

## *Electronic Supplementary Information (ESI)*

### **Cobalt-Catalyzed Dithiolation of Unactivated Alkenes with Thiols: A Facile Access to Diverse Vicinal Dithioethers**

Jing Shi,<sup>b</sup> Qian Xiao<sup>\*a</sup> and Jian-Ji Zhong<sup>\*b</sup>

<sup>a</sup> School of Chemistry and Environmental Engineering, Hanshan Normal University, Chaozhou, Guangdong 521041, P. R. China. E-mail: xiaoqian880405@hstc.edu.cn

<sup>b</sup> College of Chemistry and Chemical Engineering, and Key (Guangdong-Hong Kong Joint) Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Shantou, Guangdong 515063, P. R. China. E-mail: jjzhong@stu.edu.cn

# Table of Contents

<b>1. Experimental section .....</b>	<b>3</b>
1) General information .....	3
2) General procedure for the dithiolation reactions .....	4
3) Procedure for the gram-scale reaction.....	5
4) Radical trapping experiment .....	6
5) References .....	7
<b>2. Characterization data of the products .....</b>	<b>8</b>
<b>3. NMR spectra for the products .....</b>	<b>34</b>

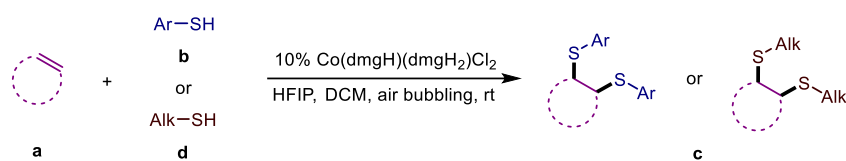
## **1. Experimental section**

### **1) General information**

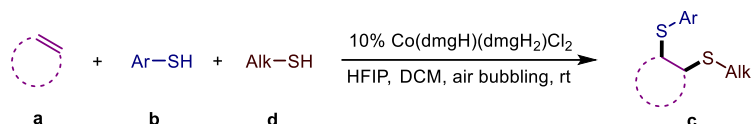
All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. Cobaloxime catalysts were synthesized according to the literature methods.<sup>1-4</sup>

The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ascend<sup>TM</sup> 400 MHz or Bruker AVANCE NEO 600 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were recorded using a Q Exactive (ESI) mass spectrometer (U3000 RS, Thermo Fisher Scientific, USA) or a Exactive GC (EI) mass spectrometer (Trace 1310, Thermo Fisher Scientific, USA), and the mass analyzer is Orbitrap.

## 2) General procedure for the dithiolation reactions

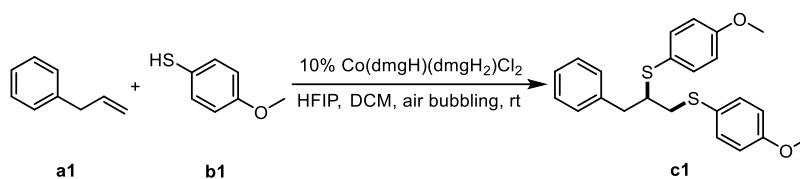


The alkenes **a** (0.2 mmol, 1.0 equiv.), thiophenols **b** or alkyl thiols **d** (0.6 mmol, 3.0 equiv.), and 10 mol% Co(dmgh)(dmgh<sub>2</sub>)Cl<sub>2</sub> were dissolved in 3.0 mL HFIP and 0.5 mL DCM in a 15 mL reaction tube equipped with magnetic stirring bar, then air bubbling was carried out at room temperature for 18 h. After the completion of the reaction, the solvent was removed and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.



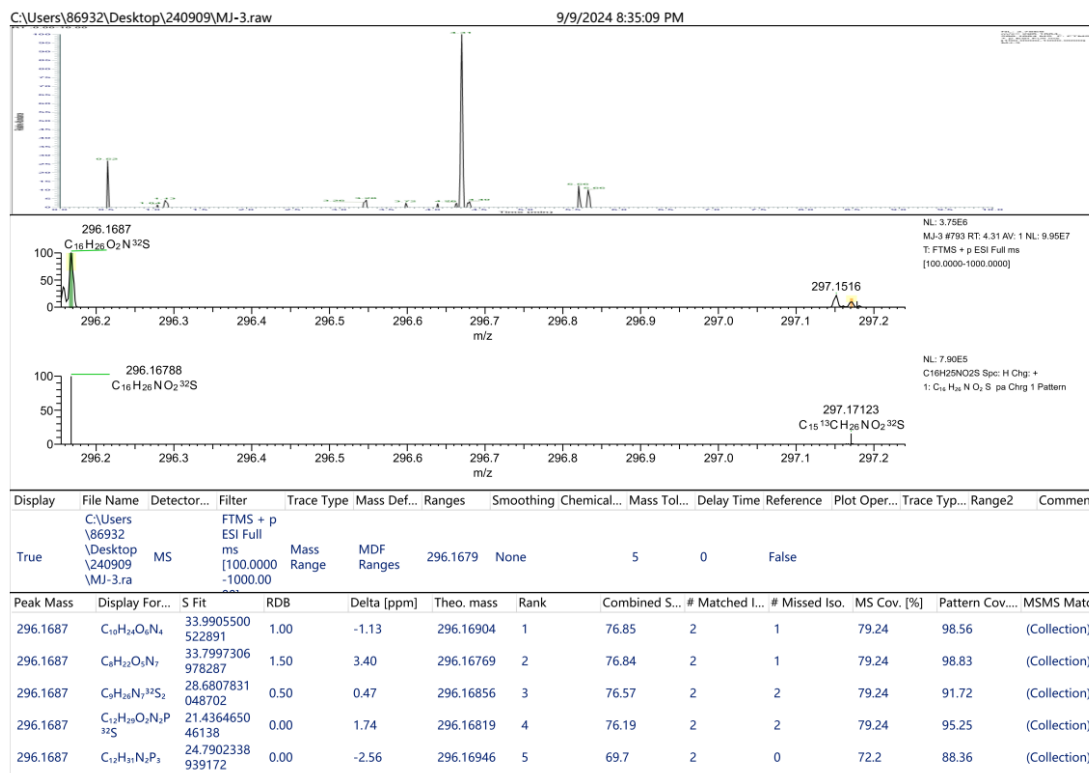
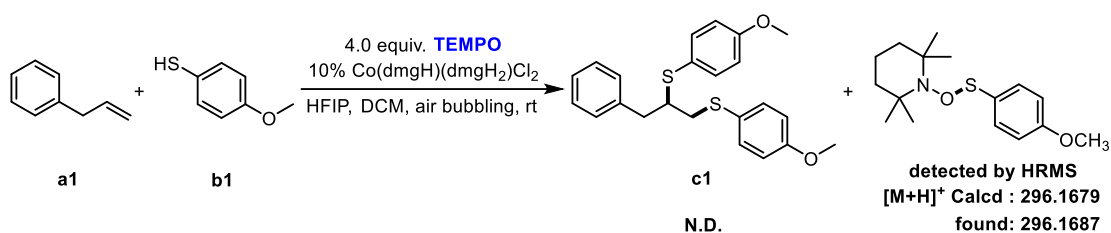
The alkenes **a** (0.3 mmol, 1.5 equiv.), thiophenols **b** (0.2 mmol, 1.0 equiv.), alkyl thiols **d** (0.4 mmol, 2.0 equiv.), and 10 mol% Co(dmgh)(dmgh<sub>2</sub>)Cl<sub>2</sub> were dissolved in 3.0 mL HFIP and 0.5 mL DCM in a 15 mL reaction tube equipped with magnetic stirring bar, then air bubbling was carried out at room temperature for 18 h. After the completion of the reaction, the solvent was removed and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.

### 3) Procedure for the gram-scale reaction



The allylbenzene **a1** (9.0 mmol, 1.0 equiv.), 4-methoxybenzenethiol **b1** (18.0 mmol, 2.0 equiv.), and 10 mol% Co(dmgh)(dmgh<sub>2</sub>)Cl<sub>2</sub> were dissolved in 60 mL HFIP and 10 mL DCM in a flask equipped with a magnetic stir bar, then air bubbling was carried out at room temperature for 36 h. After the completion of the reaction, the solvent was removed and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford **c1** (2.90 g, 81%).

#### 4) Radical trapping experiment

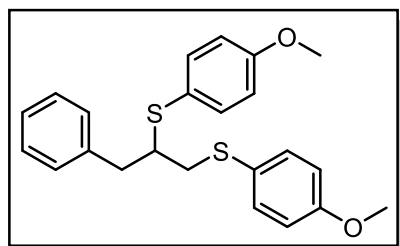


The alkylbenzene **a1** (0.2 mmol, 1.0 equiv.), 4-methoxybenzenethiol **b1** (0.6 mmol, 3.0 equiv.), TEMPO (0.8 mmol, 4.0 equiv.), and 10 mol% Co(dmgh)(dmgh<sub>2</sub>)Cl<sub>2</sub> were dissolved in 3.0 mL HFIP and 0.5 mL DCM in a 15 mL reaction tube equipped with magnetic stirring bar, then air bubbling was carried out at room temperature for 18 h. After the completion of the reaction, the mixture was analyzed by HRMS.

## 5) References

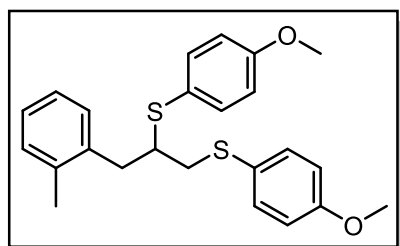
1. J. H. Espenson and R. Russell, *Inorg. Chem.*, 1974, **13**, 7.
2. A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1984, **106**, 5197.
3. M. Razavet, V. Artero and M. Fontecave, *Inorg. Chem.*, 2005, **44**, 4786.
4. Y. Z. Voloshin, A. S. Belov, A. V. Vologzhanina, G. G. Aleksandrov, A. V. Dolganov, V. V. Novikov, O. A. Varzatskii and Y. N. Bubnov, *Dalton Trans.*, 2012, **41**, 6078.

## 2. Characterization data of the products



**c1**

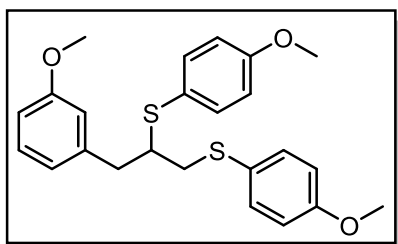
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c1** as a light-yellow oil (78 mg, 97% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.36 – 7.29 (m, 2H), 7.28 – 7.25 (m, 3H), 7.24 – 7.18 (m, 4H), 6.85 – 6.75 (m, 4H), 3.82 (s, 3H), 3.82 (s, 3H), 3.29 – 3.17 (m, 2H), 3.14 – 3.07 (m, 1H), 2.94 – 2.81 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.6, 158.9, 138.8, 135.6, 133.0, 129.4, 128.3, 126.5, 125.9, 124.2, 114.6, 114.5, 55.4, 55.3, 50.7, 40.1, 39.0. HRMS (ESI) (m/z) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{23}\text{H}_{25}\text{O}_2\text{S}_2^+$ : 397.1290; found: 397.1293.



**c2**

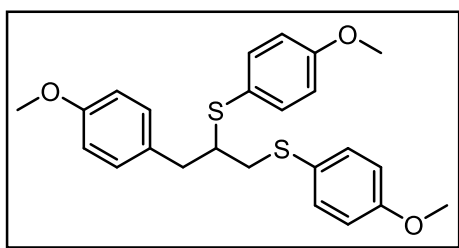
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c2** as a light-yellow oil (81 mg, 99% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.21 (d,  $J$  = 8.8 Hz, 2H), 7.15 – 7.08 (m, 6H), 6.73 (dd,  $J$  = 19.1, 8.9 Hz, 4H), 3.75 (s, 3H), 3.74 (s, 3H), 3.23 – 3.14 (m, 2H), 3.10 (dd,  $J$  = 13.6, 4.8 Hz, 1H), 2.91 (dd,  $J$  = 13.6, 7.6 Hz, 1H), 2.77 (dd,  $J$  = 13.9, 7.8 Hz, 1H), 2.21 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.6, 158.8, 137.3, 136.4, 135.8, 132.6, 130.4, 130.2, 126.6, 126.2, 125.8, 124.4, 114.6, 114.5, 55.4, 50.3, 40.6, 37.2, 19.6. HRMS (ESI) (m/z) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{24}\text{H}_{26}\text{O}_2\text{S}_2\text{Na}^+$ : 433.1266; found: 433.1264.





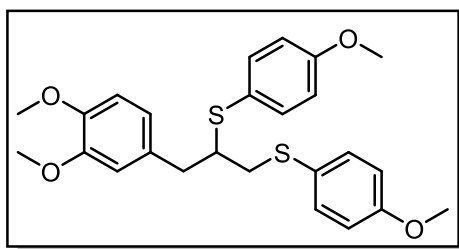
**c3**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c3** as a light-yellow oil (84 mg, 98% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.29 – 7.19 (m, 5H), 6.85 – 6.77 (m, 6H), 6.76 – 6.75 (m, 1H), 3.81 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.27 – 3.15 (m, 2H), 3.15 – 3.05 (m, 1H), 2.93 – 2.79 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.6, 159.6, 158.9, 140.4, 135.6, 133.0, 129.3, 125.9, 124.1, 121.8, 115.0, 114.6, 114.5, 111.9, 55.3, 55.1, 50.5, 40.0, 39.0. HRMS (ESI) (m/z) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{24}\text{H}_{27}\text{O}_3\text{S}_2^+$ : 427.1396; found: 427.1396.



