

# **Supporting Information**

## **Copper-Catalyzed Oxysulfenylation of Enolates with Sodium Sulfinate: A Strategy to Construct Sulfenylated Cyclic Ethers**

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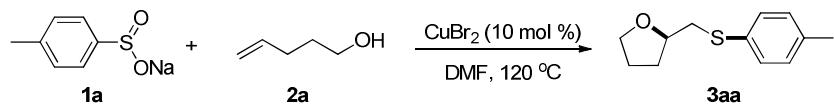
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## A. Experimental Procedures

### I. General Methods

<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> at 400 MHz, <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> at 100 MHz, and <sup>19</sup>F NMR were recorded in CDCl<sub>3</sub> at 565 MHz respectively, and the chemical shifts ( $\delta$ ) were referenced to TMS. GC–MS was obtained using electron ionization. HRMS was carried out on a MAT 95XP (Thermo). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF<sub>254</sub>), and visualization was effected at 254 nm.

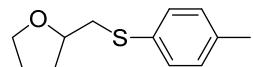
### II. General Procedure for Synthesis of Sulfenylated Cyclic Ethers



Sodium 4-methylbenzenesulfinate (**1a**, 0.25 mmol), pent-4-en-1-ol (**2a**, 0.25 mmol), and CuBr<sub>2</sub> (10 mol %) in 2.0 mL DMF were added to a tube equipped with magnetic stirrer bar. The reaction was under air and the mixture was stirred at 120 °C (oil bath temperature) for the desired reaction time. After the reaction was finished (monitored by TLC), the mixture was cooled to room temperature and quenched with aqueous NH<sub>4</sub>Cl, and the crude product was extracted with ethyl acetate. The organic extracts were concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate as eluent to afford the desired products.

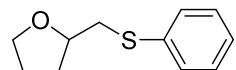
### B. Characterization Data for Compounds 3aa-6

#### 2-((*p*-Tolylthio)methyl)tetrahydrofuran (**3aa**)



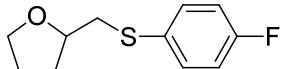
Yellow liquid (42 mg, 83%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 (d,  $J$  = 7.2 Hz, 2H), 7.09 (d,  $J$  = 7.3 Hz, 2H), 4.12 – 3.96 (m, 1H), 3.89 (q,  $J$  = 6.4 Hz, 1H), 3.75 (q,  $J$  = 6.7 Hz, 1H), 3.11 (dd,  $J$  = 12.5, 4.4 Hz, 1H), 2.94 (d,  $J$  = 6.0 Hz, 1H), 2.31 (s, 3H), 2.03 (dt,  $J$  = 21.5, 11.2 Hz, 1H), 1.97 (s, 2H), 1.65 (dt,  $J$  = 16.0, 6.7 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.2, 132.6, 130.1, 129.6, 77.7, 68.3, 39.6, 30.9, 25.7, 20.9. IR (KBr, cm<sup>-1</sup>): 3679, 2923, 1741, 1492, 1056, 804; ESI-HRMS calcd for C<sub>12</sub>H<sub>16</sub>OS[M+Na]<sup>+</sup> 231.0814; found, 231.0816.

#### 5-((Phenylthio)methyl)dihydrofuran-2(3*H*)-one (**3ba**)



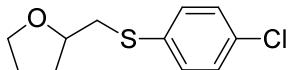
Yellow liquid (39 mg, 81%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 7.4$  Hz, 2H), 7.30 – 7.22 (m, 2H), 7.18 (d,  $J = 6.9$  Hz, 1H), 4.19 – 3.96 (m, 1H), 3.96 – 3.85 (m, 1H), 3.76 (q,  $J = 6.9$  Hz, 1H), 3.16 (dd,  $J = 12.9, 5.3$  Hz, 1H), 2.97 (dd,  $J = 12.9, 6.6$  Hz, 1H), 2.06 (d,  $J = 4.6$  Hz, 1H), 1.98 – 1.79 (m, 2H), 1.74 – 1.62 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.4, 129.3, 128.9, 126.0, 77.6, 68.3, 38.9, 30.9, 25.8. IR (KBr,  $\text{cm}^{-1}$ ): 3668, 2923, 1941, 1496, 1246, 804; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{14}\text{OS}[\text{M}+\text{H}]^+$  195.0838; found, 195.0842.

### 5-((4-Fluorophenyl)thio)methyl)dihydrofuran-2(3*H*)-one (3ca)



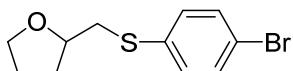
Yellow liquid (45 mg, 85%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 6.5$  Hz, 2H), 6.99 (t,  $J = 8.5$  Hz, 2H), 4.02 (dd,  $J = 12.9, 6.4$  Hz, 1H), 3.90 (dd,  $J = 14.2, 7.3$  Hz, 1H), 3.76 (dd,  $J = 14.5, 7.4$  Hz, 1H), 3.08 (dd,  $J = 13.1, 5.8$  Hz, 1H), 2.93 (dd,  $J = 13.1, 6.5$  Hz, 1H), 2.03 (dt,  $J = 22.5, 8.1$  Hz, 1H), 1.88 (dt,  $J = 45.7, 22.7$  Hz, 2H), 1.63 (dd,  $J = 19.8, 7.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8 (d,  $J = 246.2$  Hz), 132.3 (d,  $J = 8.0$  Hz), 131.3 (d,  $J = 3.0$  Hz), 116.0 (d,  $J = 21.9$  Hz), 77.6, 68.3, 40.3, 30.9, 25.8.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.7. IR (KBr,  $\text{cm}^{-1}$ ): 3431, 2924, 1491, 1225, 1055, 826; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{13}\text{FOS}[\text{M}+\text{Na}]^+$  235.0563; found, 235.0561.

### 2-((4-Chlorophenyl)thio)methyltetrahydrofuran (3da)



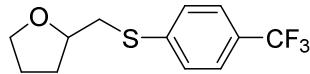
Yellow liquid (47 mg, 83%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (d,  $J = 7.4$  Hz, 2H), 7.16 (d,  $J = 8.2$  Hz, 2H), 3.97 (p,  $J = 6.0$  Hz, 1H), 3.82 (dd,  $J = 14.3, 7.2$  Hz, 1H), 3.69 (q,  $J = 7.2$  Hz, 1H), 3.04 (dd,  $J = 13.0, 5.8$  Hz, 1H), 2.89 (dd,  $J = 13.6, 5.6$  Hz, 1H), 1.96 (dd,  $J = 12.4, 6.4$  Hz, 1H), 1.84 (td,  $J = 13.9, 6.5$  Hz, 2H), 1.63 – 1.52 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.0, 131.9, 130.5, 128.9, 77.5, 68.3, 39.1, 30.9, 25.7. IR (KBr,  $\text{cm}^{-1}$ ): 3310, 2963, 1475, 1094, 746; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{13}\text{ClOS}[\text{M}+\text{Na}]^+$  251.0268; found, 251.0270.

### 2-((4-Bromophenyl)thio)methyltetrahydrofuran (3ea)



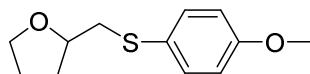
Yellow liquid (55 mg, 81%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 7.7$  Hz, 2H), 7.25 (d,  $J = 5.3$  Hz, 2H), 4.04 (d,  $J = 6.0$  Hz, 1H), 3.90 (d,  $J = 6.7$  Hz, 1H), 3.76 (d,  $J = 7.3$  Hz, 1H), 3.11 (dd,  $J = 12.4, 4.4$  Hz, 1H), 2.97 (dd,  $J = 12.9, 5.8$  Hz, 1H), 2.06 (d,  $J = 6.1$  Hz, 1H), 1.92 (d,  $J = 7.4$  Hz, 2H), 1.71 – 1.62 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.8, 131.9, 130.7, 119.8, 77.5, 68.4, 39.0, 31.0, 25.8. IR (KBr,  $\text{cm}^{-1}$ ): 2925, 2856, 1472, 808, 481; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{13}\text{BrOS}[\text{M}+\text{Na}]^+$  294.9763; found, 294.9764.

**2-(((4-(Trifluoromethyl)phenyl)thio)methyl)tetrahydrofuran (3fa)**



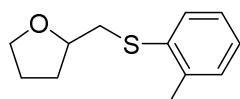
Yellow liquid (53 mg, 81%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 7.6$  Hz, 2H), 7.41 (d,  $J = 7.8$  Hz, 2H), 4.17 – 4.01 (m, 1H), 3.98 – 3.84 (m, 1H), 3.78 (dd,  $J = 13.7, 6.5$  Hz, 1H), 3.19 (dd,  $J = 12.6, 5.0$  Hz, 1H), 3.06 (dd,  $J = 12.6, 5.8$  Hz, 1H), 2.14 – 2.03 (m, 1H), 2.02 – 1.83 (m, 2H), 1.70 (dd,  $J = 17.6, 8.5$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.2, 127.7, 127.7, 127.4, 125.7 (q,  $J^3 = 4.0$  Hz), 122.81, 77.2, 68.5, 37.9, 31.0, 25.8.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.4. IR (KBr,  $\text{cm}^{-1}$ ): 3445, 2927, 1327, 1123, 826; ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{13}\text{F}_3\text{OS} [\text{M}+\text{Na}]^+$  285.0531; found, 285.0534.

**2-(((4-Methoxyphenyl)thio)methyl)tetrahydrofuran (3ga)**



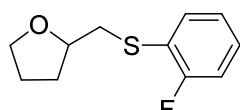
Yellow liquid (51 mg, 90%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 7.7$  Hz, 2H), 6.83 (d,  $J = 7.7$  Hz, 2H), 4.04 – 3.94 (m, 1H), 3.88 (dd,  $J = 14.3, 7.1$  Hz, 1H), 3.79 (s, 3H), 3.77 – 3.70 (m, 1H), 3.05 (dd,  $J = 12.9, 5.6$  Hz, 1H), 2.87 (dd,  $J = 12.8, 6.7$  Hz, 1H), 2.03 (dt,  $J = 13.0, 6.7$  Hz, 1H), 1.88 (tt,  $J = 13.1, 6.6$  Hz, 2H), 1.78 – 1.47 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 133.1, 126.5, 114.5, 77.8, 68.2, 55.3, 40.9, 30.8, 25.7. IR (KBr,  $\text{cm}^{-1}$ ): 3454, 2925, 1492, 1244; ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{16}\text{O}_2\text{S} [\text{M}+\text{Na}]^+$  247.0763; found, 247.0766.

**2-((o-Tolylthio)methyl)tetrahydrofuran (3ha)**



Yellow liquid (47 mg, 90%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J = 7.5$  Hz, 1H), 7.18 (t,  $J = 7.2$  Hz, 2H), 7.14 – 7.07 (m, 1H), 4.10 (dd,  $J = 12.6, 6.1$  Hz, 1H), 3.95 (dd,  $J = 13.5, 6.4$  Hz, 1H), 3.80 (q,  $J = 6.5$  Hz, 1H), 3.16 (dd,  $J = 12.0, 4.9$  Hz, 1H), 2.96 (dd,  $J = 12.4, 6.7$  Hz, 1H), 2.41 (s, 3H), 2.10 (dt,  $J = 12.3, 6.3$  Hz, 1H), 2.02 – 1.86 (m, 2H), 1.78 – 1.67 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6, 135.6, 130.1, 128.0, 126.4, 125.7, 77.6, 68.3, 38.2, 31.1, 25.7, 20.4. IR (KBr,  $\text{cm}^{-1}$ ): 3455, 2925, 2864, 1466, 1058, 745; ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{16}\text{OS} [\text{M}+\text{Na}]^+$  231.0814; found, 231.0817.

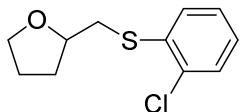
**2-((2-Fluorophenyl)thio)methyl)tetrahydrofuran (3ia)**



Yellow liquid (44 mg, 83%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (t,  $J = 7.3$  Hz, 1H), 7.21 (d,  $J = 6.2$  Hz, 1H), 7.06 (dd,  $J = 19.9, 8.8$  Hz, 2H), 4.09 – 3.99 (m, 1H), 3.89 (q,  $J = 6.4$  Hz, 1H), 3.76 (q,  $J = 6.6$

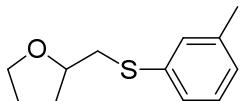
Hz, 1H), 3.12 (dd,  $J$  = 12.8, 4.6 Hz, 1H), 2.96 (dd,  $J$  = 12.7, 6.5 Hz, 1H), 2.06 (dd,  $J$  = 12.0, 6.4 Hz, 1H), 1.99 – 1.81 (m, 2H), 1.73 – 1.61 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5 (d,  $J$  = 245.2 Hz), 132.3 (d,  $J$  = 1.0 Hz), 128.4 (d,  $J$  = 7.8 Hz), 124.4 (d,  $J$  = 3.7 Hz), 123.1 (d,  $J$  = 18.0 Hz), 115.7 (d,  $J$  = 22.5 Hz), 77.7, 68.3, 38.5, 30.9, 25.8.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -109.2. IR (KBr,  $\text{cm}^{-1}$ ): 3680, 2927, 1473, 1057, 754; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{13}\text{FOS}[\text{M}+\text{Na}]^+$  235.0563; found, 235.0563.

### 2-((2-Chlorophenyl)thio)methyltetrahydrofuran (3ja)



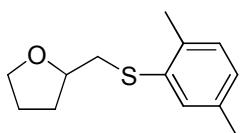
Yellow liquid (49 mg, 86%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J$  = 7.8 Hz, 2H), 7.21 (t,  $J$  = 7.6 Hz, 1H), 7.11 (t,  $J$  = 7.6 Hz, 1H), 4.10 (dd,  $J$  = 12.6, 6.4 Hz, 1H), 3.92 (dd,  $J$  = 14.0, 6.9 Hz, 1H), 3.78 (dd,  $J$  = 14.6, 7.2 Hz, 1H), 3.17 (dd,  $J$  = 12.7, 5.4 Hz, 1H), 2.99 (dd,  $J$  = 13.5, 7.7 Hz, 1H), 2.10 (dt,  $J$  = 12.3, 6.3 Hz, 1H), 1.92 (td,  $J$  = 12.3, 6.1 Hz, 2H), 1.72 (dt,  $J$  = 15.9, 7.5 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.7, 133.6, 129.7, 128.7, 127.1, 126.6, 77.3, 68.4, 37.7, 31.1, 25.7. IR (KBr,  $\text{cm}^{-1}$ ): 3658, 2925, 2859, 1453, 1058, 746; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{13}\text{ClOS}[\text{M}+\text{Na}]^+$  251.0268; found, 251.0271.

### 2-((*m*-Tolylthio)methyl)tetrahydrofuran (3ka)



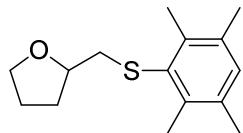
Yellow liquid (47 mg, 90%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (t,  $J$  = 10.4 Hz, 3H), 6.98 (s, 1H), 4.05 (dd,  $J$  = 12.7, 6.2 Hz, 1H), 3.90 (q,  $J$  = 6.5 Hz, 1H), 3.76 (q,  $J$  = 6.6 Hz, 1H), 3.15 (dd,  $J$  = 12.9, 4.3 Hz, 1H), 2.95 (dd,  $J$  = 12.7, 6.9 Hz, 1H), 2.31 (s, 3H), 2.06 (td,  $J$  = 12.4, 6.1 Hz, 1H), 1.98 – 1.79 (m, 2H), 1.71 – 1.62 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6, 136.1, 129.8, 128.7, 126.9, 126.2, 77.7, 68.3, 38.9, 30.9, 25.7, 21.3. IR (KBr,  $\text{cm}^{-1}$ ): 2960, 2868, 1492, 1058, 804; ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{16}\text{OS}[\text{M}+\text{Na}]^+$  231.0814; found, 231.0817.

### 2-((2,5-Dimethylphenylthio)methyl)tetrahydrofuran (3la)



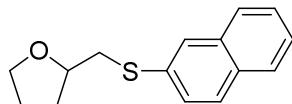
Yellow liquid (50 mg, 90%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11 (d,  $J$  = 14.0 Hz, 1H), 7.03 (d,  $J$  = 7.5 Hz, 1H), 6.87 (t,  $J$  = 11.2 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.92 (q,  $J$  = 7.0 Hz, 1H), 3.77 (q,  $J$  = 7.2 Hz, 1H), 3.13 (dd,  $J$  = 12.5, 5.2 Hz, 1H), 2.98 – 2.84 (m, 1H), 2.34 (s, 3H), 2.29 (s, 3H), 2.07 (dt,  $J$  = 12.6, 6.4 Hz, 1H), 1.89 (dt,  $J$  = 19.4, 10.4 Hz, 2H), 1.69 (dt,  $J$  = 15.5, 7.2 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.8, 135.1, 134.5, 129.9, 128.8, 126.5, 77.5, 68.3, 38.2, 31.0, 25.7, 20.9, 19.8. IR (KBr,  $\text{cm}^{-1}$ ): 2922, 2864, 1485, 1059, 808. ESI-HRMS calcd for  $\text{C}_{13}\text{H}_{18}\text{OS}[\text{M}+\text{Na}]^+$  245.0971; found, 245.0976.

**2-(((2,3,5,6-Tetramethylphenyl)thio)methyl)tetrahydrofuran (3ma)**



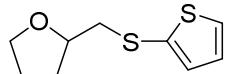
Yellow liquid (56 mg, 89%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.93 (s, 1H), 3.88 (d,  $J = 6.9$  Hz, 2H), 3.78 – 3.65 (m, 1H), 2.86 – 2.73 (m, 1H), 2.65 – 2.57 (m, 1H), 2.51 (s, 6H), 2.23 (s, 6H), 2.03 (d,  $J = 5.1$  Hz, 1H), 1.93 – 1.82 (m, 2H), 1.64 (d,  $J = 8.9$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.5, 134.2, 134.0, 131.8, 78.1, 68.2, 41.0, 31.0, 25.7, 20.9, 18.4. IR (KBr,  $\text{cm}^{-1}$ ): 2925, 2859, 1460, 1059, 749; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{22}\text{OS}[\text{M}+\text{Na}]^+$  273.1284; found, 273.1282.

**2-((Naphthalen-2-ylthio)methyl)tetrahydrofuran (3na)**



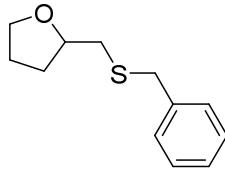
Yellow liquid (52 mg, 86%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (dd,  $J = 16.0, 8.2$  Hz, 4H), 7.44 (dd,  $J = 16.5, 7.7$  Hz, 3H), 4.18 – 4.06 (m, 1H), 3.93 (q,  $J = 7.0$  Hz, 1H), 3.83 – 3.72 (m, 1H), 3.27 (dd,  $J = 12.9, 5.4$  Hz, 1H), 3.08 (dd,  $J = 12.9, 6.7$  Hz, 1H), 2.08 (dt,  $J = 12.3, 6.3$  Hz, 1H), 2.01 – 1.83 (m, 2H), 1.78 – 1.65 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.9, 133.7, 131.7, 128.4, 127.7, 127.4, 127.0, 126.8, 126.5, 125.6, 77.6, 68.4, 38.7, 31.0, 25.8. IR (KBr,  $\text{cm}^{-1}$ ): 3061, 2914, 1377, 1182, 870; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{16}\text{OS}[\text{M}+\text{Na}]^+$  267.0814; found, 267.0817.

**2-((Thiophen-2-ylthio)methyl)tetrahydrofuran (3oa)**



Yellow liquid (31 mg, 62%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 5.3$  Hz, 1H), 7.14 (d,  $J = 3.1$  Hz, 1H), 7.00 – 6.90 (m, 1H), 4.10 – 3.95 (m, 1H), 3.89 (dd,  $J = 14.6, 7.0$  Hz, 1H), 3.76 (dd,  $J = 14.5, 7.3$  Hz, 1H), 3.01 (dd,  $J = 13.1, 6.2$  Hz, 1H), 2.86 (dd,  $J = 13.1, 6.4$  Hz, 1H), 2.07 (dt,  $J = 13.0, 6.7$  Hz, 1H), 1.91 (td,  $J = 12.9, 5.8$  Hz, 2H), 1.65 (dd,  $J = 13.6, 5.8$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.3, 133.5, 129.1, 127.5, 77.7, 68.3, 43.9, 30.7, 25.8. IR (KBr,  $\text{cm}^{-1}$ ): 3680, 3084, 2923, 1461, 1269, 748; ESI-HRMS calcd for  $\text{C}_9\text{H}_{12}\text{OS}_2[\text{M}+\text{Na}]^+$  223.0222; found, 223.0219.

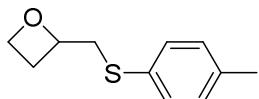
**2-((Benzylthio)methyl)tetrahydrofuran (3pa)**



Yellow liquid (40 mg, 76%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (q,  $J = 7.8$  Hz, 4H), 7.11 (t,  $J = 6.7$  Hz, 1H), 3.89 (p,  $J = 6.4$  Hz, 1H), 3.76 (dd,  $J = 14.5, 7.1$  Hz, 1H), 3.71 – 3.58 (m, 3H), 2.48 (dd,  $J =$

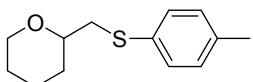
13.2, 6.1 Hz, 1H), 2.40 (dd,  $J$  = 13.1, 6.0 Hz, 1H), 1.87 (tt,  $J$  = 11.4, 5.8 Hz, 1H), 1.82 – 1.65 (m, 2H), 1.47 (dt,  $J$  = 15.5, 7.5 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2, 128.7, 128.4, 128.1, 126.6, 78.3, 67.9, 36.5, 35.9, 30.2, 25.9, 25.5. IR (KBr,  $\text{cm}^{-1}$ ): 3419; 3130; 2025; 1618; 1401; 1111; 621; MS (EI, 70 eV):  $m/z$  (%) = 208 [M] $^+$ , 190, 175, 138, 122, 91, 71.

### 2-((*p*-Tolylthio)methyl)oxetane (3ab)



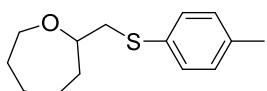
Yellow liquid (14 mg, 29%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J$  = 7.6 Hz, 2H), 7.11 (d,  $J$  = 7.6 Hz, 2H), 4.09 – 4.02 (m, 1H), 3.94 (dd,  $J$  = 15.0, 7.4 Hz, 1H), 3.84 (dd,  $J$  = 14.2, 7.2 Hz, 1H), 3.74 (dd,  $J$  = 12.5, 6.1 Hz, 1H), 3.69 – 3.63 (m, 1H), 2.33 (s, 3H), 2.27 (dd,  $J$  = 14.0, 7.1 Hz, 1H), 1.90 (td,  $J$  = 12.6, 6.1 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 131.7, 131.6, 129.8, 73.6, 67.60, 45.5, 33.1, 21.0. IR (KBr,  $\text{cm}^{-1}$ ): 3467, 2926, 1746, 1481, 1224, 749; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{14}\text{OS}[\text{M}+\text{Na}]^+$  217.0658; found, 217.0655.

### 2-((*p*-Tolylthio)methyl)tetrahydro-2*H*-pyran (3ac)



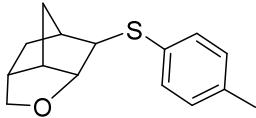
Yellow liquid (45 mg, 81%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (d,  $J$  = 7.7 Hz, 2H), 7.09 (d,  $J$  = 7.5 Hz, 2H), 4.01 (d,  $J$  = 11.1 Hz, 1H), 3.43 (t,  $J$  = 10.7 Hz, 2H), 3.05 (dd,  $J$  = 12.8, 6.4 Hz, 1H), 2.95 – 2.78 (m, 1H), 2.31 (s, 3H), 1.81 (dd,  $J$  = 24.4, 12.7 Hz, 2H), 1.54 – 1.43 (m, 2H), 1.30 (dd,  $J$  = 23.6, 11.7 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.0, 132.9, 129.8, 129.6, 76.4, 68.7, 40.3, 31.2, 25.8, 23.2, 21.0. IR (KBr,  $\text{cm}^{-1}$ ): 3676, 2930, 1493, 1090, 805; ESI-HRMS calcd for  $\text{C}_{13}\text{H}_{18}\text{OS}[\text{M}+\text{Na}]^+$  245.0971; found, 245.0975.

