

# Metal-Free Photoredox Catalyzed Formation of S-C-S and C-S Bonds from Coupling of Diaryl Sulfide/Benzyl Chlorides with Dichloromethyl Derivatives

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## Supporting Information

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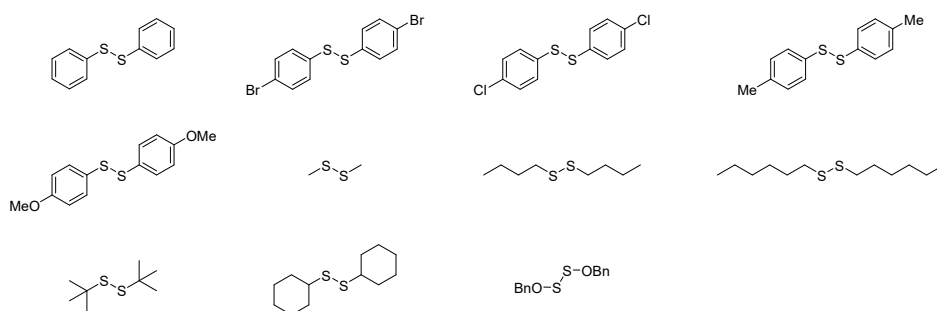
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## I. General methods and materials

All manipulations were performed under an argon atmosphere unless otherwise statement.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC-P 400 spectrometer (400 MHz for  $^1\text{H}$ , 101 MHz for  $^{13}\text{C}$ ) in  $\text{CDCl}_3$ . Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), q (quartet) or m (multiplet). Copies of their  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are provided in the Supporting Information. Emission intensities were recorded using an FS5 Spectrofluorometer. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". The crude products were purified by flash column chromatography on silica gel and the reported yields are the actual isolated yields of pure products. Unless stated otherwise, commercial reagents were used without further purification. All reagents were weighed and handled in air at room temperature.

## II. Synthesis of substrates

Disulfides were purchased from commercial sources.



**Figure S1** commercially purchased disulfides

### General Procedure for the Preparation of various 1,2-diphenyldisulfane

The substrates of various 1,2-diphenyldisulfane were synthesized according to procedures described in the previous literature studies.<sup>1,2</sup>

### General Procedure for the Preparation of various (dichloromethyl)benzene

The substrates of various (dichloromethyl)benzene were synthesized according to procedures described in the previous literature studies.<sup>3,4</sup>

## III. General procedure

### Procedure for the Synthesis of 3a

To a solution of 1,2-diphenyldisulfane **1a** (0.2 mmol) and 4CzIPN (5 mol%) in DCM (2 mL) were

placed in a flame-dried Schlenk-tube equipped with a magnetic stir bar, followed by addition of DIPEA (3 equiv.) *via* syringe. The reaction was stirred at room temperature in argon atmosphere and irradiated with a 25 W blue light-emitting diode (LED) lamp for 24 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was removed under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel using petroleum ether and ethyl acetate (100:1) as an eluent to afford the bis(phenylthio)methane **3a** in 92% yield.

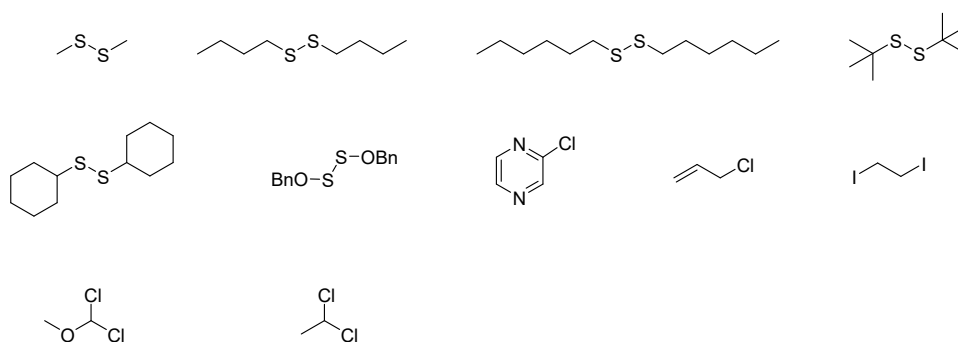
#### Procedure for the Synthesis of **3o**

To a solution of 1,2-diphenyldisulfane **1a** (0.2 mmol) and 4CzIPN (5 mol%) in H<sub>2</sub>O (1 mL) were placed in a flame-dried Schlenk-tube equipped with a magnetic stir bar, followed by addition of DIPEA (3 equiv.) and (dichloromethyl)benzene (0.34 mmol) *via* syringe. The reaction was stirred at room temperature in argon atmosphere and irradiated with a 25 W blue light-emitting diode (LED) lamp for 24 h. The progress of the reaction was monitored by TLC. After completion, extracted with water and dichloromethane, washed with saturated salt water, and dried with anhydrous sodium sulfate. The organic phase was removed under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel using petroleum ether and ethyl acetate (100:1) as an eluent to afford the (phenylmethylene)bis(phenylsulfane) **3o** in 60% yield.

#### Procedure for the Synthesis of **5a**

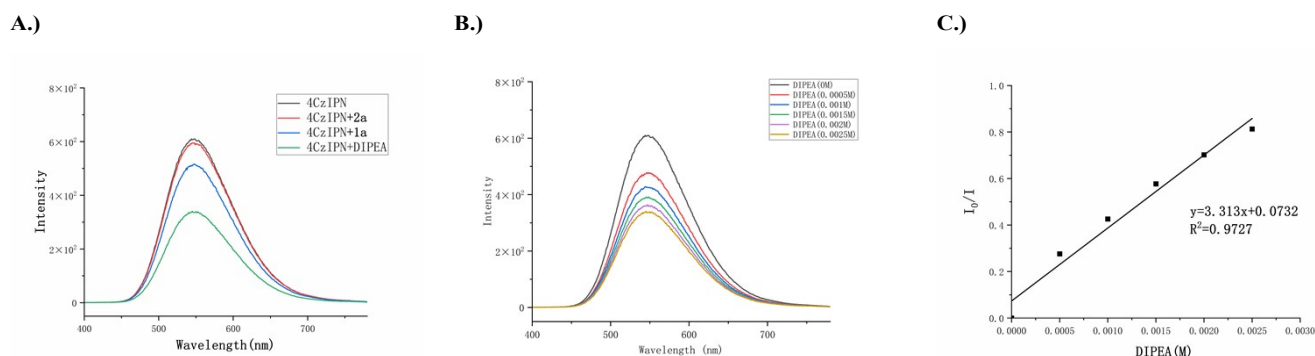
To a solution of 1,2-diphenyldisulfane **1a** (0.2 mmol) and 4CzIPN (5 mol%) in H<sub>2</sub>O (1 mL) were placed in a flame-dried Schlenk-tube equipped with a magnetic stir bar, followed by addition of DIPEA (3 equiv.) and (chloromethyl)benzene (0.34 mmol) *via* syringe. The reaction was stirred at room temperature in argon atmosphere and irradiated with a 25 W blue light-emitting diode (LED) lamp for 24 h. The progress of the reaction was monitored by TLC. After completion, extracted with water and dichloromethane, washed with saturated salt water, and dried with anhydrous sodium sulfate. The organic phase was removed under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel using petroleum ether and ethyl acetate (70:1) as an eluent to afford the benzyl(phenyl)sulfane **5a** in 64% yield.

## IV. Unsuitable substrates



**Figure S2** Substrates unsuitable for conditions A or B

## V. Procedure for emission quenching experiments

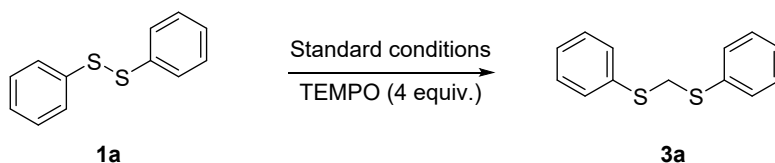


**Figure S3** Luminescence quenching study

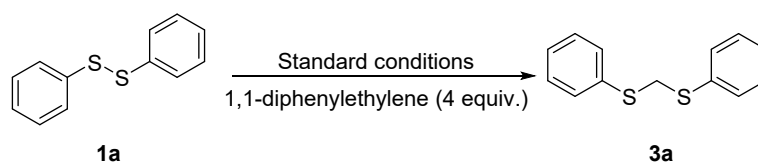
Emission intensities were recorded using an FS5 Spectrofluorometer. First, the emission intensity of 4CzIPN solutions was observed at 550 nm. The solutions were irradiated at 378 nm (Maximum absorption wavelength of 4CzIPN) and fluorescence was measured from 400 nm to 800 nm. In a typical experiment, the emission spectrum of a  $5 \times 10^{-4}$  M solution of 4CzIPN with different concentration of **1a**, **2a** and DIPEA in degassed anhydrous  $\text{CH}_3\text{CN}$  in 10 mm path length quartz cuvette was collected: A) the emission spectra of  $5 \times 10^{-4}$  M solutions of 4CzIPN with reactants (**1a**, **2a** and DIPEA) in degassed anhydrous  $\text{CH}_3\text{CN}$ ; B) the emission spectra of a  $5 \times 10^{-4}$  M solution of 4CzIPN with various concentrations of DIPEA in degassed anhydrous  $\text{CH}_3\text{CN}$ . C) the linear relationship between  $I_0/I$  and the increasing concentration of DIPEA ( $I_0$  and  $I$  are the fluorescence intensities before and after the increasing the concentration of DIPEA, respectively.).

## VI. Mechanistic Experiments

### Control experiment

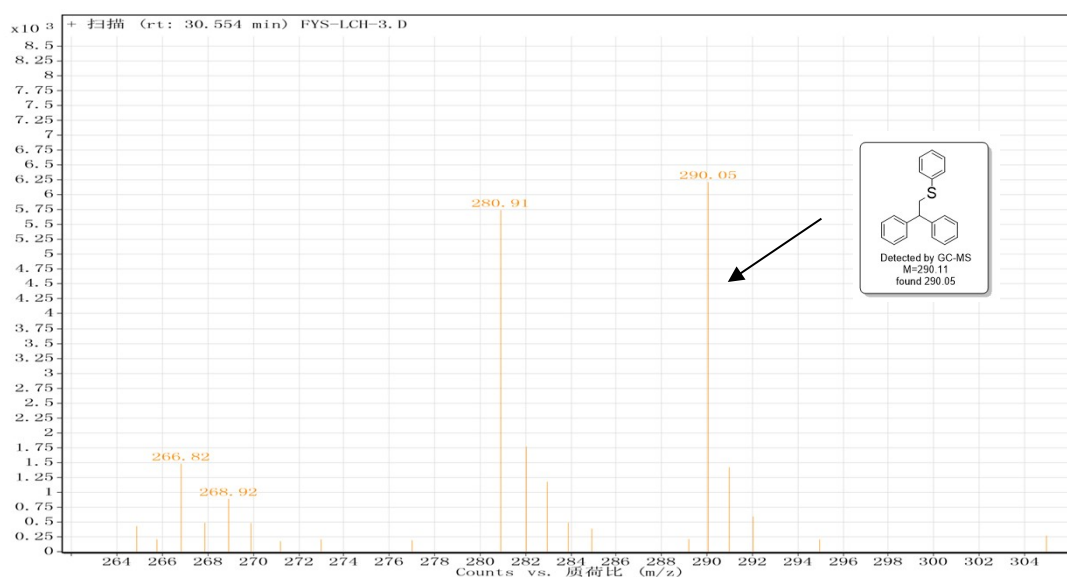


To a solution of 1,2-diphenyldisulfane **1a** (0.2 mmol), 4CzIPN (5 mol%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (4.0 equiv.) in DCM (2 mL) were placed in a flame-dried Schlenk-tube equipped with a magnetic stir bar, followed by addition of DIPEA (3 equiv.) *via* syringe. The reaction was stirred at room temperature and irradiated with a 25 W blue light-emitting diode (LED) lamp for 24 h. the reaction mixture was removed under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel using petroleum ether and ethyl acetate (100:1) as an eluent to afford the bis(phenylthio)methane **3a** in 28% yield.



To a solution of 1,2-diphenyldisulfane **1a** (0.2 mmol), 4CzIPN (5 mol%) and 1,1-diphenylethylene (4.0 equiv.) in DCM (2 mL) were placed in a flame-dried Schlenk-tube equipped with a magnetic stir bar, followed by addition of DIPEA (3 equiv.) *via* syringe. The reaction was stirred at room temperature and irradiated with a 25 W blue light-emitting diode (LED) lamp for 24 h. the reaction mixture was removed under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel using petroleum ether and ethyl acetate (100:1) as an eluent to afford the bis(phenylthio)methane **3a** in 34% yield.

To a solution of 1,2-diphenyldisulfane **1a** (0.2 mmol), 4CzIPN (5 mol%) and ethene-1,1-diylidibenzene (4.0 equiv.) in DCM (2 mL) were placed in a flame-dried Schlenk-tube equipped with a magnetic stir bar, followed by addition of DIPEA (3 equiv.) *via* syringe. The reaction was stirred at room temperature and irradiated with a 25 W blue light-emitting diode (LED) lamp for 3 h. The target product **3a** was not detected by TLC and thiophenol free radical (PhS $\cdot$ ) were successfully detected by Gas Chromatography-Mass Spectrometry (GC-MS) (Figure S4).



**Figure S4** The GC-MS analysis of thiophenol free radical

## VII. Additional experiment

### Gram-scale synthesis of **3a**

To a solution of 1,2-diphenyldisulfane **1a** (1.31 g, 6 mmol) and 4CzIPN (5 mol%) in DCM (0.1 M) were placed in a flame-dried Schlenk-tube equipped with a magnetic stir bar, followed by addition of

DIPEA (3 equiv.) *via* syringe. The reaction was stirred at room temperature in argon atmosphere and irradiated with a 25 W blue light-emitting diode (LED) lamp for 24 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was removed under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel using petroleum ether and ethyl acetate (100:1) as an eluent to afford the bis(phenylthio)methane **3a** (0.7 g) in 50% yield.

### Sunlight-driven synthesis of **3a**

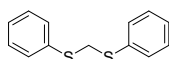
To a solution of 1,2-diphenyldisulfane **1a** (0.2 mmol) and 4CzIPN (5 mol%) in DCM (2 mL) were placed in a flame-dried Schlenk-tube equipped with a magnetic stir bar, followed by addition of DIPEA (3 equiv.) *via* syringe. The reaction was stirred at room temperature in argon atmosphere and irradiated of the sun light source for 24 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was removed under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel using petroleum ether and ethyl acetate (100:1) as an eluent to afford the bis(phenylthio)methane **3a** in 64% yield.

### Procedure for the Synthesis of **6a**

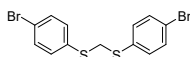
Synthesis with reference to previous reports of the literature<sup>5</sup>

## VIII. Characterization data of **3a-6a**

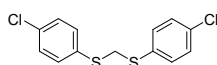
Compounds **3a-3m**, **3p-3t**, **3v**, **3x**, **3aa**, **3ac-6a** are known compounds<sup>5-18</sup>, so only <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum were included in the Supporting Information.



*bis(phenylthio)methane (3a)*. a colourless oily liquid (92% yield, 43 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44–7.40 (m, 4H), 7.33–7.29 (m, 4H), 7.26–7.22 (m, 2H), 4.34 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  134.90, 130.65, 128.97, 127.09, 40.50. The spectral characteristics data were consistent with it reported previously in the literature.<sup>6</sup>

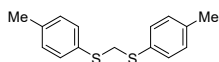


*bis((4-bromophenyl)thio)methane (3b)*. a yellowish solid (77% yield, 60 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44–7.41 (m, 4H), 7.27–7.23 (m, 4H), 4.27 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  133.56, 132.46, 132.10, 121.49, 40.73. The spectral characteristics data were consistent with it reported previously in the literature.<sup>6</sup>

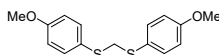


*bis((4-chlorophenyl)thio)methane (3c)*. a yellow oily liquid (76% yield, 43 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35–7.32 (m, 4H), 7.30–7.27 (m, 4H), 4.27 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  133.61, 132.98, 132.43, 129.23, 41.24. The spectral

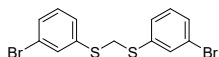
ral characteri stics data were consistent with it reported previously in the literature.<sup>6</sup>



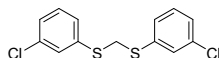
*bis(p-tolylthio)methane (3d)*. a white solid (64% yield, 33.2 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35–7.32 (m, 4H), 7.14–7.12 (m, 4H), 4.26 (s, 2H), 2.34 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.41, 131.54, 131.30, 129.80, 42.01, 21.17. The spectral characteri stics data were consistent with it reported previously in the literature.<sup>6</sup>



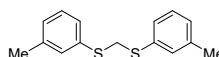
*bis((4-methoxyphenyl)thio)methane (3e)*. a yellowish oily liquid (50% yield, 29.2 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42–7.39 (m, 4H), 6.87–6.84 (m, 4H), 4.15 (s, 2H), 3.81 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.60, 134.47, 125.25, 114.60, 55.36, 44.53. The spectral characteri stics data were consistent with it reported previously in the literature.<sup>6</sup>



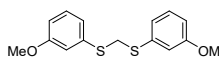
*bis((3-bromophenyl)thio)methane (3f)*. a yellowish solid (46% yield, 36 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (t, *J* = 1.8 Hz, 2H), 7.40–7.37 (m, 2H), 7.34–7.31 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 2H), 4.33 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.74, 133.04, 130.31, 130.29, 129.11, 122.78, 40.15. The spectral characteri stics data were consistent with it reported previously in the literature.<sup>6</sup>



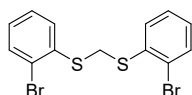
*bis((3-chlorophenyl)thio)methane (3g)*. a yellow oily liquid (88% yield, 53 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38–7.37 (m, 2H), 7.27–7.22 (m, 6H), 4.34 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.55, 134.73, 130.23, 130.03, 128.63, 127.43, 40.10. The spectral characteri stics data were consistent with it reported previously in the literature.<sup>6</sup>



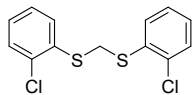
*bis(m-tolylthio)methane (3h)*. a pink oily liquid (88% yield, 46 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24–7.20 (m, 6H), 7.06–7.05 (m, 2H), 4.34 (s, 2H), 2.33 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.82, 134.82, 131.26, 128.86, 127.99, 127.64, 40.50, 21.39. The spectral characteri stics data were consistent with it reported previously in the literature.<sup>6</sup>



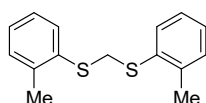
*bis((3-methoxyphenyl)thio)methane (3i)*. a yellowish oily liquid (68% yield, 40 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 (t, *J* = 8.0 Hz, 2H), 6.98–6.93 (m, 4H), 6.77–6.74 (m, 2H), 4.33 (s, 2H), 3.76 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.84, 136.30, 129.87, 122.54, 115.70, 112.91, 55.33, 40.08. The spectral characteri stics data were consistent with it reported previously in the literature.<sup>6</sup>



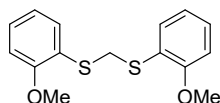
*bis((2-bromophenyl)thio)methane (3j)*. a white solid (83% yield, 65 mg). (PET/EtOAc = 10:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59–7.56 (m, 2H), 7.48–7.45 (m, 2H), 7.33–7.29 (m, 2H), 7.13–7.09 (m, 2H), 4.41 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.84, 133.15, 130.64, 128.06, 127.88, 124.97, 37.77. The spectral characteristics data were consistent with it reported previously in the literature.<sup>6</sup>



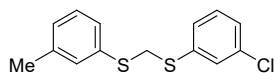
*bis((2-chlorophenyl)thio)methane (3k)*. a yellow liquid (67% yield, 40 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48–7.46 (m, 2H), 7.40–7.38 (m, 2H), 7.25–7.19 (m, 4H), 4.41 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 134.89, 133.69, 131.07, 129.87, 128.07, 127.23, 37.07. The spectral characteristics data were consistent with it reported previously in the literature.<sup>6</sup>



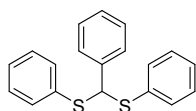
*bis(o-tolylthio)methane (3l)*. a pink oily liquid (75% yield, 39 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41–7.39 (m, 2H), 7.19–7.13 (m, 6H), 4.29 (s, 2H), 2.35 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.43, 134.43, 130.21, 129.71, 126.78, 126.47, 38.41, 20.40. The spectral characteristics data were consistent with it reported previously in the literature.<sup>6</sup>



*bis((2-methoxyphenyl)thio)methane (3m)*. a yellowish oily liquid (77% yield, 45 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (t, *J* = 8.0 Hz, 2H), 7.01–6.98 (m, 2H), 6.97–6.96 (m, 2H), 6.79–6.76 (m, 2H), 4.35 (s, 2H), 3.78 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.73, 136.20, 129.77, 122.42, 115.59, 112.80, 55.22, 39.96. The spectral characteristics data were consistent with it reported previously in the literature.<sup>7</sup>



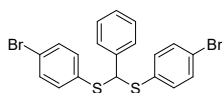
*(3-chlorophenyl)((m-tolylthio)methyl)sulfane (3n)*. a colorless liquid (71% yield, 40 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.38–7.36 (t, *J* = 3.3 Hz, 1H), 7.28–7.17 (m, 6H), 7.08–7.04 (m, 1H), 4.33 (d, *J* = 2.0 Hz, 1H), 4.33 (s, 1H), 2.33 (d, *J* = 3.1 Hz, 1H), 2.32 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 136.48, 134.73, 134.67, 131.58, 131.15, 130.13, 130.01, 129.90, 129.75, 128.86, 128.77, 128.55, 128.26, 128.16, 127.95, 127.90, 127.53, 127.37, 126.99, 40.37, 40.20, 39.97, 21.31.



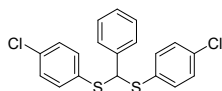
*(phenylmethylene)bis(phenylsulfane) (3p)*. a yellowish solid (60% yield, 36.9 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37–7.33 (m, 6H), 7.28–7.26 (m, 2H), 7.24–7.22 (m, 7H), 5.42 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.65, 134.53, 132.54, 128.87, 128.51, 128.09, 127.90, 127.83, 60.41. The spectral characteristics data were consistent



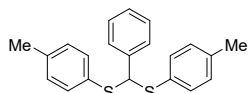
with it reported previously in the literature.<sup>8</sup>



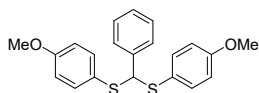
(*phenylmethylene*)bis((4-bromophenyl)sulfane) (**3q**). a colourless oil liquid (38% yield, 35.4 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d,  $J$  = 8.4 Hz, 4H), 7.30–7.25 (m, 5H), 7.17 (d,  $J$  = 8.4 Hz, 4H), 5.34 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  138.77, 134.24, 133.15, 131.96, 128.60, 128.36, 127.79, 122.37, 60.43. The spectral characteristics data were consistent with it reported previously in the literature.<sup>8</sup>



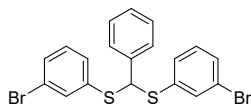
(*phenylmethylene*)bis((4-chlorophenyl)sulfane) (**3r**). a yellowish oily liquid (35% yield, 26.3 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.31–7.30 (m, 2H), 7.29–7.28 (m, 2H), 7.24–7.21 (m, 7H), 7.20 (d,  $J$  = 4.2 Hz, 2H), 5.33 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 138.83, 134.29, 134.16, 132.45, 129.03, 128.59, 128.34, 127.79, 60.76. The spectral characteristics data were consistent with it reported previously in the literature.<sup>8</sup>



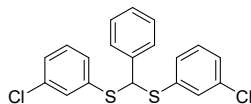
(*phenylmethylene*)bis(*p*-tolylsulfane) (**3s**). a yellowish solid (38% yield, 25.5 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27–7.24 (m, 2H), 7.19–7.15 (m, 3H), 7.17–7.15 (m, 4H), 6.97 (d,  $J$  = 7.9 Hz, 4H), 5.24 (s, 1H), 2.23 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  139.91, 137.99, 133.10, 130.78, 129.54, 128.33, 127.85, 61.22, 21.16. The spectral characteristics data were consistent with it reported previously in the literature.<sup>8</sup>



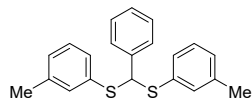
(*phenylmethylene*)bis((4-methoxyphenyl)sulfane) (**3t**). a white solid (26% yield, 19.2 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28–7.24 (m, 4H), 7.23–7.20 (m, 5H), 6.77–6.73 (m, 4H), 5.13 (s, 1H), 3.76 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.55, 139.74, 135.58, 127.93, 127.50, 124.40, 113.94, 62.59, 54.93. The spectral characteristics data were consistent with it reported previously in the literature.<sup>9</sup>



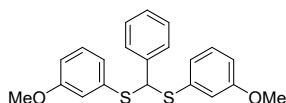
(*phenylmethylene*)bis((3-bromophenyl)sulfane) (**3u**). a colorless liquid (53% yield, 50 mg). (PET/EtOAc = 25:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.47 (t,  $J$  = 1.8 Hz, 2H), 7.39–7.38 (m, 1H), 7.37–7.35 (m, 3H), 7.32–7.30 (m, 3H), 7.27–7.26 (m, 1H), 7.25–7.24 (m, 1H), 7.12 (t,  $J$  = 7.9 Hz, 2H), 5.43 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 138.56, 136.30, 134.85, 130.96, 130.86, 130.15, 128.68, 128.50, 127.79, 122.51, 60.20.



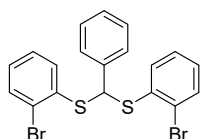
(*phenylmethylene*)bis(*(3-chlorophenyl)sulfane*) (**3v**). a yellowish liquid (41% yield, 31 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38–7.36 (m, 2H), 7.32–7.31 (m, 3H), 7.30–7.28 (m, 2H), 7.24–7.18 (m, 6H), 5.45 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.60, 136.06, 134.43, 131.98, 130.35, 129.85, 128.67, 128.48, 128.05, 127.79, 60.09. The spectral characteristics data were consistent with it reported previously in the literature.<sup>8</sup>



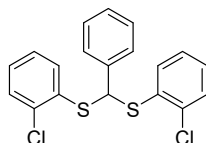
(*phenylmethylene*)bis(*m*-tolylsulfane) (**3w**). a yellowish liquid (34% yield, 23 mg). (PET/EtOAc = 25:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.40–7.37 (m, 2H), 7.31–7.29 (m, 2H), 7.27–7.26 (m, 1H), 7.17–7.13 (m, 6H), 7.06–7.04 (m, 2H), 5.43 (s, 1H), 2.28 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 139.86, 138.51, 134.32, 133.04, 129.37, 128.58, 128.52, 128.38, 127.86, 127.14, 60.37, 21.23;



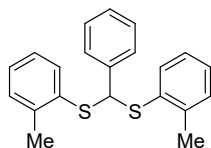
(*phenylmethylene*)bis(*(3-methoxyphenyl)sulfane*) (**3x**). a yellowish liquid (27% yield, 20 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40–7.37 (m, 2H), 7.29–7.28 (m, 1H), 7.26–7.24 (m, 2H), 7.17–7.13 (m, 2H), 6.96–6.94 (m, 2H), 6.85–6.84 (m, 2H), 6.78–6.75 (m, 2H), 5.45 (s, 1H), 3.70 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.51, 139.59, 135.66, 129.57, 128.50, 128.06, 127.88, 124.31, 117.04, 113.84, 59.90, 55.18. The spectral characteristics data were consistent with it reported previously in the literature.<sup>8</sup>



(*phenylmethylene*)bis(*(2-bromophenyl)sulfane*) (**3y**). a yellowish oily liquid (54% yield, 51 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55–7.53 (m, 2H), 7.52–7.49 (m, 2H), 7.45–7.43 (m, 2H), 7.31–7.28 (m, 1H), 7.27–7.24 (m, 2H), 7.19–7.15 (m, 2H), 7.09–7.05 (m, 2H), 5.74 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.05, 135.47, 133.45, 133.07, 128.80, 128.63, 128.43, 127.99, 127.70, 126.56, 57.21.

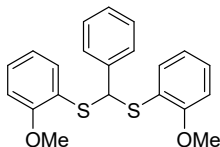


(*phenylmethylene*)bis(*(2-chlorophenyl)sulfane*) (**3z**). a yellowish oily liquid (62% yield, 47 mg). (PET/EtOAc = 100:1 as the eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51–7.49 (m, 2H), 7.46–7.44 (m, 2H), 7.38–7.35 (m, 2H), 7.29–7.25 (m, 3H), 7.19–7.11 (m, 4H), 5.77 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.22, 136.06, 133.57, 133.41, 129.75, 128.75, 128.60, 128.40, 127.91, 127.06, 56.53.

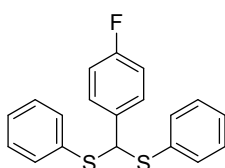


(*phenylmethylene*)bis(*o*-tolylsulfane) (**3aa**). a yellowish liquid (58% yield, 39 mg). (PET/EtOAc =

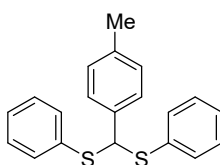
100:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.39 (m, 2H), 7.36–7.34 (d,  $J$  = 7.5 Hz, 2H), 7.30–7.25 (m, 3H), 7.16–7.15 (m, 4H), 7.11–7.07 (m, 3H), 5.31 (s, 1H), 2.31 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.10, 139.87, 133.98, 132.95, 130.23, 128.43, 128.00, 127.78, 127.75, 126.30, 59.78, 20.58. The spectral characteristics data were consistent with it reported previously in the literature.<sup>11</sup>



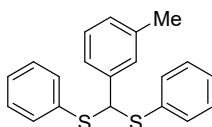
(*phenylmethylene*)bis(*(2-methoxyphenyl)sulfane*) (**3ab**). a yellowish liquid (31% yield, 23 mg). (PET/EtOAc = 100:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.37 (m, 2H), 7.21–7.24 (m, 3H), 7.18–7.14 (t,  $J$  = 8.0 Hz, 2H), 6.96–6.94 (m, 2H), 6.86–6.85 (m, 2H), 6.78–6.76 (m, 2H), 5.46 (s, 1H), 3.70 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.52, 139.61, 135.67, 129.58, 128.51, 128.06, 127.89, 124.33, 117.06, 113.86, 59.92, 55.20.



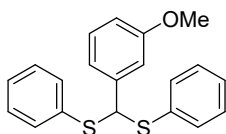
((*4-fluorophenyl*)methylene)bis(*phenylsulfane*) (**3ac**). a yellow liquid (34% yield, 22 mg). (PET/EtOAc = 100:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.31 (m, 4H), 7.30–7.28 (s, 2H), 7.25–7.23 (m, 6H), 6.95–6.91 (m, 2H), 5.39 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.42, 160.97, 135.43, 135.40, 134.09, 132.67, 129.60, 129.51, 128.87, 127.96, 115.42, 115.21, 59.53. The spectral characteristics data were consistent with it reported previously in the literature.<sup>8</sup>



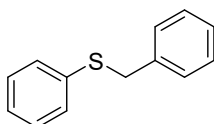
(*p-tolylmethylene*)bis(*phenylsulfane*) (**3ad**). a yellow solid (30% yield, 19.2 mg). (PET/EtOAc = 100:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.32 (m, 4H), 7.28–7.26 (m, 3H), 7.24–7.23 (m, 5H), 7.08 (d,  $J$  = 7.8 Hz, 2H), 5.41 (s, 1H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.47, 138.19, 134.64, 132.37, 128.84, 128.78, 128.43, 128.31, 127.69, 124.85, 60.39, 21.36. The spectral characteristics data were consistent with it reported previously in the literature.<sup>8</sup>



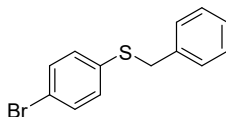
(*m-tolylmethylene*)bis(*phenylsulfane*) (**3ae**). a pink solid (43% yield, 28 mg). (PET/EtOAc = 100:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.33 (m, 4H), 7.26–7.24 (m, 6H), 7.19 (s, 1H), 7.17–7.15 (m, 2H), 7.08–7.04 (m, 1H), 5.40 (s, 1H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.84, 136.59, 134.75, 132.25, 129.17, 128.78, 127.69, 127.62, 60.06, 21.17. The spectral characteristics data were consistent with it reported previously in the literature.<sup>10</sup>



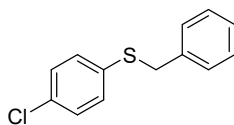
((3-methoxyphenyl)methylene)bis(phenylsulfane) (**3af**). a yellowish oily solid (66% yield, 45 mg). (PET/EtOAc = 100:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37–7.35 (m, 4H), 7.27–7.24 (m, 6H), 7.18 (t,  $J$  = 7.9 Hz, 1H), 6.95 (d,  $J$  = 7.7 Hz, 1H), 6.92–6.91 (m, 1H), 6.80–6.77 (m, 1H), 5.40 (s, 1H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.54, 141.11, 134.47, 132.46, 129.43, 128.81, 127.77, 120.19, 114.02, 112.92, 60.32, 55.22. The spectral characteristics data were consistent with it reported previously in the literature.<sup>11</sup>



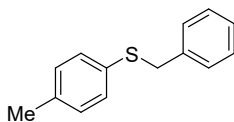
benzyl(phenyl)sulfane (**5a**). a pink solid (64% yield, 44 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (t,  $J$  = 1.8 Hz, 1H), 7.29–7.27 (m, 5H), 7.26–7.25 (m, 1H), 7.24–7.22 (m, 2H), 7.19–7.15 (m, 1H), 4.11 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.37, 136.30, 129.71, 128.79, 128.77, 128.44, 127.13, 126.27, 38.94. The spectral characteristics data were consistent with it reported previously in the literature.<sup>12</sup>



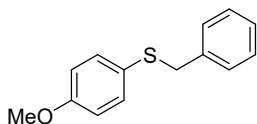
benzyl(4-bromophenyl)sulfane (**5b**). a white solid (94% yield, 90 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38–7.34 (m, 2H), 7.30–7.24 (m, 5H), 7.16–7.13 (m, 2H), 4.09 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.98, 135.36, 131.83, 131.42, 128.76, 128.54, 127.31, 120.28, 39.02. The spectral characteristics data were consistent with it reported previously in the literature.<sup>12</sup>



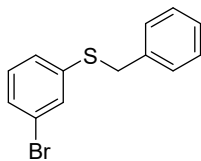
benzyl(4-chlorophenyl)sulfane (**5c**). a white solid (77% yield, 61 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.25 (m, 5H), 7.23–7.21 (m, 4H), 4.08 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.06, 134.60, 132.42, 131.36, 128.91, 128.76, 128.52, 127.28, 39.25. The spectral characteristics data were consistent with it reported previously in the literature.<sup>12</sup>



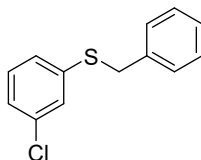
benzyl(p-tolyl)sulfane (**5d**). a white solid (82% yield, 60 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26–7.24 (m, 4H), 7.22–7.18 (m, 3H), 7.04 (d,  $J$  = 8.0 Hz, 2H), 4.05 (s, 2H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.85, 136.61, 132.54, 130.73, 129.69, 128.91, 128.51, 127.15, 39.81, 21.15. The spectral characteristics data were consistent with it reported previously in the literature.<sup>12</sup>



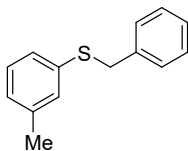
*benzyl(4-methoxyphenyl)sulfane (5e)*. a white solid (76% yield, 48 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27–7.21 (m, 5H), 7.20–7.16 (m, 3H), 6.79–6.75 (m, 2H), 3.97 (s, 2H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.23, 138.17, 134.13, 128.95, 128.42, 127.04, 126.07, 114.46, 55.34, 41.26. The spectral characteristics data were consistent with it reported previously in the literature.<sup>12</sup>



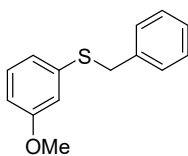
*benzyl(3-bromophenyl)sulfane (5f)*. a white solid (63% yield, 60 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (t,  $J$  = 1.8 Hz, 1H), 7.33–7.26 (m, 6H), 7.23–7.20 (m, 1H), 7.14 (t,  $J$  = 7.9 Hz, 1H), 4.14 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.81, 136.63, 131.68, 130.05, 129.13, 128.79, 128.55, 127.73, 127.37, 122.62, 38.60. The spectral characteristics data were consistent with it reported previously in the literature.<sup>14</sup>



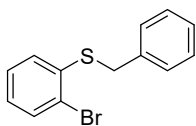
*benzyl(3-chlorophenyl)sulfane (5g)*. a white solid (86% yield, 69 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.26 (m, 6H), 7.20–7.15 (m, 3H), 4.15 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.54, 136.63, 134.46, 129.75, 128.76, 128.53, 127.34, 127.17, 126.19, 38.49. The spectral characteristics data were consistent with it reported previously in the literature.<sup>14</sup>



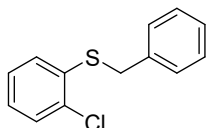
*benzyl(m-tolyl)sulfane (5h)*. a yellow oily liquid (82% yield, 60 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32–7.30 (m, 4H), 7.27–7.22 (m, 1H), 7.16–7.11 (m, 3H), 7.01–7.00 (d,  $J$  = 7.2 Hz, 1H), 4.13 (s, 2H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.56, 137.50, 136.13, 130.36, 128.83, 128.65, 128.44, 127.15, 127.12, 126.64, 38.97, 21.29. The spectral characteristics data were consistent with it reported previously in the literature.<sup>12</sup>



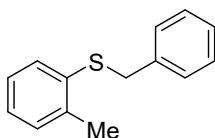
*benzyl(3-methoxyphenyl)sulfane (5i)*. a colorless liquid (76% yield, 60 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.27 (m, 4H), 7.26–7.22 (m, 1H), 7.17 (t,  $J$  = 8.0 Hz, 1H), 6.92–6.90 (m, 1H), 6.84–6.82 (m, 1H), 6.74–6.71 (m, 1H), 4.13 (s, 2H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.63, 137.67, 137.30, 129.60, 128.78, 128.46, 127.15, 121.59, 114.60, 112.11, 55.15, 38.70. The spectral characteristics data were consistent with it reported previously in the literature.<sup>13</sup>



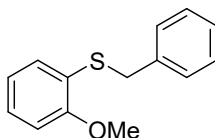
*benzyl(2-bromophenyl)sulfane (5j)*. a white solid (71% yield, 68 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58–7.56 (m, 1H), 7.40–7.38 (m, 2H), 7.36–7.32 (m, 2H), 7.31–7.27 (m, 1H), 7.26–7.21 (m, 2H), 7.07–7.02 (m, 1H), 4.17 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.82, 136.03, 132.83, 128.88, 128.67, 128.53, 127.65, 127.36, 126.80, 123.52, 37.80. The spectral characteristics data were consistent with it reported previously in the literature.<sup>12</sup>



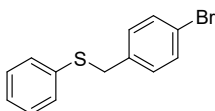
*benzyl(2-chlorophenyl)sulfane (5k)*. a white solid (86% yield, 69 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41–7.37 (m, 3H), 7.35–7.31 (m, 2H), 7.30–7.26 (m, 2H), 7.20–7.16 (m, 1H), 7.15–7.11 (m, 1H), 4.18 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.18, 135.69, 133.45, 129.53, 129.02, 128.84, 128.51, 127.32, 127.00, 126.73, 37.33. The spectral characteristics data were consistent with it reported previously in the literature.<sup>12</sup>



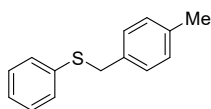
*benzyl(o-tolyl)sulfane (5l)*. a colorless liquid (71% yield, 54 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.20 (m, 6H), 7.15–7.06 (m, 3H), 4.07 (s, 2H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.79, 137.19, 135.73, 129.99, 128.83, 128.77, 128.45, 127.15, 126.36, 126.02, 38.21, 20.26. The spectral characteristics data were consistent with it reported previously in the literature.<sup>12</sup>



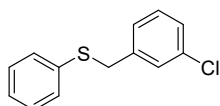
*benzyl(2-methoxyphenyl)sulfane (5m)*. a white solid (78% yield, 61 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.27 (m, 2H), 7.26–7.24 (m, 2H), 7.22–7.16 (m, 3H), 6.88–6.83 (m, 2H), 4.09 (s, 2H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.41, 137.40, 130.28, 128.84, 128.34, 127.52, 127.00, 124.32, 120.91, 110.35, 55.71, 37.13. The spectral characteristics data were consistent with it reported previously in the literature.<sup>13</sup>



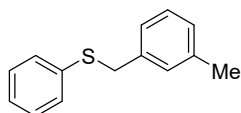
*(4-bromobenzyl)(phenyl)sulfane (5n)*. a white solid (79% yield, 76 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.38 (m, 2H), 7.31–7.24 (m, 4H), 7.23–7.18 (m, 1H), 7.16–7.13 (m, 2H), 4.05 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.73, 135.68, 131.63, 130.54, 130.32, 129.00, 126.76, 121.10, 38.66. The spectral characteristics data were consistent with it reported previously in the literature.<sup>16</sup>



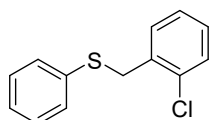
(4-methylbenzyl)(phenyl)sulfane (**5o**). a white solid (90% yield, 66 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.31 (m, 2H), 7.28–7.25 (m, 2H), 7.21–7.16 (m, 3H), 7.11 (d,  $J$  = 7.9 Hz, 2H), 4.11 (s, 2H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.90, 136.69, 134.35, 129.63, 129.26, 128.88, 128.77, 126.25, 38.71, 21.18. The spectral characteristics data were consistent with it reported previously in the literature.<sup>17</sup>



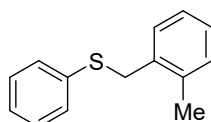
(3-chlorobenzyl)(phenyl)sulfane (**5p**). a yellow oily liquid (81% yield, 65 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.26 (m, 5H), 7.24–7.19 (m, 3H), 7.17–7.15 (m, 1H), 4.07 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.69, 135.65, 134.26, 130.27, 129.73, 128.98, 128.95, 127.39, 126.99, 126.77, 38.73. The spectral characteristics data were consistent with it reported previously in the literature.<sup>16</sup>



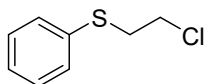
(3-methylbenzyl)(phenyl)sulfane (**5q**). a colorless oily liquid (85% yield, 62 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.27 (m, 2H), 7.25–7.21 (m, 2H), 7.17–7.13 (m, 2H), 7.10–7.06 (m, 2H), 7.03 (d,  $J$  = 7.5 Hz, 1H), 4.06 (s, 2H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.16, 137.25, 136.66, 129.60, 128.84, 128.40, 127.99, 126.24, 125.89, 38.94, 21.39. The spectral characteristics data were consistent with it reported previously in the literature.<sup>17</sup>



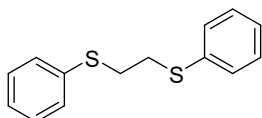
(2-chlorobenzyl)(phenyl)sulfane (**5r**). a colorless oily liquid (54% yield, 43 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39–7.37 (m, 1H), 7.36–7.33 (m, 2H), 7.30–7.15 (m, 6H), 4.23 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.77, 135.25, 134.11, 130.75, 130.72, 129.71, 128.94, 128.64, 126.81, 126.80, 37.03. The spectral characteristics data were consistent with it reported previously in the literature.<sup>16</sup>