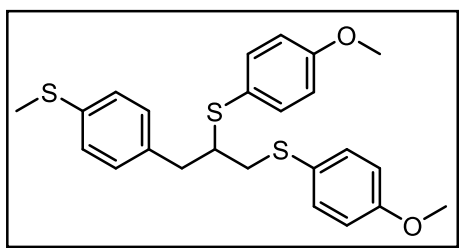
**c4**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c4** as a light-yellow oil (81 mg, 95% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.27 – 7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 7.16 – 7.10 (m, 2H), 6.89 – 6.75 (m, 6H), 3.81 – 3.80 (m, 9H), 3.22 – 3.12 (m, 2H), 3.08 (dd,  $J = 13.6, 4.3$  Hz, 1H), 2.91 – 2.76 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.5, 158.9, 158.2, 135.5, 133.0, 130.8, 130.3, 126.0, 124.3, 114.6, 114.5, 113.7, 55.3, 55.2, 50.9, 39.9, 38.0. HRMS (ESI) (m/z) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{24}\text{H}_{27}\text{O}_3\text{S}_2^+$ : 427.1396; found: 427.1401.



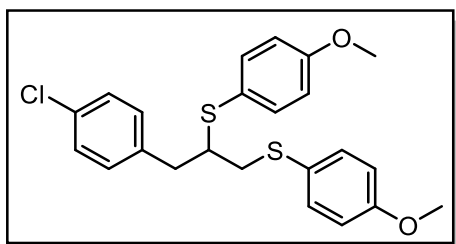
**c5**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **c5** as a light-yellow oil (89 mg, 97% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.27 – 7.24 (m, 2H), 7.21 – 7.14 (m, 2H), 6.82 – 6.77 (m, 4H), 6.77 – 6.72 (m, 2H), 6.70 (d,  $J = 2.0$  Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.21 – 3.11 (m, 2H), 3.07 (dd,  $J = 13.6, 4.4$  Hz, 1H), 2.90 – 2.77 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.6, 158.9, 148.7, 147.6, 135.6, 132.9, 131.3, 125.9, 124.2, 121.4, 114.6, 114.5, 112.6, 111.1, 55.9, 55.8, 55.3, 50.8, 39.8, 38.4. HRMS (ESI) (m/z) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{25}\text{H}_{29}\text{O}_4\text{S}_2^+$ : 457.1502; found: 457.1500.



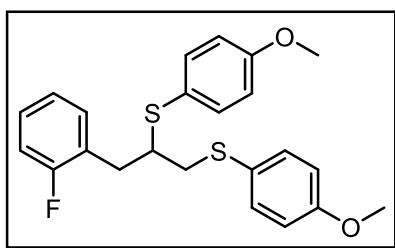
**c6**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c6** as a light-yellow oil (74 mg, 84% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.24 (d,  $J = 2.2$  Hz, 1H), 7.23 – 7.18 (m, 4H), 7.17 (d,  $J = 2.2$  Hz, 1H), 7.15 – 7.09 (m, 2H), 6.84 – 6.73 (m, 4H), 3.81 (s, 6H), 3.24 – 3.03 (m, 3H), 2.81 (ddd,  $J = 13.4, 10.5, 7.7$  Hz, 2H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.6, 158.9, 143.9, 136.2, 135.7, 135.5, 133.0, 129.9, 126.7, 125.8, 124.0, 114.6, 114.5, 55.3, 50.6, 40.0, 38.3. HRMS (ESI) (m/z) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{24}\text{H}_{27}\text{O}_2\text{S}_3^+$ : 443.1168; found: 443.1169.



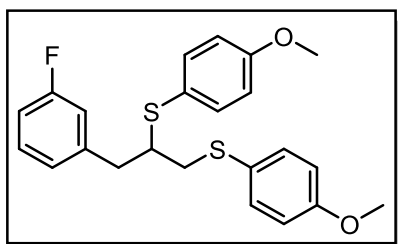
**c7**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c7** as a light-yellow oil (76 mg, 88% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.28 – 7.17 (m, 6H), 7.16 – 7.08 (m, 2H), 6.84 – 6.74 (m, 4H), 3.81 (s, 6H), 3.22 (dd,  $J$  = 14.0, 5.0 Hz, 1H), 3.17 – 3.06 (m, 2H), 2.87 – 2.74 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.6, 159.0, 137.3, 135.6, 133.1, 132.2, 130.7, 128.4, 125.6, 123.8, 114.6, 114.5, 55.4, 50.6, 40.1, 38.1. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{23}\text{H}_{24}\text{ClO}_2\text{S}_2^+$ : 431.0901; found: 431.0899.



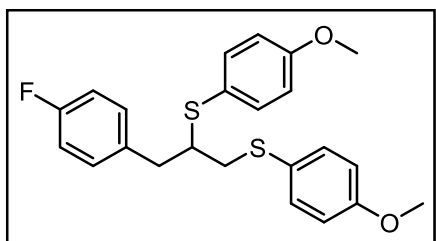
**c8**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c8** as a light-yellow oil (70 mg, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.27 – 7.18 (m, 6H), 7.12 – 6.98 (m, 2H), 6.78 (d,  $J$  = 8.4 Hz, 4H), 3.81 (s, 6H), 3.36 – 3.20 (m, 2H), 3.11 (dd,  $J$  = 13.6, 4.6 Hz, 1H), 2.92 – 2.77 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 161.2 (d,  $J$  = 245.9 Hz), 159.5, 159.0, 135.5, 133.3, 131.7 (d,  $J$  = 4.8 Hz), 128.3, 128.2, 126.0, 125.9, 123.9, 115.3 (d,  $J$  = 22.5 Hz), 114.6, 114.5, 55.3, 49.5, 40.8, 32.8.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = -117.04. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{23}\text{H}_{24}\text{FO}_2\text{S}_2^+$ : 415.1196; found: 415.1195.



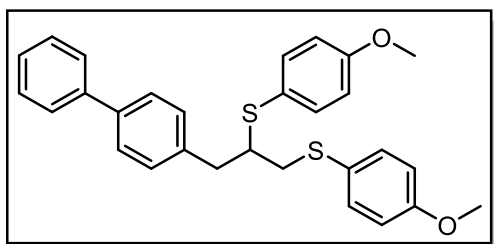
**c9**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c9** as a light-yellow oil (81 mg, 98% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.28 – 7.19 (m, 5H), 7.00 – 6.88 (m, 3H), 6.80 (dd,  $J$  = 8.7, 4.8 Hz, 4H), 3.81 (s, 6H), 3.25 (dd,  $J$  = 14.0, 5.2 Hz, 1H), 3.20 – 3.08 (m, 2H), 2.83 (dt,  $J$  = 14.7, 7.5 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 162.8 (d,  $J$  = 246.6 Hz), 159.7, 159.0, 141.4 (d,  $J$  = 7.4 Hz), 135.6, 133.1, 129.7 (d,  $J$  = 8.5 Hz), 125.6, 125.0, 123.9, 116.2 (d,  $J$  = 21.0 Hz), 114.7, 114.6, 113.4 (d,  $J$  = 21.4 Hz), 55.3, 50.4, 40.2, 38.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = -113.45. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{23}\text{H}_{24}\text{FO}_2\text{S}_2^+$ : 415.1196; found: 415.1192.



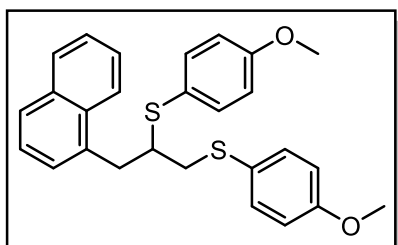
**c10**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c10** as a light-yellow oil (81 mg, 97% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.27 – 7.14 (m, 6H), 6.99 (t,  $J$  = 8.7 Hz, 2H), 6.79 (dd,  $J$  = 8.8, 5.0 Hz, 4H), 3.81 (s, 6H), 3.22 (dd,  $J$  = 13.9, 5.3 Hz, 1H), 3.18 – 3.07 (m, 2H), 2.82 (ddd,  $J$  = 13.3, 7.9, 4.8 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 162.8 (d,  $J$  = 245.2 Hz), 159.6, 159.0, 135.5, 134.5, 133.0, 130.8 (d,  $J$  = 8.1 Hz), 125.7, 124.0, 115.1 (d,  $J$  = 21.4 Hz), 114.6, 114.5, 55.3, 50.8, 40.0, 38.0.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = -116.58. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{23}\text{H}_{24}\text{FO}_2\text{S}_2^+$ : 415.1196; found: 415.1193.



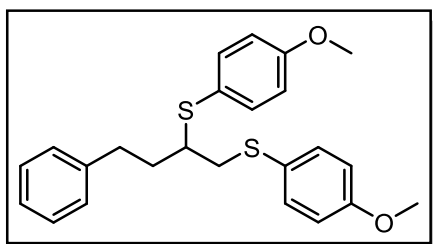
**c11**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c11** as a light-yellow oil (84 mg, 89% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.62 (d,  $J$  = 7.5 Hz, 2H), 7.55 (d,  $J$  = 8.2 Hz, 2H), 7.46 (t,  $J$  = 7.7 Hz, 2H), 7.36 (t,  $J$  = 7.3 Hz, 1H), 7.29 (d,  $J$  = 3.5 Hz, 4H), 7.22 (d,  $J$  = 8.8 Hz, 2H), 6.90 – 6.69 (m, 4H), 3.82 (s, 3H), 3.81 (s, 3H), 3.34 – 3.18 (m, 2H), 3.13 (dd,  $J$  = 13.5, 4.3 Hz, 1H), 2.90 (dd,  $J$  = 13.4, 7.9 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.6, 158.9, 140.9, 139.3, 137.9, 135.6, 133.0, 129.8, 128.8, 127.1, 127.0, 125.8, 124.1, 114.6, 114.5, 55.3, 50.7, 40.1, 38.6. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{29}\text{H}_{29}\text{O}_2\text{S}_2^+$ : 473.1603; found: 473.1599.



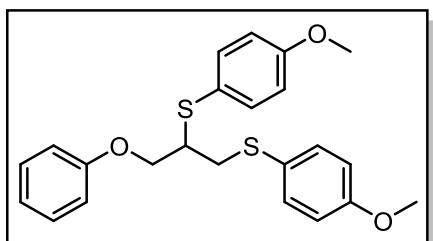
**c12**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 120/1, v/v) afforded **c12** as a light-yellow oil (88 mg, 98% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.95 (d,  $J$  = 8.3 Hz, 1H), 7.88 (d,  $J$  = 7.8 Hz, 1H), 7.78 (d,  $J$  = 7.8 Hz, 1H), 7.53 – 7.36 (m, 4H), 7.27 – 7.24 (m, 2H), 7.20 – 7.11 (m, 2H), 6.85 – 6.76 (m, 2H), 6.76 – 6.68 (m, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.78 – 3.71 (m, 1H), 3.44 (p,  $J$  = 7.8 Hz, 1H), 3.30 – 3.15 (m, 2H), 3.00 (dd,  $J$  = 13.7, 7.9 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.6, 158.8, 135.9, 134.9, 134.0, 132.6, 131.9, 128.8, 128.0, 127.4, 126.1, 125.9, 125.5, 125.3, 124.1, 123.8, 114.6, 114.5, 55.3, 50.1, 40.6, 37.2. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{27}\text{H}_{27}\text{O}_2\text{S}_2^+$ : 447.1447; found: 447.1443.



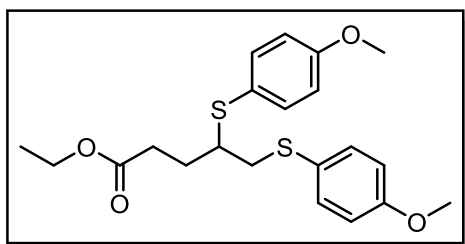
**c13**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c13** as a light-yellow oil (76 mg, 92% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.33 (ddd,  $J = 9.2, 6.3, 1.0$  Hz, 2H), 7.25 (td,  $J = 6.2, 2.4$  Hz, 5H), 7.13 – 7.05 (m, 2H), 6.85 – 6.77 (m, 2H), 6.77 – 6.68 (m, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 3.14 (dd,  $J = 13.2, 3.8$  Hz, 1H), 3.02 – 2.73 (m, 4H), 2.33 (dddd,  $J = 14.3, 9.0, 7.7, 3.6$  Hz, 1H), 1.80 (dtd,  $J = 14.2, 8.8, 5.0$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.5, 159.0, 141.6, 135.4, 133.7, 128.6, 128.4, 125.9, 125.8, 123.9, 114.6, 114.5, 55.3, 47.9, 41.5, 33.8, 32.9. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{24}\text{H}_{27}\text{O}_2\text{S}_2^+$ : 411.1447; found: 411.1447.



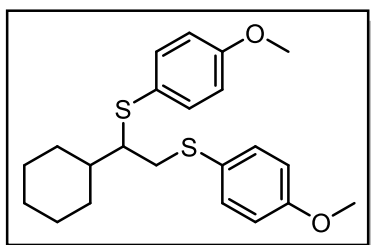
**c14**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 120/1, v/v) afforded **c14** as a light-yellow oil (68 mg, 83% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.40 (d,  $J = 8.8$  Hz, 2H), 7.30 – 7.26 (m, 4H), 6.97 (t,  $J = 7.3$  Hz, 1H), 6.91 – 6.81 (m, 4H), 6.78 (d,  $J = 8.8$  Hz, 2H), 4.21 (qd,  $J = 9.8, 5.2$  Hz, 2H), 3.82 (s, 3H), 3.79 (s, 3H), 3.40 – 3.22 (m, 2H), 3.17 (dd,  $J = 13.6, 5.4$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.9, 159.0, 158.4, 136.1, 133.0, 129.4, 125.8, 123.4, 121.0, 114.7, 114.6, 114.6, 68.0, 55.4, 55.3, 48.7, 37.4. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{23}\text{H}_{25}\text{O}_3\text{S}_2^+$ : 413.1240; found: 413.1245.