### 2-((*p*-Tolylthio)methyl)oxepane (3ad)



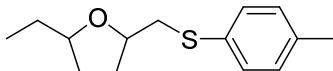
Yellow liquid (51 mg, 87%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (d,  $J$  = 7.6 Hz, 2H), 7.08 (d,  $J$  = 7.4 Hz, 2H), 3.93 – 3.78 (m, 1H), 3.64 (d,  $J$  = 2.5 Hz, 1H), 3.54 (dd,  $J$  = 12.2, 7.1 Hz, 1H), 3.06 (dd,  $J$  = 12.6, 7.1 Hz, 1H), 2.95 – 2.80 (m, 1H), 2.31 (s, 3H), 1.95 – 1.85 (m, 1H), 1.74 (s, 2H), 1.60 (dd,  $J$  = 17.5, 13.8 Hz, 4H), 1.49 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.9, 133.0, 129.9, 129.6, 78.2, 68.8, 40.7, 34.9, 30.9, 26.7, 25.6, 20.9. IR (KBr,  $\text{cm}^{-1}$ ): 2926, 2858, 1491, 1102, 806; ESI-HRMS calcd for  $\text{C}_{14}\text{H}_{20}\text{OS}[\text{M}+\text{Na}]^+$  259.1127; found, 259.1134.

### 6-(*p*-Tolylthio)hexahydro-2*H*-3,5-methanocyclopenta[b]furan (3ae)



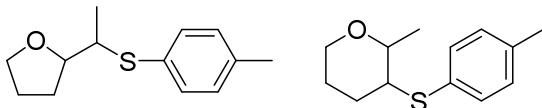
Yellow liquid (49 mg, 79%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 7.3$  Hz, 2H), 7.09 (d,  $J = 7.5$  Hz, 2H), 4.15 (d,  $J = 4.5$  Hz, 1H), 3.84 – 3.75 (m, 1H), 3.71 (d,  $J = 8.0$  Hz, 1H), 2.95 (s, 1H), 2.66 (s, 1H), 2.39 (d,  $J = 10.5$  Hz, 1H), 2.29 (s, 3H), 2.17 (s, 1H), 2.03 (dd,  $J = 17.6, 7.1$  Hz, 2H), 1.55 (d,  $J = 10.7$  Hz, 1H), 1.18 (d,  $J = 12.6$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.8, 132.0, 129.8, 129.7, 85.7, 74.5, 57.1, 46.3, 39.4, 38.0, 37.8, 35.9, 20.9. IR (KBr,  $\text{cm}^{-1}$ ): 3459, 2961, 1762, 1243, 741; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{18}\text{OS}[\text{M}+\text{Na}]^+$  269.0971; found, 269.0972.

#### 2-Ethyl-5-((*p*-Tolylthio)methyl)tetrahydrofuran (3af)



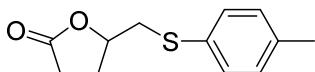
Yellow liquid (46 mg, 80%, dr = 1:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (d,  $J = 7.4$  Hz, 2H), 7.08 (d,  $J = 7.3$  Hz, 2H), 4.19 – 3.97 (m, 1H), 3.96 – 3.72 (m, 1H), 3.15 (d,  $J = 12.6$  Hz, 1H), 2.95 – 2.82 (m, 1H), 2.30 (s, 3H), 2.15 – 1.87 (m, 2H), 1.75 – 1.56 (m, 2H), 1.45 (ddd,  $J = 20.1, 16.2, 9.0$  Hz, 2H), 1.18 – 0.39 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.0, 136.0, 132.7, 132.6, 129.9, 129.8, 129.6, 81.4, 80.8, 77.8, 39.7, 31.4, 31.3, 30.5, 30.4, 28.7, 28.6, 20.9, 10.2, 10.2. IR (KBr,  $\text{cm}^{-1}$ ): 2964, 2926, 1493, 1091, 803; ESI-HRMS calcd for  $\text{C}_{14}\text{H}_{20}\text{OS}[\text{M}+\text{Na}]^+$  259.1127; found, 259.1131.

#### 2-(1-*(p*-Tolylthio)ethyl)tetrahydrofuran (3ag) and 2-Methyl-3-(*p*-Tolylthio)tetrahydro-2*H*-pyran (3ag')



Yellow liquid (44 mg, 80%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (t,  $J = 7.6$  Hz, 2H), 7.11 (d,  $J = 7.7$  Hz, 2H), 3.99 – 3.83 (m, 2H), 3.78 (m, 1H), 3.33 (m, 1H), 2.33 (s, 3H), 2.17 – 2.00 (m, 1H), 2.00 – 1.82 (m, 2H), 1.81 – 1.71 (m, 1H), 1.31 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.4, 137.1, 136.9, 133.5, 133.0, 132.6, 131.1, 130.9, 129.6, 129.5, 82.3, 81.5, 78.0, 68.6, 68.4, 67.8, 51.1, 48.5, 47.5, 31.7, 29.6, 28.2, 27.2, 26.2, 26.0, 21.0, 20.4, 18.0, 16.9. IR (KBr,  $\text{cm}^{-1}$ ): 3456, 3137, 2865, 1632, 1402, 1058, 702; ESI-HRMS calcd for  $\text{C}_{13}\text{H}_{18}\text{OS}[\text{M}+\text{Na}]^+$  245.0971; found, 245.0974.

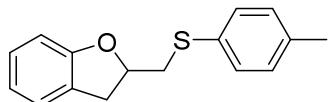
#### 5-((*p*-Tolylthio)methyl)dihydrofuran-2(3*H*)-one (3ah)



Yellow liquid (43 mg, 78%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 7.6$  Hz, 2H), 7.12 (d,  $J = 7.6$  Hz, 2H), 4.64 – 4.54 (m, 1H), 3.31 (dd,  $J = 13.6, 4.4$  Hz, 1H), 2.98 (dd,  $J = 13.8, 7.8$  Hz, 1H), 2.64 – 2.46 (m, 2H), 2.44 – 2.36 (m, 1H), 2.33 (s, 3H), 2.09 – 1.93 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$

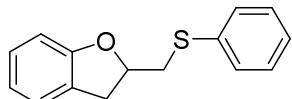
176.5, 137.4, 131.1, 130.0, 78.7, 77.2, 39.3, 28.4, 26.9, 21.0. IR (KBr,  $\text{cm}^{-1}$ ): 3624, 2924, 1775, 1493, 1170, 804; ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{S}[\text{M}+\text{Na}]^+$  245.0607; found, 245.0610.

**2-((*p*-Tolylthio)methyl)-2,3-dihydrobenzofuran (3ai)**



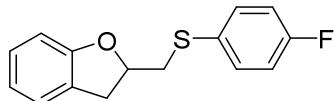
Yellow liquid (51 mg, 80%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 7.5$  Hz, 2H), 7.16 – 7.06 (m, 4H), 6.83 (t,  $J = 7.1$  Hz, 1H), 6.75 (d,  $J = 7.8$  Hz, 1H), 4.93 – 4.77 (m, 1H), 3.38 – 3.26 (m, 2H), 3.03 (dd,  $J = 10.5, 7.7$  Hz, 2H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 136.8, 131.5, 130.7, 129.8, 128.0, 126.0, 125.0, 120.5, 109.5, 81.1, 39.6, 34.8, 21.0. IR (KBr,  $\text{cm}^{-1}$ ): 2924, 2854, 1480, 1383, 1132, 750; ESI-HRMS calcd for  $\text{C}_{16}\text{H}_{16}\text{OS}[\text{M}+\text{Na}]^+$  279.0814; found, 279.0815.

**2-((Phenylthio)methyl)-2,3-dihydrobenzofuran (3bi)**



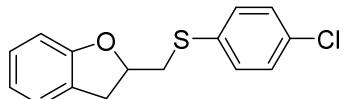
Yellow liquid (53 mg, 87%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 7.9$  Hz, 2H), 7.29 (t,  $J = 7.5$  Hz, 1H), 7.21 (t,  $J = 7.2$  Hz, 2H), 7.14 (d,  $J = 7.3$  Hz, 1H), 7.10 (t,  $J = 7.7$  Hz, 1H), 6.84 (t,  $J = 7.4$  Hz, 1H), 6.75 (d,  $J = 8.0$  Hz, 1H), 4.96 – 4.83 (m, 1H), 3.41 – 3.27 (m, 2H), 3.15 – 3.01 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 135.4, 129.9, 129.0, 128.1, 126.5, 126.0, 125.0, 120.6, 109.5, 81.1, 39.0, 34.8. IR (KBr,  $\text{cm}^{-1}$ ): 3453, 2922, 1478, 1227, 745; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{14}\text{OS}[\text{M}+\text{Na}]^+$  265.0658; found, 265.0656.

**2-((4-Fluorophenylthio)methyl)-2,3-dihydrobenzofuran (3ci)**



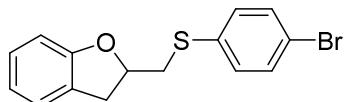
Yellow liquid (53 mg, 81%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.35 (m, 2H), 7.16 – 7.06 (m, 2H), 6.99 (t,  $J = 8.5$  Hz, 2H), 6.91 – 6.78 (m, 1H), 6.73 (t,  $J = 8.9$  Hz, 1H), 4.93 – 4.78 (m, 1H), 3.39 – 3.22 (m, 2H), 3.14 – 2.96 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1 (d,  $J = 247.0$  Hz), 159.1, 133.1 (d,  $J = 9.0$  Hz), 130.3 (d,  $J = 3.0$  Hz), 128.1, 125.9, 125.0, 120.6, 116.1 (d,  $J = 22.0$  Hz), 109.5, 81.1, 40.3, 34.8.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.7. IR (KBr,  $\text{cm}^{-1}$ ): 3675, 3053, 1484, 1228, 750; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{13}\text{FOS}[\text{M}+\text{Na}]^+$  283.0563; found, 283.0567.

**2-((4-Chlorophenylthio)methyl)-2,3-dihydrobenzofuran (3di)**



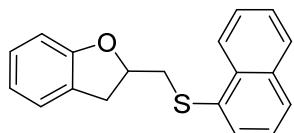
Yellow liquid (55 mg, 80%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 8.2$  Hz, 2H), 7.25 (d,  $J = 8.1$  Hz, 2H), 7.17 – 7.06 (m, 2H), 6.84 (t,  $J = 7.4$  Hz, 1H), 6.74 (d,  $J = 8.0$  Hz, 1H), 4.93 – 4.80 (m, 1H), 3.39 – 3.25 (m, 2H), 3.14 – 3.02 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 134.0, 132.6, 131.3, 129.1, 128.1, 125.8, 125.0, 120.7, 109.5, 80.9, 39.2, 34.8. IR (KBr,  $\text{cm}^{-1}$ ): 2924, 1477, 1229, 1095.29, 750; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{13}\text{ClOS} [\text{M}+\text{Na}]^+$  299.0268; found, 299.0265.

### 2-((4-Bromophenylthio)methyl)-2,3-dihydrobenzofuran (3ei)



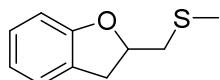
Yellow liquid (70 mg, 88%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 8.3$  Hz, 2H), 7.26 (d,  $J = 6.9$  Hz, 2H), 7.19 – 7.06 (m, 2H), 6.85 (t,  $J = 7.4$  Hz, 1H), 6.74 (d,  $J = 8.0$  Hz, 1H), 4.95 – 4.82 (m, 1H), 3.43 – 3.25 (m, 2H), 3.08 (ddd,  $J = 21.6, 14.7, 6.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 134.7, 132.1, 131.4, 128.2, 125.9, 125.0, 120.7, 120.5, 109.5, 80.9, 39.1, 34.8. IR (KBr,  $\text{cm}^{-1}$ ): 3677, 3053, 2923, 1475, 1230, 749; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{13}\text{BrOS} [\text{M}+\text{Na}]^+$  342.9763; found, 342.9758.

### 2-((Naphthalen-1-ylthio)methyl)-2,3-dihydrobenzofuran (3pi)



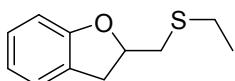
Yellow liquid (62 mg, 85%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (d,  $J = 8.3$  Hz, 1H), 7.85 (d,  $J = 7.9$  Hz, 1H), 7.77 (d,  $J = 8.2$  Hz, 1H), 7.69 (d,  $J = 7.2$  Hz, 1H), 7.54 (dt,  $J = 21.9, 7.2$  Hz, 2H), 7.40 (t,  $J = 7.7$  Hz, 1H), 7.18 – 7.04 (m, 2H), 6.88 – 6.79 (m, 1H), 6.76 (t,  $J = 11.6$  Hz, 1H), 5.18 – 4.53 (m, 1H), 3.37 (ddd,  $J = 24.8, 14.6, 7.3$  Hz, 2H), 3.19 – 3.01 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 134.1, 133.4, 132.3, 129.9, 128.6, 128.1, 128.1, 126.6, 126.3, 126.0, 125.5, 125.2, 125.0, 120.6, 109.51, 81.1, 39.6, 34.9. IR (KBr,  $\text{cm}^{-1}$ ): 3677, 3051, 2855, 1476, 1229, 753; ESI-HRMS calcd for  $\text{C}_{19}\text{H}_{16}\text{OS} [\text{M}+\text{Na}]^+$  315.0814; found, 315.0822.

### 2-((Methylthio)methyl)-2,3-dihydrobenzofuran (3qi)



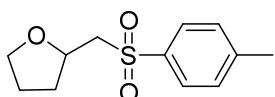
Yellow liquid (34 mg, 76%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 – 7.04 (m, 2H), 6.89 – 6.72 (m, 2H), 4.94 (dd,  $J = 13.5, 6.7$  Hz, 1H), 3.35 (dd,  $J = 15.6, 8.9$  Hz, 1H), 3.06 (dd,  $J = 15.6, 6.8$  Hz, 1H), 2.89 (dd,  $J = 13.4, 5.5$  Hz, 1H), 2.77 (dd,  $J = 13.6, 6.6$  Hz, 1H), 2.20 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 128.0, 126.2, 125.0, 120.5, 109.4, 82.0, 39.2, 34.9, 16.4. IR (KBr,  $\text{cm}^{-1}$ ): 2925, 1493, 1244, 1056, 826; ESI-HRMS calcd for  $\text{C}_{10}\text{H}_{12}\text{OS} [\text{M}+\text{Na}]^+$  203.0501; found, 203.0500.

**2-((Ethylthio)methyl)-2,3-dihydrobenzofuran (3ri)**



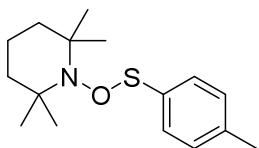
Yellow liquid (37 mg, 77%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (d,  $J = 7.3$  Hz, 1H), 7.10 (t,  $J = 7.7$  Hz, 1H), 6.84 (t,  $J = 7.4$  Hz, 1H), 6.77 (d,  $J = 8.0$  Hz, 1H), 4.97 – 4.87 (m, 1H), 3.35 (dd,  $J = 15.7, 9.0$  Hz, 1H), 3.06 (dd,  $J = 15.7, 6.9$  Hz, 1H), 2.94 (dd,  $J = 13.4, 5.5$  Hz, 1H), 2.78 (dd,  $J = 13.2, 6.7$  Hz, 1H), 2.65 (d,  $J = 7.1$  Hz, 2H), 1.28 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 128.0, 126.2, 125.0, 120.5, 109.4, 82.2, 36.7, 35.0, 27.0, 14.8. IR (KBr,  $\text{cm}^{-1}$ ): 2924, 2855, 1483, 1227, 750; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{14}\text{OS}[\text{M}+\text{Na}]^+$  217.0658; found, 217.0655.

**2-(Tosylmethyl)tetrahydrofuran (4)**



Yellow liquid (59 mg, 95%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J = 7.5$  Hz, 2H), 7.09 (d,  $J = 7.6$  Hz, 2H), 4.03 (p,  $J = 6.5$  Hz, 1H), 3.89 (dd,  $J = 14.4, 7.1$  Hz, 1H), 3.75 (q,  $J = 7.3$  Hz, 1H), 3.11 (dd,  $J = 12.9, 5.5$  Hz, 1H), 2.92 (dd,  $J = 12.6, 6.7$  Hz, 1H), 2.31 (s, 3H), 2.04 (dt,  $J = 12.8, 6.4$  Hz, 1H), 1.96 – 1.79 (m, 2H), 1.68 – 1.60 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.2, 132.6, 130.1, 129.6, 77.7, 68.3, 39.6, 30.9, 25.7, 20.9. R (KBr,  $\text{cm}^{-1}$ ): 3692, 2925, 2362, 1763, 1564, 1244. ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{16}\text{O}_3\text{S} [\text{M}+\text{Na}]^+$  263.0712; found, 263.0709.

**2,2,6,6-Tetramethyl-1-((*p*-tolylthio)oxy)piperidine (6)**

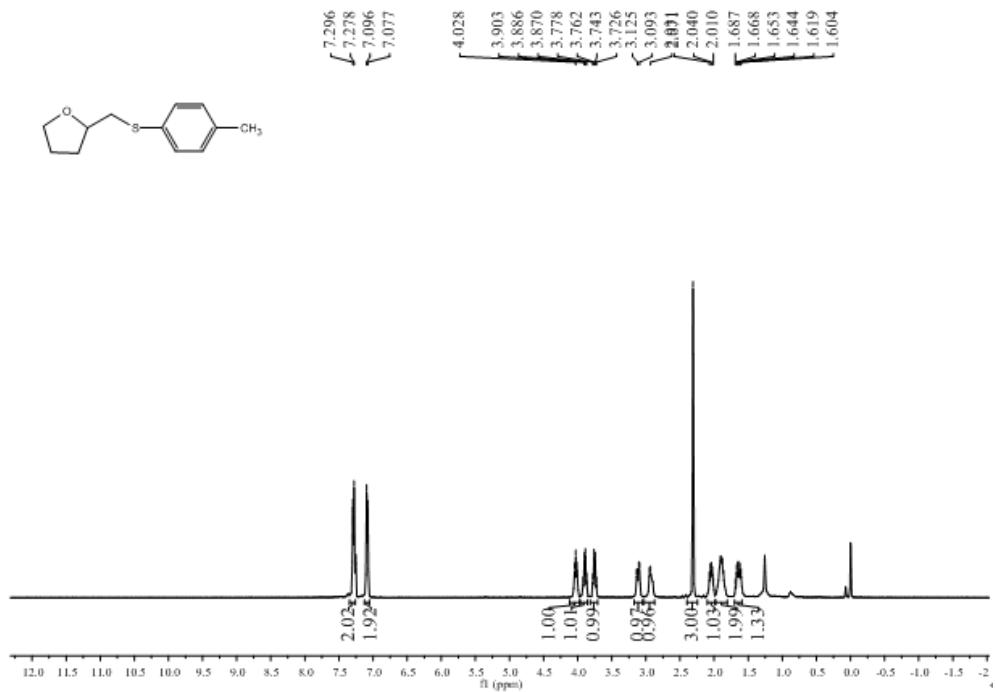


Light yellow solid (42 mg, 60%, m.p. 62–64°C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.2$  Hz, 2H), 7.23 (d,  $J = 8.1$  Hz, 2H), 2.39 (s, 3H), 1.66 (s, 6H), 1.57 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.5, 141.7, 129.1, 126.1, 60.7, 43.9, 31.1, 21.3, 16.7. IR (KBr,  $\text{cm}^{-1}$ ): 3750, 3453, 2924, 1656, 1384, 1139. MS (EI, 70 eV):  $m/z$  (%) = 280 [ $\text{M}+\text{H}]^+$ , 212, 172, 155, 109, 91.

