H), 2.38 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.8, 142.2, 139.1, 136.6, 134.3, 130.2, 128.6, 127.9, 124.7, 124.5, 21.5, 21.2. ESI HRMS: calculated for  $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  279.0513, found 279.0524.



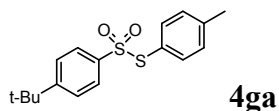
**S-p-tolyl 2-methylbenzenesulfonothioate** Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47 - 7.43 (m, 1H), 7.42-7.39 (m, 1H), 7.33 (d,  $J = 7.5$  Hz, 2H), 7.15 - 7.11 (m, 3H), 7.07 (d,  $J = 8.1$  Hz, 2H), 2.70 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.1, 140.4, 137.8, 136.5, 133.7, 132.8, 130.3, 130.1, 125.7, 124.3, 21.5, 20.5. ESI HRMS: calculated for  $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  279.0513, found 279.0507.



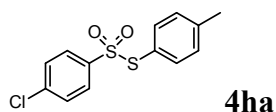
**S-p-tolyl 4-methoxybenzenesulfonothioate** White solid, mp, 61 - 62 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 (d,  $J = 9.0$  Hz, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 7.14 (d,  $J = 8.0$  Hz, 2H), 6.86 (d,  $J = 9.0$  Hz, 2H), 3.87 (s, 3H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm)  $\delta$  163.5, 142.0, 136.5, 135.1, 130.2, 129.9, 124.7, 113.8, 55.7, 21.5. ESI HRMS: calculated for  $\text{C}_{14}\text{H}_{15}\text{O}_3\text{S}_2$   $[\text{M}+\text{H}]^+$  295.0463, found 295.0462.



**S-p-tolyl 3-methoxybenzenesulfonothioate** Yellow solid, mp, 46 - 47 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41 (t,  $J = 8.0$  Hz, 1H), 7.35-7.33 (m, 2H), 7.26-7.23 (m, 3H), 7.20-7.17 (m, 1H), 7.10 (t,  $J = 2.0$  Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.5, 144.0, 142.2, 136.6, 130.3, 129.8, 124.5, 120.6, 119.8, 111.5, 55.6, 21.5. ESI HRMS: calculated for  $\text{C}_{14}\text{H}_{15}\text{O}_3\text{S}_2$   $[\text{M}+\text{H}]^+$  295.0463, found 295.0470.

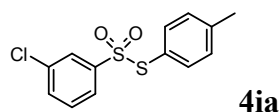


**S-p-tolyl 4-tert-butylbenzenesulfonothioate** Yellow solid, mp, 87 - 88 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50 (d,  $J = 8.7$  Hz, 2H), 7.42 (d,  $J = 8.7$  Hz, 2H), 7.23 (d,  $J = 8.1$  Hz, 2H), 7.13 (t,  $J = 8.0$  Hz, 2H), 2.38 (s, 3H), 1.33 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.6, 142.1, 140.3, 136.6, 130.2, 127.5, 125.8, 124.6, 35.3, 31.1, 21.5. ESI HRMS: calculated for  $\text{C}_{17}\text{H}_{21}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$  321.0983, found 321.0954.

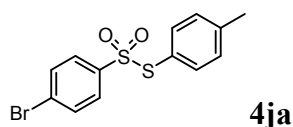


**S-p-tolyl 4-chlorobenzenesulfonothioate** White solid, mp, 122 - 123 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 (d,  $J = 8.7$  Hz, 2H), 7.39 (d,  $J = 8.7$  Hz, 2H), 7.24 (d,  $J = 8.2$  Hz, 2H), 7.16 (d,  $J = 8.0$  Hz, 2H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm)

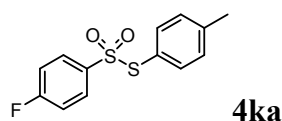
$\delta$  142.5, 141.5, 140.2, 136.5, 130.4, 129.1, 129.0, 124.1, 21.6. ESI HRMS: calculated for  $C_{13}H_{12}ClO_2S_2$   $[M+H]^+$  284.9811, found 284.9826.



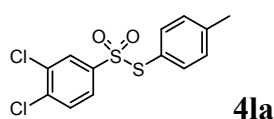
**S-p-tolyl 3-chlorobenzenesulfonothioate** Yellow solid, mp, 70 - 71 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.55-7.53 (m, 1H), 7.48 (t,  $J = 1.7$  Hz, 1H), 7.47-7.44 (m, 1H), 7.37 (t,  $J = 7.9$  Hz, 1H), 7.24 (d,  $J = 8.2$  Hz, 2H), 7.17 (d,  $J = 8.2$  Hz, 2H), 2.39 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  144.3, 142.6, 136.5, 135.0, 133.6, 130.4, 130.0, 127.7, 125.6, 123.9, 21.5. ESI HRMS: calculated for  $C_{13}H_{11}ClNaO_2S_2$   $[M+Na]^+$  320.9787, found 320.9794.



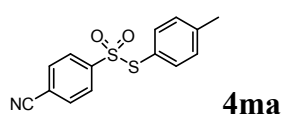
**S-p-tolyl 4-bromobenzenesulfonothioate** White solid, mp, 115 - 116 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.56 (d,  $J = 8.6$  Hz, 2H), 7.42 (d,  $J = 8.36$  Hz, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.17 (d,  $J = 8.1$  Hz, 2H), 2.39 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  142.6, 142.2, 136.6, 132.2, 130.5, 129.1, 128.9, 124.2, 21.6. ESI HRMS: calculated for  $C_{13}H_{12}BrO_2S_2$   $[M+H]^+$  342.9462, found 342.9471.



**S-p-tolyl 4-fluorobenzenesulfonothioate** White solid, mp, 97 - 98 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.60 - 7.56 (m, 2H), 7.23 (d,  $J = 8.2$  Hz, 2H), 7.15 (d,  $J = 8.2$  Hz, 2H), 7.09 (t,  $J = 8.2$  Hz, 2H), 2.38 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz, ppm)  $\delta$  165.6 (d,  $J_{C-F} = 255.1$  Hz), 142.5, 139.1 (d,  $J_{C-F} = 3.0$  Hz), 136.5, 130.4 (d,  $J_{C-F} = 9.6$  Hz), 130.3, 124.2, 116.1 (d,  $J_{C-F} = 22.7$  Hz), 21.5. ESI HRMS: calculated for  $C_{13}H_{12}FO_2S_2$   $[M+H]^+$  283.0263, found 283.0277.

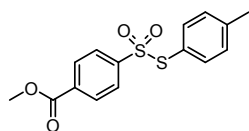


**S-p-tolyl 3,4-dichlorobenzenesulfonothioate** White solid, mp, 98 - 99 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.56 (d,  $J = 2.1$  Hz, 2H), 7.51 (d,  $J = 8.4$  Hz, 2H), 7.38 (dd,  $J = 2.1$  Hz,  $J = 8.4$  Hz, 2H), 7.27 (d,  $J = 7.9$  Hz, 2H), 7.19 (d,  $J = 8.1$  Hz, 1H), 2.41 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  142.8, 142.3, 138.5, 136.5, 133.5, 130.8, 130.6, 129.5, 126.4, 123.8, 21.5. ESI HRMS: calculated for  $C_{13}H_{10}Cl_2NaO_2S_2$   $[M+Na]^+$  354.9397, found 354.9383.



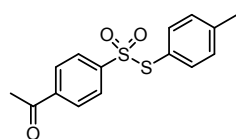
**S-p-tolyl 4-cyanobenzenesulfonothioate** White solid, mp, 105 - 106 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.72 (d,  $J = 8.6$  Hz, 2H), 7.66 (d,  $J = 8.6$  Hz, 2H), 7.23 (d,  $J =$

8.2 Hz, 2H), 7.17 (d,  $J = 8.2$  Hz, 2H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm)  $\delta$  146.6, 142.9, 136.4, 132.7, 130.6, 128.1, 123.5, 117.1, 117.1, 21.6. ESI HRMS: calculated for  $\text{C}_{14}\text{H}_{11}\text{NNaO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  312.0129, found 312.0121.



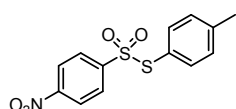
**4na**

**methyl 4-(p-tolylthiosulfonyl)benzoate** White solid, mp, 96 - 97 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.07 (d,  $J = 8.2$  Hz, 2H), 7.62 (d,  $J = 8.3$  Hz, 2H), 7.21 (d,  $J = 8.1$  Hz, 2H), 7.14 (d,  $J = 7.9$  Hz, 2H), 3.96 (s, 3H), 1.39 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.5, 146.5, 142.6, 136.5, 134.4, 130.5, 130.0, 127.6, 123.9, 52.8, 21.5. ESI HRMS: calculated for  $\text{C}_{15}\text{H}_{14}\text{NaO}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  345.0231, found 345.0220.



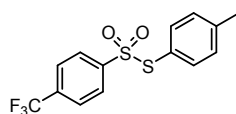
**4oa**

**S-p-tolyl 4-acetylbenzenesulfonothioate** White solid, mp, 79 - 80 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.97 (d,  $J = 8.5$  Hz, 2H), 7.65 (d,  $J = 8.5$  Hz, 2H), 7.23 (d,  $J = 8.1$  Hz, 2H), 7.15 (d,  $J = 8.1$  Hz, 2H), 2.64 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm)  $\delta$  196.7, 146.5, 142.6, 140.4, 136.4, 130.5, 128.7, 127.8, 123.9, 27.0, 21.5. ESI HRMS: calculated for  $\text{C}_{15}\text{H}_{15}\text{O}_3\text{S}_2$   $[\text{M}+\text{H}]^+$  307.0463, found 307.0428.



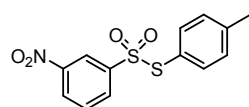
**4pa**

**S-p-tolyl 4-nitrobenzenesulfonothioate** White solid, mp, 137 - 138 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.27 (d,  $J = 8.8$  Hz, 2H), 7.73 (d,  $J = 8.5$  Hz, 2H), 7.24 (d,  $J = 8.0$  Hz, 2H), 7.18 (d,  $J = 8.0$  Hz, 2H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm)  $\delta$  150.3, 148.0, 143.0, 136.4, 130.7, 128.8, 124.1, 123.4, 21.6. MS (ESI); ESI HRMS: calculated for  $\text{C}_{13}\text{H}_{11}\text{NNaO}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  332.0027, found 332.0022.



**4qa**

**S-p-tolyl 4-(trifluoromethyl)benzenesulfonothioate** White solid, mp, 85 - 86 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70 (s, 4H), 7.24 (d,  $J = 8.2$  Hz, 2H), 7.17 (d,  $J = 8.1$  Hz, 2H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.2, 142.7, 136.5, 135.1 (q,  $J = 32.9$  Hz), 130.5, 128.0, 126.0 (q,  $J = 3.7$  Hz), 123.8, 123.1 (q,  $J = 271.5$  Hz), 21.5. ESI HRMS: calculated for  $\text{C}_{14}\text{H}_{11}\text{F}_3\text{NaO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  355.0050, found 355.0010.



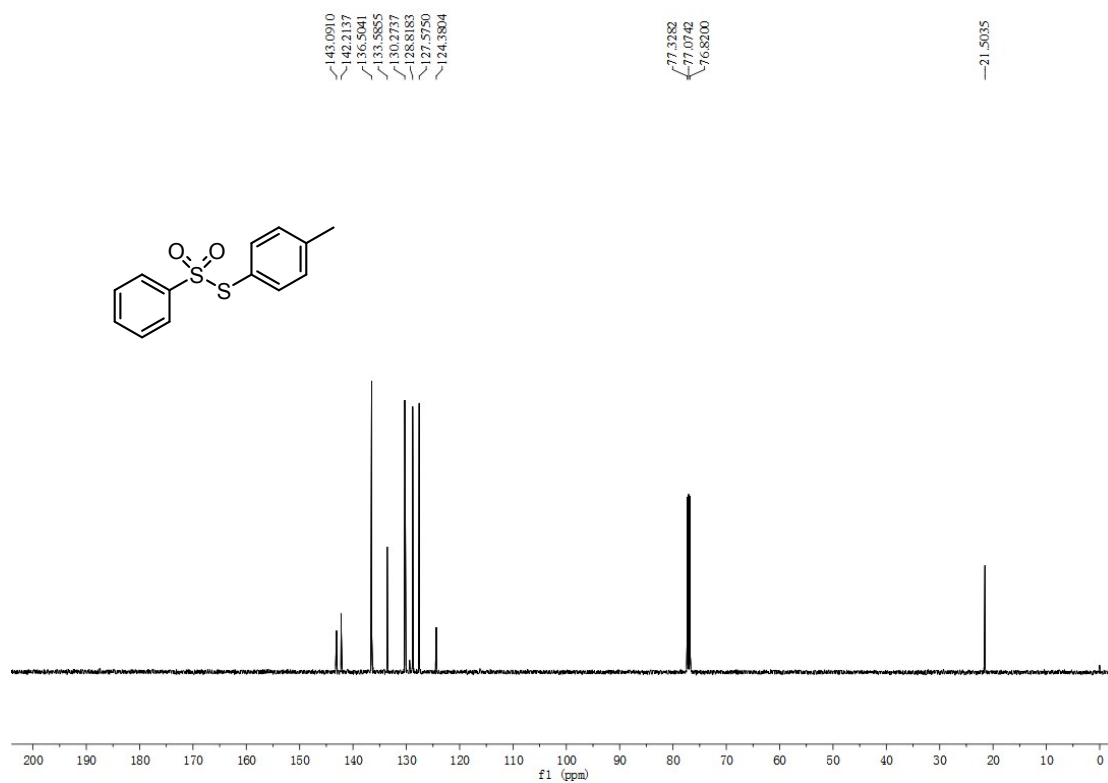
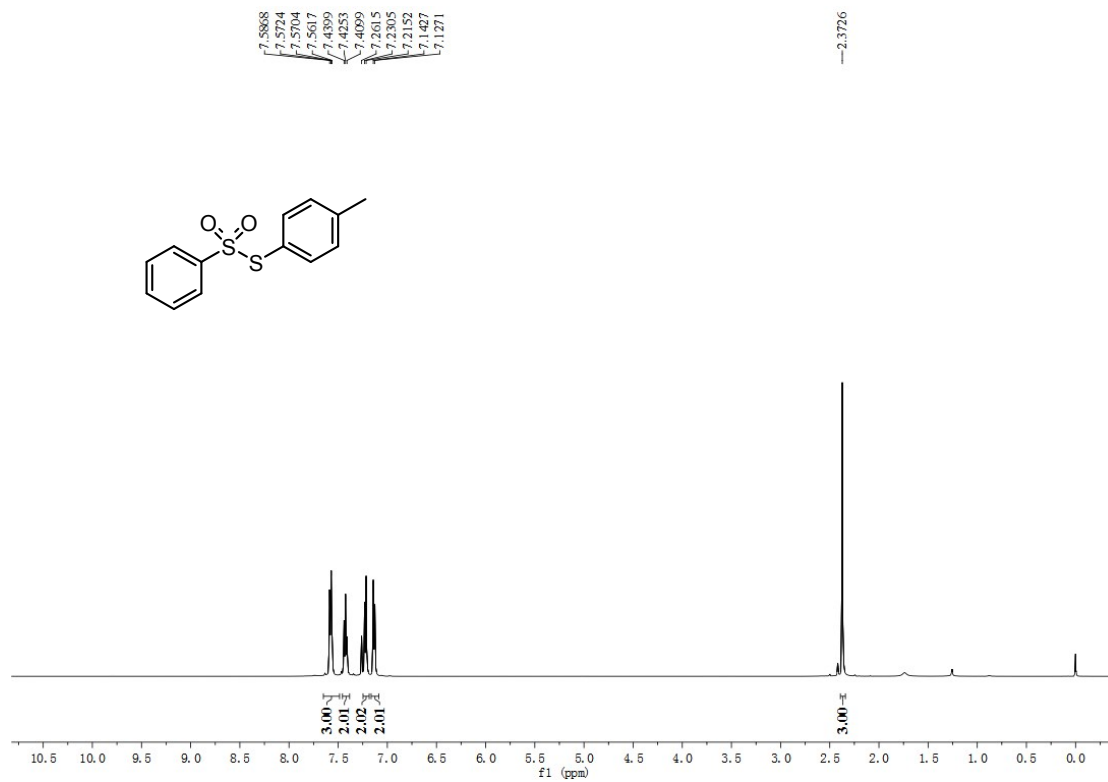
**4ra**

**S-p-tolyl 3-nitrobenzenesulfonothioate** White solid, mp, 102 - 103 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.43-8.41 (m, 1H), 8.27 (t,  $J = 1.9$  Hz, 2H), 7.90 (d,  $J = 7.9$  Hz,

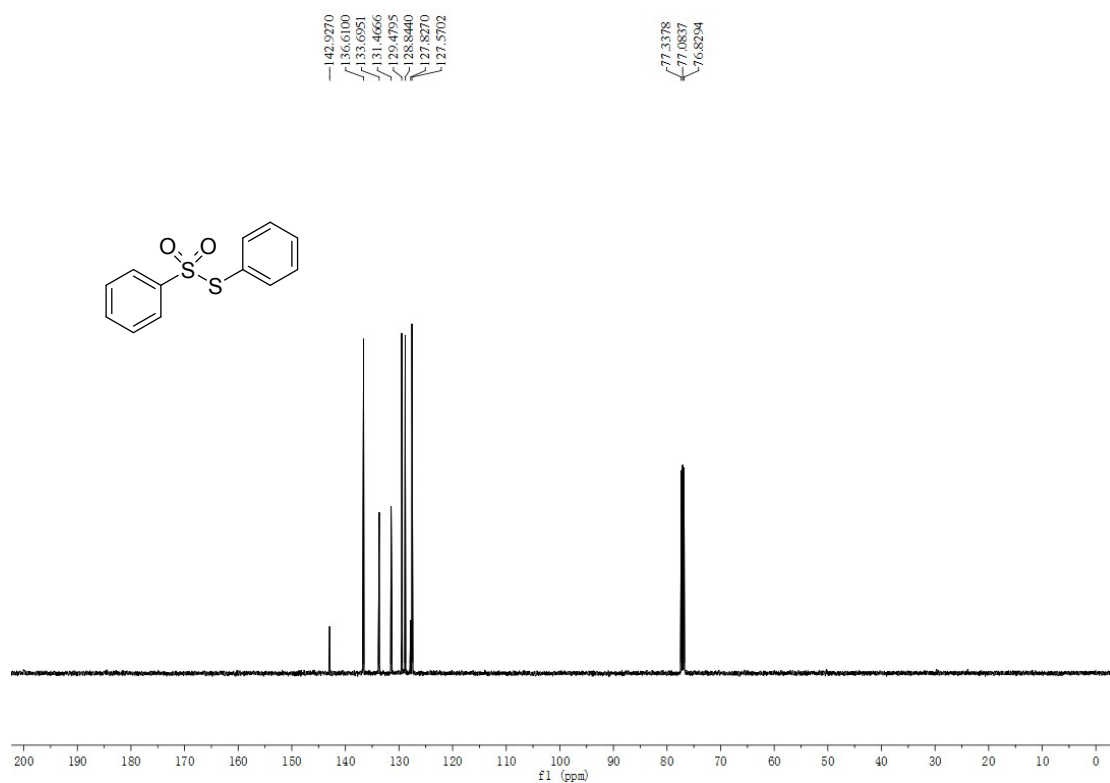
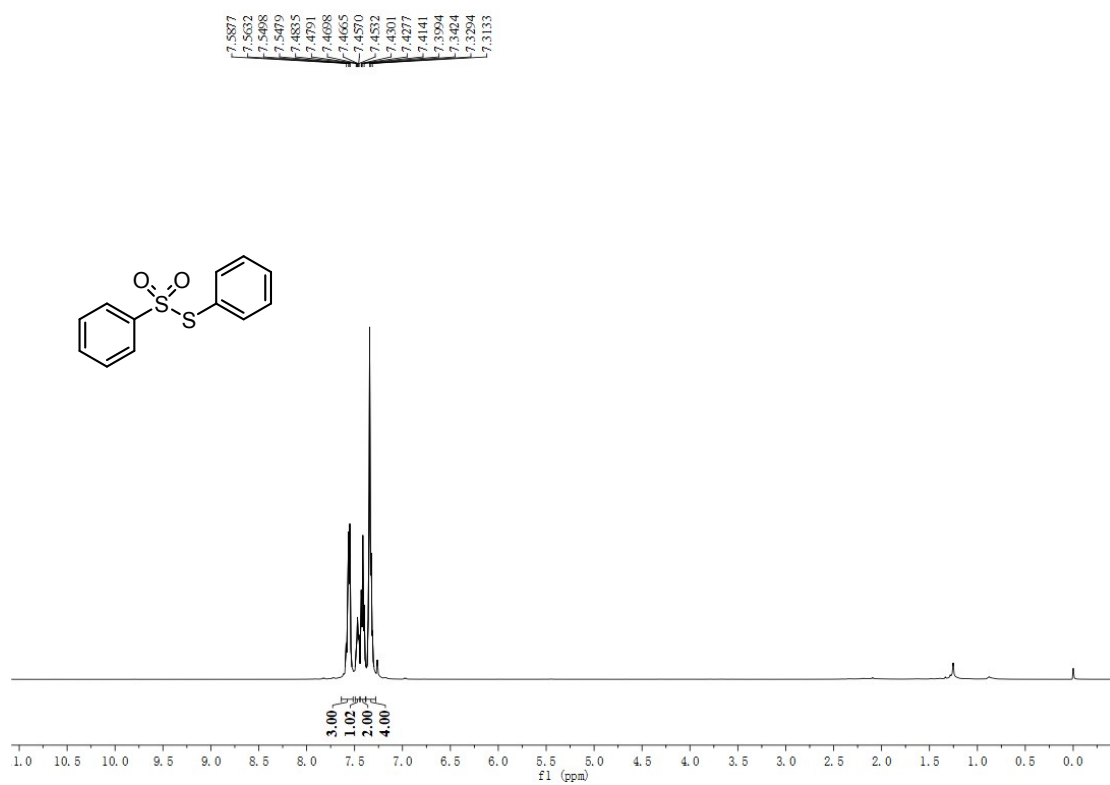
1H), 7.67 (t,  $J = 7.9$  Hz, 1H), 7.23 (d,  $J = 8.2$  Hz, 2H), 7.17 (d,  $J = 8.2$  Hz, 2H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.9, 144.6, 143.2, 136.4, 132.7, 130.7, 130.3, 127.9, 123.5, 122.9, 21.5. ESI HRMS: calculated for  $\text{C}_{13}\text{H}_{11}\text{NNaO}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  332.0027, found 332.0012.