**c15**

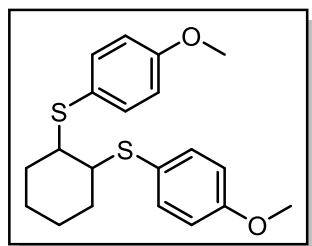
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) afforded **c15** as a light-yellow oil (70 mg, 86% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.29 (d,  $J = 8.8$  Hz, 2H), 7.21 (d,  $J = 8.8$  Hz, 2H), 6.79 (dd,  $J = 11.1$ , 8.7 Hz, 4H), 4.13 (q,  $J = 7.1$  Hz, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 3.14 (dd,  $J = 13.4$ , 4.3 Hz, 1H), 2.90 (tt,  $J = 9.2$ , 4.0 Hz, 1H), 2.76 (dd,  $J = 13.4$ , 9.4 Hz, 1H), 2.64 (ddd,  $J = 14.8$ , 9.2, 5.6 Hz, 1H), 2.52 (ddd,  $J = 16.0$ , 9.0, 6.8 Hz, 1H), 2.30 (ddt,  $J = 16.0$ , 6.4, 3.5 Hz, 1H), 1.74 (dq,  $J = 10.3$ , 5.4, 4.5 Hz, 1H), 1.25 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 173.1, 159.7, 159.0, 135.9, 133.3, 125.8, 123.3, 114.6, 114.5, 60.4, 55.3, 48.7, 41.2, 31.8, 27.6, 14.2. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{21}\text{H}_{27}\text{O}_4\text{S}_2^+$ : 407.1345; found: 407.1346.



**c16**

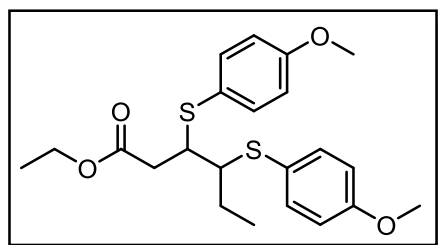
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c16** as a light-yellow oil (73 mg, 94% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.28 – 7.26 (m, 2H), 7.15 (d,  $J = 8.8$  Hz, 2H), 6.84 – 6.70 (m, 4H), 3.81 (s, 3H), 3.79 (s, 3H), 3.13 – 3.01 (m, 2H), 2.89 (ddd,  $J = 8.2$ , 5.9, 3.5 Hz, 1H), 2.02 – 1.89 (m, 1H), 1.84 – 1.72 (m, 3H), 1.68 (d,  $J = 13.1$  Hz, 2H), 1.53 (qd,  $J = 12.5$ , 3.6 Hz, 1H), 1.36 – 1.25 (m, 1H), 1.24 – 1.04 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.2, 158.8, 135.0, 133.0, 126.3, 125.8, 114.5, 57.0, 55.3, 39.3, 38.7, 31.5, 28.2,

26.5, 26.4. HRMS (ESI) (m/z) for  $[M+H]^+$  calculated for  $C_{22}H_{29}O_2S_2^+$ : 389.1603; found: 389.1605.



**c17**

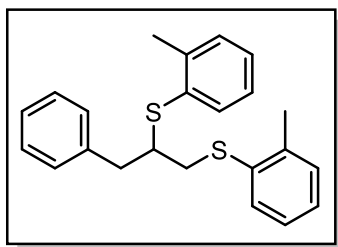
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c17** as a light-yellow oil (45 mg, 62% yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm = 7.40 – 7.31 (m, 4H), 6.87 – 6.78 (m, 4H), 3.82 (s, 6H), 3.01 (dt,  $J$  = 5.9, 2.6 Hz, 2H), 2.22 – 2.09 (m, 2H), 1.68 – 1.62 (m, 2H), 1.58 – 1.49 (m, 2H), 1.38 – 1.29 (m, 2H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  ppm = 159.45, 135.63, 124.67, 114.38, 55.31, 50.80, 30.69, 23.96. HRMS (ESI) (m/z) for  $[M+H]^+$  calculated for  $C_{20}H_{25}O_2S_2^+$ : 361.1290; found: 361.1292.



**c18**

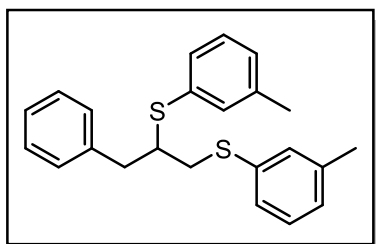
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 80/1, v/v) afforded **c18** as a light-yellow oil (52 mg, 61% yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm = 7.44 – 7.34 (m, 4H), 6.82 (d,  $J$  = 8.3 Hz, 4H), 4.11 (q,  $J$  = 7.1 Hz, 2H), 3.80 (d,  $J$  = 1.1 Hz, 6H), 3.54 – 3.49 (m, 1H), 3.04 (dd,  $J$  = 15.9, 5.3 Hz, 1H), 2.92 (ddd,  $J$  = 8.9, 6.5, 4.3 Hz, 1H), 2.60 (dd,  $J$  = 16.0, 8.9 Hz, 1H), 2.03 – 1.92 (m, 1H), 1.64 – 1.53 (m, 1H), 1.24 (t,  $J$  = 7.2 Hz, 3H), 1.06 (t,  $J$  = 7.3 Hz, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  ppm = 171.6, 159.7, 159.4, 135.8, 135.3, 125.3, 124.3, 114.5, 114.5, 60.6, 57.1, 55.3, 51.2, 38.4, 25.3, 14.2, 11.9. HRMS (ESI) (m/z) for  $[M+H]^+$  calculated for  $C_{22}H_{29}O_4S_2^+$ : 421.1502; found: 421.1501.





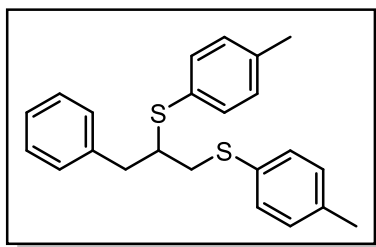
**c19**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c19** as a light-yellow oil (62 mg, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.39 – 7.34 (m, 2H), 7.32 – 7.19 (m, 7H), 7.17 – 7.10 (m, 2H), 7.05 (t,  $J = 7.5$  Hz, 1H), 6.97 (d,  $J = 7.7$  Hz, 1H), 3.48 – 3.35 (m, 2H), 3.24 (dd,  $J = 13.6, 3.9$  Hz, 1H), 3.06 – 2.91 (m, 2H), 2.41 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 140.4, 138.6, 138.3, 134.8, 133.7, 132.6, 130.5, 130.3, 129.5, 128.9, 128.4, 127.4, 126.6, 126.5, 126.4, 126.2, 49.1, 39.2, 37.6, 20.7, 20.5. HRMS (ESI) (m/z) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{23}\text{H}_{24}\text{S}_2\text{Na}^+$ : 387.1212; found: 387.1219.



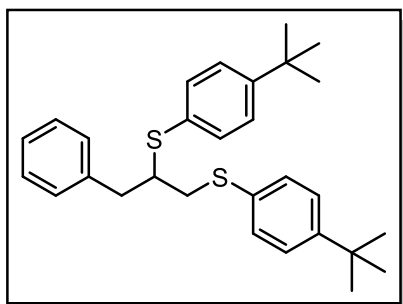
**c20**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c20** as a light-yellow oil (72 mg, 99% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.40 – 7.34 (m, 2H), 7.32 – 7.27 (m, 3H), 7.22 – 7.13 (m, 4H), 7.12 – 7.02 (m, 4H), 3.47 (tt,  $J = 8.8, 4.8$  Hz, 1H), 3.32 (ddd,  $J = 26.9, 13.9, 5.0$  Hz, 2H), 3.00 (ddd,  $J = 17.4, 13.9, 8.3$  Hz, 2H), 2.34 (s, 3H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 138.8, 138.6, 135.4, 134.0, 133.2, 130.4, 129.5, 129.5, 128.8, 128.8, 128.4, 128.2, 127.2, 126.8, 126.6, 49.8, 39.1, 38.4, 21.4, 21.3. HRMS (ESI) (m/z) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{23}\text{H}_{24}\text{S}_2\text{Na}^+$ : 387.1212; found: 387.1219.



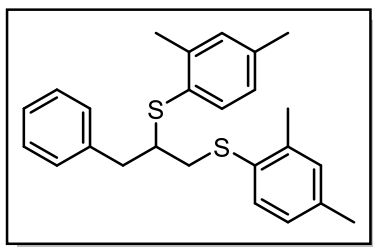
**c21**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c21** as a light-yellow oil (63 mg, 86% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.39 – 7.32 (m, 2H), 7.31 – 7.24 (m, 5H), 7.20 – 7.03 (m, 6H), 3.44 – 3.26 (m, 2H), 3.22 (dd,  $J$  = 13.6, 4.5 Hz, 1H), 2.96 (td,  $J$  = 13.6, 8.1 Hz, 2H), 2.39 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 138.73, 137.48, 136.37, 133.16, 132.03, 130.39, 130.32, 129.74, 129.48, 128.36, 126.56, 50.11, 39.05, 38.93, 21.17, 21.07. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{23}\text{H}_{24}\text{S}_2\text{Na}^+$ : 387.1212; found: 387.1215.



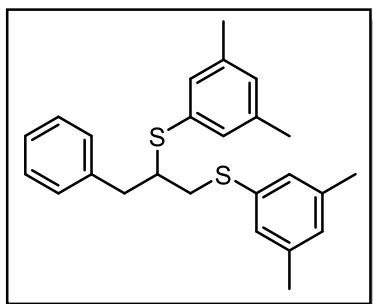
**c22**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c22** as a light-yellow oil (89 mg, 99% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.41 – 7.34 (m, 3H), 7.34 – 7.27 (m, 8H), 7.23 – 7.16 (m, 2H), 3.46 (dq,  $J$  = 13.1, 4.6, 4.2 Hz, 1H), 3.33 (ddd,  $J$  = 30.6, 13.9, 4.8 Hz, 2H), 3.03 – 2.96 (m, 2H), 2.38 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 150.6, 149.6, 138.7, 132.6, 132.2, 130.64, 129.9, 129.6, 128.4, 126.6, 126.0, 49.8, 39.0, 38.7, 34.6, 34.5, 31.4. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{29}\text{H}_{37}\text{S}_2^+$ : 449.2331; found: 449.2330.



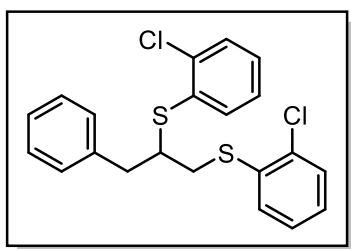
**c23**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c23** as a light-yellow oil (65 mg, 83% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.40 – 7.33 (m, 2H), 7.31 – 7.27 (m, 3H), 6.98 (s, 2H), 6.89 (t,  $J = 10.7$  Hz, 4H), 3.52 – 3.40 (m, 1H), 3.30 (ddd,  $J = 18.8, 13.9, 5.1$  Hz, 2H), 3.00 (ddd,  $J = 20.2, 13.9, 8.2$  Hz, 2H), 2.29 (s, 6H), 2.27 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 138.7, 138.5, 135.2, 133.7, 130.2, 129.6, 129.2, 128.4, 128.2, 127.4, 126.6, 49.8, 39.2, 38.4, 21.2. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{25}\text{H}_{28}\text{S}_2\text{Na}^+$ : 415.1525; found: 415.1529.



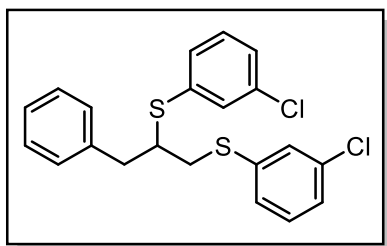
**c24**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c24** as a light-yellow oil (77 mg, 98% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.39 – 7.33 (m, 2H), 7.32 – 7.27 (m, 3H), 7.19 (d,  $J = 7.8$  Hz, 1H), 7.05 (d,  $J = 7.0$  Hz, 2H), 6.94 (d,  $J = 7.8$  Hz, 2H), 6.87 (d,  $J = 7.2$  Hz, 1H), 3.45 – 3.28 (m, 2H), 3.18 (dd,  $J = 13.4, 3.9$  Hz, 1H), 2.98 – 2.91 (m, 2H), 2.38 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 140.6, 138.8, 138.6, 137.5, 136.2, 133.5, 131.4, 131.2, 130.0, 129.9, 129.5, 128.3, 127.2, 127.1, 126.5, 49.5, 39.3, 38.1, 21.1, 21.0, 20.6, 20.4. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{25}\text{H}_{28}\text{S}_2\text{Na}^+$ : 415.1525; found: 415.1525.



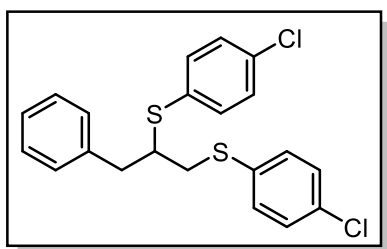
**c25**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c25** as a light-yellow oil (65 mg, 80% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.41 (t,  $J = 7.0$  Hz, 2H), 7.36 – 7.26 (m, 6H), 7.14 (ddt,  $J = 36.4, 22.3, 6.8$  Hz, 5H), 3.61 (tt,  $J = 9.0, 5.0$  Hz, 1H), 3.41 (dd,  $J = 14.2, 5.4$  Hz, 1H), 3.26 (dd,  $J = 13.6, 4.2$  Hz, 1H), 3.10 – 2.99 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 138.0, 136.8, 134.8, 134.7, 133.5, 133.3, 130.1, 130.0, 129.9, 129.5, 128.5, 128.4, 127.4, 127.2, 126.8, 48.5, 39.1, 37.5. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{S}_2\text{Na}^+$ : 427.0119; found: 427.0112.



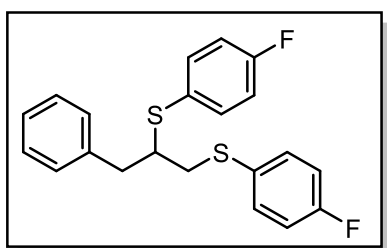
**c26**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c26** as a light-yellow oil (34 mg, 42% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.39 – 7.34 (m, 2H), 7.32 – 7.29 (m,  $J = 2.6$  Hz, 2H), 7.28 – 7.21 (m, 5H), 7.21 – 7.15 (m, 3H), 7.13 – 7.04 (m, 1H), 3.49 – 7.42 (m, 1H), 3.25 (ddd,  $J = 34.0, 14.0, 5.3$  Hz, 2H), 3.01 (ddd,  $J = 29.6, 13.9, 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 138.0, 137.6, 136.3, 134.8, 134.7, 131.8, 130.1, 129.4, 129.2, 128.6, 127.6, 127.6, 126.9, 126.7, 50.0, 39.2, 38.2. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{S}_2\text{Na}^+$ : 427.0119; found: 427.0119.