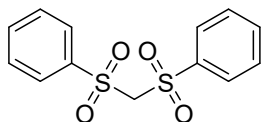
(2-methylbenzyl)(phenyl)sulfane (**5s**). a yellowish oily liquid (85% yield, 62 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.37 (m, 2H), 7.35–7.31 (m, 2H), 7.28–7.24 (m, 1H), 7.24–7.21 (m, 3H), 7.18–7.13 (m, 1H), 4.17 (s, 2H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.77, 136.66, 135.05, 130.51, 130.18, 129.81, 128.87, 127.56, 126.45, 126.05, 37.39, 19.23. The spectral characteristics data were consistent with it reported previously in the literature.<sup>17</sup>



(2-chloroethyl)(phenyl)sulfane (**5t**). a colorless liquid (79% yield, 54 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.37 (m, 2H), 7.33–7.29 (m, 2H), 7.26–7.22 (m, 1H), 3.62–3.58 (m, 2H), 3.23–3.19 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.16, 130.41, 129.16, 127.01, 42.25, 36.06. The spectral characteristics data were consistent with it reported previously in the literature.<sup>15</sup>



1,2-bis(phenylthio)ethane (**5u**). a white solid (89% yield, 44 mg). (PET/EtOAc = 70:1 as the eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (t,  $J = 2.2$  Hz, 1H), 7.30 (d,  $J = 1.6$  Hz, 4H), 7.28 (d,  $J = 2.0$  Hz, 2H), 7.26 (t,  $J = 1.8$  Hz, 1H), 7.24–7.19 (m, 2H), 3.09 (s, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.03, 130.06, 129.08, 126.61, 33.38. The spectral characteristics data were consistent with it reported previously in the literature.<sup>18</sup>

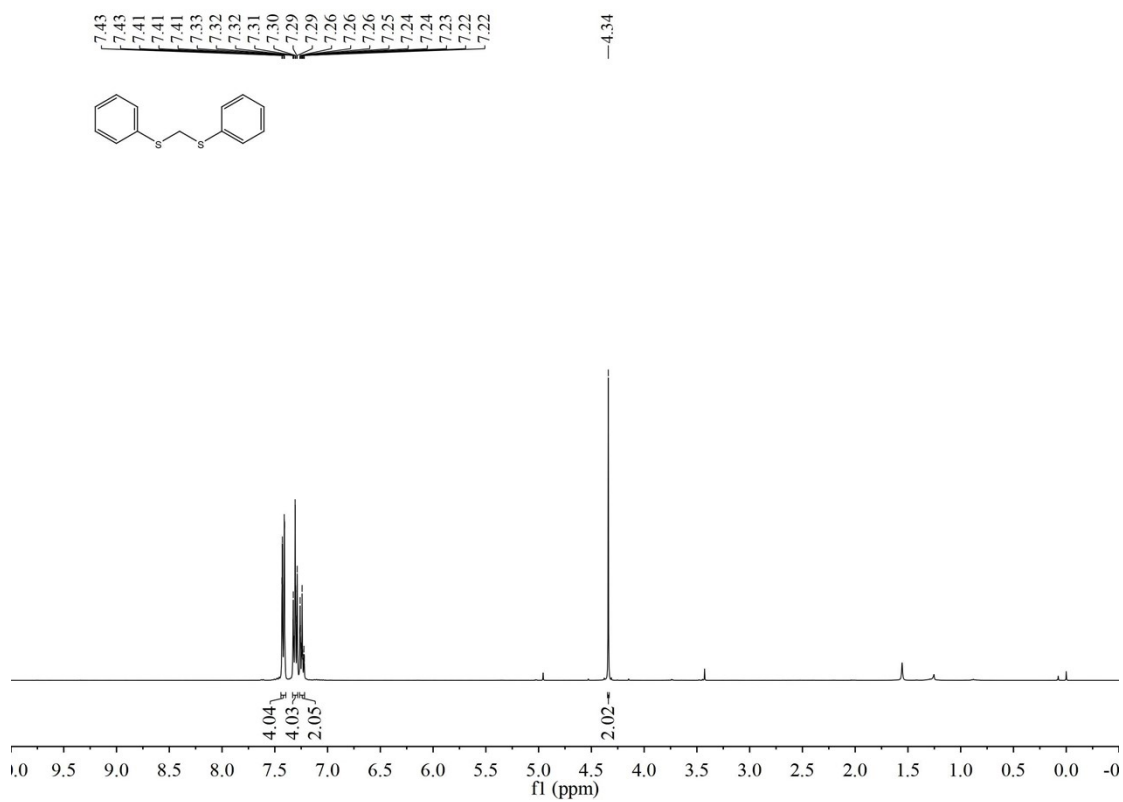


bis(phenylsulfonyl)methane (**6a**). a white solid (70% yield, 180 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98–7.95 (m, 4H), 7.74–7.70 (m, 2H), 7.61–7.57 (m, 4H), 4.76 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.45, 134.90, 129.45, 128.93, 74.54. The spectral characteristics data were consistent with it reported previously in the literature.<sup>5</sup>