## 5. Copies of NMR spectra

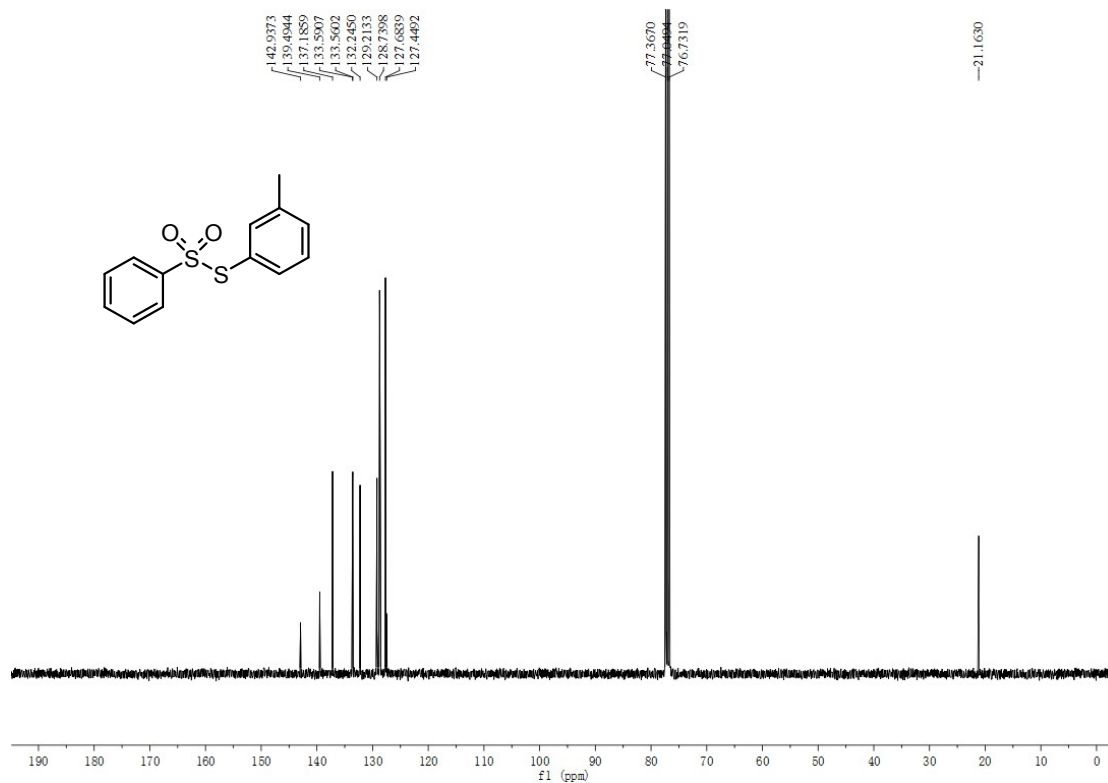
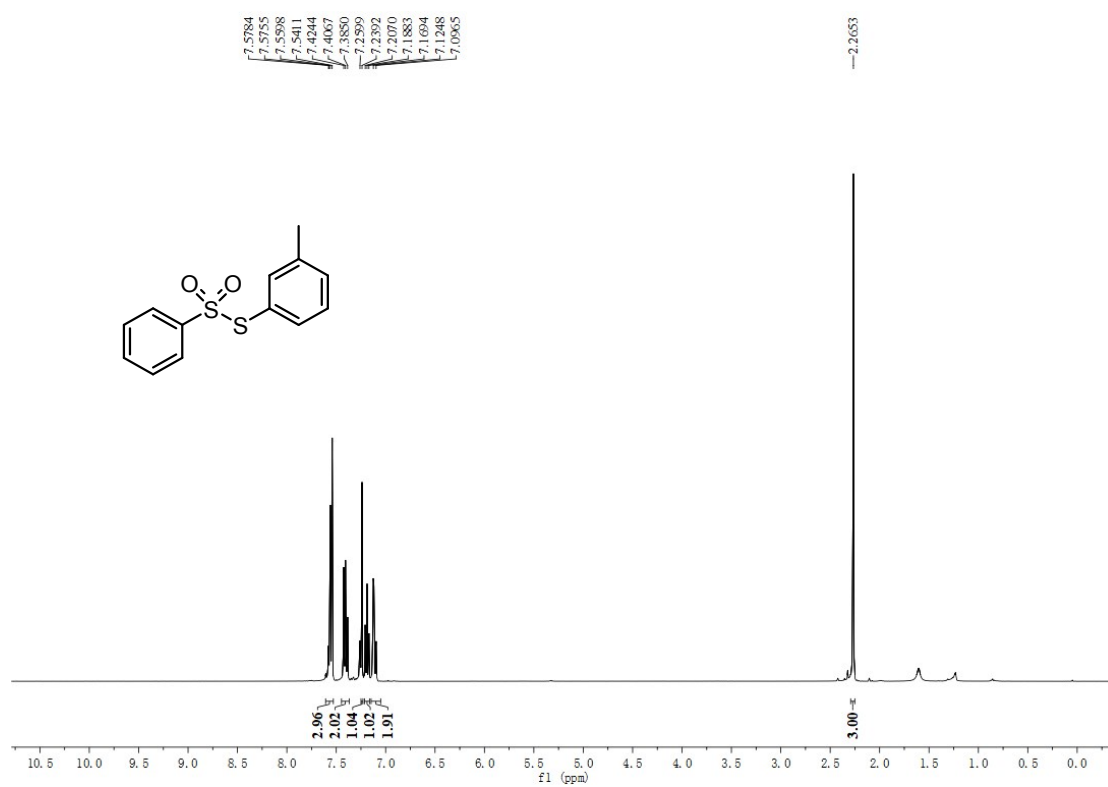
### 4aa



4ab

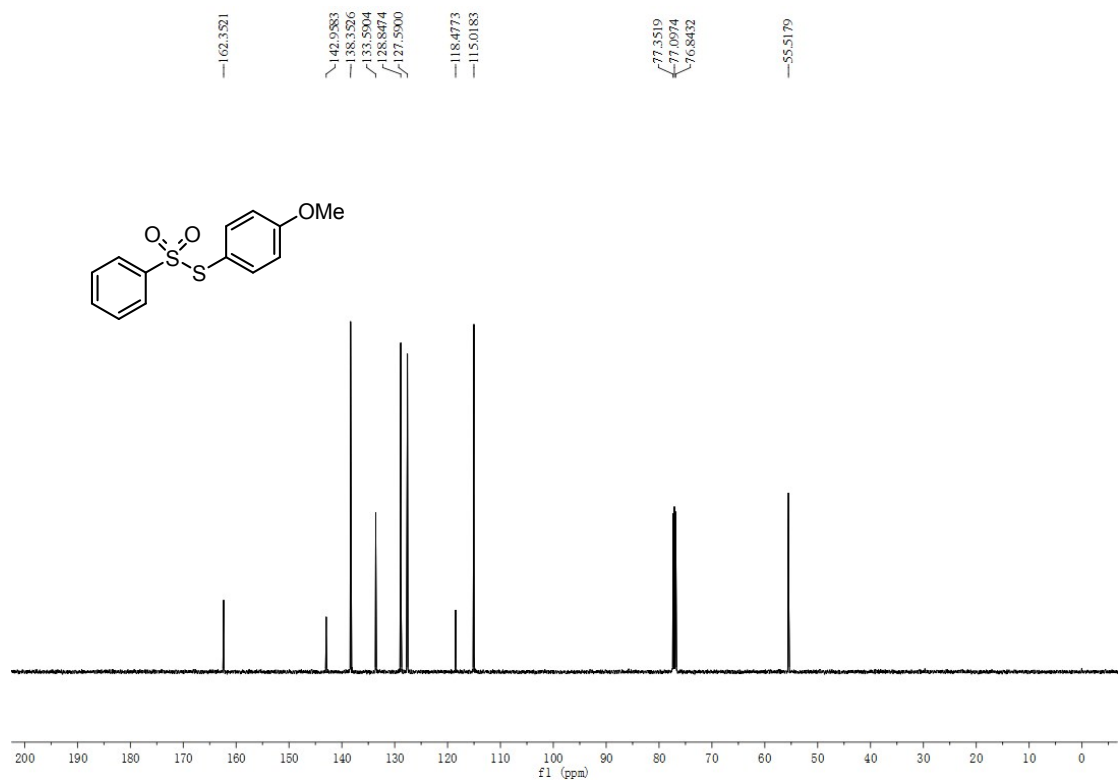
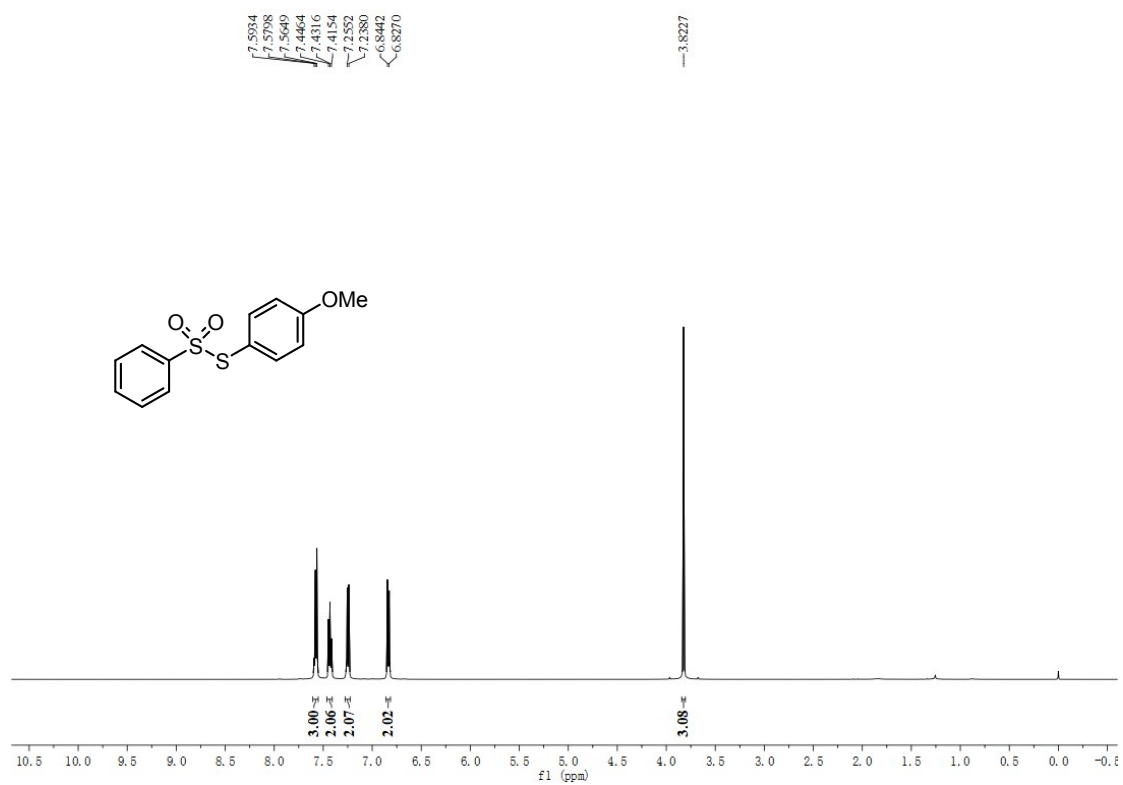


4ac

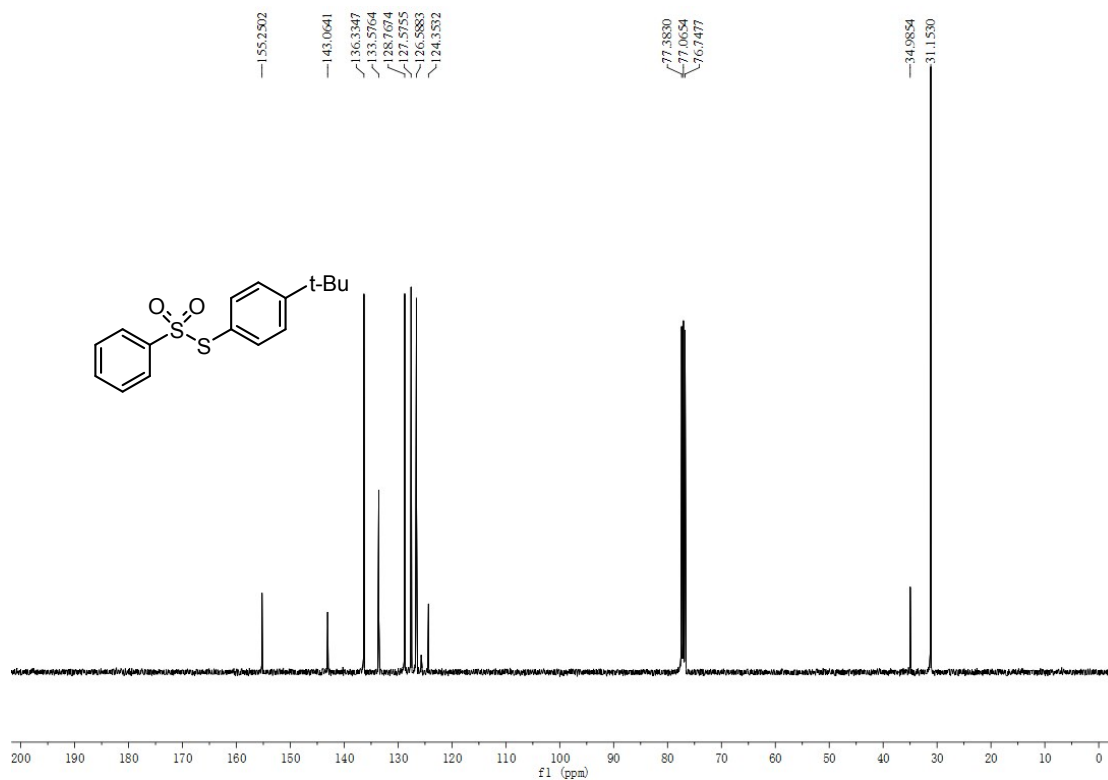
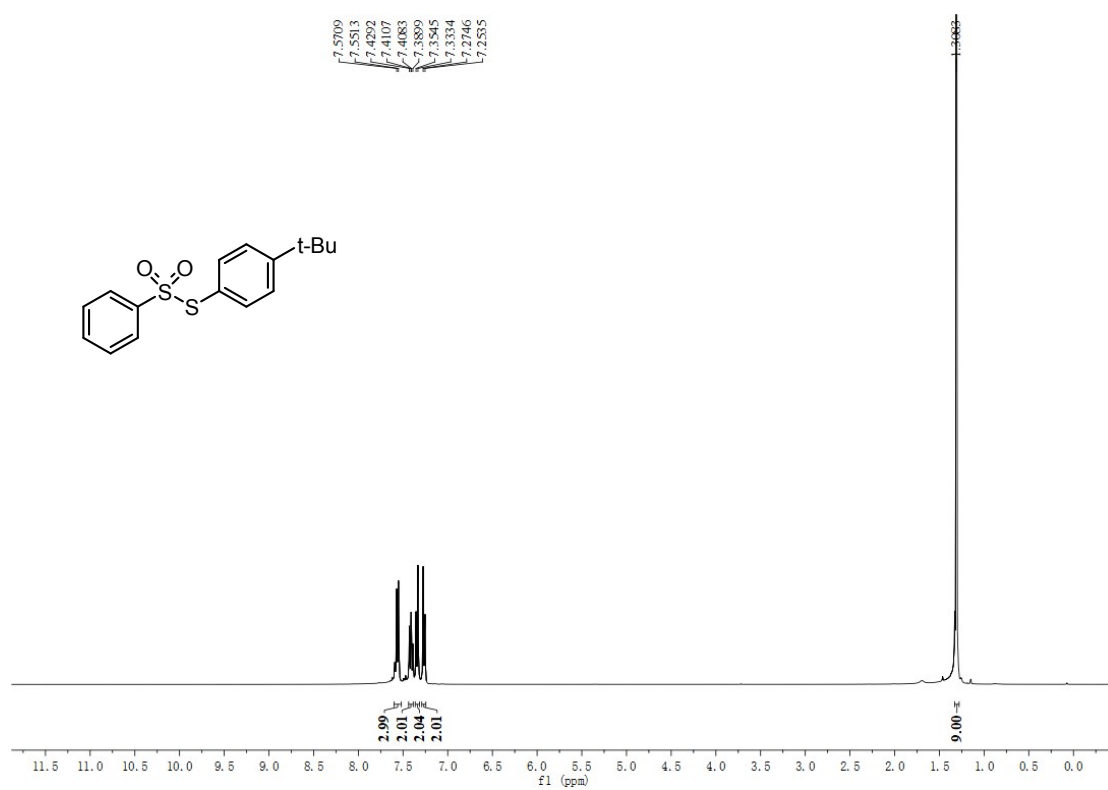




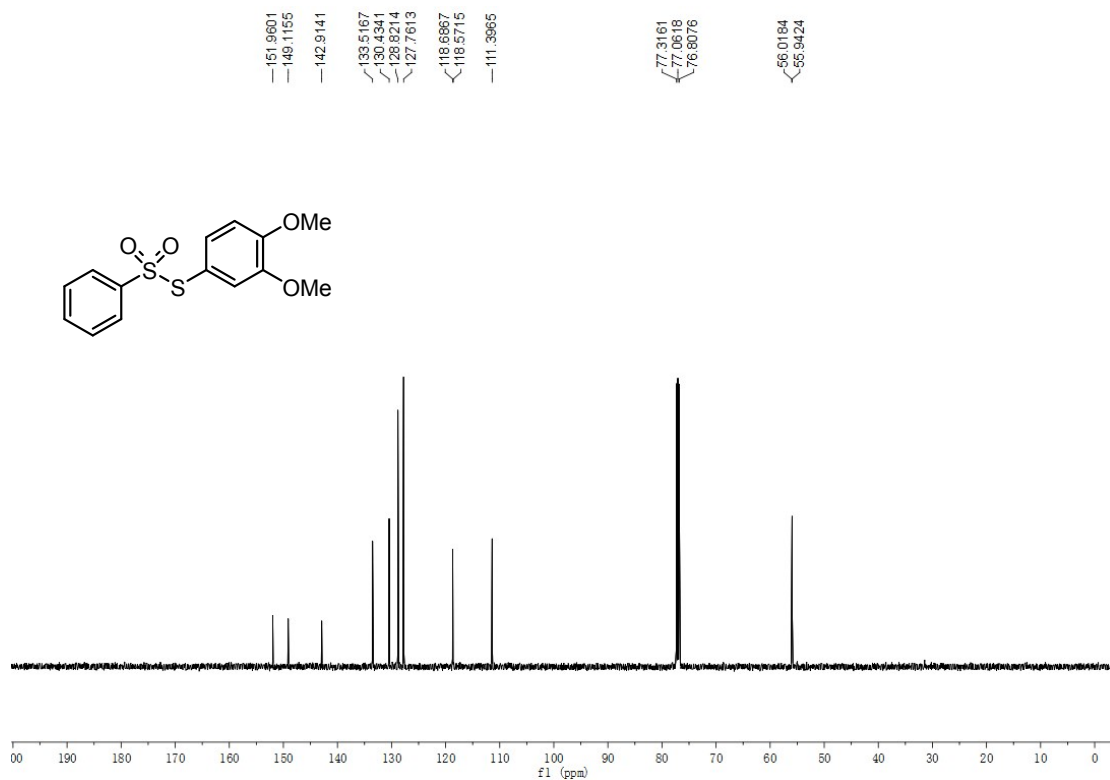
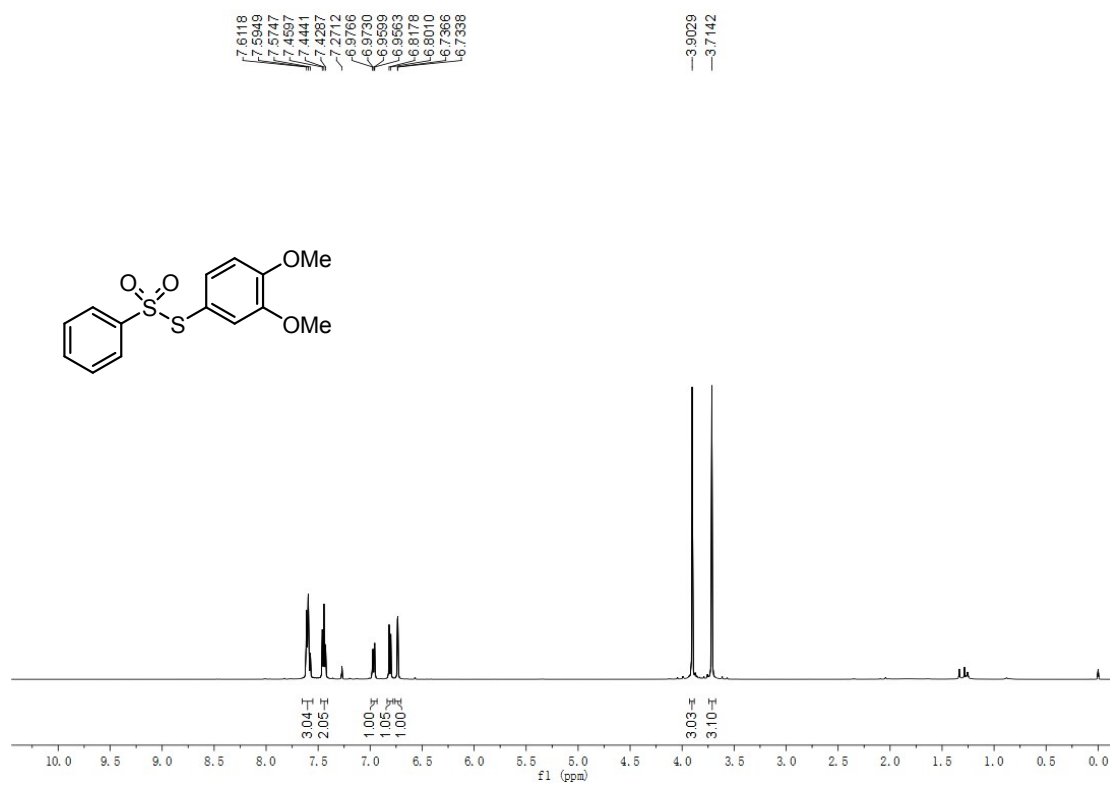
4ad



4ae

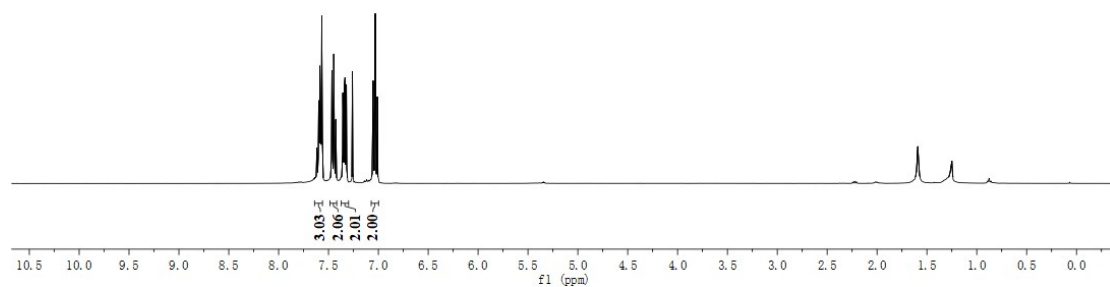
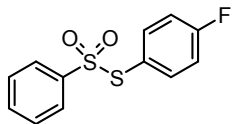