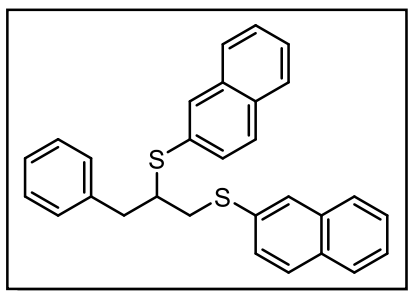
**c27**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c27** as a light-yellow oil (54 mg, 67% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.36 – 7.33 (m, 2H), 7.31 – 7.20 (m, 9H), 7.11 (d,  $J$  = 8.6 Hz, 2H), 3.34 (ddd,  $J$  = 13.1, 7.9, 5.1 Hz, 1H), 3.19 (ddd,  $J$  = 46.6, 13.9, 5.4 Hz, 2H), 3.02 – 2.90 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 138.2, 134.1, 134.0, 133.7, 132.6, 132.5, 131.2, 129.4, 129.2, 128.5, 126.8, 50.5, 39.3, 38.7. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{S}_2\text{Na}^+$ : 427.0119; found: 427.0121.



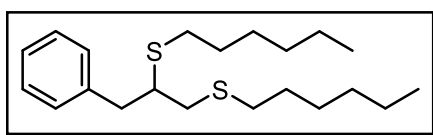
**c28**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c28** as a light-yellow oil (56 mg, 75% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.28 (t,  $J$  = 7.4 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.18 – 7.12 (m, 4H), 6.91 (dt,  $J$  = 13.4, 8.6 Hz, 4H), 3.24 – 3.17 (m, 2H), 3.05 (dd,  $J$  = 13.7, 4.7 Hz, 1H), 2.93 – 2.83 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 162.5 (d,  $J$  = 248.6 Hz), 161.9 (d,  $J$  = 247.5 Hz), 138.4, 135.4 (d,  $J$  = 8.2 Hz), 132.6 (d,  $J$  = 8.2 Hz), 130.51, 129.4, 129.0, 128.5, 126.8, 116.1 (d,  $J$  = 21.8 Hz), 116.0 (d,  $J$  = 21.8 Hz), 50.9, 39.6, 39.2.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = -113.39, -114.78. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{21}\text{H}_{19}\text{F}_2\text{S}_2^+$ : 373.0891; found: 373.0891.



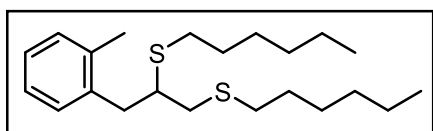
**c29**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c29** as a light-yellow oil (71 mg, 81% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.84 – 7.72 (m, 3H), 7.65 (dd,  $J$  = 19.7, 8.6 Hz, 2H), 7.60 – 7.37 (m, 7H), 7.36 – 7.27 (m, 7H), 3.59 (tt,  $J$  = 9.3, 4.9 Hz, 1H), 3.45 – 3.35 (m, 2H), 3.08 (ddd,  $J$  = 40.8, 14.1, 8.4 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 138.5, 133.7, 133.6, 132.9, 132.4, 131.9, 131.6, 131.2, 129.8, 129.5, 128.6, 128.5, 128.4, 127.7, 127.7, 127.6, 127.4, 127.1, 126.7, 126.5, 126.3, 125.8, 49.9, 39.2, 38.3. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{29}\text{H}_{25}\text{S}_2^+$ : 437.1392; found: 437.1398.



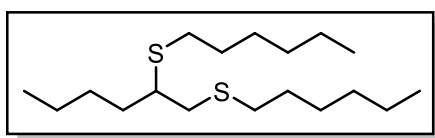
**c30**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 500/1, v/v) afforded **c30** as a light-yellow oil (68 mg, 97% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.37 – 7.20 (m, 5H), 3.15 (dd,  $J$  = 13.6, 6.0 Hz, 1H), 3.05 – 2.95 (m, 1H), 2.91 – 2.76 (m, 2H), 2.69 (dd,  $J$  = 13.1, 7.8 Hz, 1H), 2.55 (t,  $J$  = 7.5 Hz, 2H), 2.50 (t,  $J$  = 7.4 Hz, 2H), 1.63 – 1.50 (m, 4H), 1.44 – 1.23 (m, 12H), 0.91 (q,  $J$  = 6.9 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 139.2, 129.4, 128.2, 126.4, 47.4, 40.3, 37.5, 33.1, 31.5, 31.4, 29.7, 28.6, 28.6, 22.6, 14.1. HRMS (EI) ( $m/z$ ) for  $[\text{M}]^+$  calculated for  $\text{C}_{21}\text{H}_{36}\text{S}_2^+$ : 352.2253; found: 352.2246.



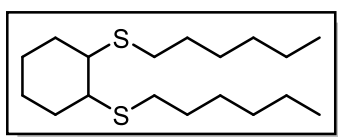
**c31**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 500/1, v/v) afforded **c31** as a light-yellow oil (48 mg, 65% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.23 – 7.19 (m, 1H), 7.17 – 7.14 (m, 3H), 3.19 (dd,  $J$  = 13.9, 6.4 Hz, 1H), 3.00 (p,  $J$  = 7.2 Hz, 1H), 2.93 – 2.66 (m, 3H), 2.55 (t,  $J$  = 7.5 Hz, 2H), 2.47 (t,  $J$  = 7.4 Hz, 2H), 2.38 (s, 3H), 1.61 – 1.47 (m, 4H), 1.42 – 1.20 (m, 12H), 0.90 (q,  $J$  = 7.1 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 137.6, 136.3, 130.3, 126.5, 125.7, 46.5, 38.1, 33.3, 31.4, 31.4, 29.7, 29.6, 28.6, 22.6, 22.5, 19.7, 14.1. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{22}\text{H}_{38}\text{S}_2\text{Na}^+$ : 389.2307; found: 389.2307.



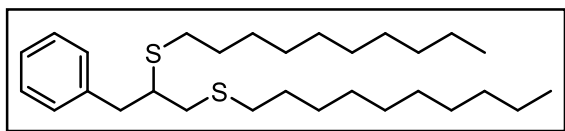
**c32**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 500/1, v/v) afforded **c32** as a light-yellow oil (62 mg, 98% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 2.84 (dd,  $J$  = 12.2, 4.3 Hz, 1H), 2.77 – 2.59 (m, 2H), 2.53 (t,  $J$  = 7.2 Hz, 4H), 1.81 (tt,  $J$  = 9.9, 5.7 Hz, 1H), 1.63 – 1.54 (m, 4H), 1.53 – 1.44 (m, 2H), 1.43 – 1.25 (m, 15H), 0.93 – 0.87 (m, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 45.8, 38.4, 33.2, 33.1, 31.4, 30.9, 29.8, 28.9, 28.7, 28.6, 22.6, 14.0. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{18}\text{H}_{39}\text{S}_2^+$ : 319.2488; found: 319.2487.



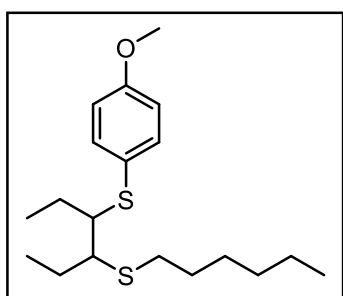
**c33**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 500/1, v/v) afforded **c33** as a light-yellow oil (57 mg, 90% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 2.77 (dt,  $J$  = 5.9, 2.6 Hz, 2H), 2.57 (t,  $J$  = 7.5 Hz, 4H), 2.21 – 2.15 (m, 2H), 1.68 (tt,  $J$  = 5.3, 2.7 Hz, 2H), 1.63 – 1.49 (m, 6H), 1.43 – 1.34 (m, 6H), 1.34 – 1.22 (m, 8H), 0.89 (t,  $J$  = 6.8 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 48.4, 31.7, 31.5, 29.8, 28.7, 24.0, 22.6, 14.0. HRMS (EI) ( $m/z$ ) for  $[\text{M}]^+$  calculated for  $\text{C}_{18}\text{H}_{36}\text{S}_2^+$ : 316.2253; found: 316.2254.



**c34**

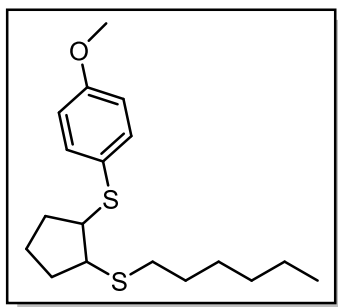
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 500/1, v/v) afforded **c34** as a light-yellow oil (65 mg, 70% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.37 – 7.28 (m, 2H), 7.28 – 7.19 (m, 3H), 3.15 (dd,  $J = 13.6, 6.1$  Hz, 1H), 3.06 – 2.94 (m, 1H), 2.91 – 2.76 (m, 2H), 2.69 (dd,  $J = 13.1, 7.8$  Hz, 1H), 2.54 (t,  $J = 7.4$  Hz, 2H), 2.49 (t,  $J = 7.4$  Hz, 2H), 1.61 – 1.49 (m, 4H), 1.41 – 1.24 (m, 28H), 0.90 (t,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 139.1, 129.4, 128.2, 126.4, 47.4, 40.2, 37.5, 33.1, 31.9, 31.4, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 28.9, 22.7, 14.1. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{29}\text{H}_{52}\text{S}_2\text{Na}^+$ : 487.3403; found: 487.3406.



**c35**

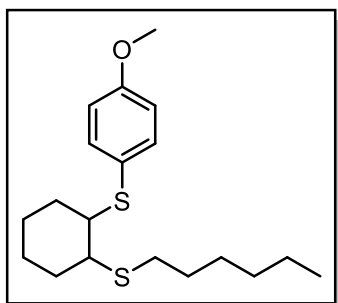
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c35** as a light-yellow oil (40 mg, 59% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.41 (d,  $J = 8.8$  Hz, 2H), 6.83 (d,  $J = 8.8$  Hz, 2H), 3.80 (s, 3H), 3.01 (dt,  $J = 9.3, 4.7$  Hz, 1H), 2.66 (dt,  $J = 9.7, 5.0$  Hz, 1H), 2.54 (t,  $J = 7.5$  Hz, 2H), 1.88 – 1.73 (m, 2H), 1.67 – 1.53 (m, 4H), 1.42 – 1.34 (m, 2H), 1.31 – 1.24 (m, 4H), 1.06 (t,  $J = 7.3$  Hz, 3H), 1.00 (t,  $J = 7.3$  Hz, 3H), 0.89 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.1, 134.9, 126.6, 114.4, 58.6, 55.3, 52.9, 32.7, 31.5, 29.8, 28.7, 26.2, 25.1, 22.6, 14.1, 12.2, 12.1. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{19}\text{H}_{32}\text{OS}_2\text{Na}^+$ : 363.1787; found: 363.1786.





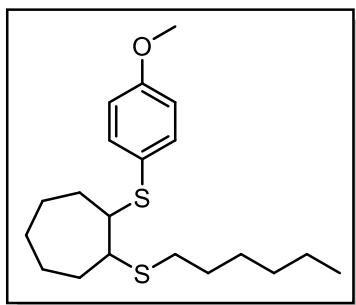
**c36**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c36** as a light-yellow oil (36 mg, 55% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.41 (d,  $J$  = 8.8 Hz, 2H), 6.83 (d,  $J$  = 8.8 Hz, 2H), 3.80 (s, 3H), 3.01 (dt,  $J$  = 9.3, 4.7 Hz, 1H), 2.66 (dt,  $J$  = 9.7, 5.0 Hz, 1H), 2.54 (t,  $J$  = 7.5 Hz, 2H), 1.88 – 1.73 (m, 2H), 1.67 – 1.53 (m, 4H), 1.42 – 1.34 (m, 2H), 1.31 – 1.24 (m, 4H), 1.06 (t,  $J$  = 7.3 Hz, 3H), 1.00 (t,  $J$  = 7.3 Hz, 3H), 0.89 (t,  $J$  = 6.9 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.1, 134.9, 126.6, 114.4, 58.6, 55.3, 52.9, 32.7, 31.5, 29.8, 28.7, 26.2, 25.1, 22.6, 14.1, 12.2, 12.1. HRMS (EI) ( $m/z$ ) for  $[\text{M}]^+$  calculated for  $\text{C}_{18}\text{H}_{28}\text{OS}_2^+$ : 324.1576; found: 324.1574.



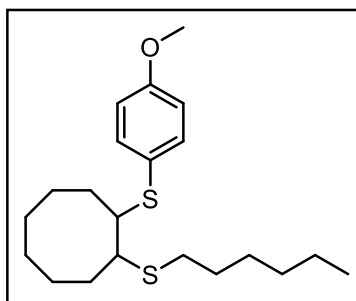
**c37**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c37** as a light-yellow oil (41 mg, 60% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.44 (d,  $J$  = 8.8 Hz, 2H), 6.86 (d,  $J$  = 8.8 Hz, 2H), 3.82 (s, 3H), 3.09 (td,  $J$  = 7.3, 4.0 Hz, 1H), 2.73 (td,  $J$  = 7.5, 4.0 Hz, 1H), 2.49 (tt,  $J$  = 7.8, 4.0 Hz, 2H), 2.32 – 2.20 (m, 1H), 2.14 – 2.01 (m, 1H), 1.72 – 1.63 (m, 2H), 1.58 – 1.47 (m, 4H), 1.39 – 1.25 (m, 8H), 0.90 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.5, 145.8, 135.8, 114.4, 55.3, 52.4, 46.9, 31.5, 31.3, 29.8, 28.7, 24.0, 23.8, 22.6, 14.0. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{19}\text{H}_{31}\text{OS}_2^+$ : 339.1811; found: 339.1807.