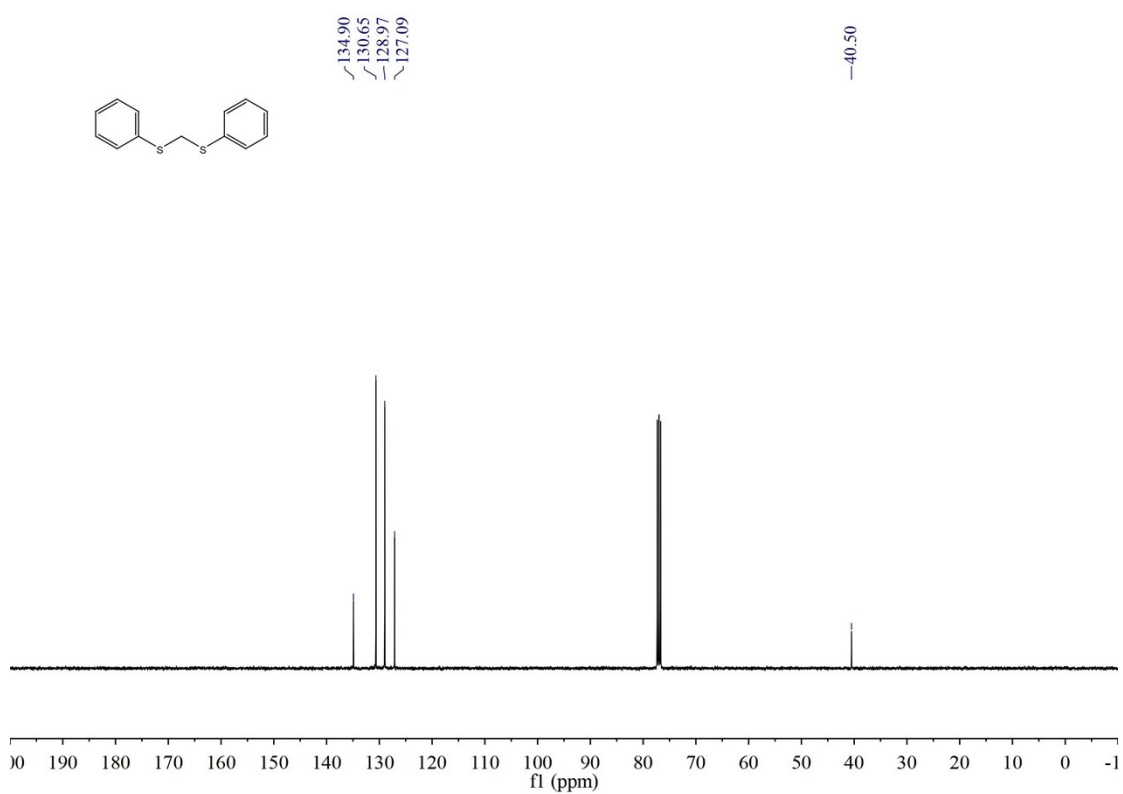


## IX. NMR charts of 3a-6a

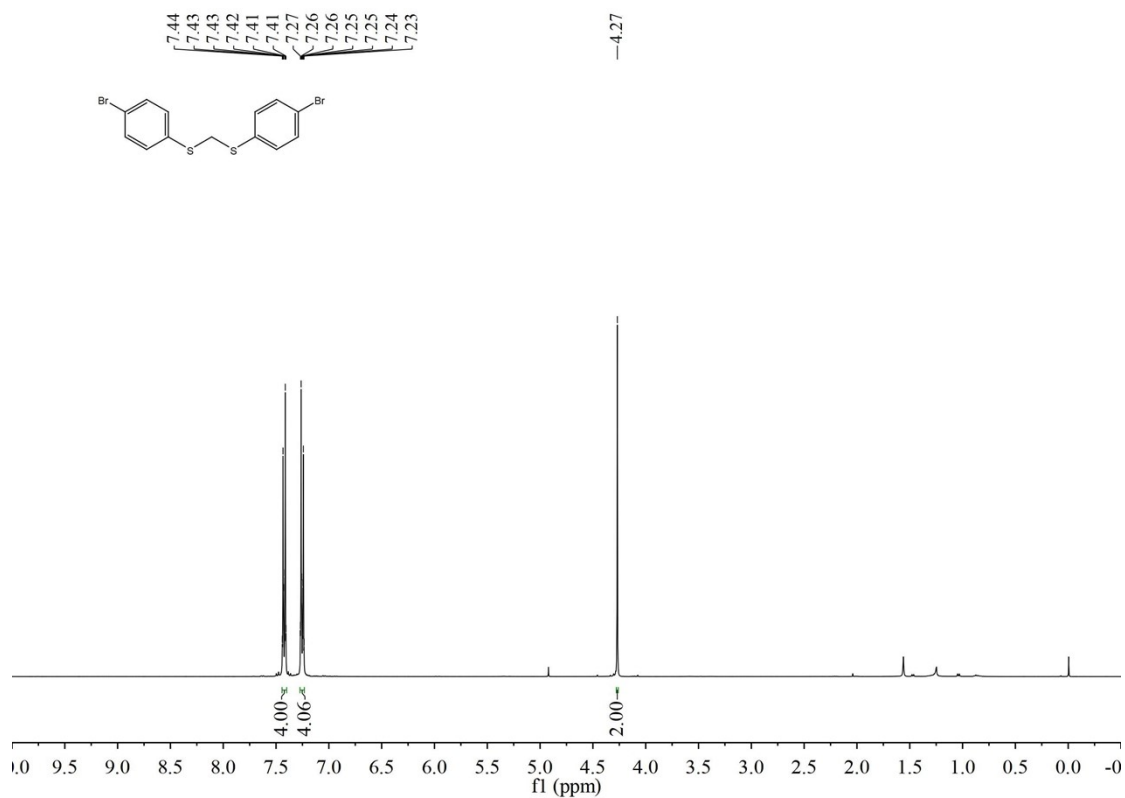
**3a-<sup>1</sup>H**



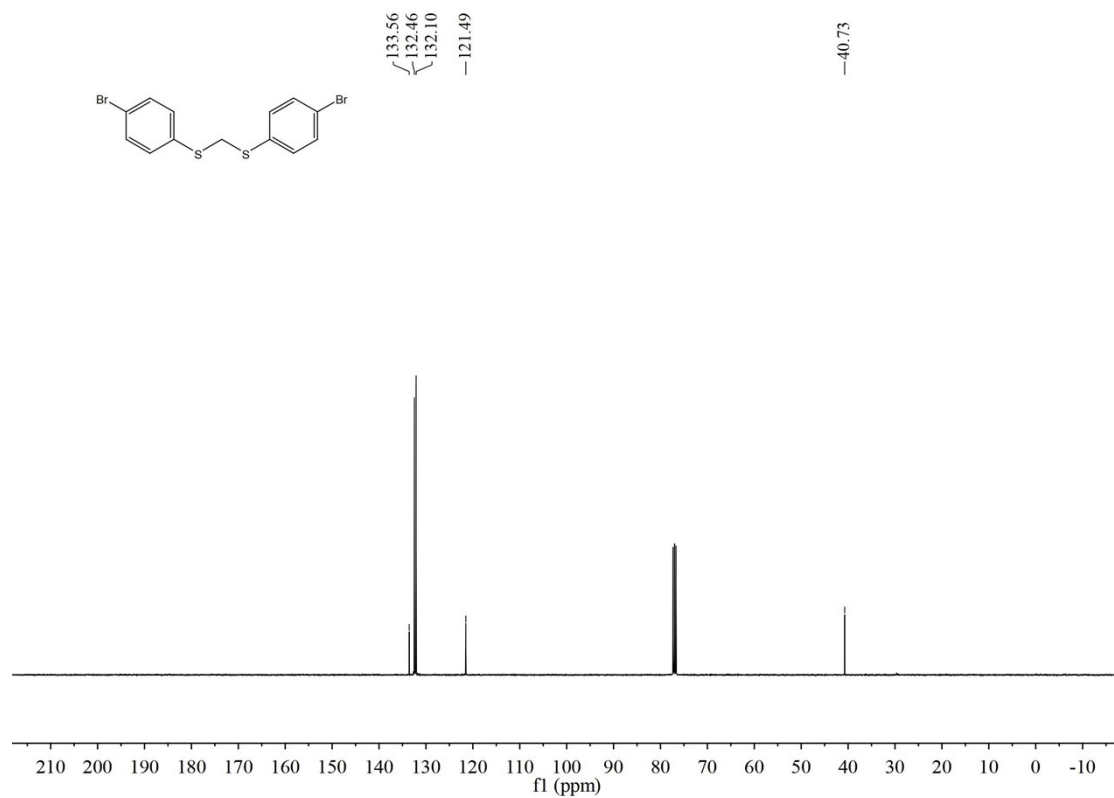
**3a-<sup>13</sup>C**



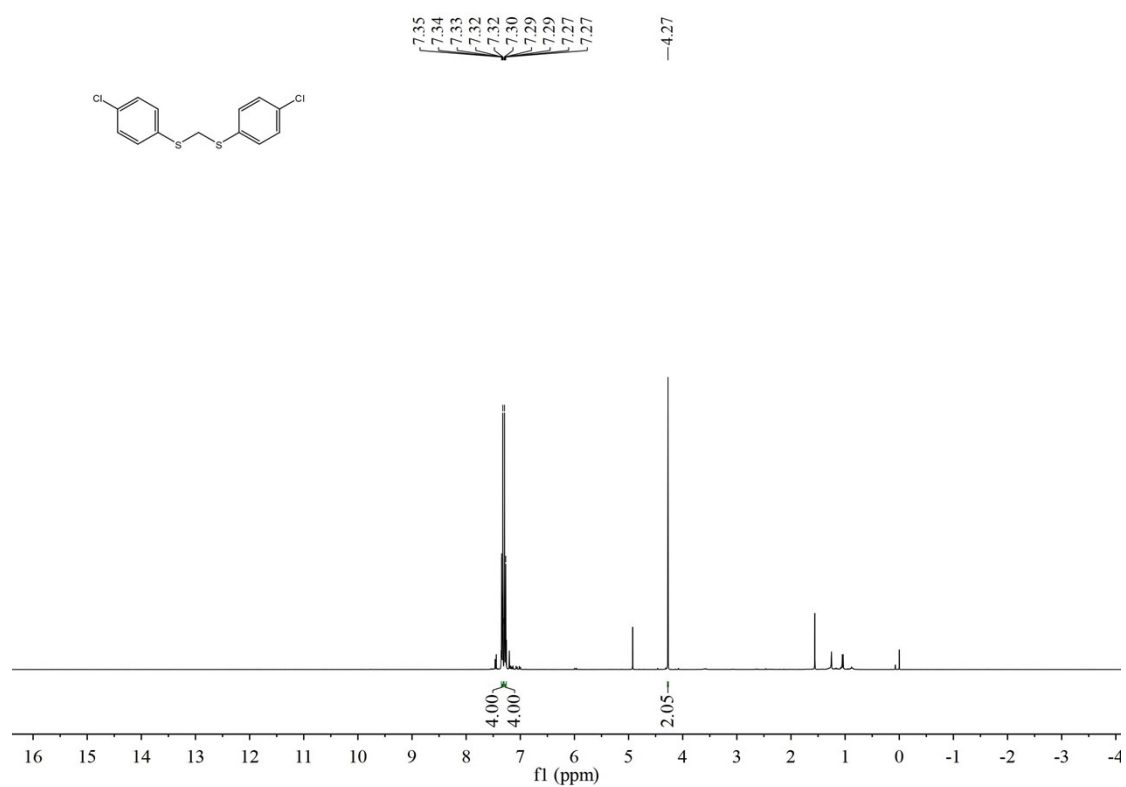
**3b-<sup>1</sup>H**



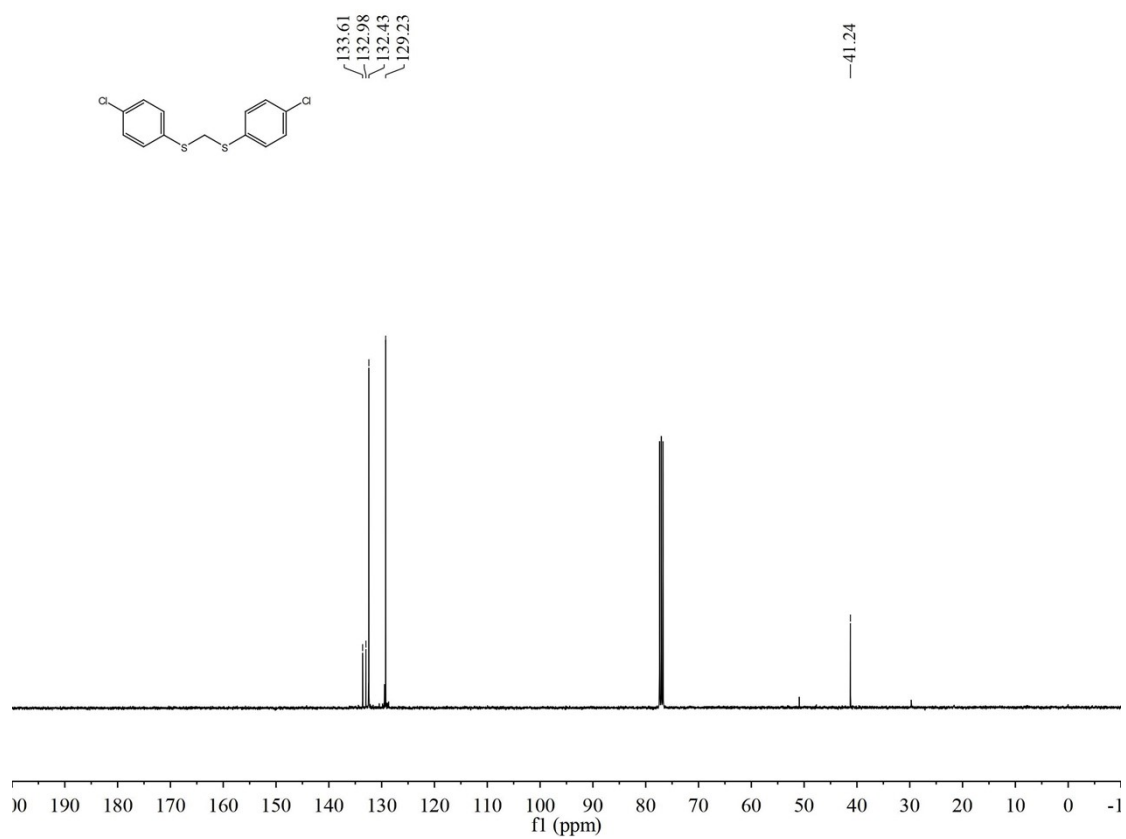
**3b-<sup>13</sup>C**



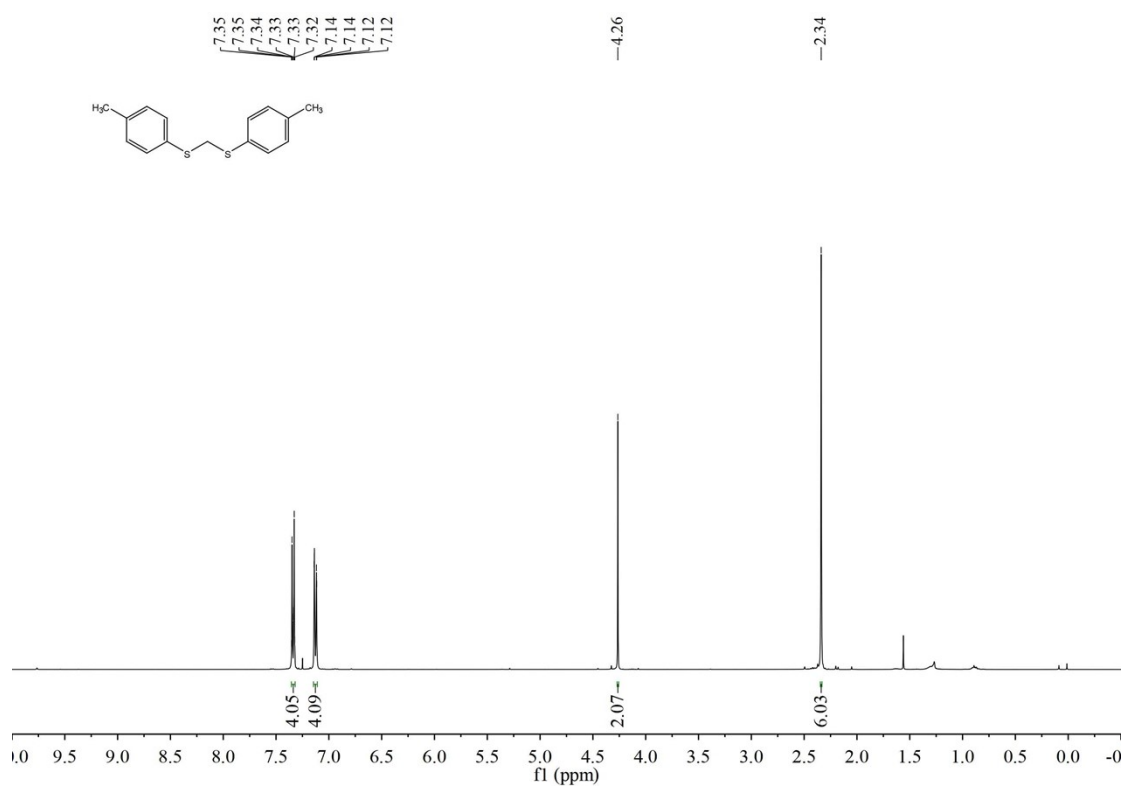
**3c-<sup>1</sup>H**



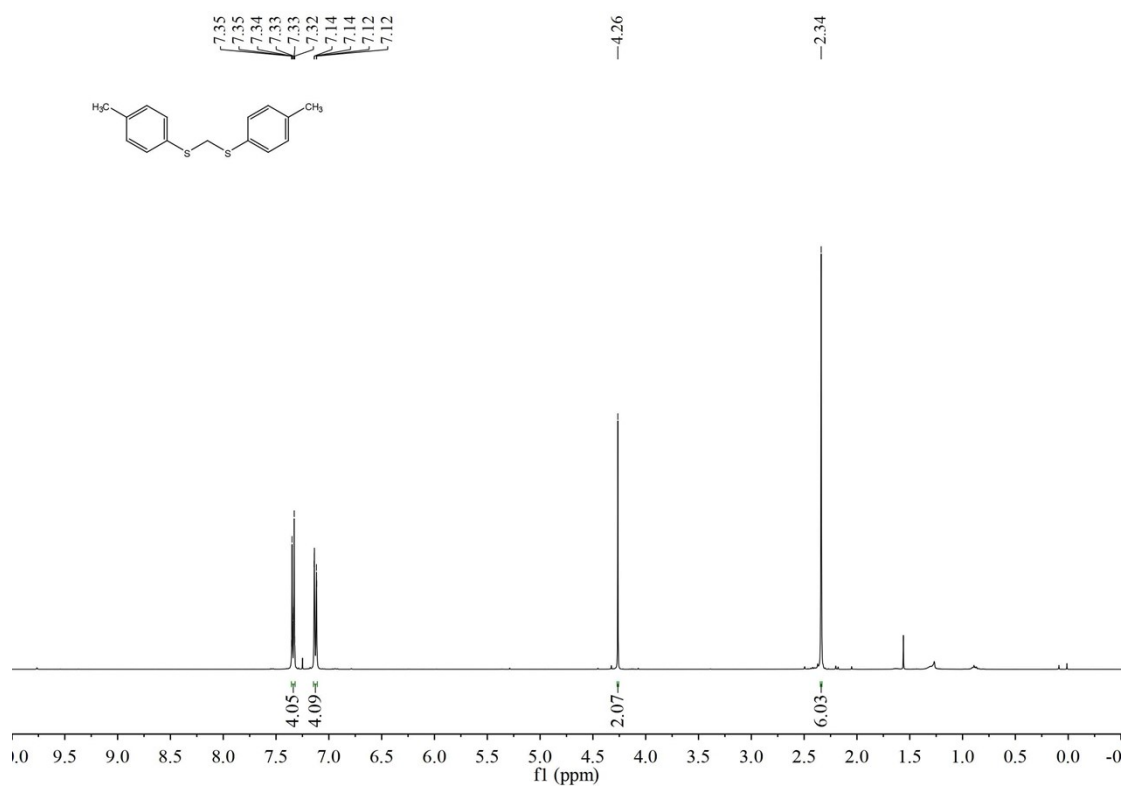
**3c-<sup>13</sup>C**



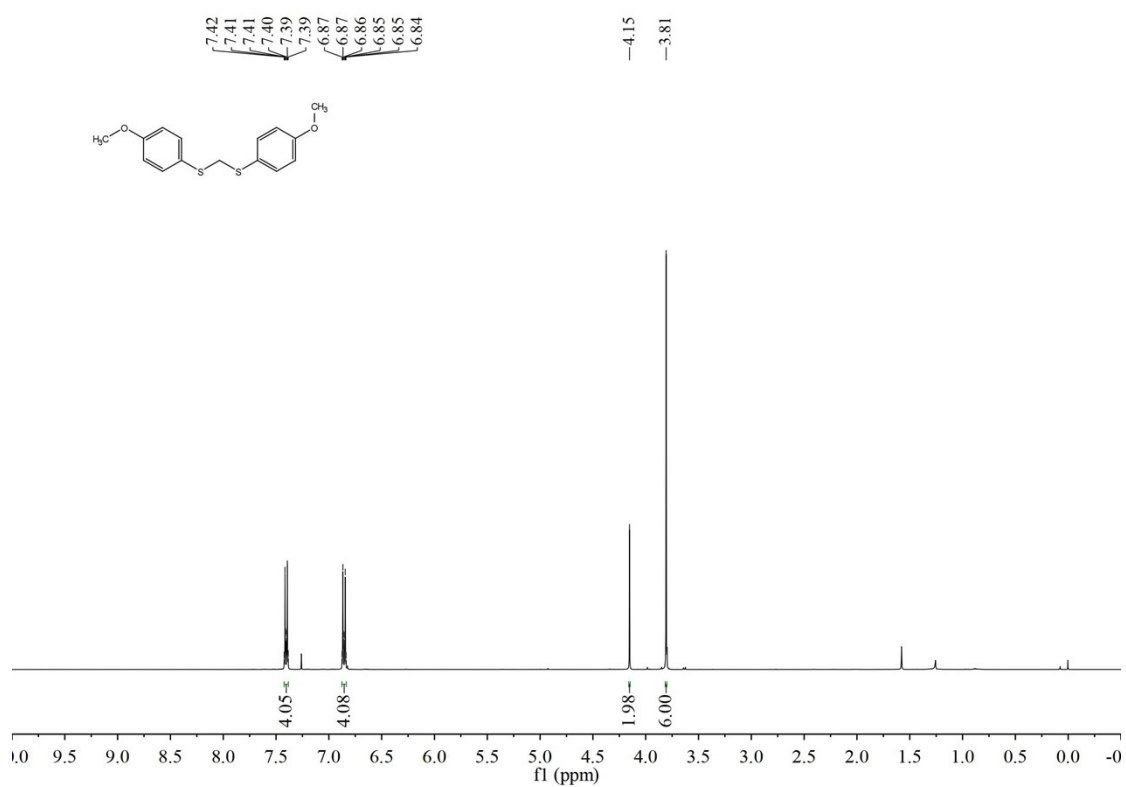
**3d-<sup>1</sup>H**



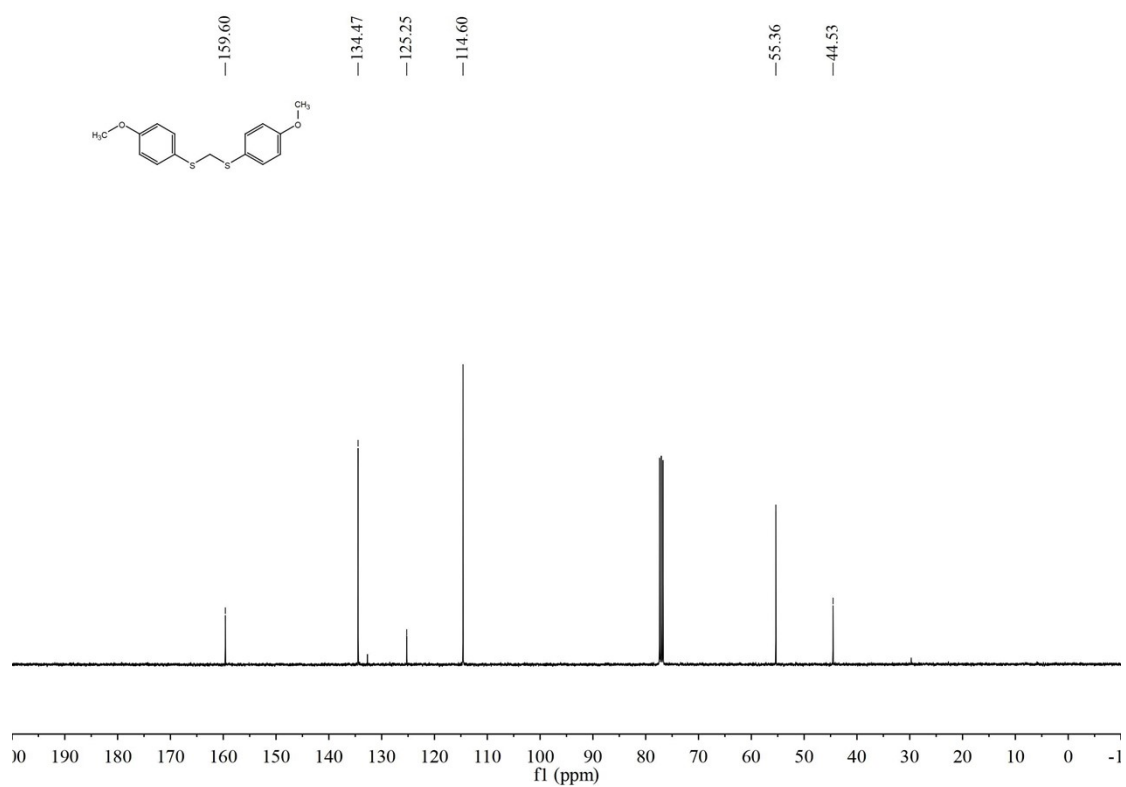
**3d-<sup>13</sup>C**



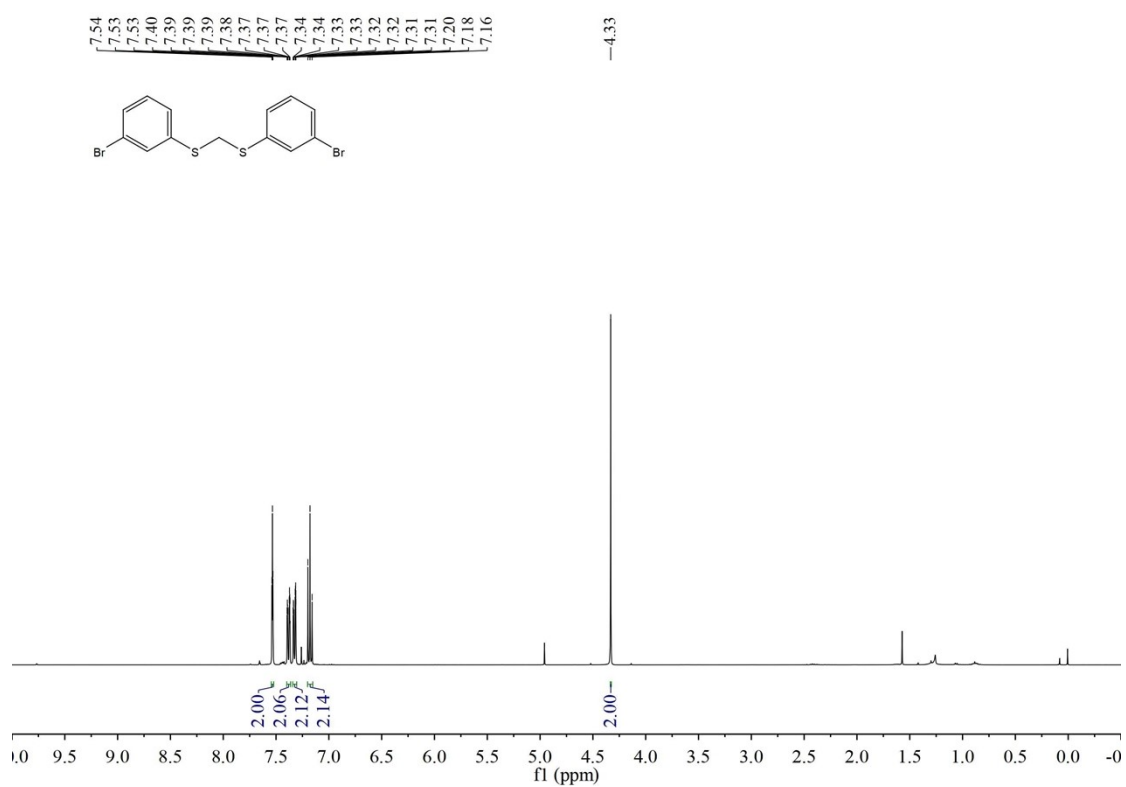
**3e-<sup>1</sup>H**



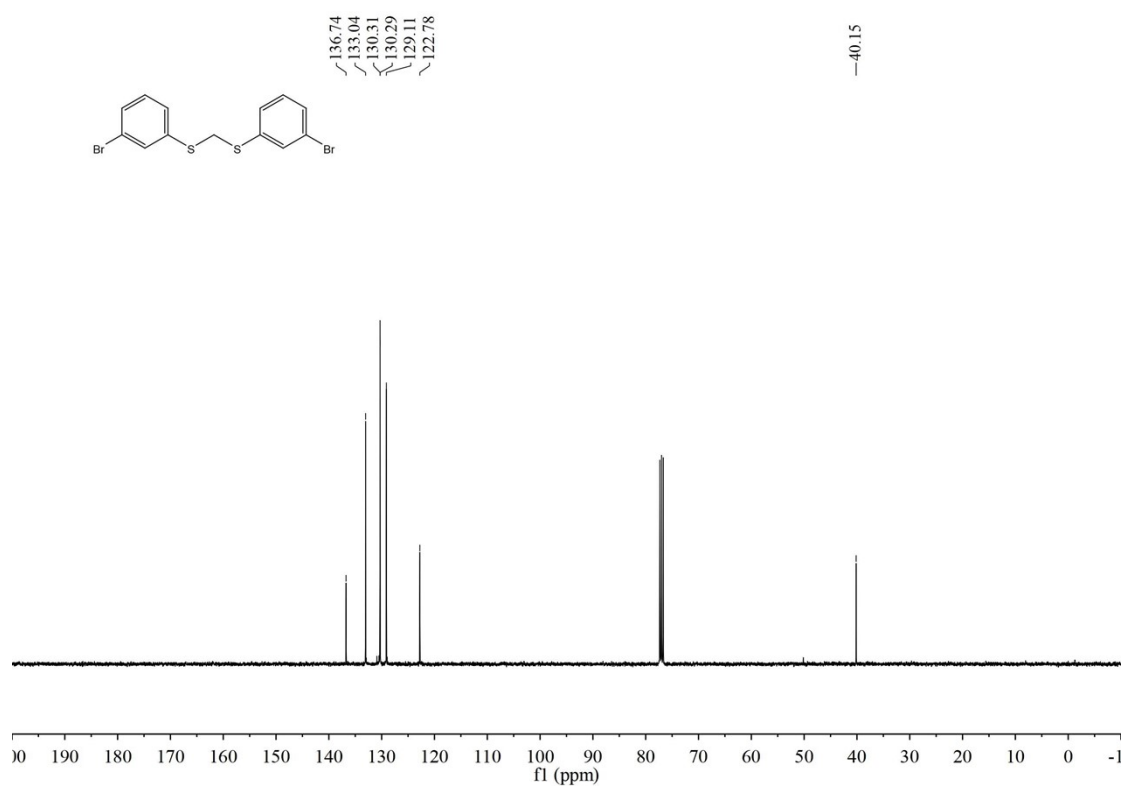
**3e-<sup>13</sup>C**



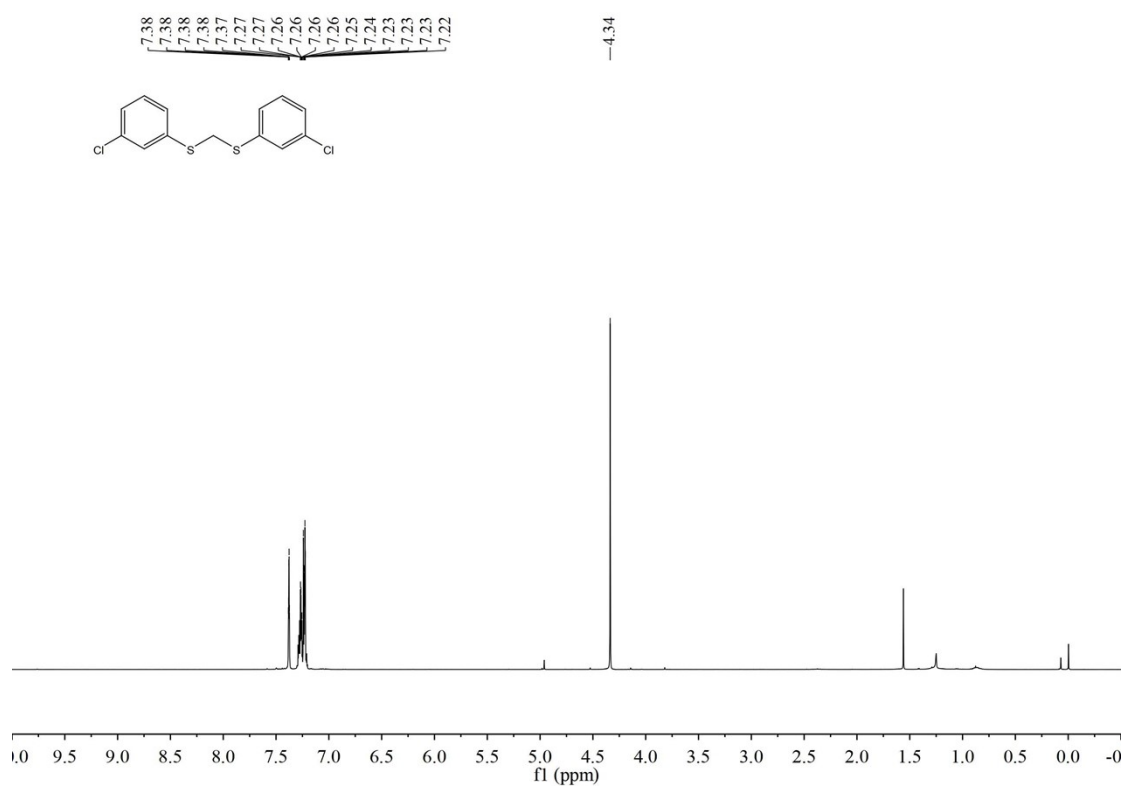
**3f-<sup>1</sup>H**



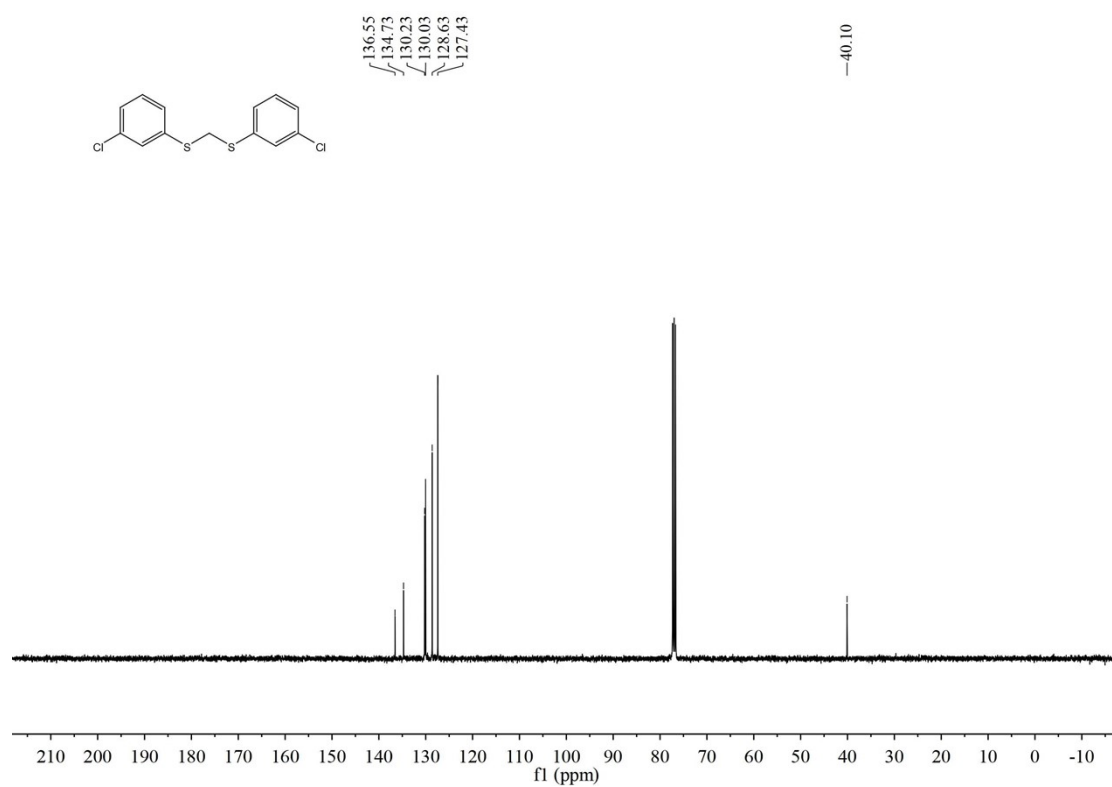
**4f-<sup>13</sup>C**



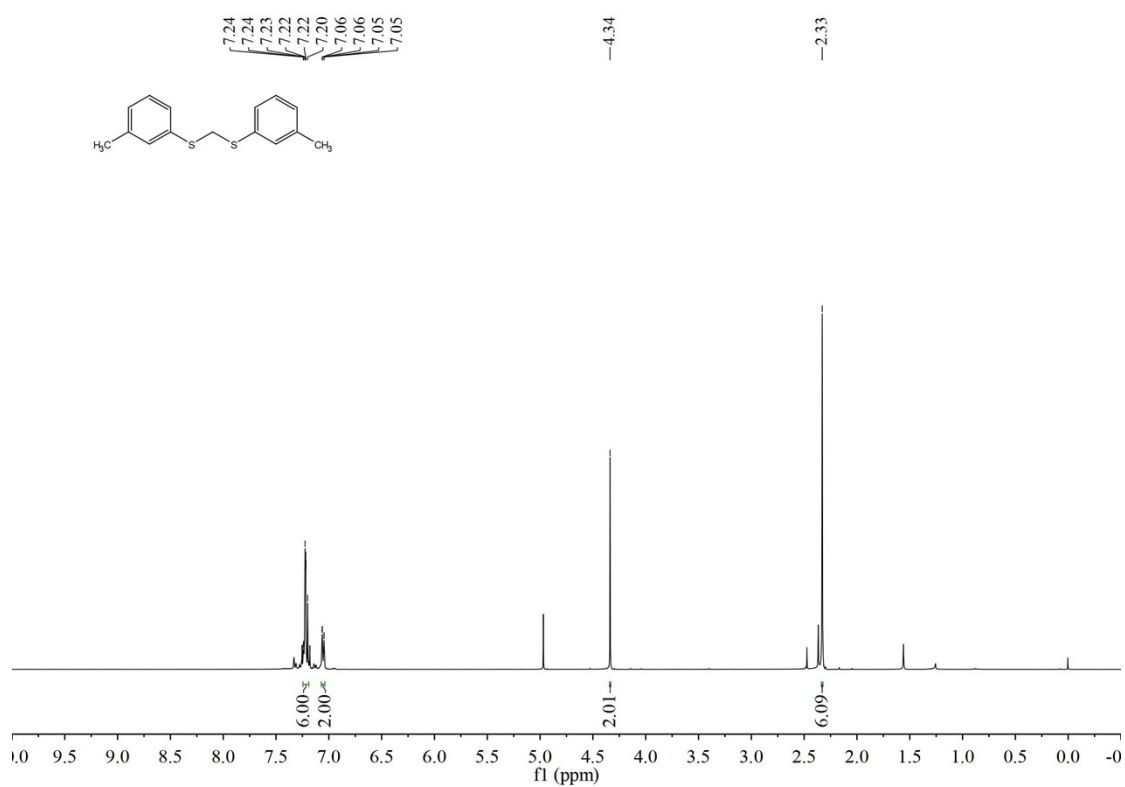
**3g-<sup>1</sup>H**



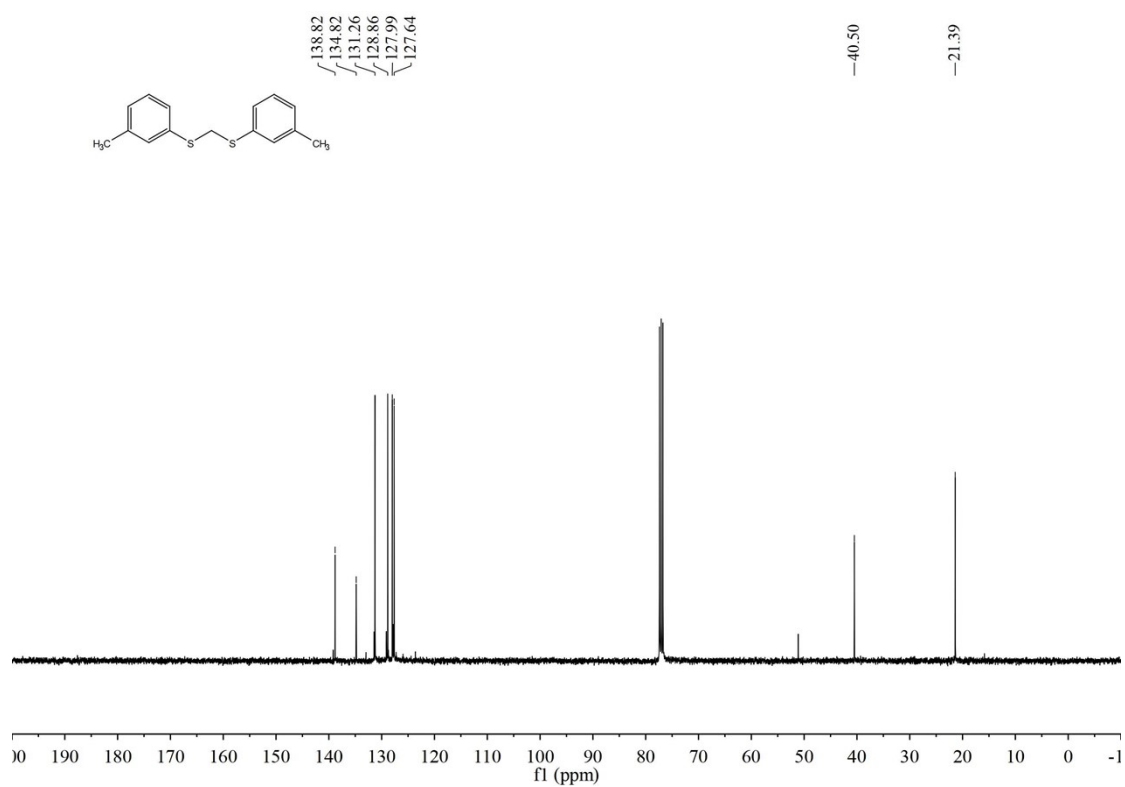
**3g-<sup>13</sup>C**



**3h-<sup>1</sup>H**

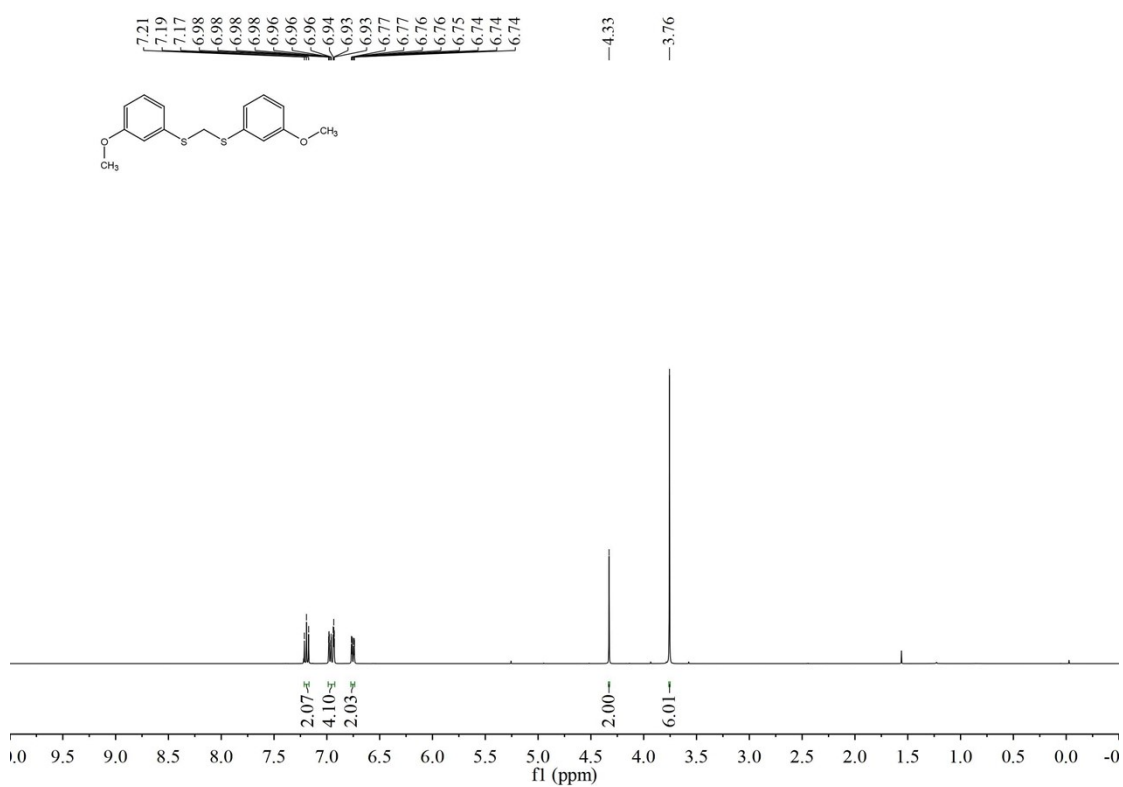


**3h-<sup>13</sup>C**

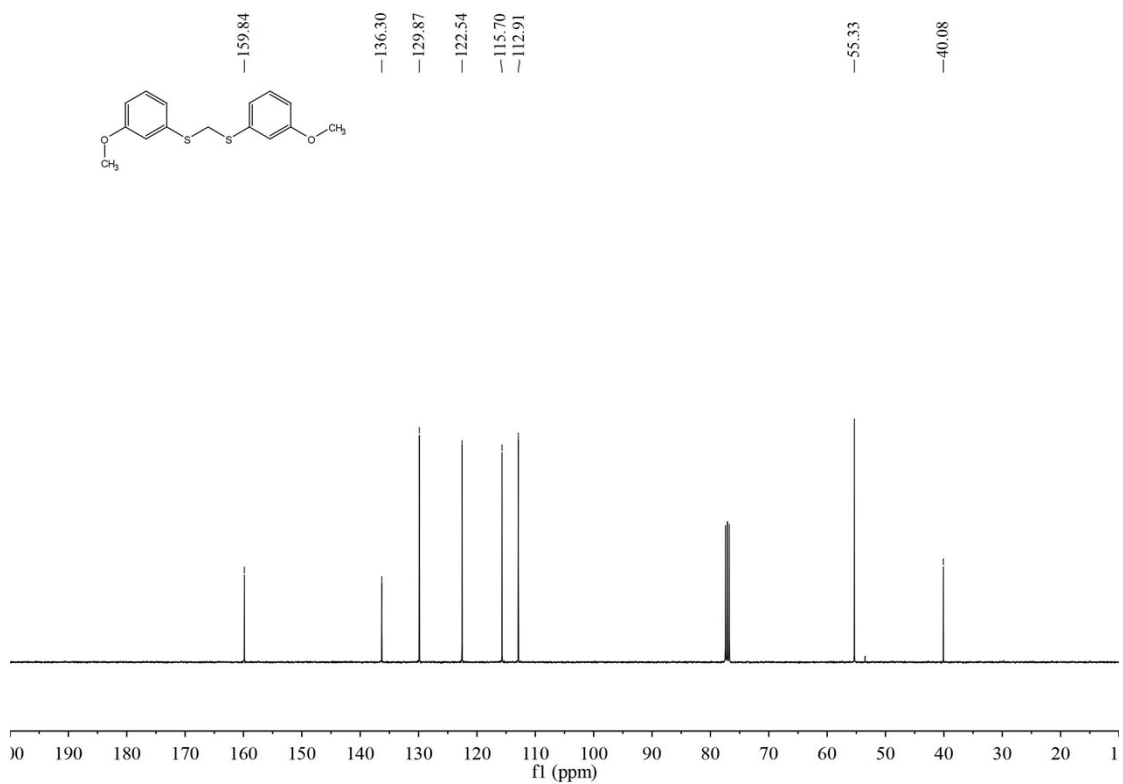




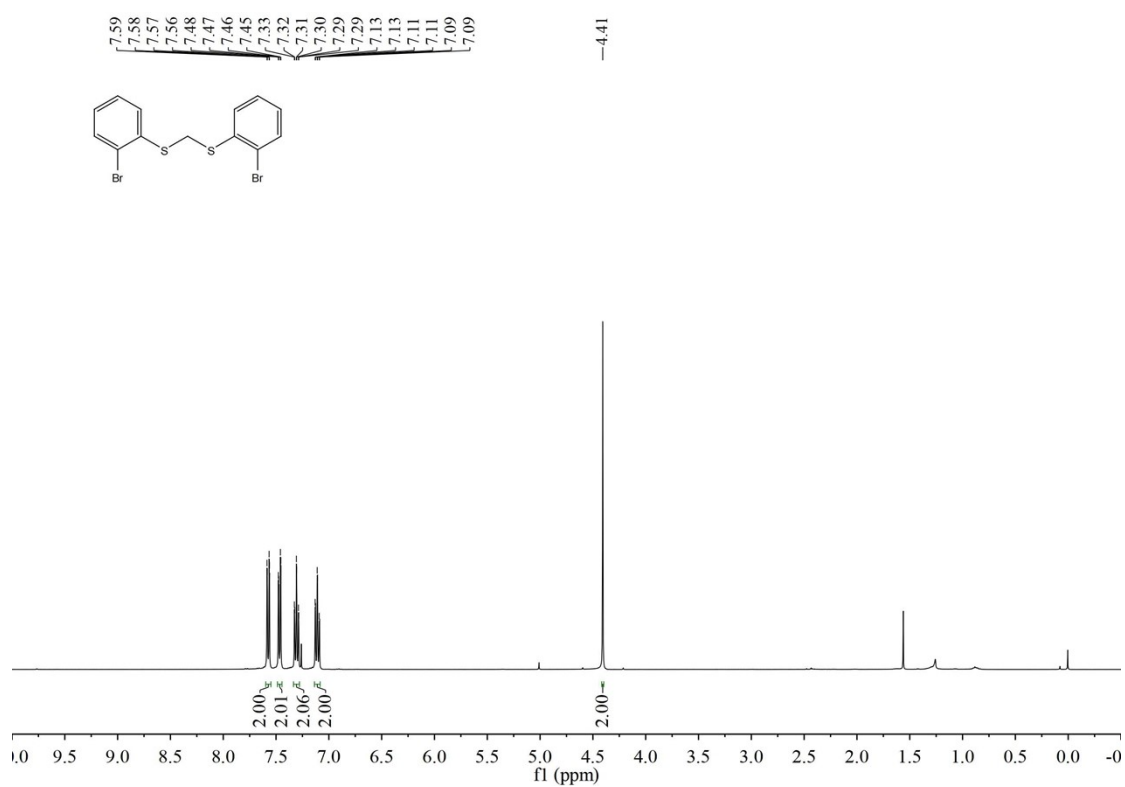
**3i-<sup>1</sup>H**



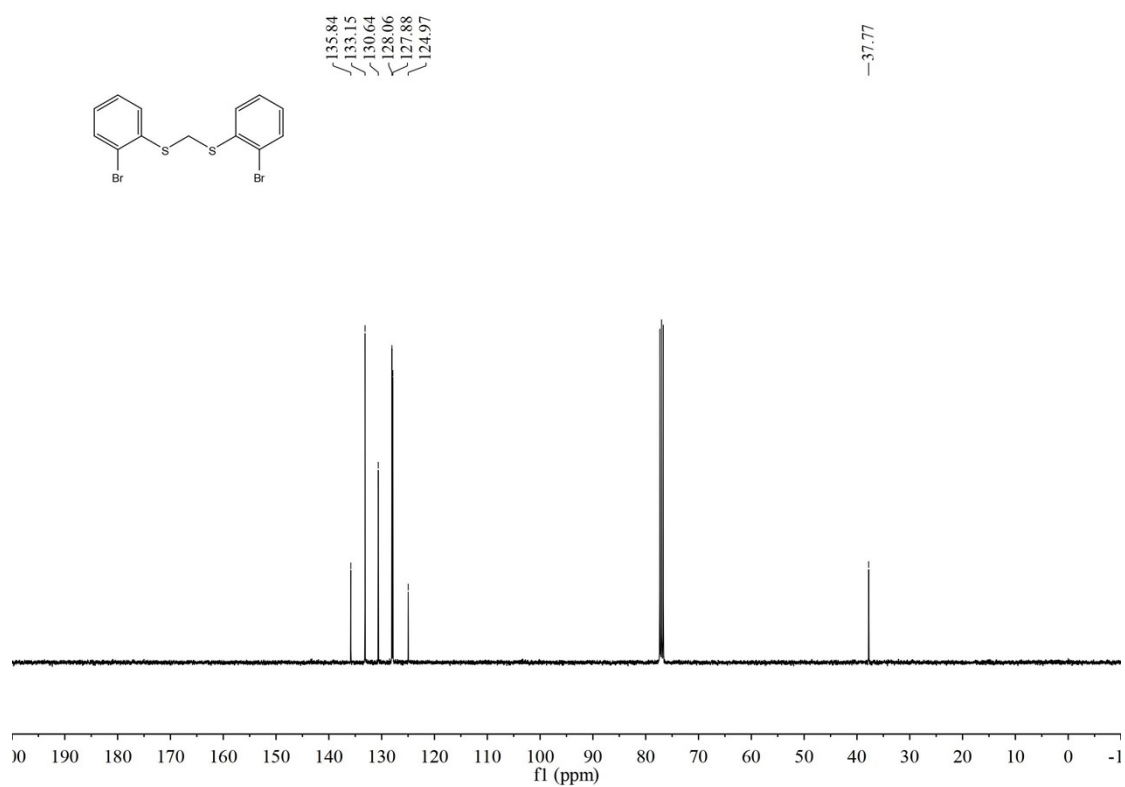
**3i-<sup>13</sup>C**



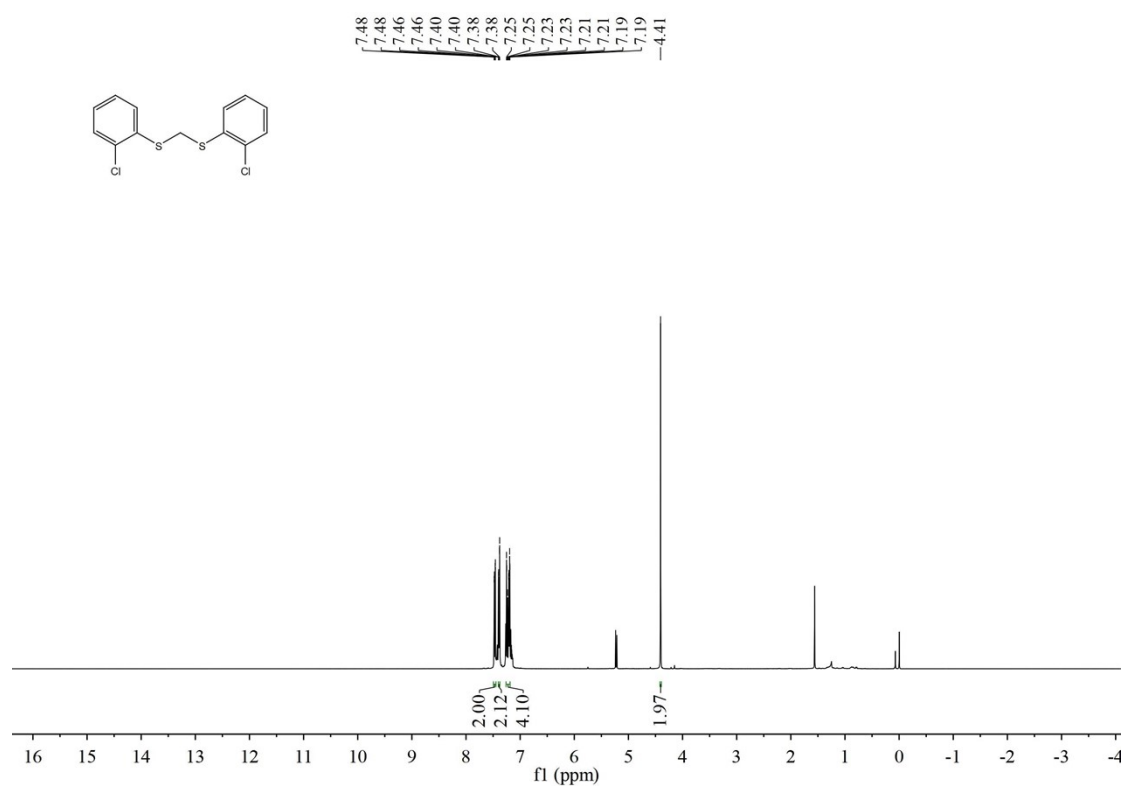
**3j-<sup>1</sup>H**



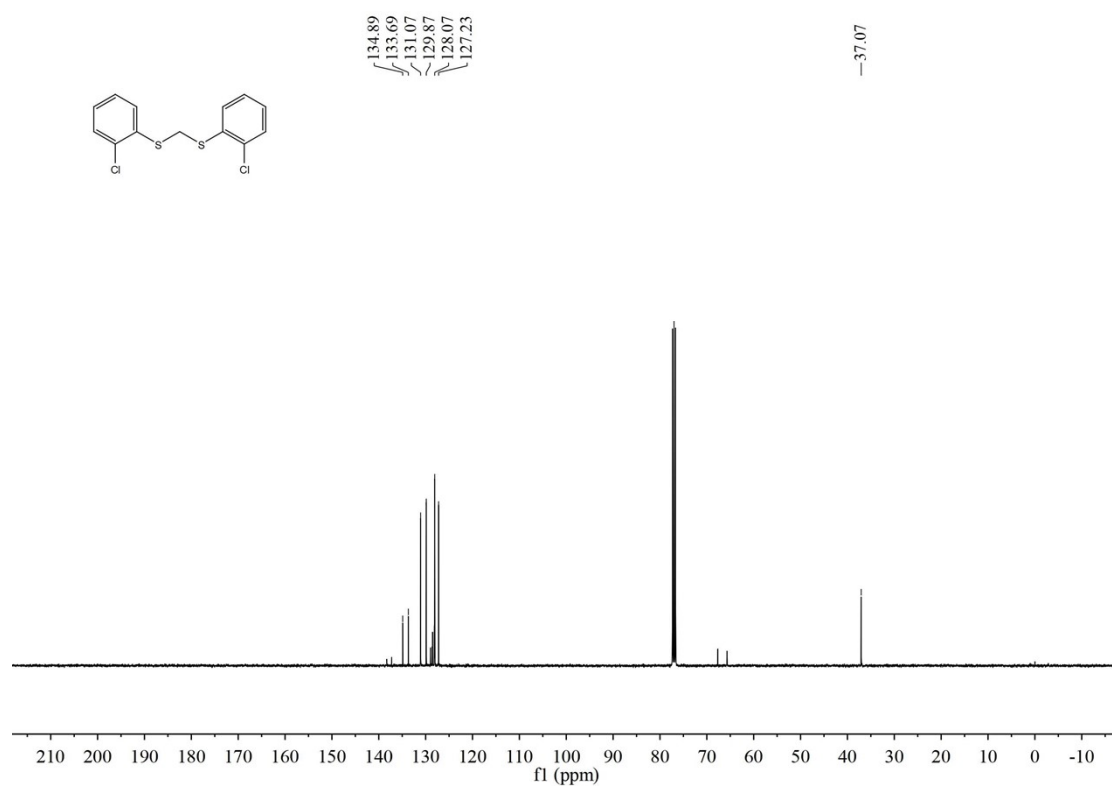
**3j-<sup>13</sup>C**



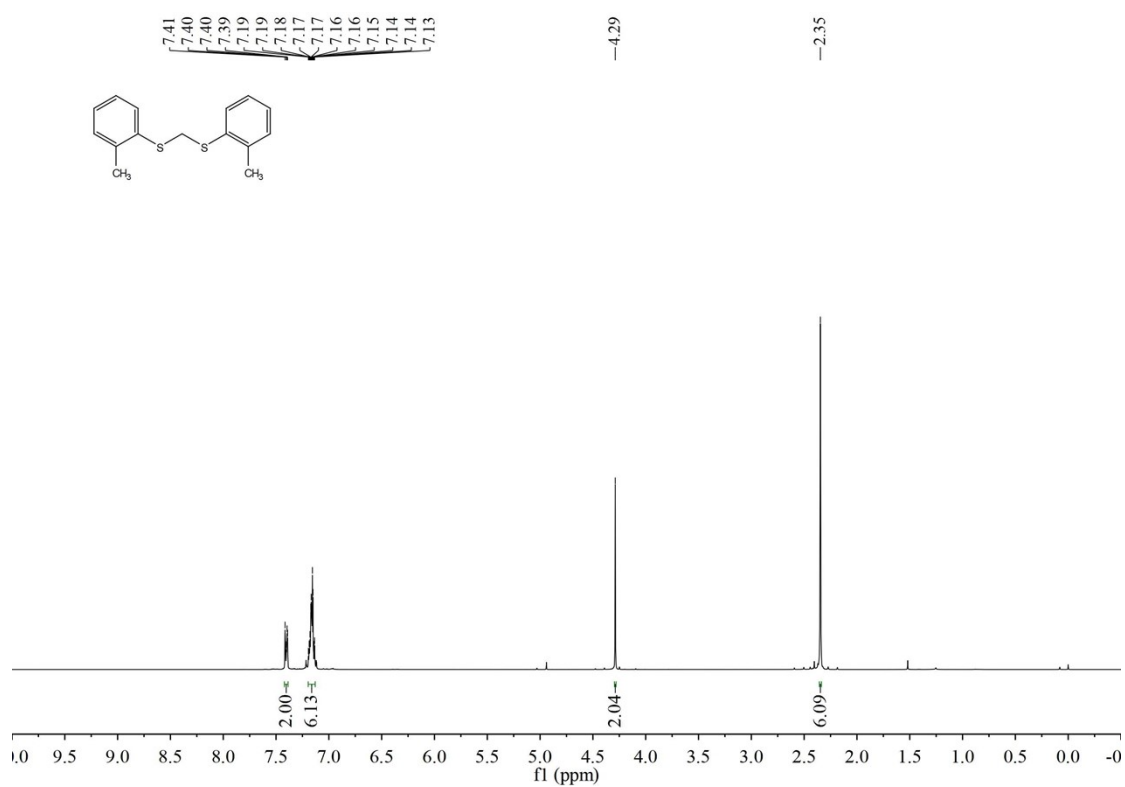
**3k-<sup>1</sup>H**



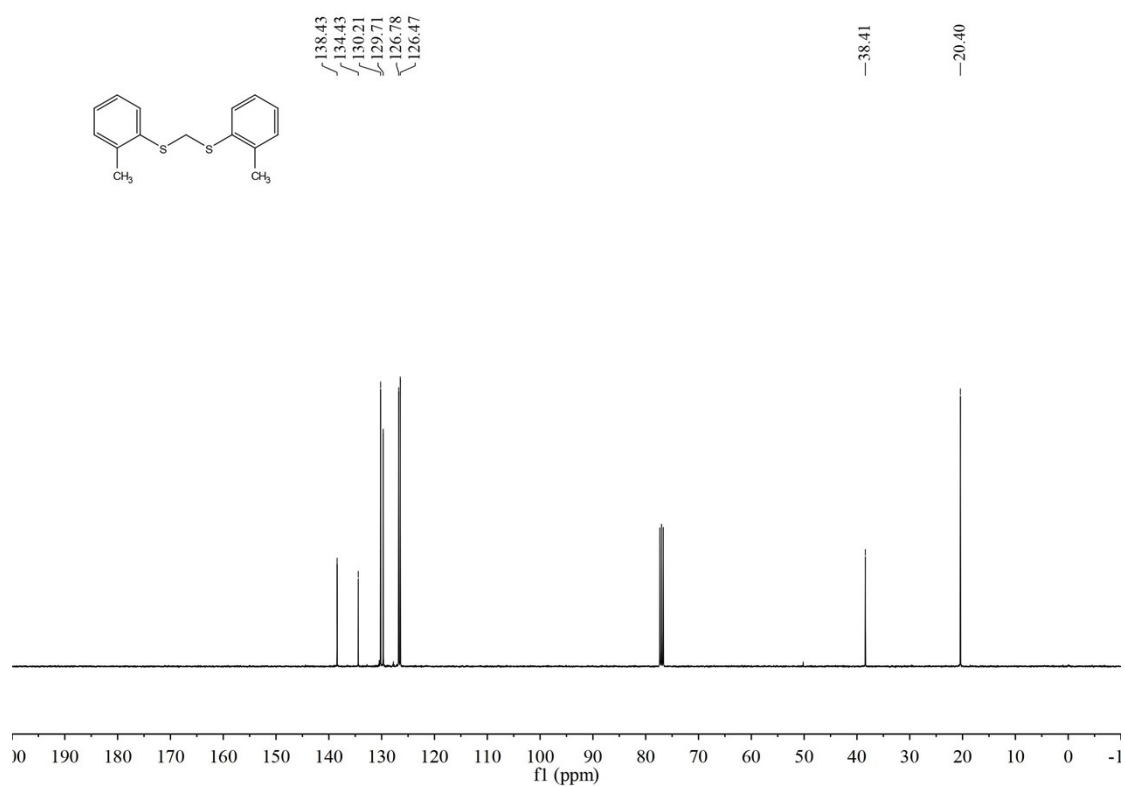
**3k-<sup>13</sup>C**



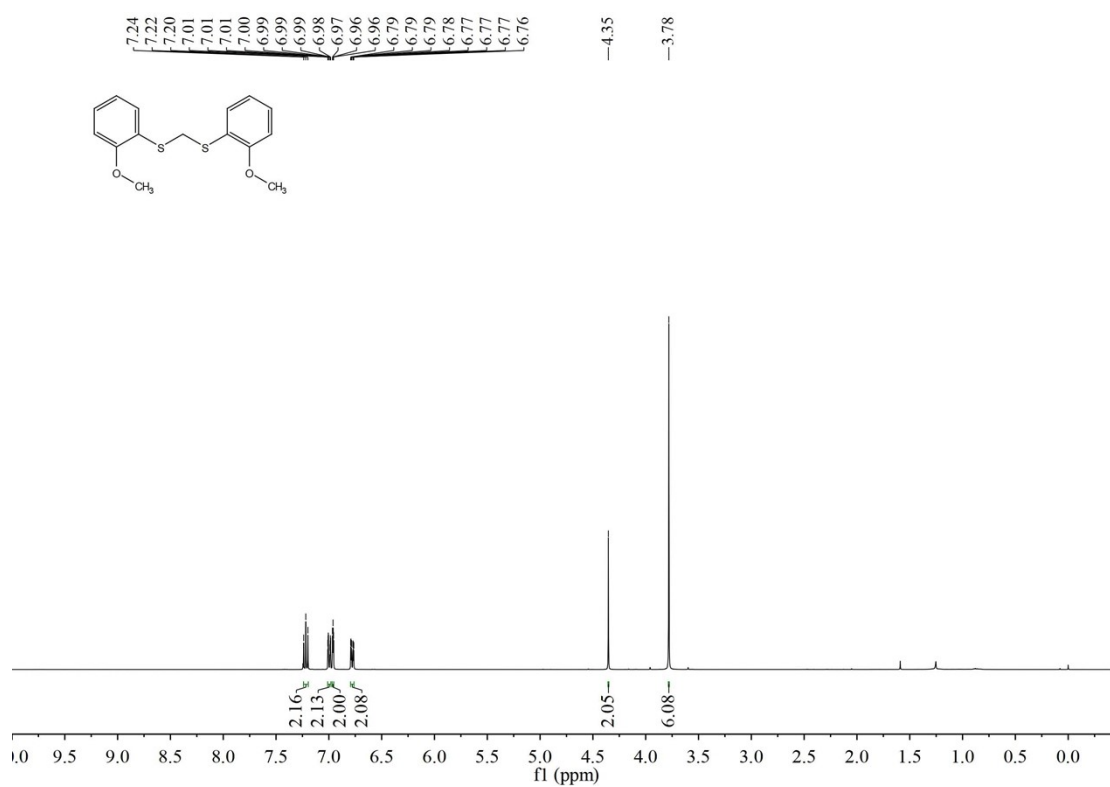
**3I-<sup>1</sup>H**



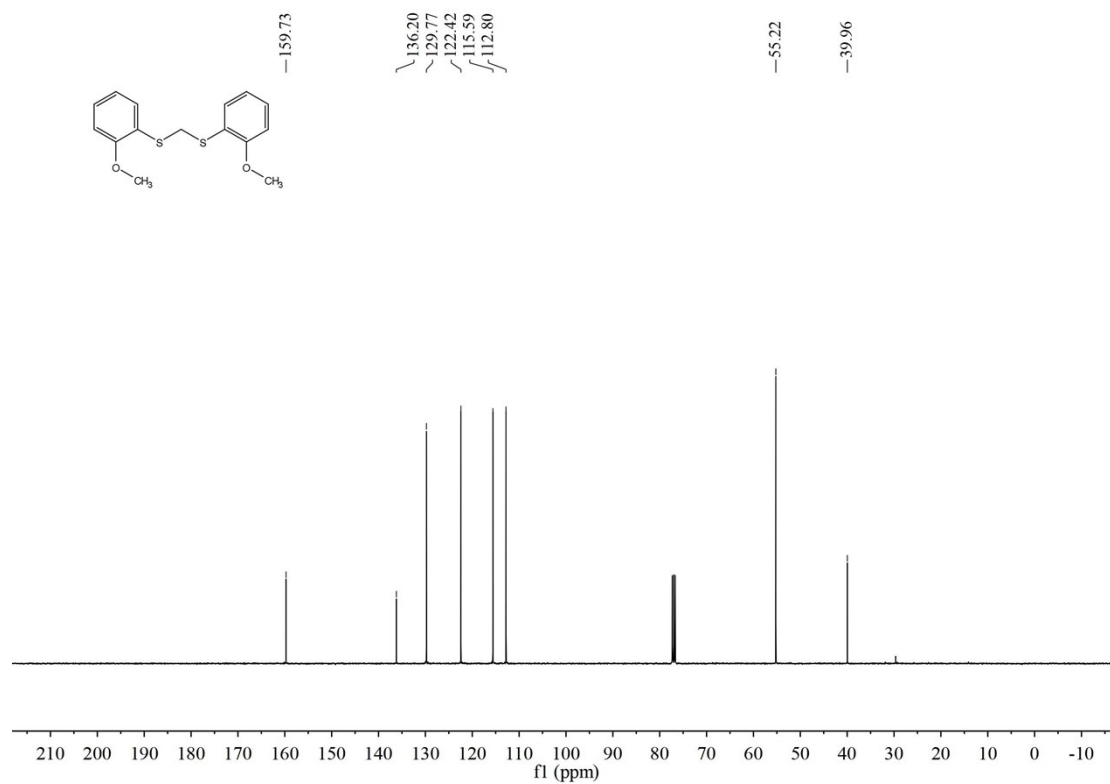
**3I-<sup>13</sup>C**



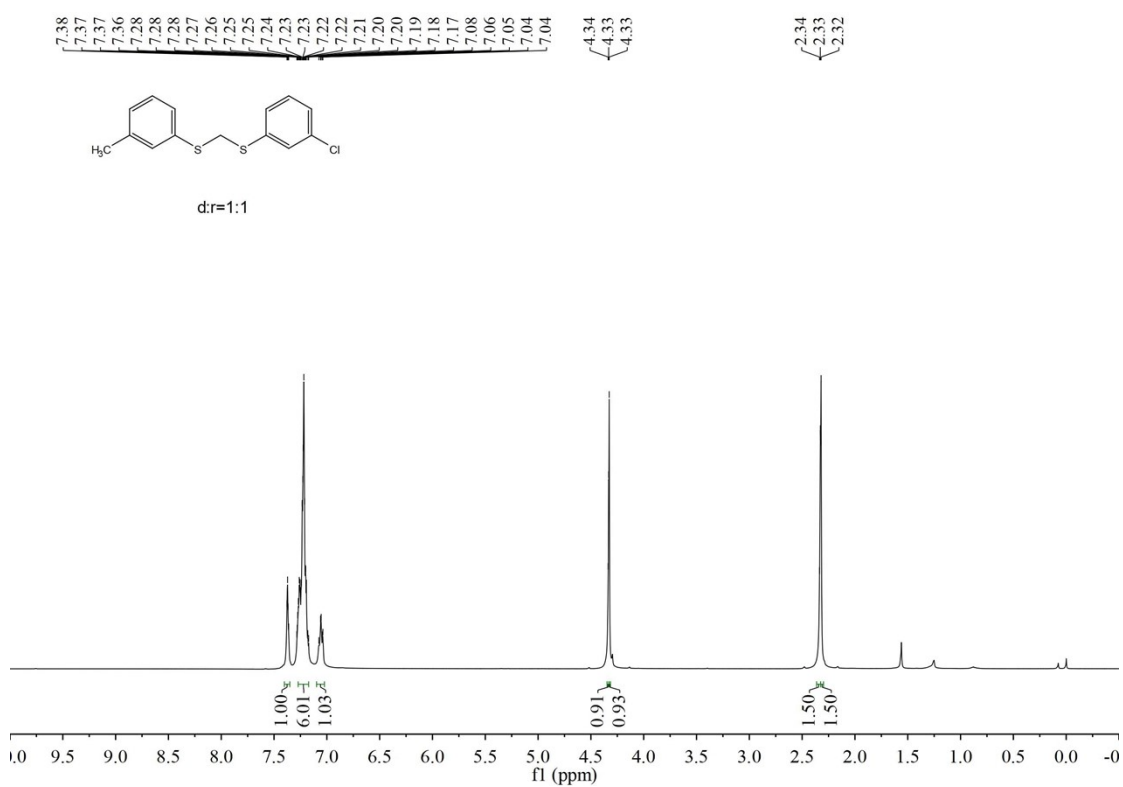
**3m-<sup>1</sup>H**



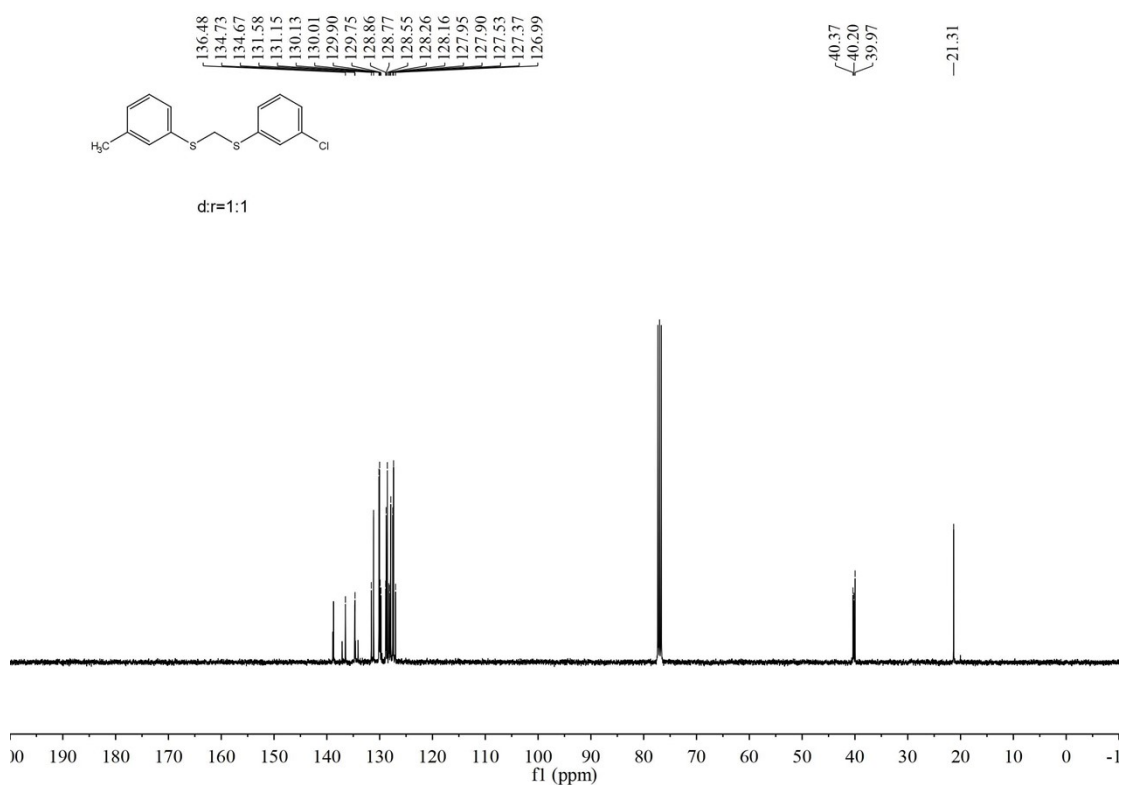
**3m-<sup>13</sup>C**



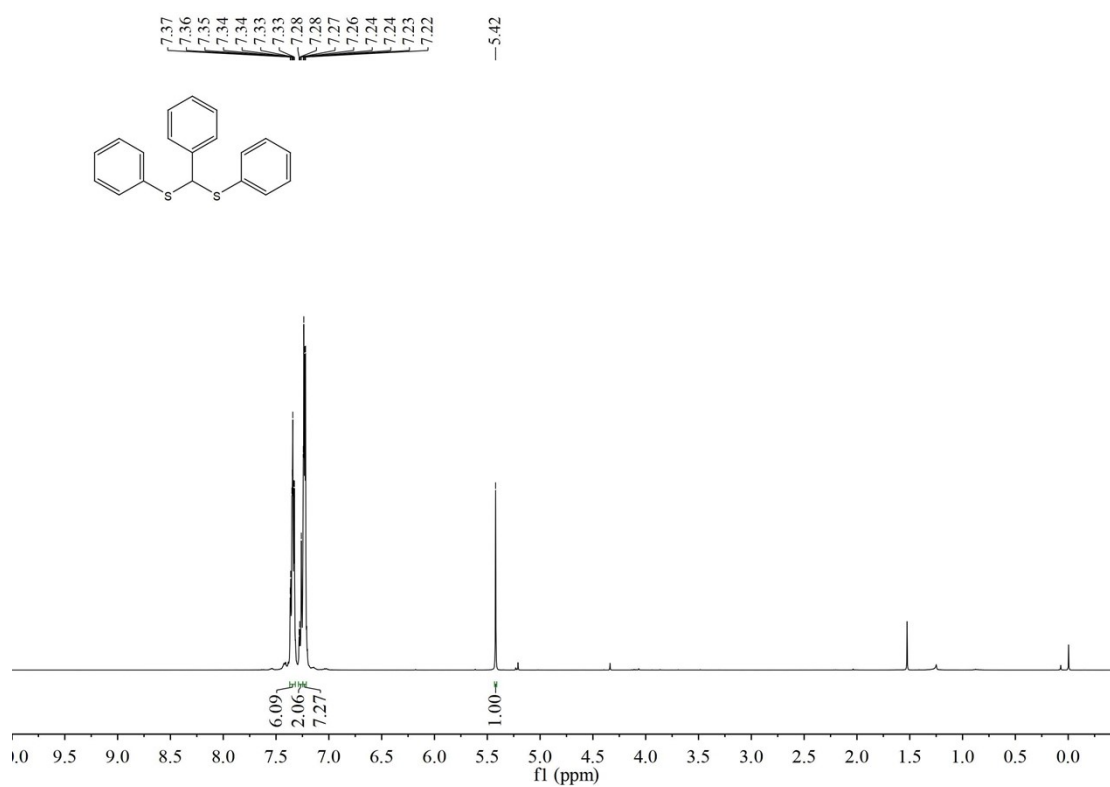