4af

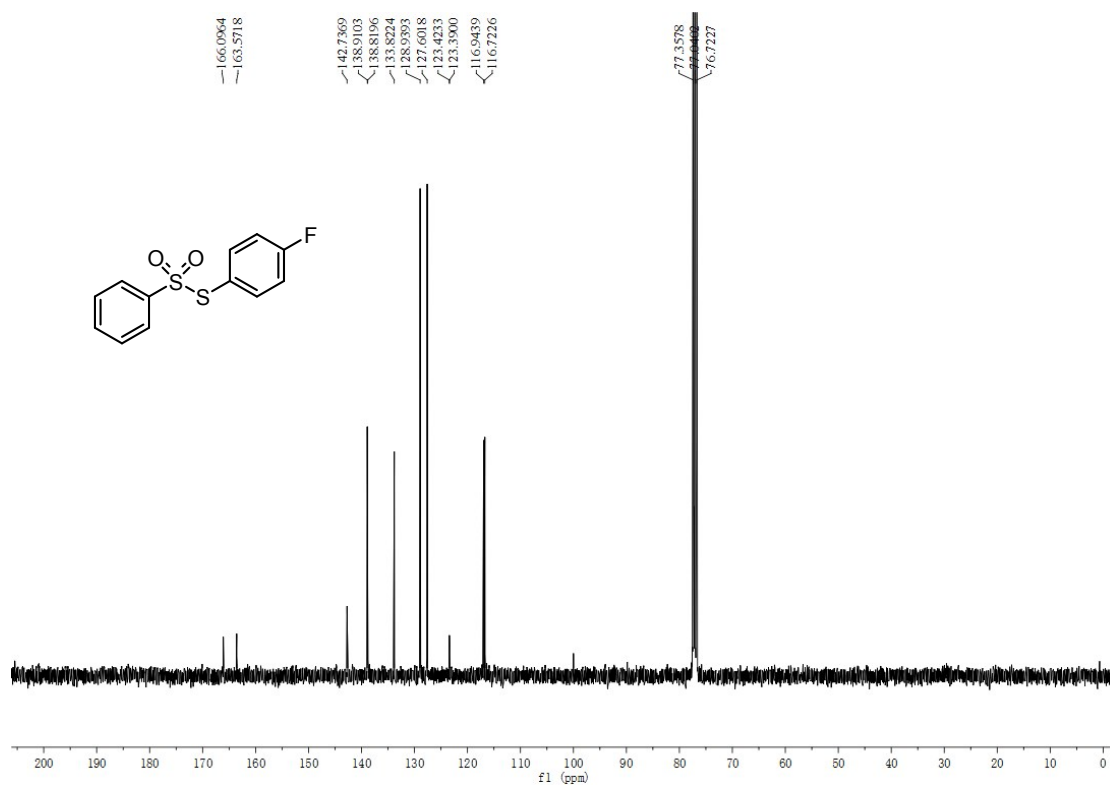
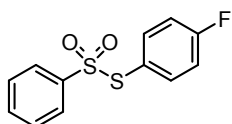


4ag

7.6162  
7.6134  
7.5977  
7.5860  
7.5769  
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7.4265  
7.3559  
7.3307  
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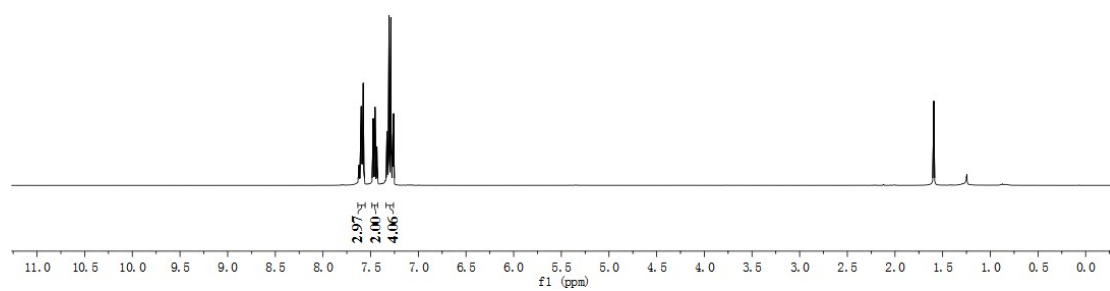
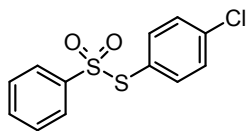


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123.3900  
116.7226



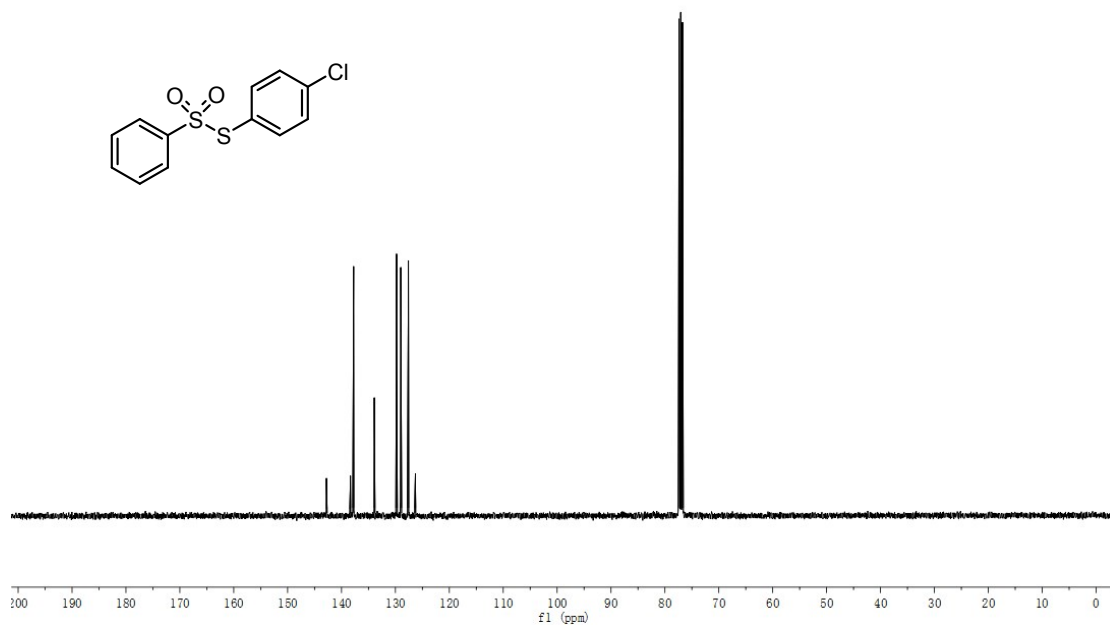
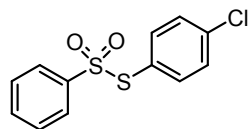
4ah

7.6218  
7.6053  
7.5884  
7.5820  
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7.2666  
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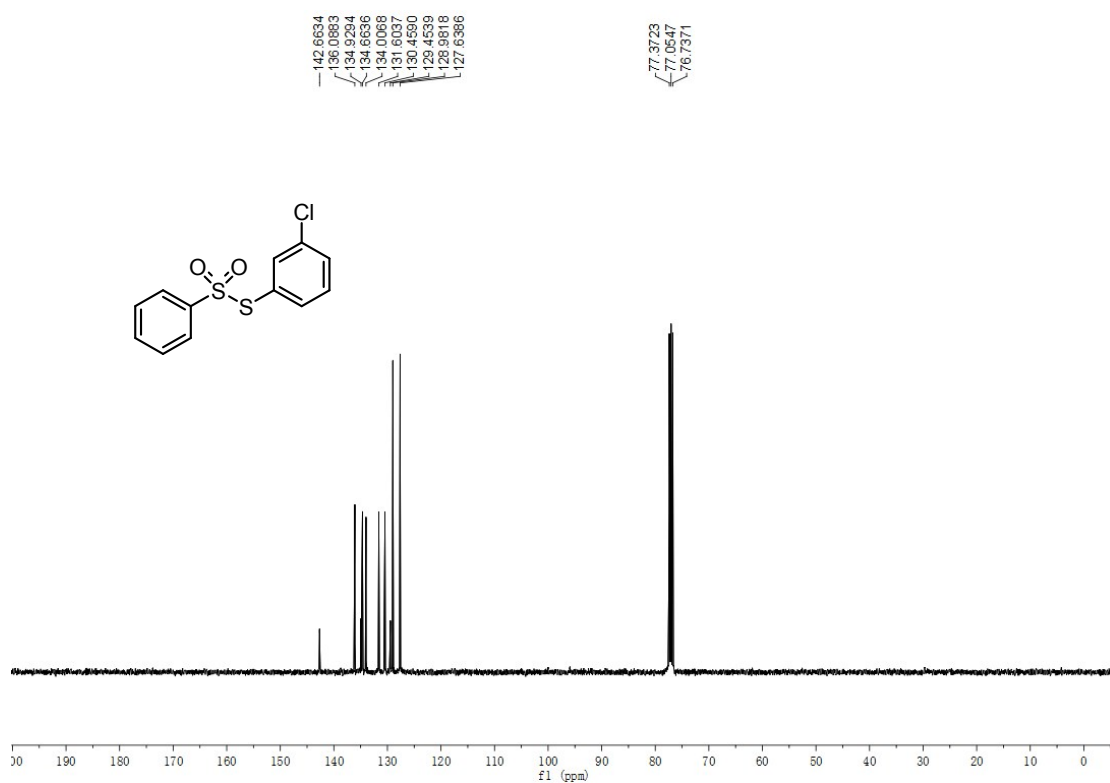
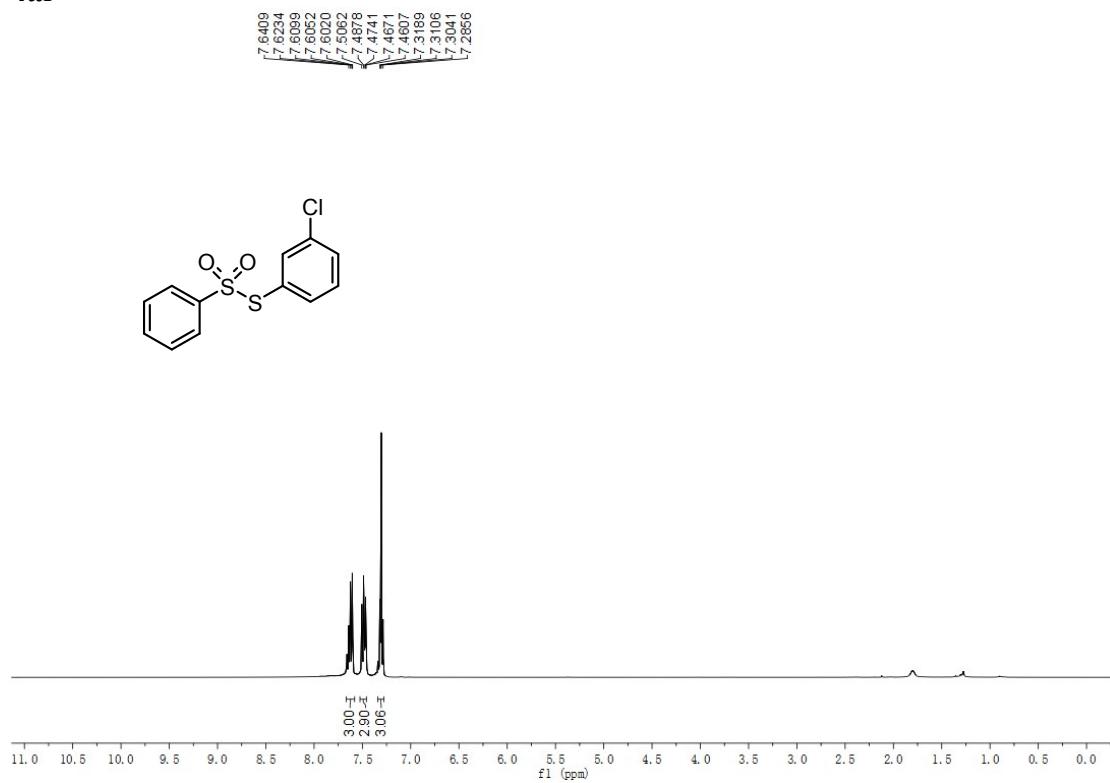


142.8023  
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126.3009

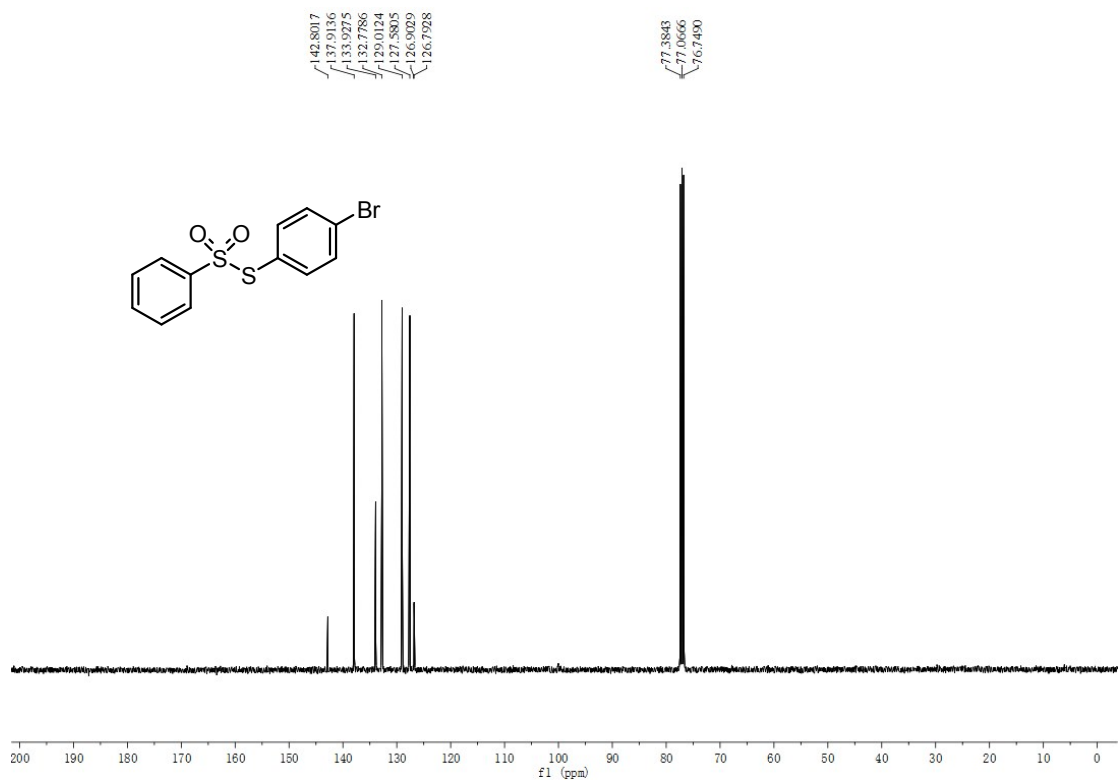
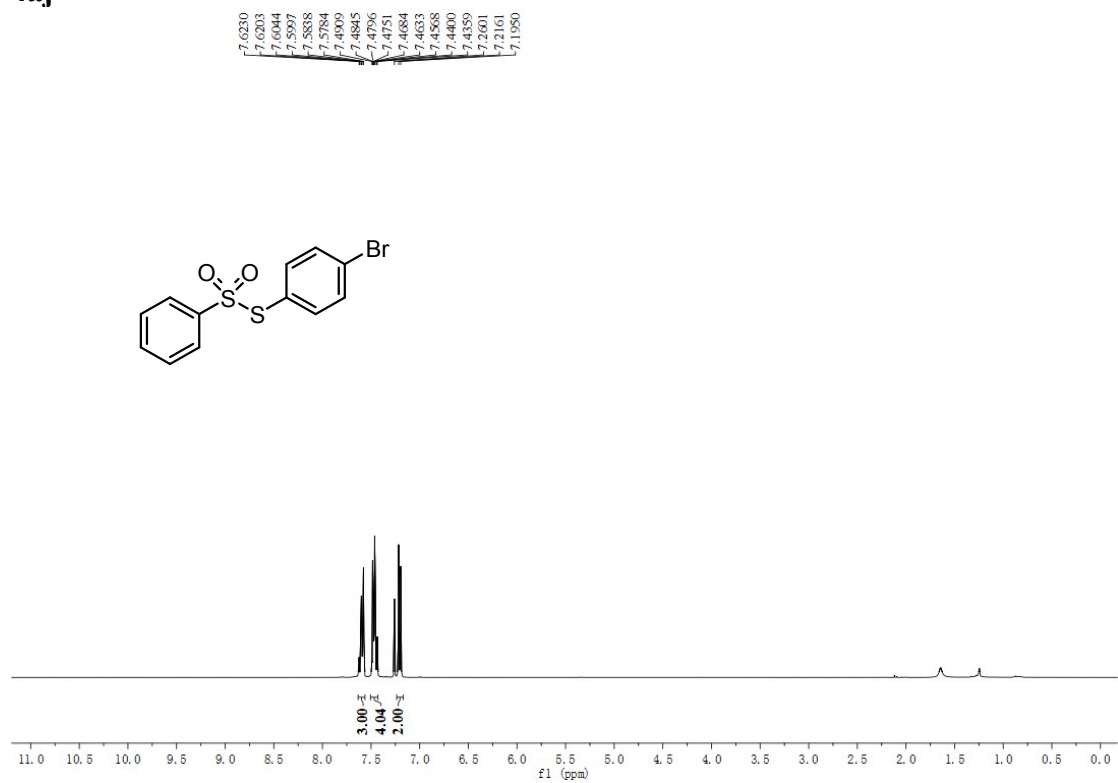
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76.7395



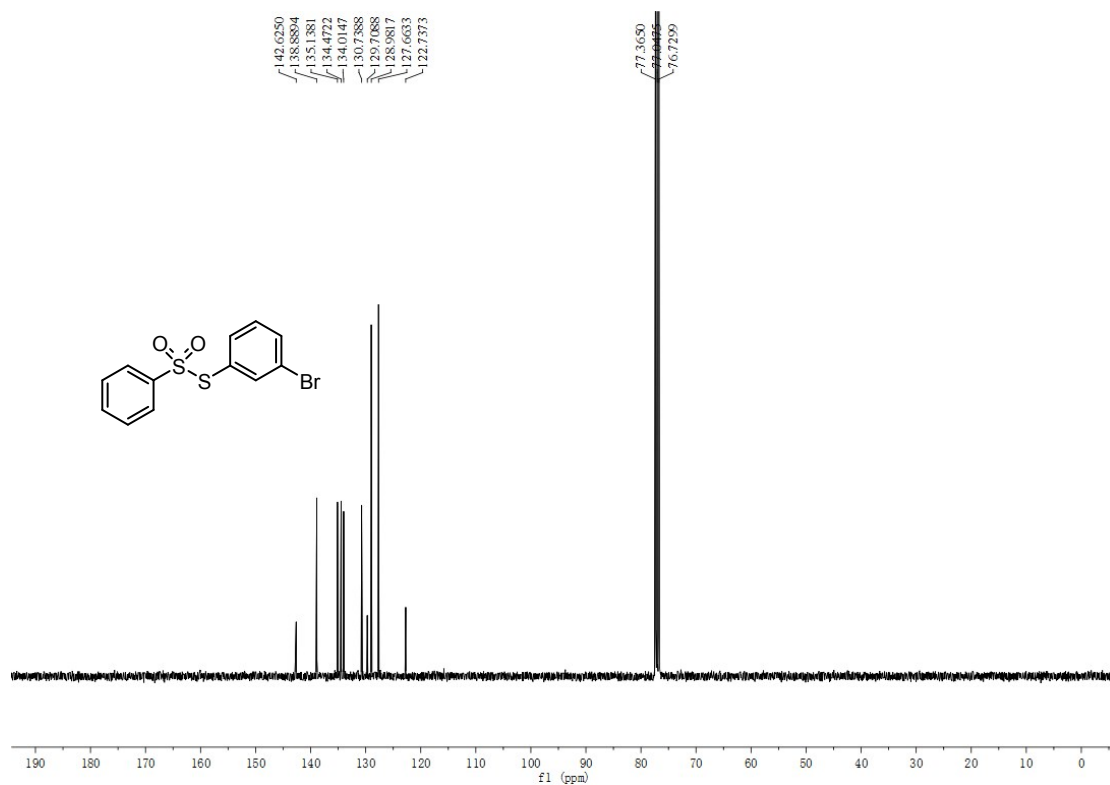
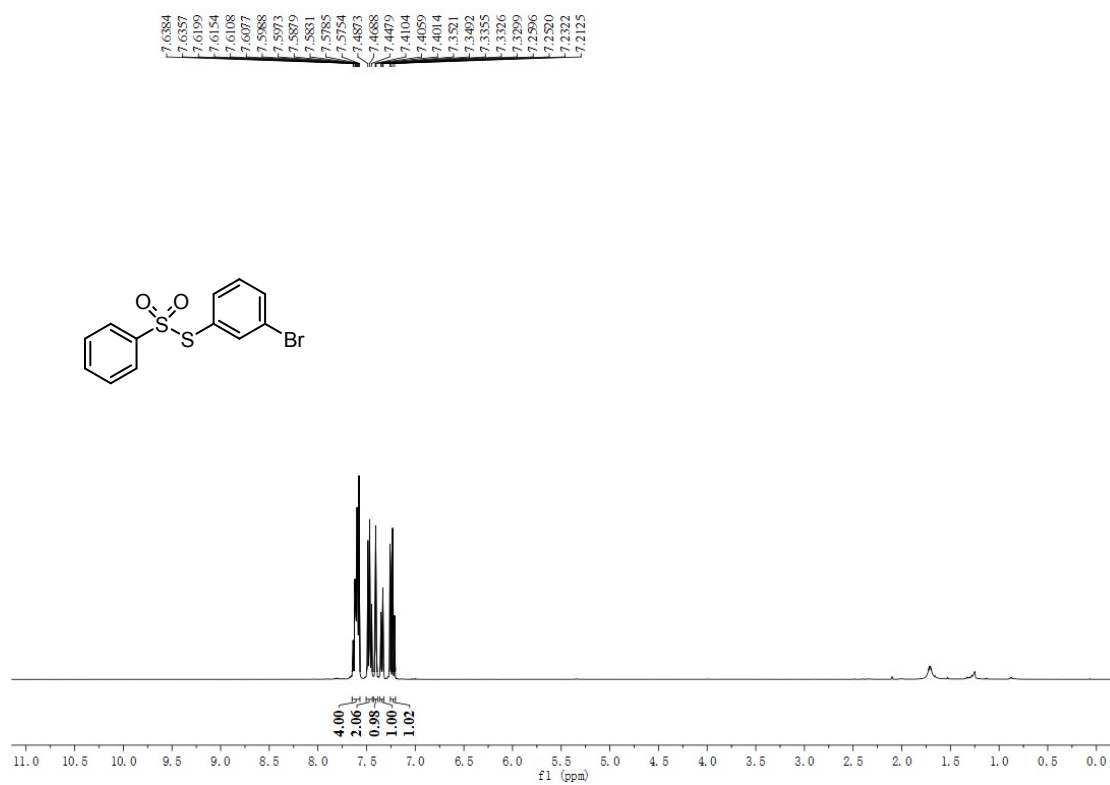
4ai