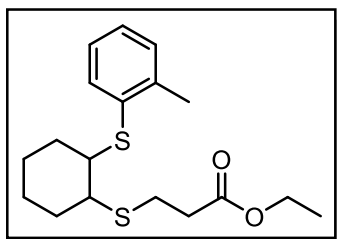
**c38**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c38** as a light-yellow oil (38 mg, 54% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.41 (d,  $J$  = 8.3 Hz, 2H), 6.84 (d,  $J$  = 8.5 Hz, 2H), 3.79 (s, 3H), 3.30 (dt,  $J$  = 8.2, 4.0 Hz, 1H), 2.96 (dt,  $J$  = 7.9, 4.1 Hz, 1H), 2.42 – 2.22 (m, 2H), 2.18 – 1.99 (m, 2H), 1.81 – 1.70 (m, 4H), 1.61 – 1.51 (m, 4H), 1.45 – 1.37 (m, 2H), 1.30 – 1.20 (m, 6H), 0.88 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.5, 135.6, 125.9, 114.5, 56.4, 55.3, 49.7, 31.8, 31.4, 30.9, 30.6, 29.6, 28.9, 28.7, 24.2, 24.1, 22.6, 14.0. HRMS (ESI) ( $m/z$ ) for  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{20}\text{H}_{32}\text{OS}_2\text{Na}^+$ : 375.1787; found: 375.1787.



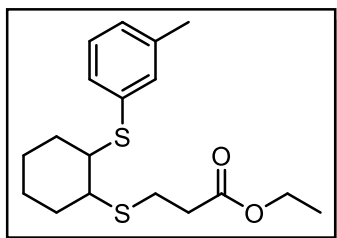
**c39**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c39** as a light-yellow oil (33 mg, 45% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.41 (d,  $J$  = 8.6 Hz, 2H), 6.84 (d,  $J$  = 8.6 Hz, 2H), 3.80 (s, 3H), 3.25 (t,  $J$  = 7.1 Hz, 1H), 2.90 (t,  $J$  = 7.1 Hz, 1H), 2.55 – 2.38 (m, 2H), 2.24 – 2.01 (m, 2H), 1.90 – 1.75 (m, 4H), 1.62 – 1.47 (m, 7H), 1.38 – 1.24 (m, 7H), 0.89 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 159.3, 135.4, 126.1, 114.4, 55.8, 55.3, 49.0, 32.0, 31.5, 29.6, 29.4, 29.3, 28.8, 26.3, 26.2, 25.4, 22.6, 14.0. HRMS (EI) ( $m/z$ ) for  $[\text{M}]^+$  calculated for  $\text{C}_{21}\text{H}_{34}\text{OS}_2^+$ : 366.2046; found: 366.2046.



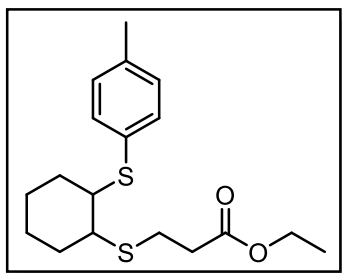
**c40**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **c40** as a light-yellow oil (37 mg, 55% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.45 – 7.36 (m, 1H), 7.23 – 7.09 (m, 3H), 4.14 (q,  $J = 7.2$  Hz, 2H), 3.28 (td,  $J = 6.9, 4.0$  Hz, 1H), 2.88 – 2.74 (m, 3H), 2.52 (t,  $J = 7.3$  Hz, 2H), 2.44 (s, 3H), 2.34 – 2.21 (m, 1H), 2.14 – 2.01 (m, 1H), 1.71 – 1.64 (m, 2H), 1.63 – 1.52 (m, 2H), 1.46 – 1.32 (m, 2H), 1.26 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 171.9, 140.1, 134.4, 132.3, 130.3, 127.0, 126.4, 60.6, 50.5, 47.5, 34.9, 30.9, 30.4, 26.5, 23.7, 23.6, 20.9, 14.2. HRMS (EI) ( $m/z$ ) for  $[\text{M}]^+$  calculated for  $\text{C}_{18}\text{H}_{26}\text{O}_2\text{S}_2^+$ : 338.1369; found: 338.1368.



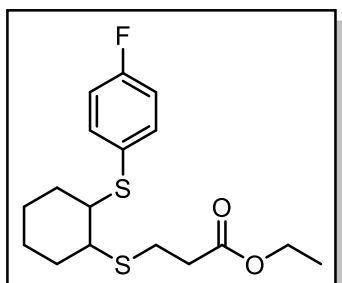
**c41**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **c41** as a light-yellow oil (37 mg, 55% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.29 – 7.14 (m, 3H), 7.04 (d,  $J = 7.5$  Hz, 1H), 4.15 (q,  $J = 7.1$  Hz, 2H), 3.27 (td,  $J = 7.1, 4.0$  Hz, 1H), 2.86 – 2.74 (m, 3H), 2.53 (t,  $J = 7.6$  Hz, 2H), 2.33 (s, 3H), 2.30 – 2.20 (m, 1H), 2.18 – 2.05 (m, 1H), 1.70 – 1.64 (m, 2H), 1.61 – 1.51 (m, 2H), 1.44 – 1.31 (m, 2H), 1.26 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 171.9, 138.7, 134.6, 133.0, 129.4, 128.7, 127.9, 60.6, 51.1, 47.4, 34.9, 30.9, 30.7, 26.4, 23.8, 23.7, 21.3, 14.2. HRMS (EI) ( $m/z$ ) for  $[\text{M}]^+$  calculated for  $\text{C}_{18}\text{H}_{26}\text{O}_2\text{S}_2^+$ : 338.1369; found: 338.1366.



**c42**

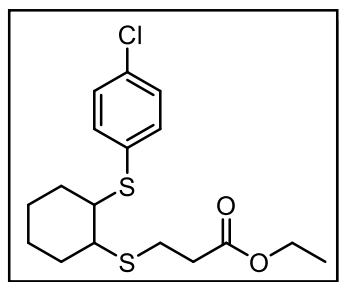
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **c42** as a light-yellow oil (39 mg, 58% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.35 (d,  $J$  = 8.1 Hz, 2H), 7.11 (d,  $J$  = 7.9 Hz, 2H), 4.15 (q,  $J$  = 7.1 Hz, 2H), 3.23 – 3.13 (m, 1H), 2.83 – 2.74 (m, 3H), 2.53 (t,  $J$  = 7.6 Hz, 2H), 2.33 (s, 3H), 2.30 – 2.18 (m, 1H), 2.14 – 2.02 (m, 1H), 1.71 – 1.62 (m, 2H), 1.60 – 1.46 (m, 2H), 1.43 – 1.30 (m, 2H), 1.27 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 171.9, 137.4, 133.2, 130.9, 129.7, 60.6, 51.6, 47.3, 34.9, 31.1, 30.9, 26.3, 23.9, 23.8, 21.1, 14.2. HRMS (EI) ( $m/z$ ) for  $[\text{M}]^+$  calculated for  $\text{C}_{18}\text{H}_{26}\text{O}_2\text{S}_2^+$ : 338.1369; found: 338.1369.



**c43**

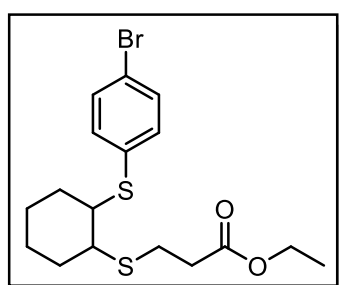
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **c43** as a light-yellow oil (41 mg, 60% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.50 – 7.40 (m, 2H), 7.00 (t,  $J$  = 8.7 Hz, 2H), 4.14 (q,  $J$  = 7.2 Hz, 2H), 3.11 (td,  $J$  = 7.7, 4.0 Hz, 1H), 2.82 – 2.69 (m, 3H), 2.58 – 2.45 (m, 2H), 2.29 – 2.17 (m, 1H), 2.12 – 2.00 (m, 1H), 1.71 – 1.61 (m, 2H), 1.58 – 1.45 (m, 2H), 1.40 – 1.29 (m, 2H), 1.26 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 171.8, 162.4 (d,  $J$  = 248.5 Hz), 135.5 (d,  $J$  = 8.1 Hz), 129.6, 116.0 (d,  $J$  = 21.7 Hz), 60.6, 52.2, 47.4, 34.8,

31.3, 31.1, 26.2, 24.0, 23.9, 14.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = -114.02.  
HRMS (EI) (m/z) for  $[\text{M}]^+$  calculated for  $\text{C}_{17}\text{H}_{23}\text{FO}_2\text{S}_2^+$ : 342.1118; found: 342.1121.



**c44**

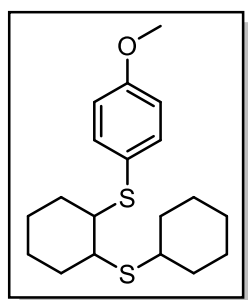
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **c44** as a light-yellow oil (41 mg, 53% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.42 – 7.32 (m, 2H), 7.30 – 7.20 (m, 2H), 4.15 (q,  $J$  = 7.2 Hz, 2H), 3.20 (td,  $J$  = 7.6, 4.0 Hz, 1H), 2.84 – 2.70 (m, 3H), 2.58 – 2.47 (m, 2H), 2.28 – 2.17 (m, 1H), 2.13 – 2.04 (m, 1H), 1.72 – 1.62 (m, 2H), 1.58 – 1.46 (m, 2H), 1.44 – 1.32 (m, 2H), 1.26 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 171.8, 133.9, 133.3, 133.2, 129.0, 60.7, 51.7, 47.5, 34.9, 31.3, 31.1, 26.3, 24.0, 23.9, 14.2. HRMS (EI) (m/z) for  $[\text{M}]^+$  calculated for  $\text{C}_{17}\text{H}_{23}\text{ClO}_2\text{S}_2^+$ : 358.0823; found: 358.0821.



**c45**

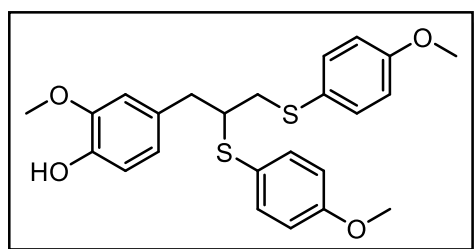
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **c45** as a light-yellow oil (44 mg, 55% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 7.46 – 7.37 (m, 2H), 7.33 – 7.28 (m, 2H), 4.15 (q,  $J$  = 7.2 Hz, 2H), 3.21 (td,  $J$  = 7.6, 4.0 Hz, 1H), 2.86 – 2.71 (m, 3H), 2.54 (t,  $J$  = 7.4 Hz, 2H), 2.29 – 2.17 (m, 1H), 2.14 – 2.04 (m, 1H), 1.71 – 1.60 (m, 2H), 1.59 – 1.46 (m, 2H), 1.42 – 1.30 (m, 2H), 1.27 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm = 171.8, 134.0, 132.0,

121.2, 60.7, 51.5, 47.5, 34.9, 31.3, 31.1, 26.3, 24.0, 23.9, 14.2. HRMS (ESI) (m/z) for  $[M+Na]^+$  calculated for  $C_{17}H_{23}BrO_2S_2Na^+$ : 425.0215; found: 425.0217.



**c46**

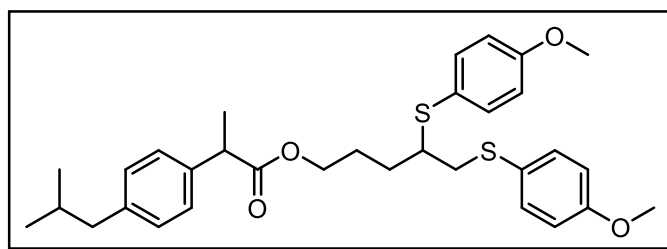
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded **c46** as a light-yellow oil (44 mg, 56% yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm = 7.43 (d,  $J$  = 8.6 Hz, 2H), 6.84 (d,  $J$  = 8.6 Hz, 2H), 3.79 (s, 3H), 3.12 (q,  $J$  = 6.5 Hz, 1H), 2.87 – 2.78 (m, 1H), 2.60 (q,  $J$  = 6.7 Hz, 1H), 2.33 – 2.20 (m, 1H), 2.11 – 2.01 (m, 1H), 1.88 – 1.68 (m, 4H), 1.65 – 1.47 (m, 5H), 1.40 – 1.18 (m, 7H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  ppm = 159.5, 135.8, 125.2, 114.4, 55.3, 52.9, 44.6, 43.4, 33.9, 31.0, 30.1, 26.2, 25.8, 23.7, 23.4. HRMS (EI) (m/z) for  $[M]^+$  calculated for  $C_{19}H_{28}OS_2^+$ : 336.1576; found: 336.1576.



**c47**

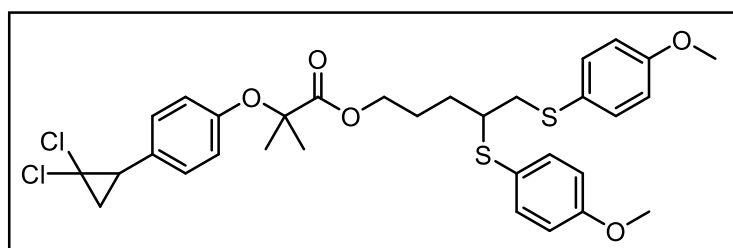
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) afforded **c47** as a light-yellow oil (87 mg, 98% yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm = 7.25 – 7.22 (m, 2H), 7.15 (d,  $J$  = 8.8 Hz, 2H), 6.83 (d,  $J$  = 7.9 Hz, 1H), 6.76 (dd,  $J$  = 12.1, 8.8 Hz, 4H), 6.71 – 6.62 (m, 2H), 5.63 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.18 – 2.99 (m, 3H), 2.89 – 2.74 (m, 2H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  ppm = 159.6, 158.9, 146.3, 144.2, 135.6, 132.9, 130.6, 125.9, 124.2, 122.1, 114.6,

114.5, 114.2, 111.9, 55.8, 55.4, 50.9, 39.7, 38.6. HRMS (ESI) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>24</sub>H<sub>27</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup>: 443.1345; found: 443.1343.