**3n-<sup>1</sup>H**



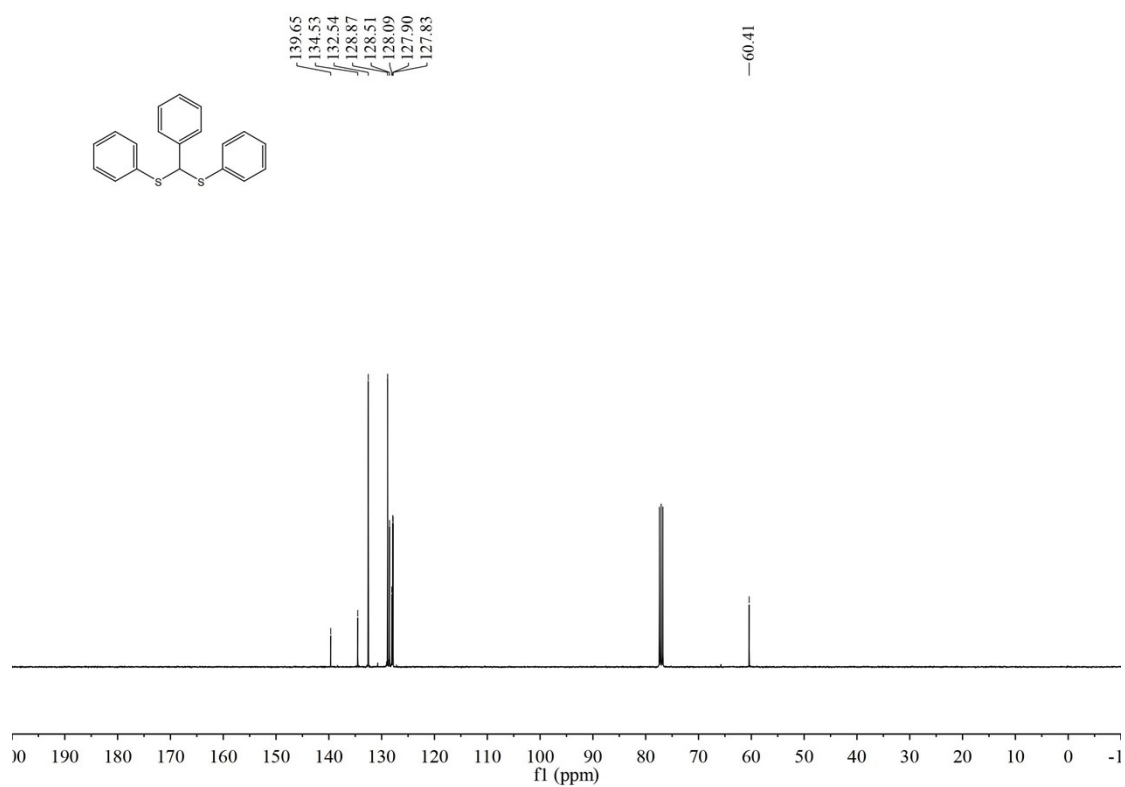
**3n-<sup>13</sup>C**



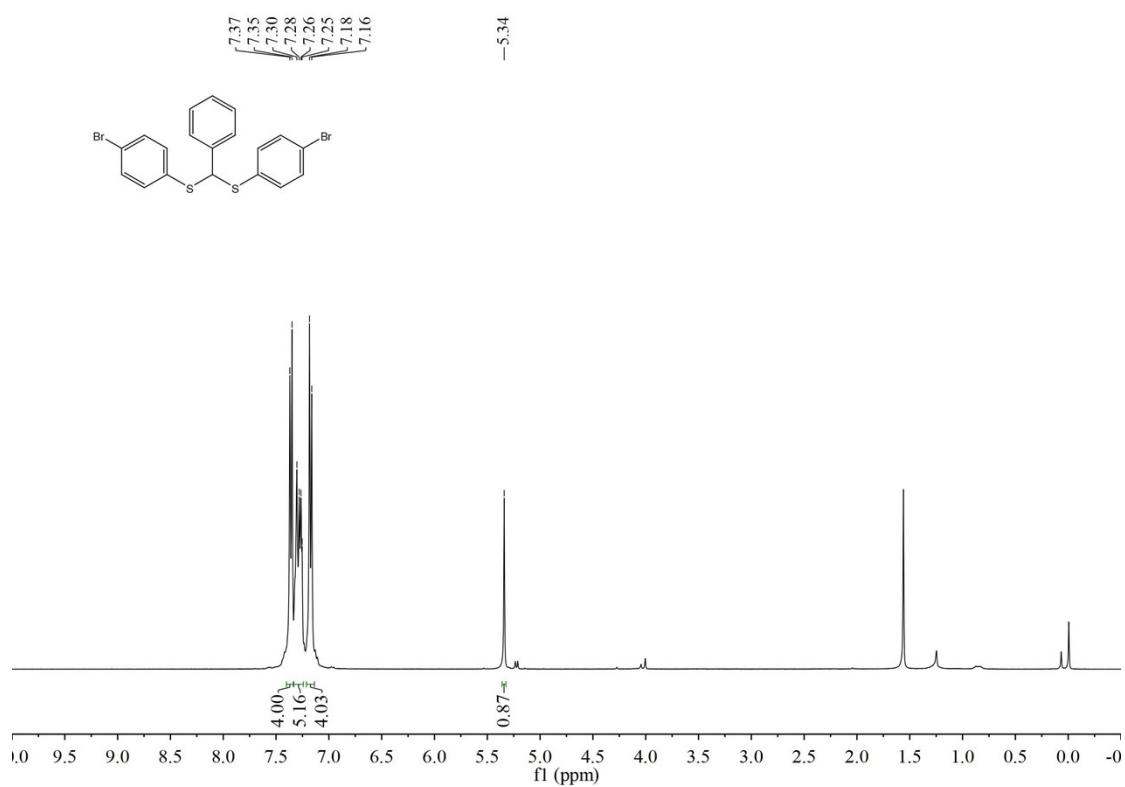
**3p-<sup>1</sup>H**



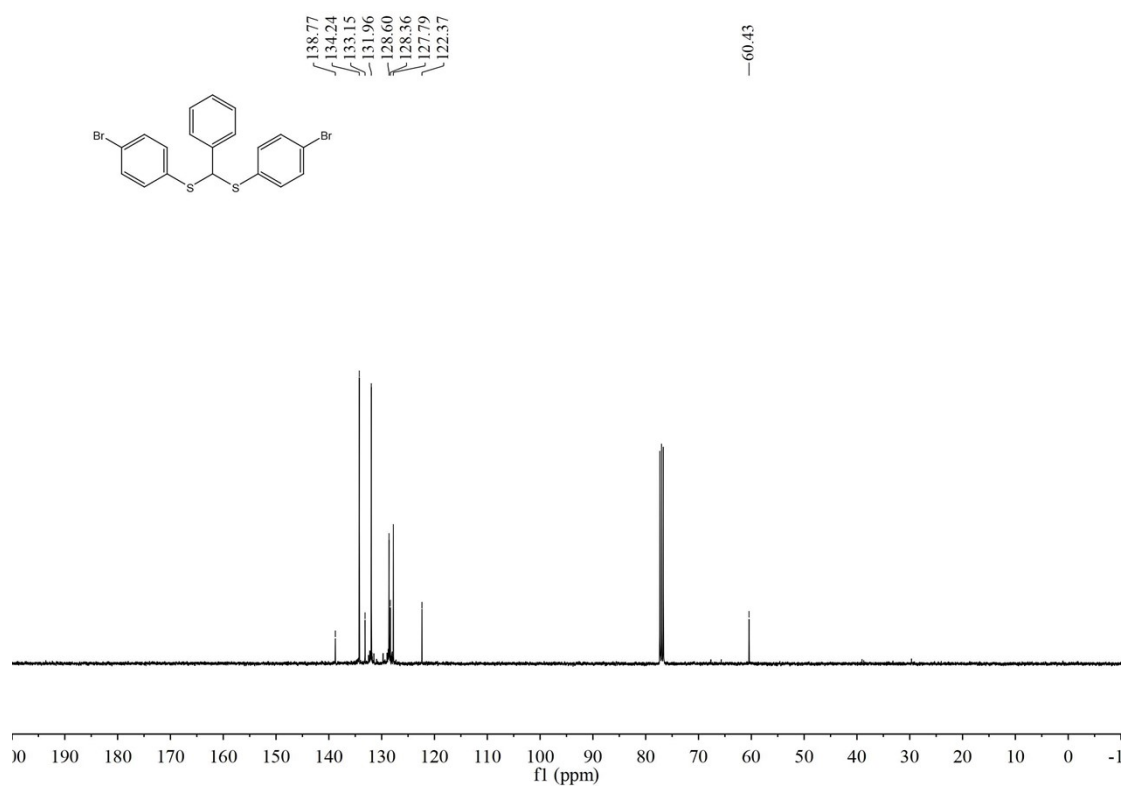
**3p-<sup>13</sup>C**



**3q-<sup>1</sup>H**



**3q-<sup>13</sup>C**





Chemical structure: Clc1ccc(SCC2SCC(c3ccccc3)S2)c(c1)

<sup>1</sup>H NMR spectrum (ppm):

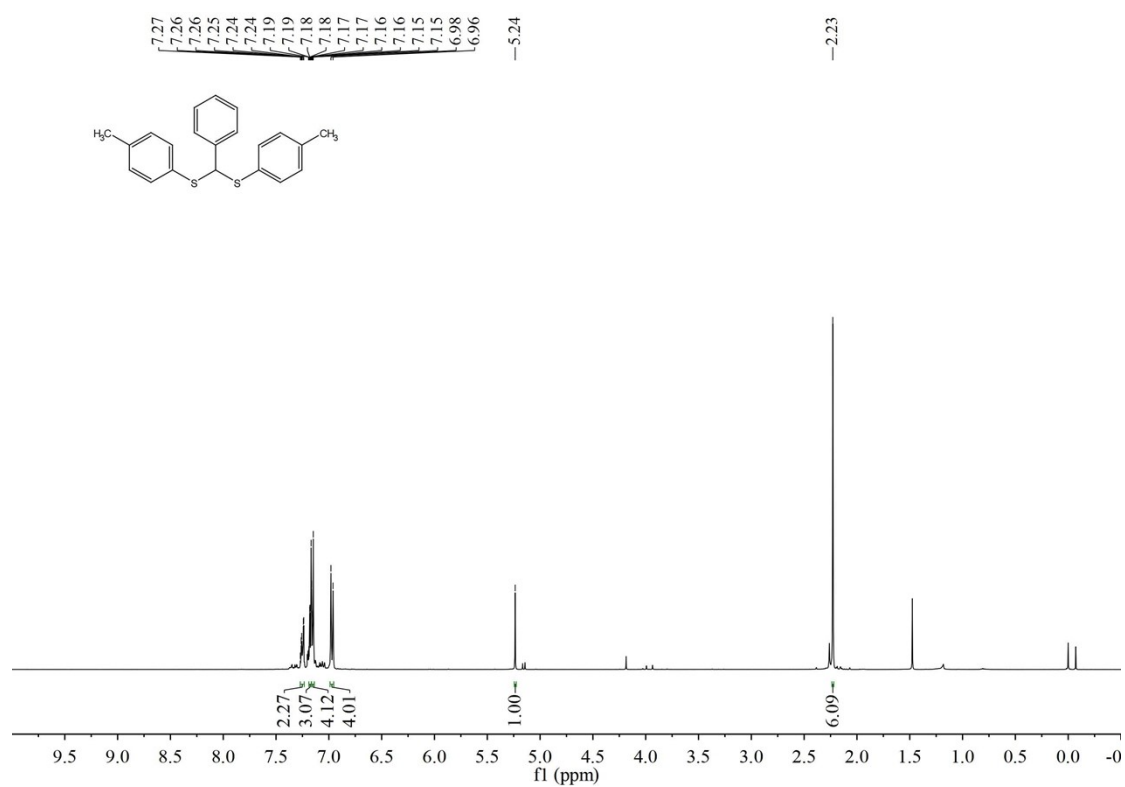
- Aromatic region (7.20 - 7.32 ppm): Multiplet, integration values: 2.19, 2.19, 7.07, 2.27.
- Reference peak (-5.33 ppm): Singlet, integration value: 1.00.
- Solvent peak (1.00 ppm): Singlet.

Chemical structure of 1,2-bis(4-chlorophenyl)-1-phenylethane-1,2-dithiolane is shown above the spectrum. The spectrum displays several peaks in the aromatic region, with the following chemical shifts (ppm) labeled above the corresponding peaks:

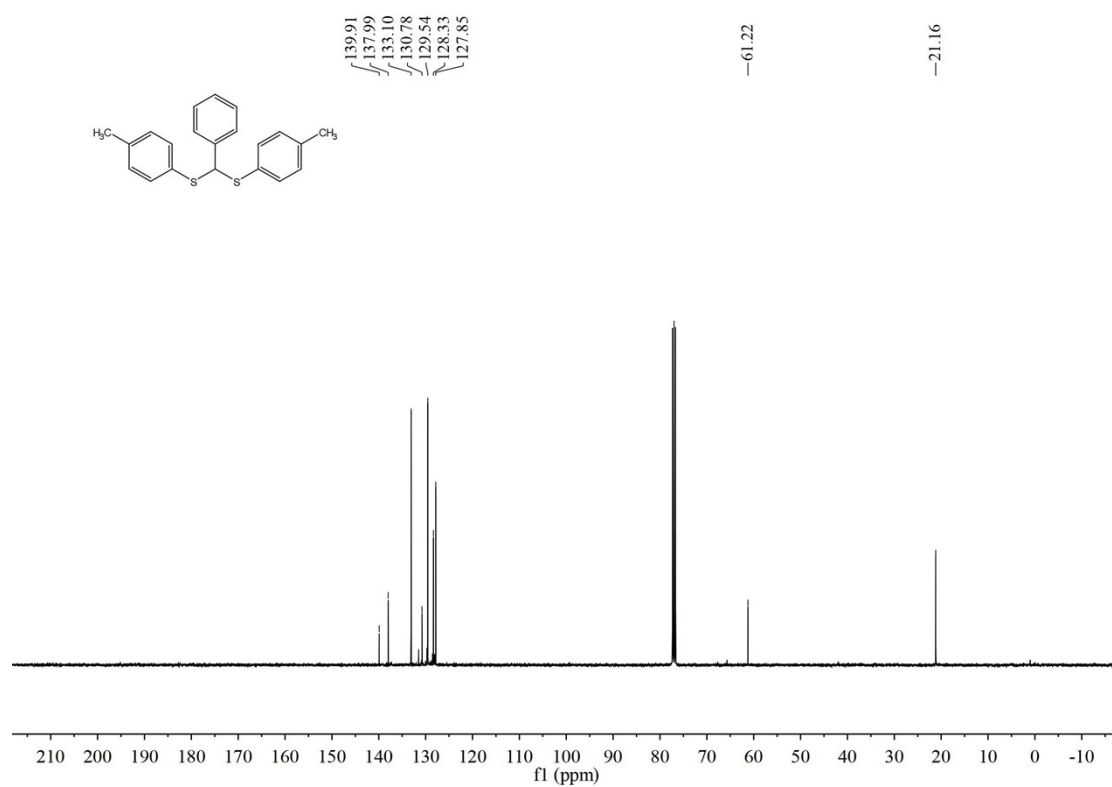
- 138.83
- 134.29
- 134.16
- 132.45
- 129.03
- 128.59
- 128.34
- 127.79

A peak at 60.76 ppm is also labeled, corresponding to the CDCl<sub>3</sub> solvent.

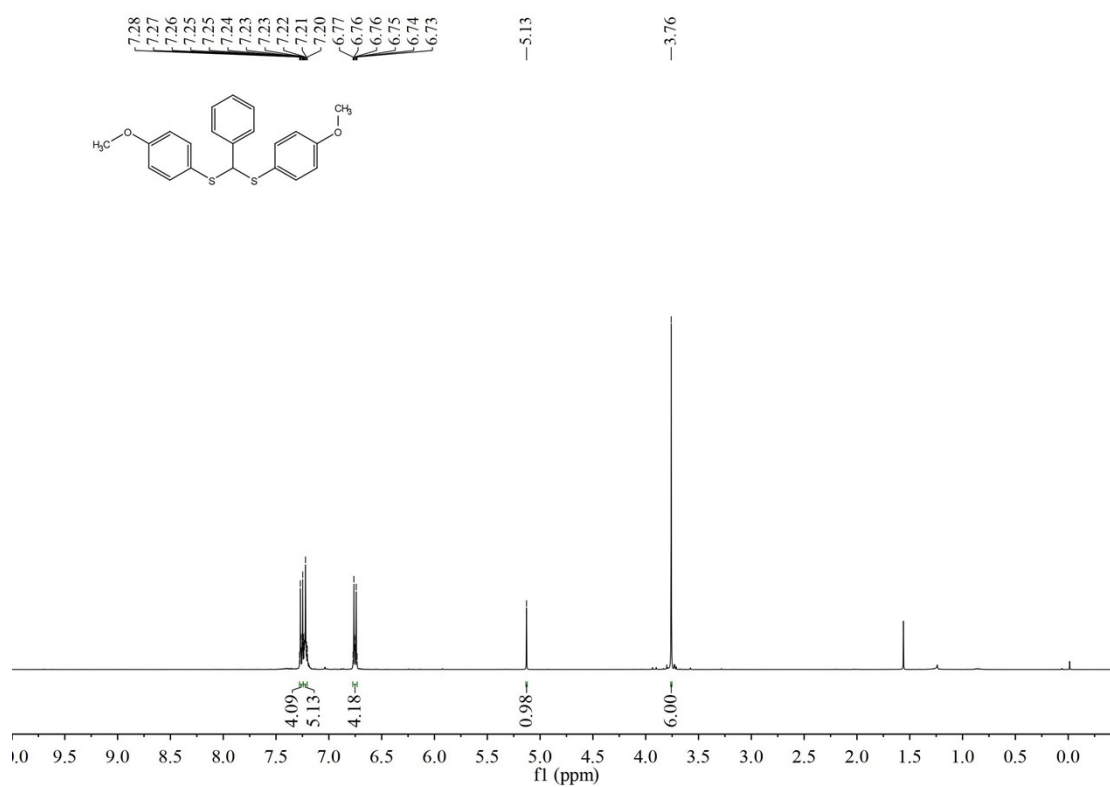
**3s-<sup>1</sup>H**



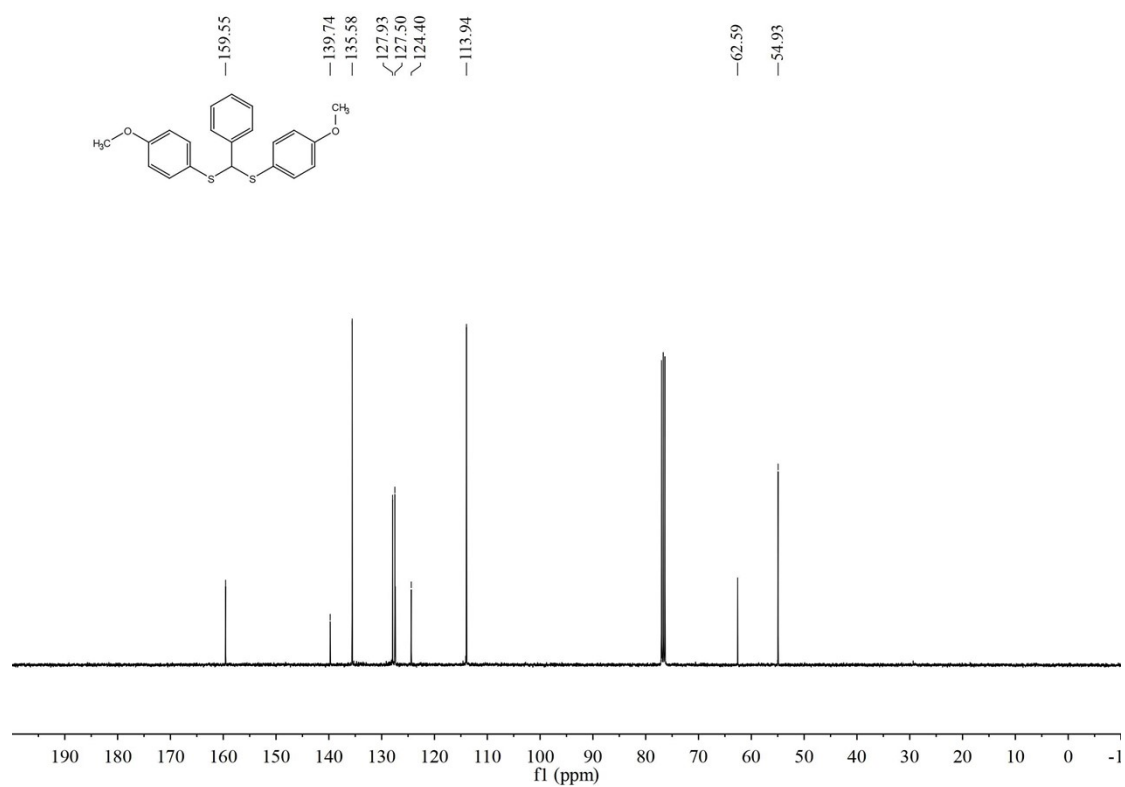
**3s-<sup>13</sup>C**



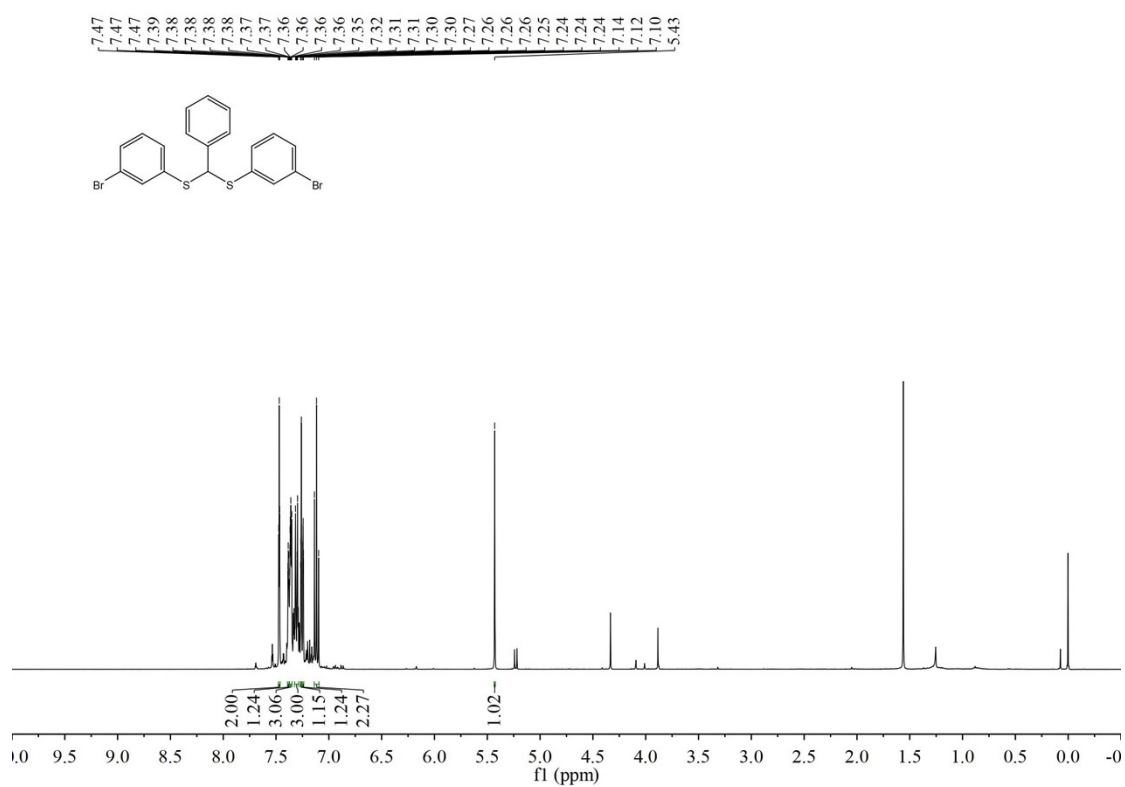
**3t-<sup>1</sup>H**



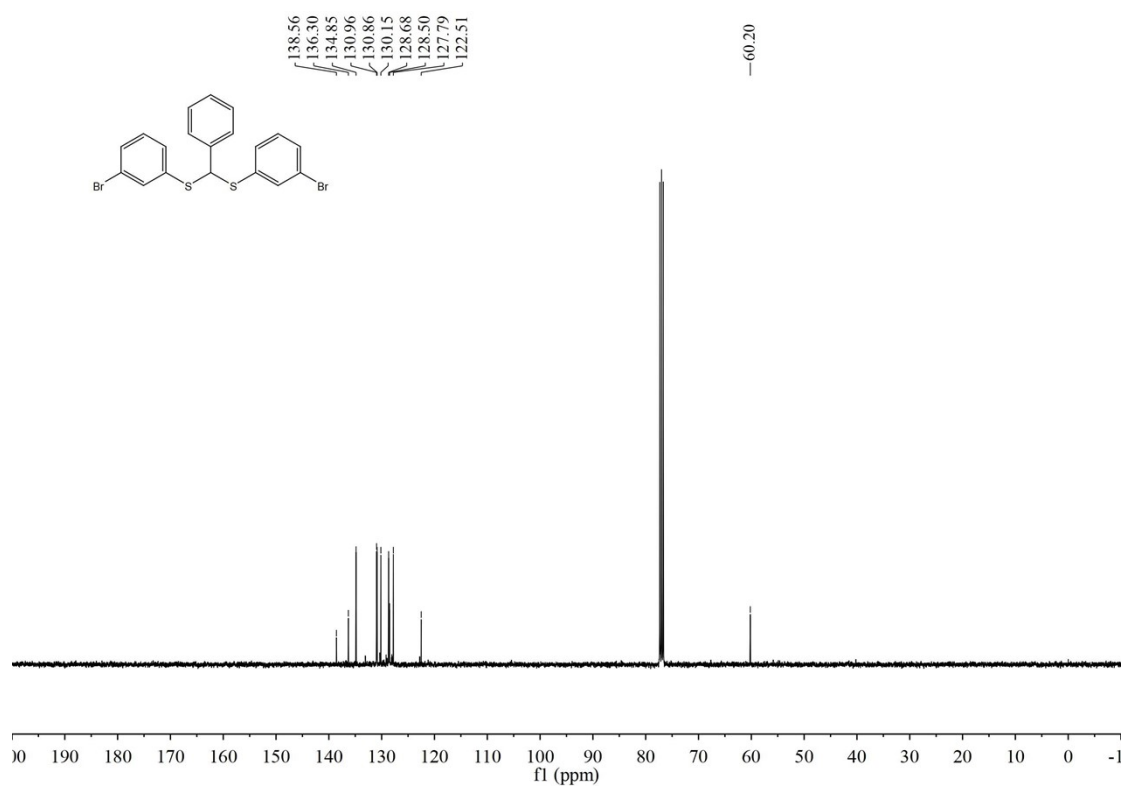
**3t-<sup>13</sup>C**



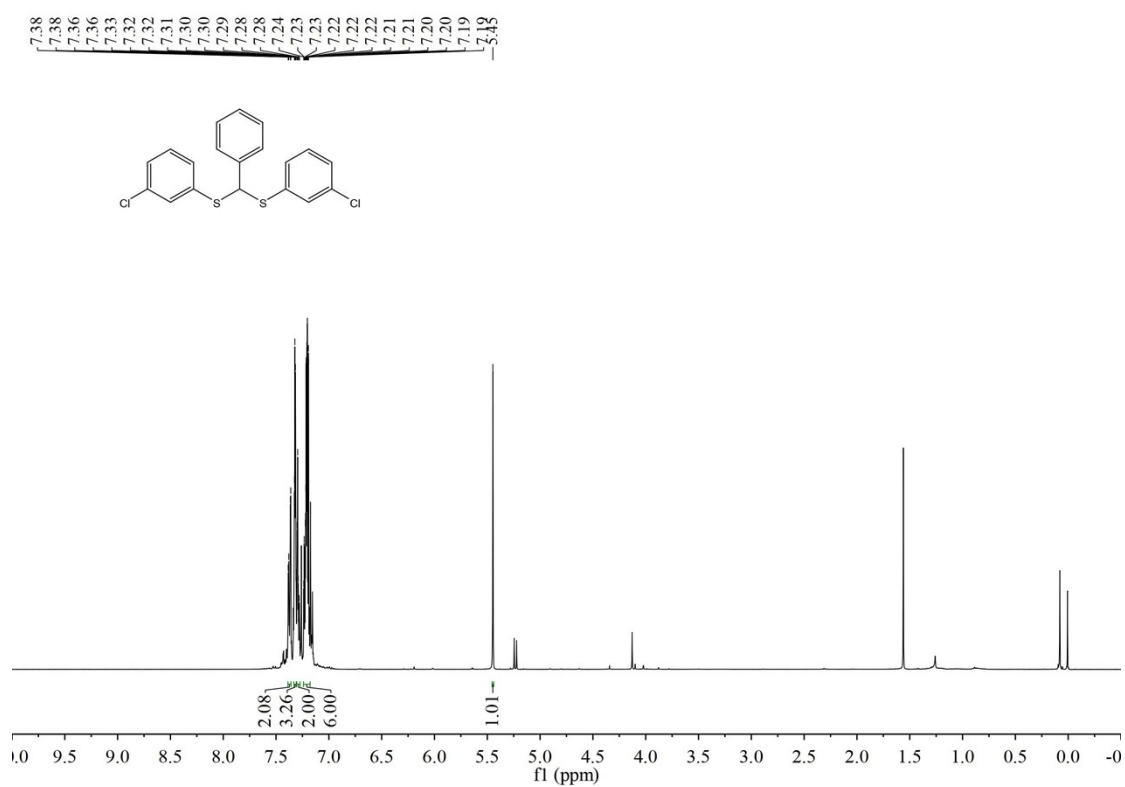
**3u-<sup>1</sup>H**



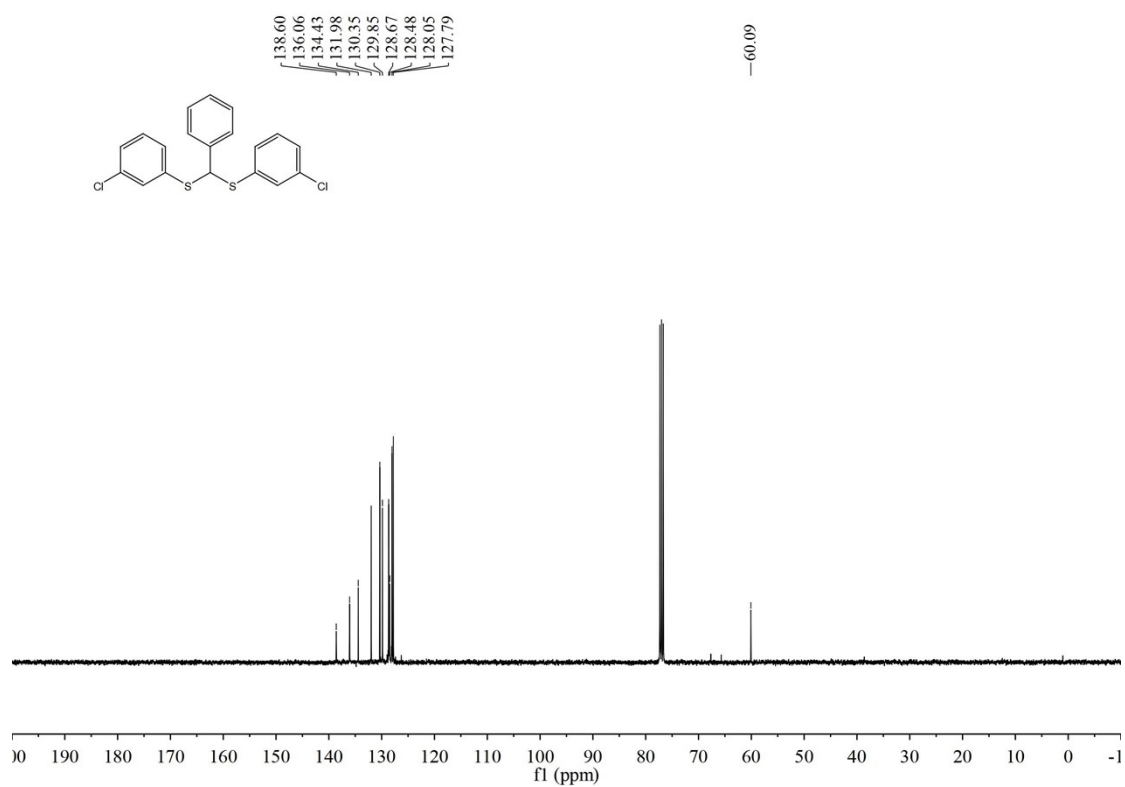
**3u-<sup>13</sup>C**



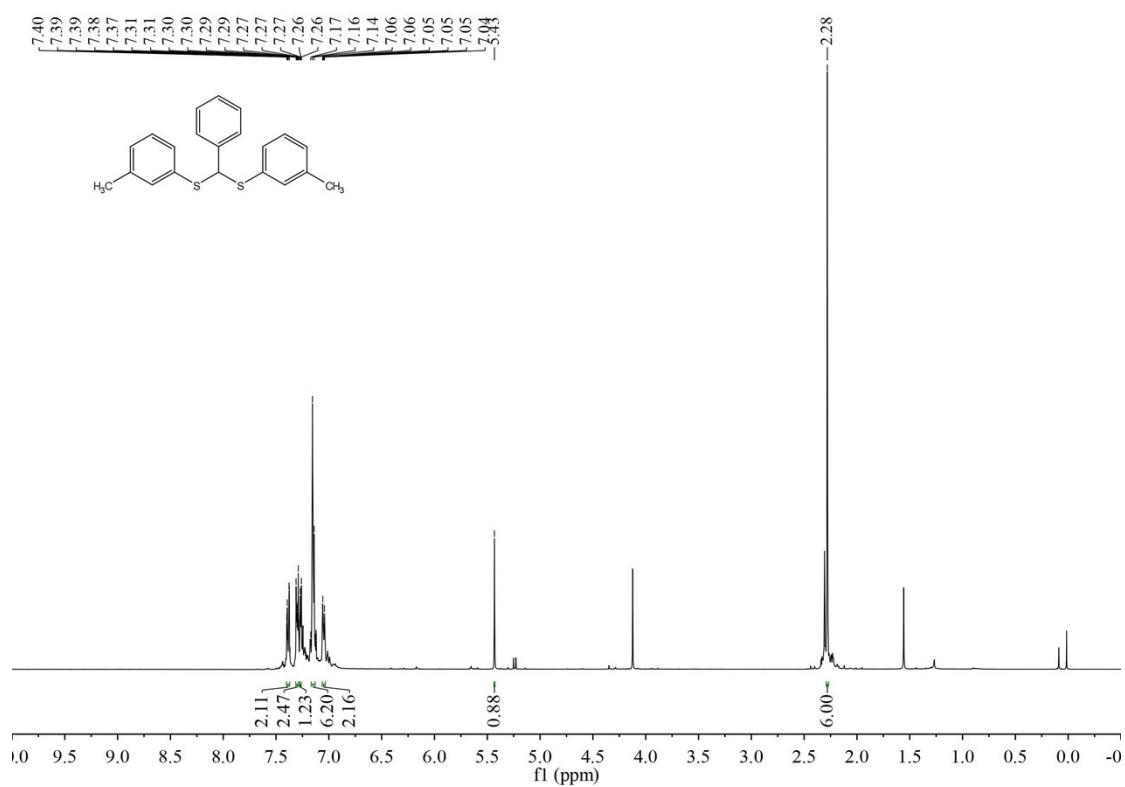
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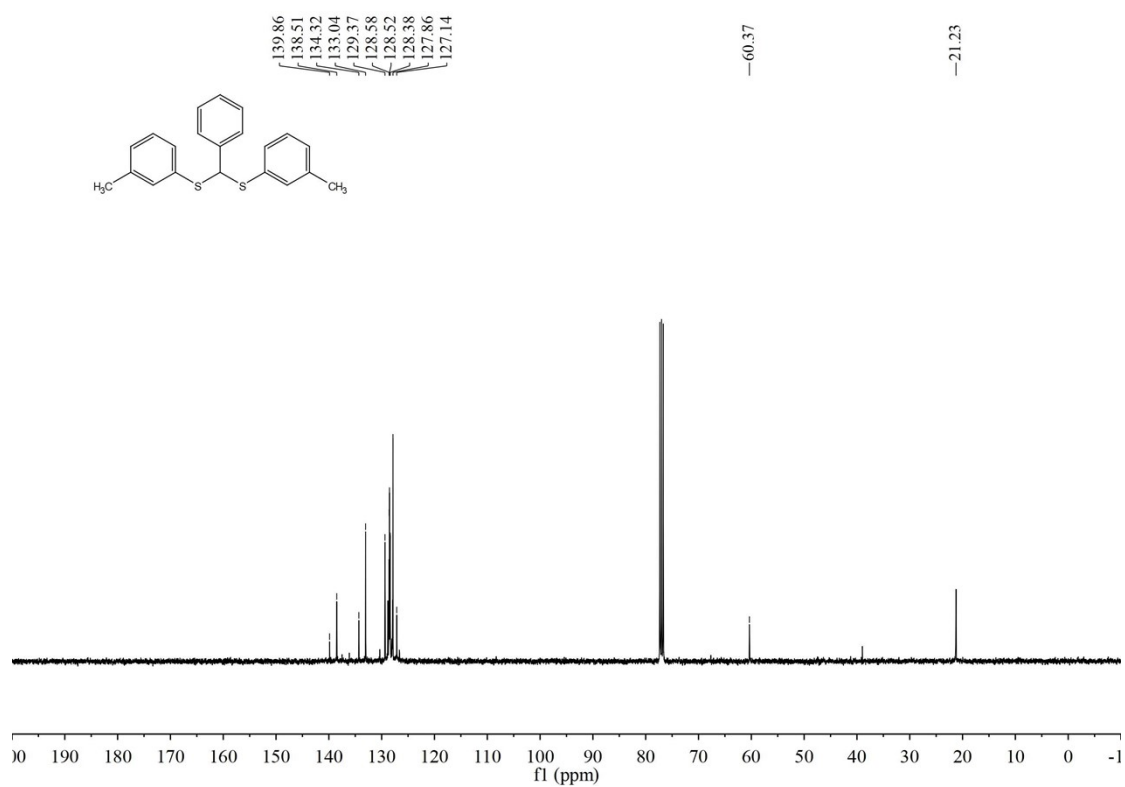
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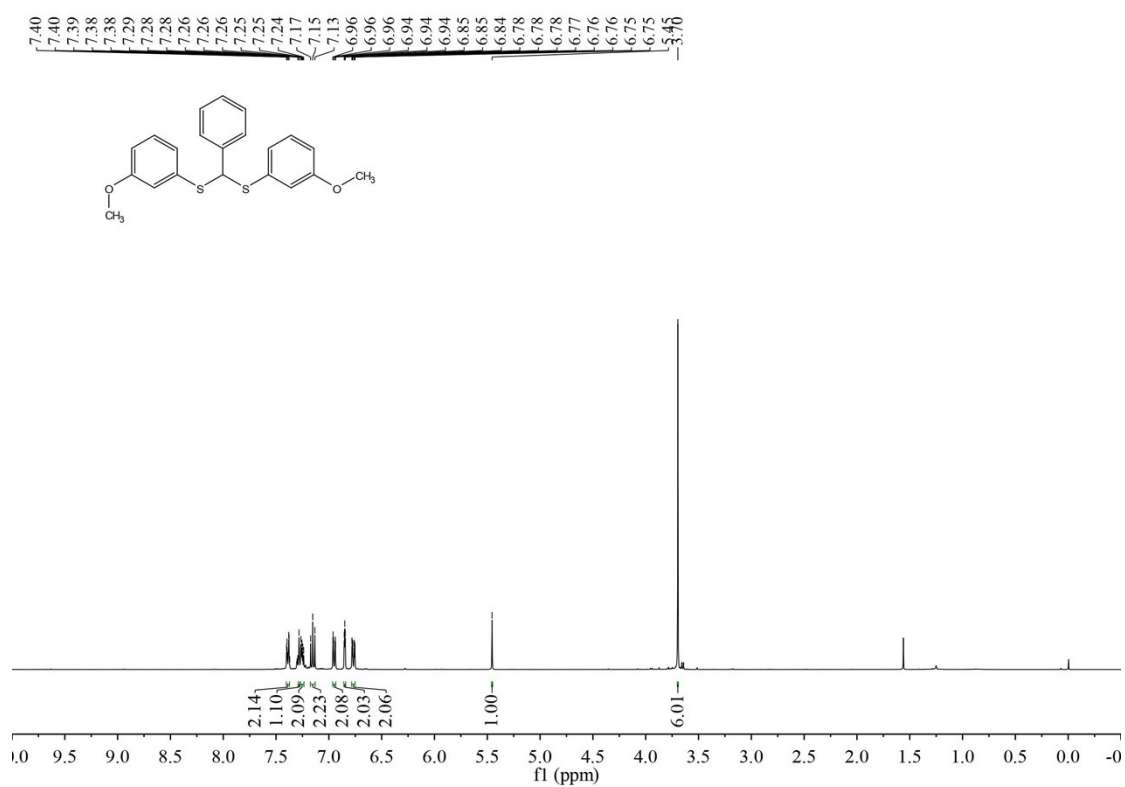
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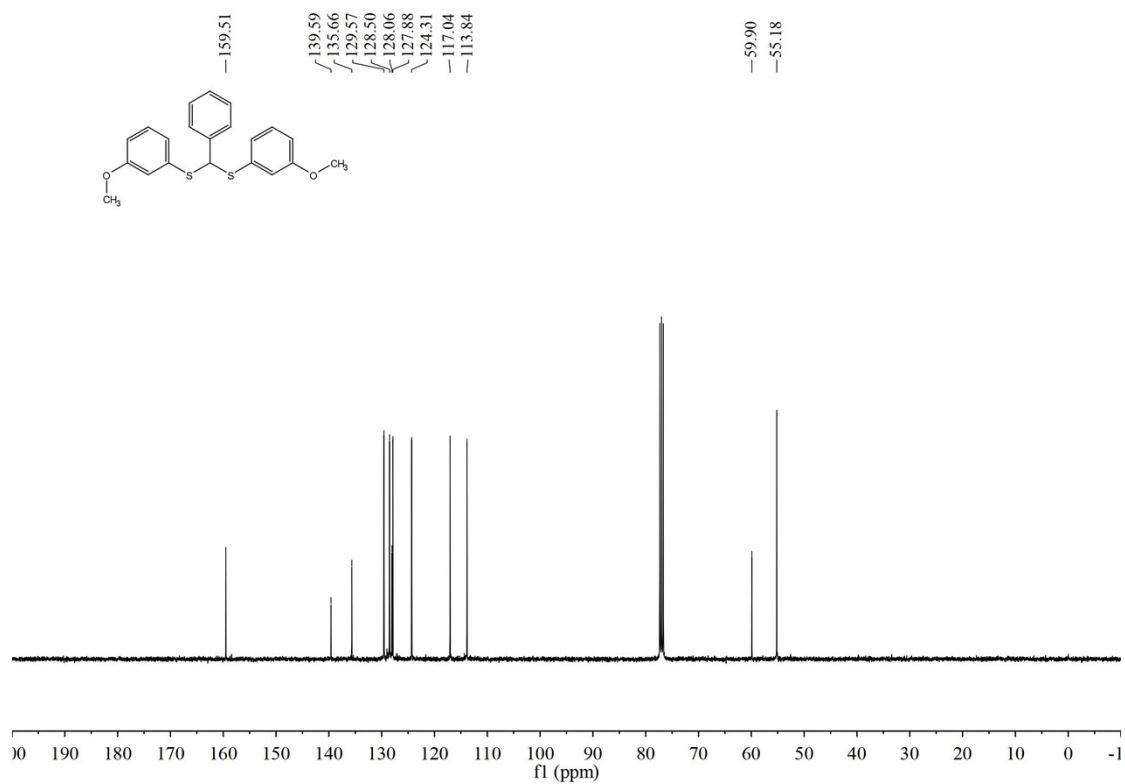
**3w-<sup>13</sup>C**