4aj

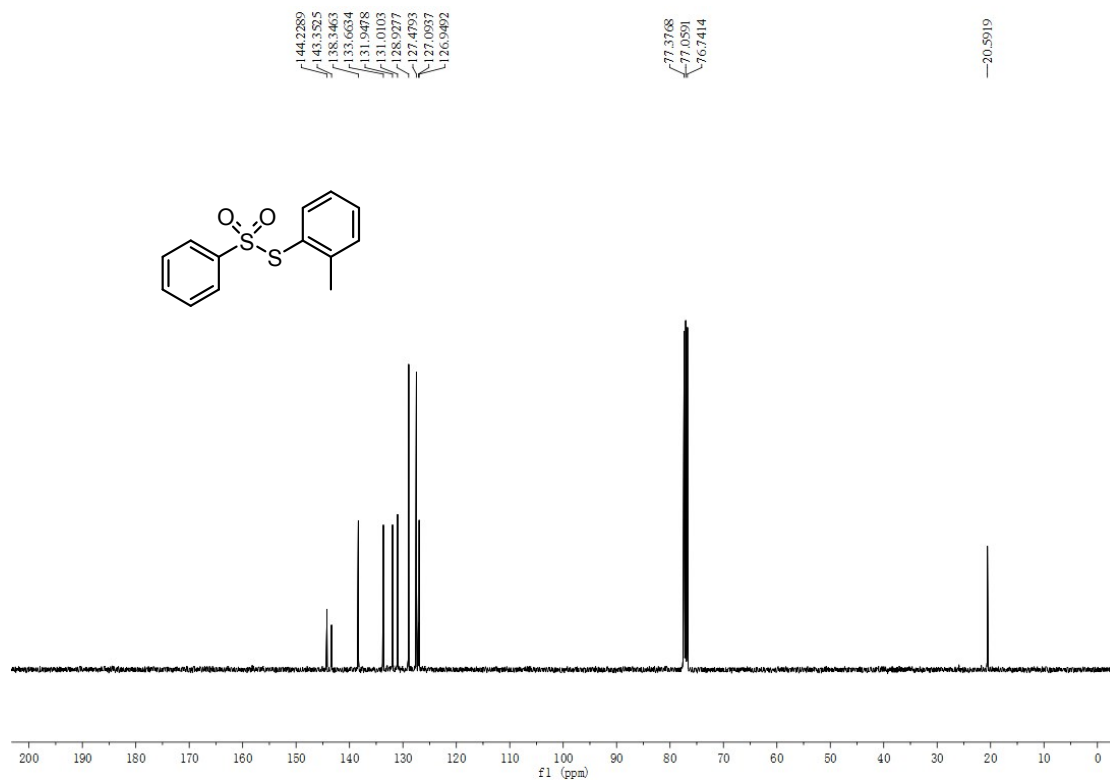
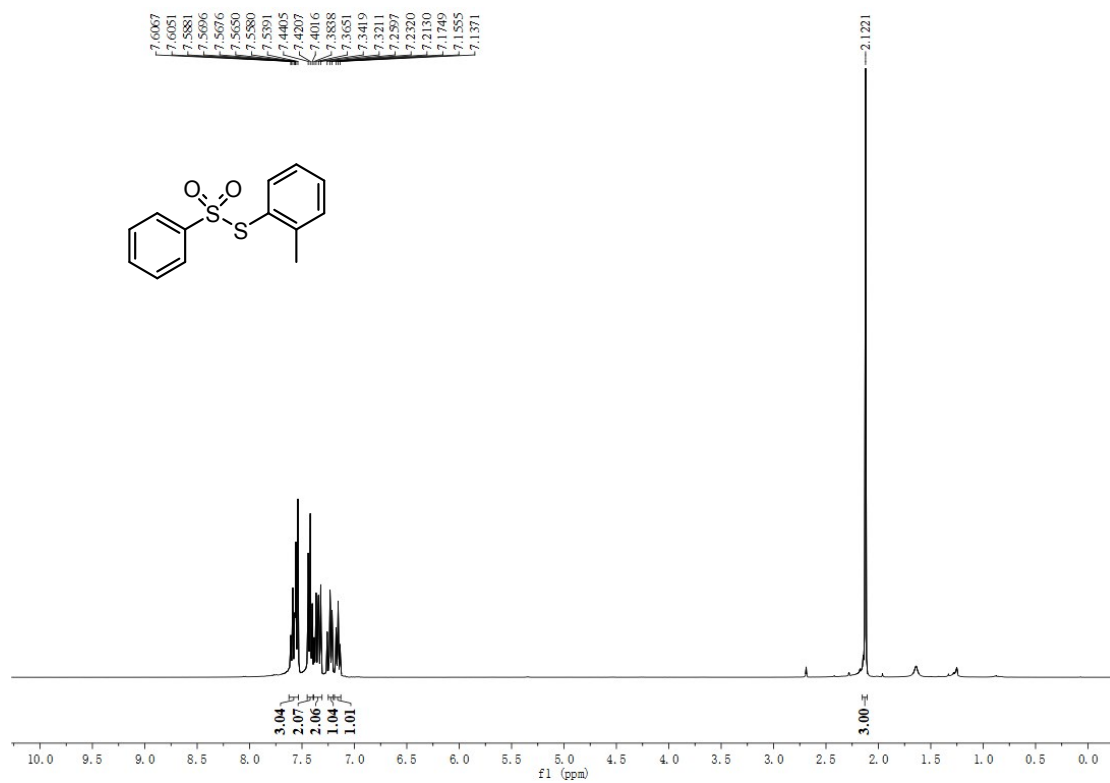


4ak



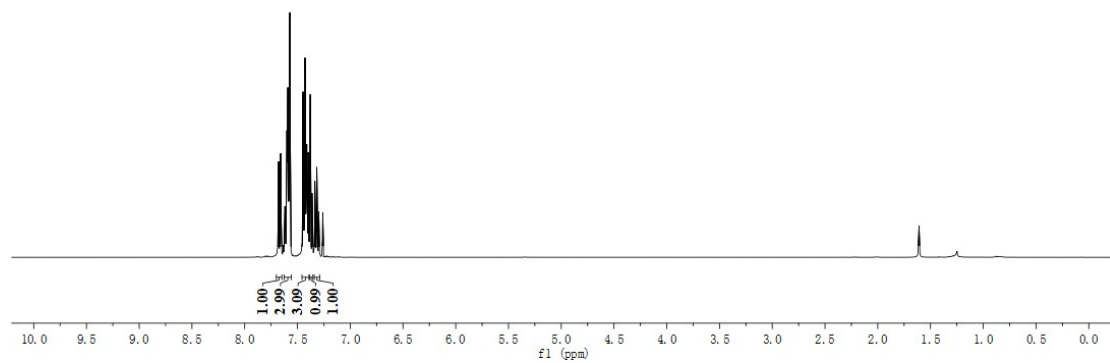
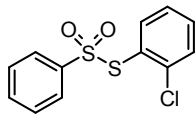


4al



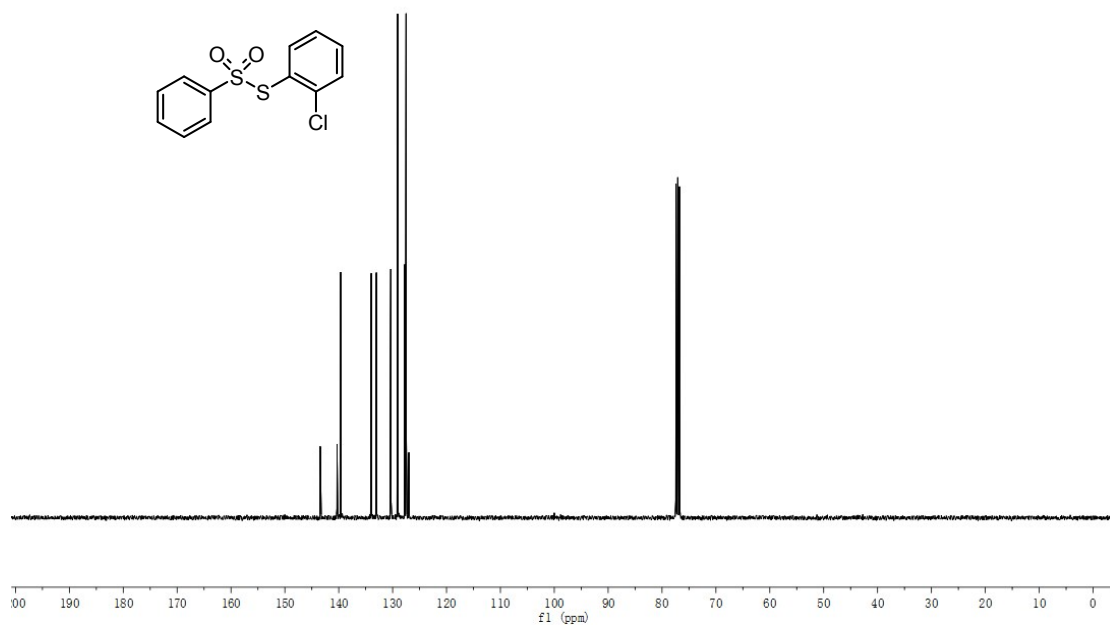
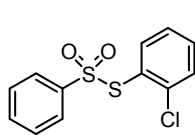
# 4am

7.6821  
7.6781  
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7.6388  
7.6182  
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7.5929  
7.5908  
7.5784  
7.5720  
7.4470  
7.4421  
7.4361  
7.4285  
7.4259  
7.4159  
7.4121  
7.4076  
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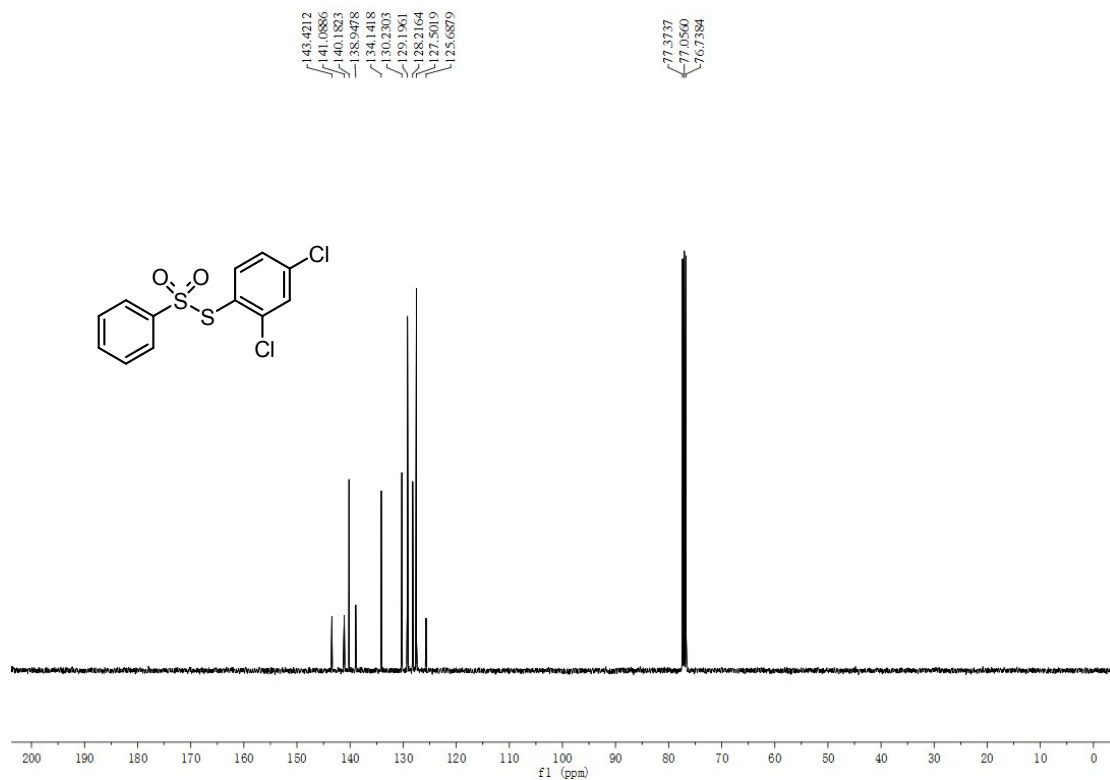
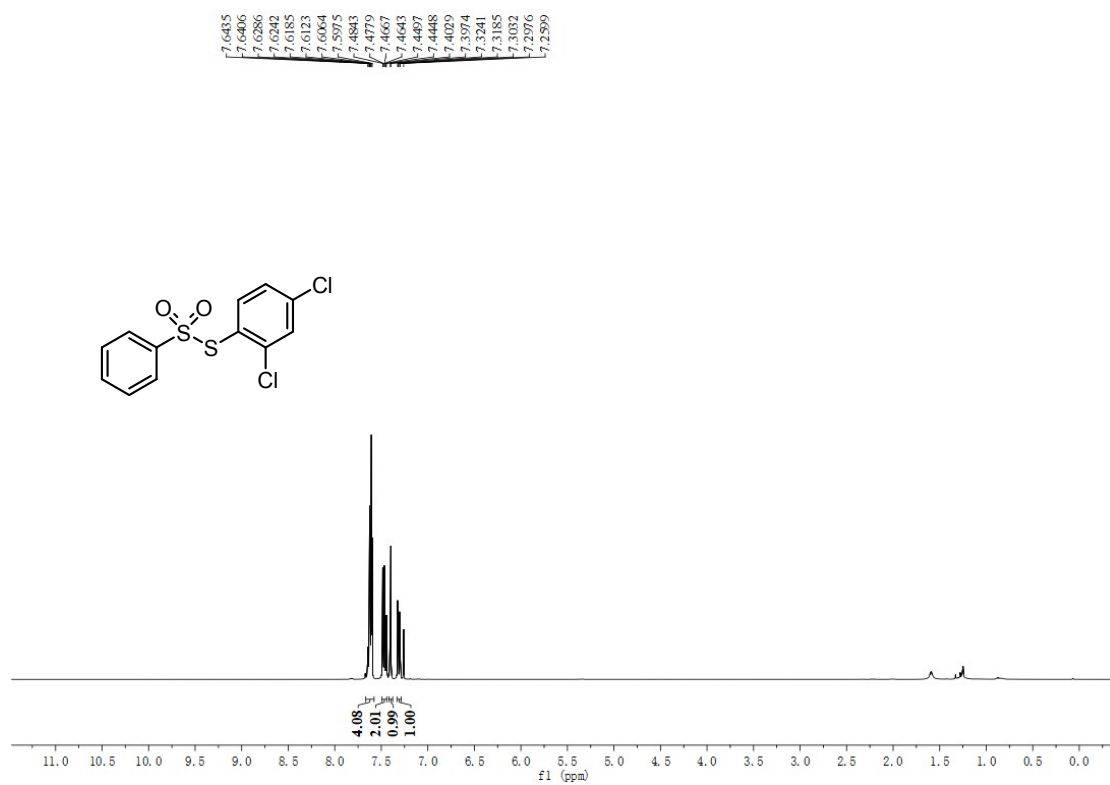


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127.5038  
126.9897

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76.7609

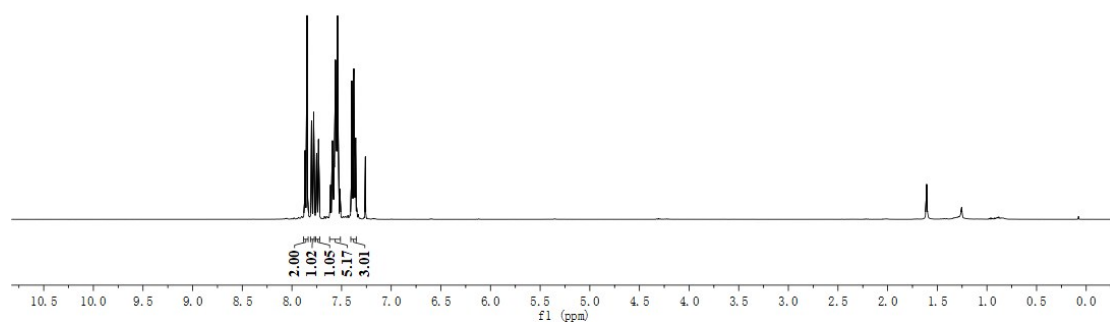
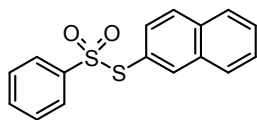


# 4an



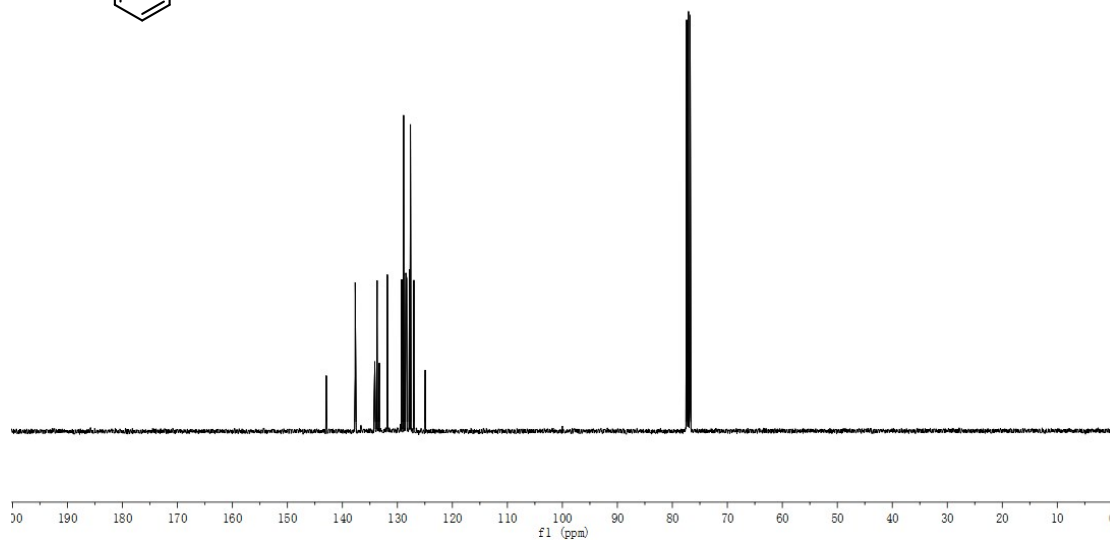
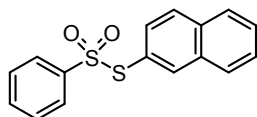
4ao

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7.8024  
7.7810  
7.7513  
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7.5552  
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7.5172  
7.5149  
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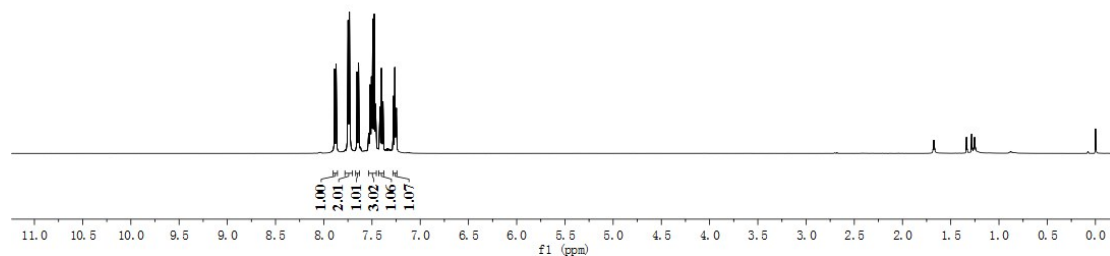
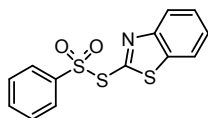
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133.2924  
131.8381  
129.2113  
128.8803  
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127.0096  
124.9321

77.3955  
77.0778  
76.7601

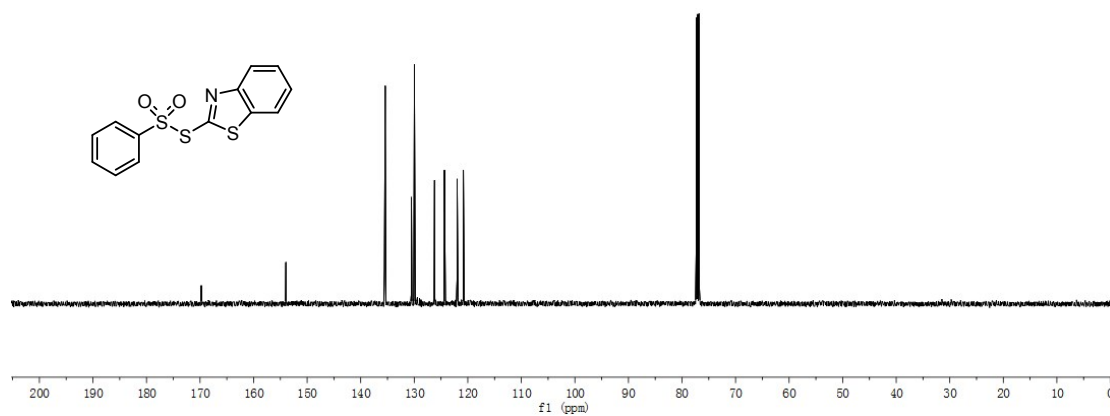
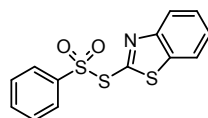


4ap

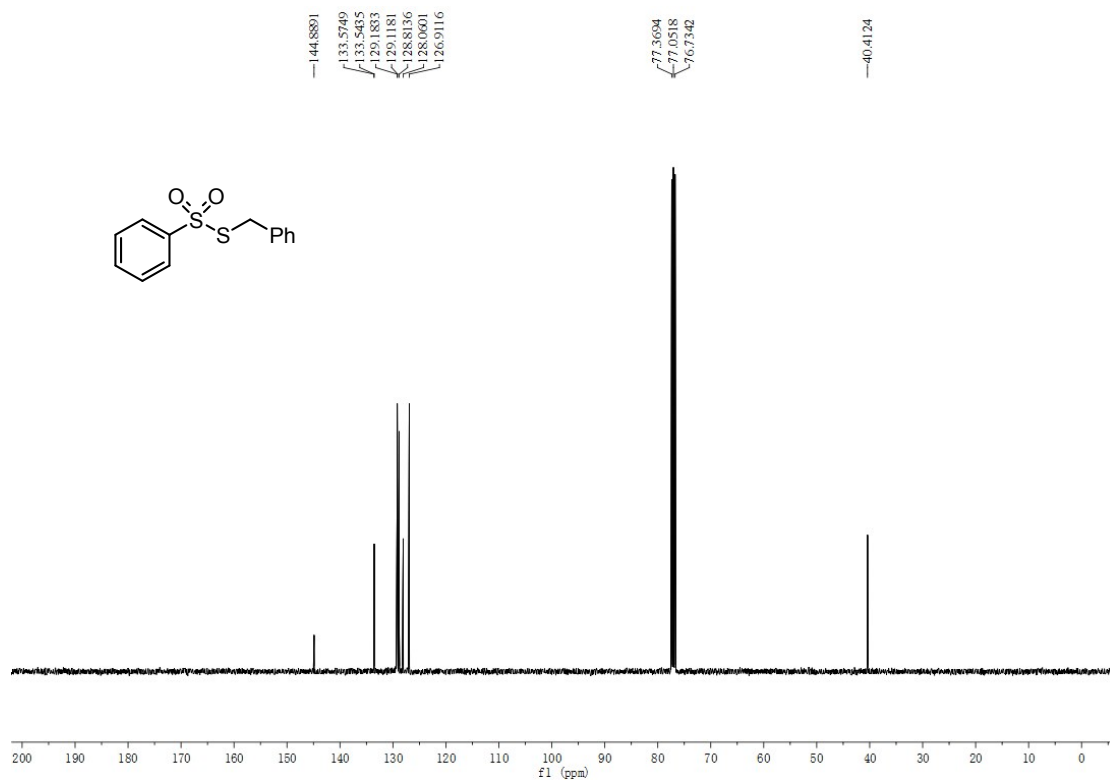
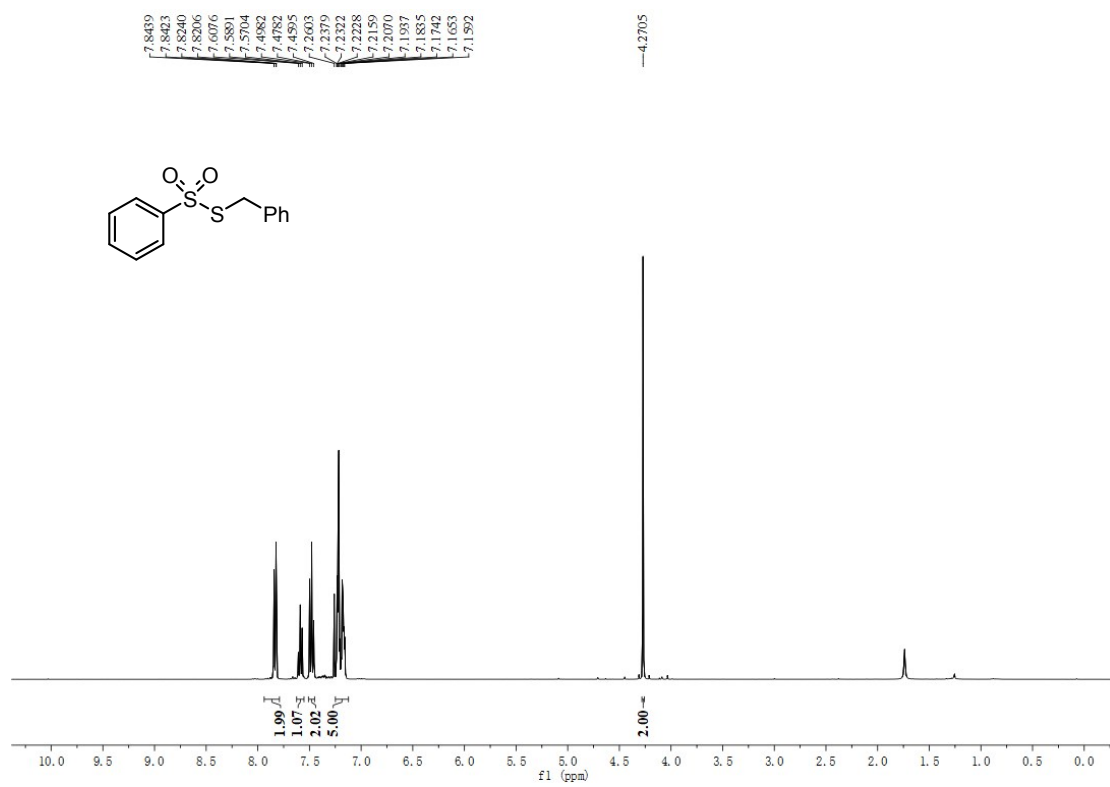
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7.2476