**c48**

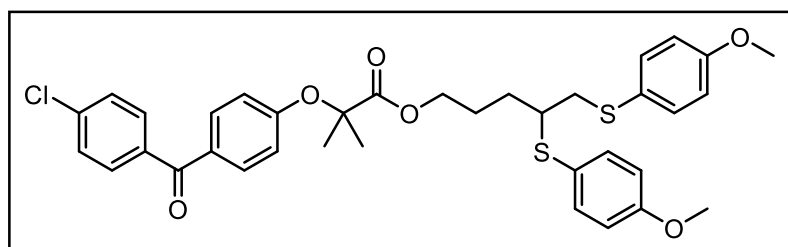
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **c48** as a light-yellow oil (66 mg, 60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.27 – 7.23 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.16 (dq, *J* = 8.4, 3.1 Hz, 2H), 7.08 (d, *J* = 7.4 Hz, 2H), 6.83 – 6.71 (m, 4H), 4.14 – 3.97 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.68 (qd, *J* = 7.2, 2.1 Hz, 1H), 3.09 (dd, *J* = 13.4, 3.7 Hz, 1H), 2.88 – 2.77 (m, 1H), 2.69 (dd, *J* = 13.3, 9.4 Hz, 1H), 2.43 (d, *J* = 6.6 Hz, 2H), 1.98 – 1.66 (m, 4H), 1.52 – 1.35 (m, 4H), 0.88 (d, *J* = 6.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ ppm = 174.7, 159.7, 159.0, 140.5, 137.8, 135.8, 133.2, 133.1, 129.3, 127.2, 125.9, 123.6, 114.6, 114.5, 64.3, 55.3, 48.8, 45.2, 45.0, 41.1, 30.2, 28.6, 26.0, 22.4, 18.5. HRMS (ESI) (m/z) for [M+Na]<sup>+</sup> calculated for C<sub>32</sub>H<sub>40</sub>O<sub>4</sub>S<sub>2</sub>Na<sup>+</sup>: 575.2260; found: 575.2264.



**c49**

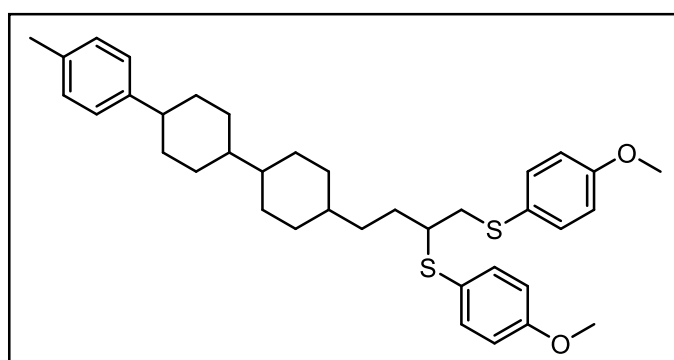
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **c49** as a light-yellow oil (80 mg, 63% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.27 – 7.24 (m, 2H), 7.19 – 7.12 (m, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.85 – 6.71 (m, 6H), 4.16 (td, *J* = 5.9, 2.7 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.08 (dd, *J* = 13.4, 3.9 Hz, 1H), 2.86 – 2.75 (m, 2H), 2.67 (dd, *J* = 13.3, 9.6 Hz, 1H), 2.00 – 1.83 (m, 3H), 1.79 – 1.69 (m, 2H), 1.61 (s, 6H), 1.47 – 1.32 (m, 1H). <sup>13</sup>C NMR (101 MHz,

CDCl<sub>3</sub>)  $\delta$  ppm = 174.2, 159.7, 159.0, 155.0, 135.8, 133.1, 129.7, 128.1, 125.8, 123.5, 118.6, 114.6, 79.2, 65.1, 60.9, 55.3, 48.8, 41.0, 34.8, 28.6, 26.0, 25.8, 25.5. HRMS (ESI) (m/z) for [M+Na]<sup>+</sup> calculated for C<sub>32</sub>H<sub>36</sub>Cl<sub>2</sub>O<sub>5</sub>S<sub>2</sub>Na<sup>+</sup>: 657.1273; found: 657.1273.



**c50**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded **c50** as a light-yellow oil (73 mg, 55% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 7.74 (d, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 4.17 (tt, *J* = 11.0, 5.8 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.08 (dd, *J* = 13.4, 3.9 Hz, 1H), 2.87 – 2.75 (m, 1H), 2.66 (dd, *J* = 13.4, 9.7 Hz, 1H), 2.02 – 1.82 (m, 2H), 1.69 (s, 7H), 1.46 – 1.32 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 194.1, 173.7, 159.7, 159.0, 138.3, 136.4, 135.8, 133.0, 132.1, 131.2, 130.4, 129.9, 128.5, 125.7, 123.4, 117.3, 114.9, 114.6, 113.8, 79.4, 65.4, 55.3, 48.7, 41.0, 28.5, 26.0, 25.5. HRMS (ESI) (m/z) for [M+Na]<sup>+</sup> calculated for C<sub>36</sub>H<sub>37</sub>ClO<sub>6</sub>S<sub>2</sub>Na<sup>+</sup>: 687.1612; found: 687.1611.



**c51**

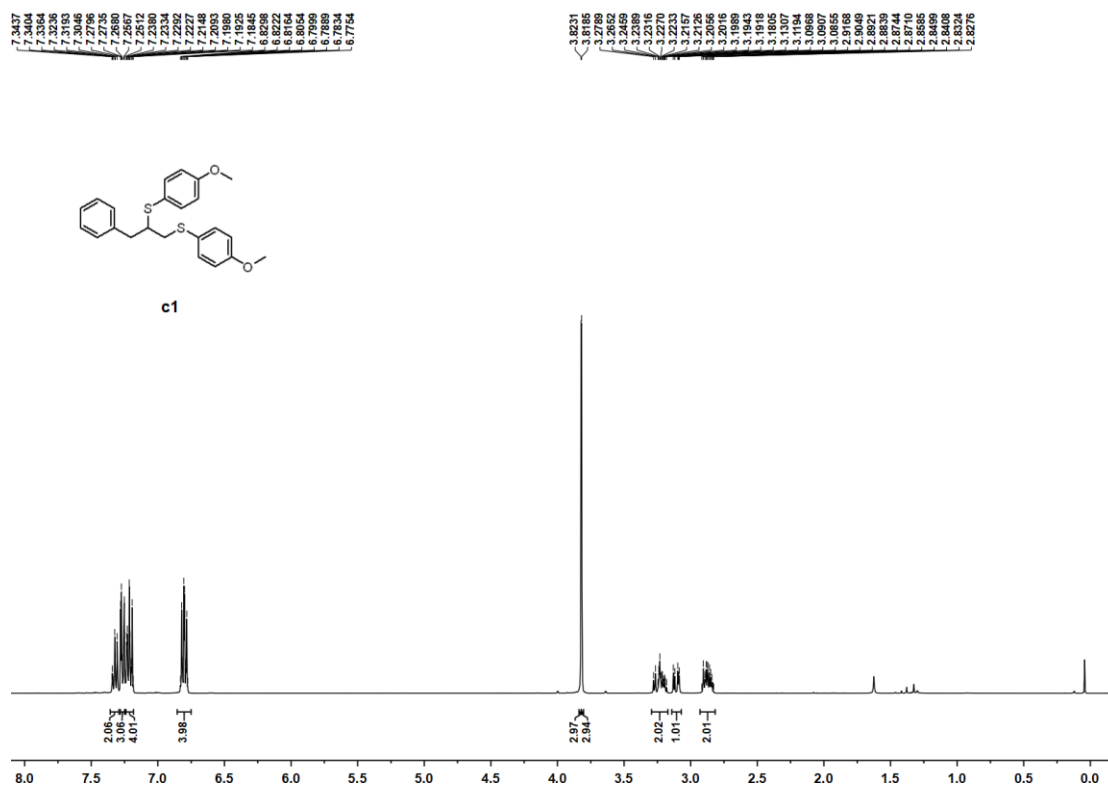
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 150/1, v/v) afforded **c51** as a light-yellow oil (76 mg, 64% yield). <sup>1</sup>H NMR (400 MHz,



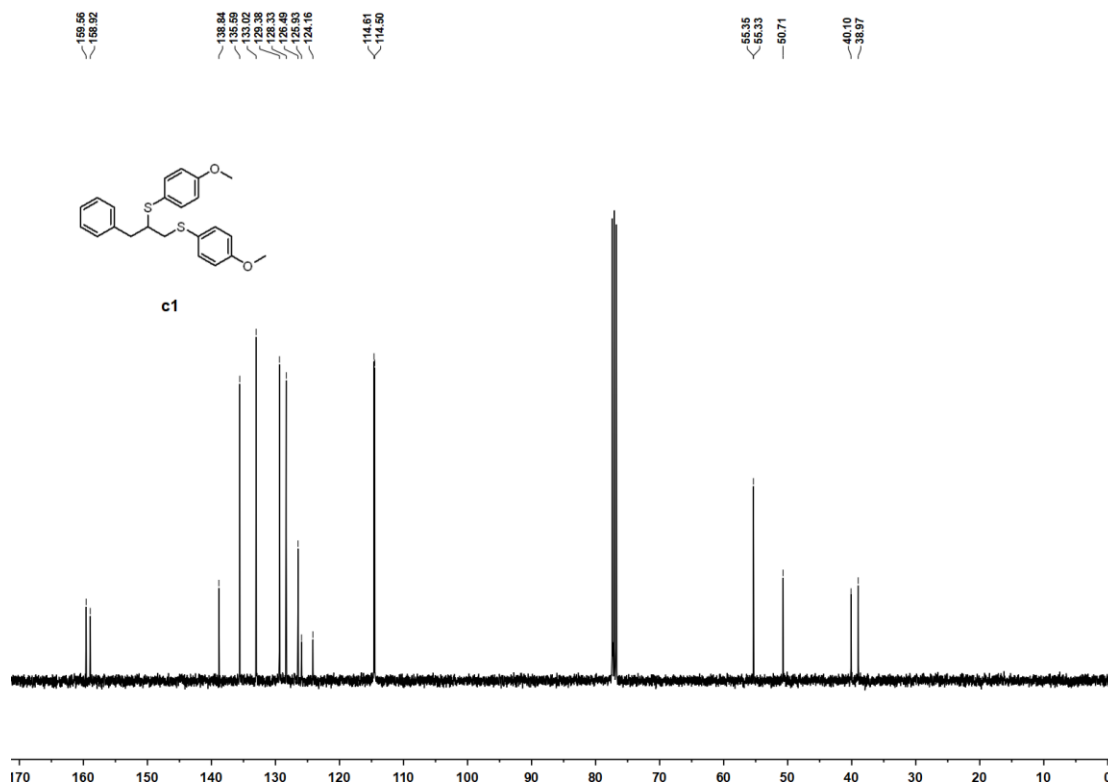
CDCl<sub>3</sub>)  $\delta$  ppm = 7.27 (d,  $J$  = 8.8 Hz, 2H), 7.18 (d,  $J$  = 8.8 Hz, 2H), 7.09 (s, 4H), 6.84 – 6.71 (m, 4H), 3.79 (s, 3H), 3.78 (s, 3H), 3.11 (dd,  $J$  = 13.1, 4.0 Hz, 1H), 2.87 (tt,  $J$  = 8.3, 4.0 Hz, 1H), 2.76 (dd,  $J$  = 13.2, 9.4 Hz, 1H), 2.41 (tt,  $J$  = 12.1, 3.4 Hz, 1H), 2.31 (s, 3H), 1.98 – 1.71 (m, 9H), 1.52 – 1.20 (m, 6H), 1.17 – 1.07 (m, 4H), 1.04 – 0.85 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  ppm = 159.5, 158.9, 144.9, 135.6, 135.2, 133.1, 129.0, 126.7, 126.2, 124.2, 114.6, 114.5, 55.3, 49.5, 44.3, 43.4, 42.9, 41.1, 37.8, 34.7, 34.4, 33.8, 33.3, 30.4, 30.1, 30.0, 29.8, 21.0, 14.2. HRMS (ESI) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>37</sub>H<sub>49</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>: 589.3168; found: 589.3165.