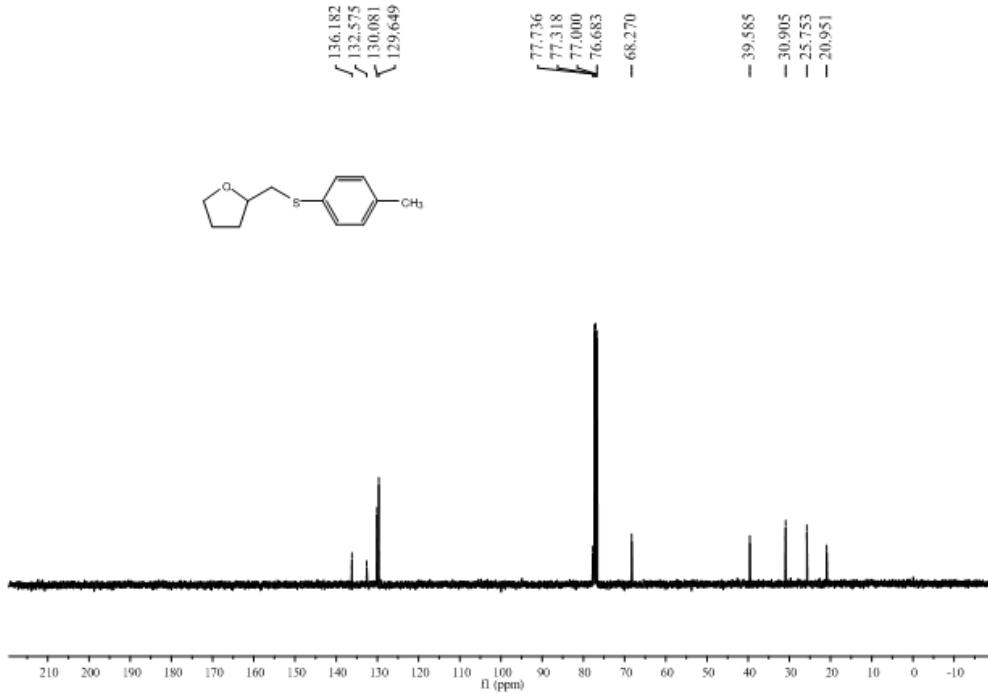
## C. NMR Spectra

### 2-((*p*-Tolylthio)methyl)tetrahydrofuran (3aa)

<sup>1</sup>H NMR

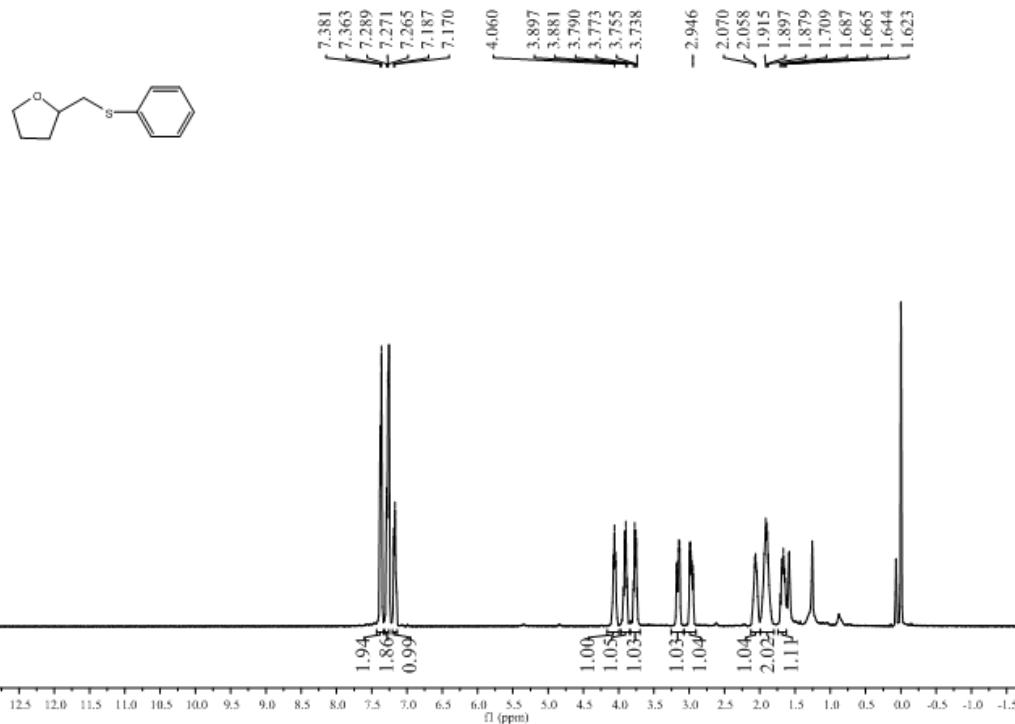


<sup>13</sup>C NMR

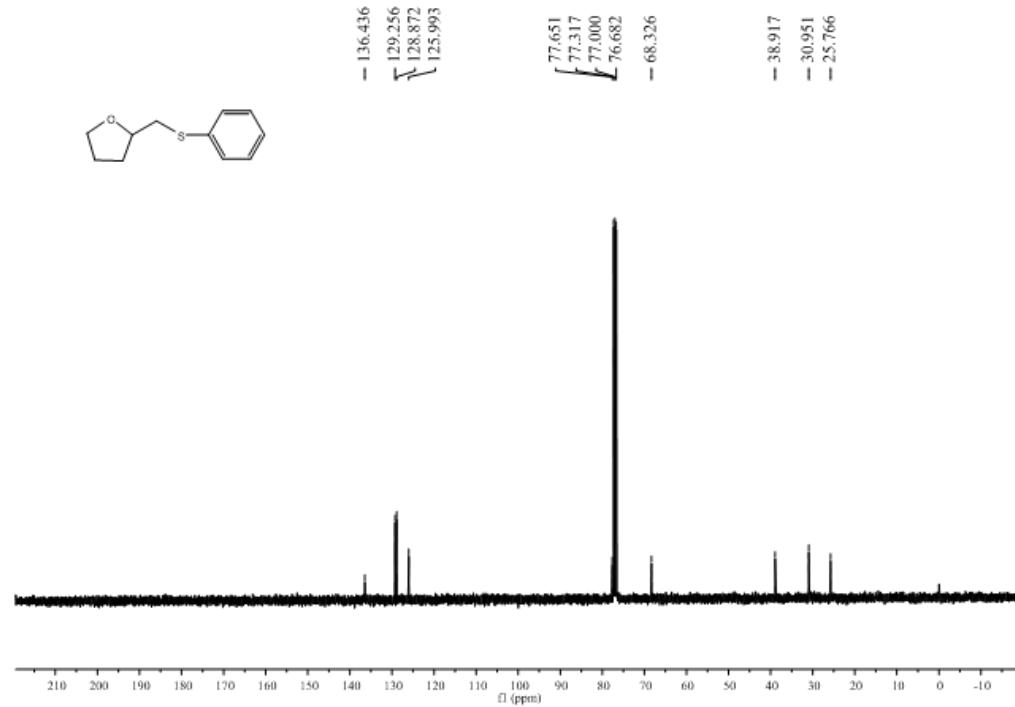


**5-((Phenylthio)methyl)dihydrofuran-2(3*H*)-one (3ba)**

<sup>1</sup>H NMR

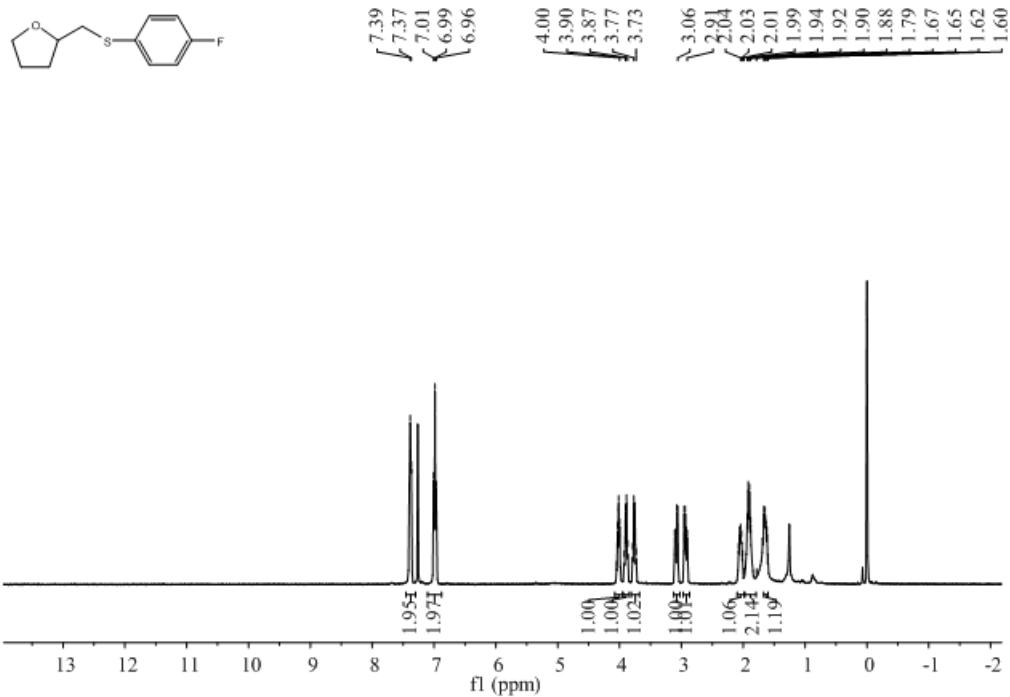


<sup>13</sup>C NMR

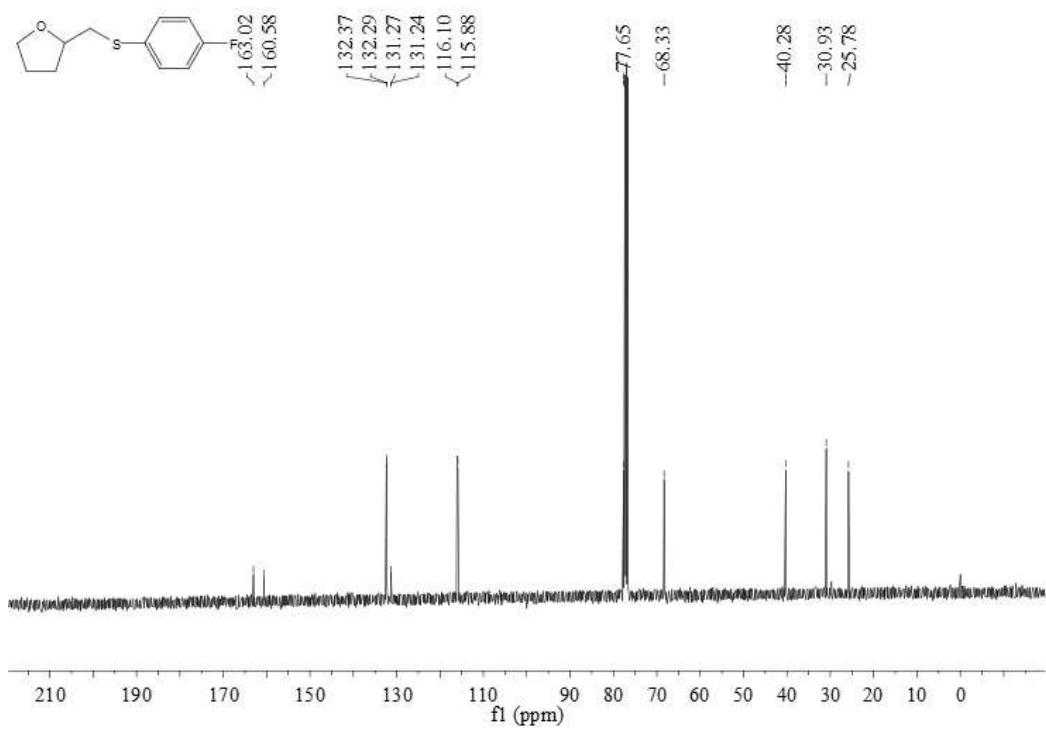


**5-((4-Fluorophenyl)thio)methyl)dihydrofuran-2(3H)-one (3ca)**

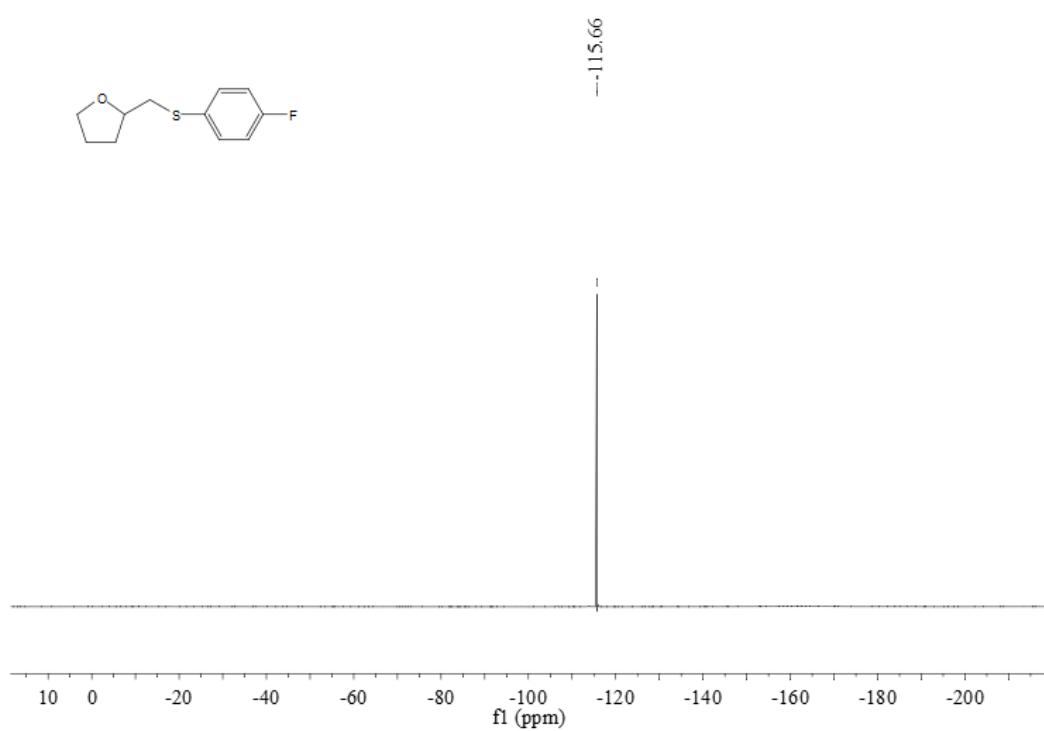
<sup>1</sup>H NMR



<sup>13</sup>C NMR

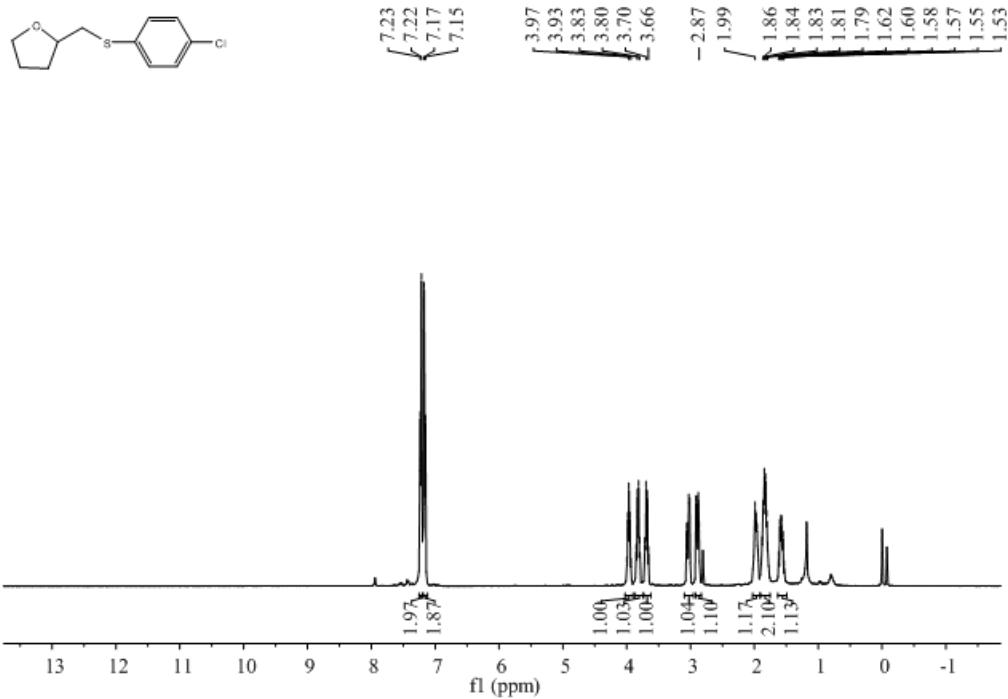


<sup>19</sup>F NMR

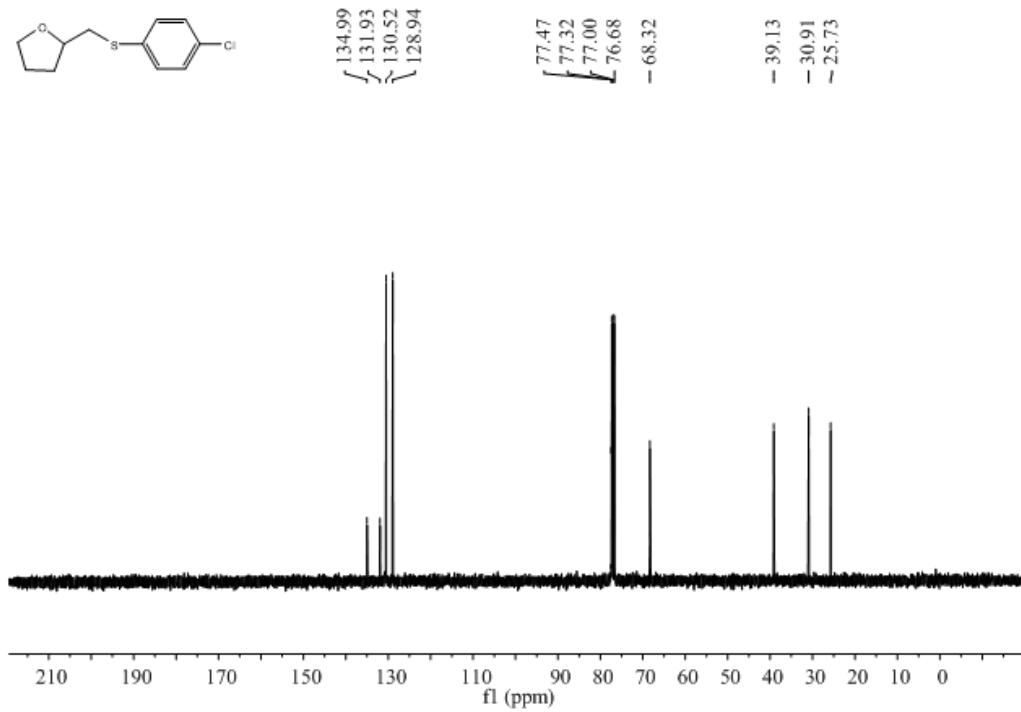


**2-(((4-Chlorophenyl)thio)methyl)tetrahydrofuran (3da)**

<sup>1</sup>H NMR

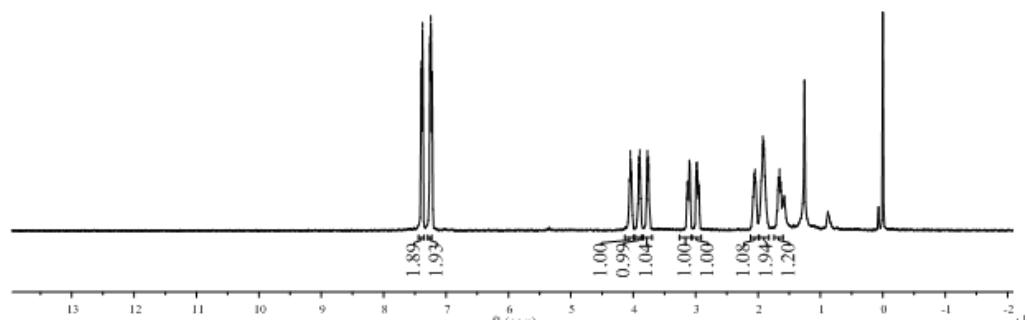


<sup>13</sup>C NMR

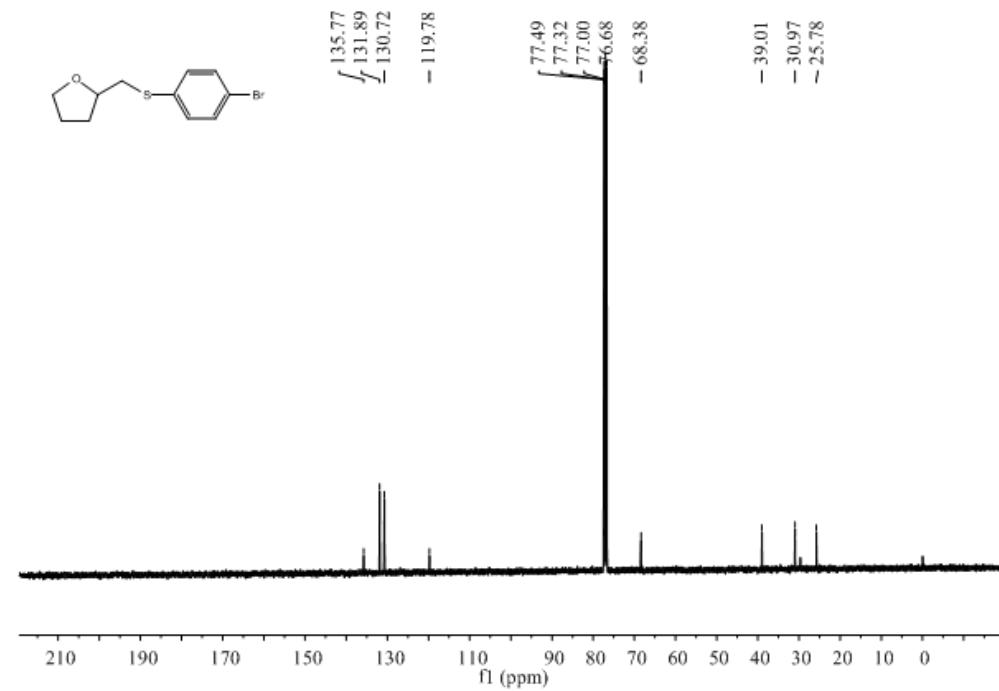


**2-(((4-Bromophenyl)thio)methyl)tetrahydrofuran (3ea)**

<sup>1</sup>H NMR

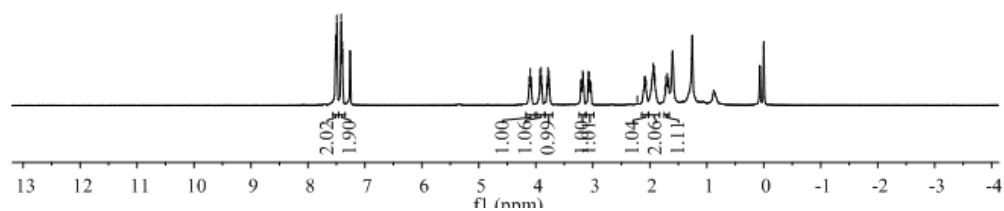


<sup>13</sup>C NMR

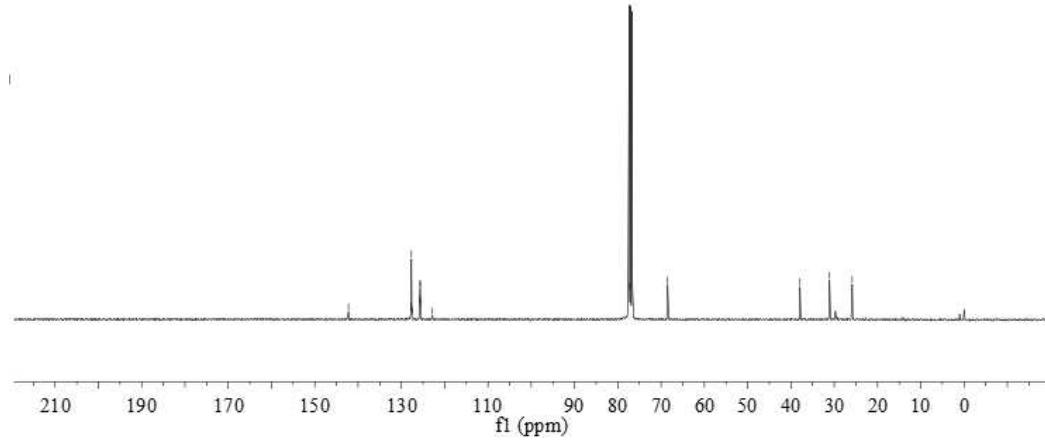
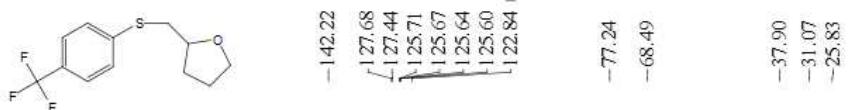