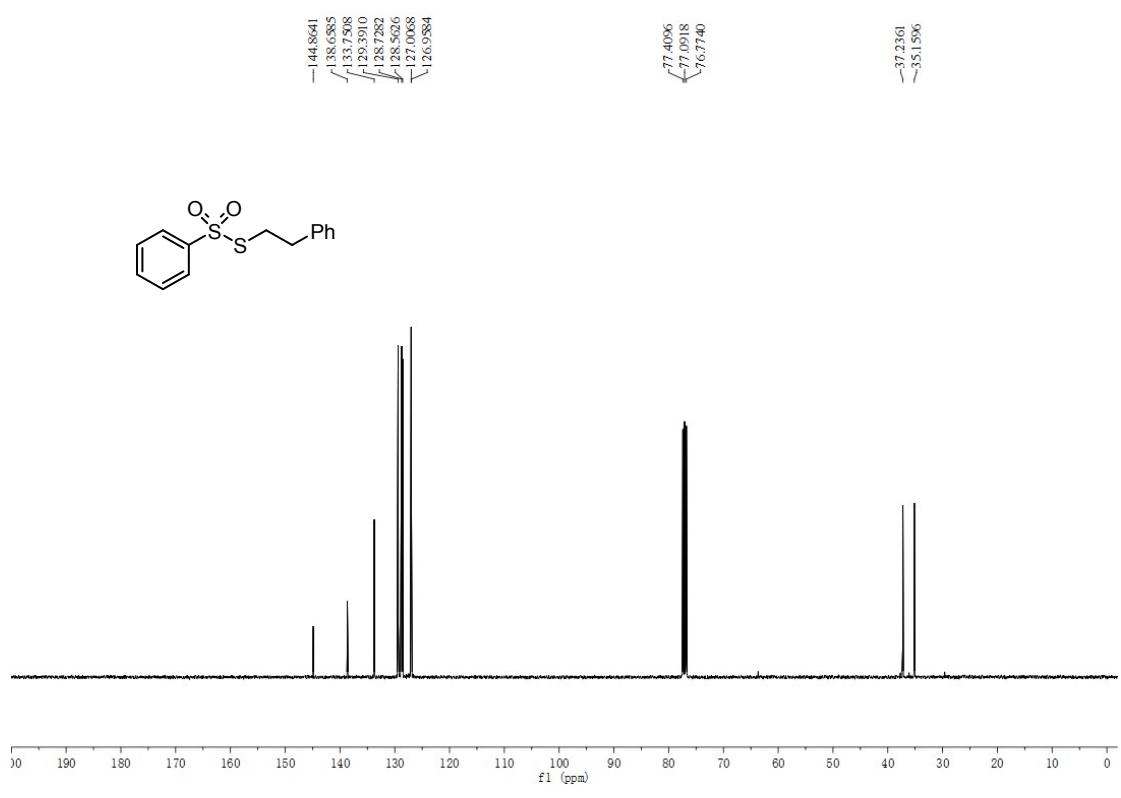
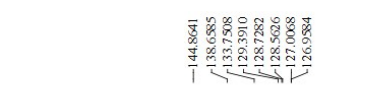
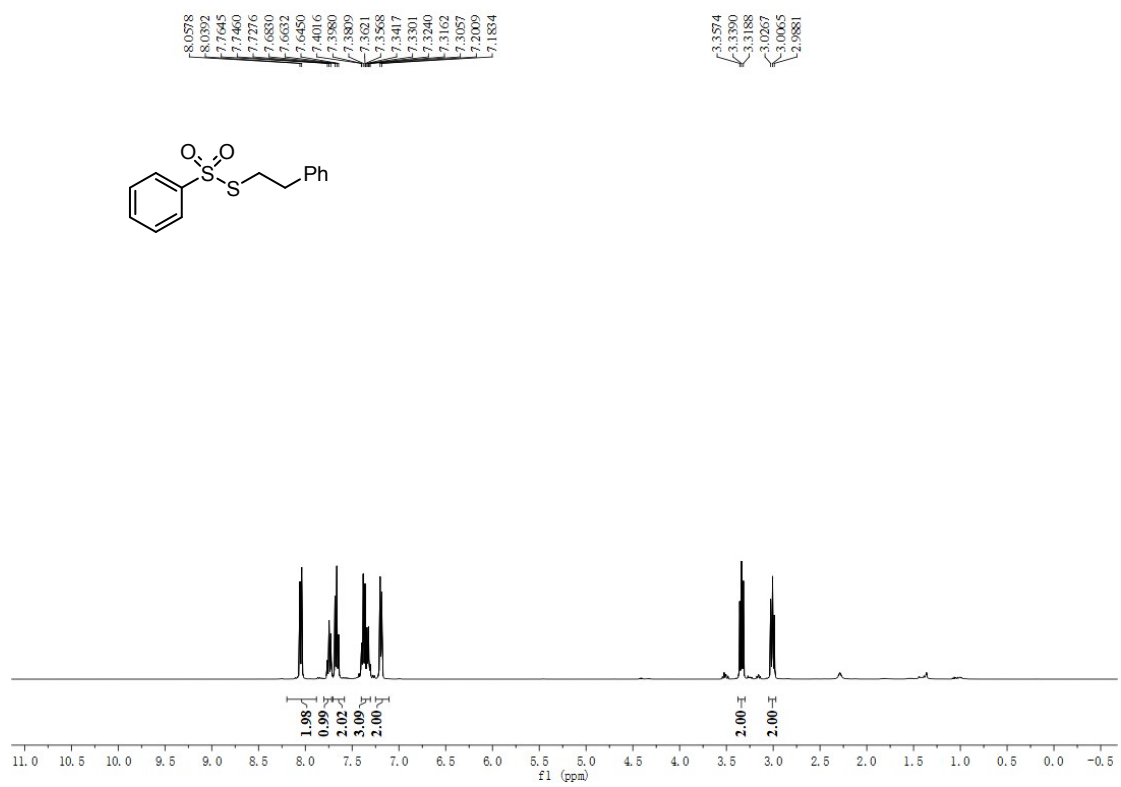
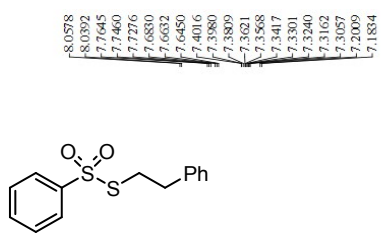
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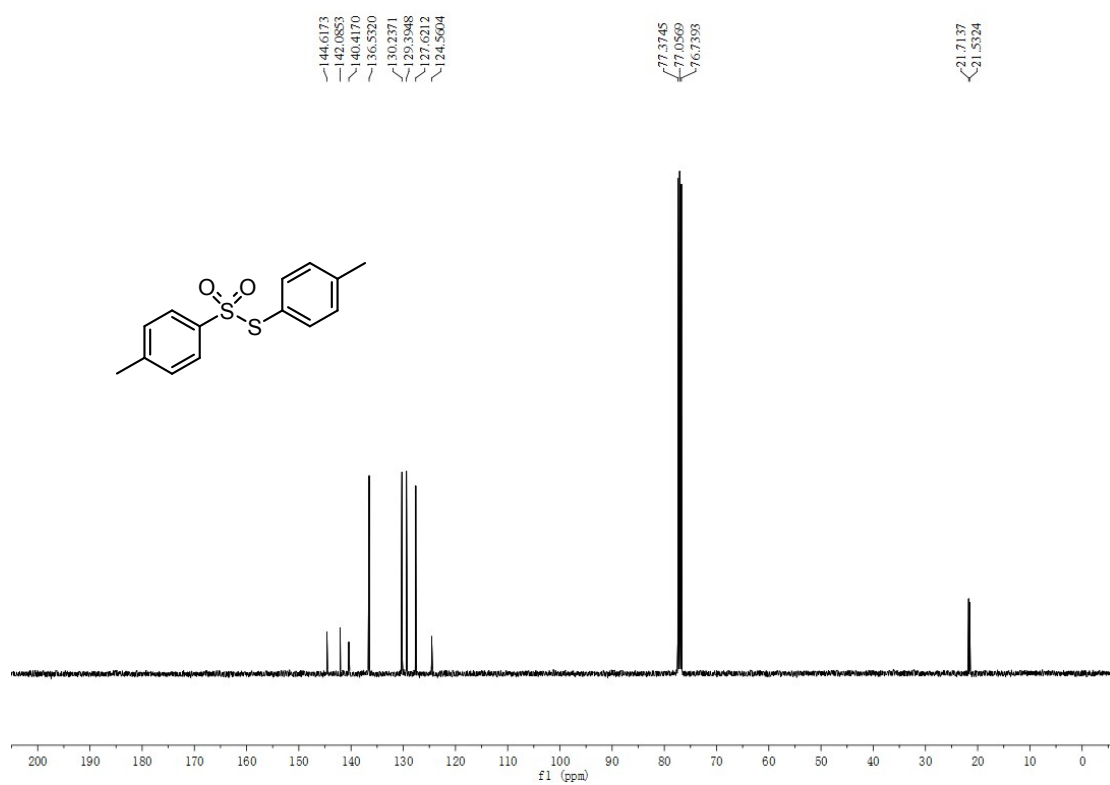
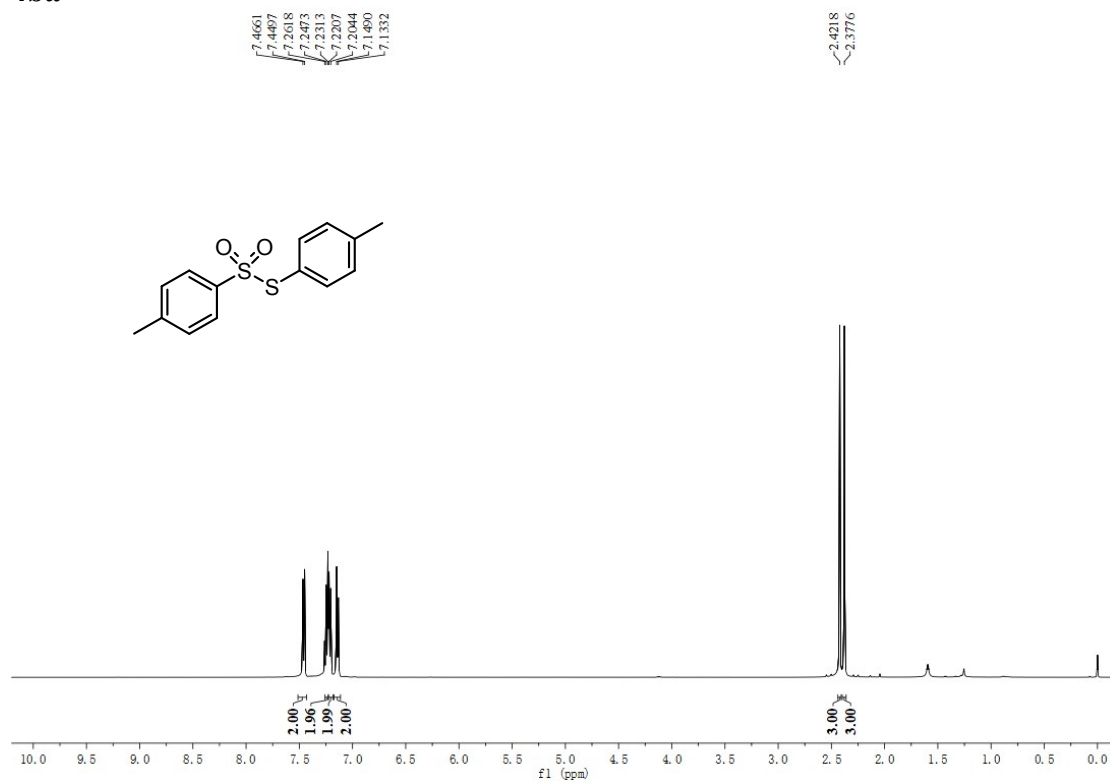
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4ar

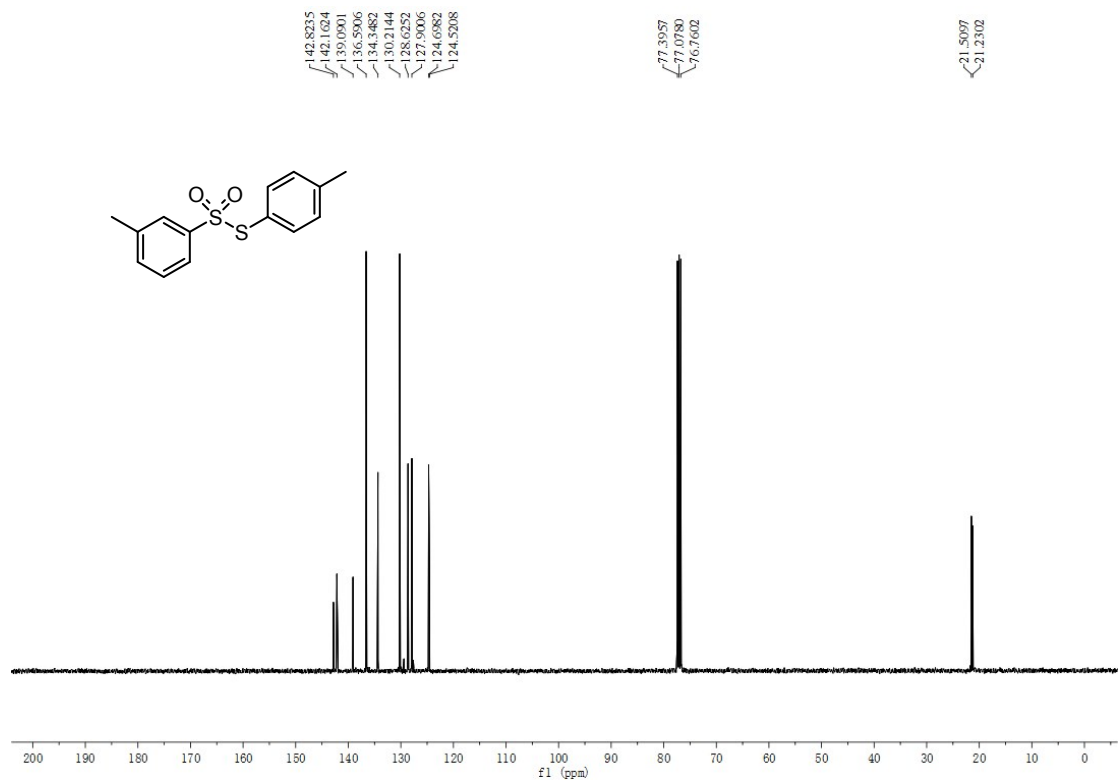
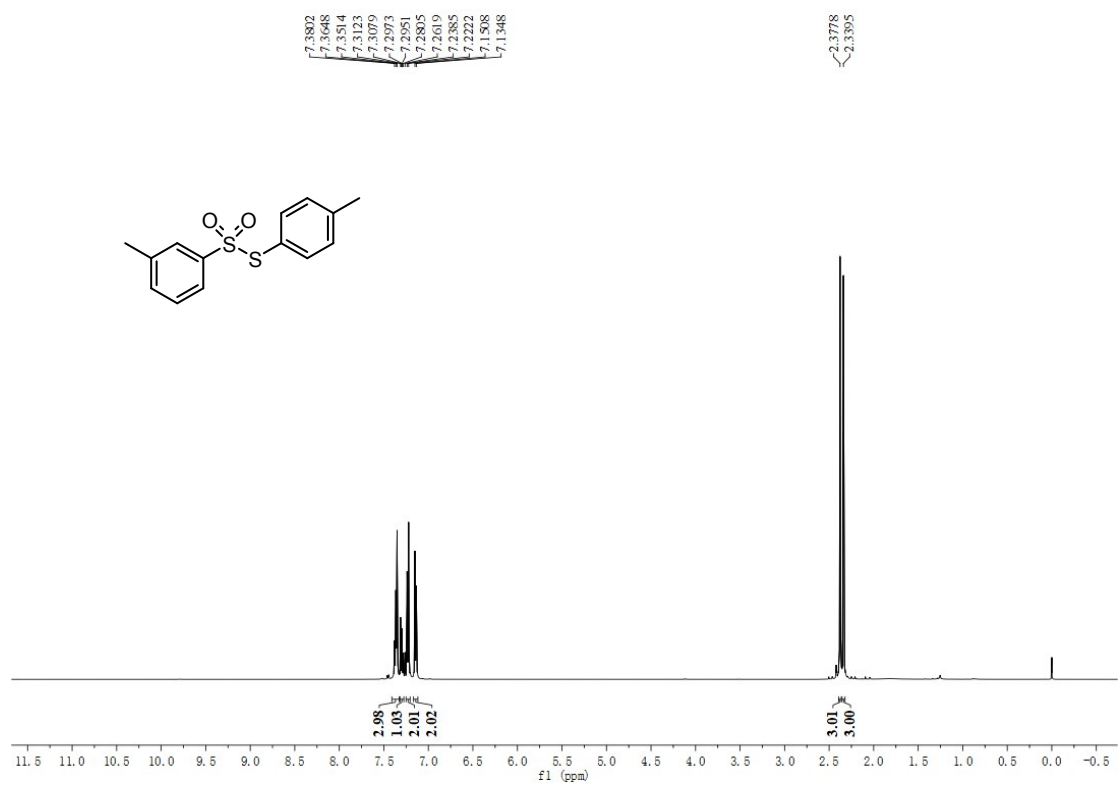


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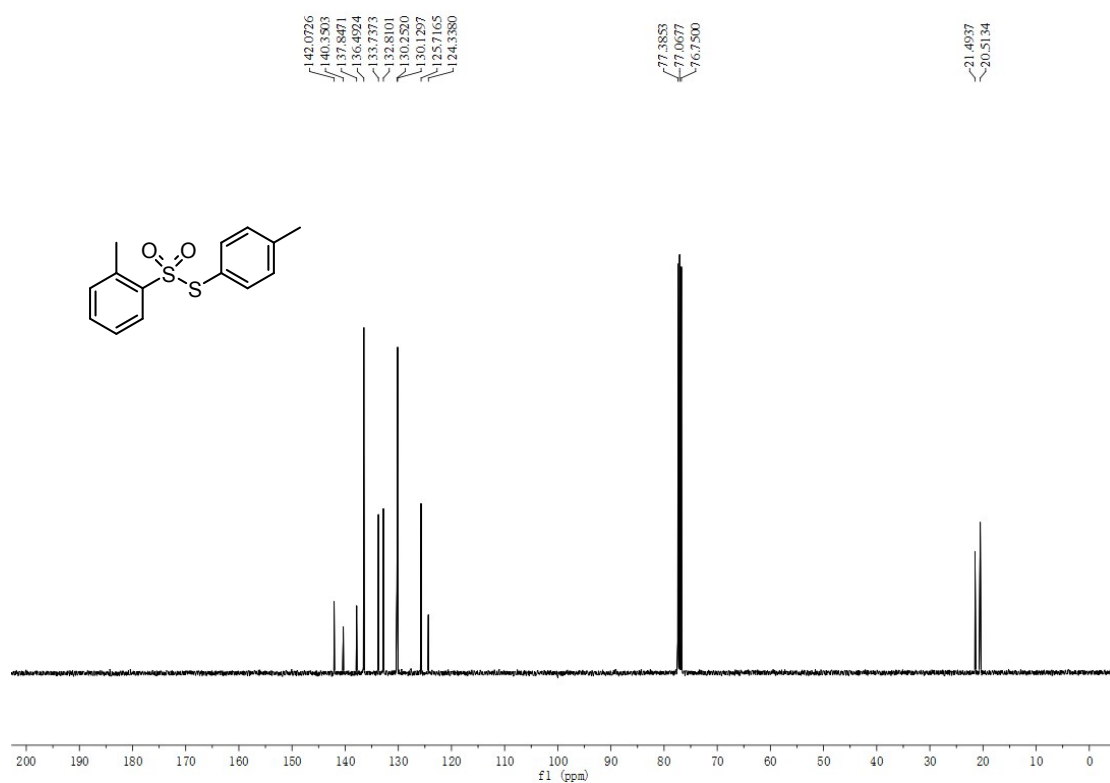
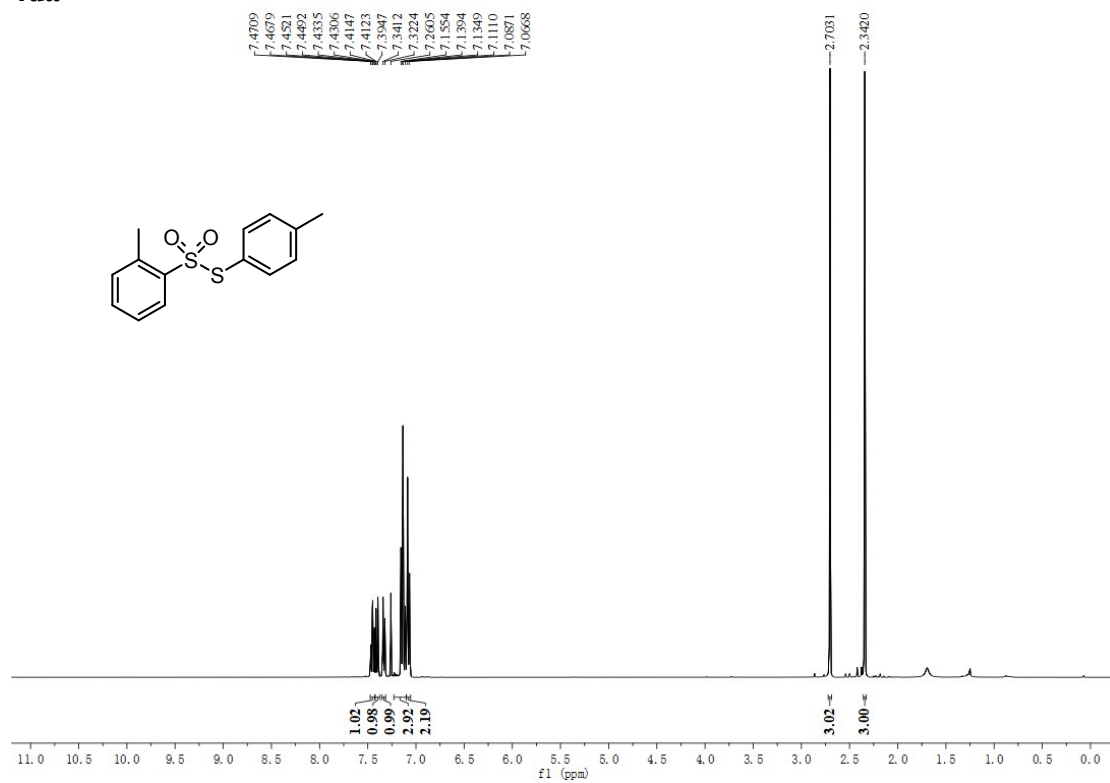