### 3. NMR spectra for the products

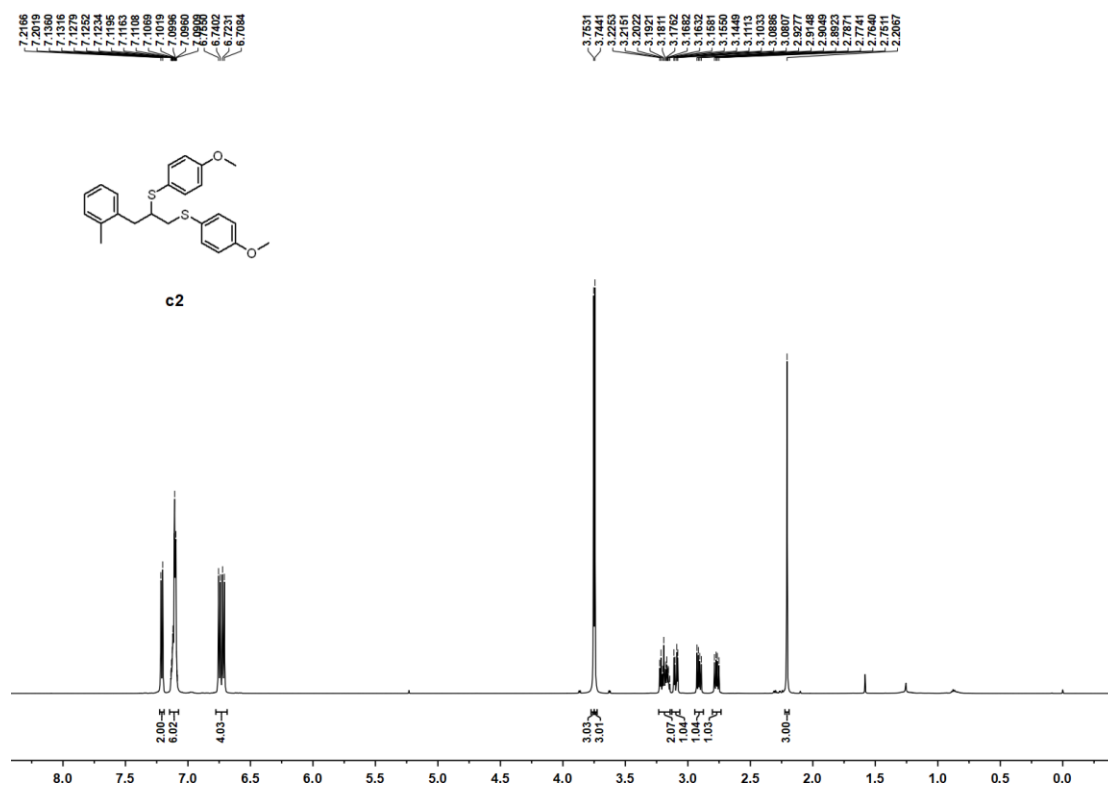
$^1\text{H}$  NMR spectra of compound **c1** in  $\text{CDCl}_3$  (400 MHz):



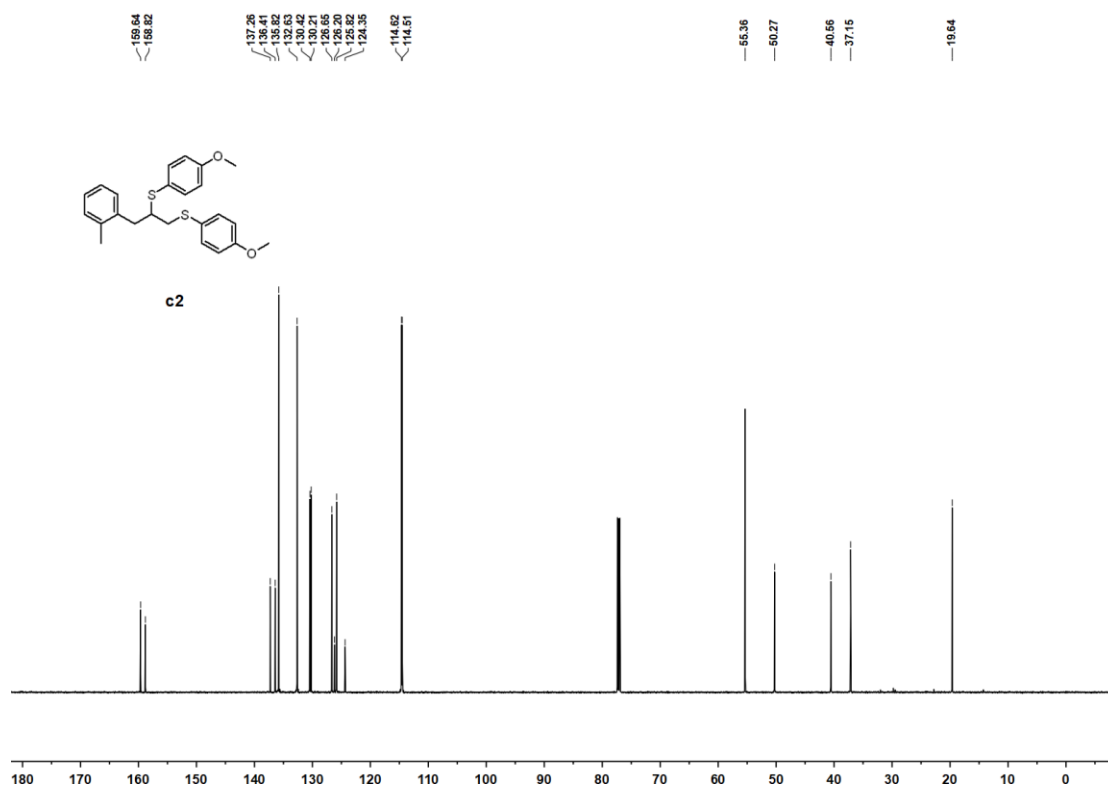
$^{13}\text{C}$  NMR spectra of compound **c1** in  $\text{CDCl}_3$  (101 MHz):



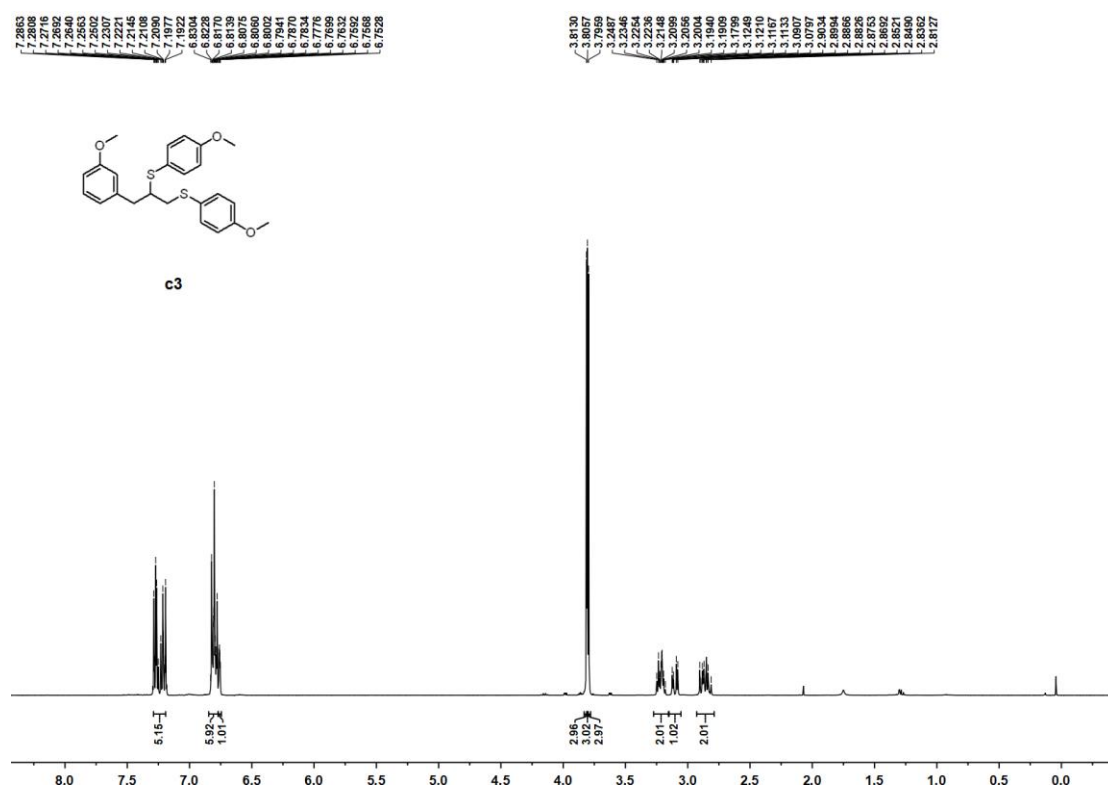
$^1\text{H}$  NMR spectra of compound **c2** in  $\text{CDCl}_3$  (600 MHz):



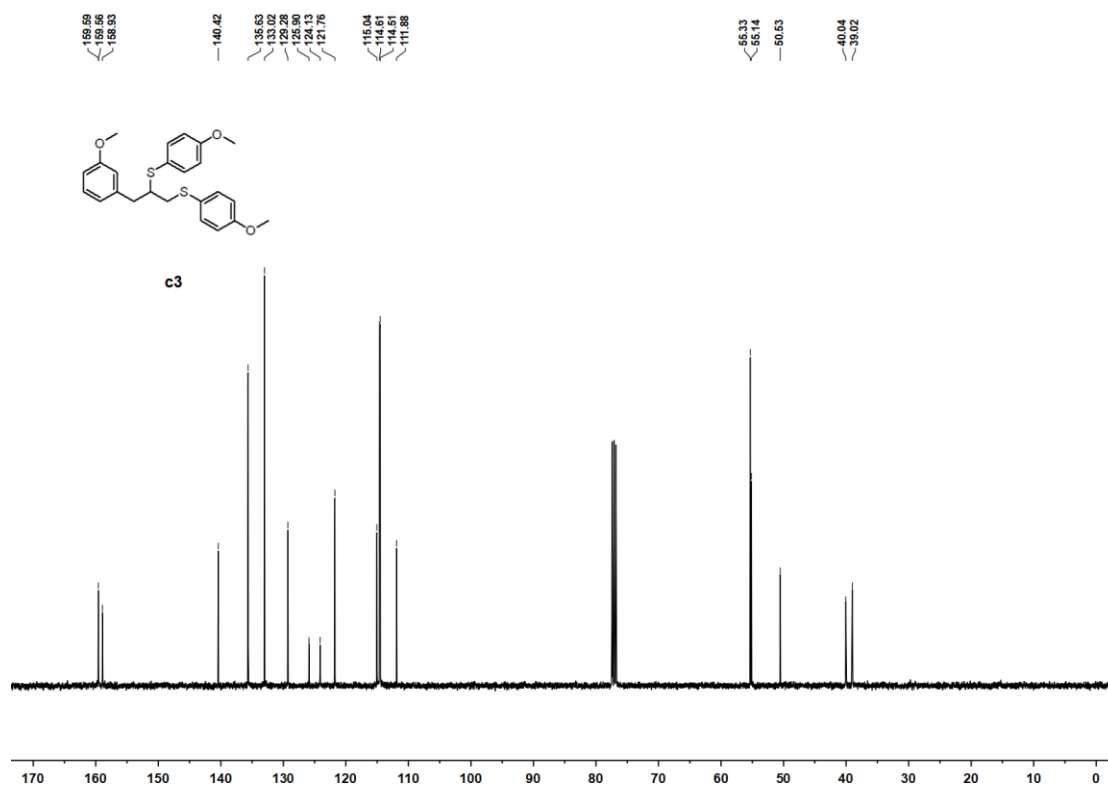
$^{13}\text{C}$  NMR spectra of compound **c2** in  $\text{CDCl}_3$  (151 MHz):



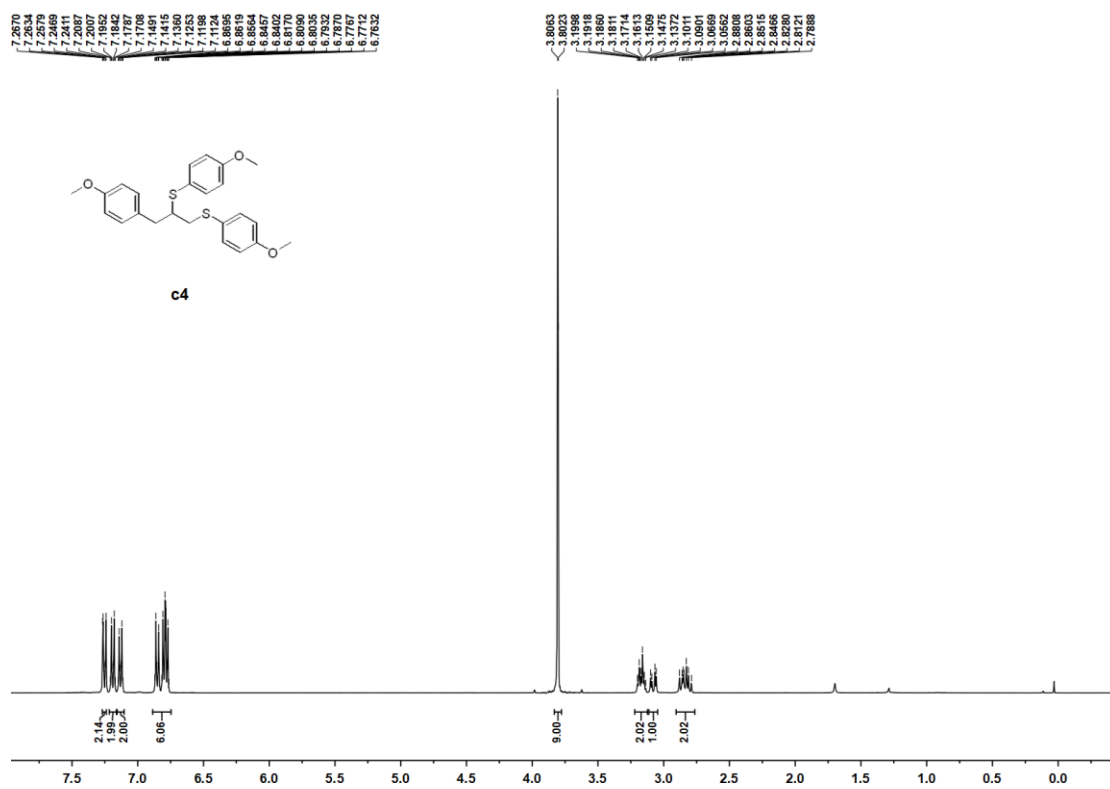
$^1\text{H}$  NMR spectra of compound **c3** in  $\text{CDCl}_3$  (400 MHz):