**2-(((4-(Trifluoromethyl)phenyl)thio)methyl)tetrahydrofuran (3fa)**

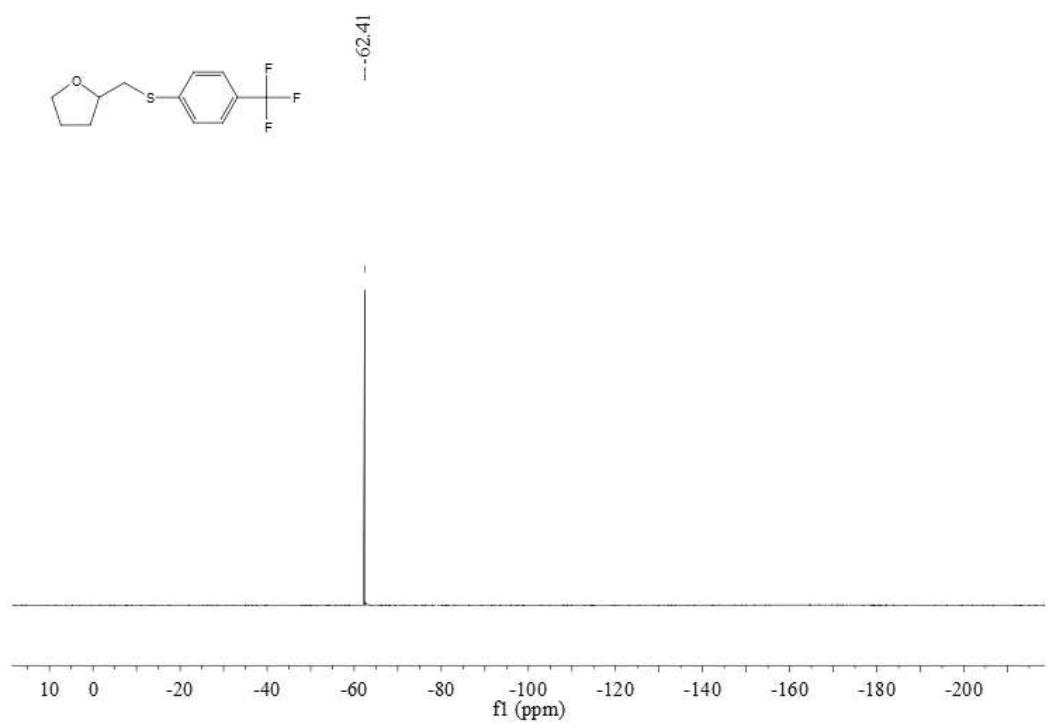
<sup>1</sup>H NMR



<sup>13</sup>C NMR

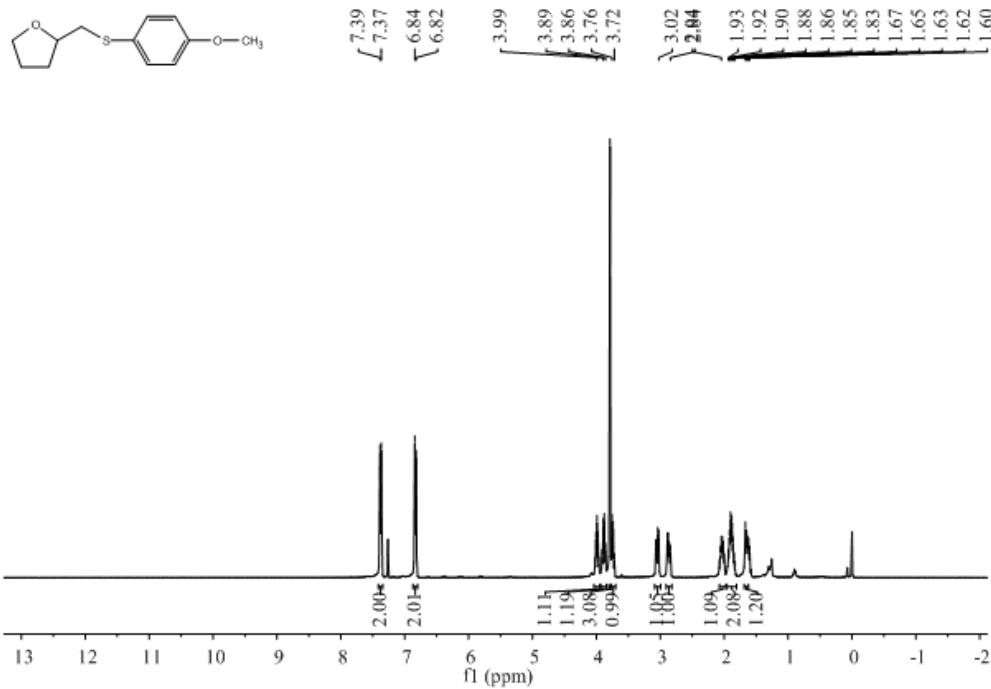


<sup>19</sup>F NMR

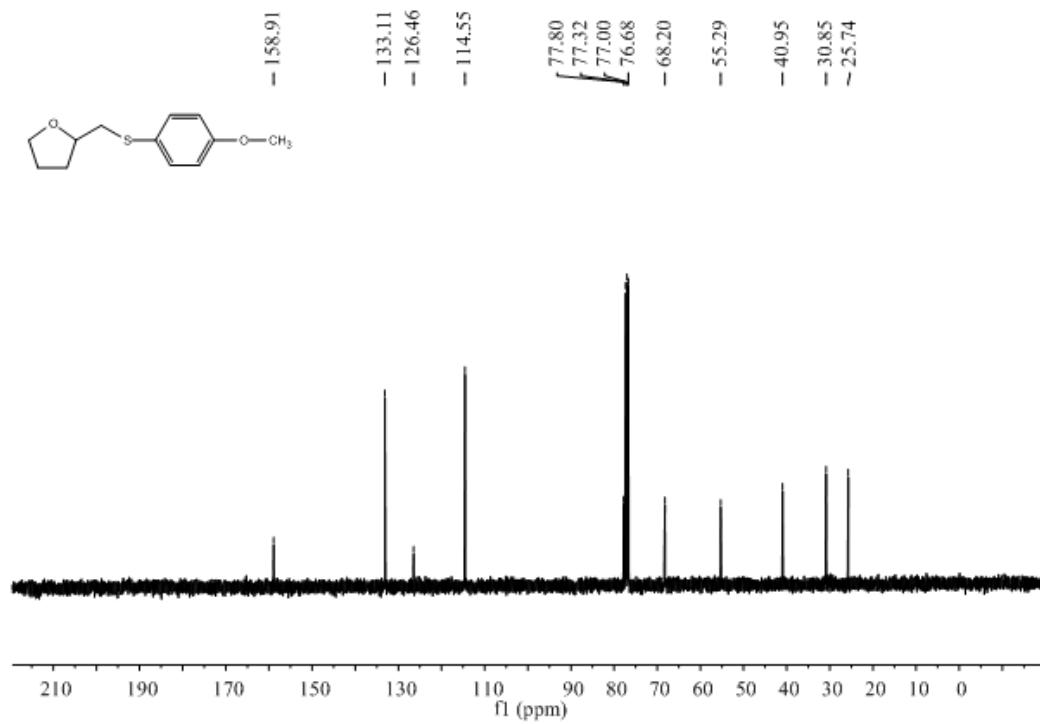


**2-(((4-Methoxyphenyl)thio)methyl)tetrahydrofuran (3ga)**

<sup>1</sup>H NMR

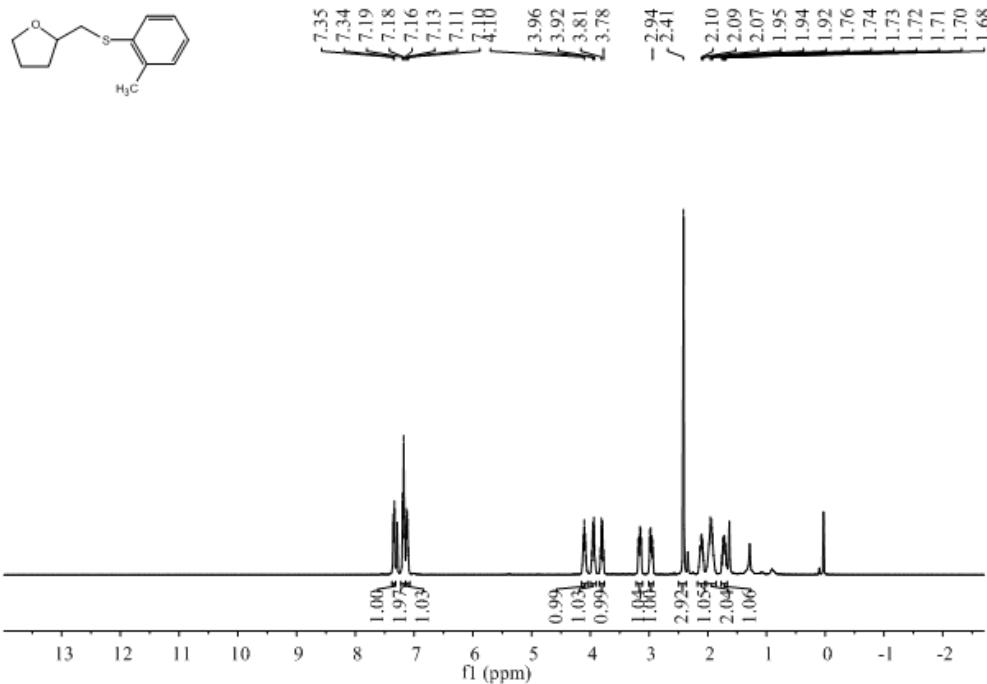


<sup>13</sup>C NMR

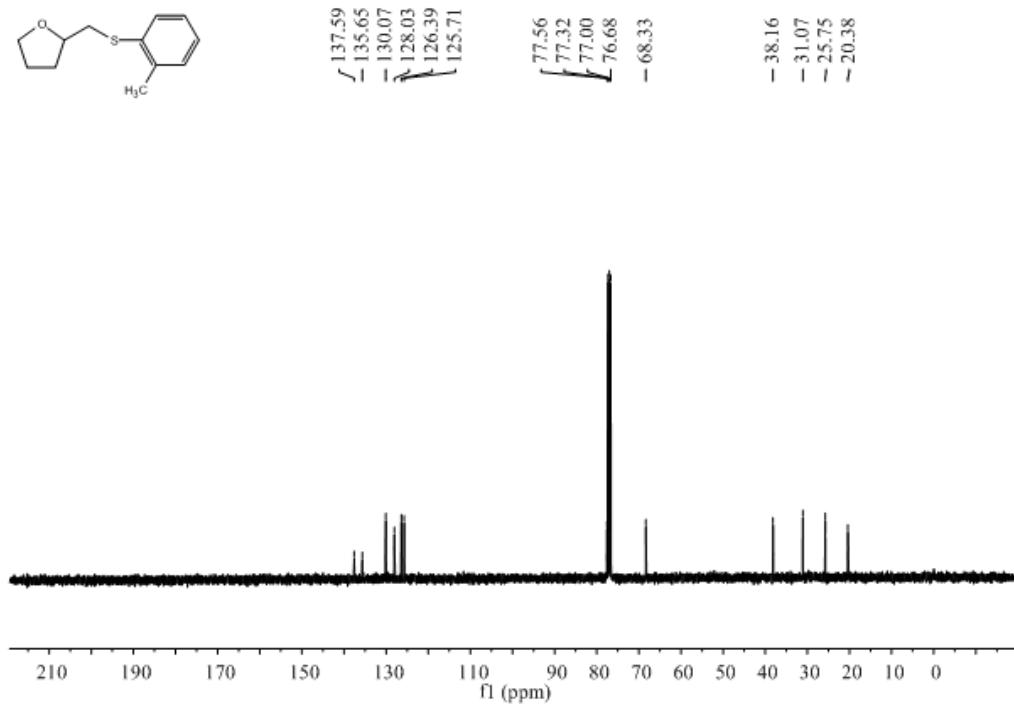


**2-((*o*-Tolylthio)methyl)tetrahydrofuran (3ha)**

<sup>1</sup>H NMR

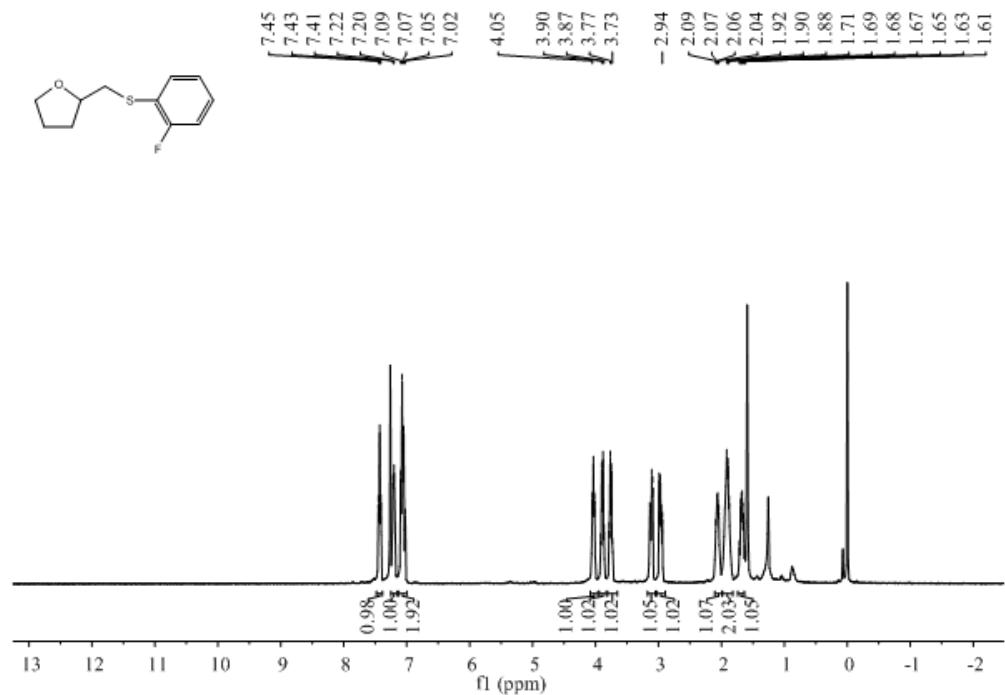


<sup>13</sup>C NMR

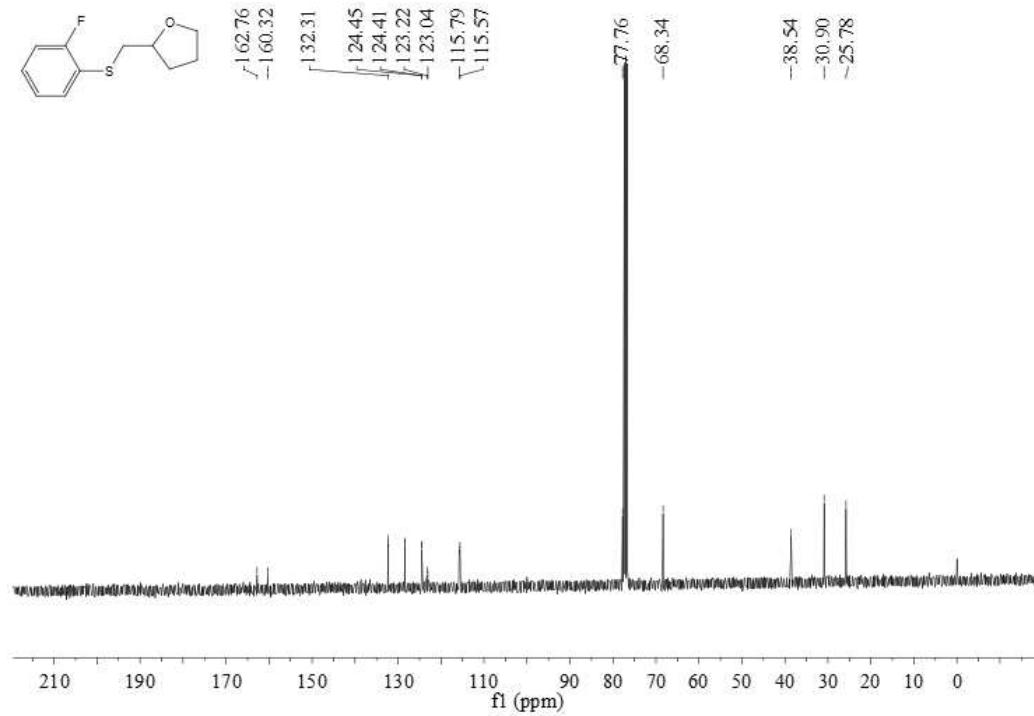


**2-(((2-Fluorophenyl)thio)methyl)tetrahydrofuran (3ia)**

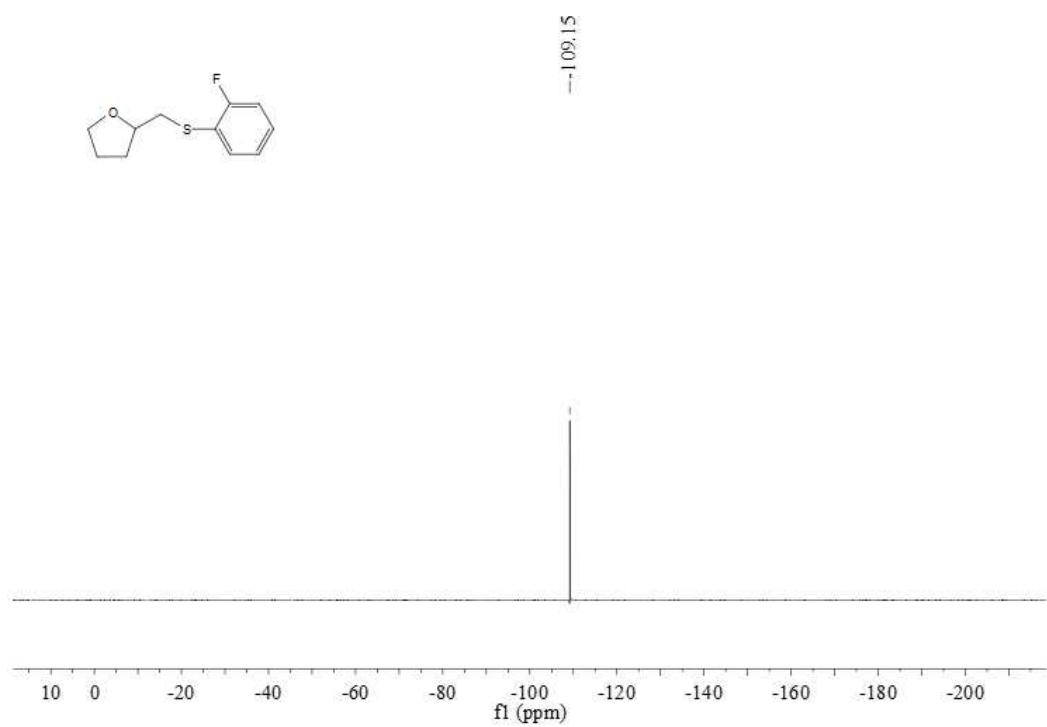
<sup>1</sup>H NMR



<sup>13</sup>C NMR

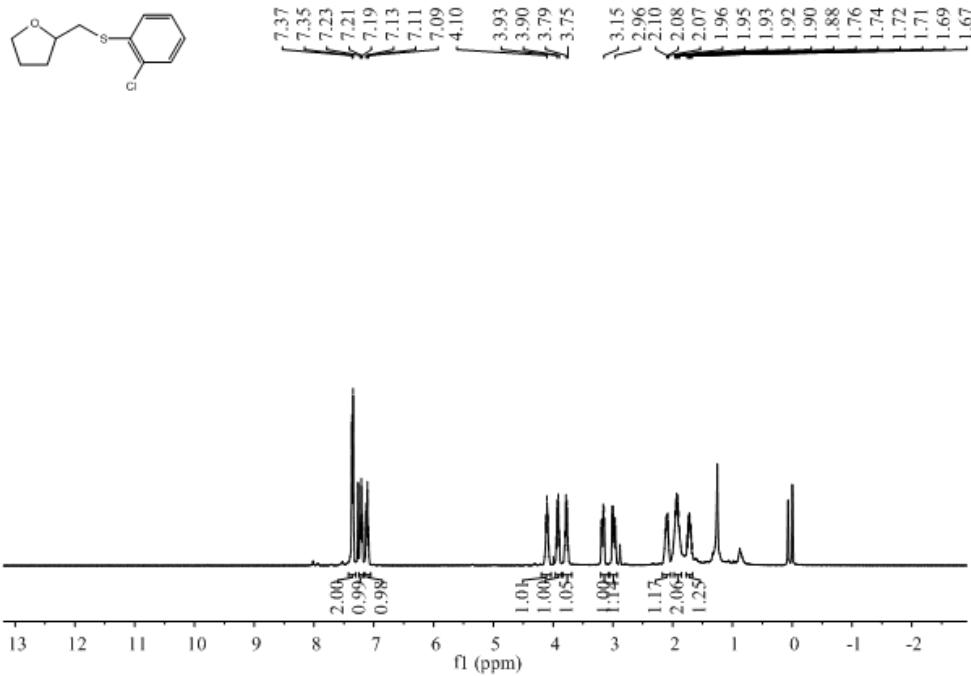


<sup>19</sup>F NMR

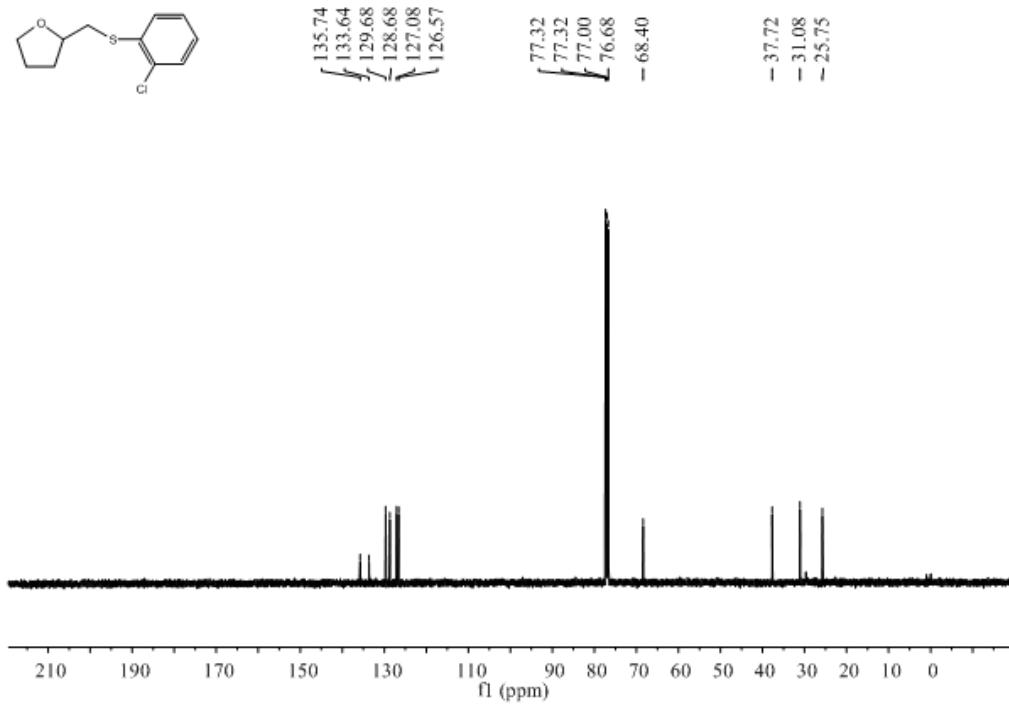


**2-((2-Chlorophenyl)thio)methyltetrahydrofuran (3ja)**

<sup>1</sup>H NMR

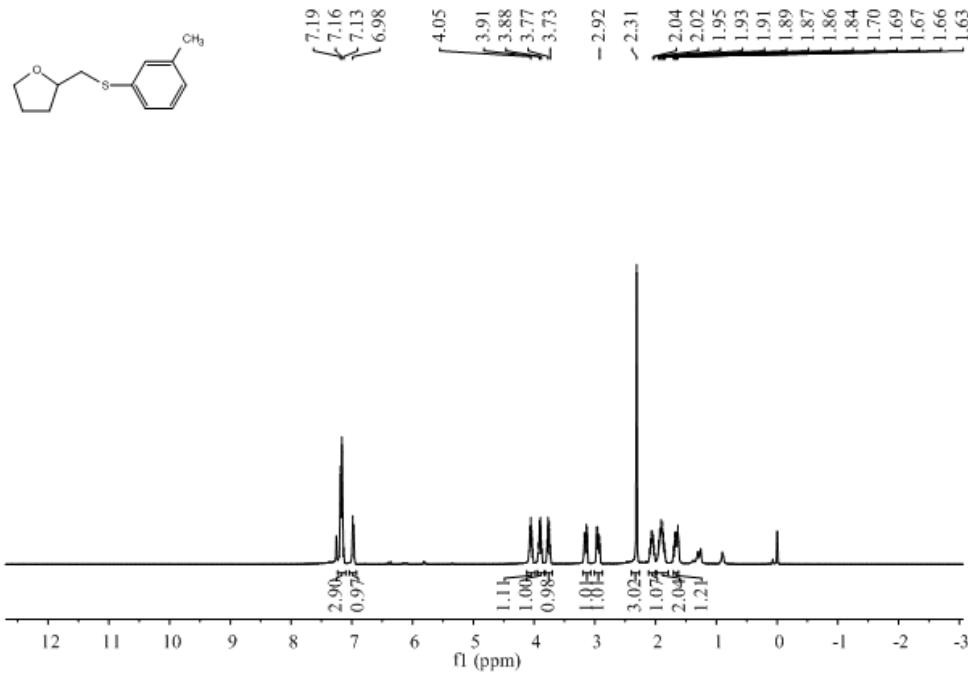


<sup>13</sup>C NMR

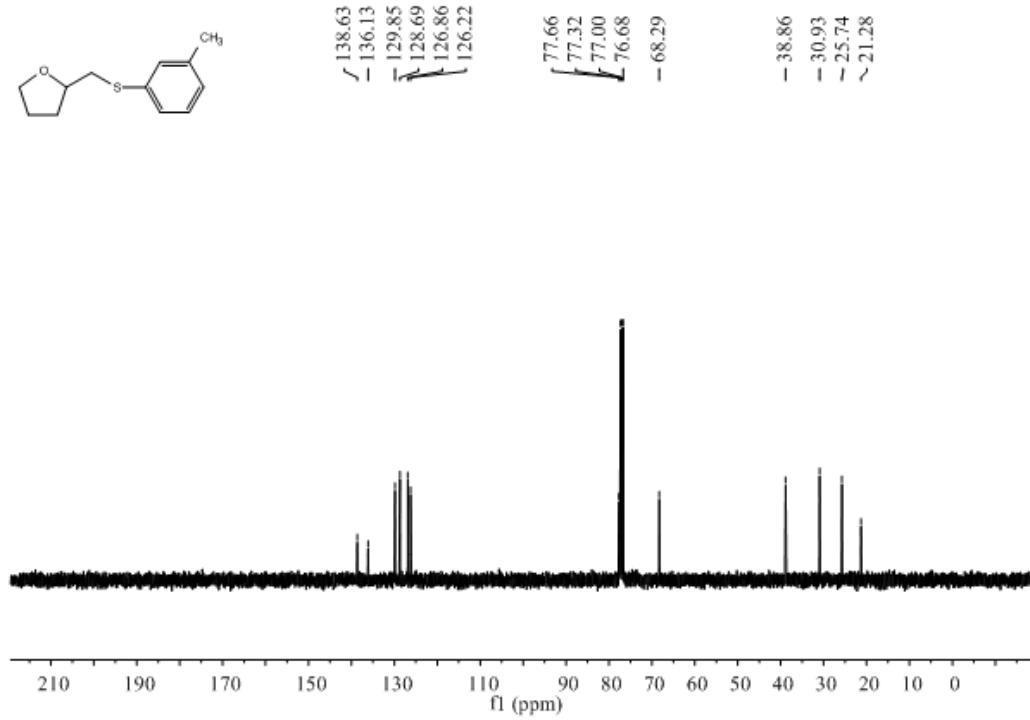