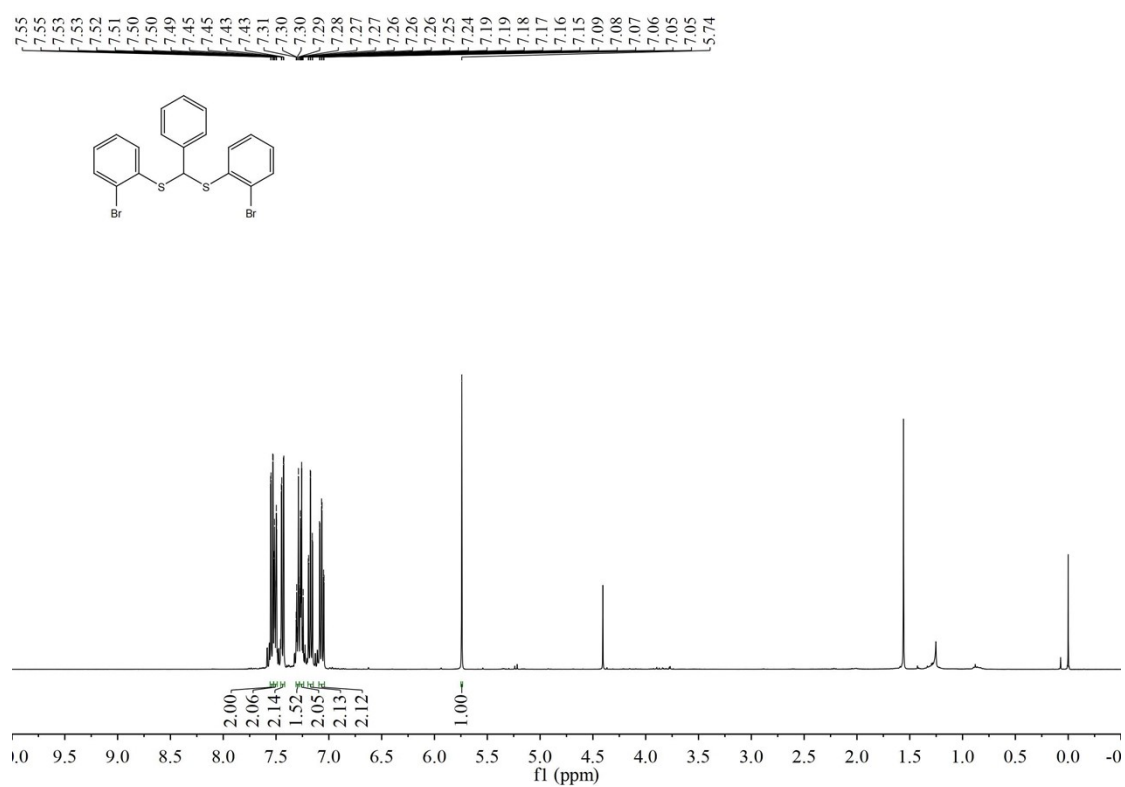
**3x-<sup>1</sup>H**



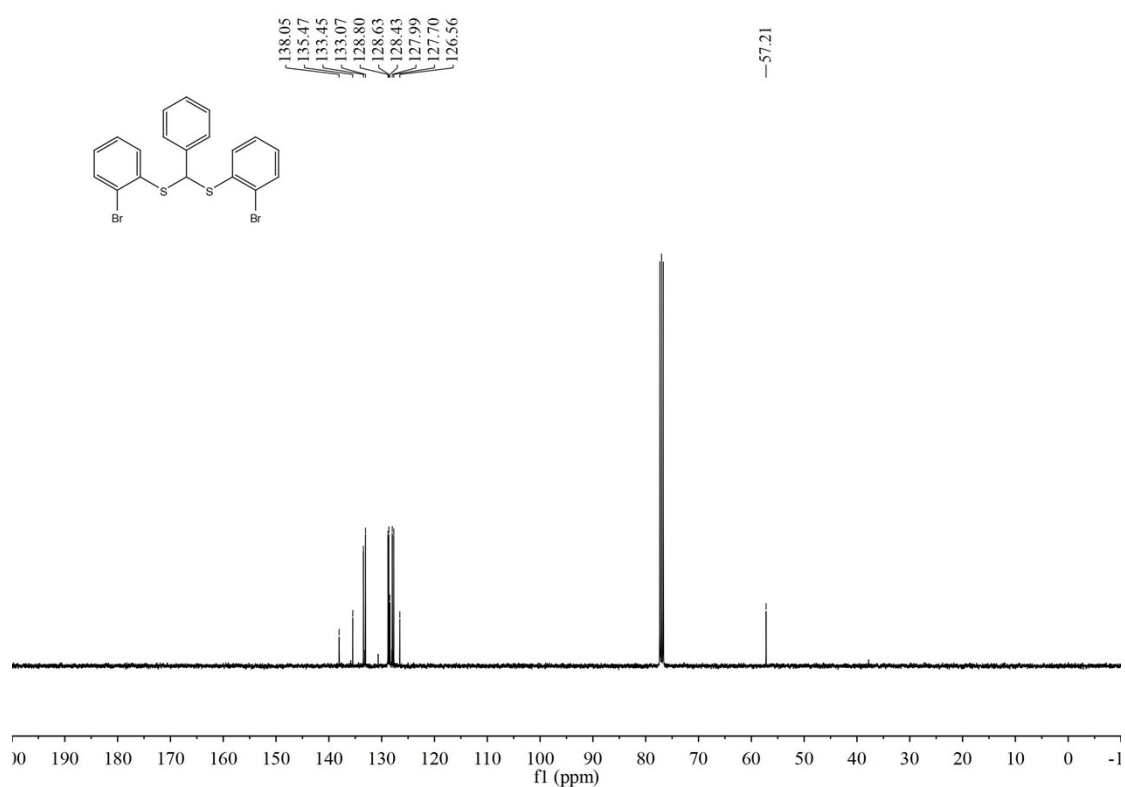
**3x-<sup>13</sup>C**



**3y-<sup>1</sup>H**

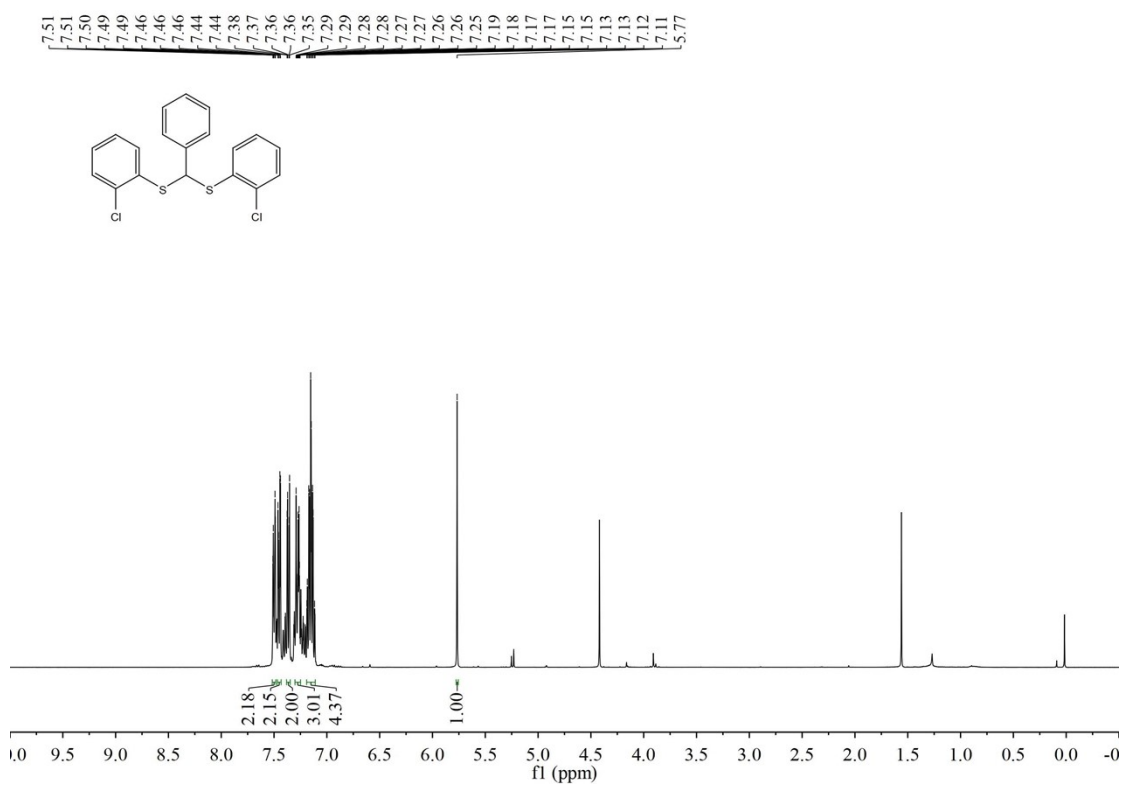


**3y-<sup>13</sup>C**

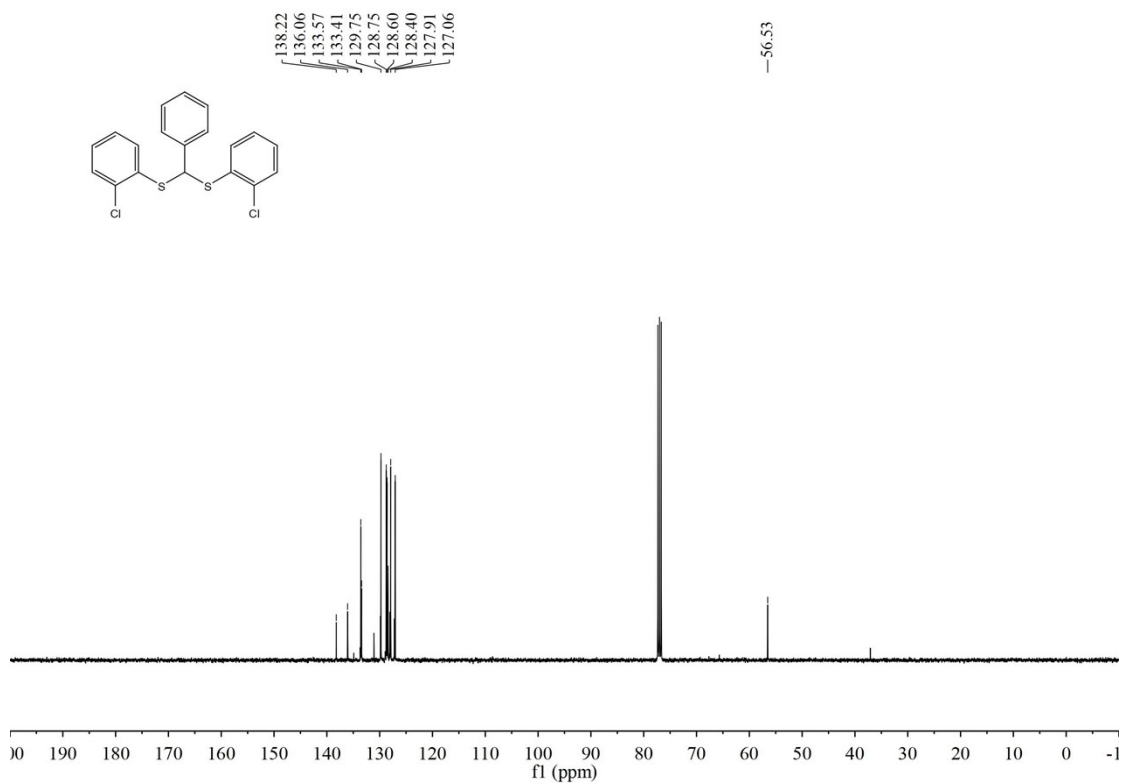




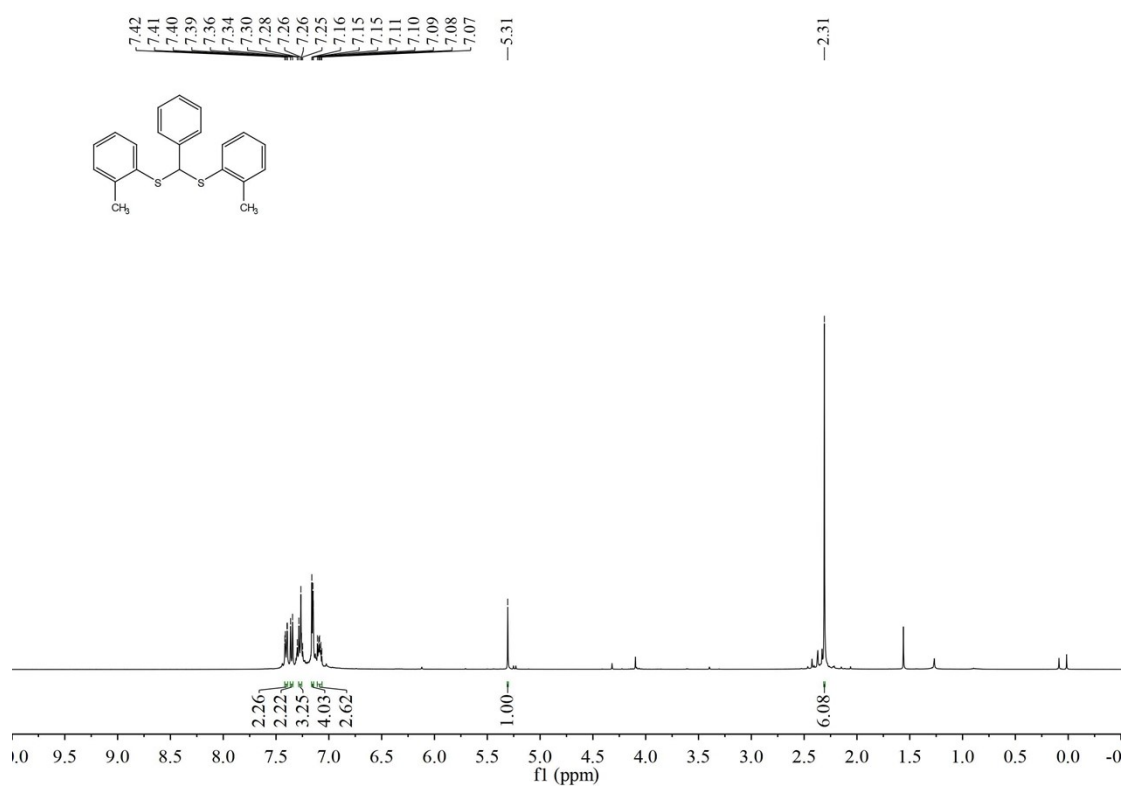
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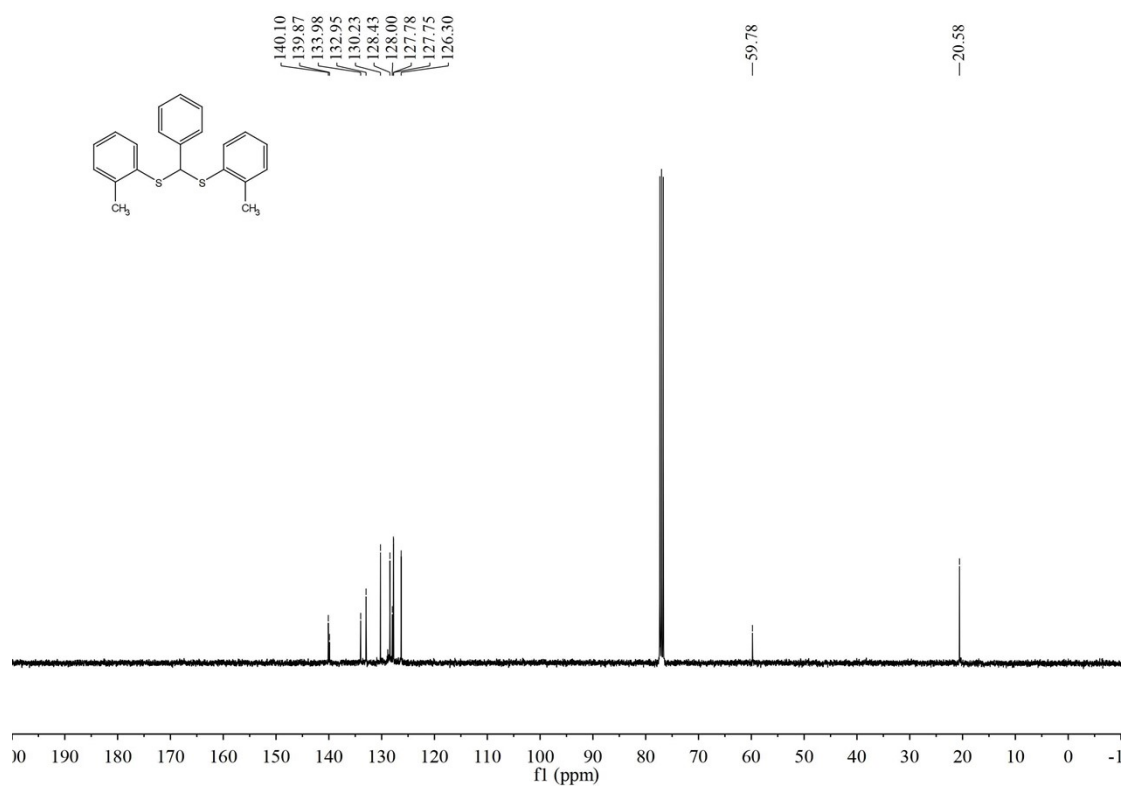
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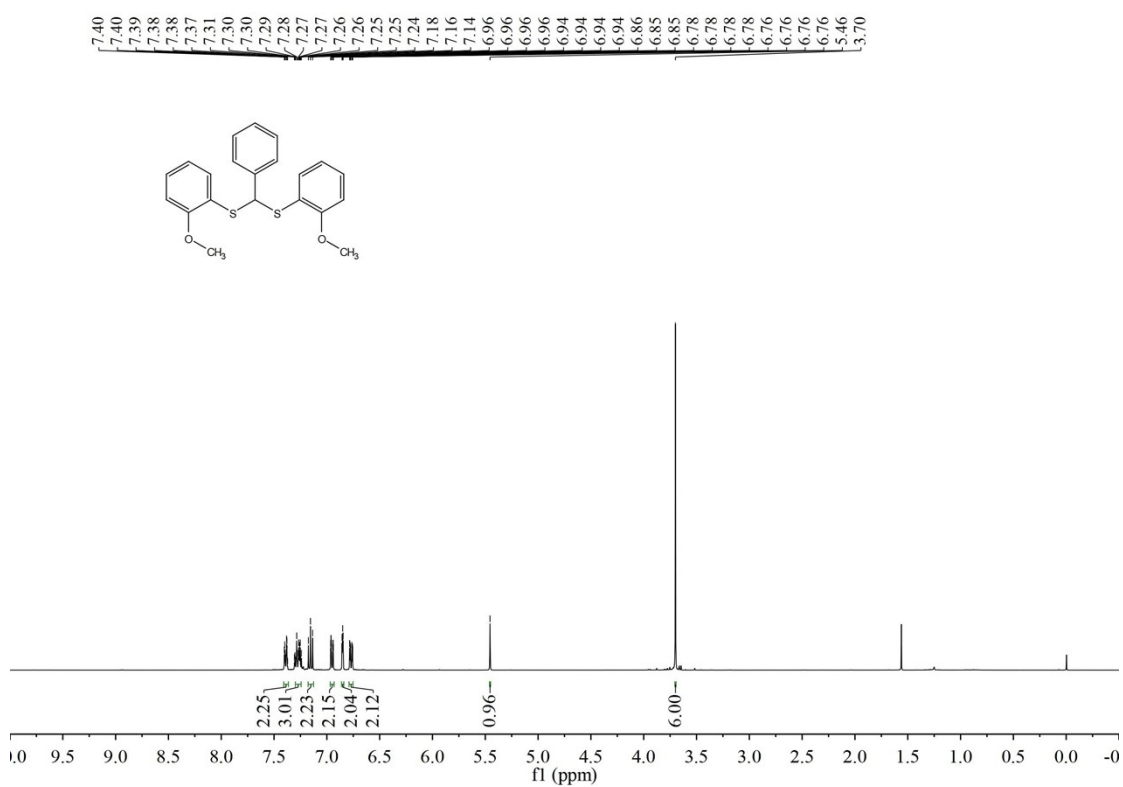
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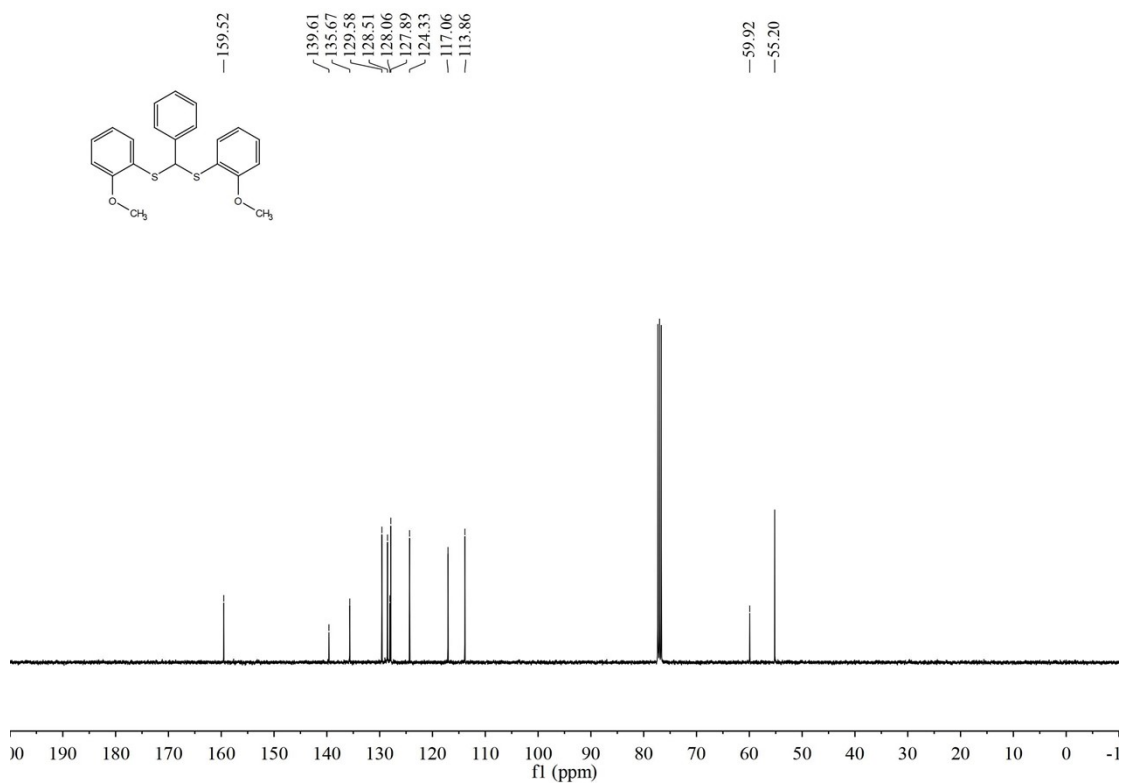
**3aa-<sup>13</sup>C**



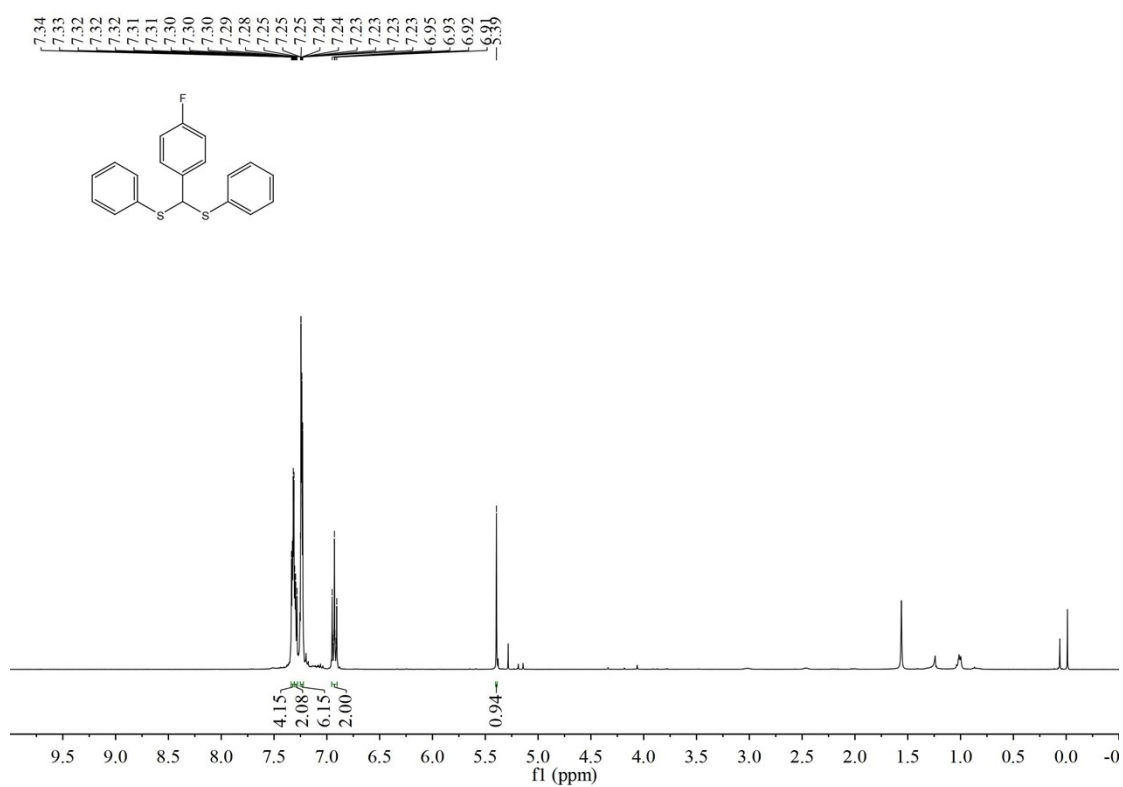
**3ab-<sup>1</sup>H**



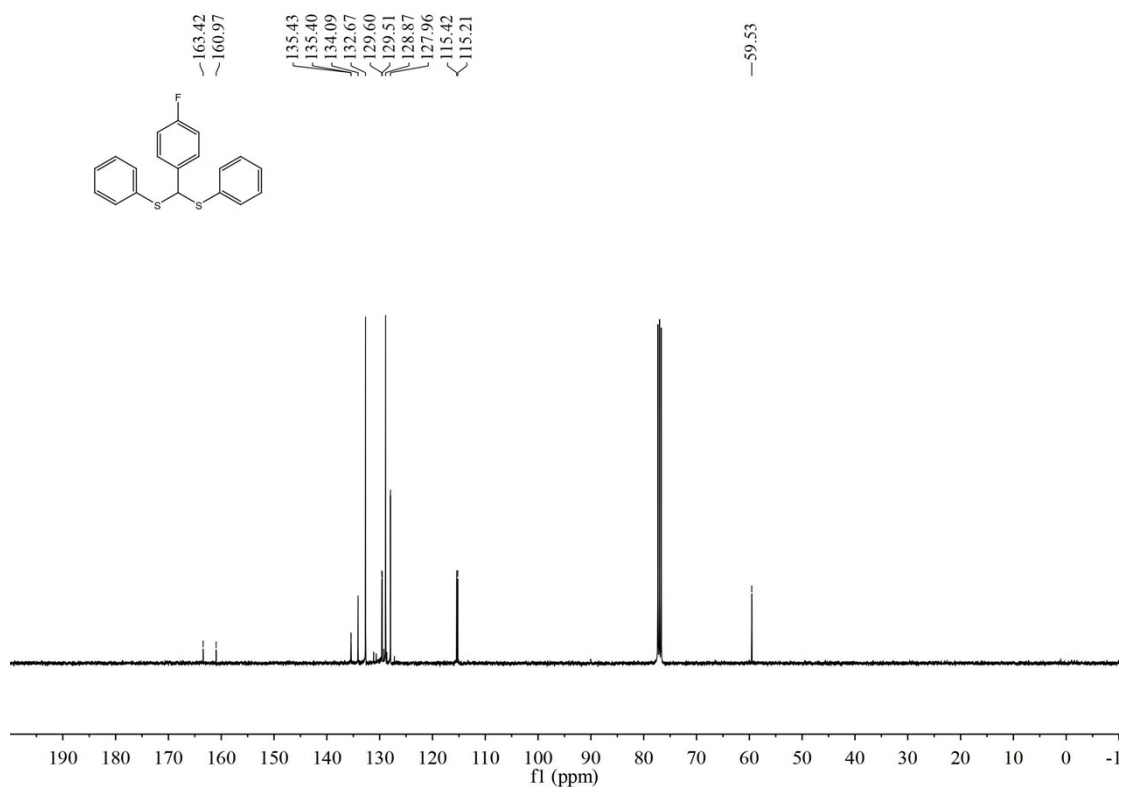
**3ab-<sup>13</sup>C**



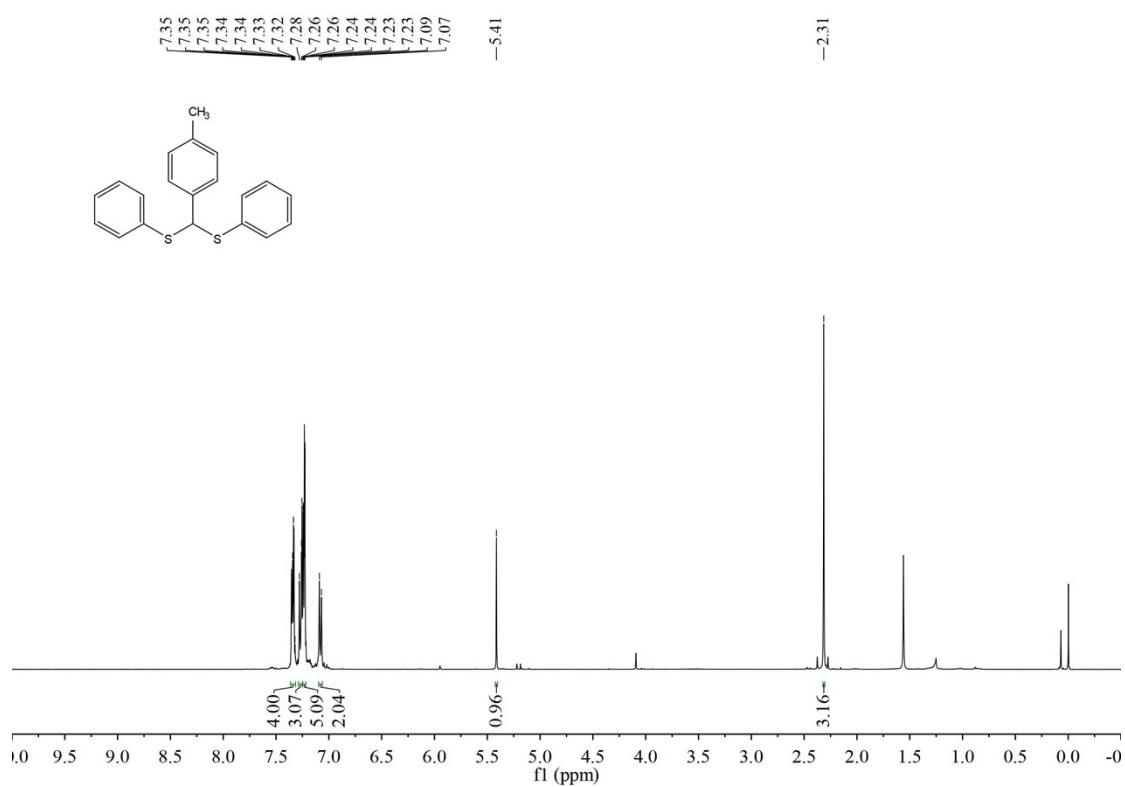
**3ac-<sup>1</sup>H**



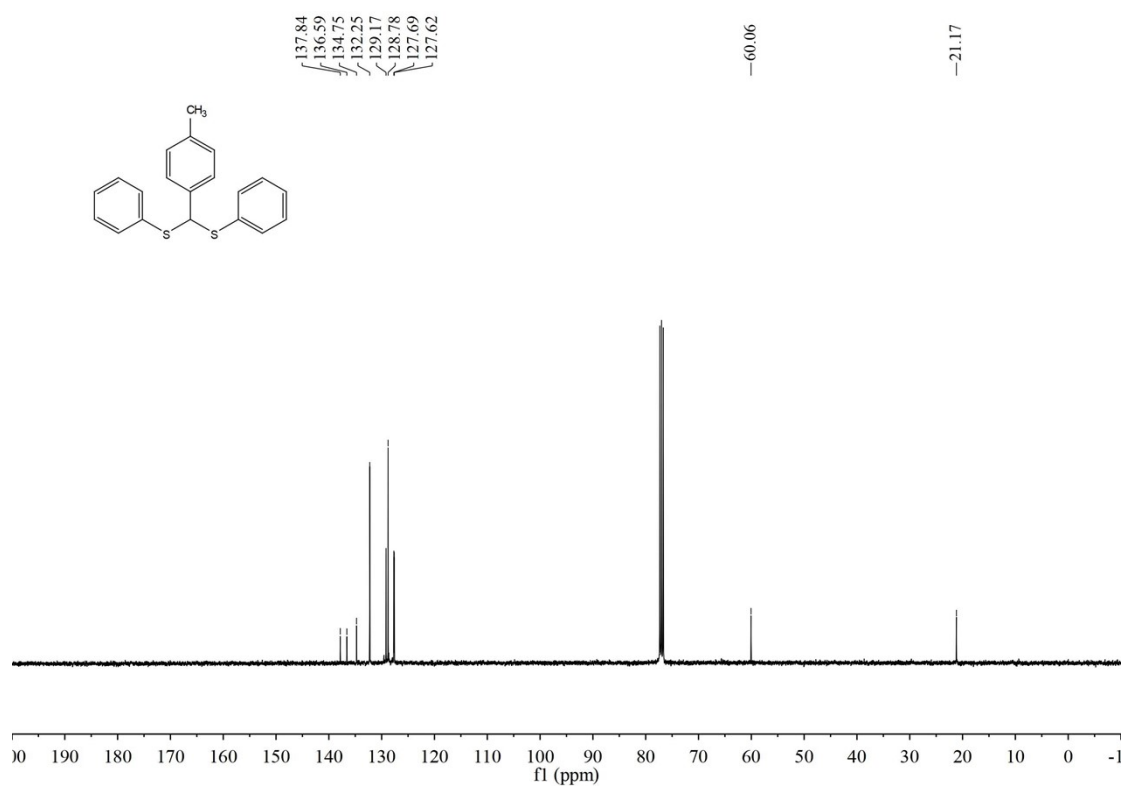
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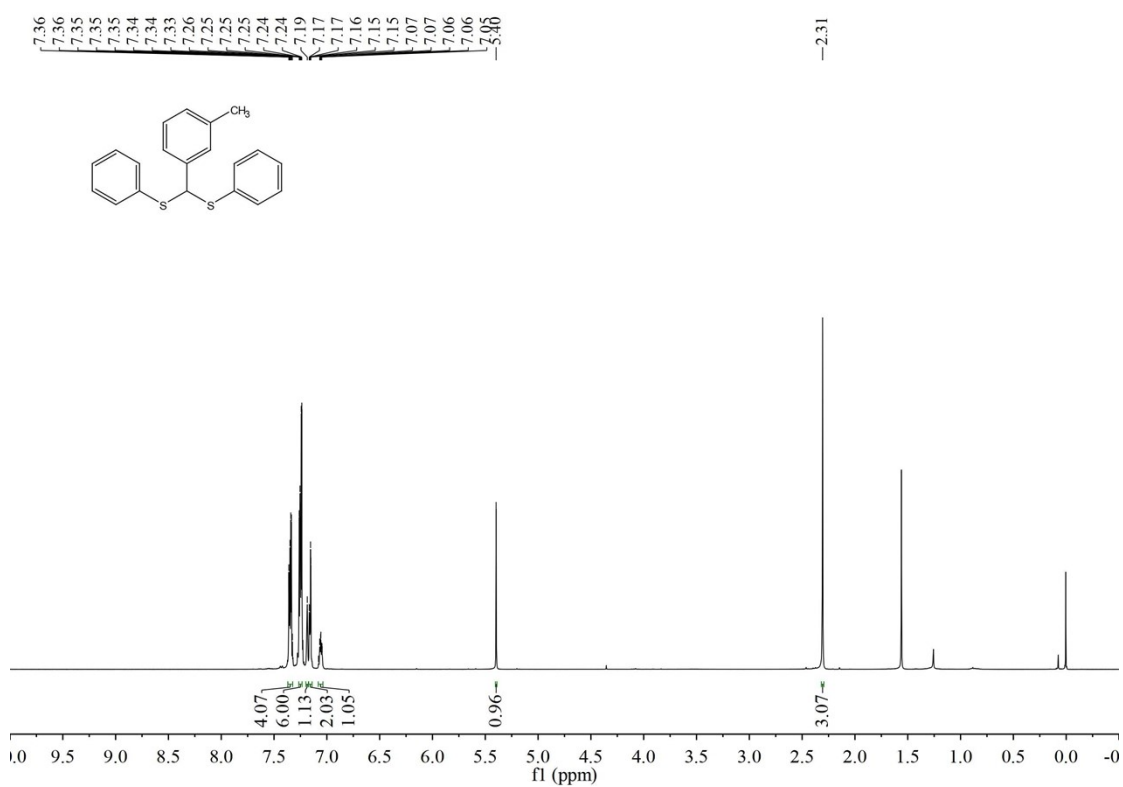
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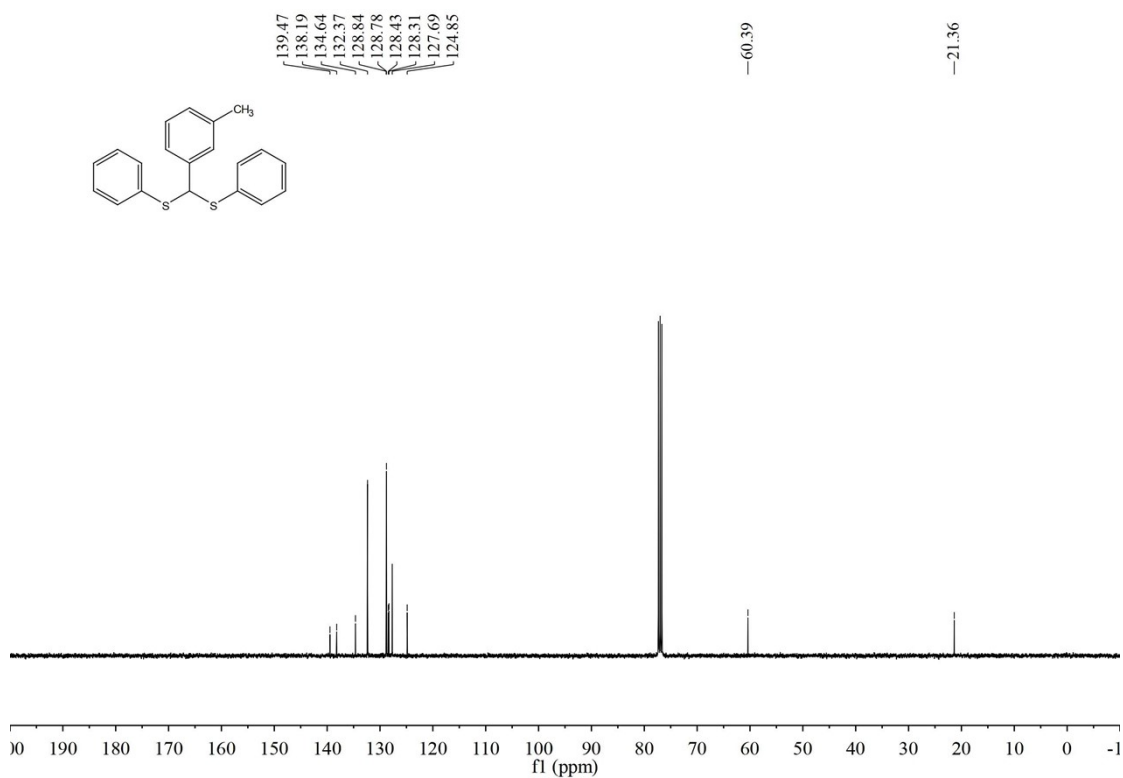
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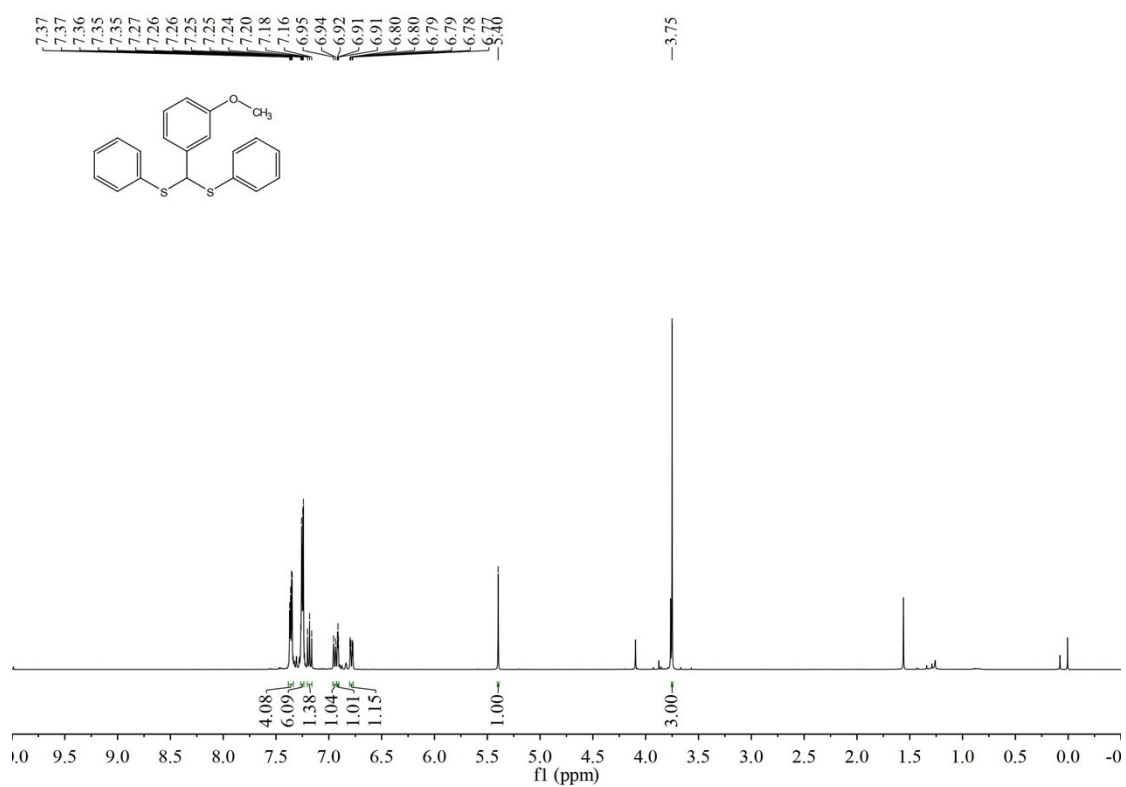
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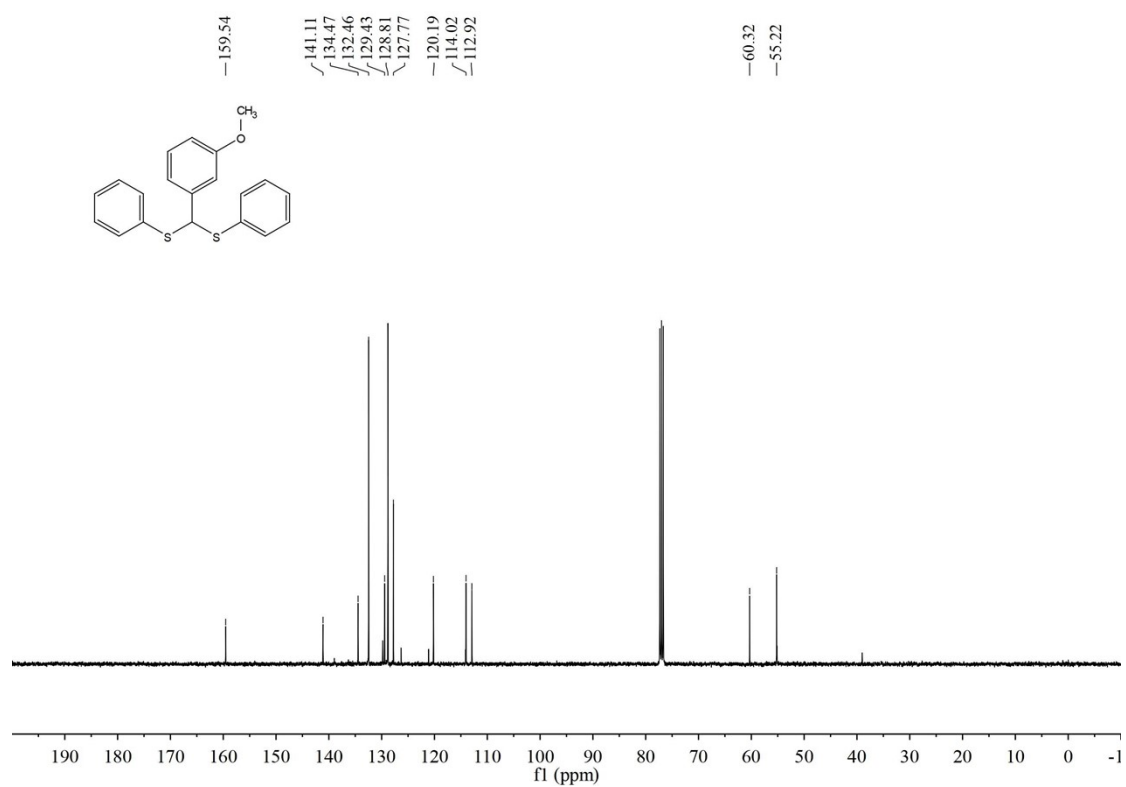
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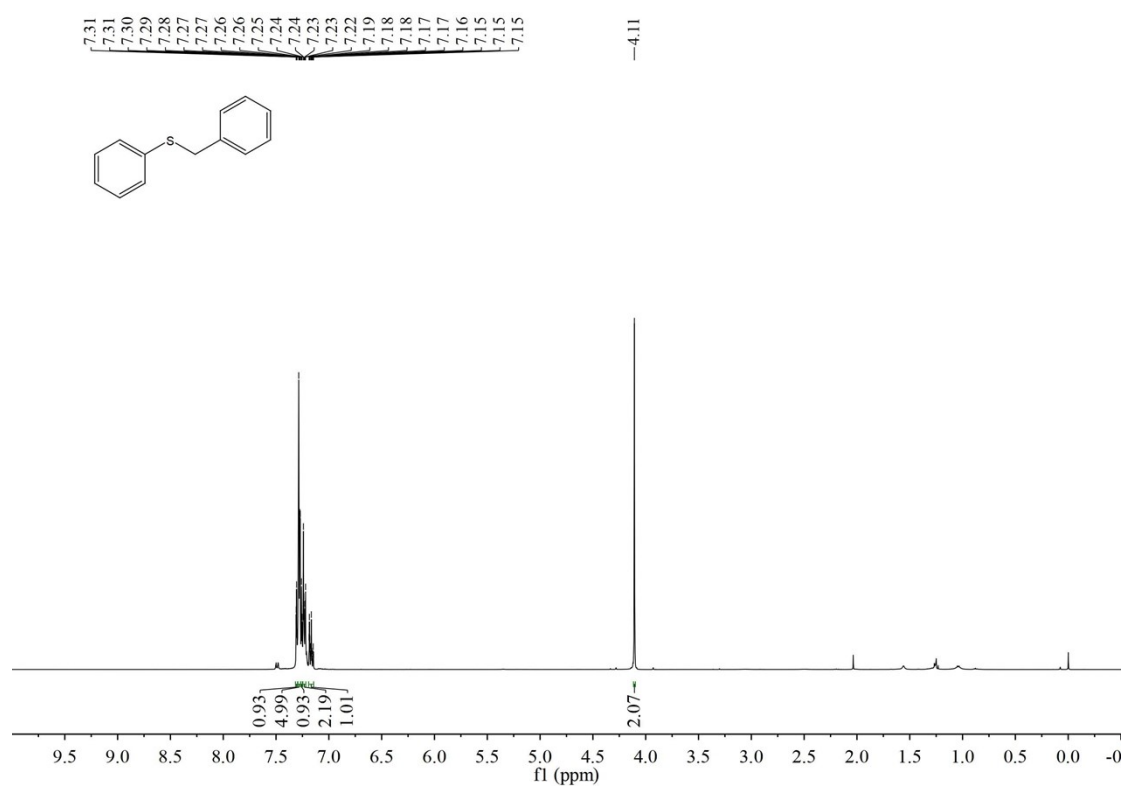
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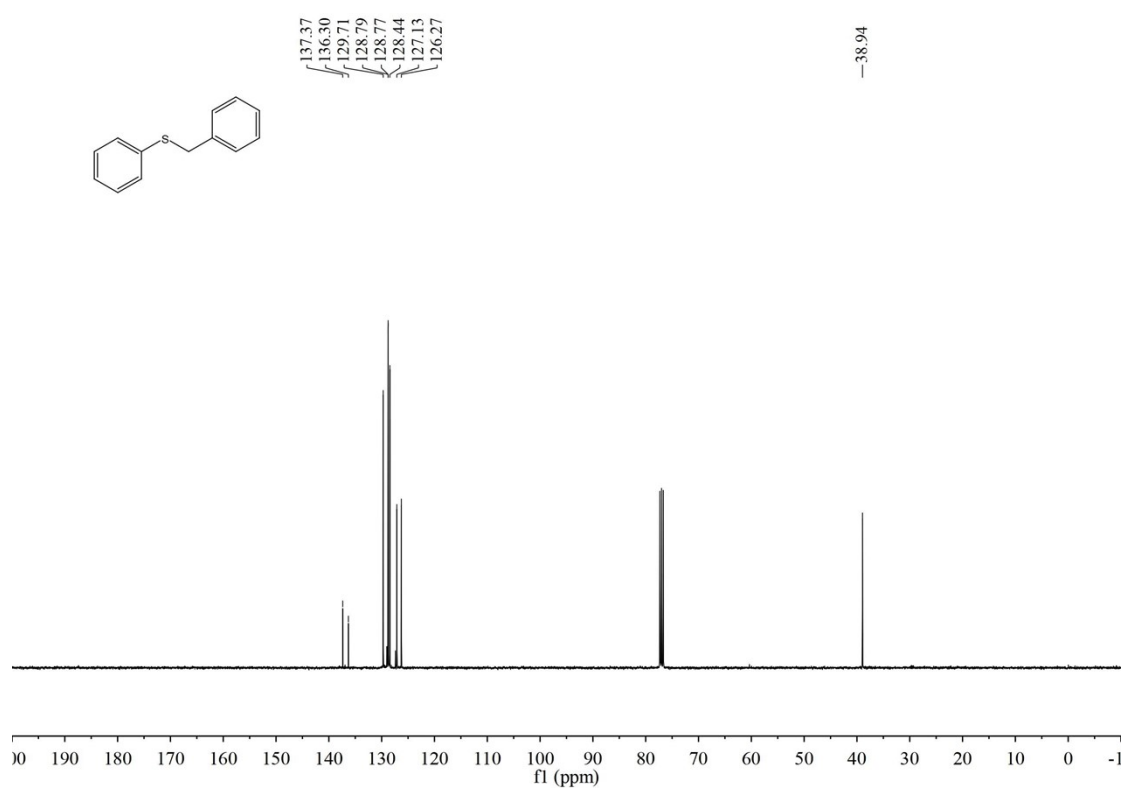
**3af-<sup>13</sup>C**