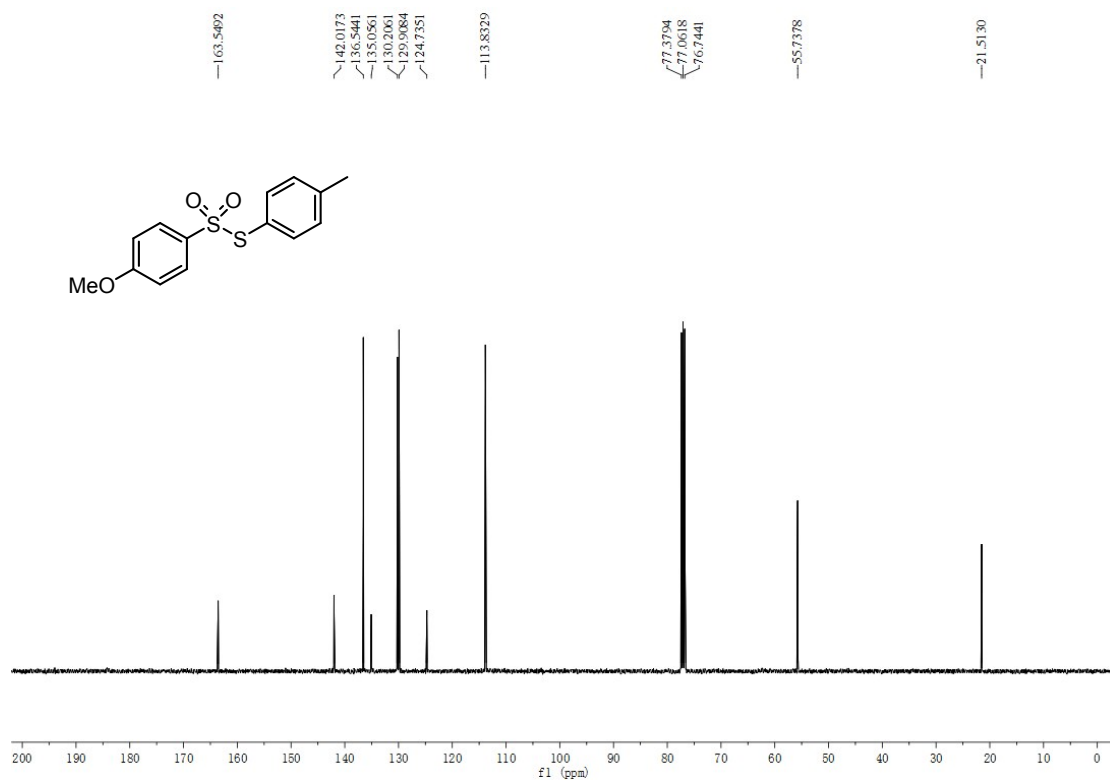
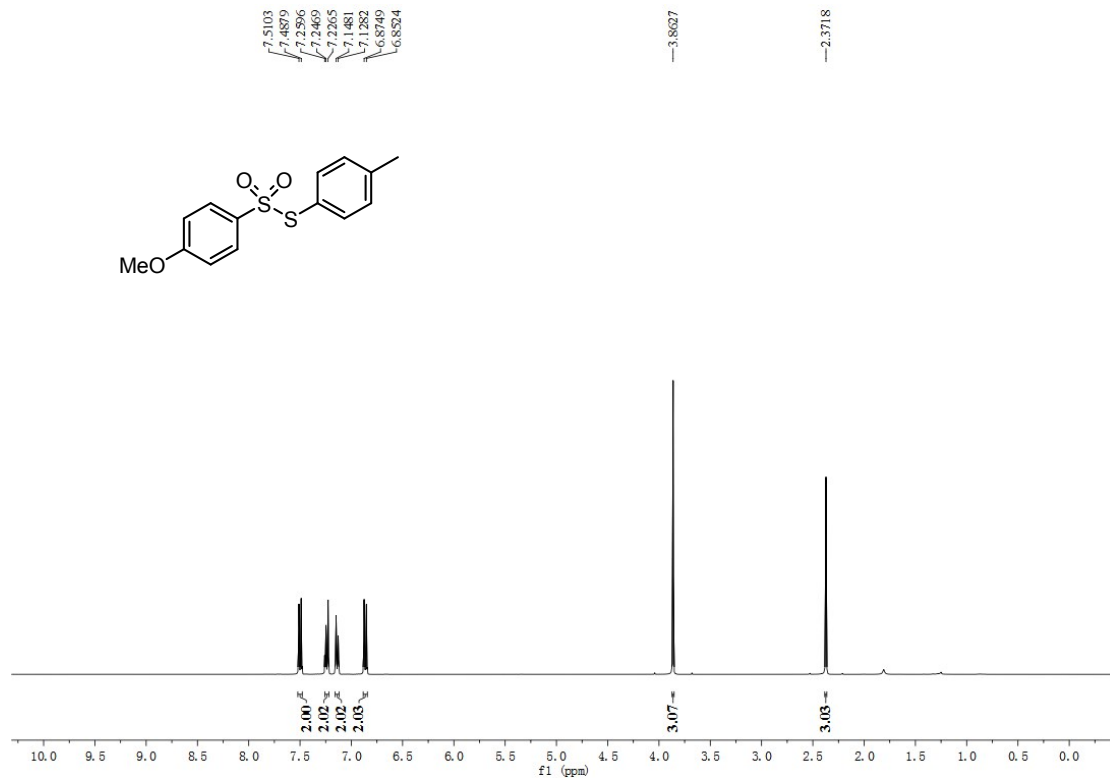
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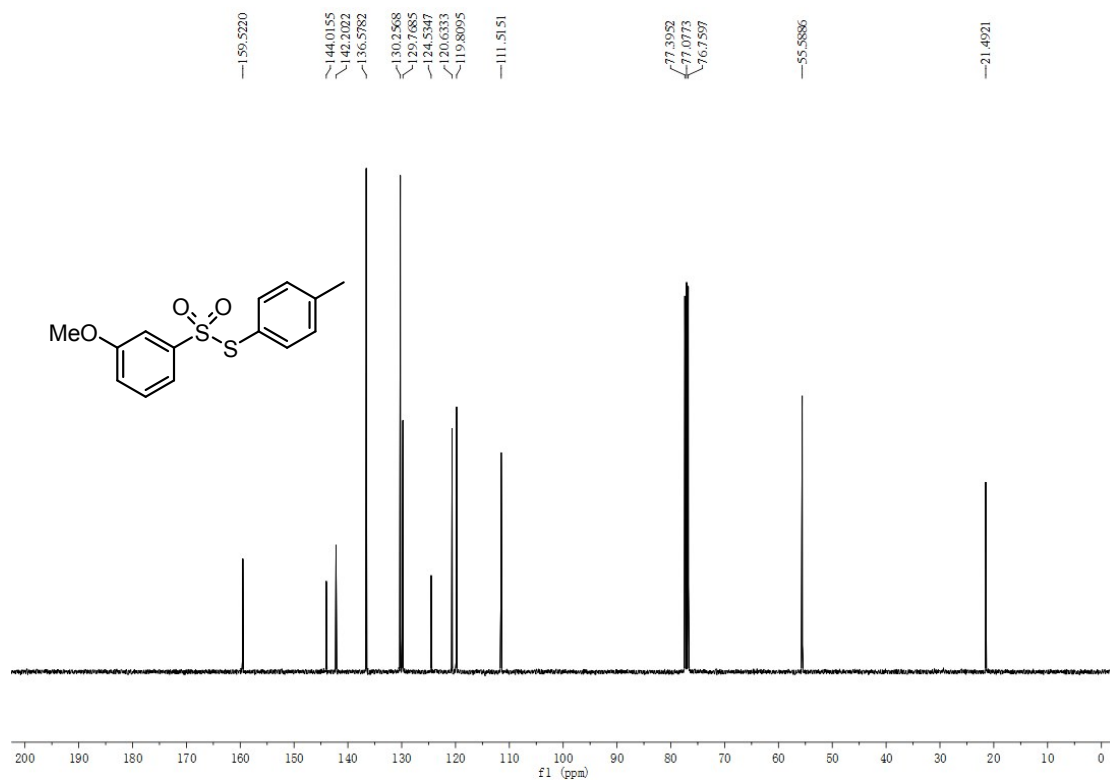
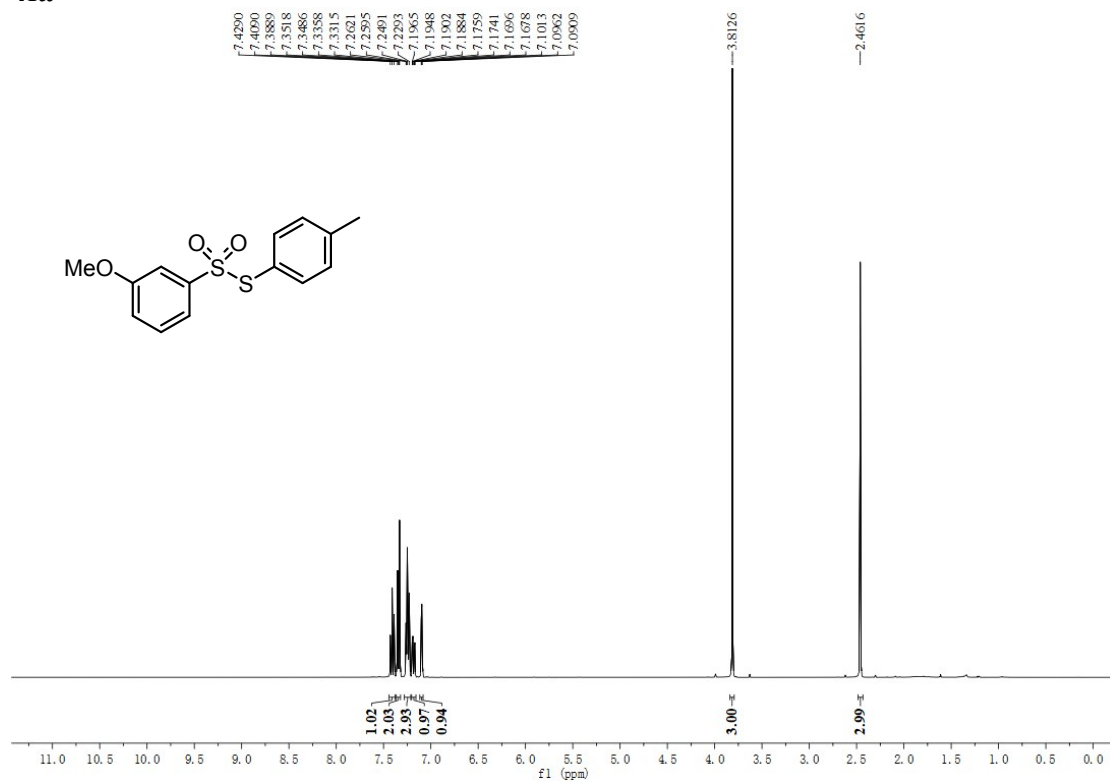
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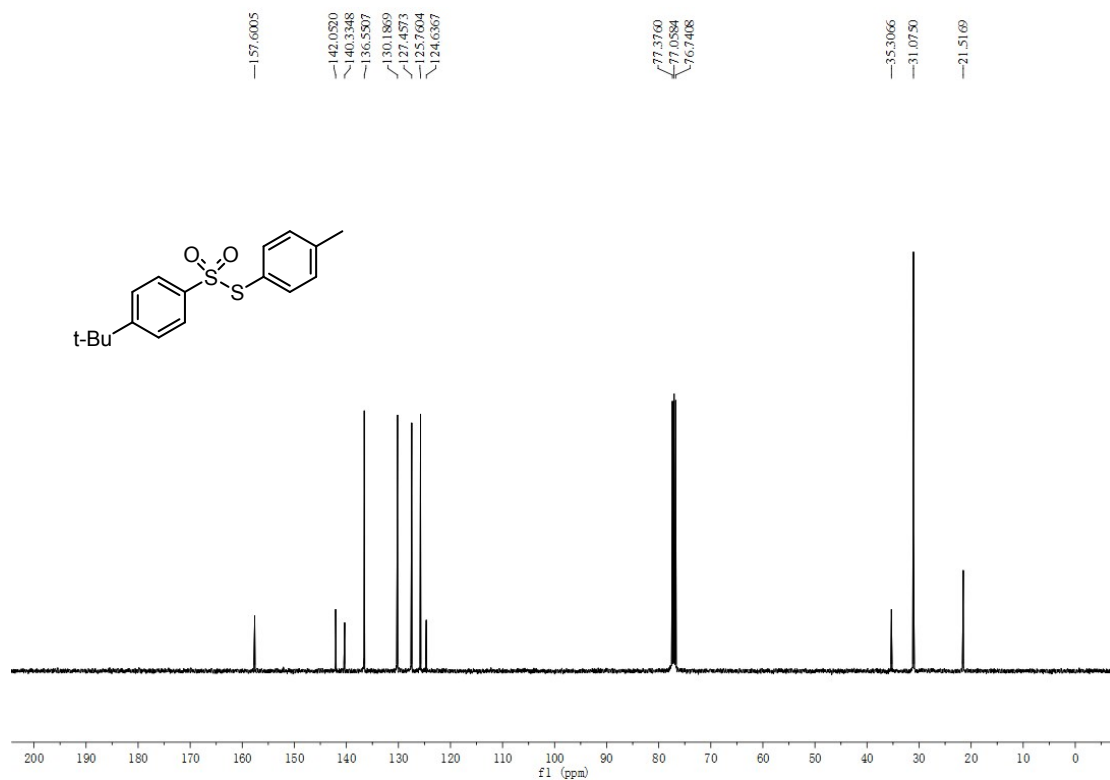
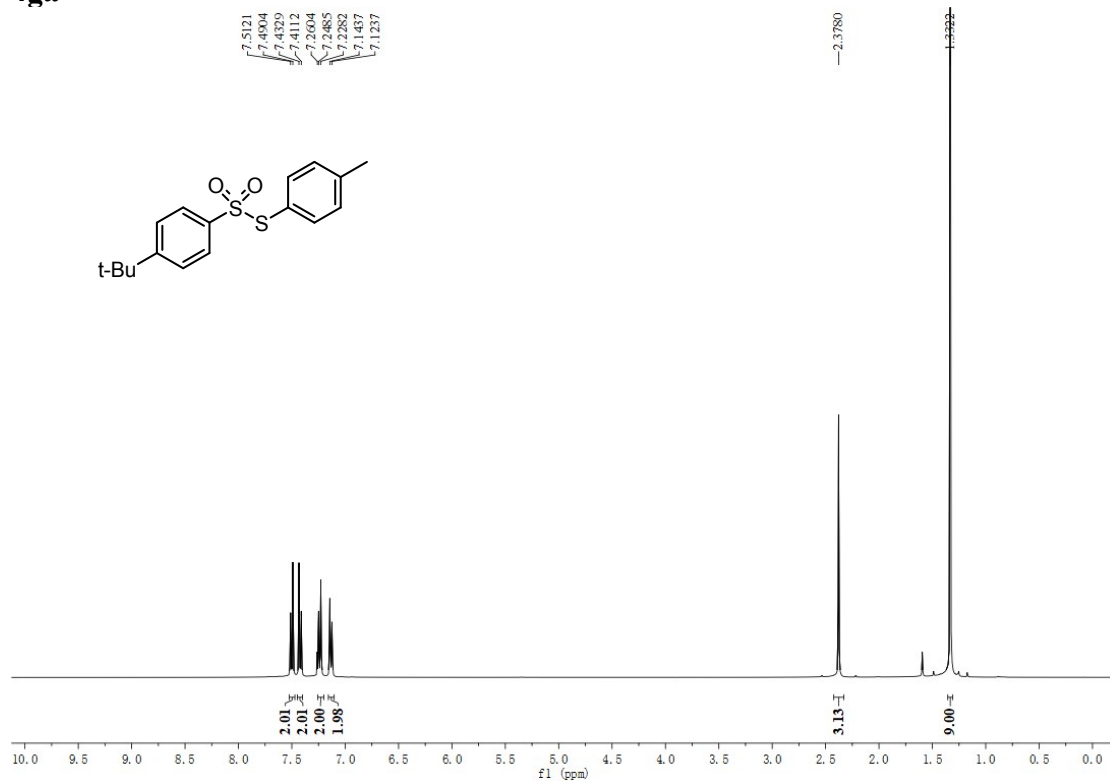
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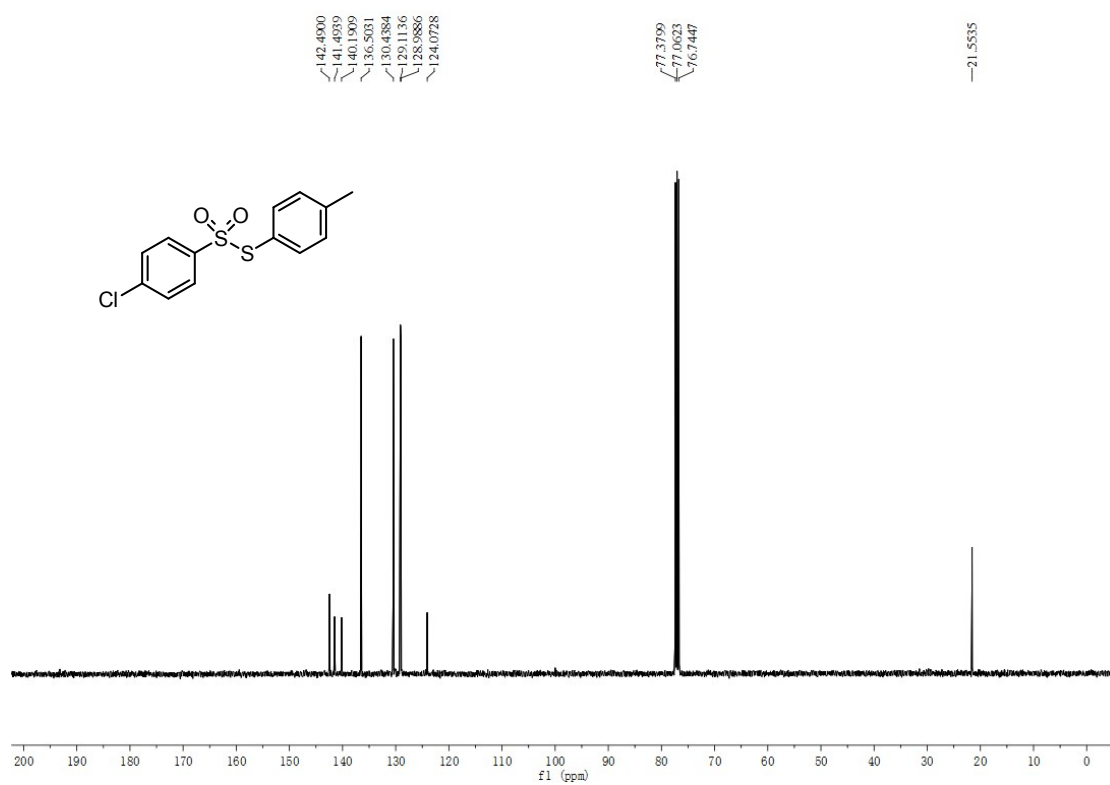
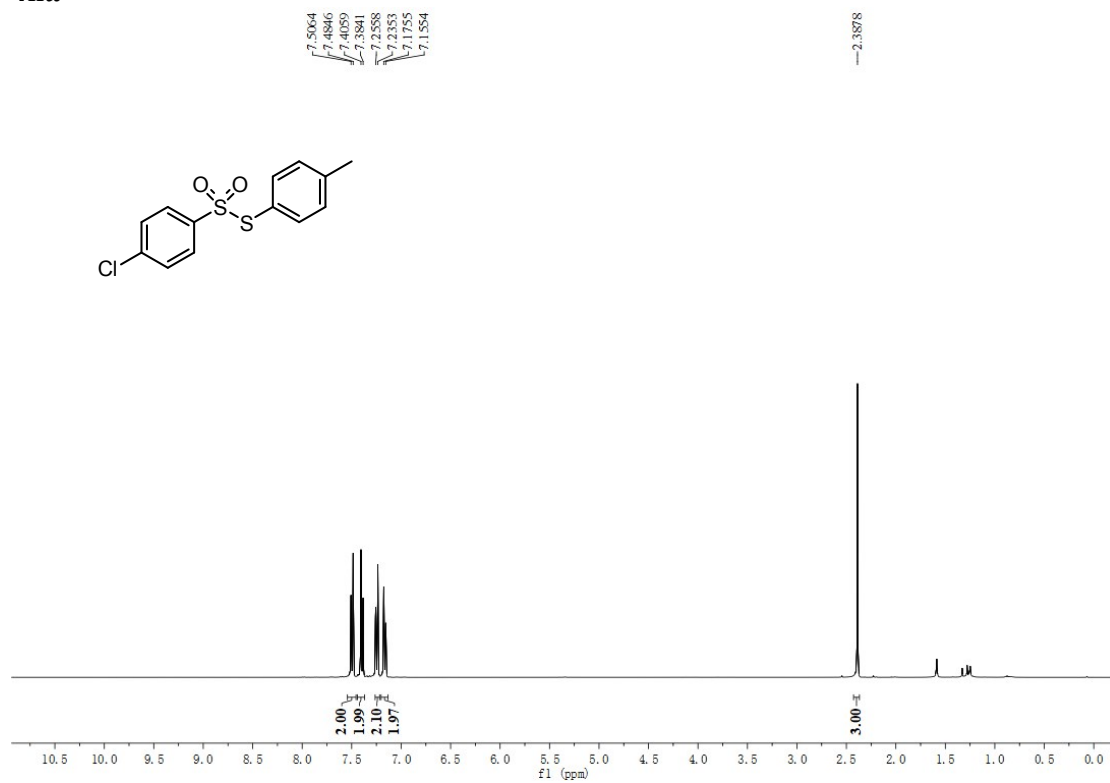
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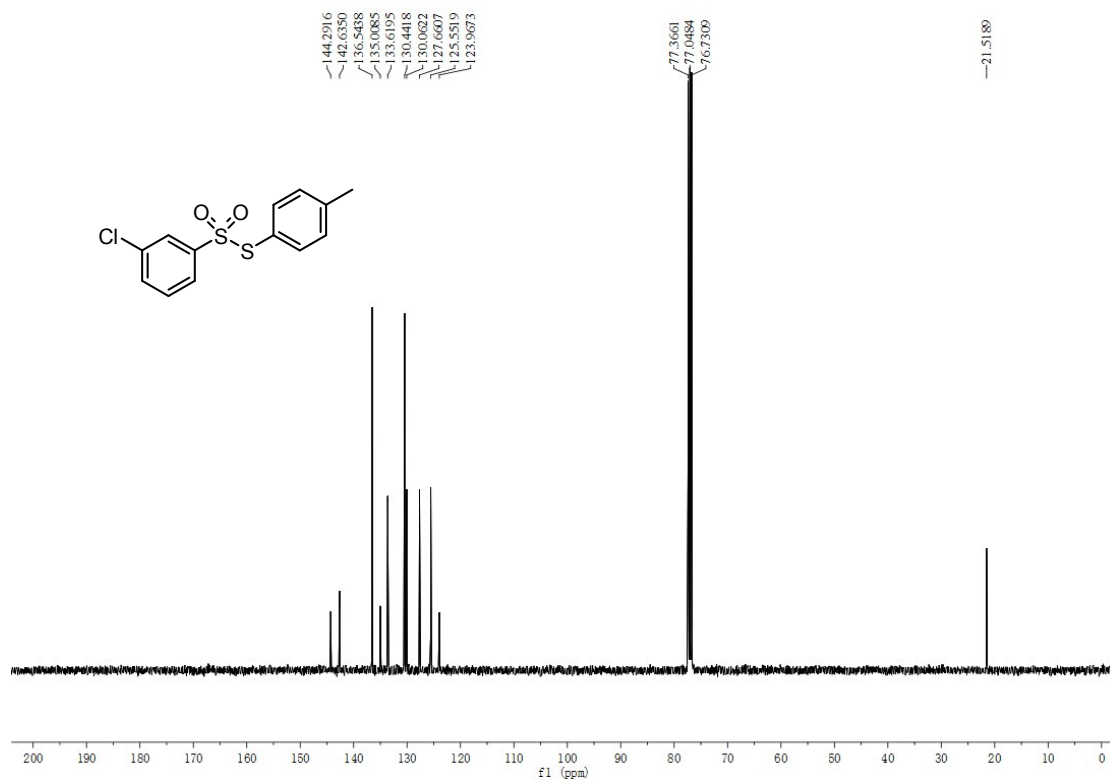
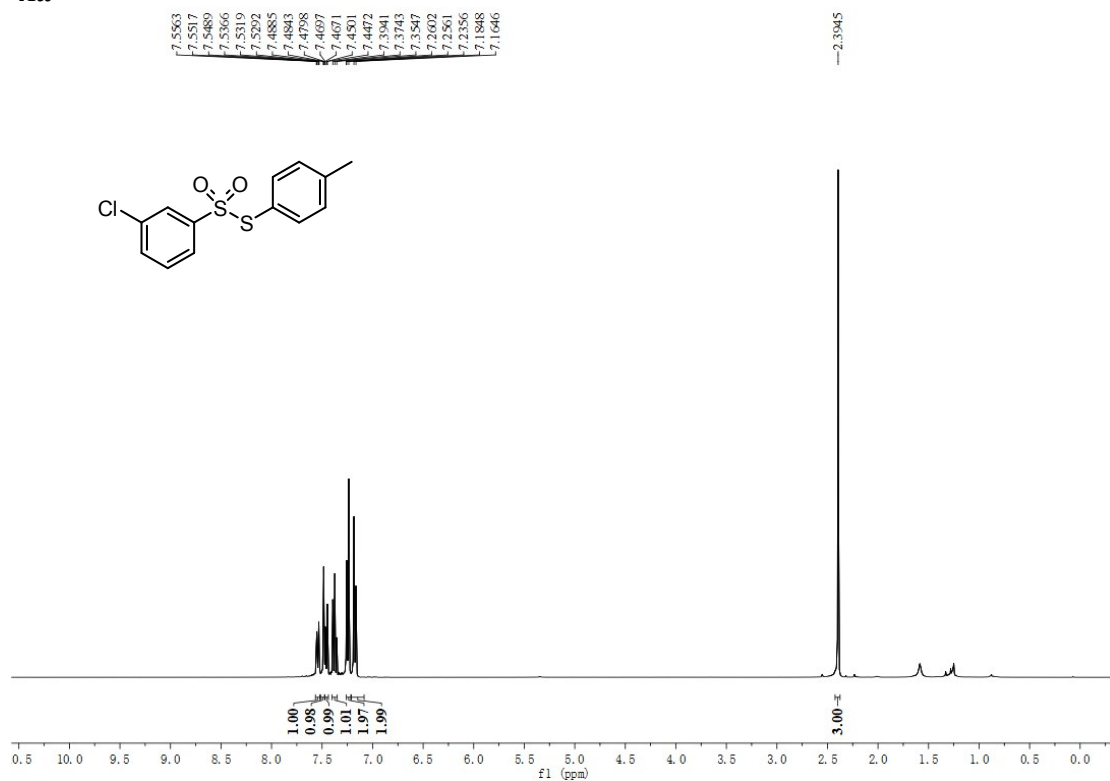
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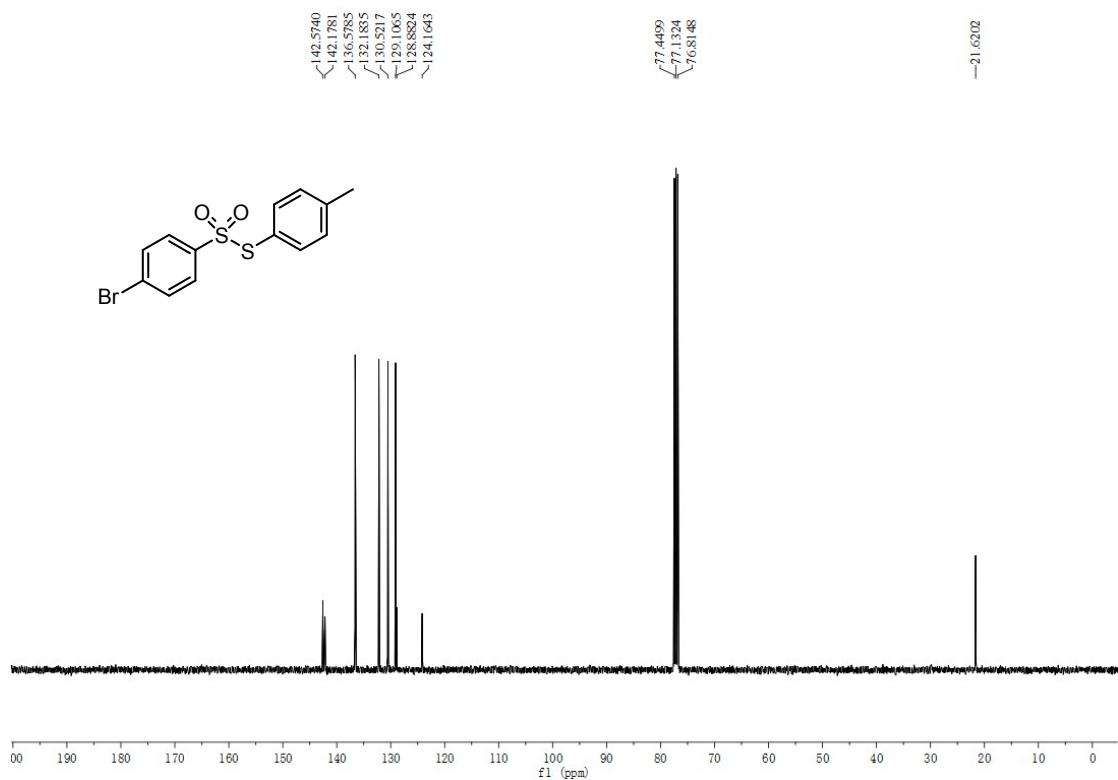
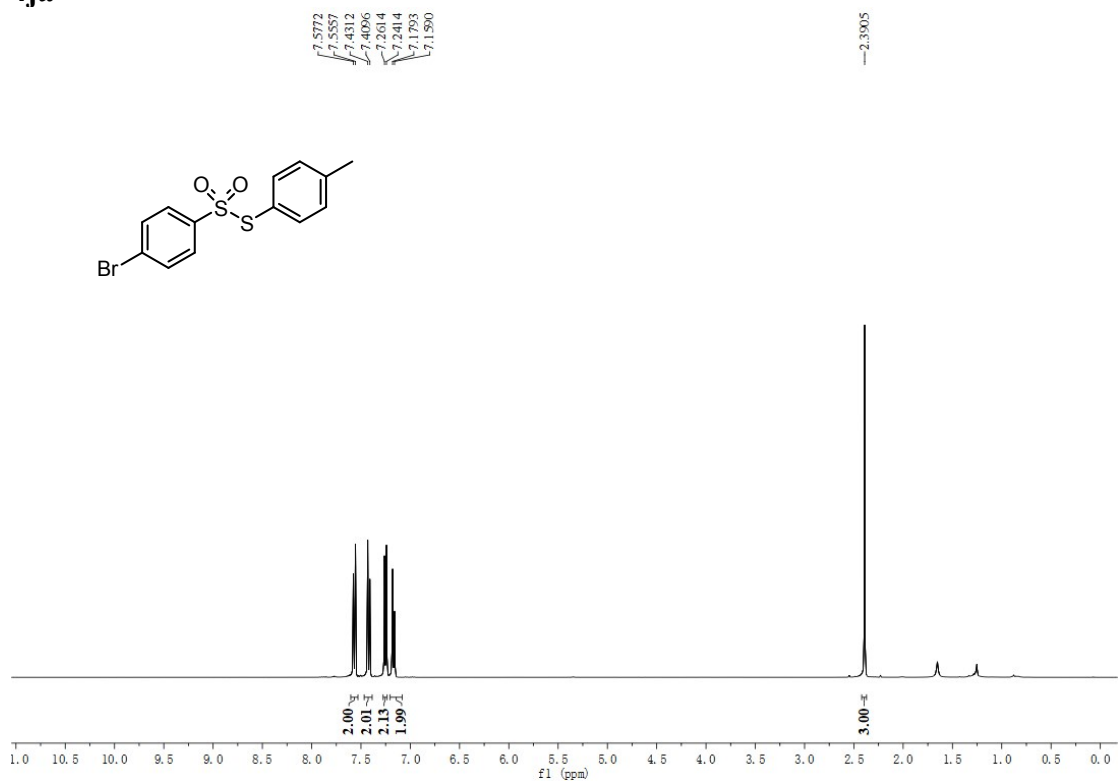
# 4ha