**2-((*m*-Tolylthio)methyl)tetrahydrofuran (3ka)**

<sup>1</sup>H NMR

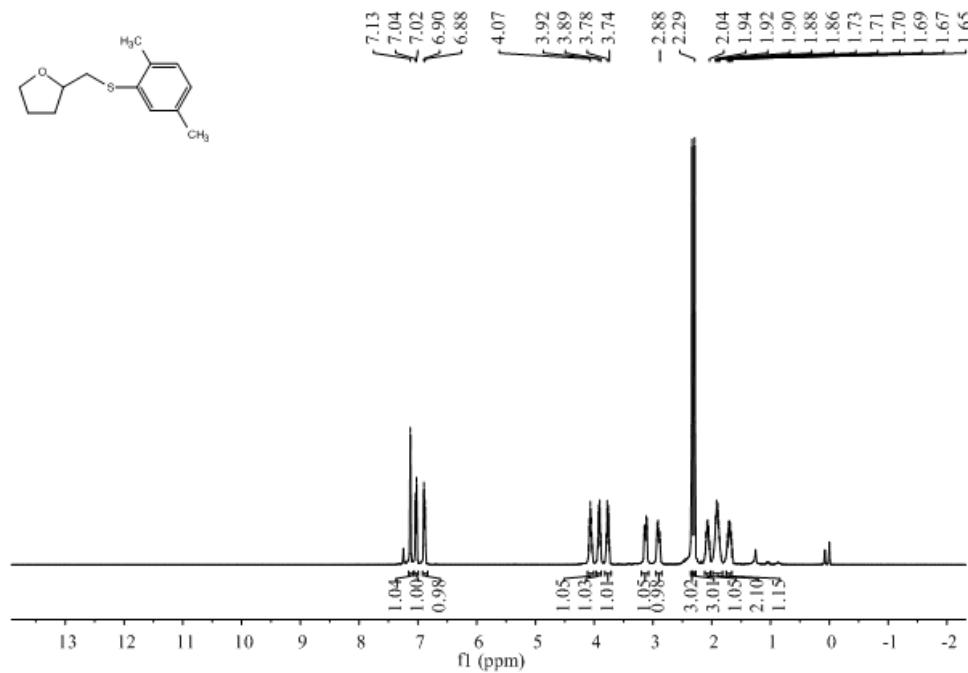


<sup>13</sup>C NMR

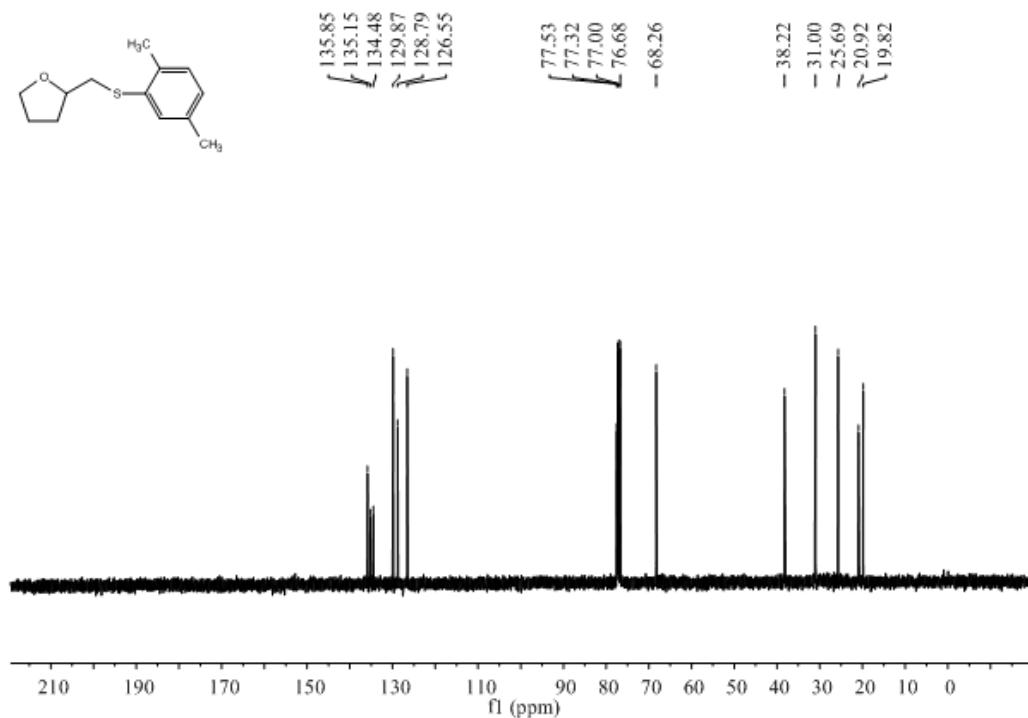


**2-((2,5-Dimethylphenylthio)methyl)tetrahydrofuran (3la)**

<sup>1</sup>H NMR

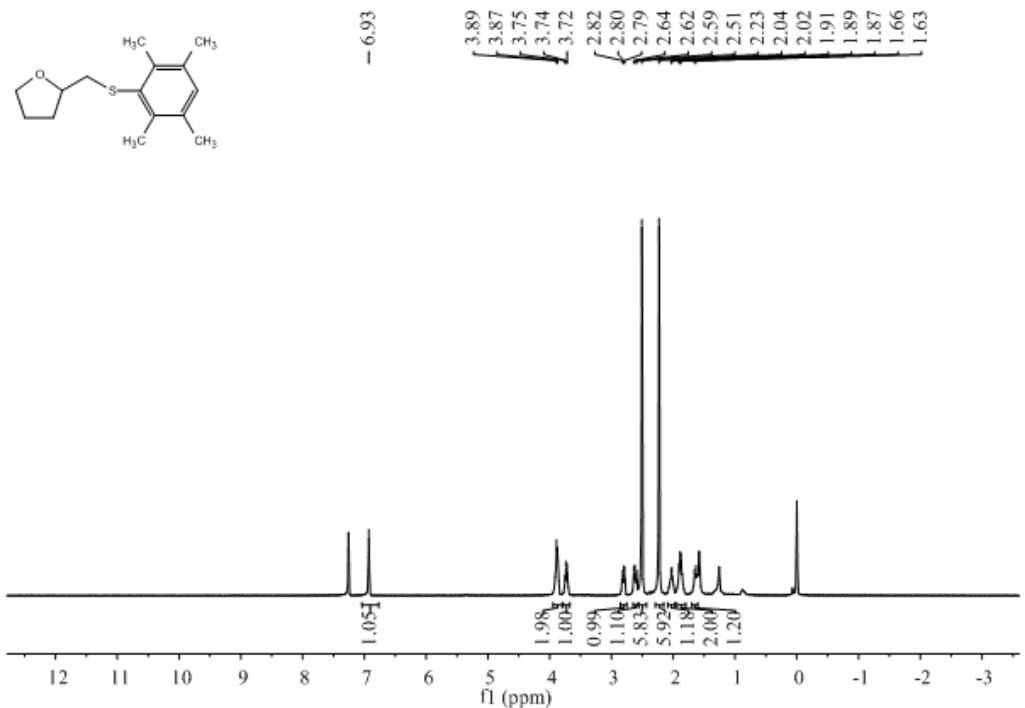


<sup>13</sup>C NMR

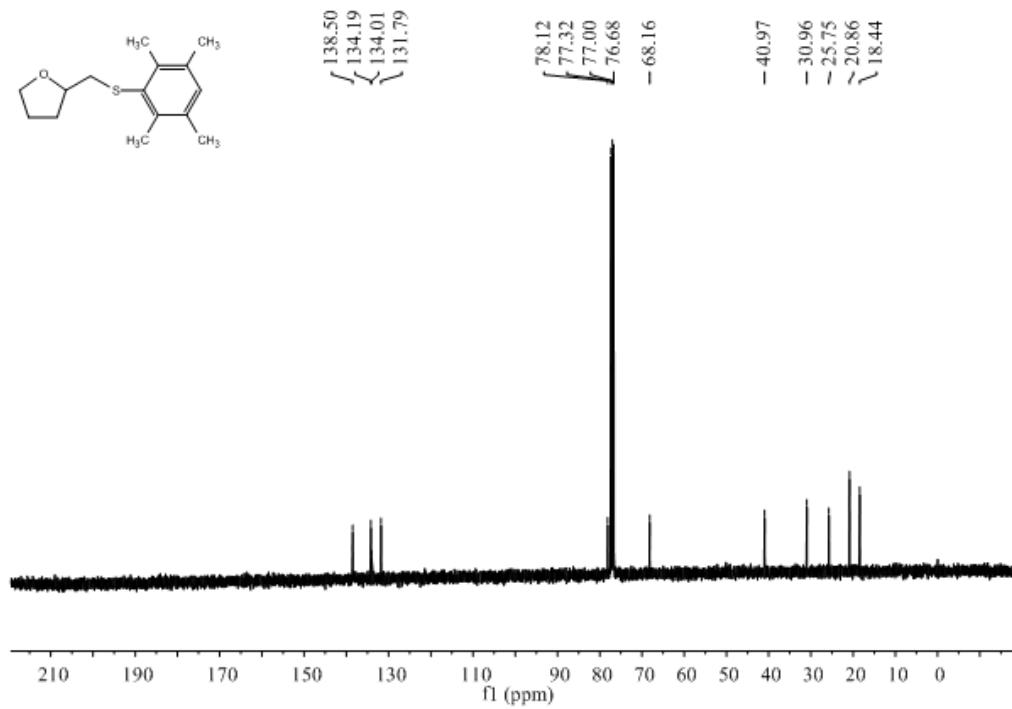


**2-((2,3,5,6-Tetramethylphenyl)thio)methyltetrahydrofuran (3ma)**

<sup>1</sup>H NMR

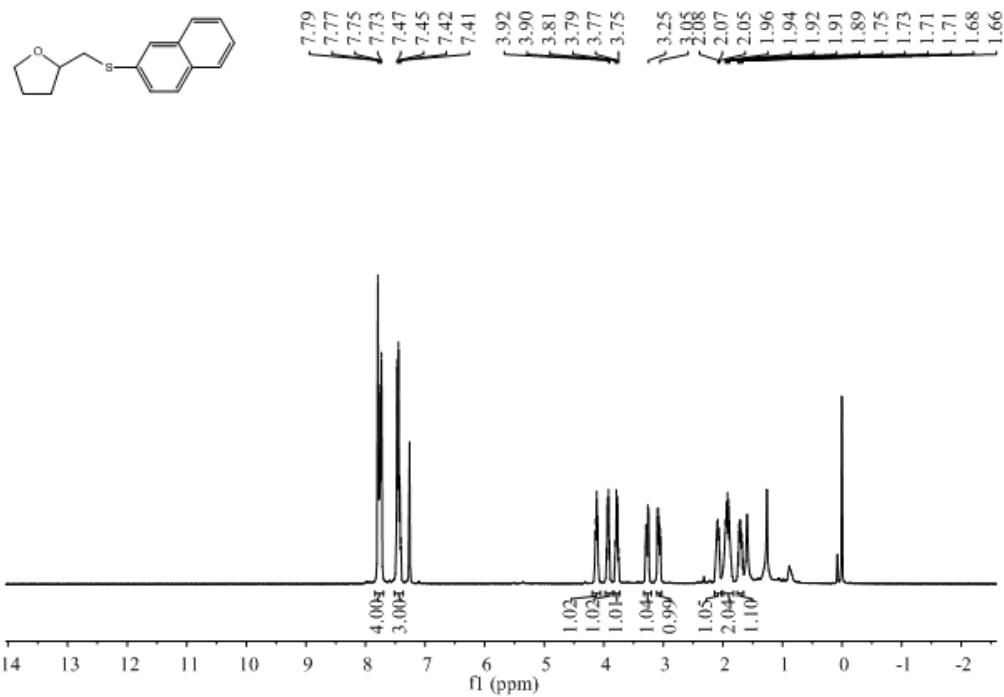


<sup>13</sup>C NMR

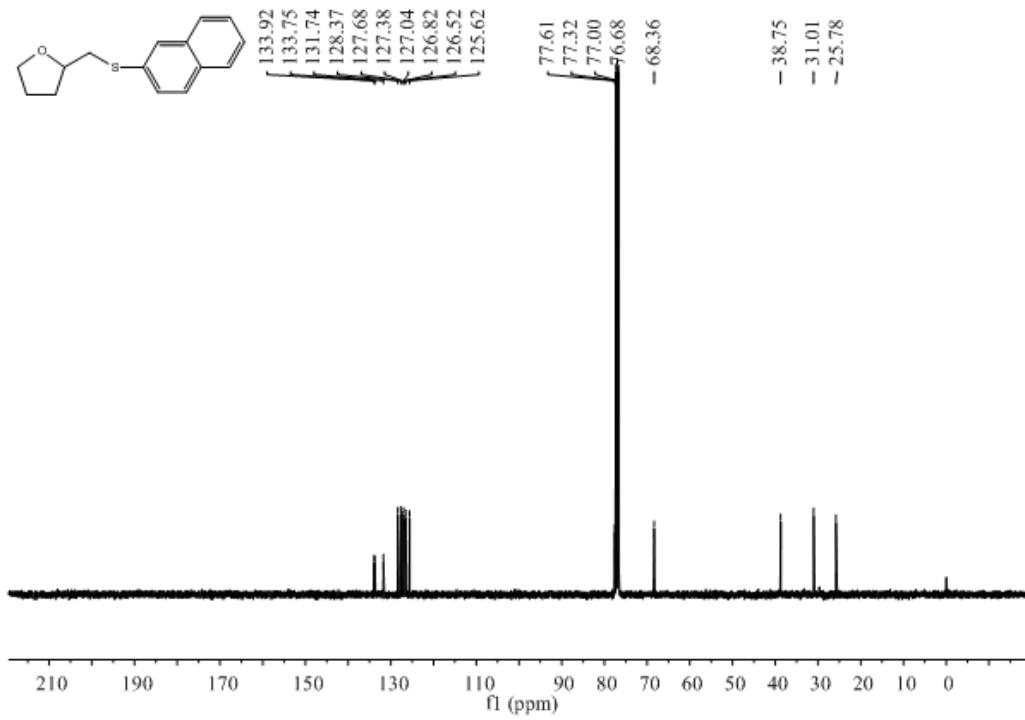


**2-((Naphthalen-2-ylthio)methyl)tetrahydrofuran (3na)**

<sup>1</sup>H NMR

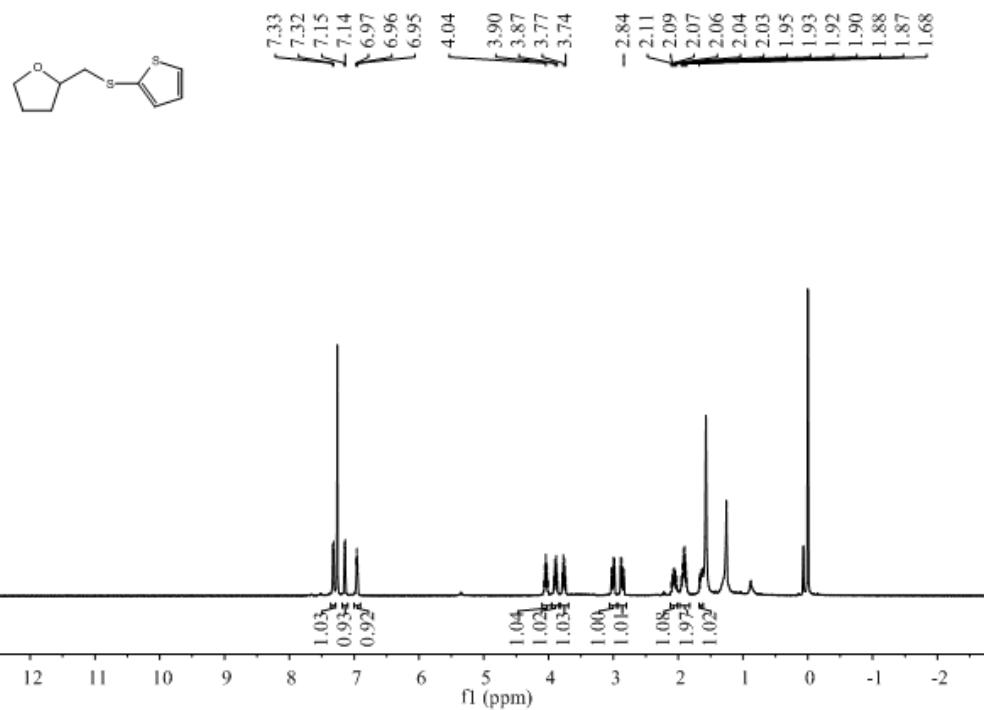


<sup>13</sup>C NMR

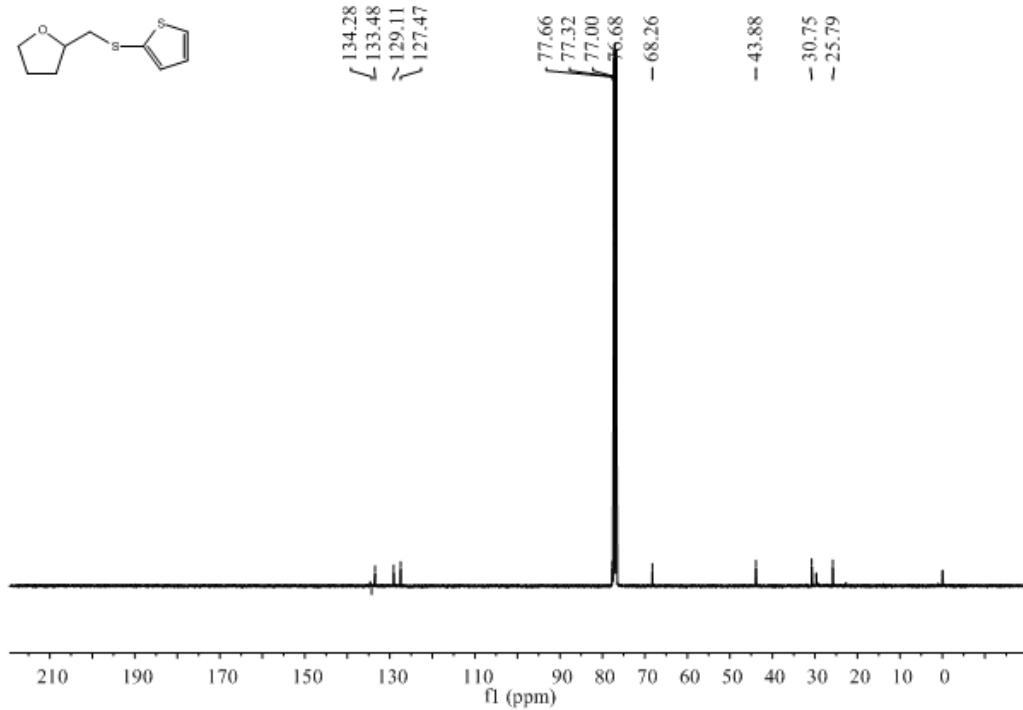


**2-((Thiophen-2-ylthio)methyl)tetrahydrofuran (3o)**

<sup>1</sup>H NMR

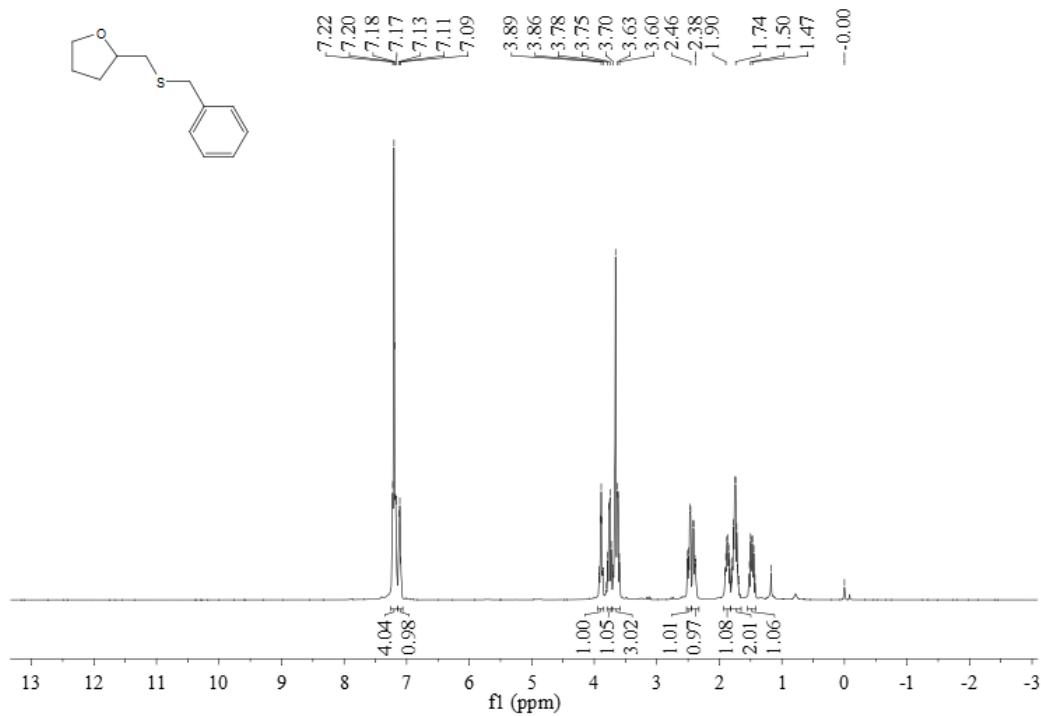


<sup>13</sup>C NMR

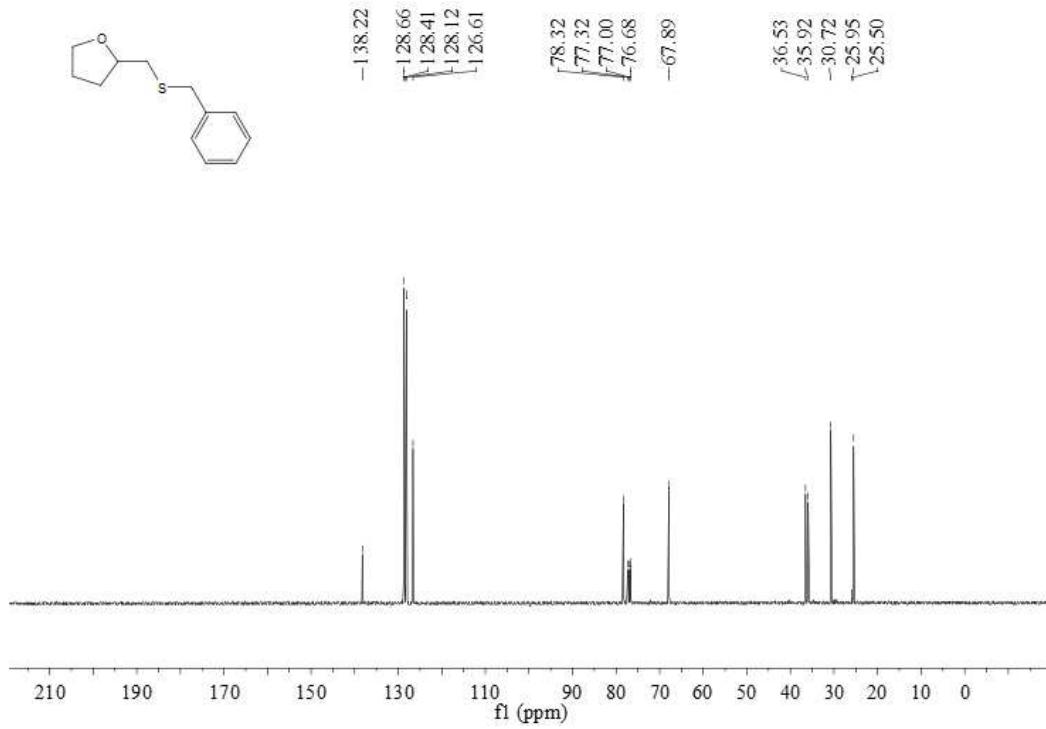


**2-((Benzylthio)methyl)tetrahydrofuran (3pa)**

<sup>1</sup>H NMR

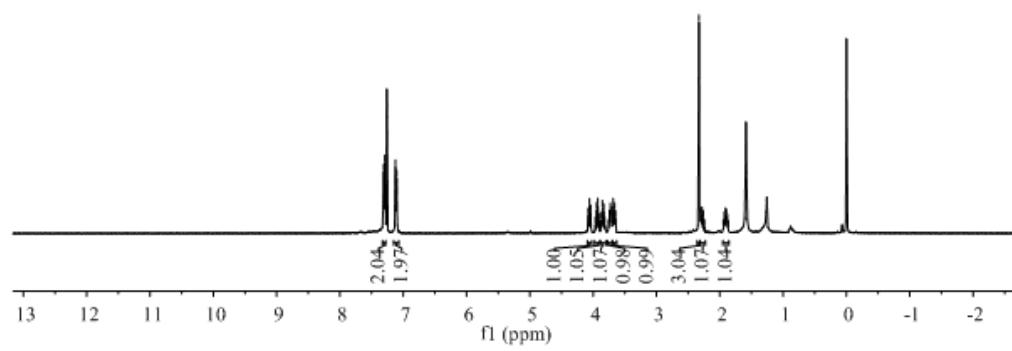
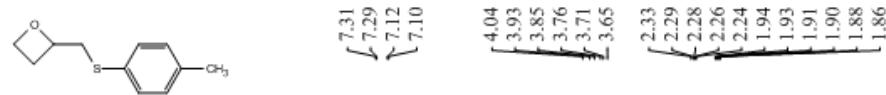