**5a-<sup>1</sup>H**

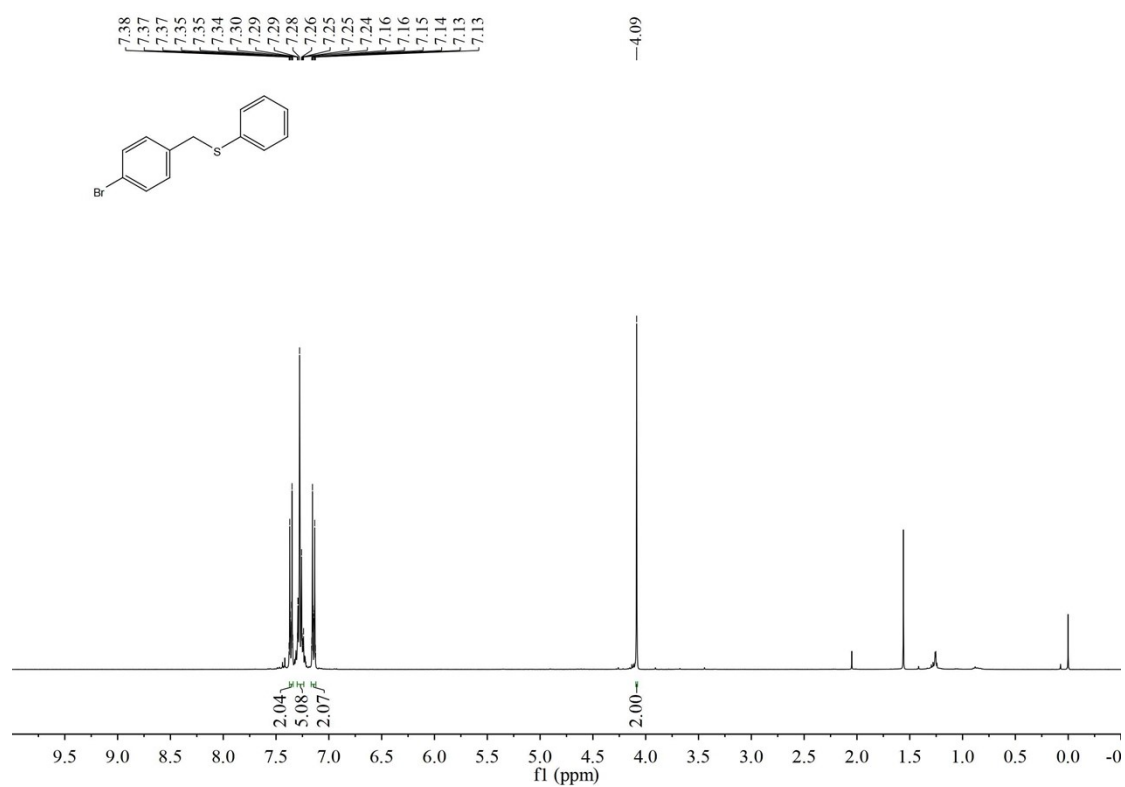


**5a-<sup>13</sup>C**

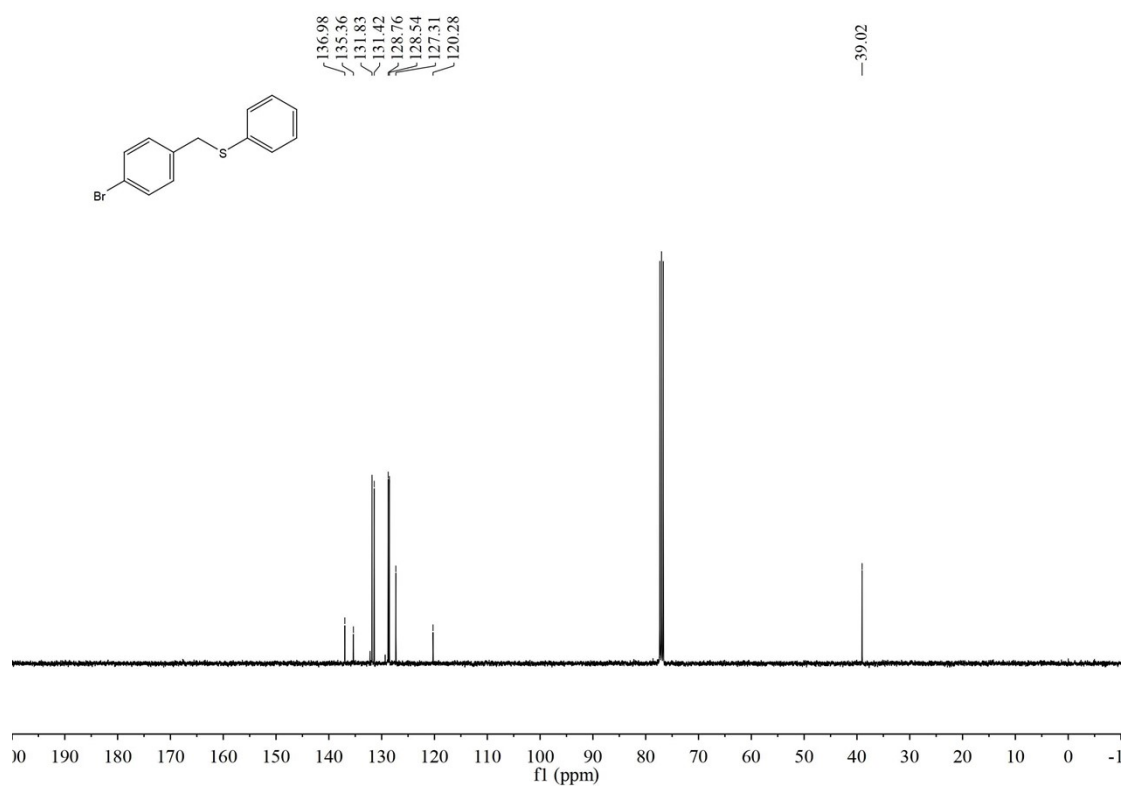




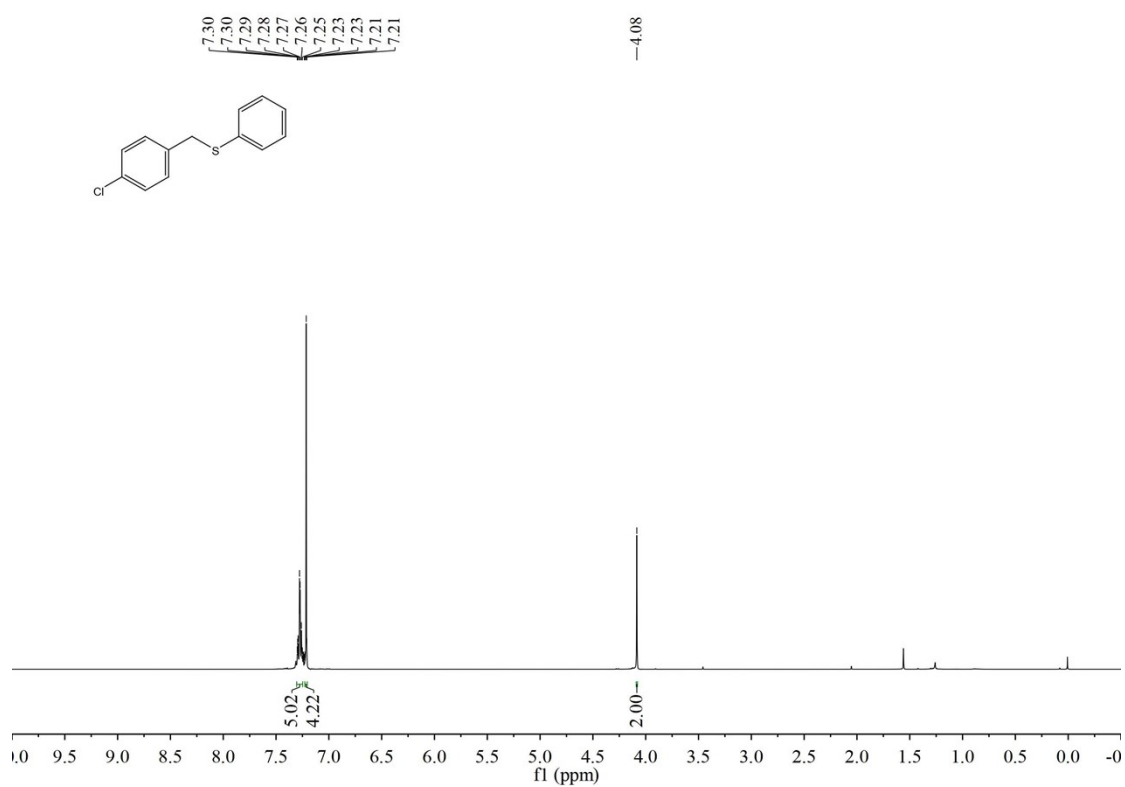
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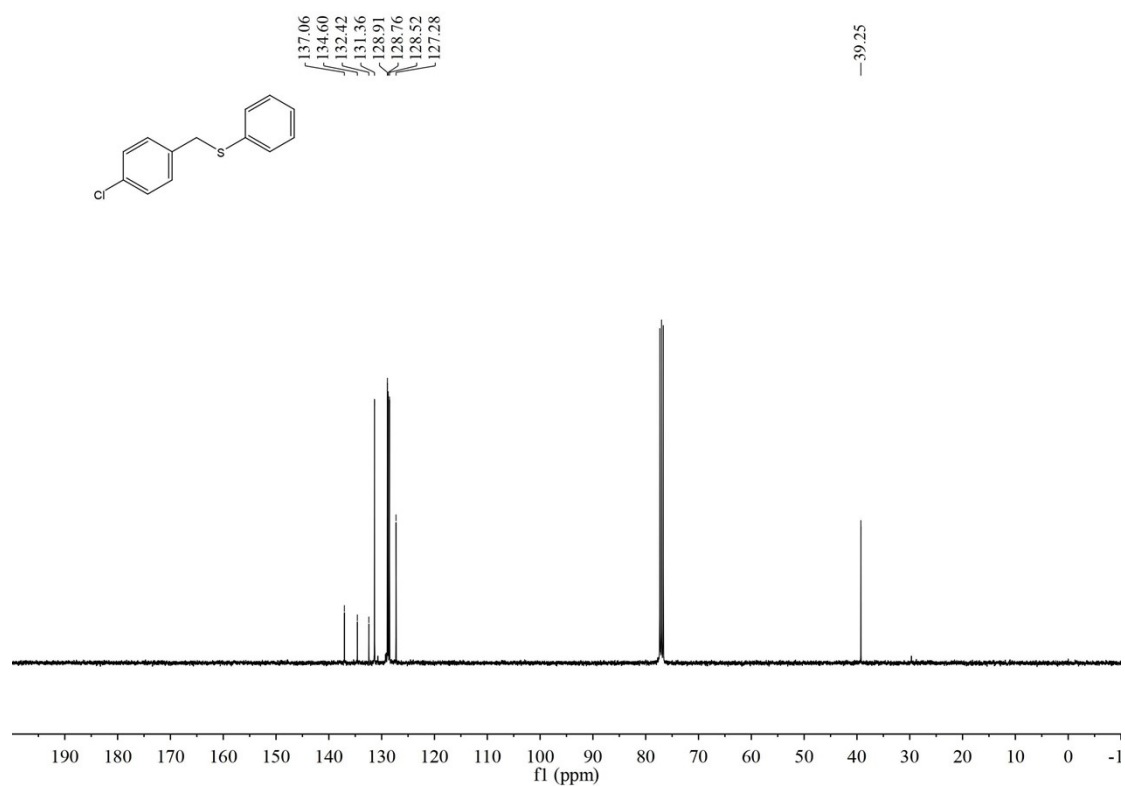
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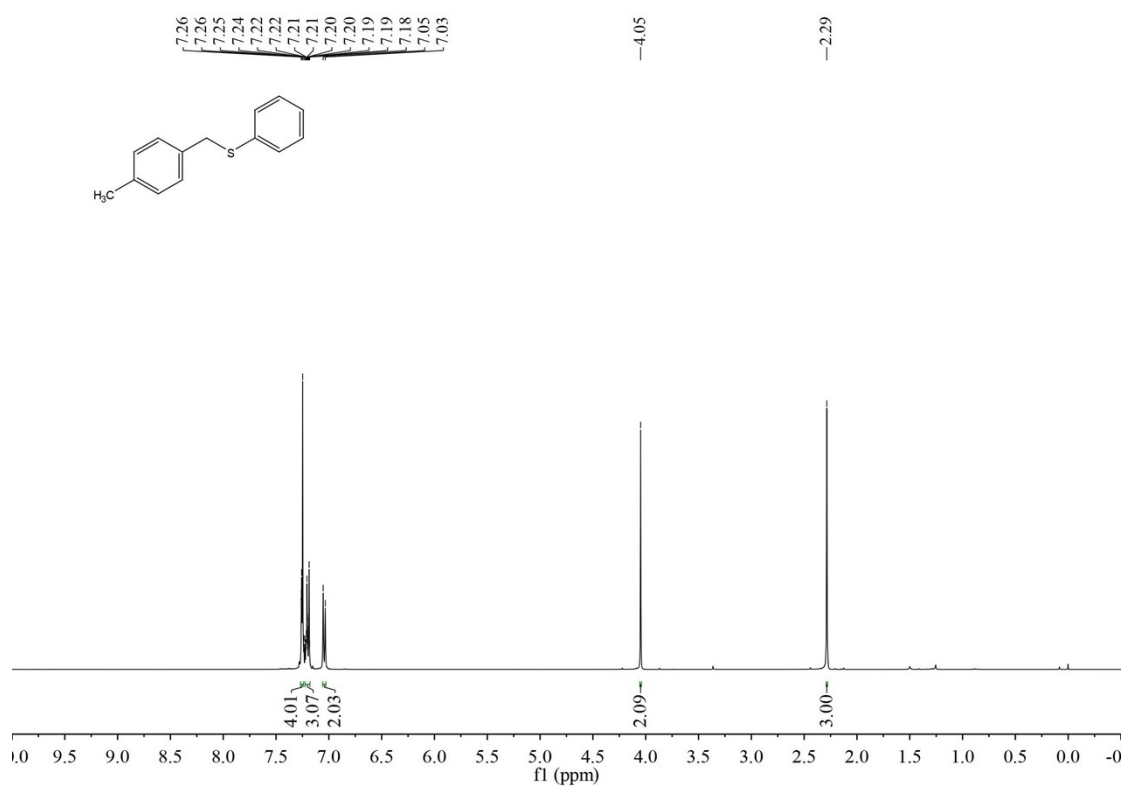
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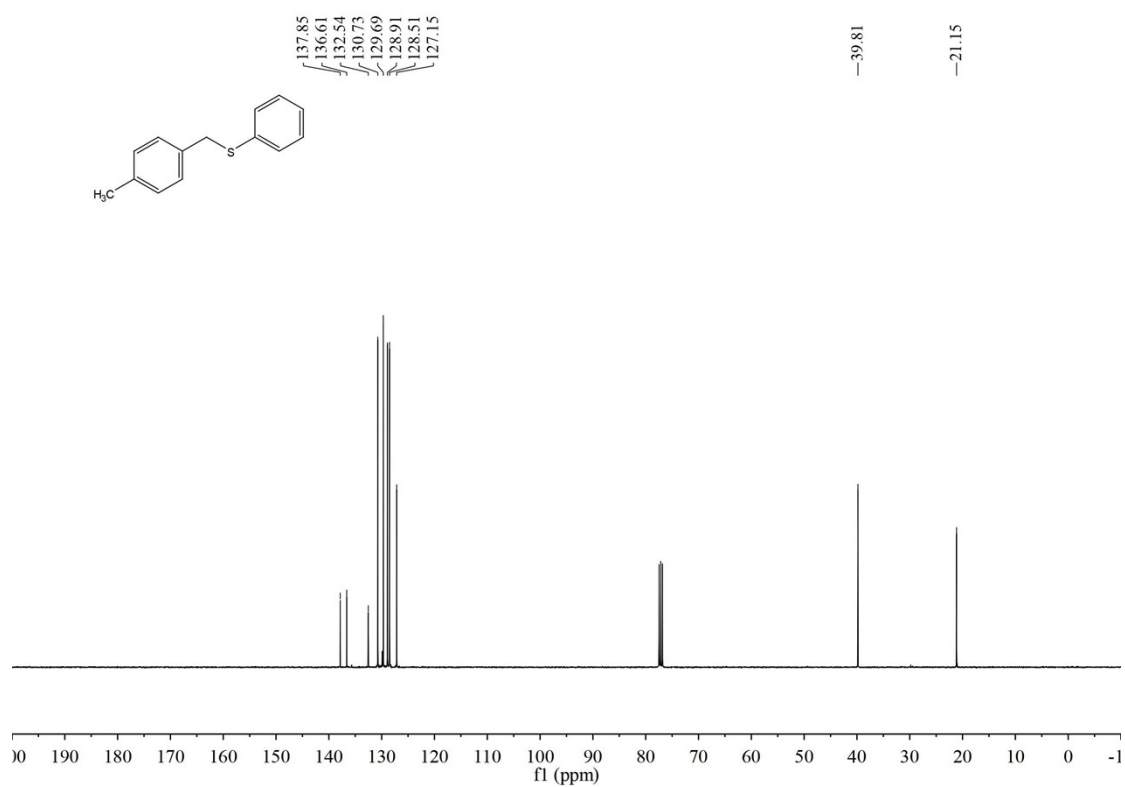
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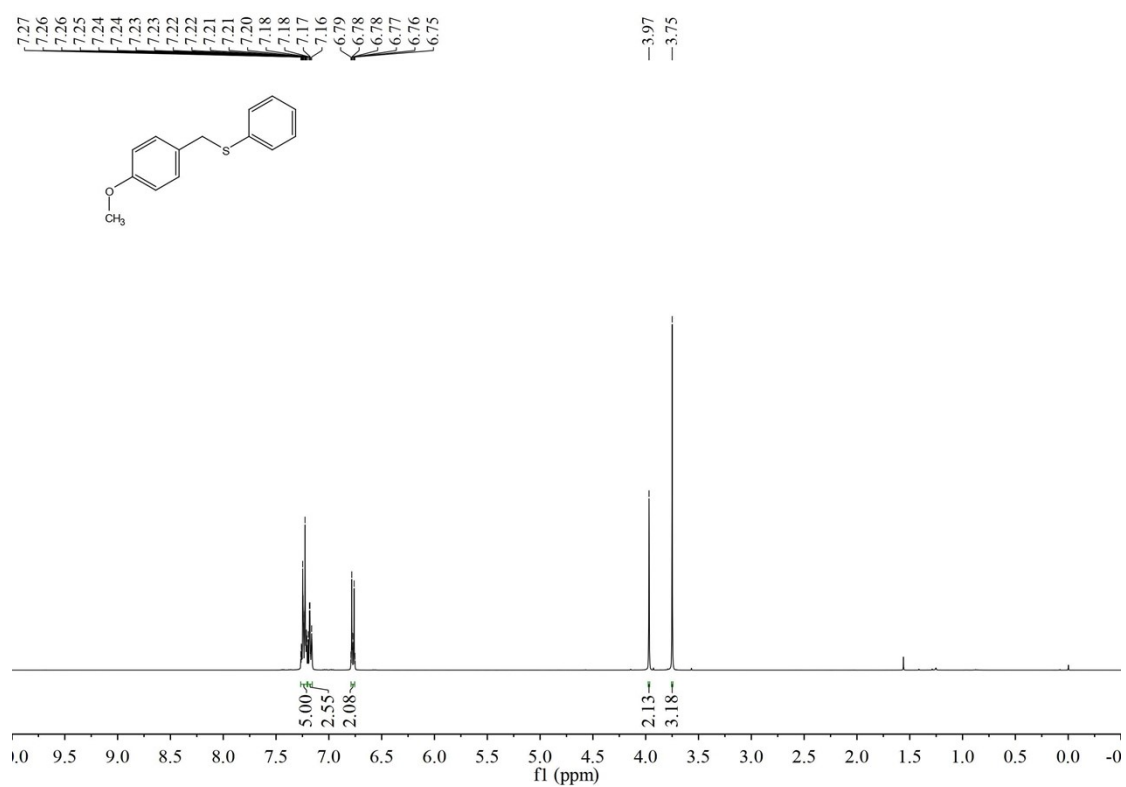
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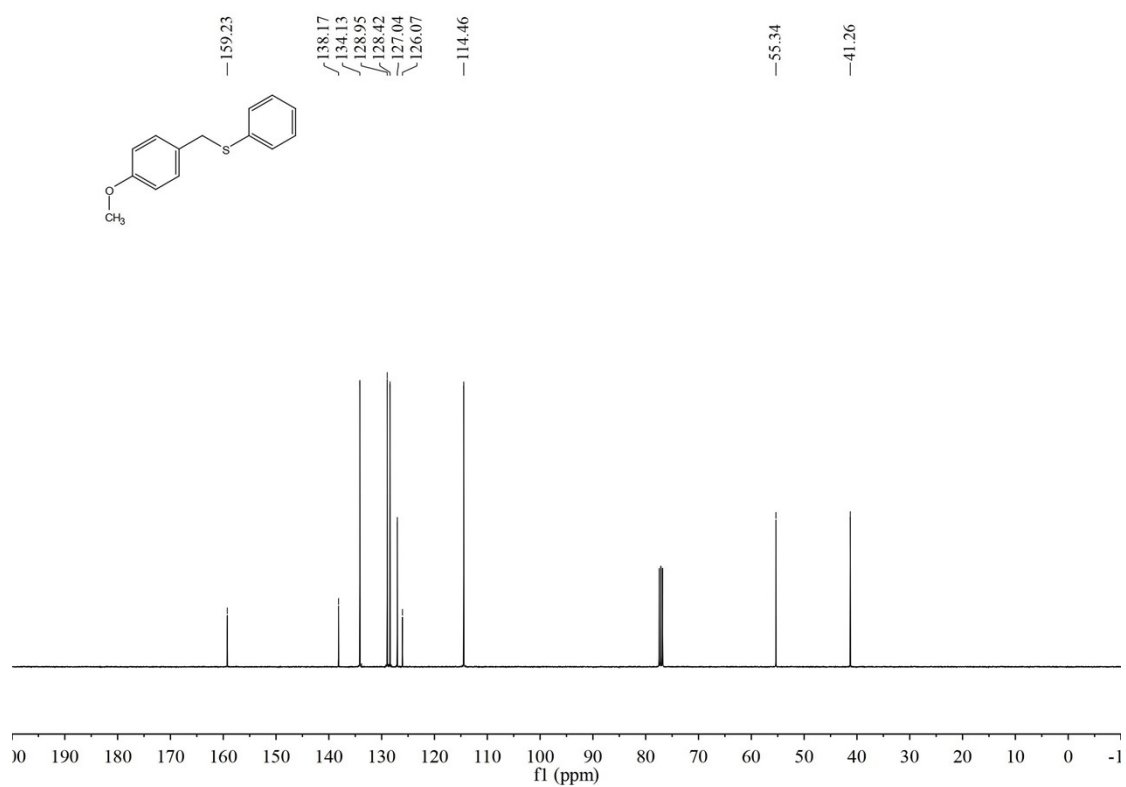
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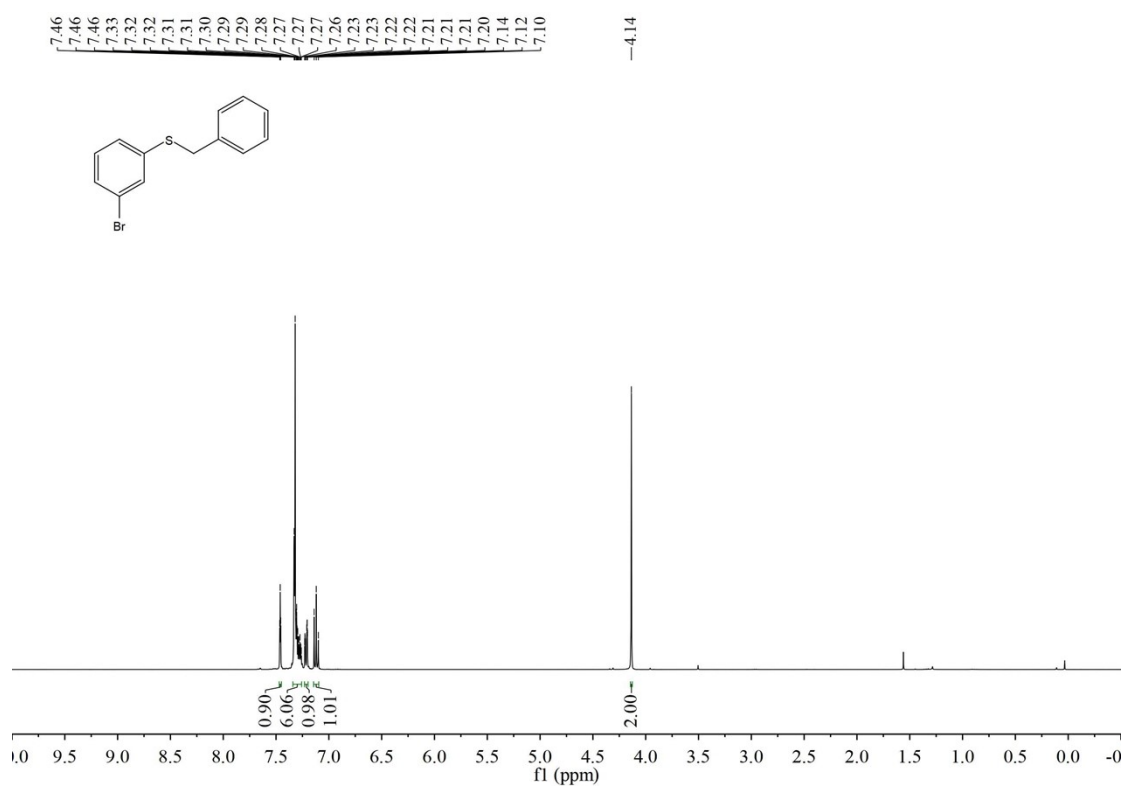
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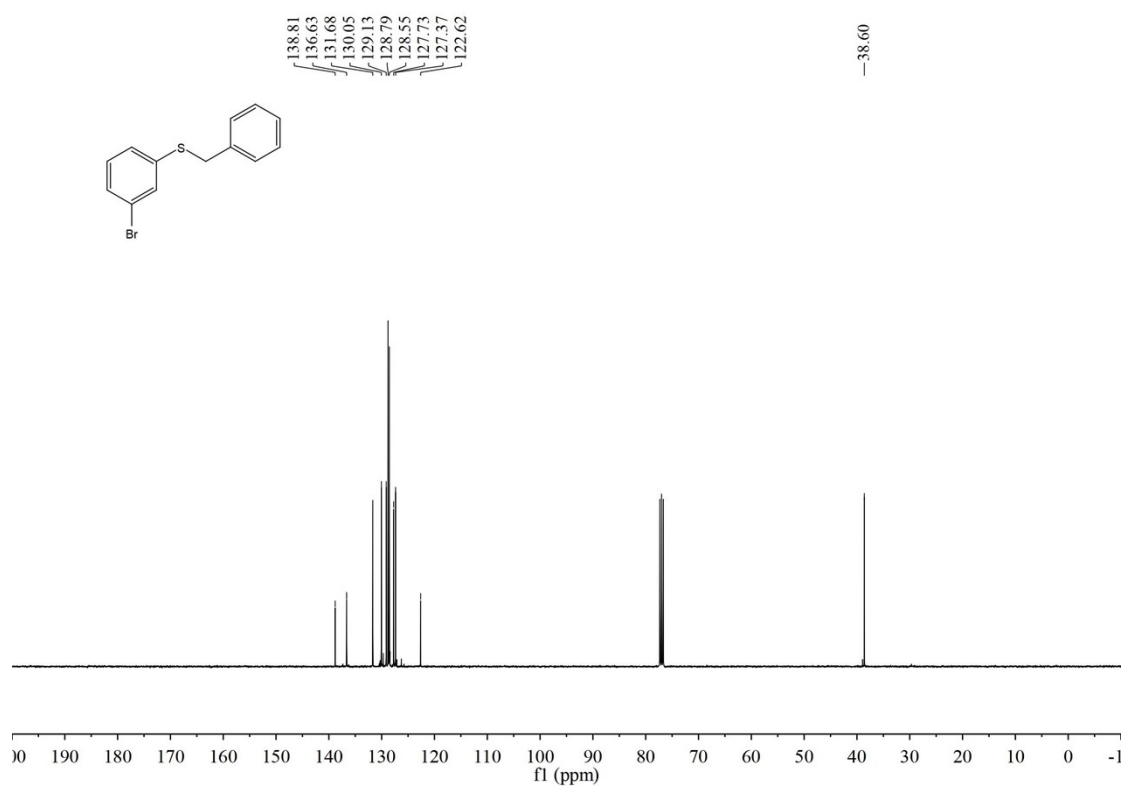
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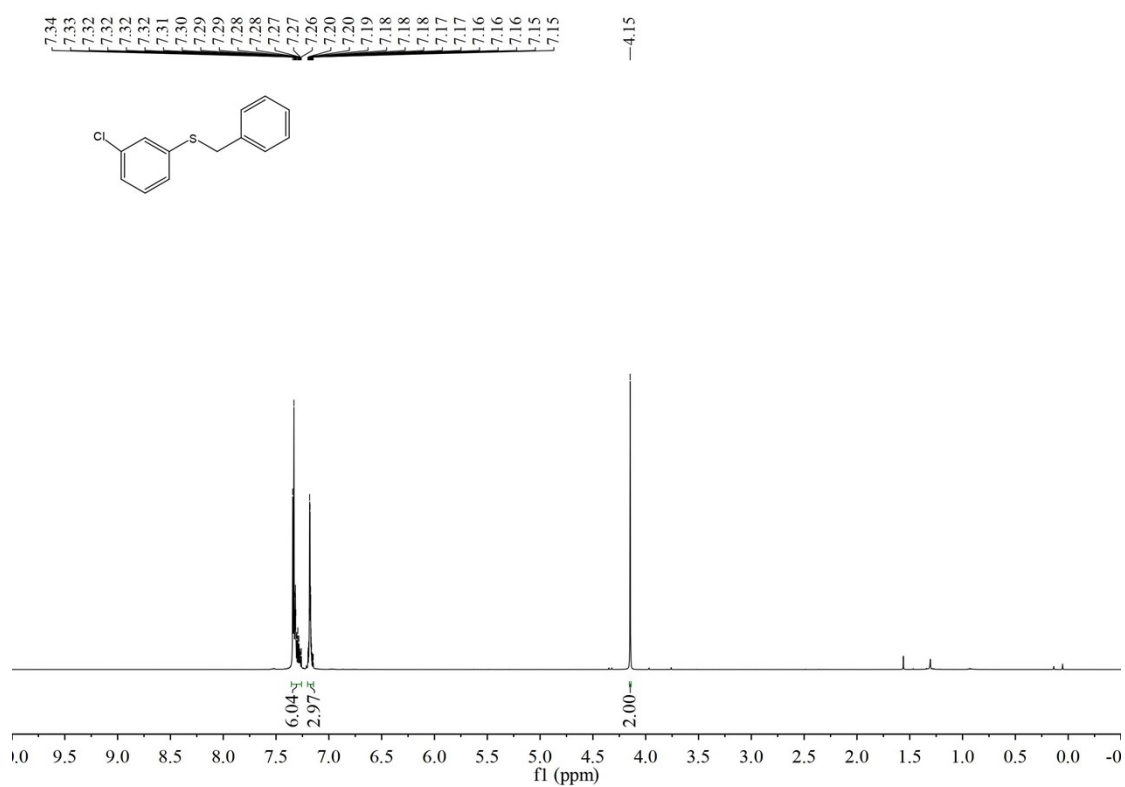
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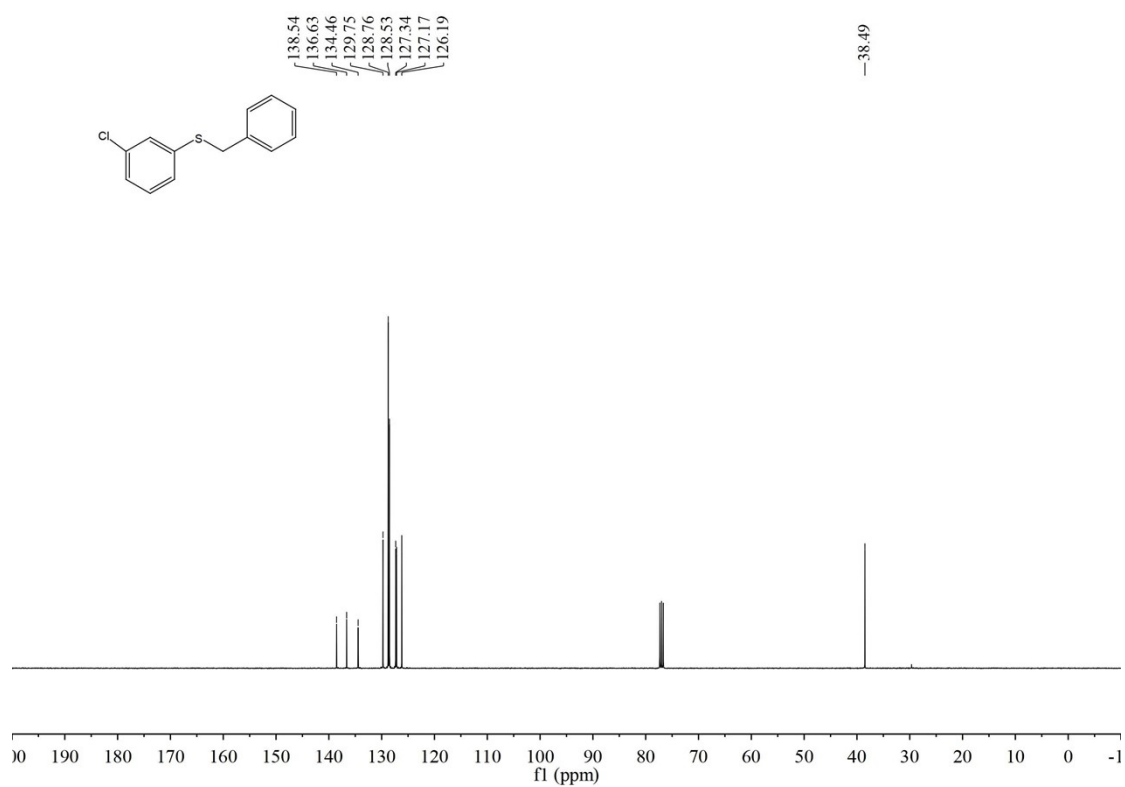
**5f-<sup>13</sup>C**