4ia

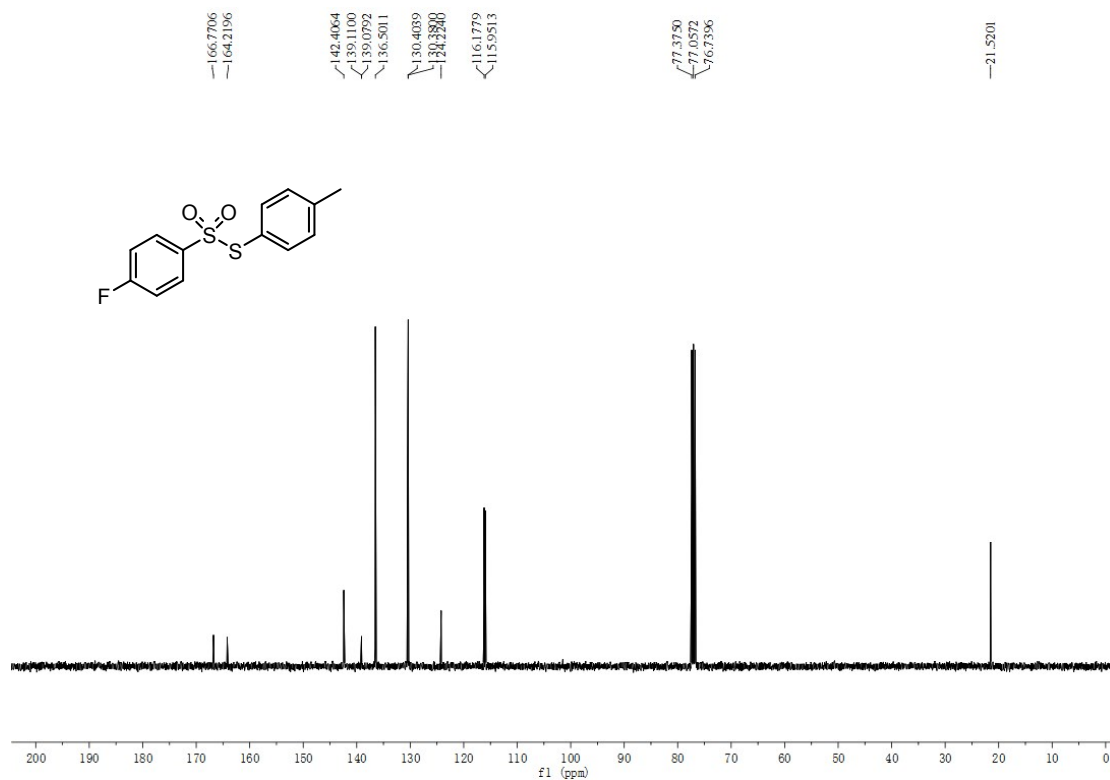
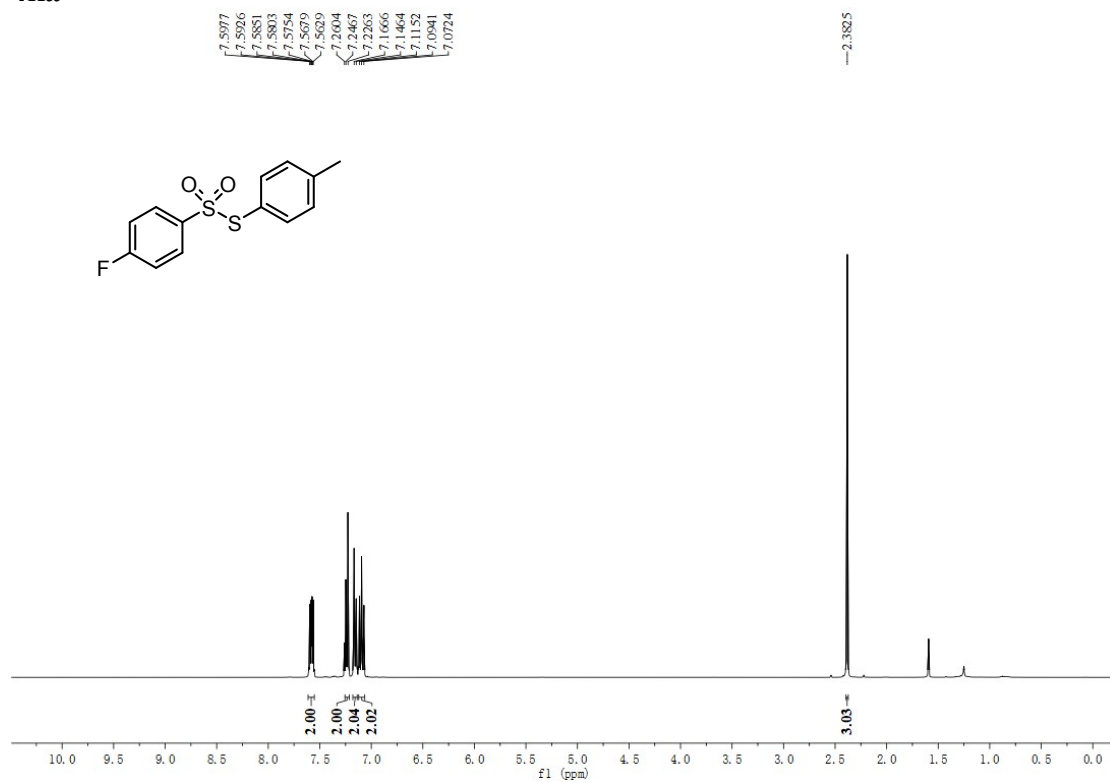


4ja

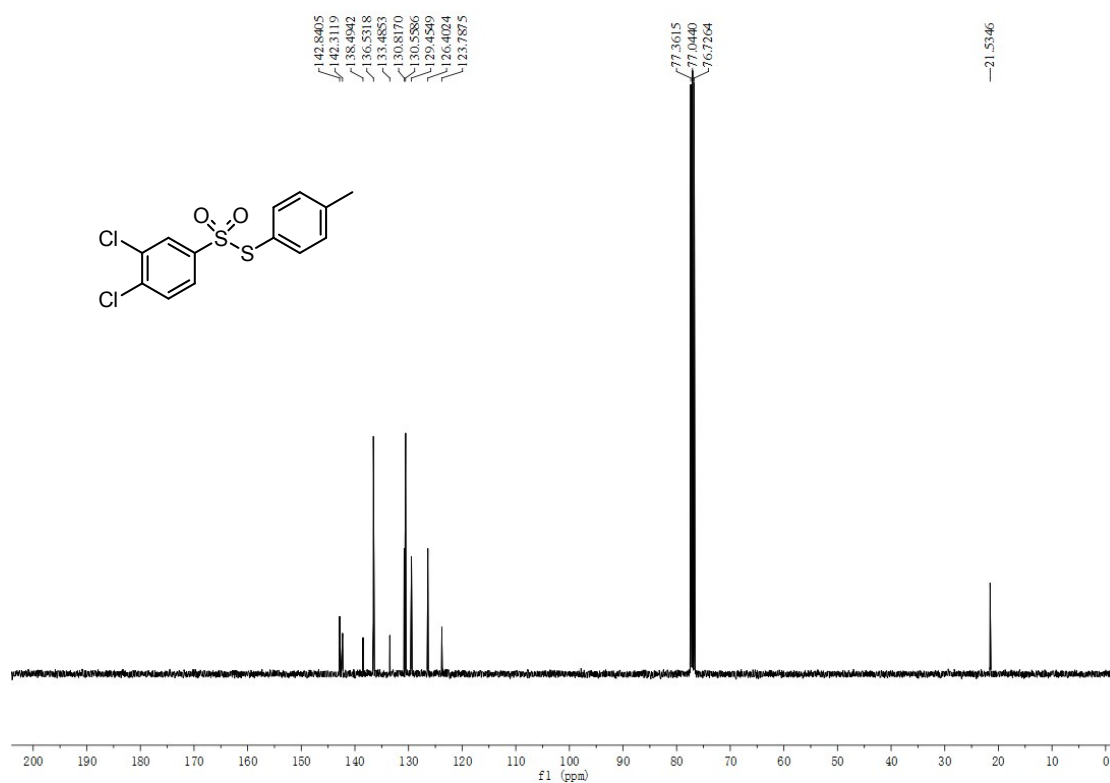
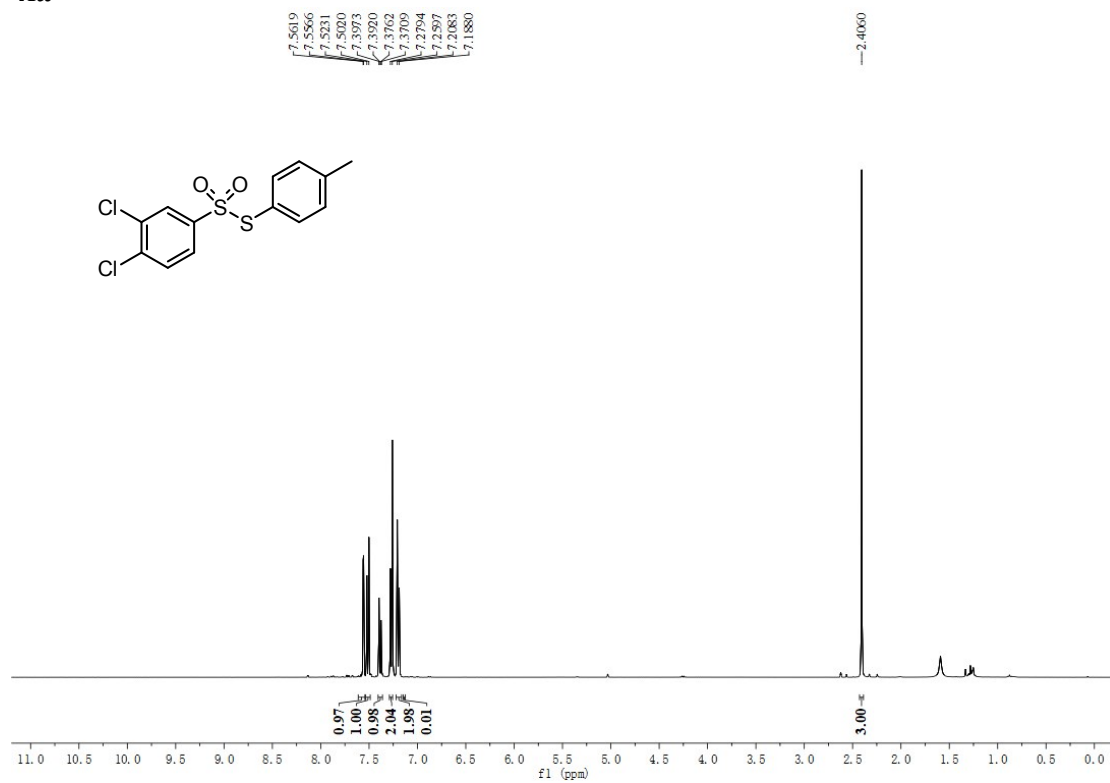