<sup>13</sup>C NMR

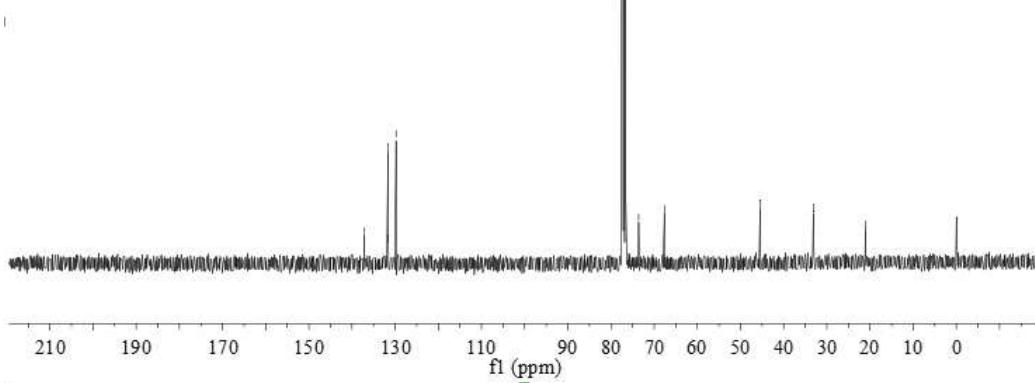


**2-((*p*-Tolylthio)methyl)oxetane (3ab)**

<sup>1</sup>H NMR

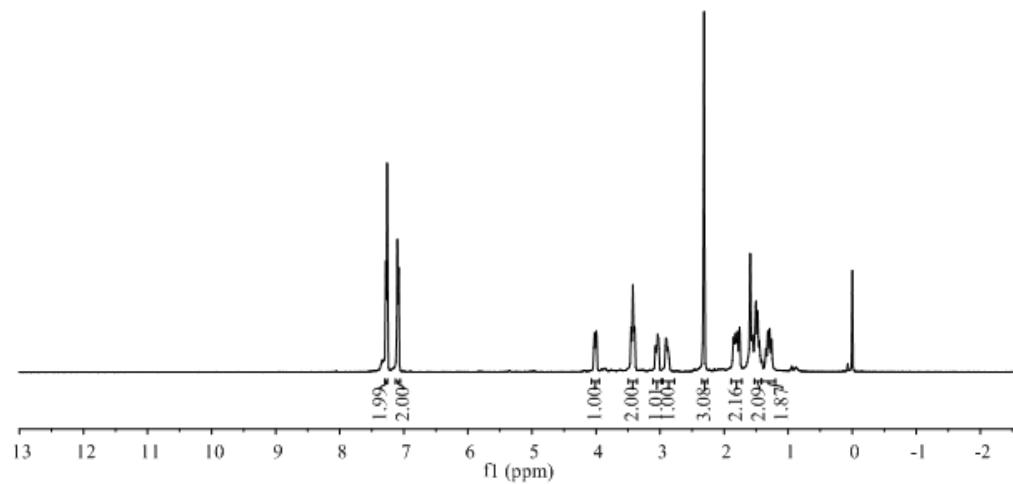
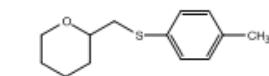