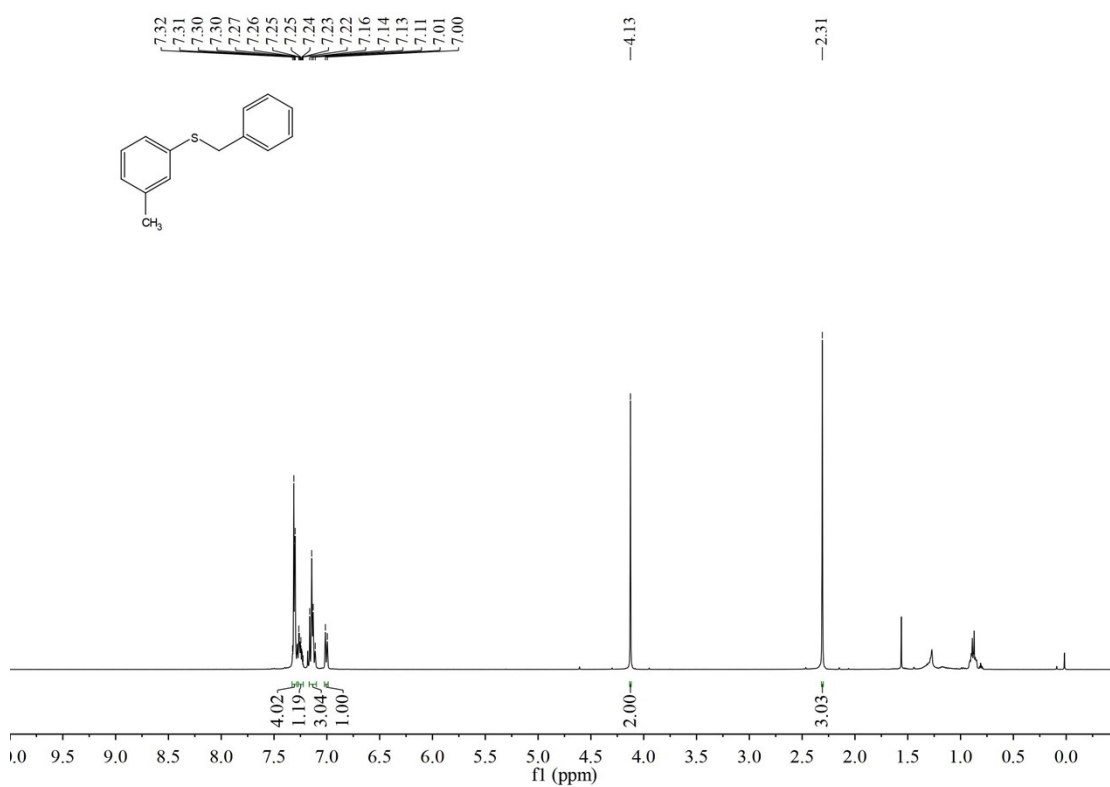
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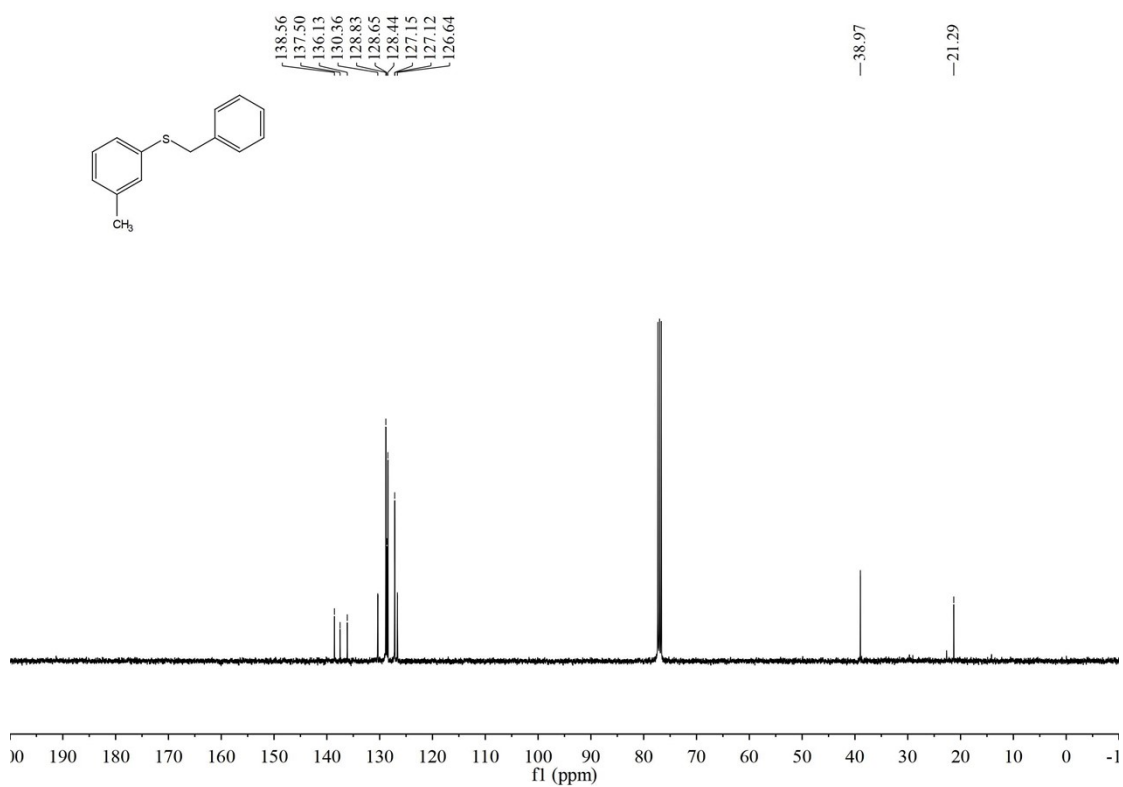
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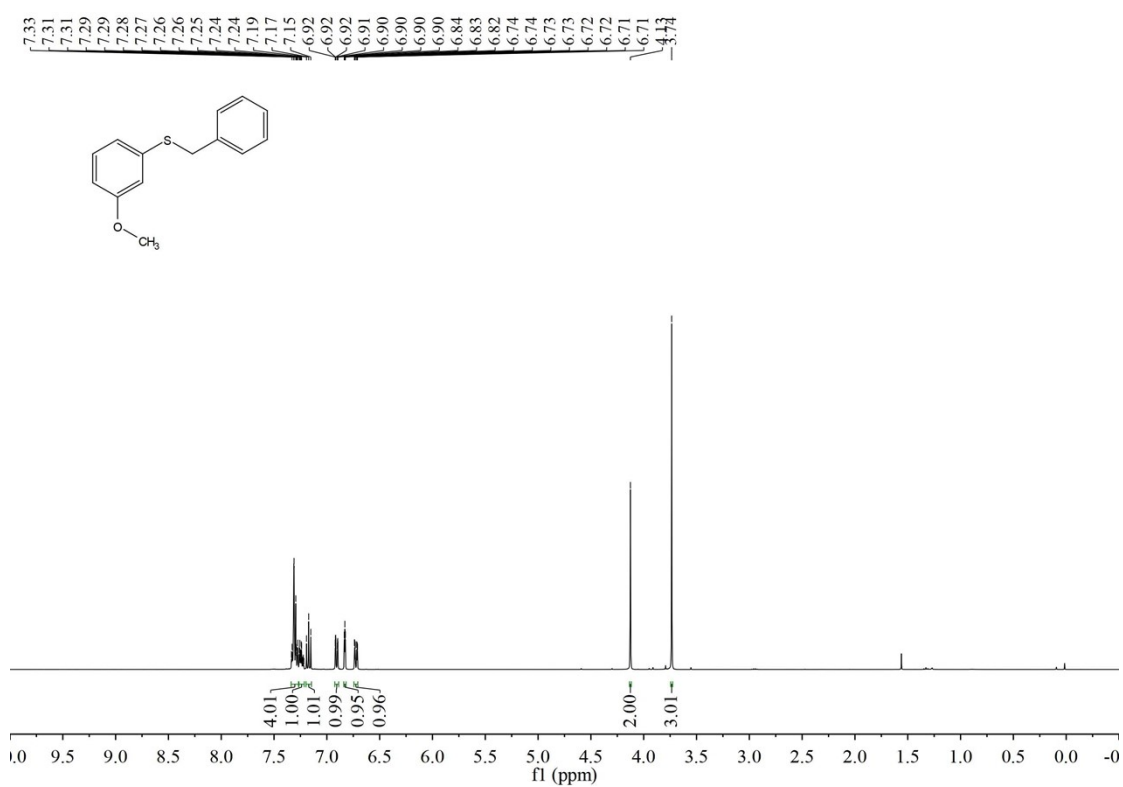
**5h-<sup>1</sup>H**



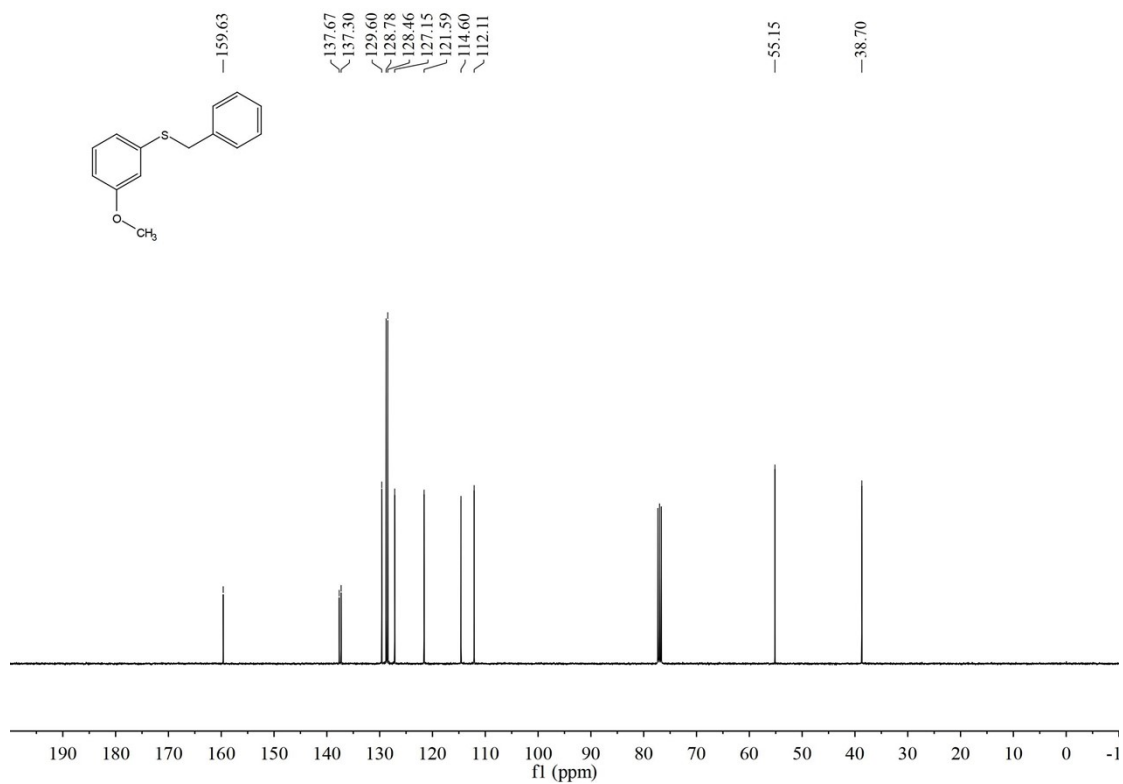
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**5i-<sup>1</sup>H**

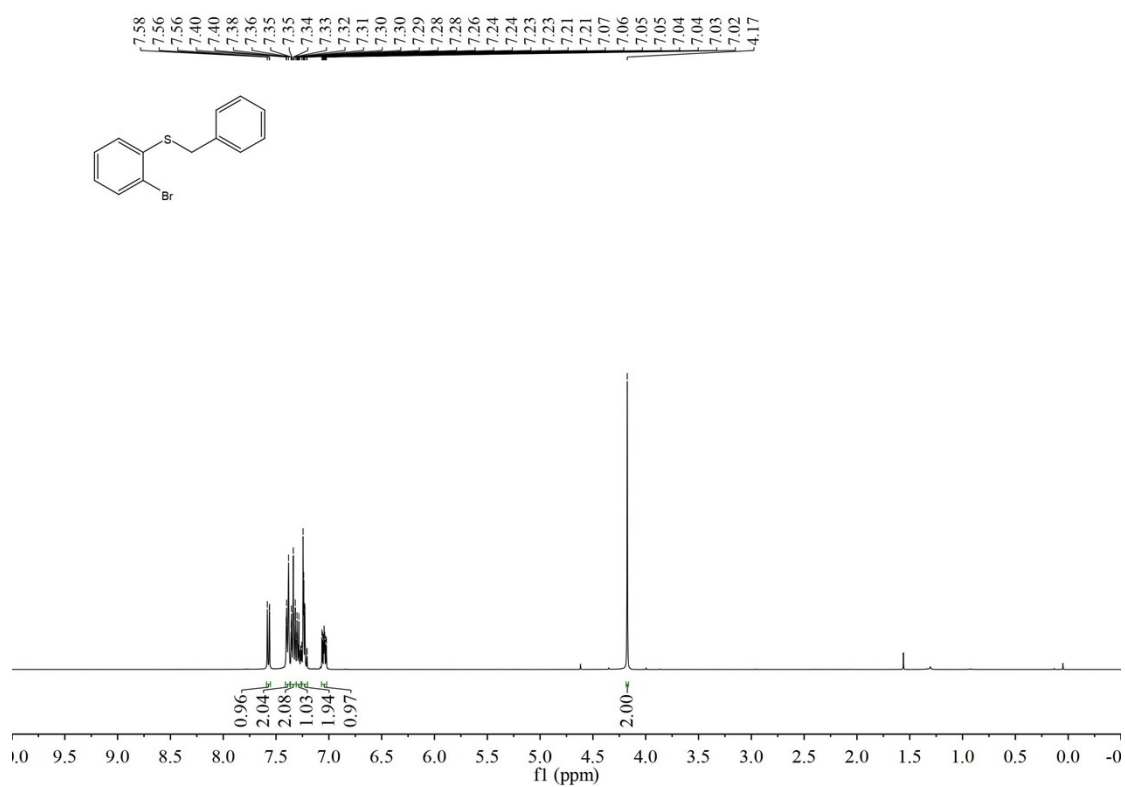


**5i-<sup>13</sup>C**

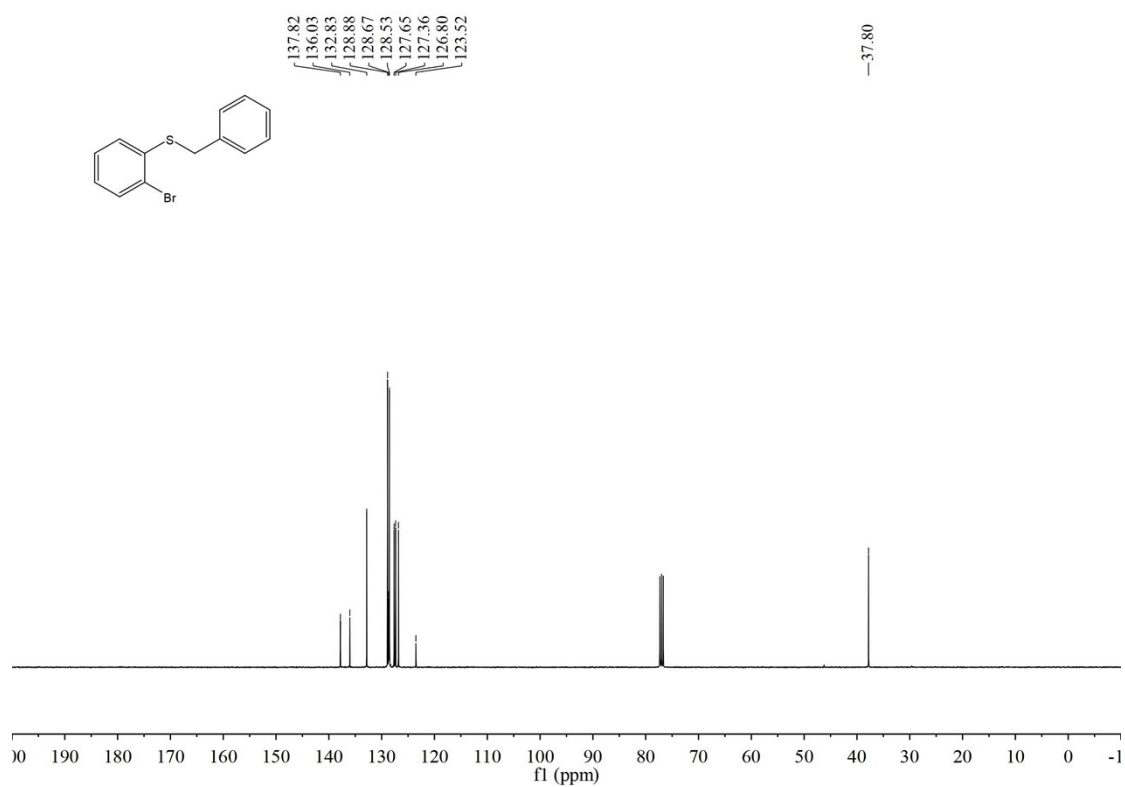




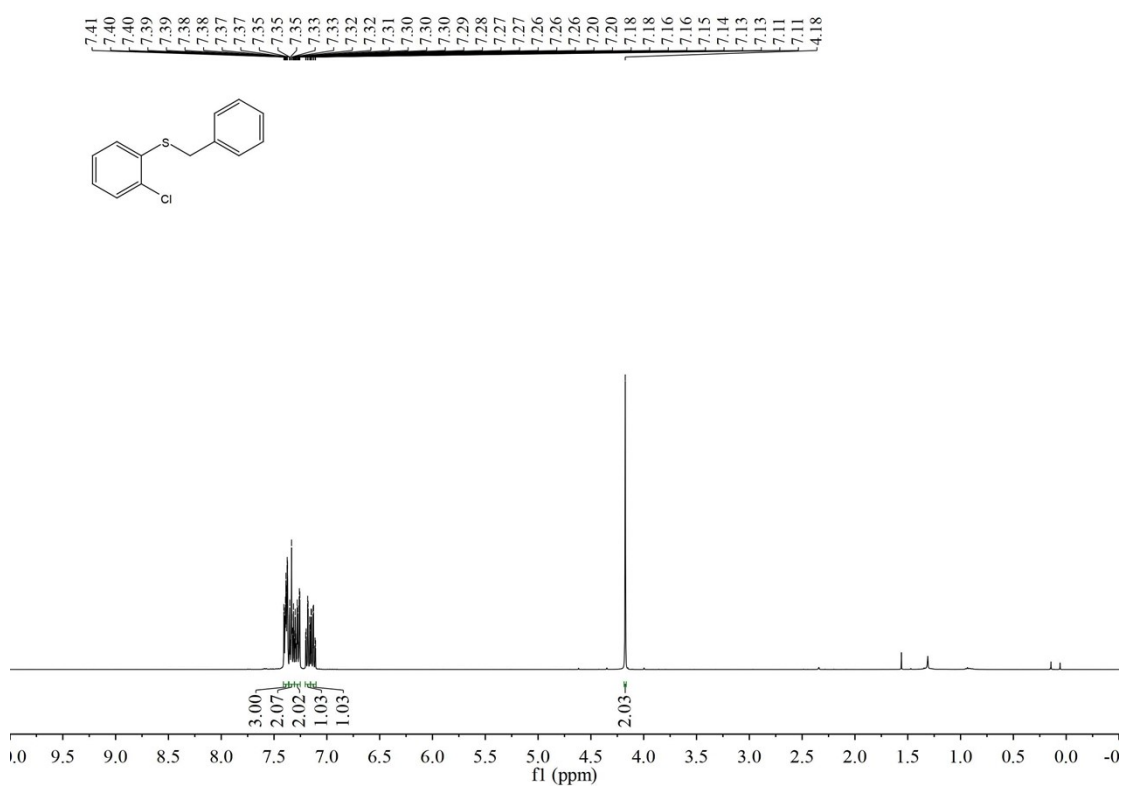
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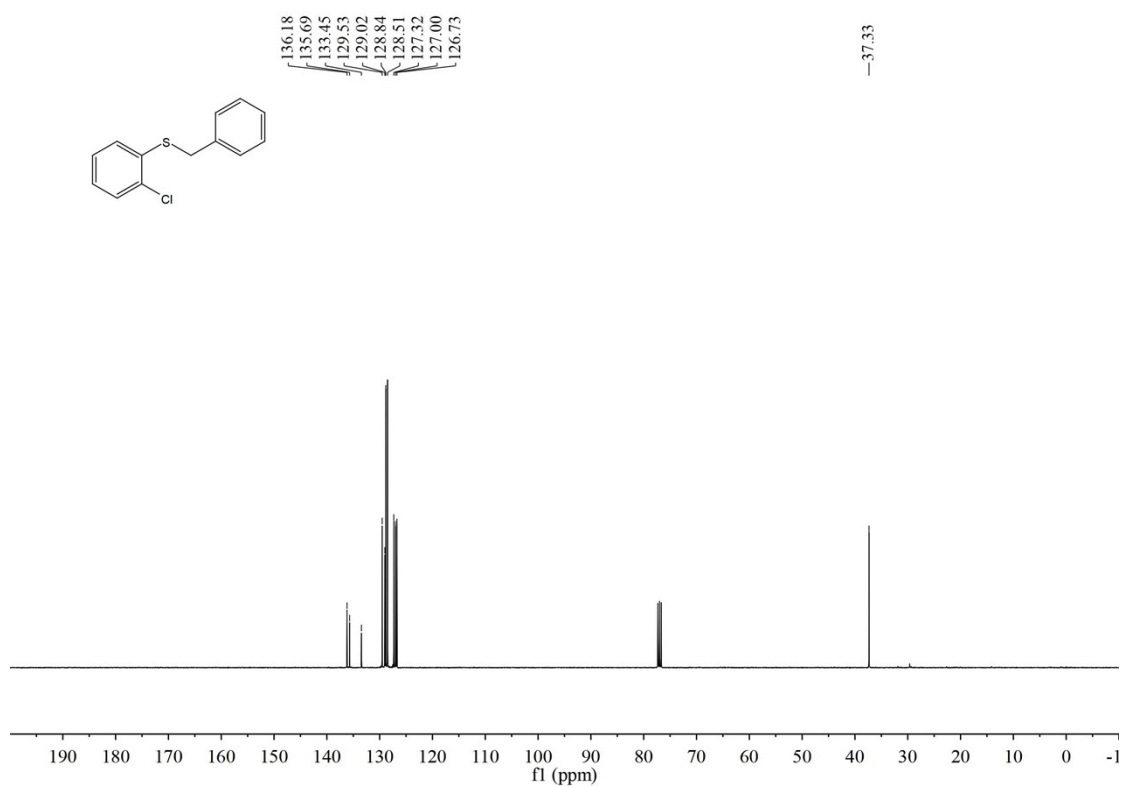
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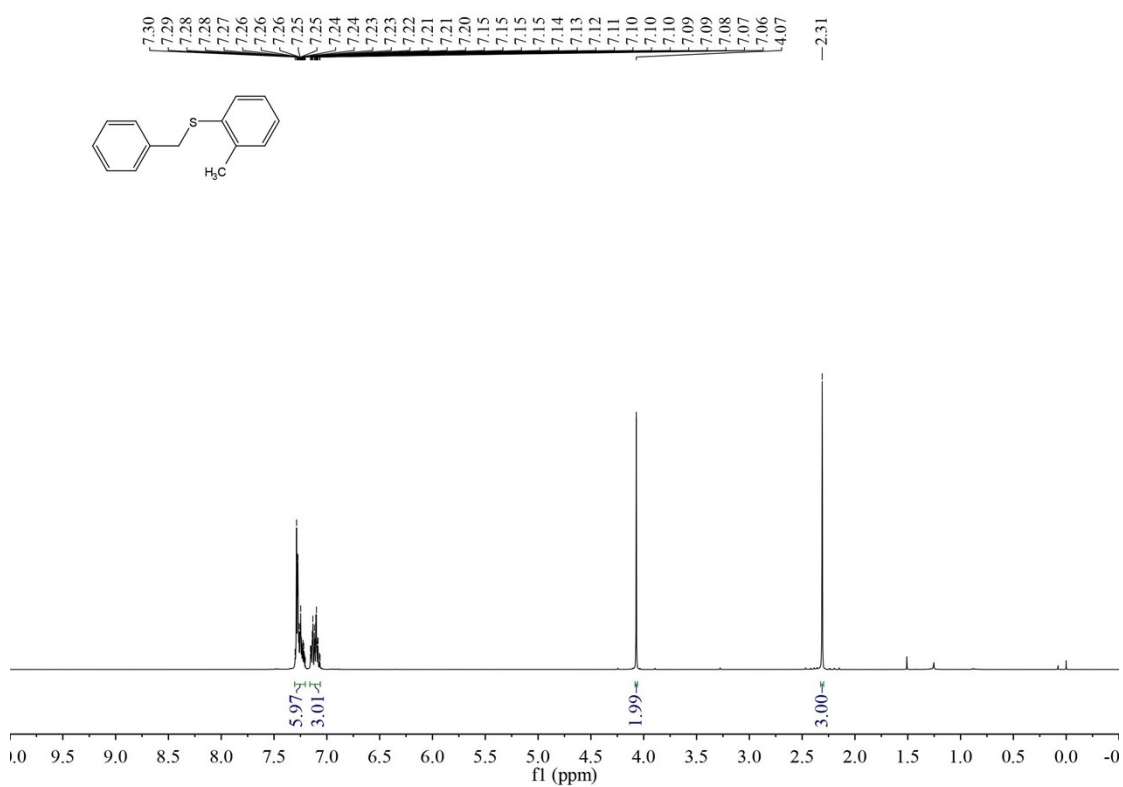
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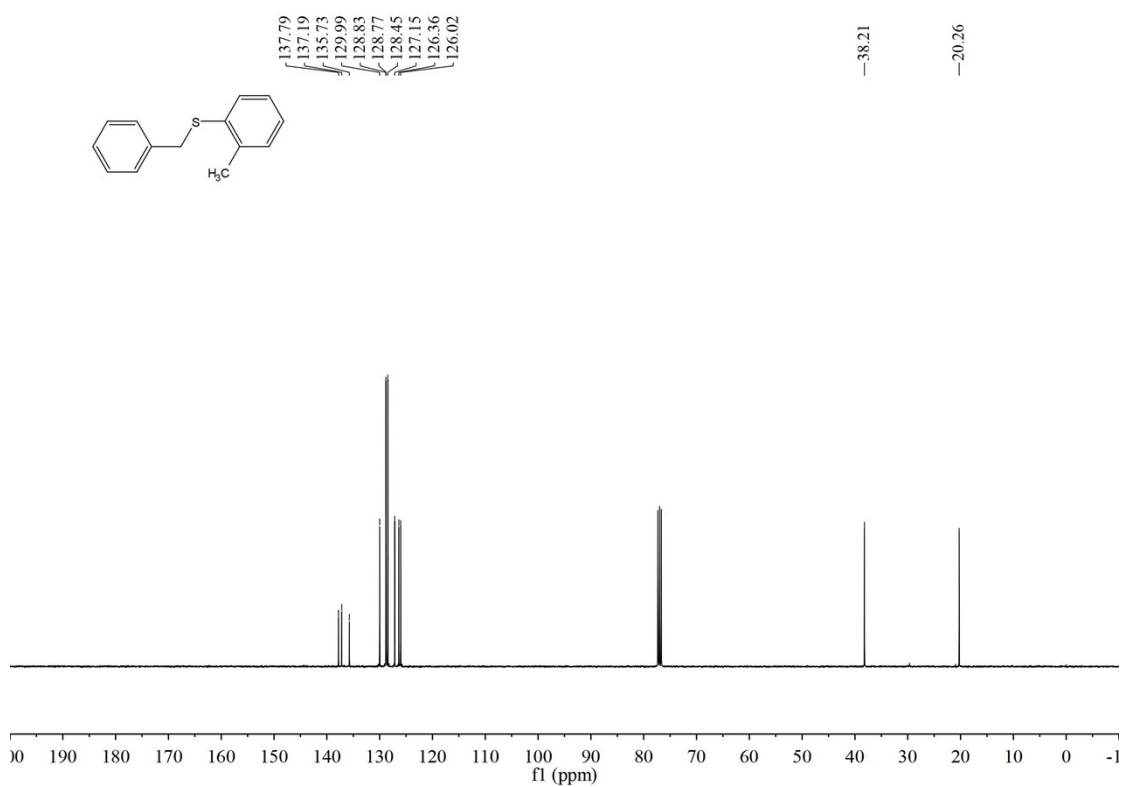
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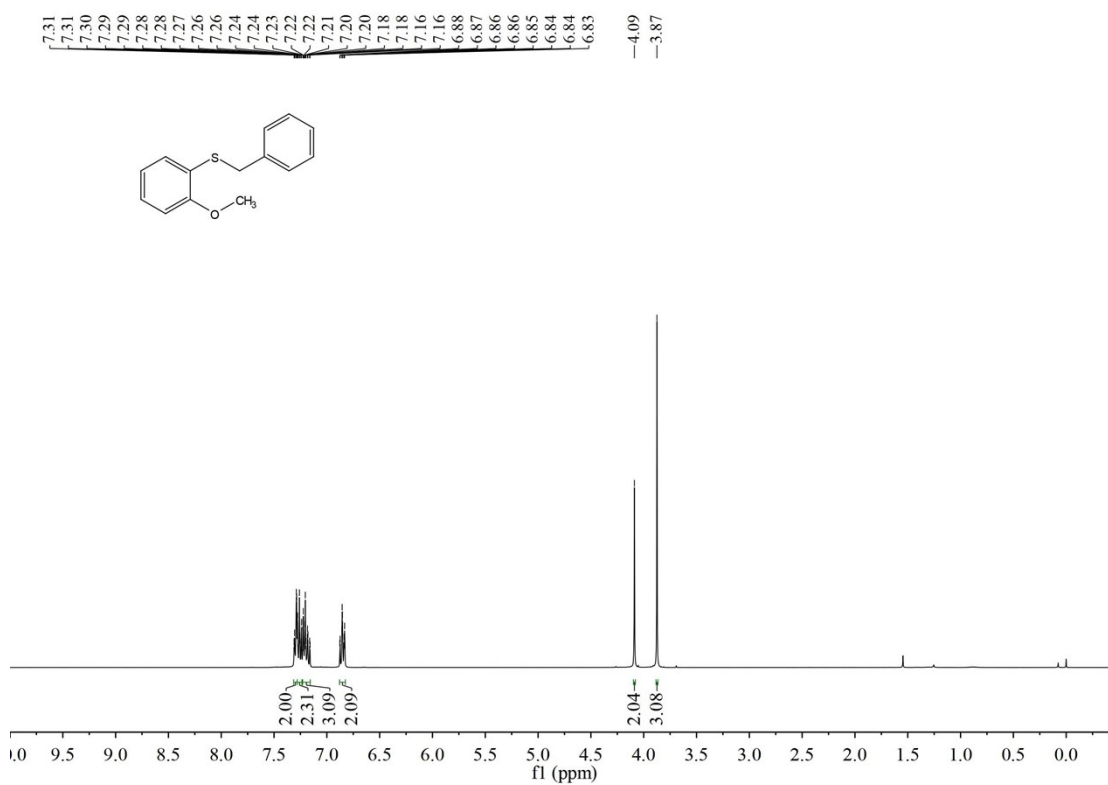
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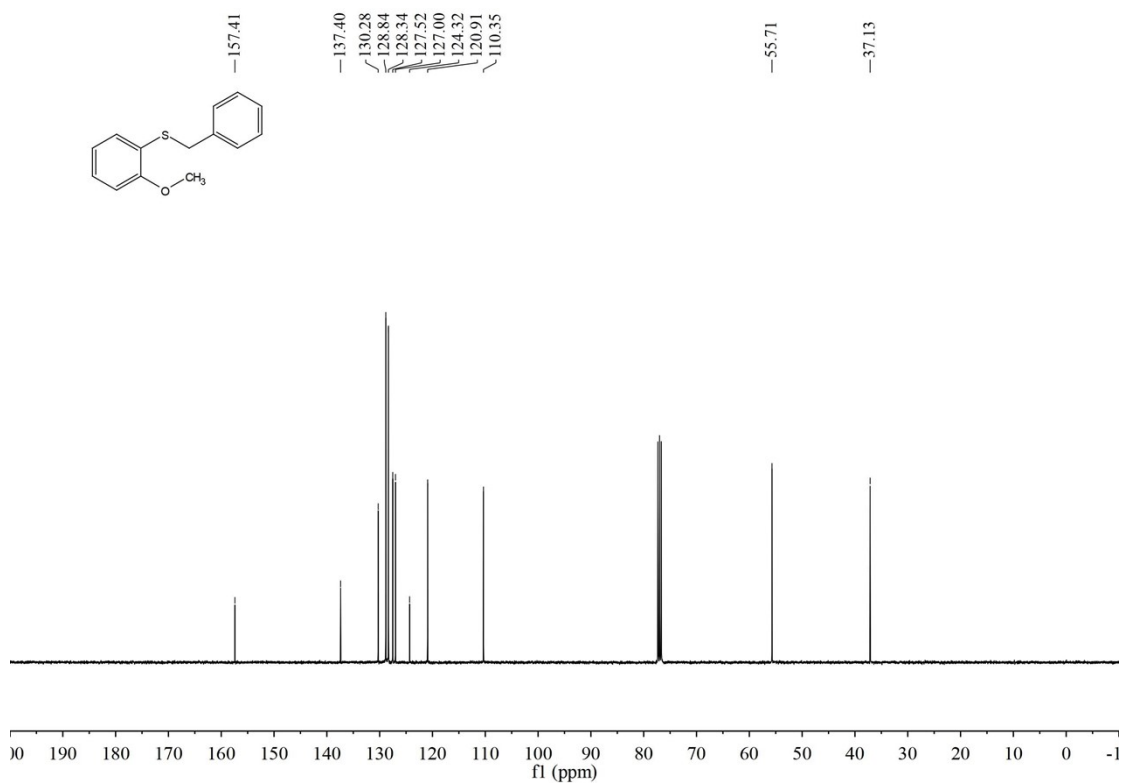
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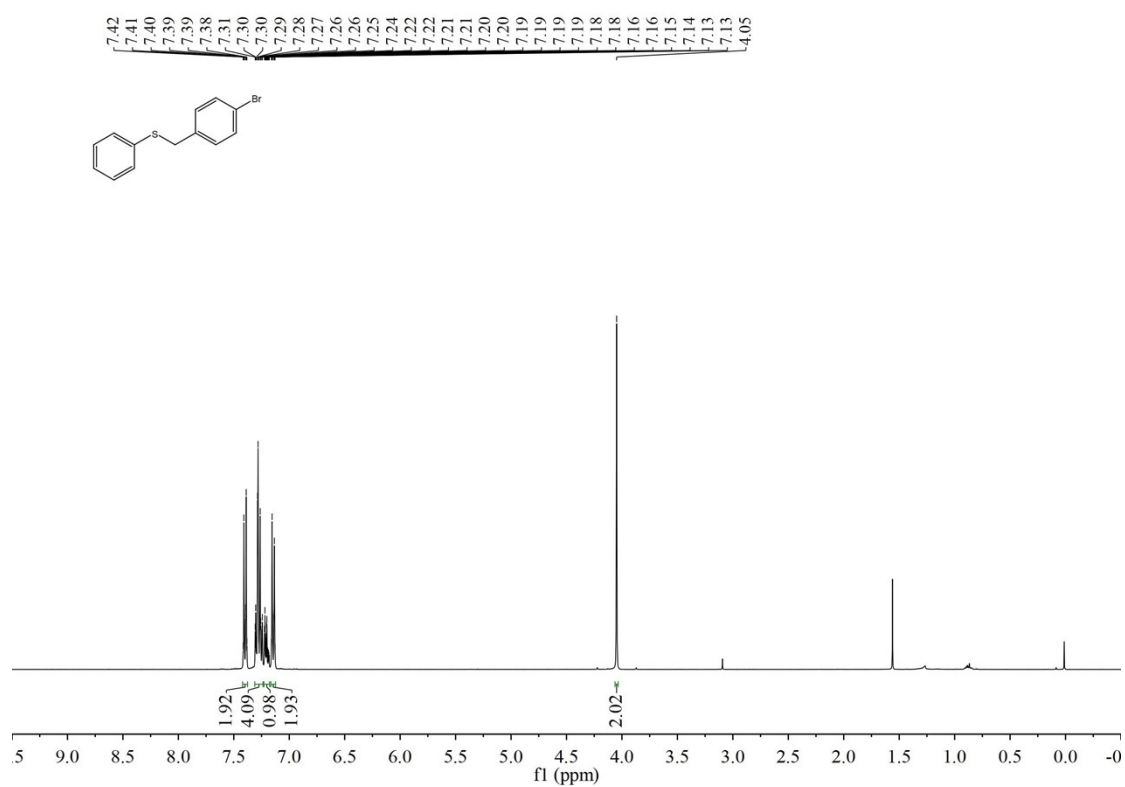
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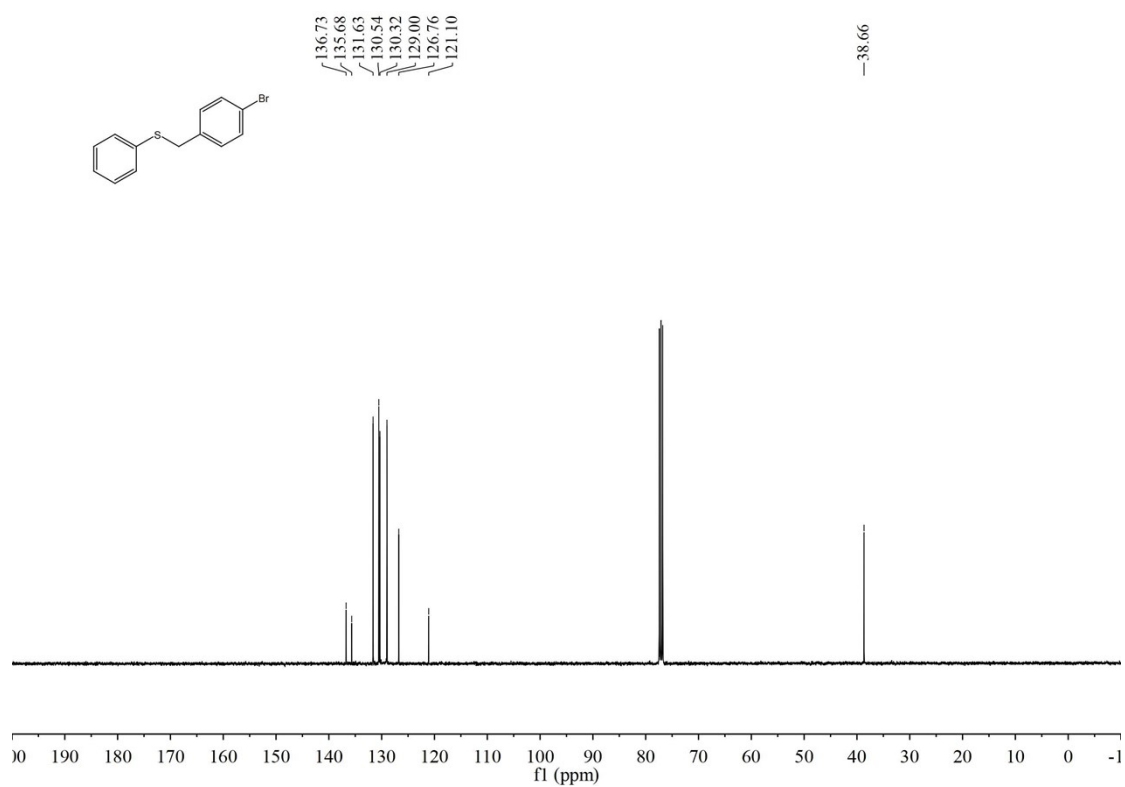
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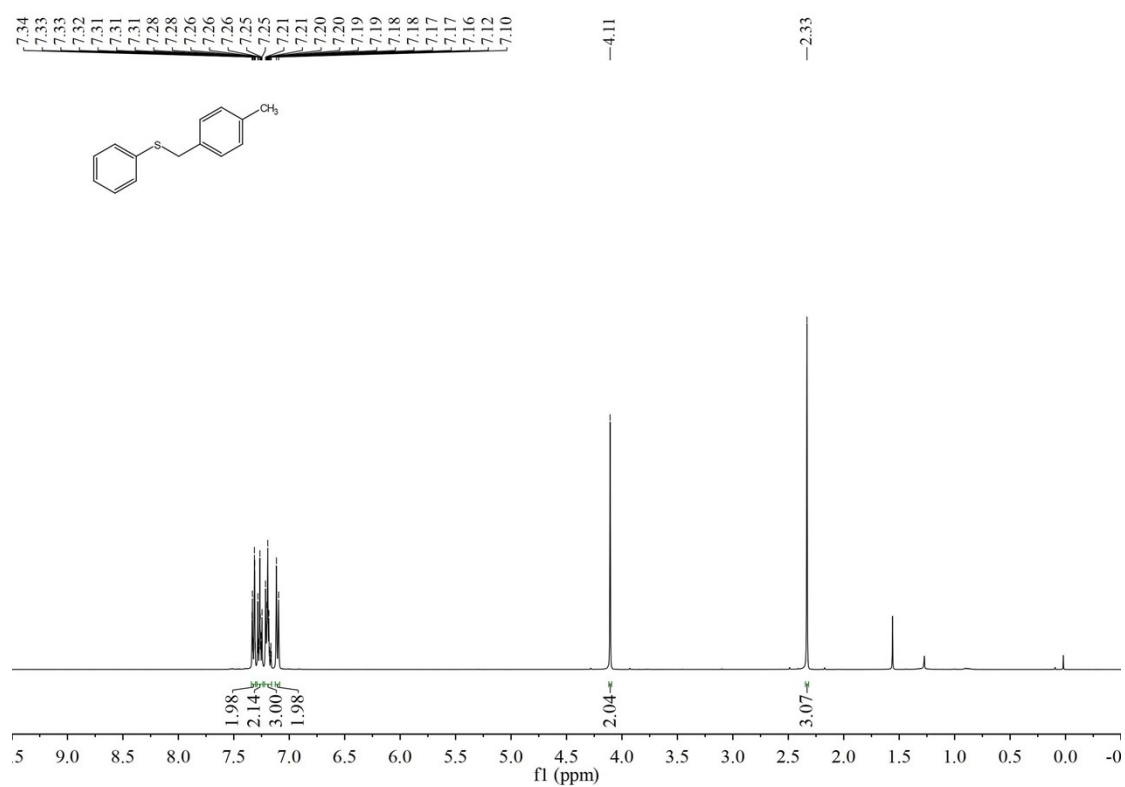
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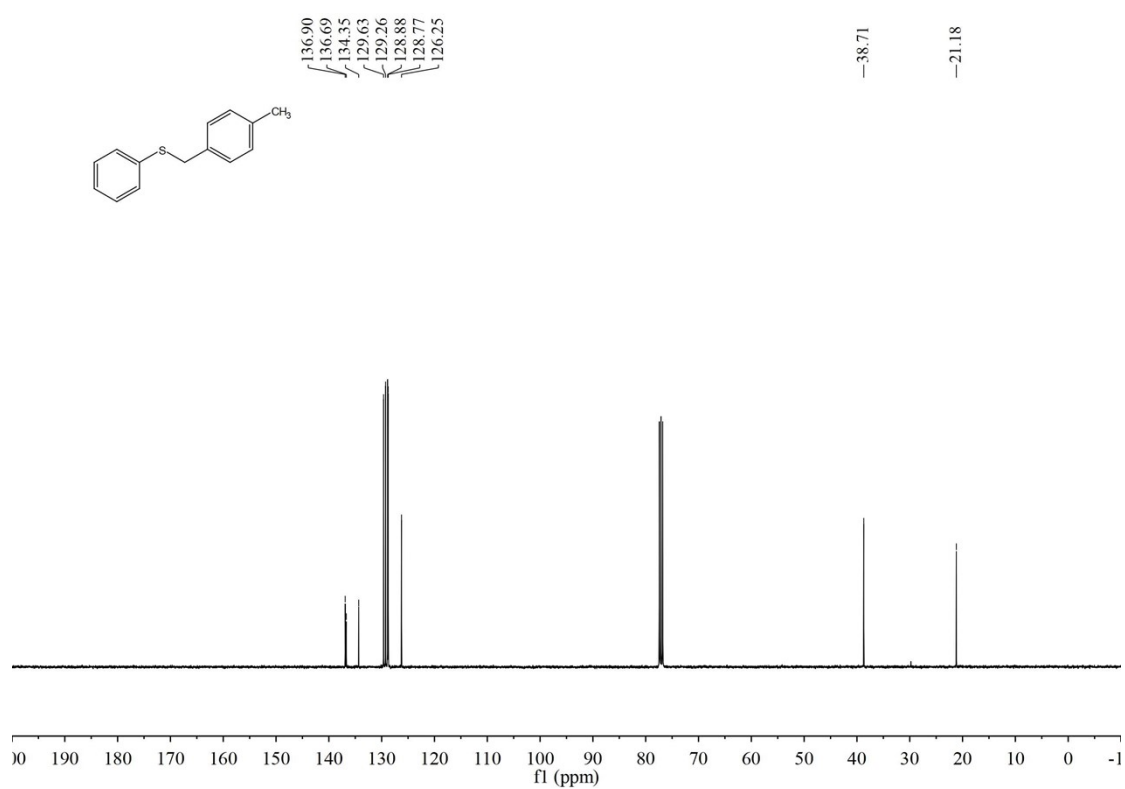
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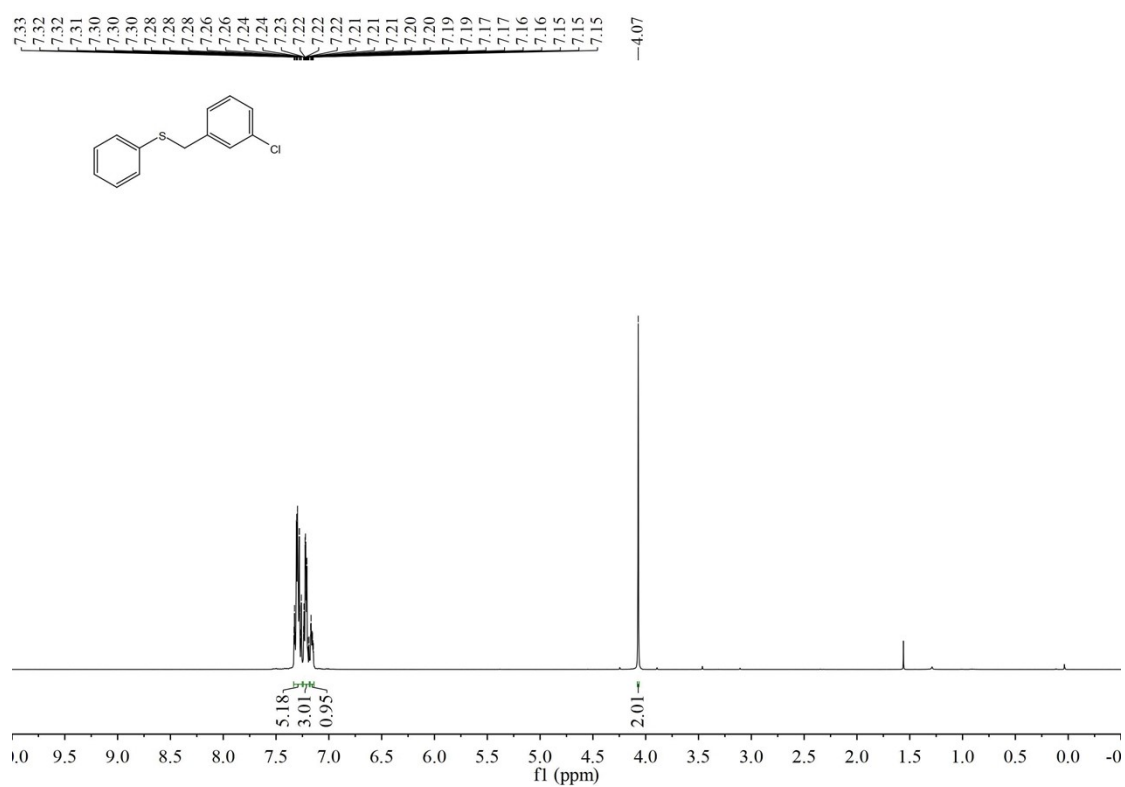
**50-<sup>1</sup>H**