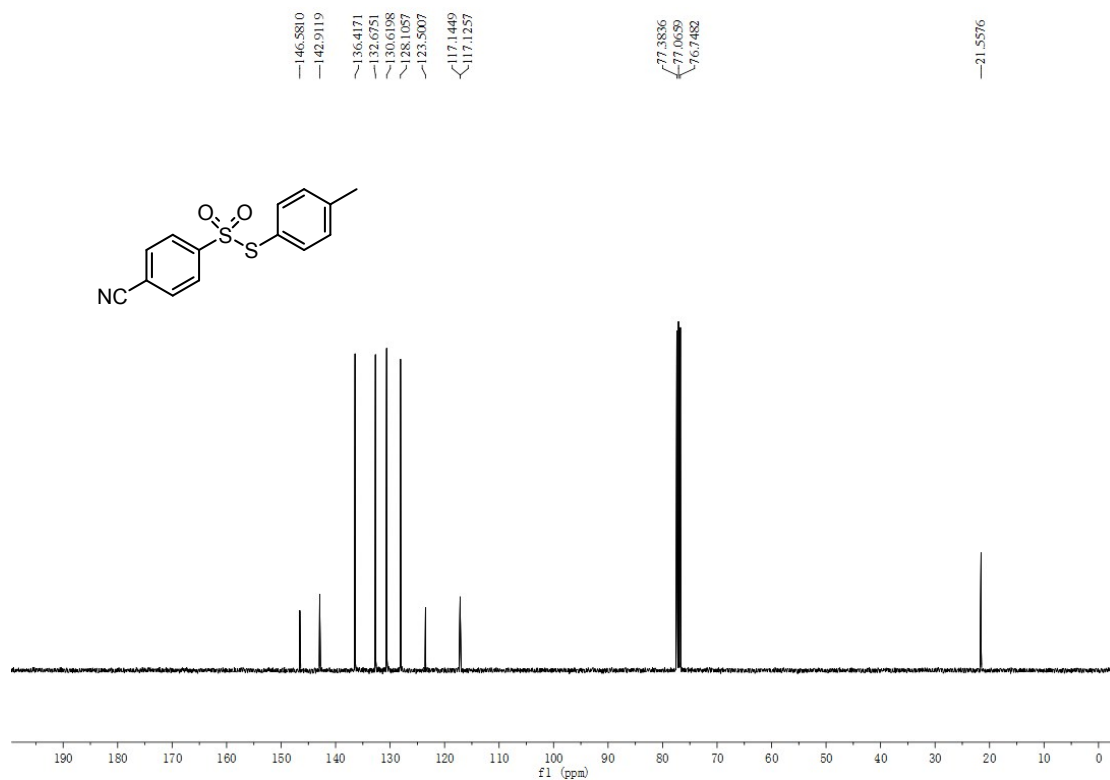
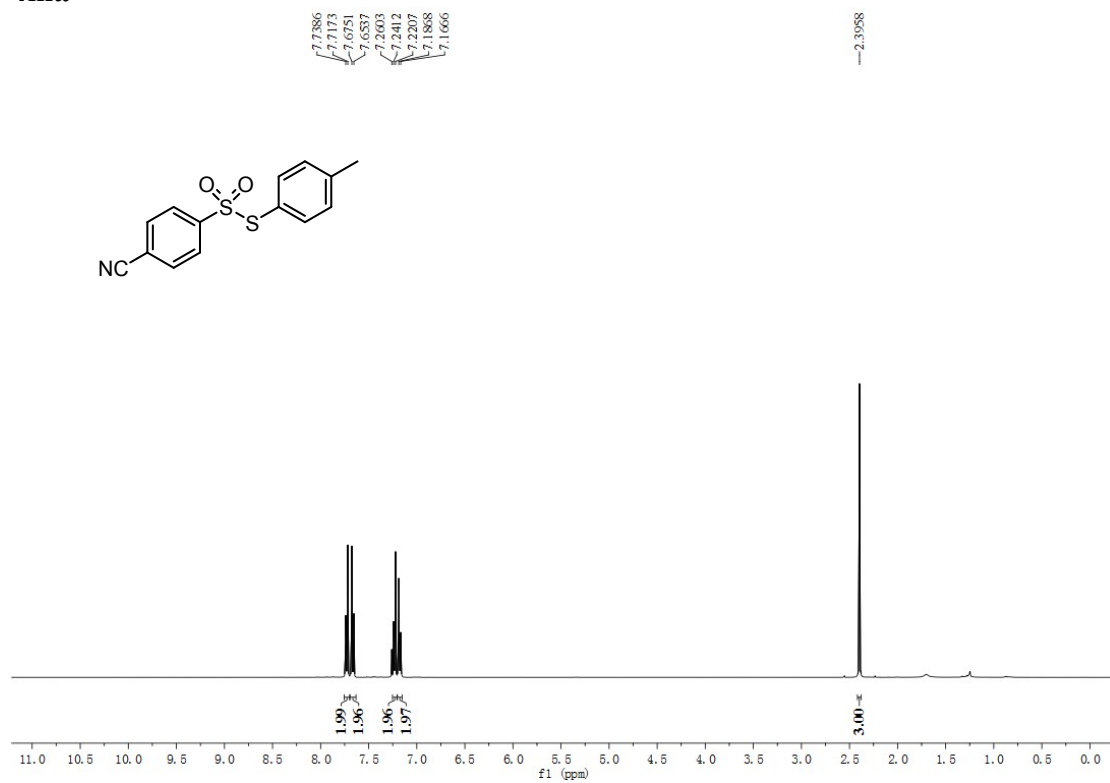
4ka



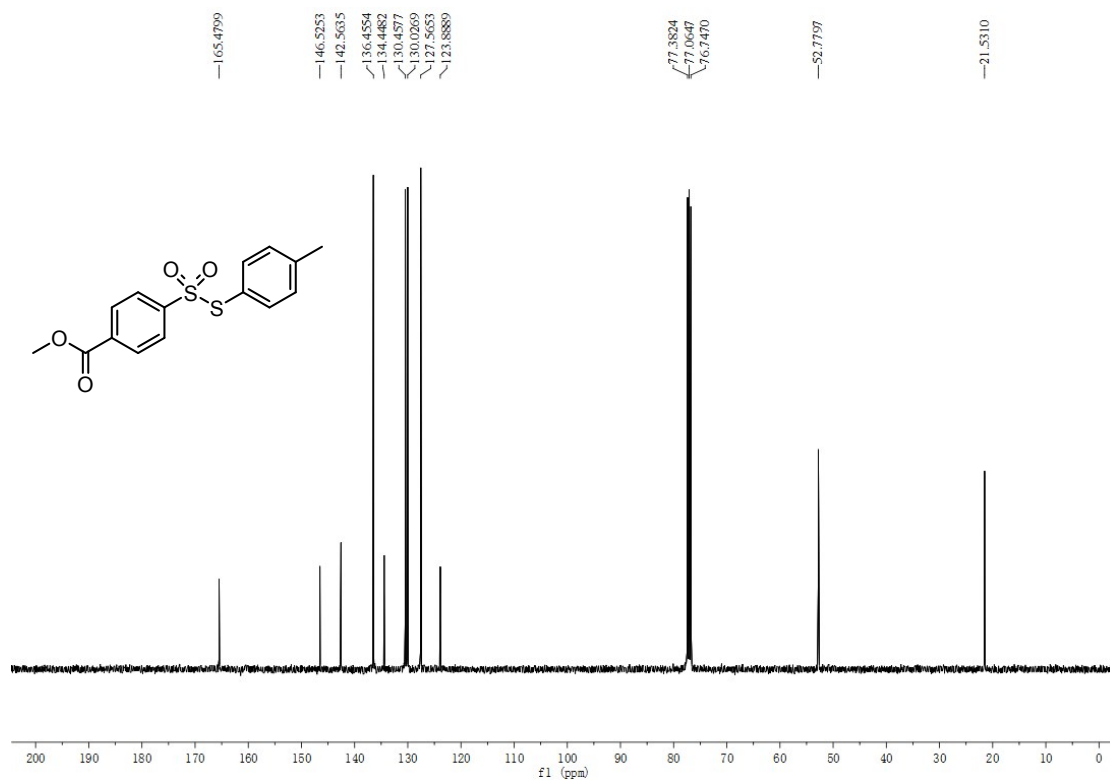
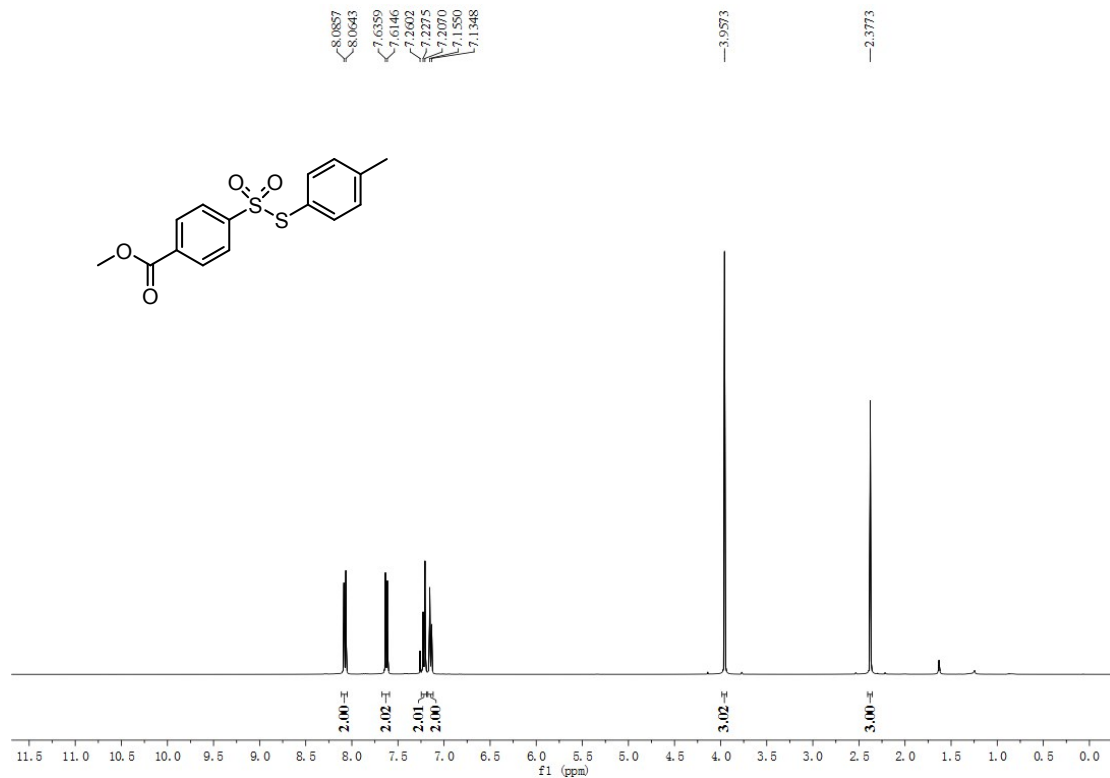
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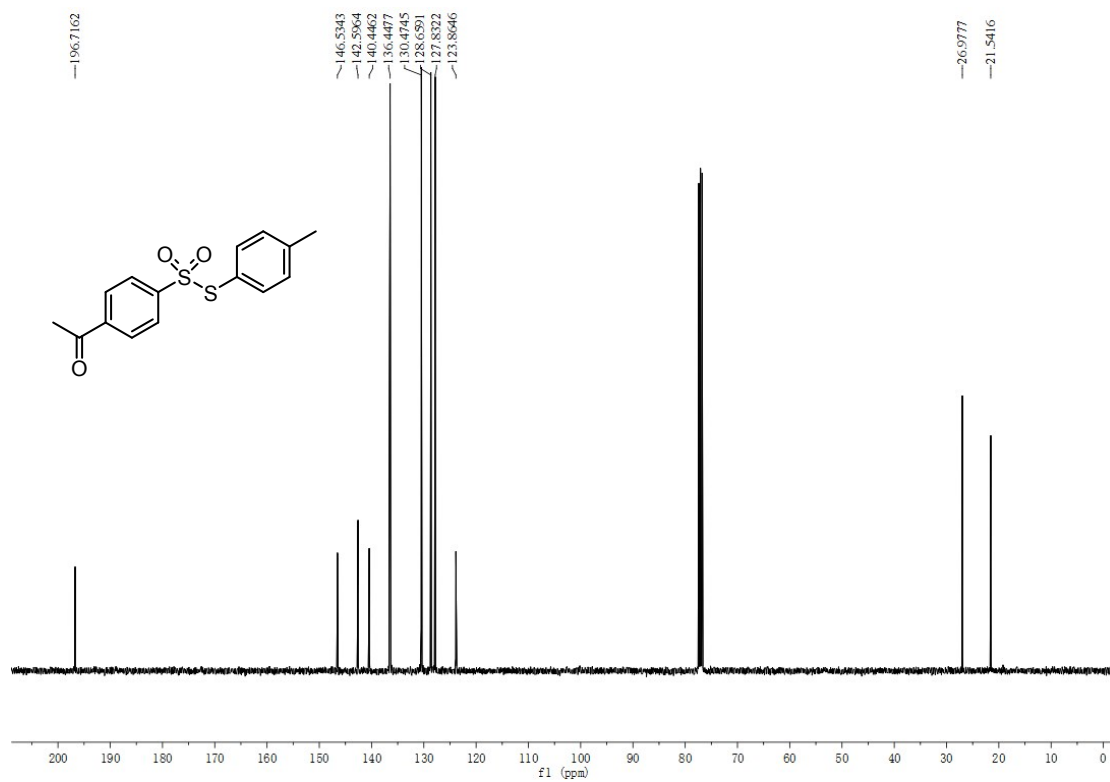
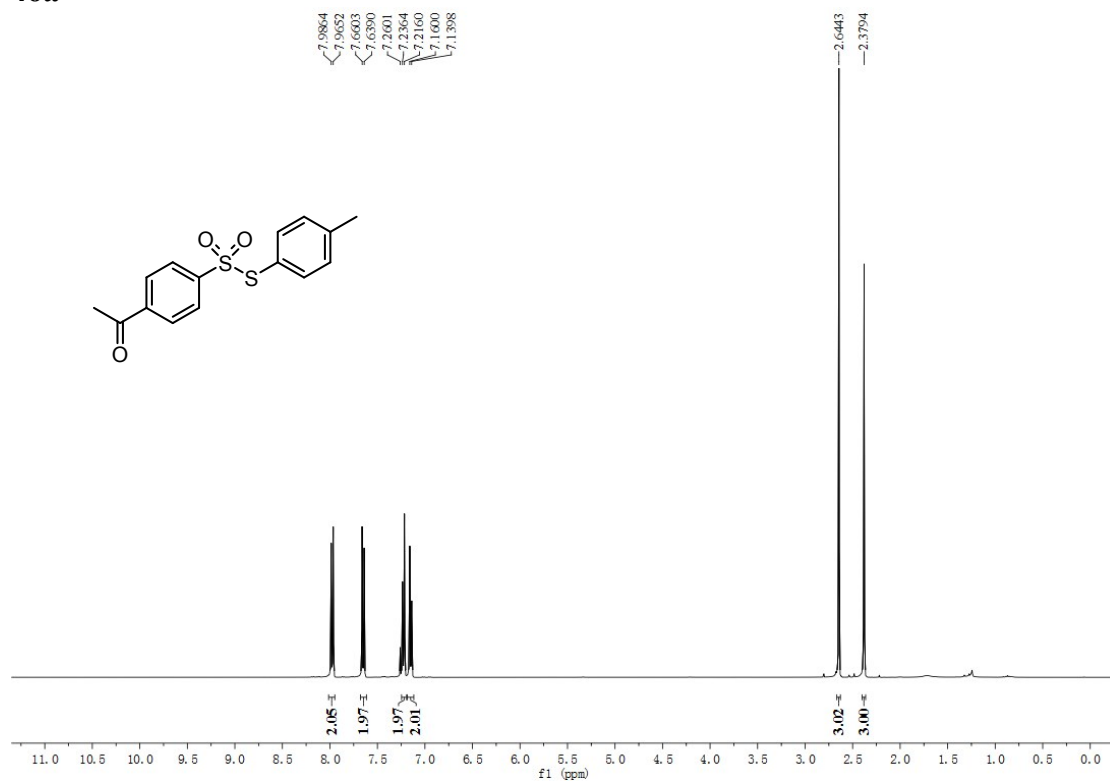
4ma



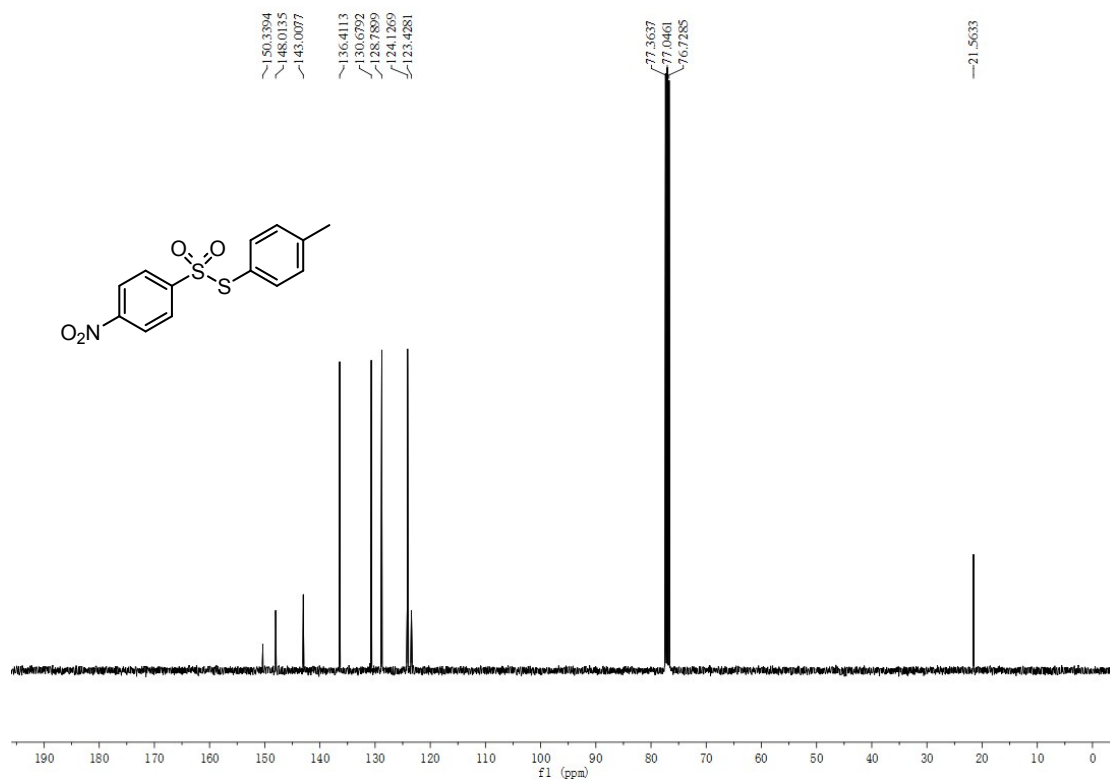
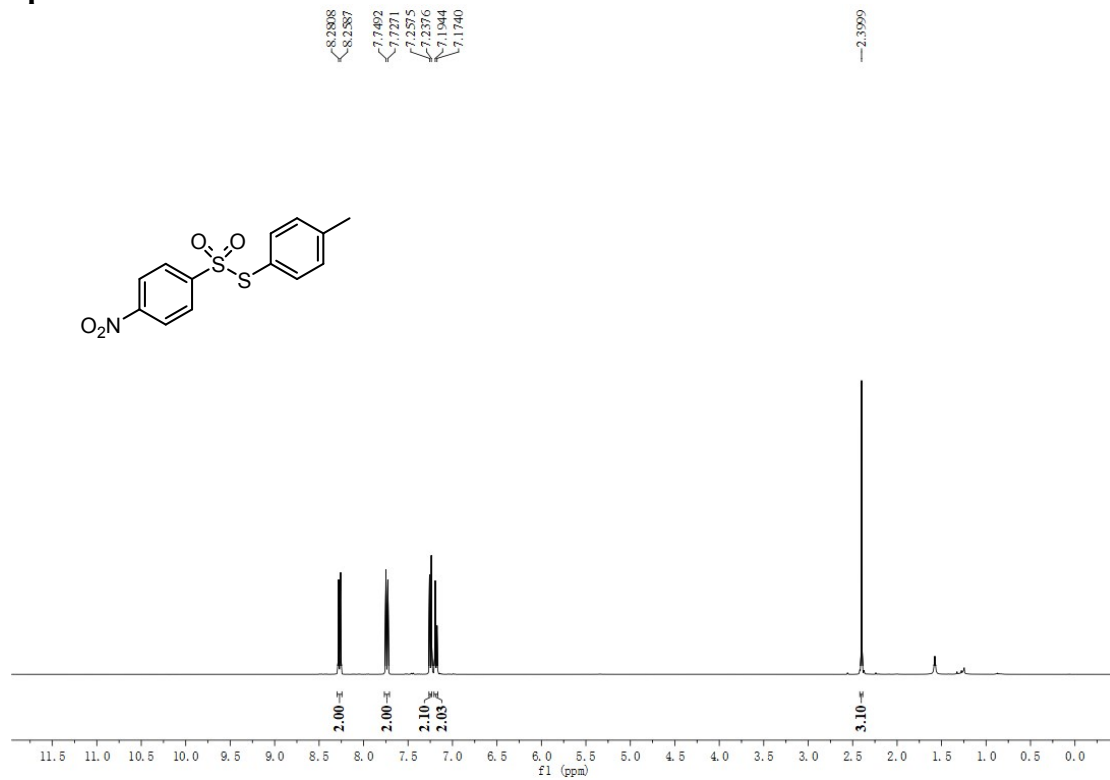
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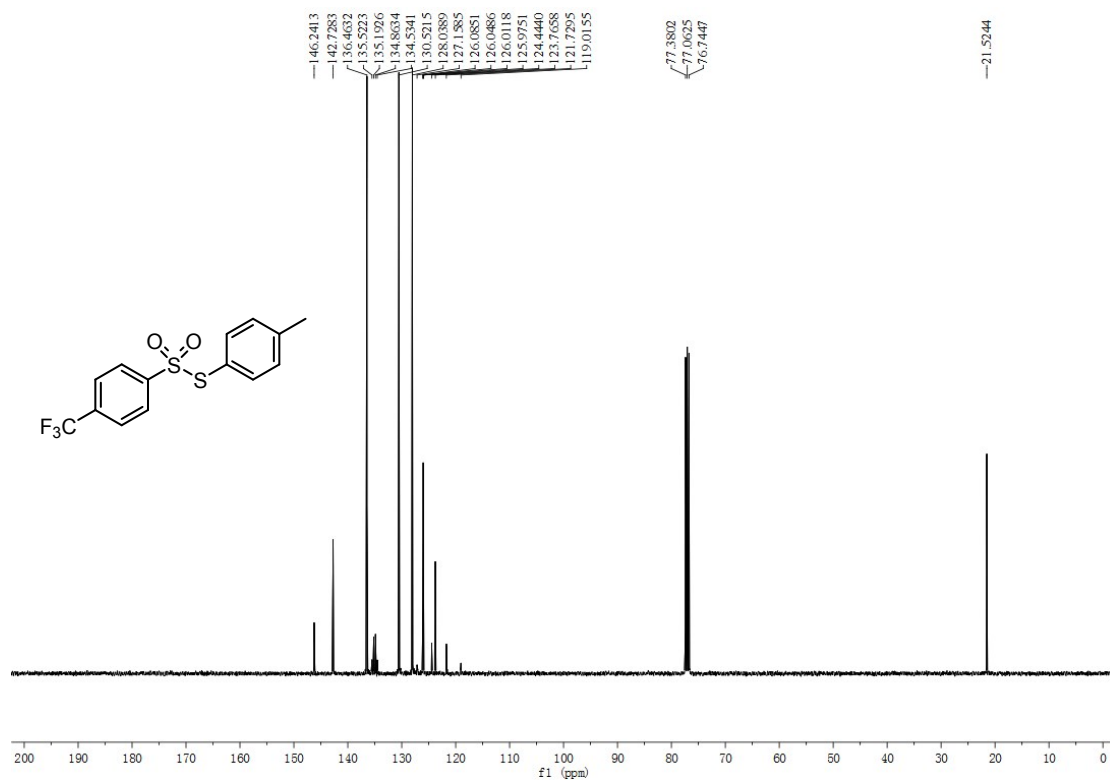
40a



4pa



4qa



4ra