<sup>13</sup>C NMR

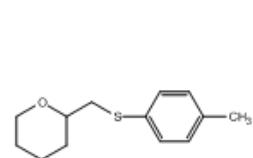


**2-((*p*-Tolylthio)methyl)tetrahydro-2*H*-pyran (3ac)**

<sup>1</sup>H NMR



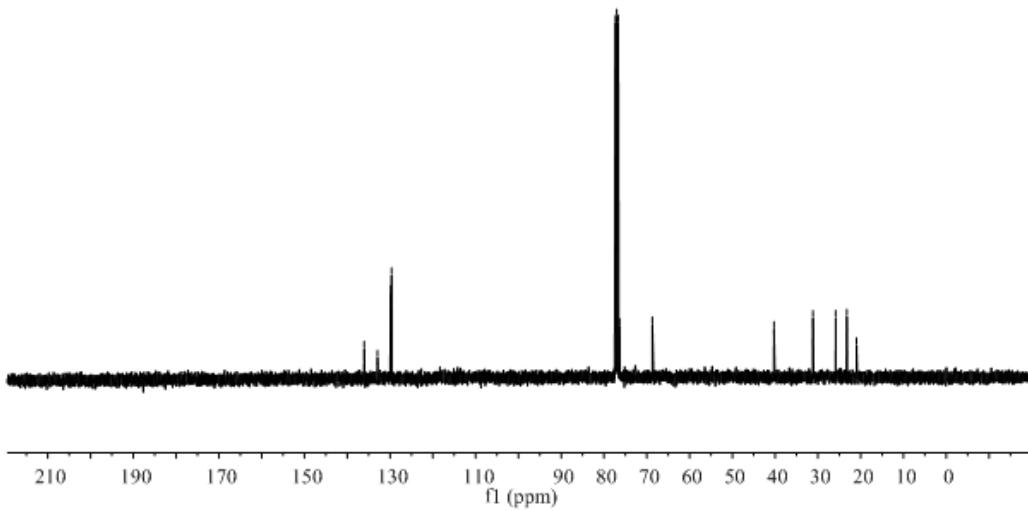
<sup>13</sup>C NMR



136.02  
132.93  
129.85  
129.64

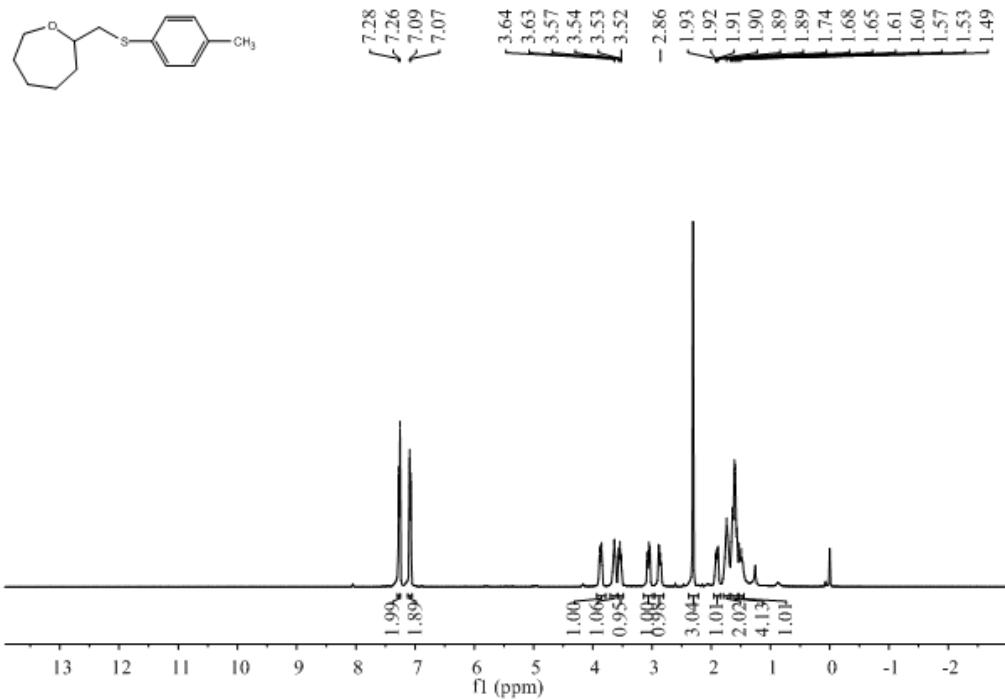
77.32  
77.00  
76.68

68.68  
-40.26  
-31.17  
-25.82  
-23.25  
20.97

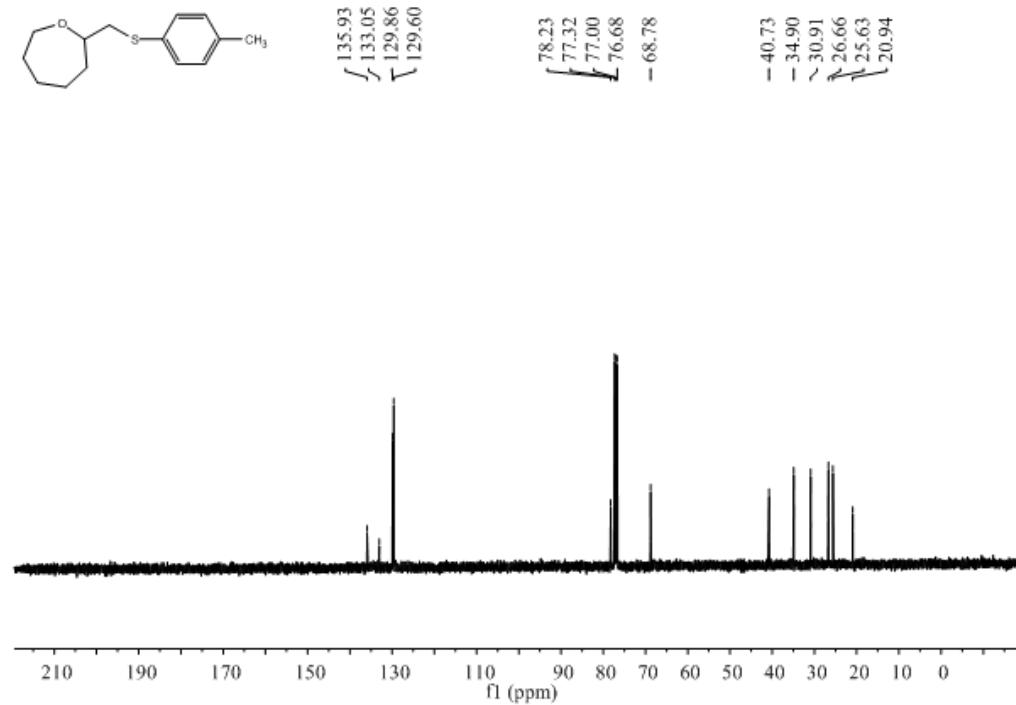


**2-((*p*-Tolylthio)methyl)oxepane (3ad)**

<sup>1</sup>H NMR

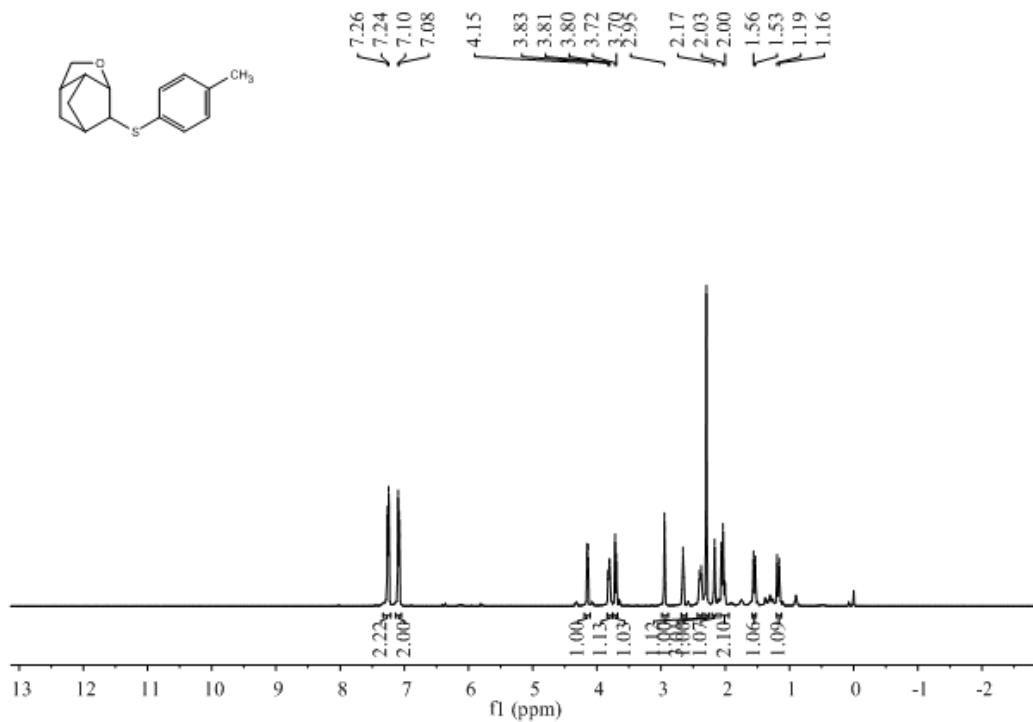


<sup>13</sup>C NMR

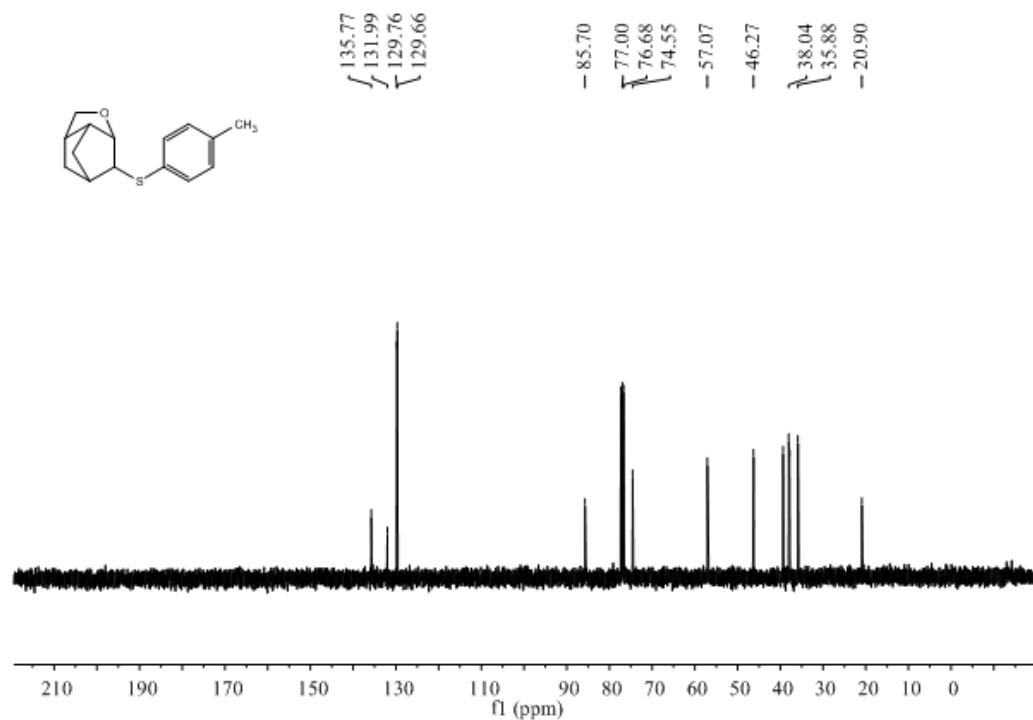


**6-(*p*-Tolylthio)hexahydro-2*H*-3,5-methanocyclopenta[b]furan (3ae)**

<sup>1</sup>H NMR

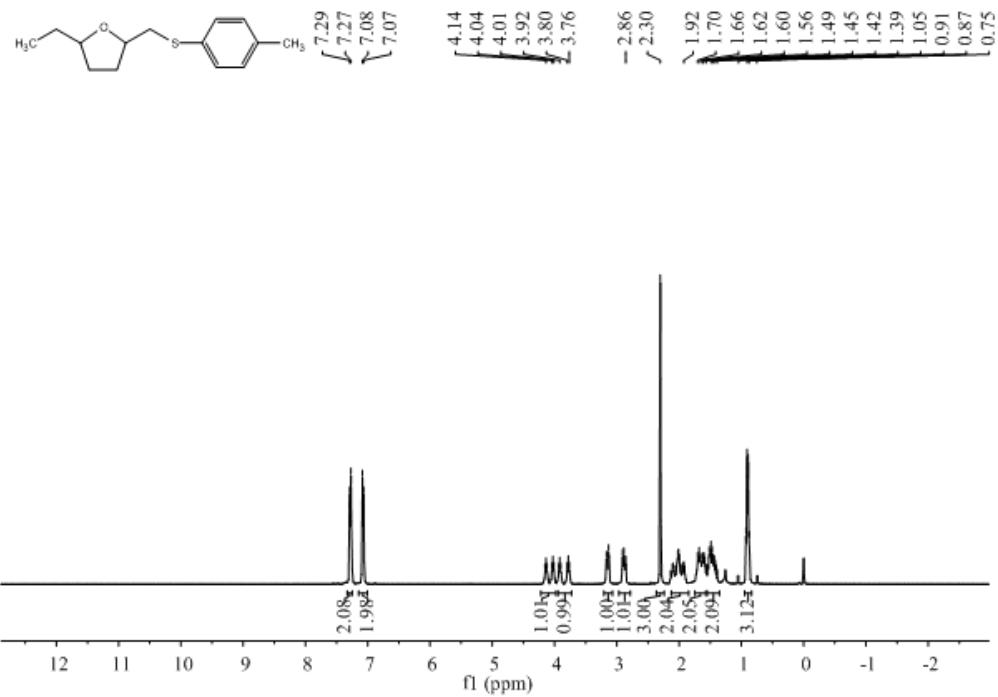


<sup>13</sup>C NMR

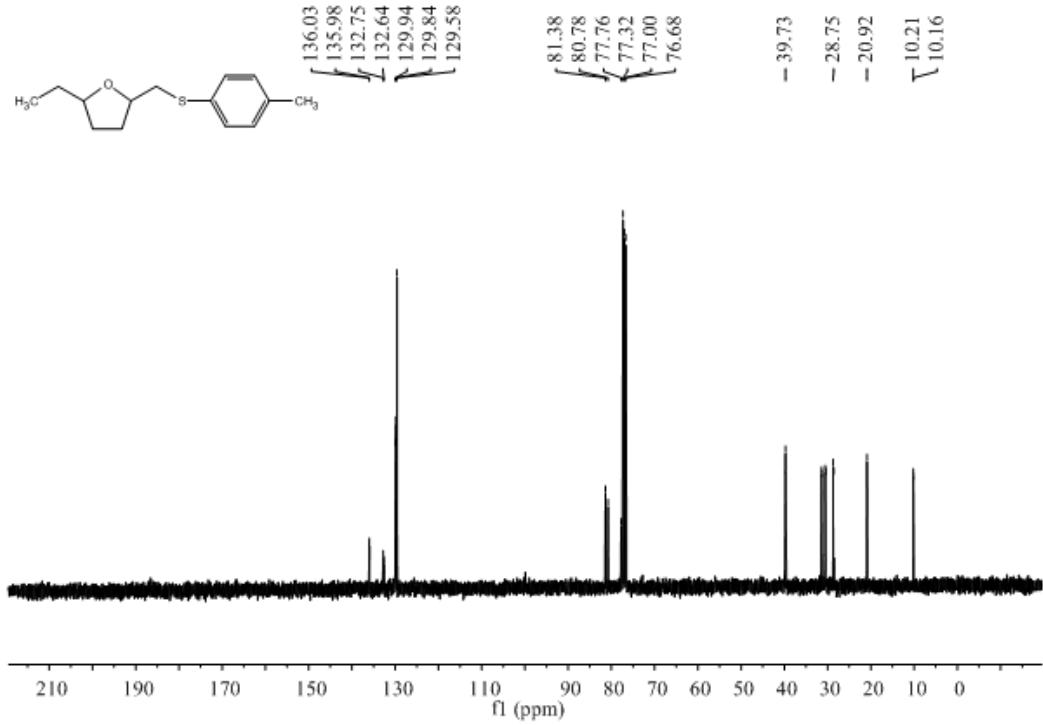


**2-Ethyl-5-((*p*-tolylthio)methyl)tetrahydrofuran (3af)**

<sup>1</sup>H NMR

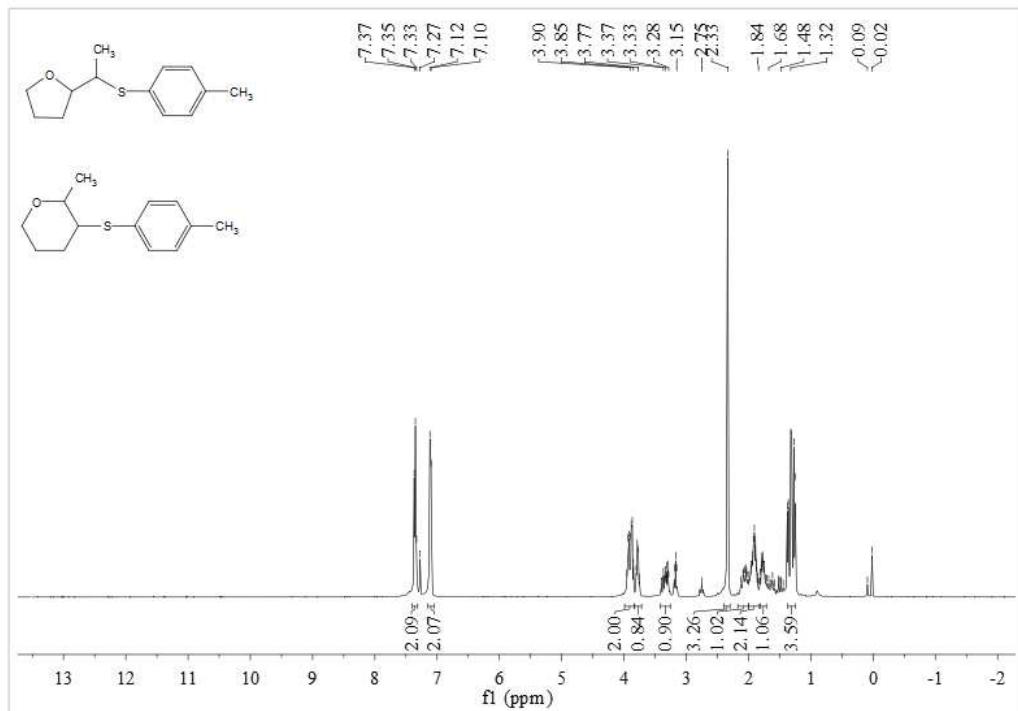


<sup>13</sup>C NMR

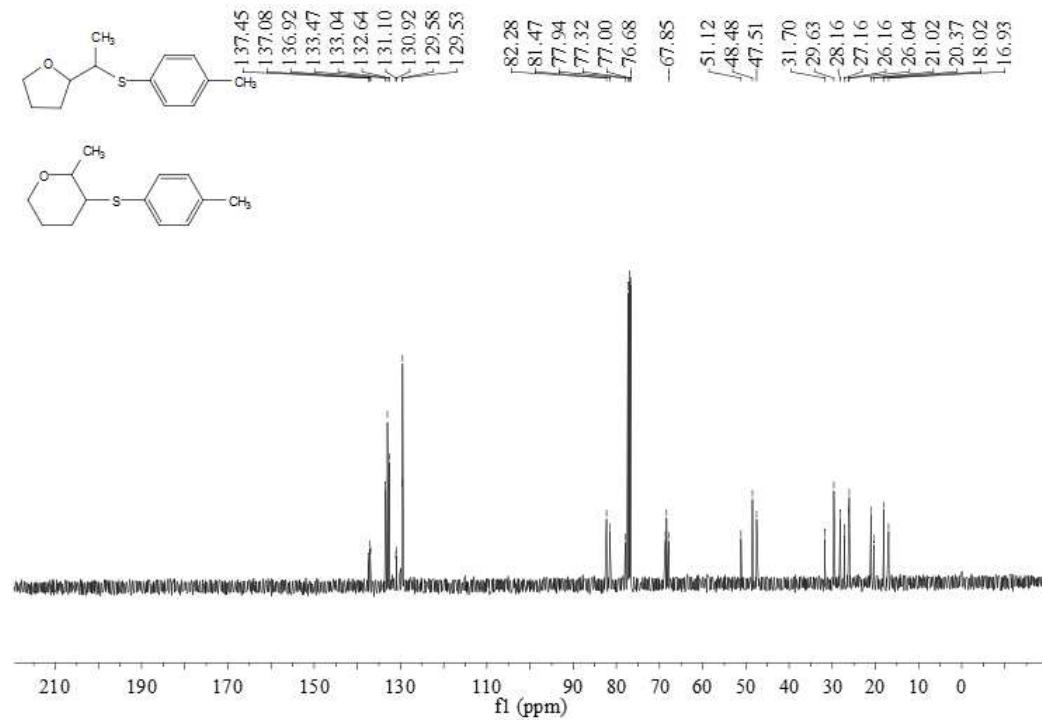


**2-(1-(*p*-Tolylthio)ethyl)tetrahydrofuran (**3ag**) and 2-Methyl-3-(*p*-tolylthio)tetrahydro-2*H*-pyran (**3ag'**)**

<sup>1</sup>H NMR

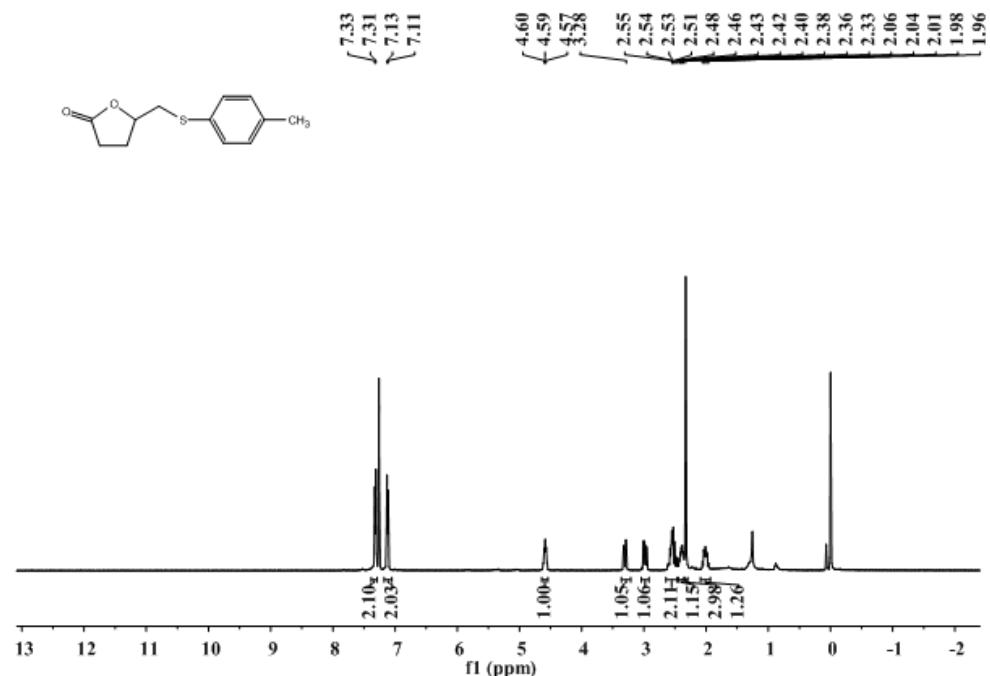


<sup>13</sup>C NMR

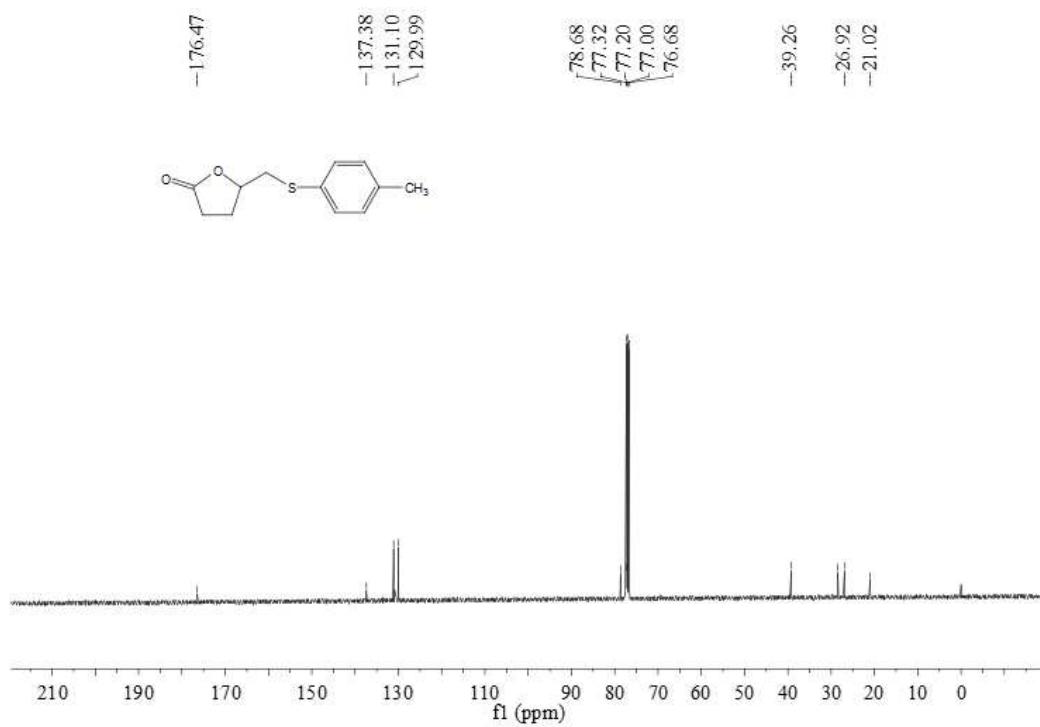


**5-((*p*-Tolylthio)methyl)dihydrofuran-2(3*H*)-one (3ah)**

<sup>1</sup>H NMR

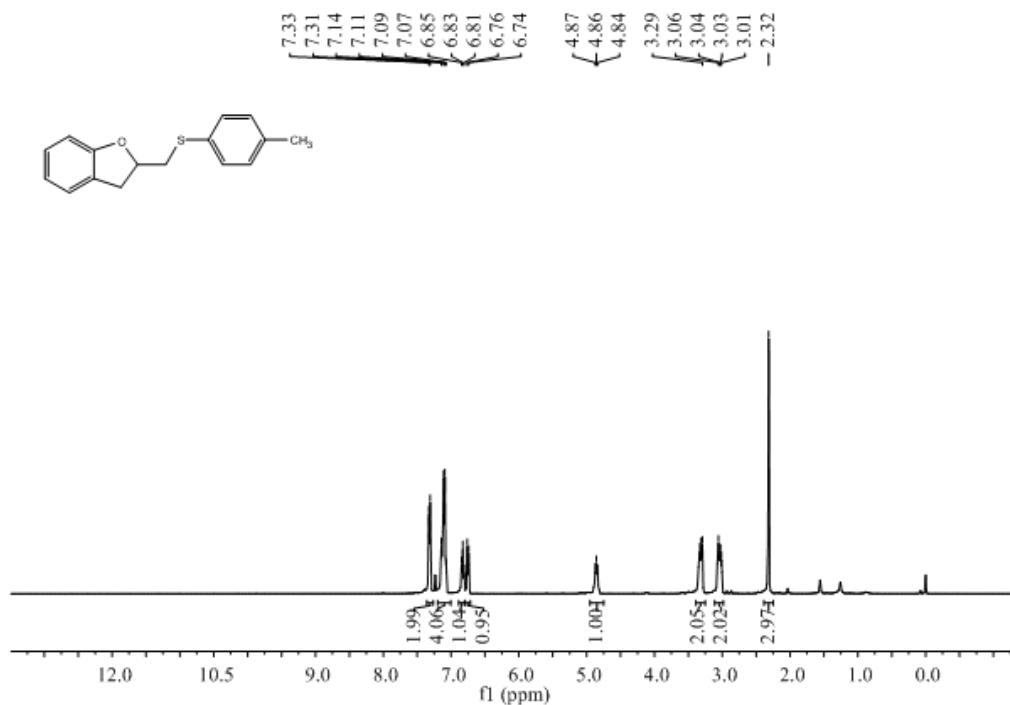


<sup>13</sup>C NMR

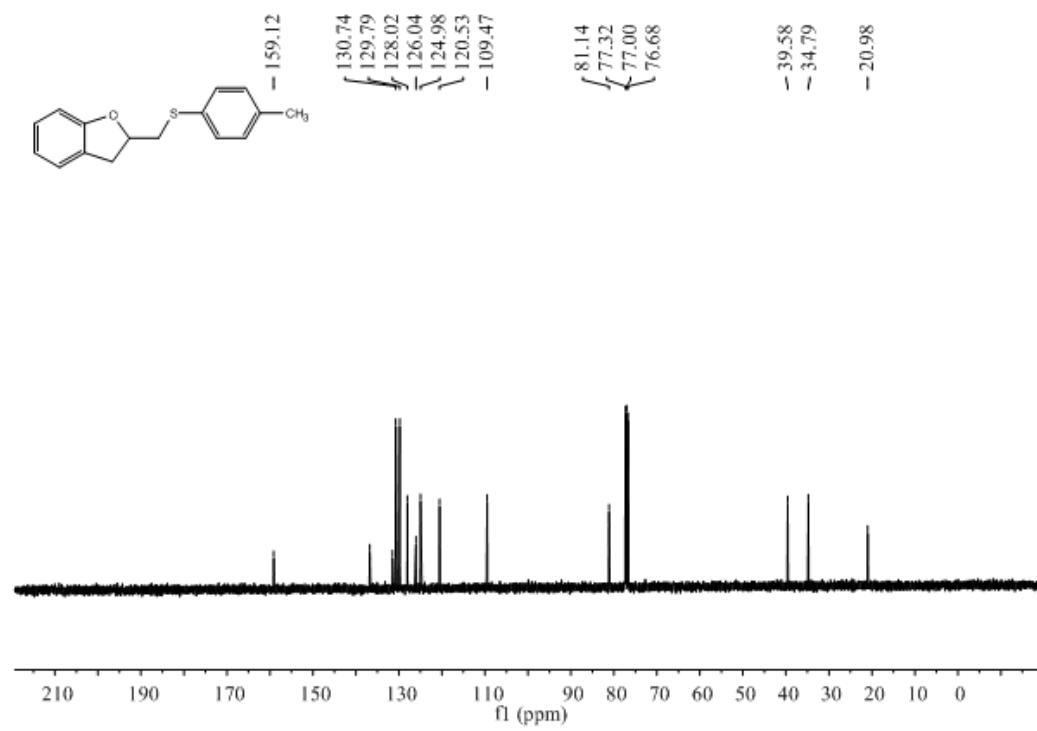


**2-((*p*-Tolylthio)methyl)-2,3-dihydrobenzofuran (3ai)**

<sup>1</sup>H NMR

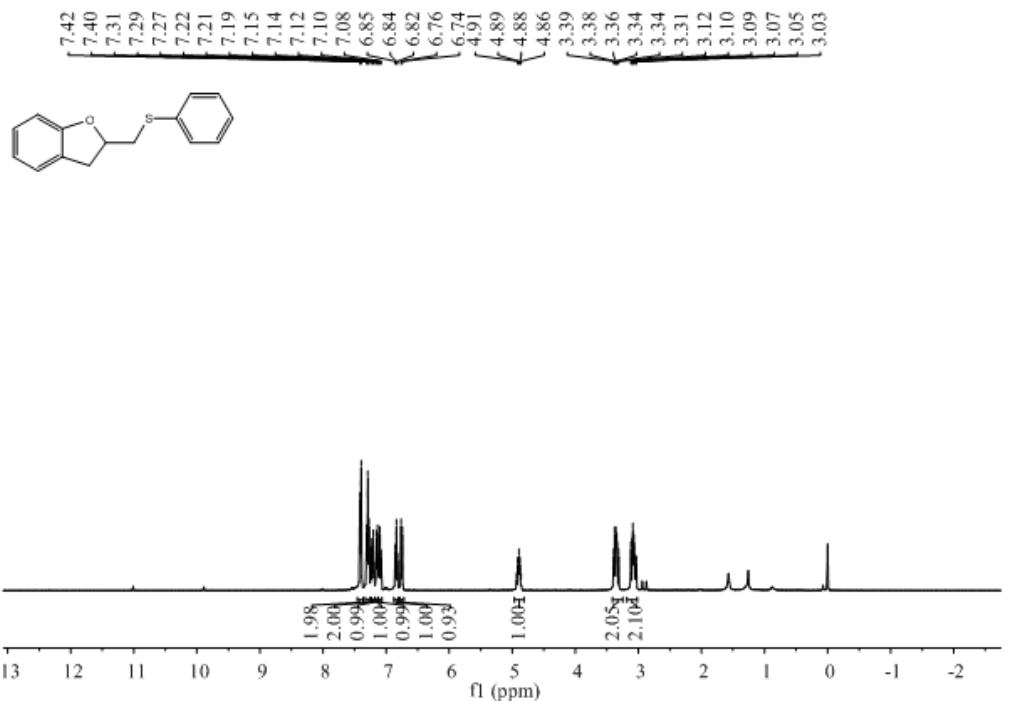


<sup>13</sup>C NMR

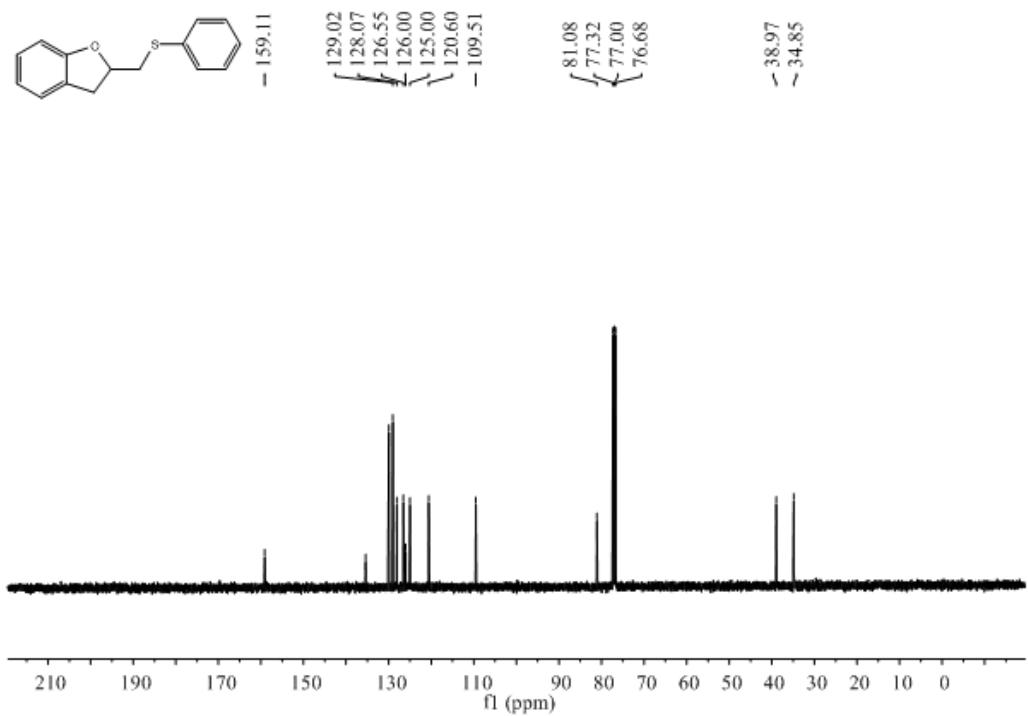


**2-((Phenylthio)methyl)-2,3-dihydrobenzofuran (3bi)**

<sup>1</sup>H NMR

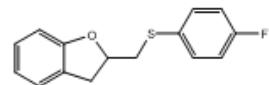
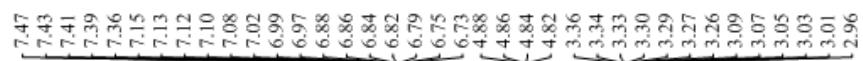