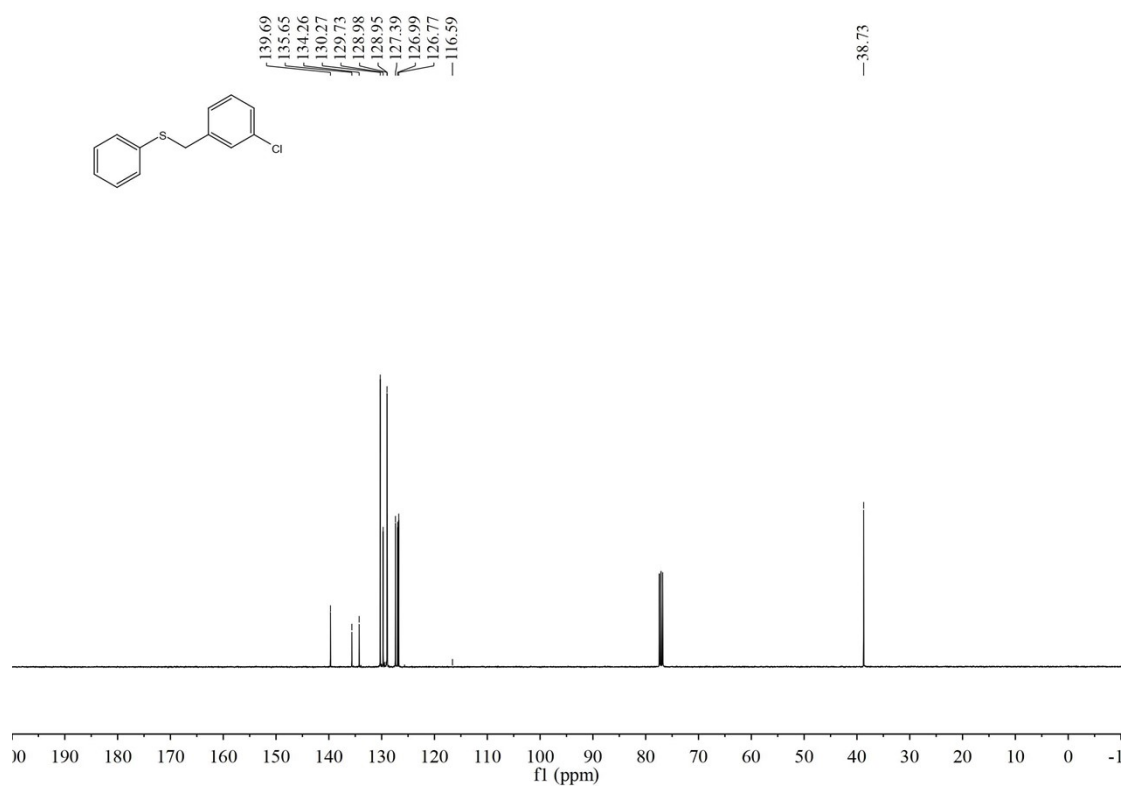
**50-<sup>13</sup>C**



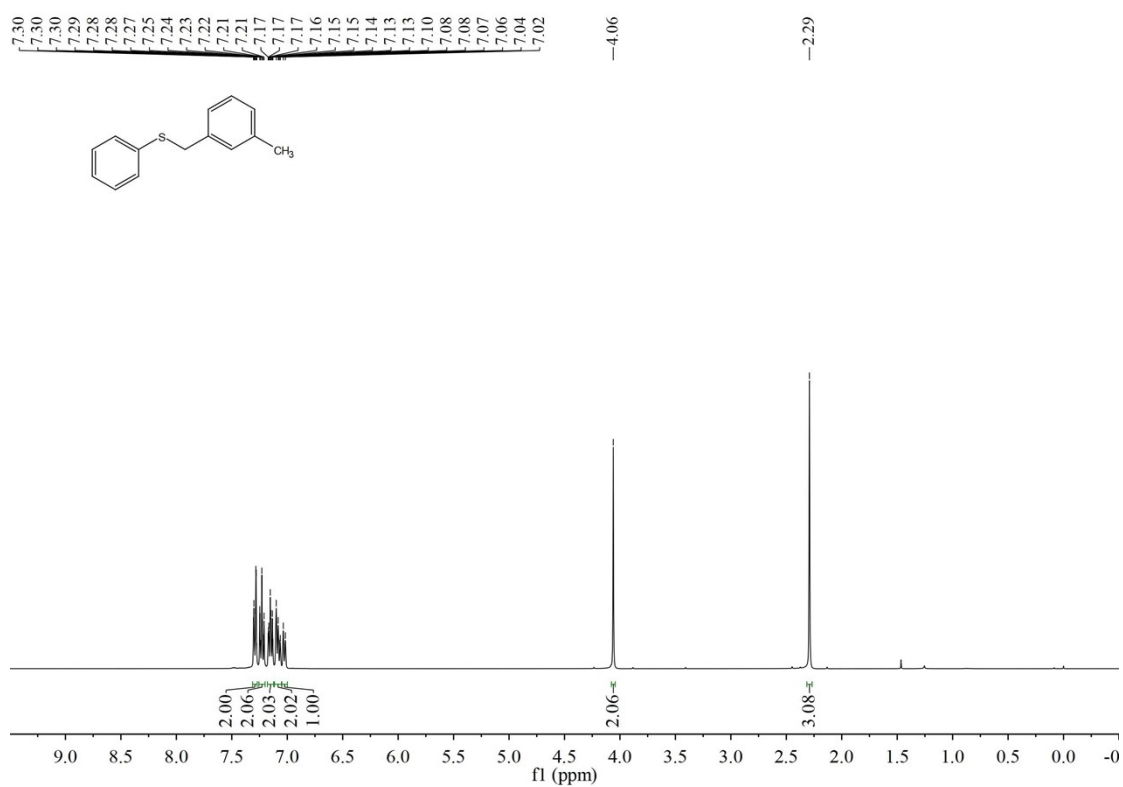
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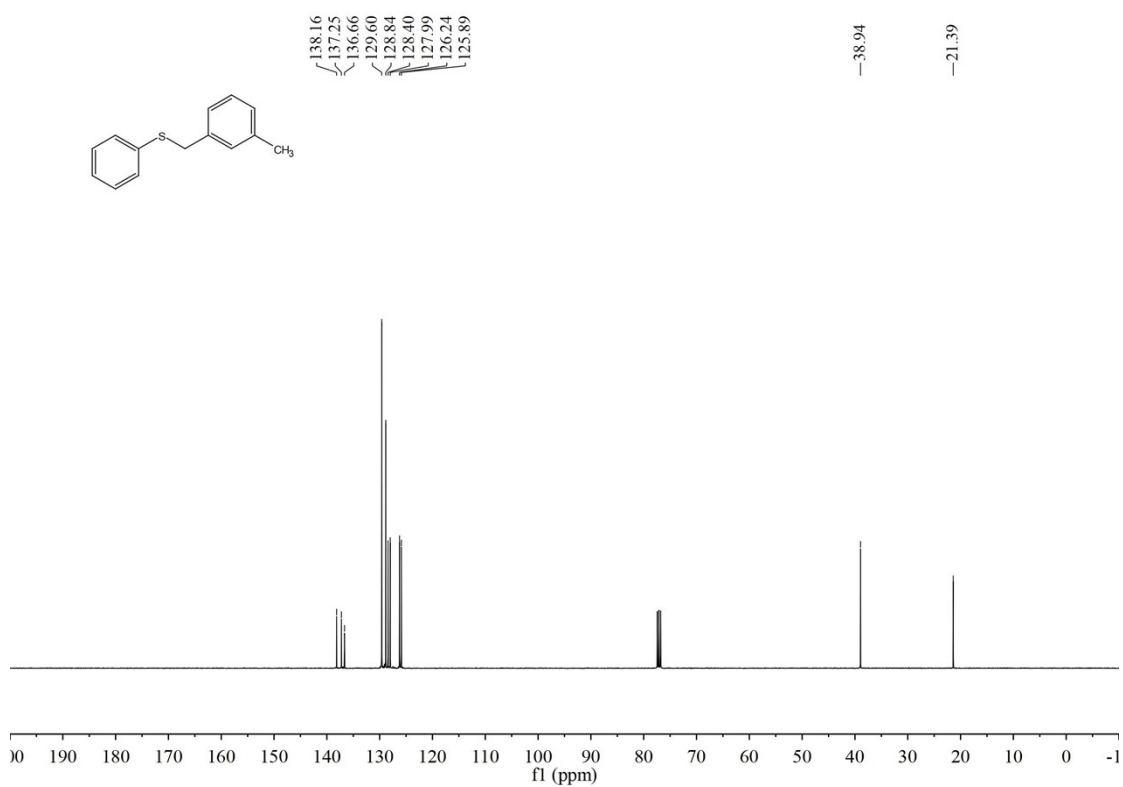
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**5q-<sup>1</sup>H**

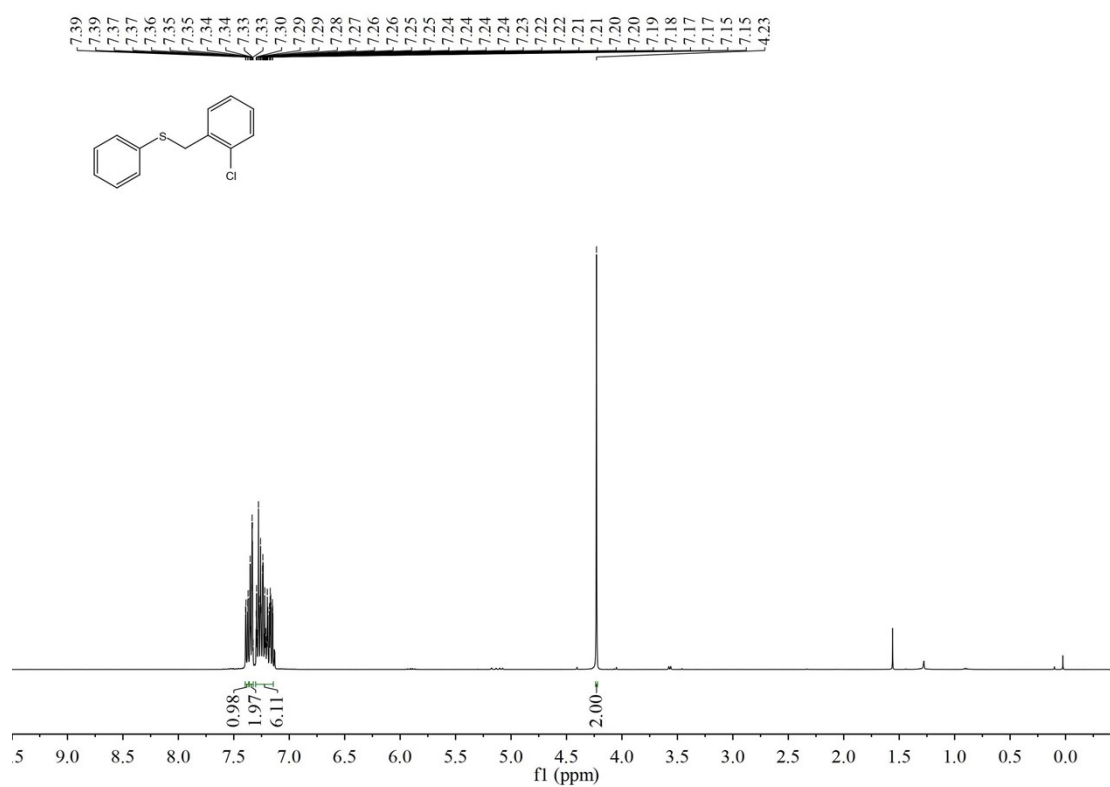


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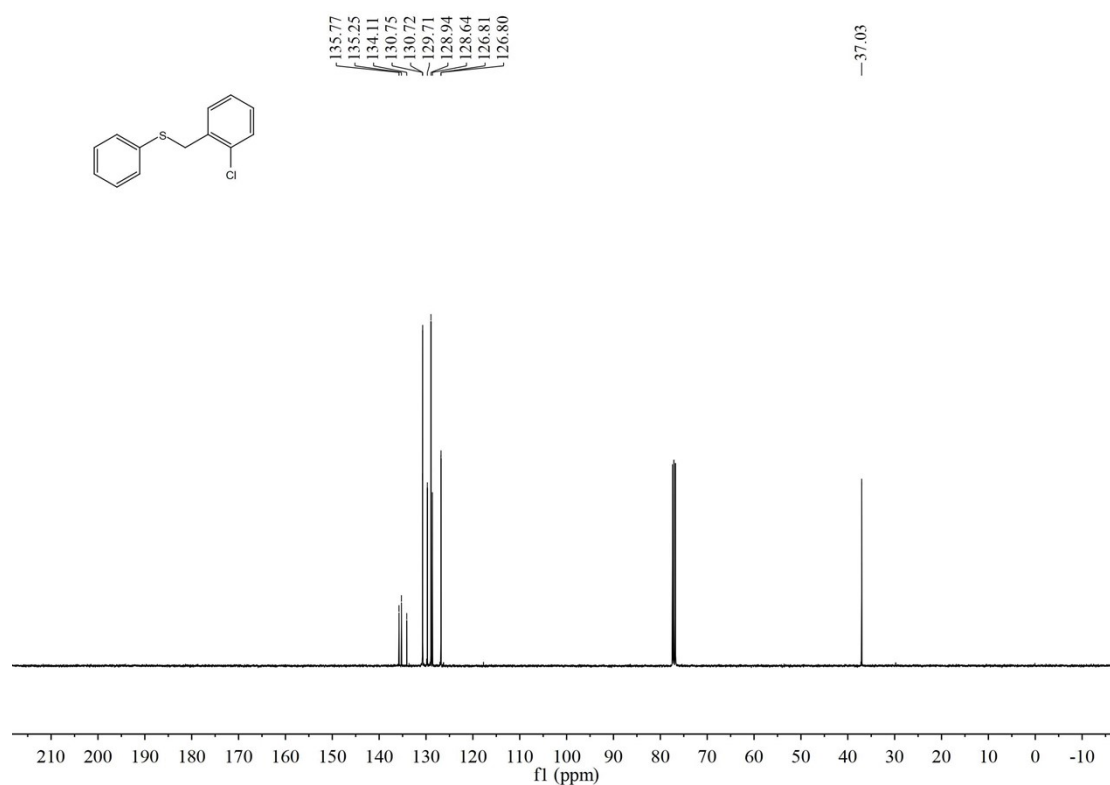




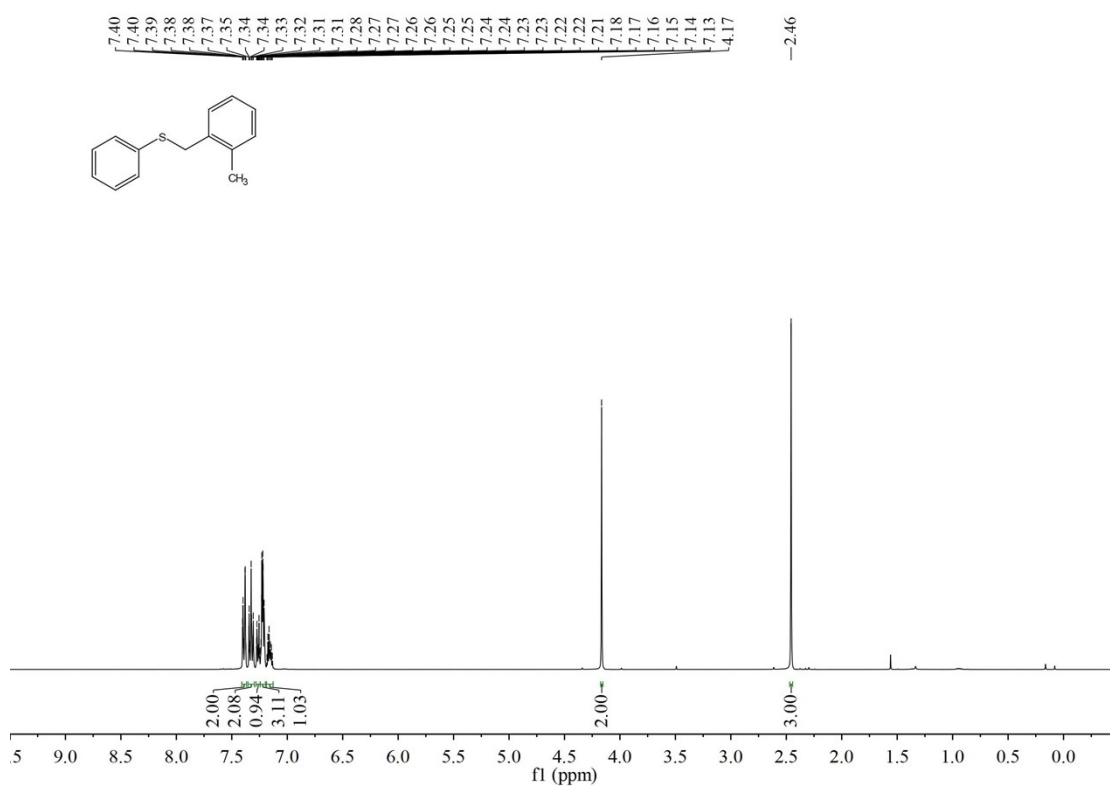
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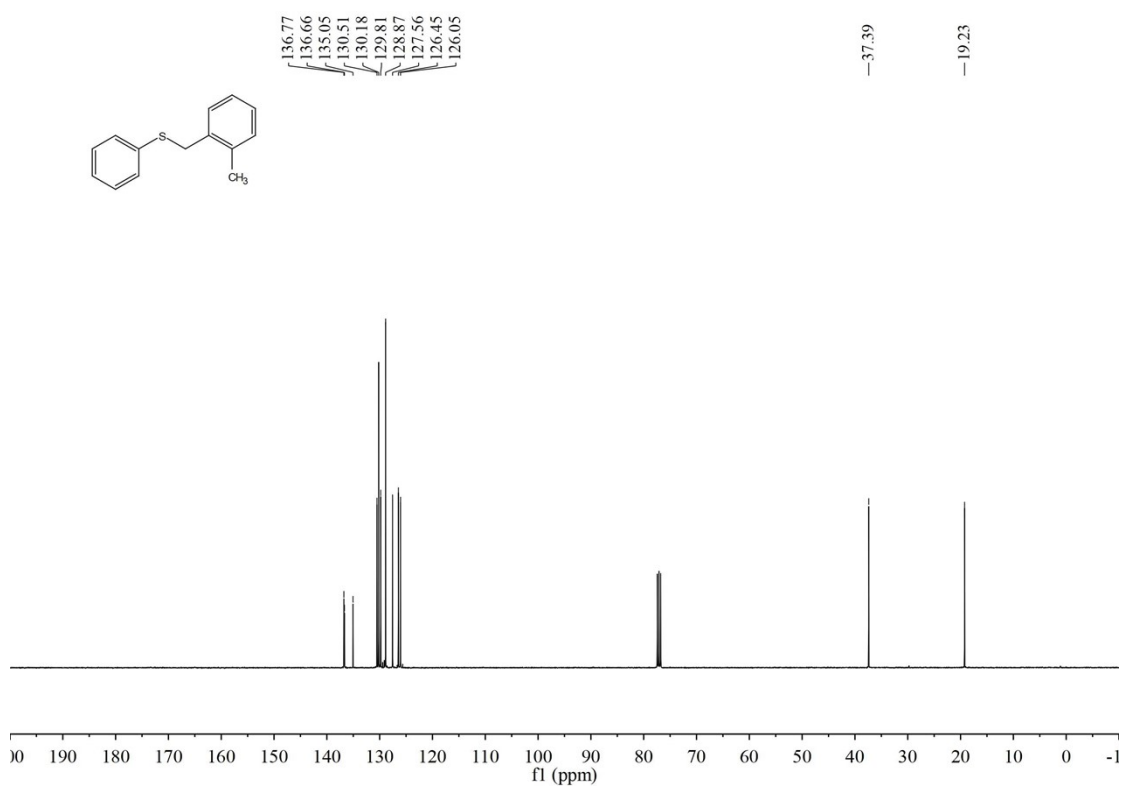
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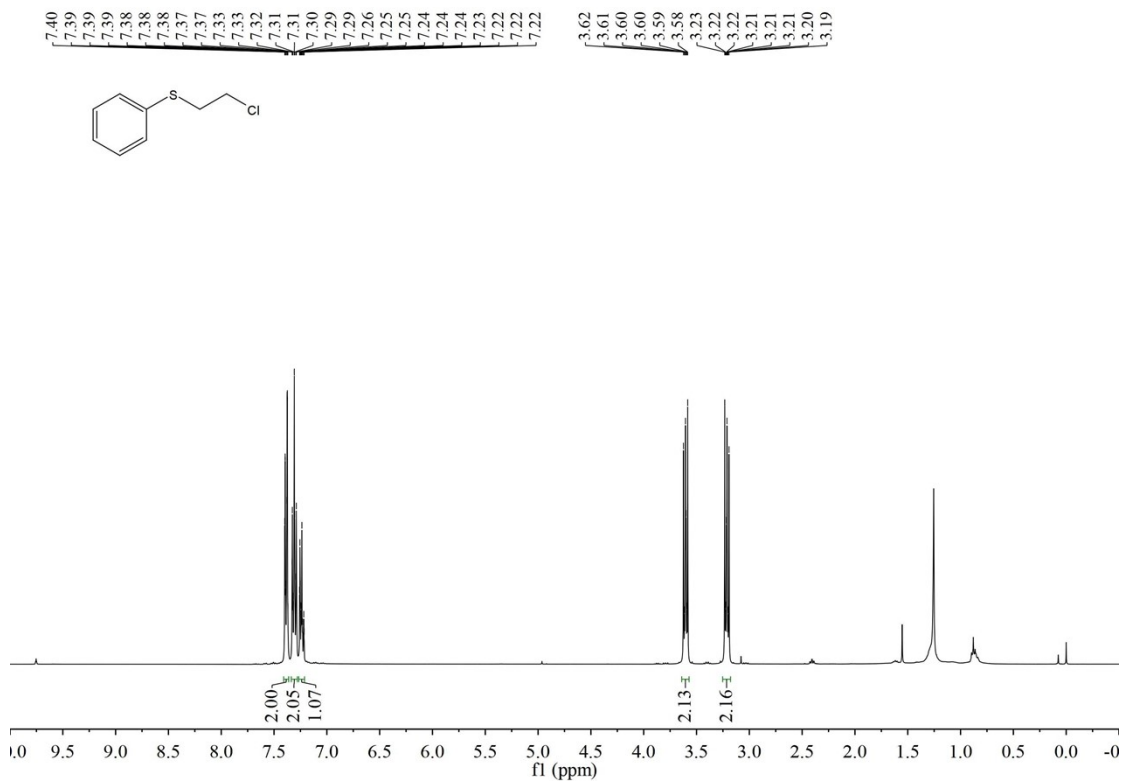
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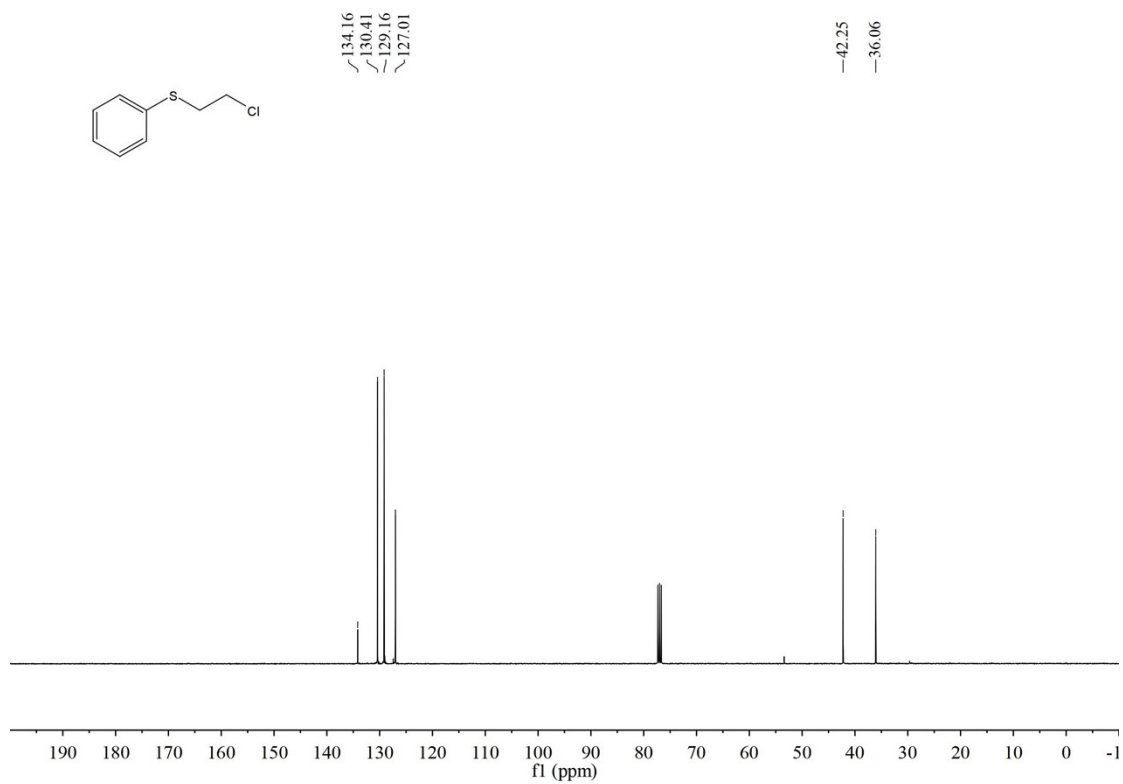
**5s-<sup>13</sup>C**



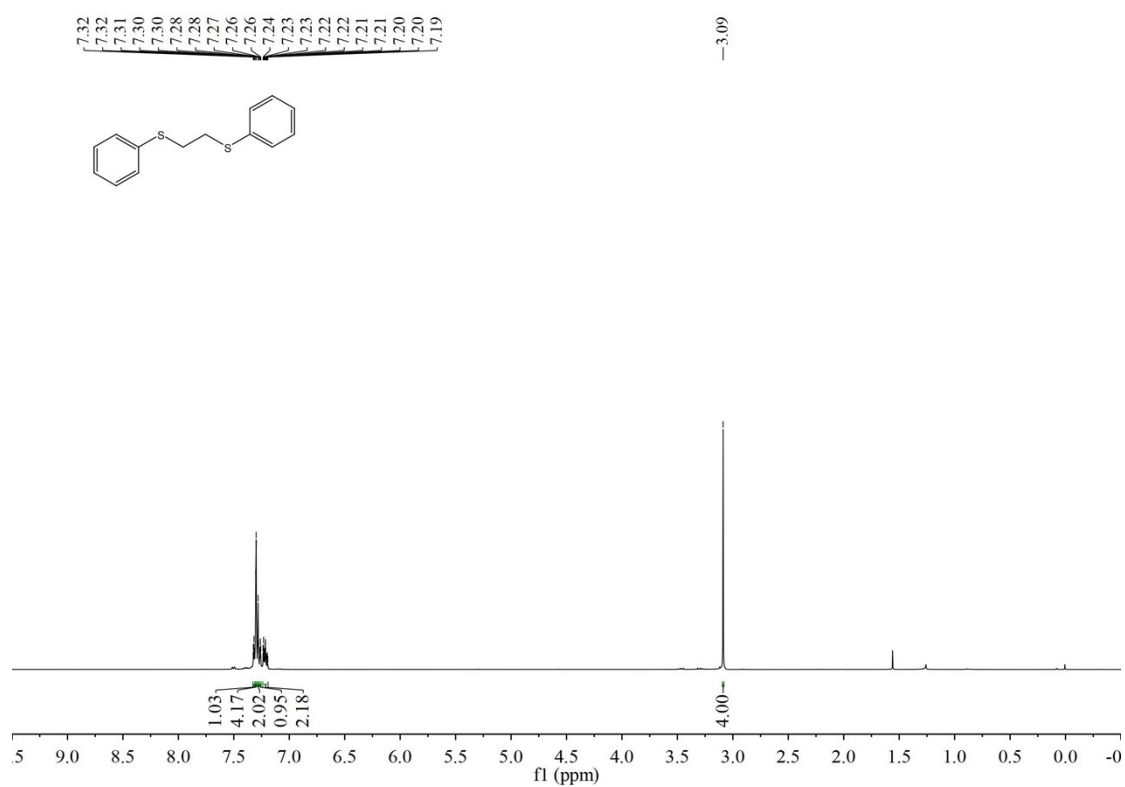
**5t-<sup>1</sup>H**



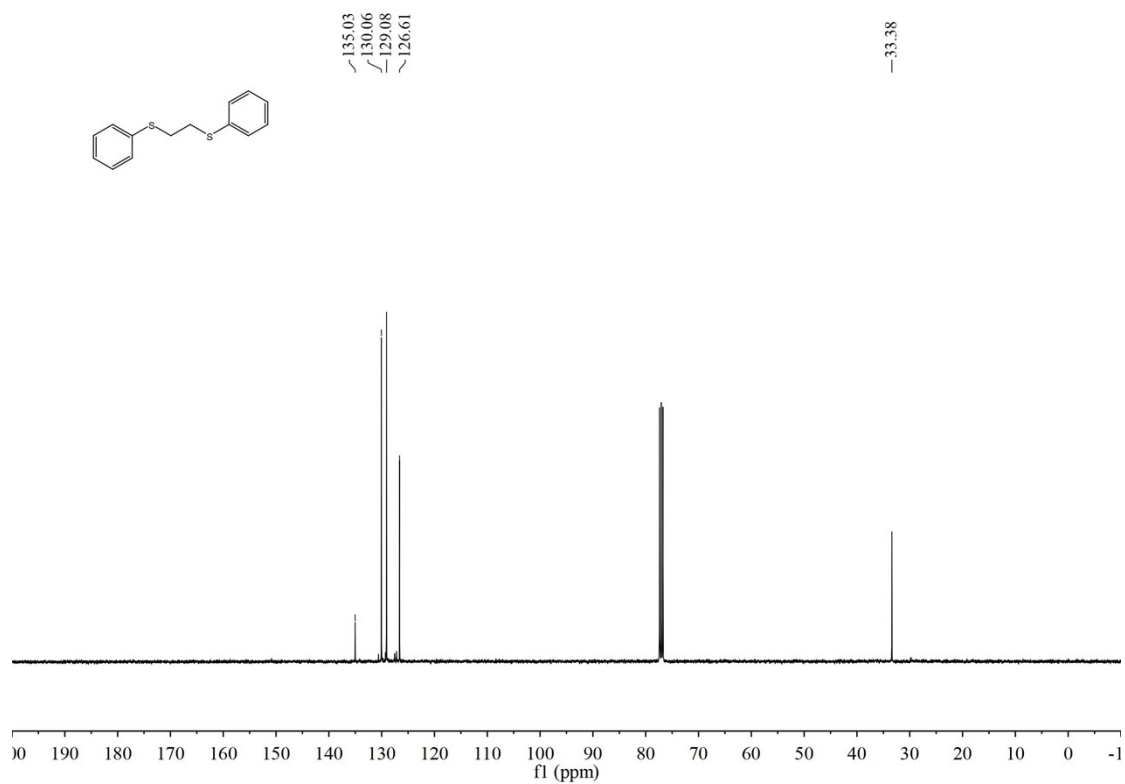
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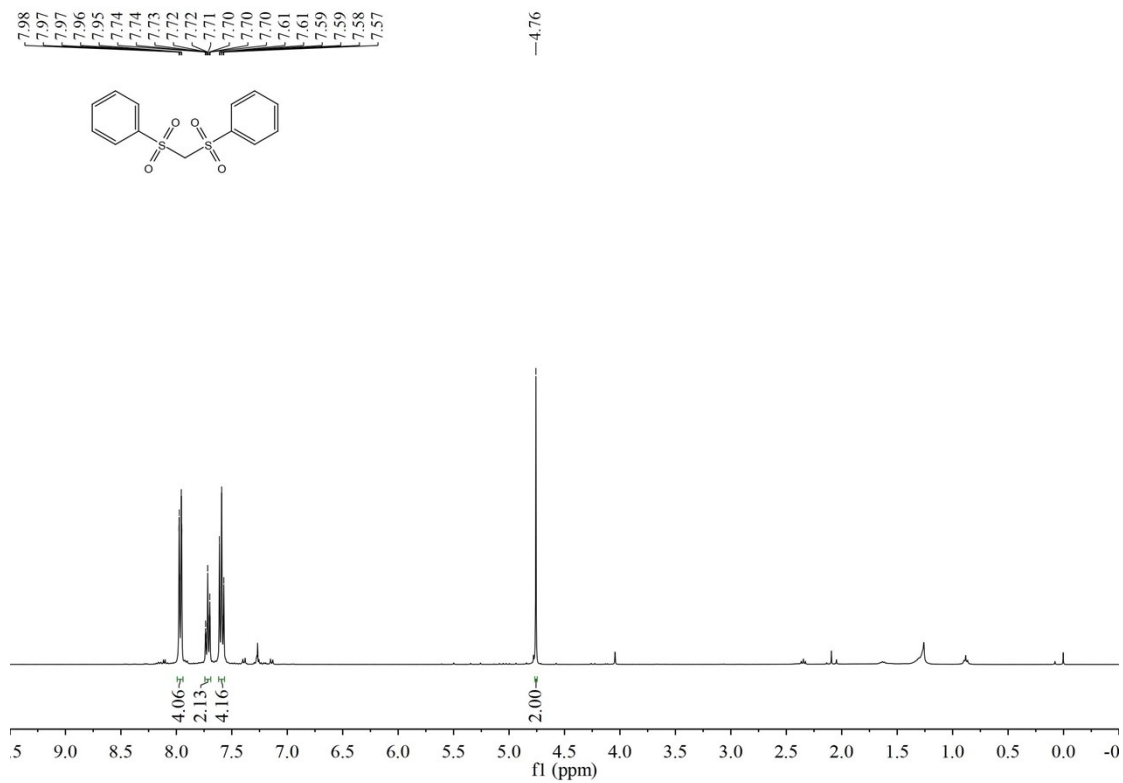
**5u-<sup>1</sup>H**



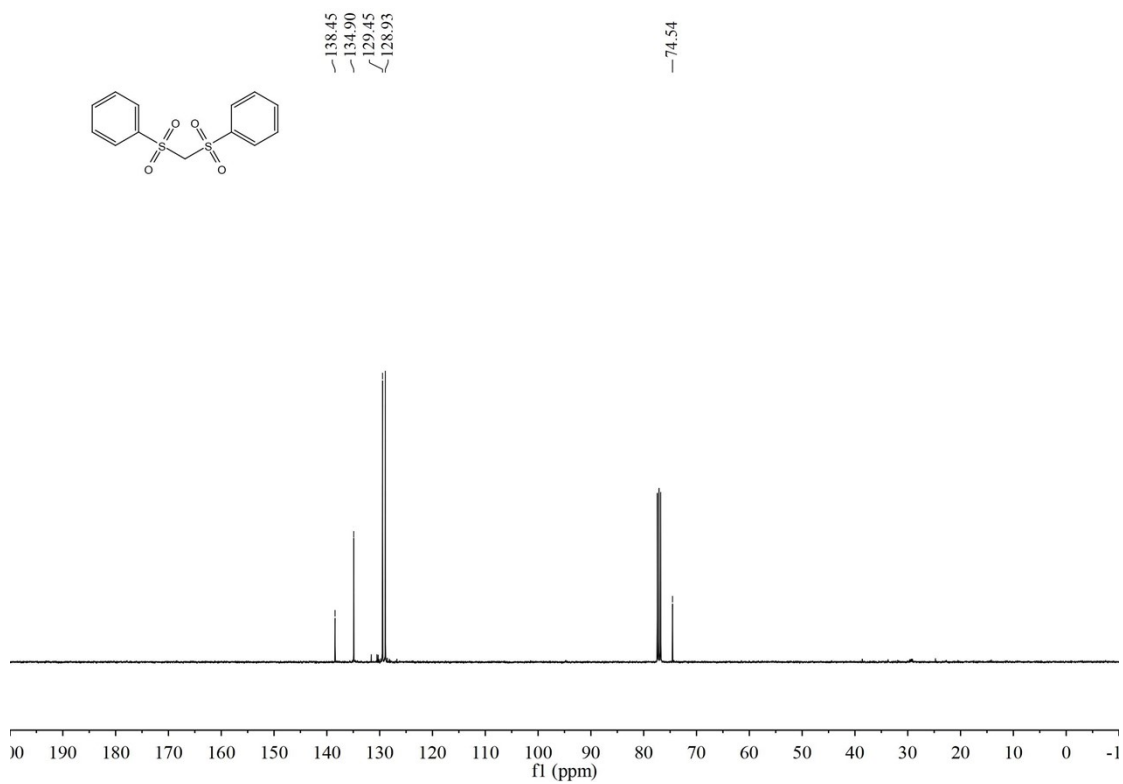
**5u-<sup>13</sup>C**



**6a-<sup>1</sup>H**



**6a-<sup>13</sup>C**



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