<sup>13</sup>C NMR

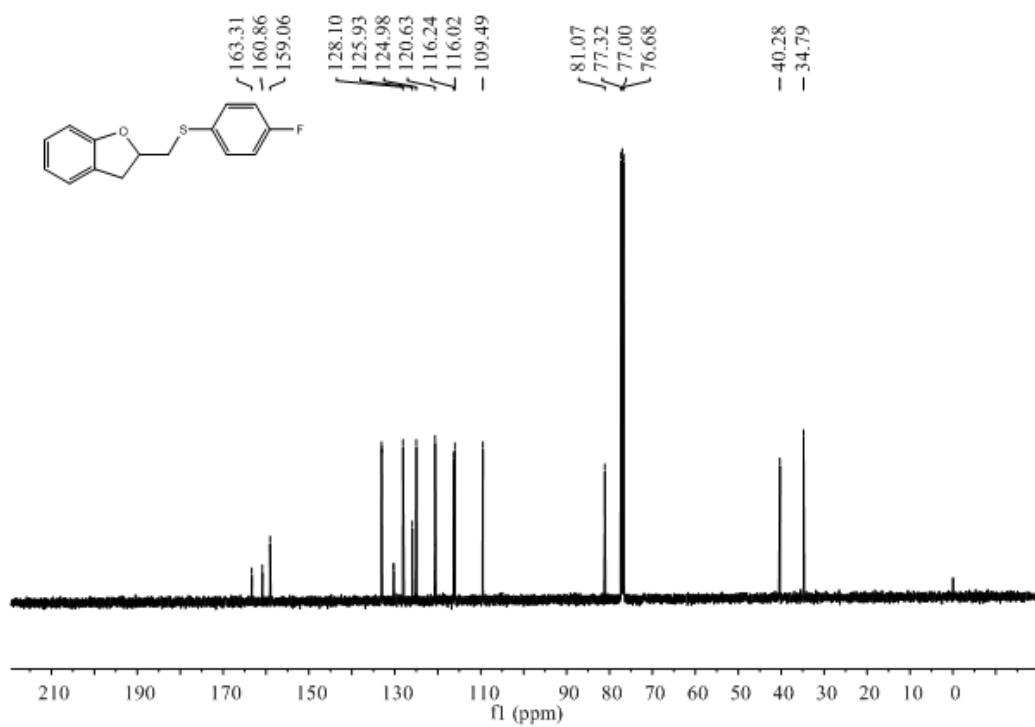


**2-((4-Fluorophenyl)thio)methyl-2,3-dihydrobenzofuran (3ci)**

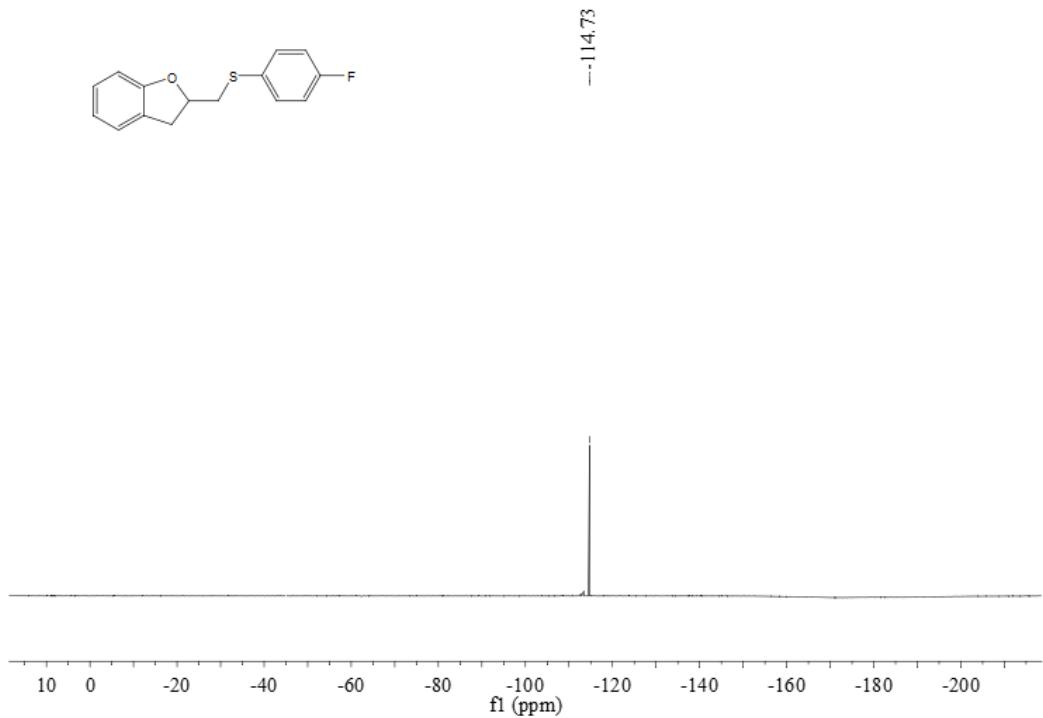
<sup>1</sup>H NMR



<sup>13</sup>C NMR

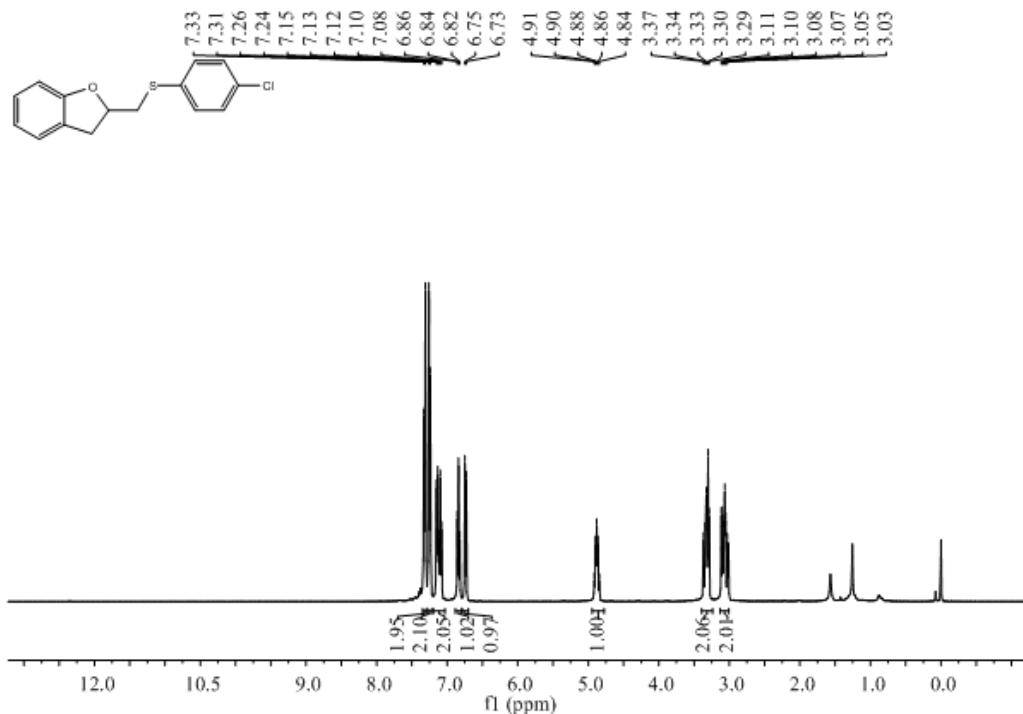


<sup>19</sup>F NMR

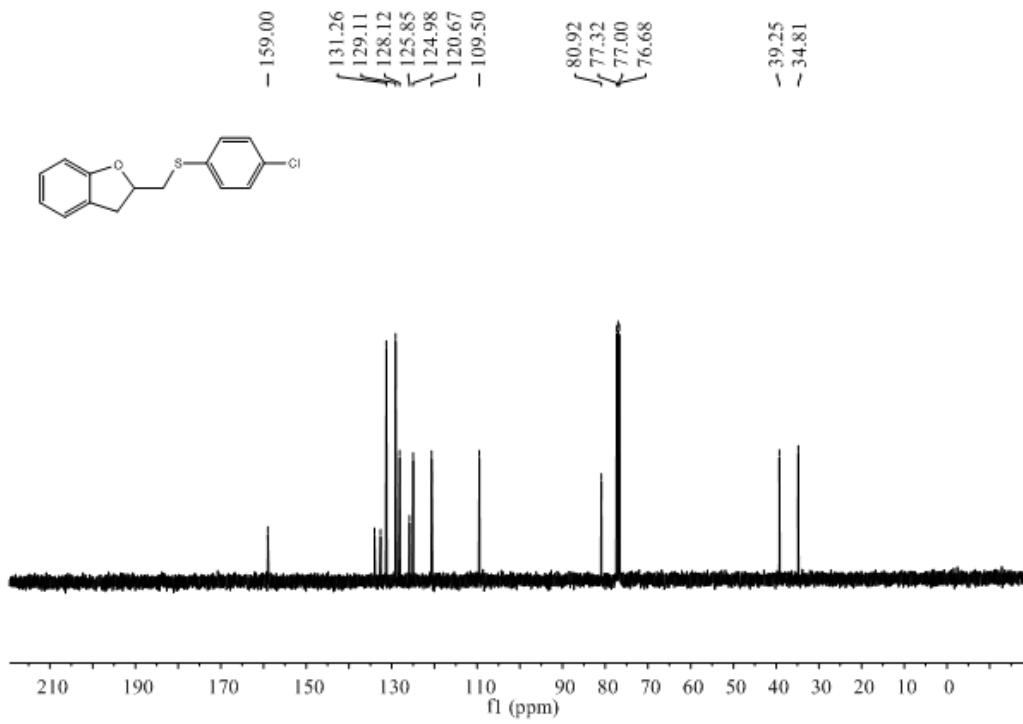


**2-(((4-Chlorophenyl)thio)methyl)-2,3-dihydrobenzofuran (3di)**

<sup>1</sup>H NMR

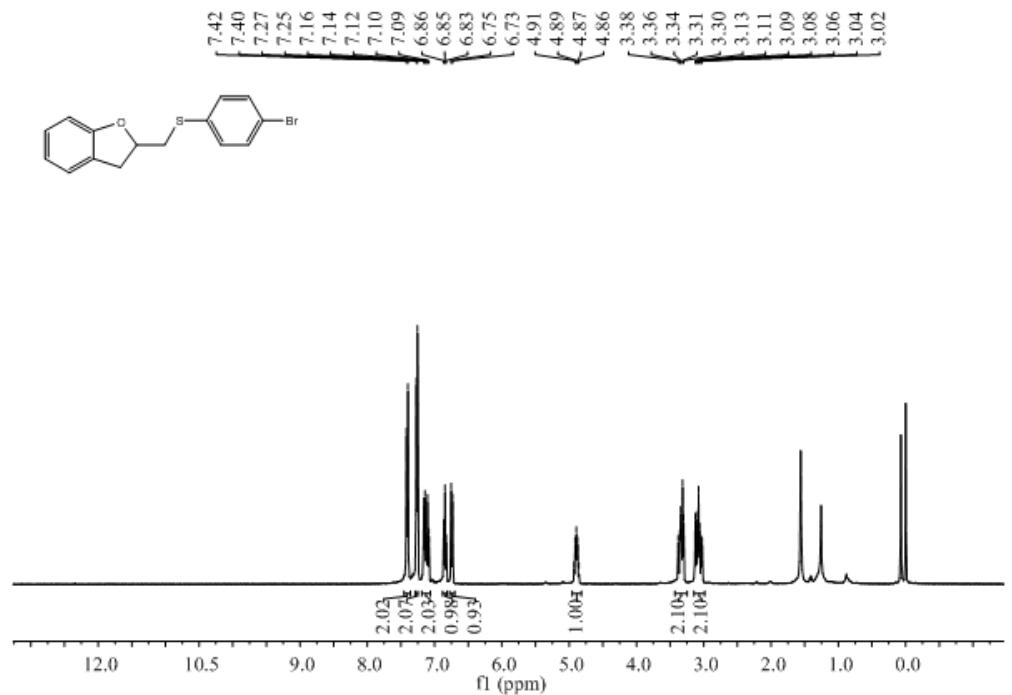


<sup>13</sup>C NMR

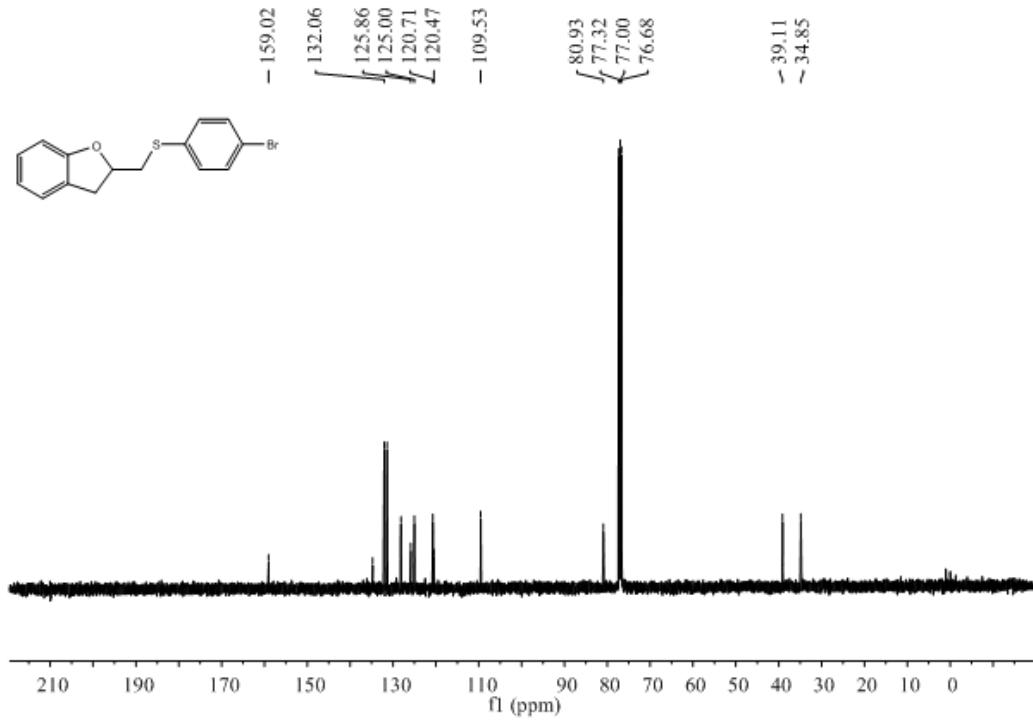


**2-(((4-Bromophenyl)thio)methyl)-2,3-dihydrobenzofuran (3ei)**

<sup>1</sup>H NMR

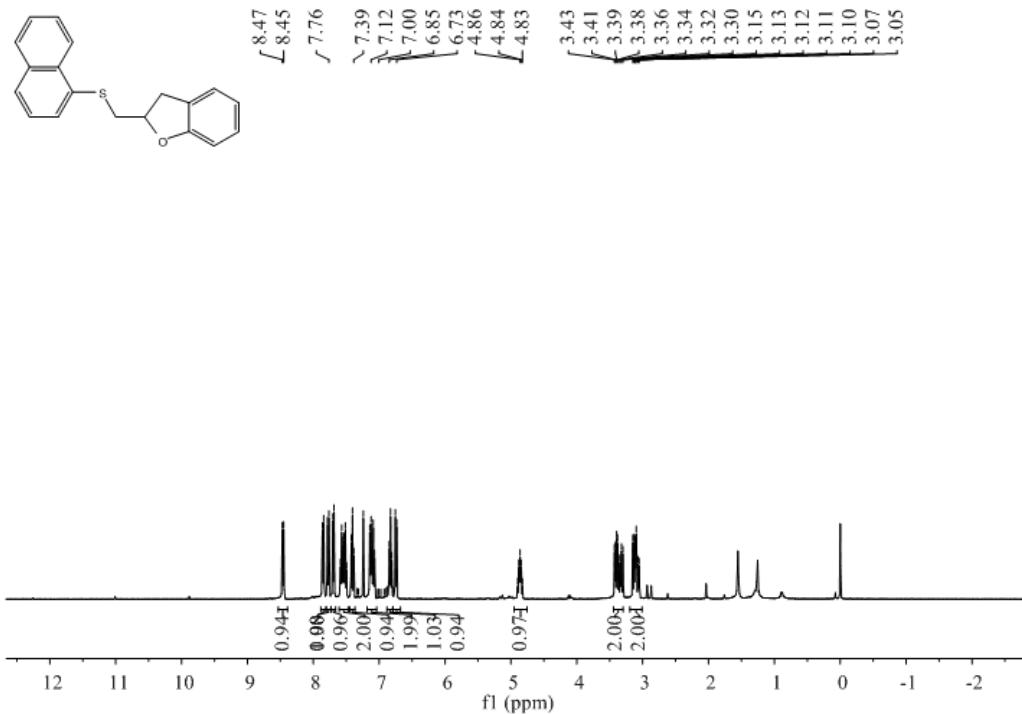


<sup>13</sup>C NMR

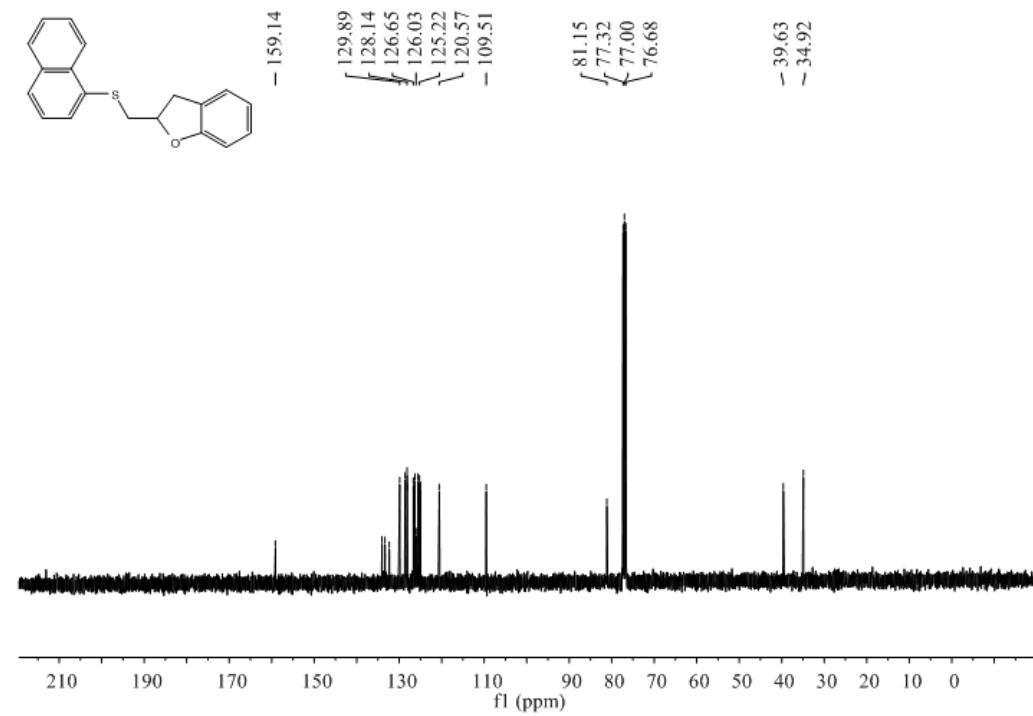


**2-((Naphthalen-1-ylthio)methyl)-2,3-dihydrobenzofuran (3pi)**

<sup>1</sup>H NMR

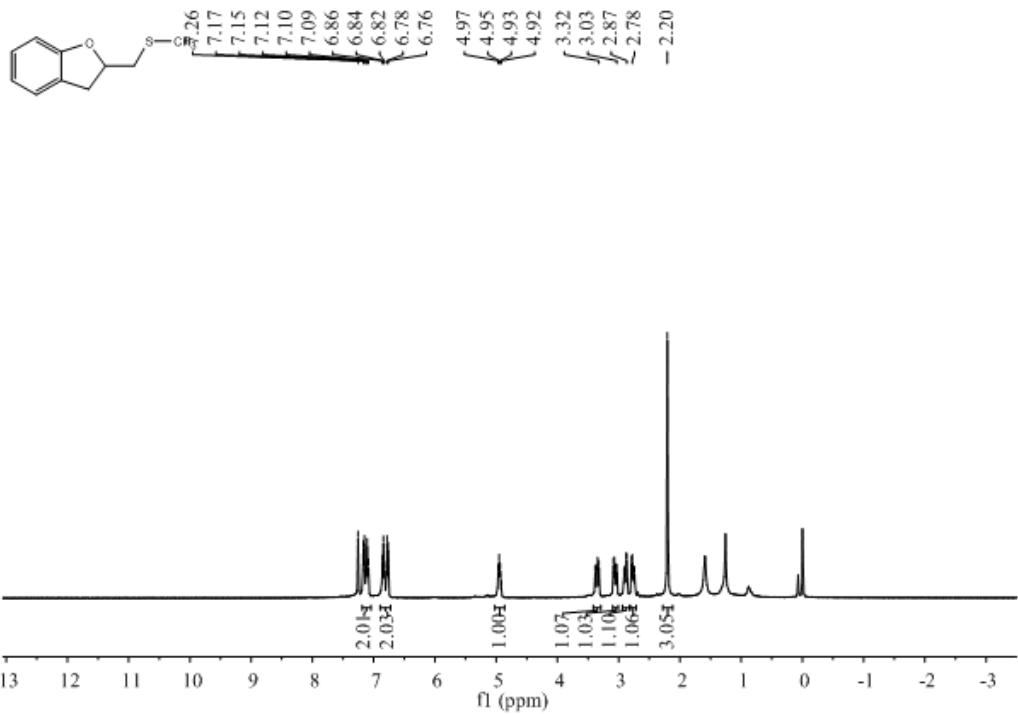


<sup>13</sup>C NMR

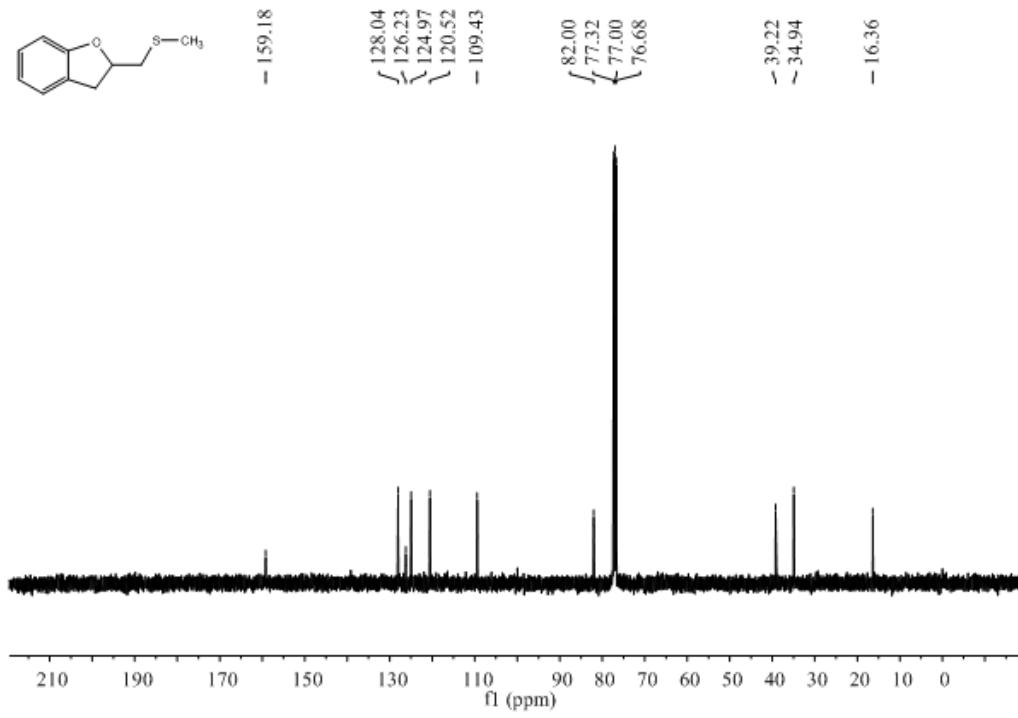


**2-((Methylthio)methyl)-2,3-dihydrobenzofuran (3qi)**

<sup>1</sup>H NMR

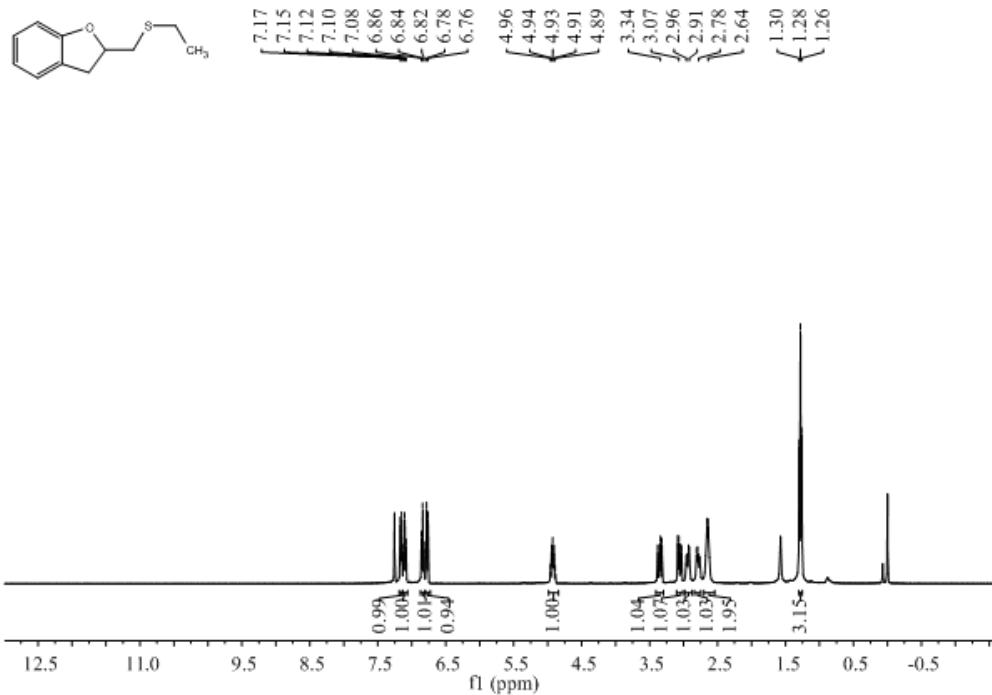


<sup>13</sup>C NMR

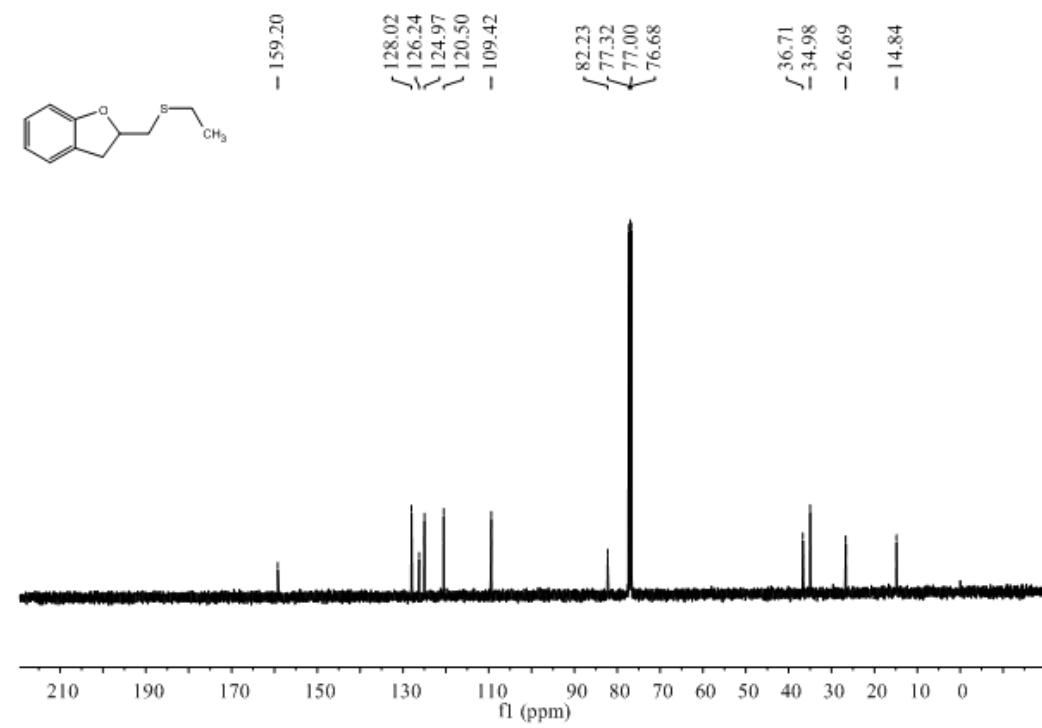


**2-((Ethylthio)methyl)-2,3-dihydrobenzofuran (3ri)**

<sup>1</sup>H NMR

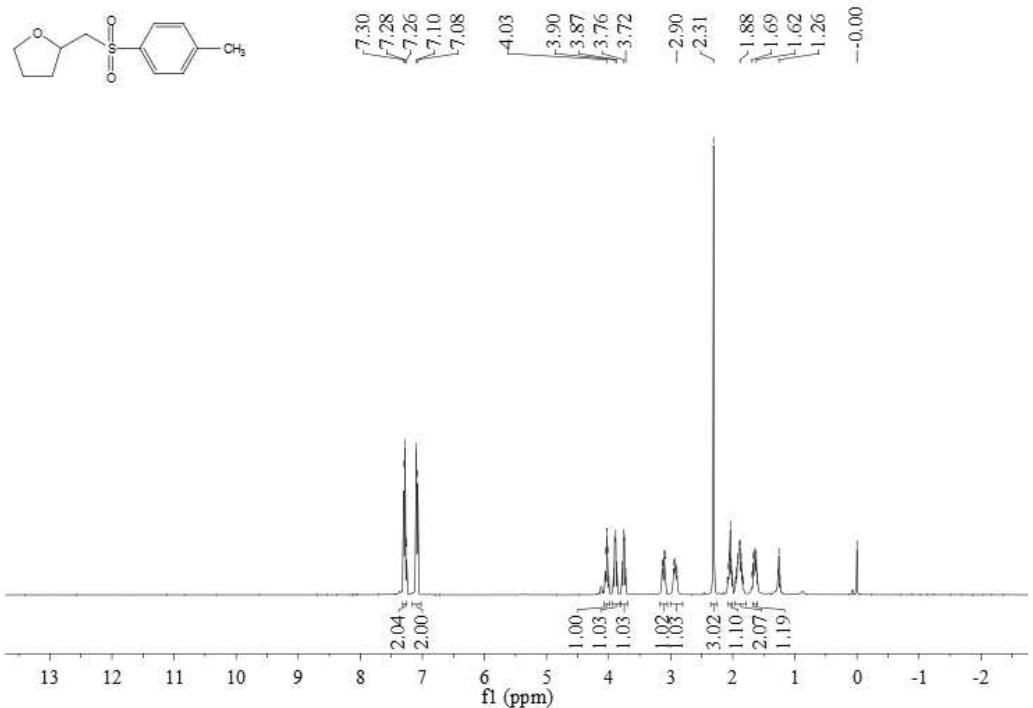


<sup>13</sup>C NMR

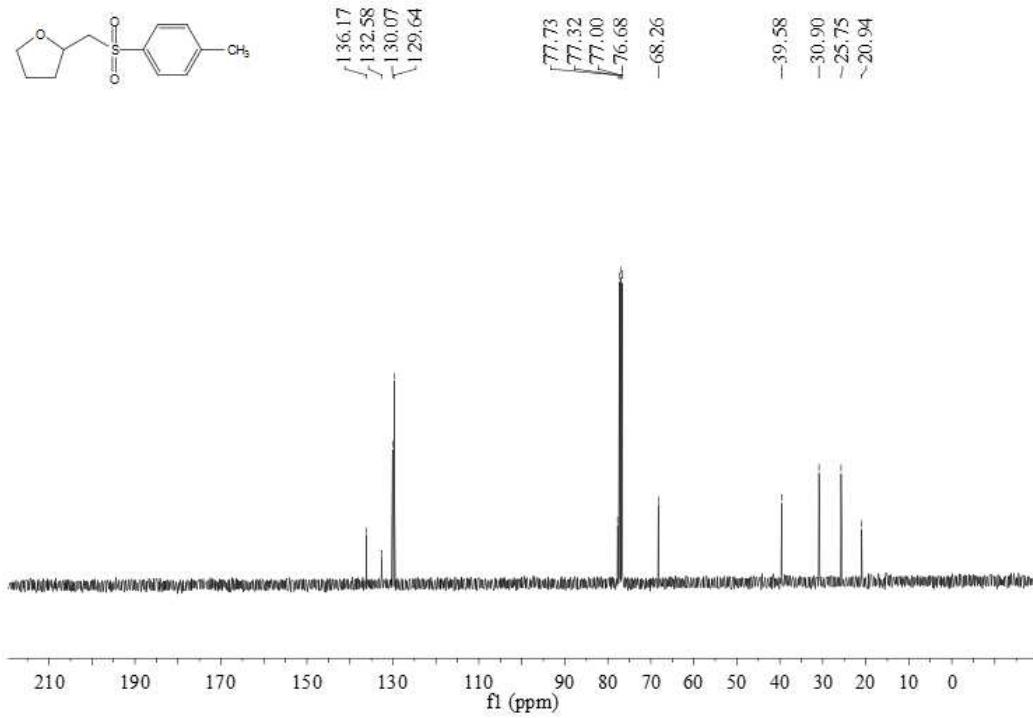


**2-(Tosylmethyl)tetrahydrofuran (4)**

<sup>1</sup>H NMR

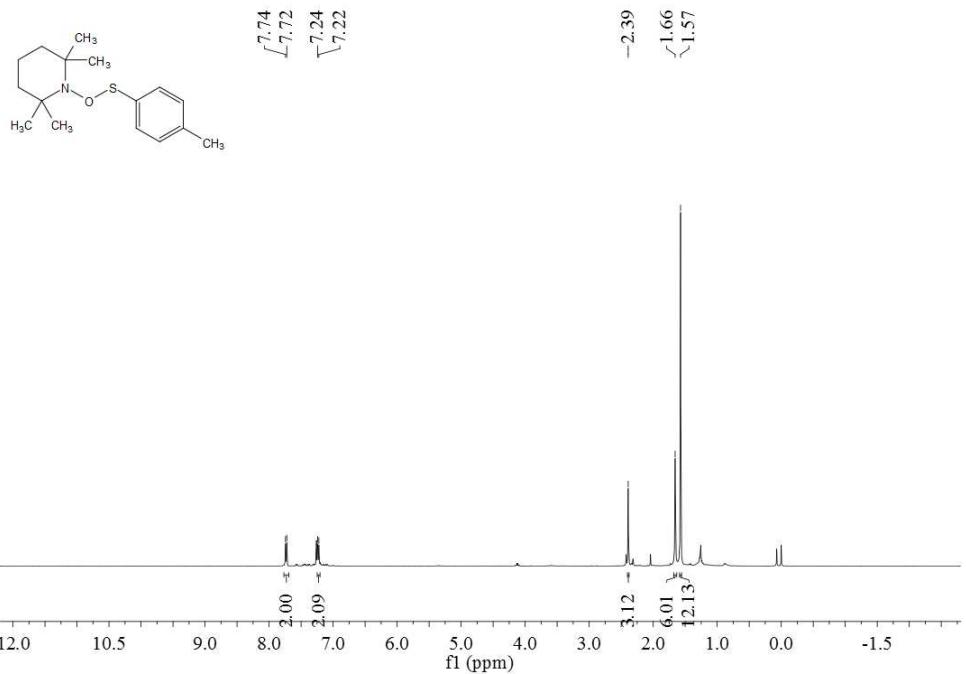


<sup>13</sup>C NMR



**2,2,6,6-Tetramethyl-1-((p-tolylthio)oxy)piperidine (6)**

<sup>1</sup>H NMR



<sup>13</sup>C NMR