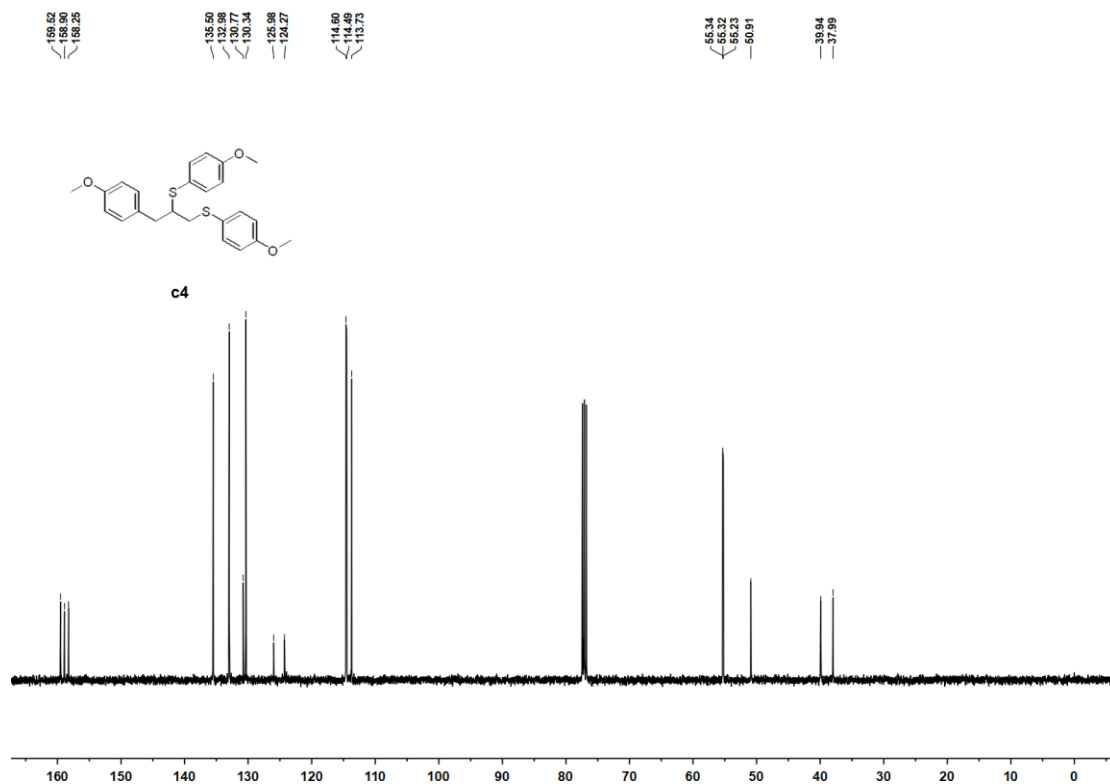
$^{13}\text{C}$  NMR spectra of compound **c3** in  $\text{CDCl}_3$  (101 MHz):



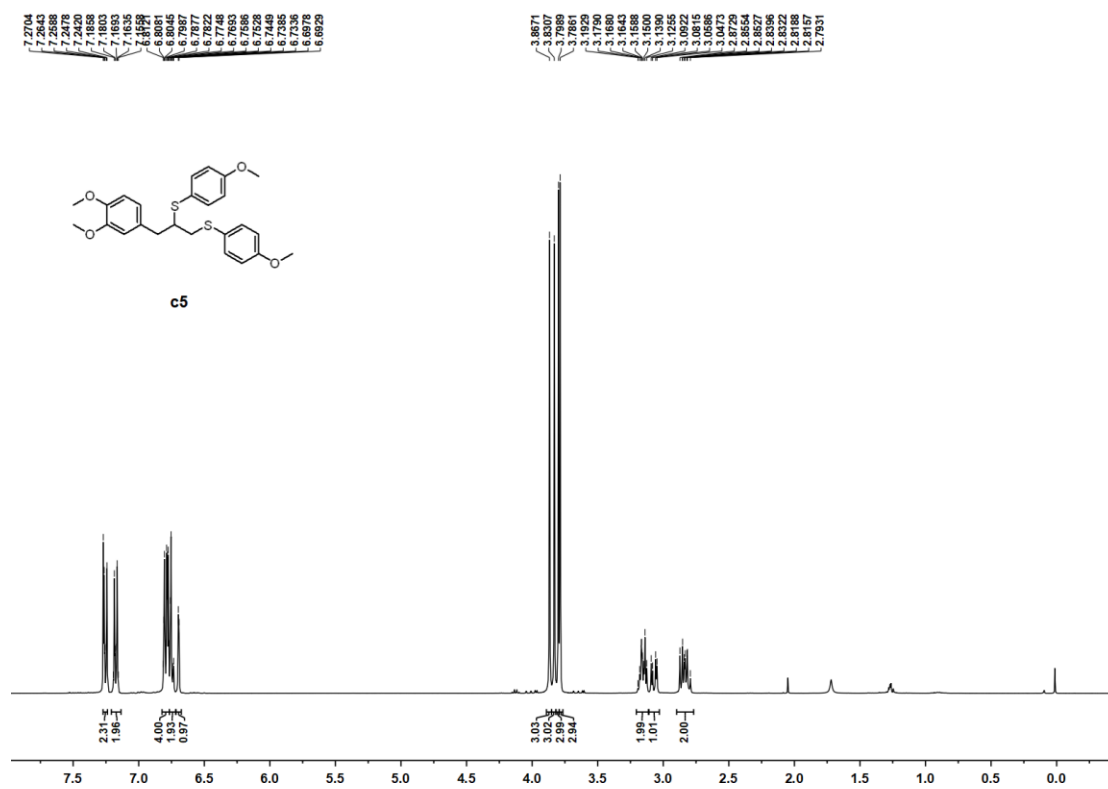
$^1\text{H}$  NMR spectra of compound **c4** in  $\text{CDCl}_3$  (400 MHz):



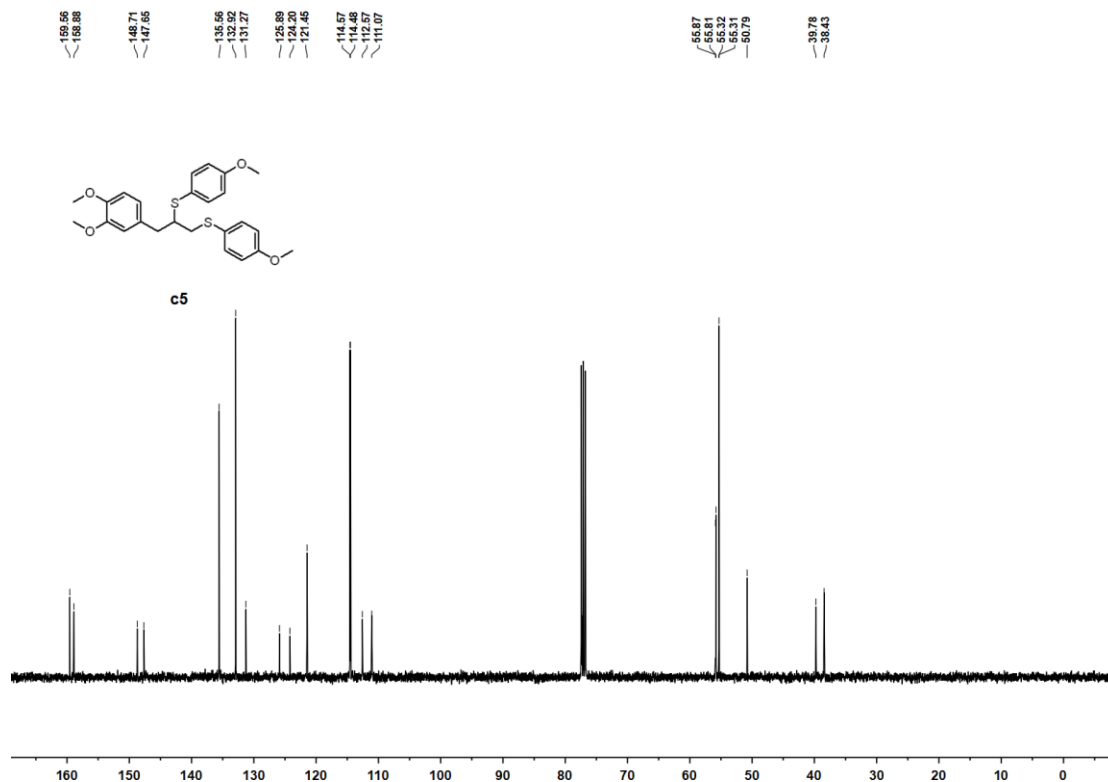
$^{13}\text{C}$  NMR spectra of compound **c4** in  $\text{CDCl}_3$  (101 MHz):



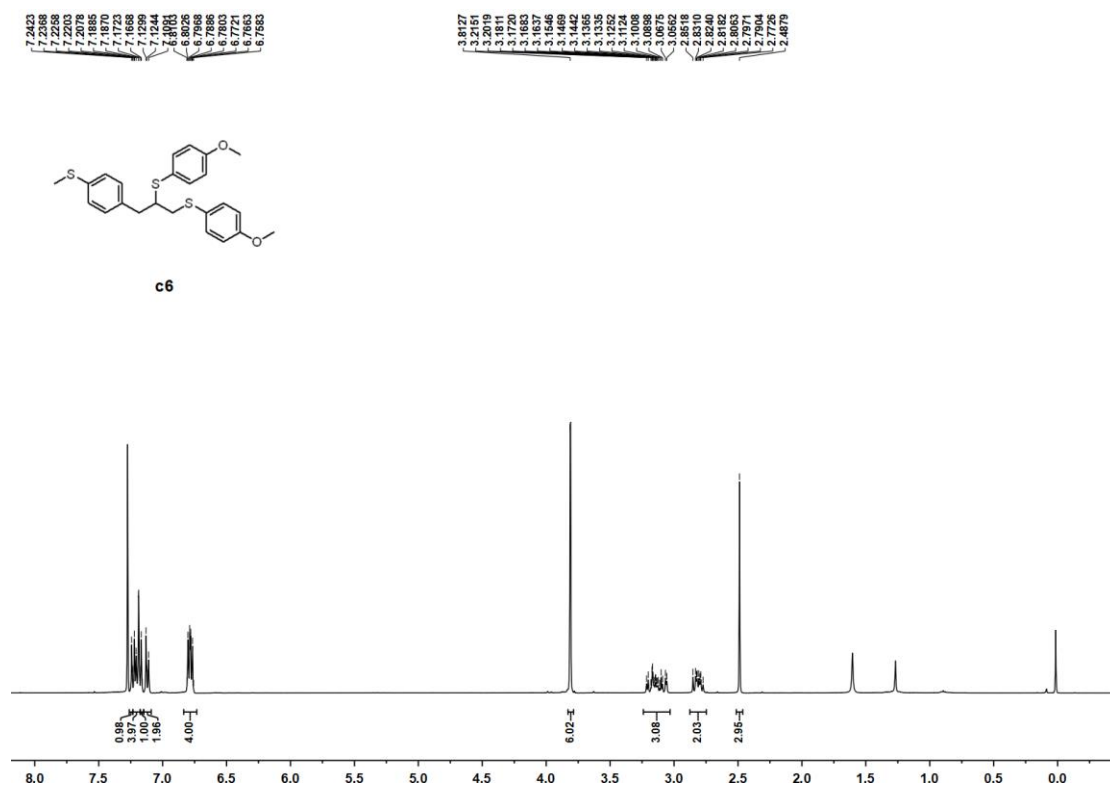
$^1\text{H}$  NMR spectra of compound **c5** in  $\text{CDCl}_3$  (400 MHz):



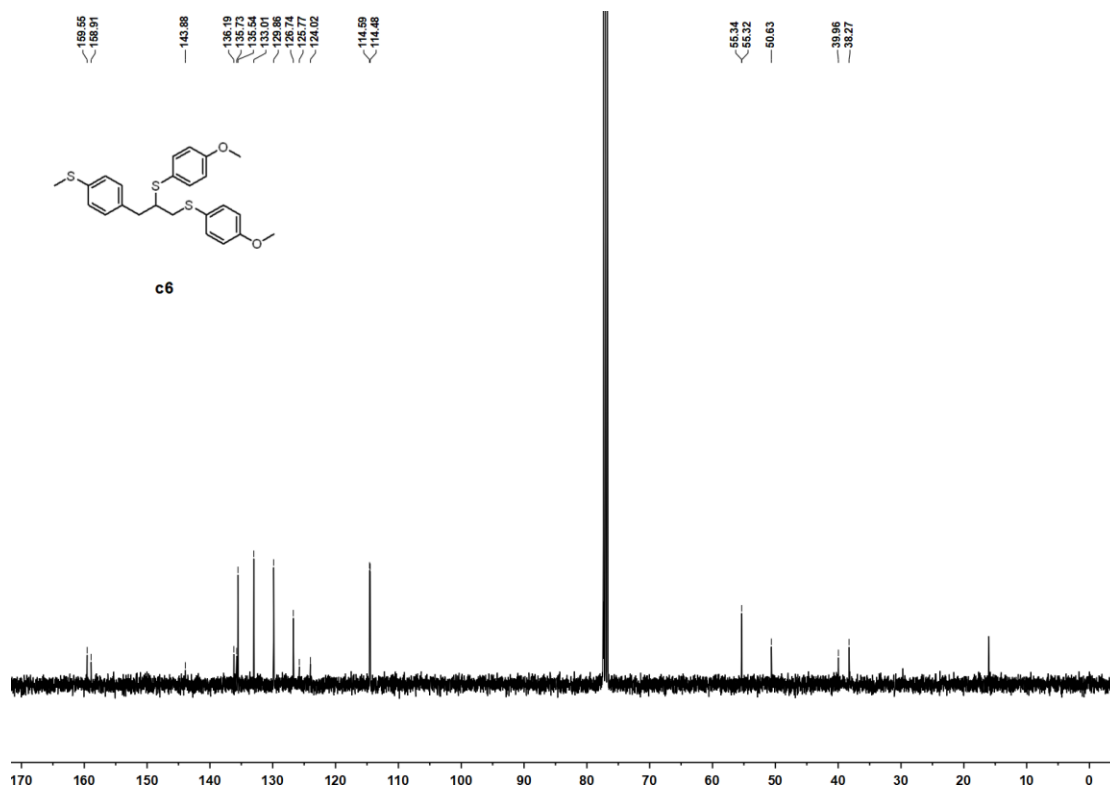
$^{13}\text{C}$  NMR spectra of compound **c5** in  $\text{CDCl}_3$  (101 MHz):



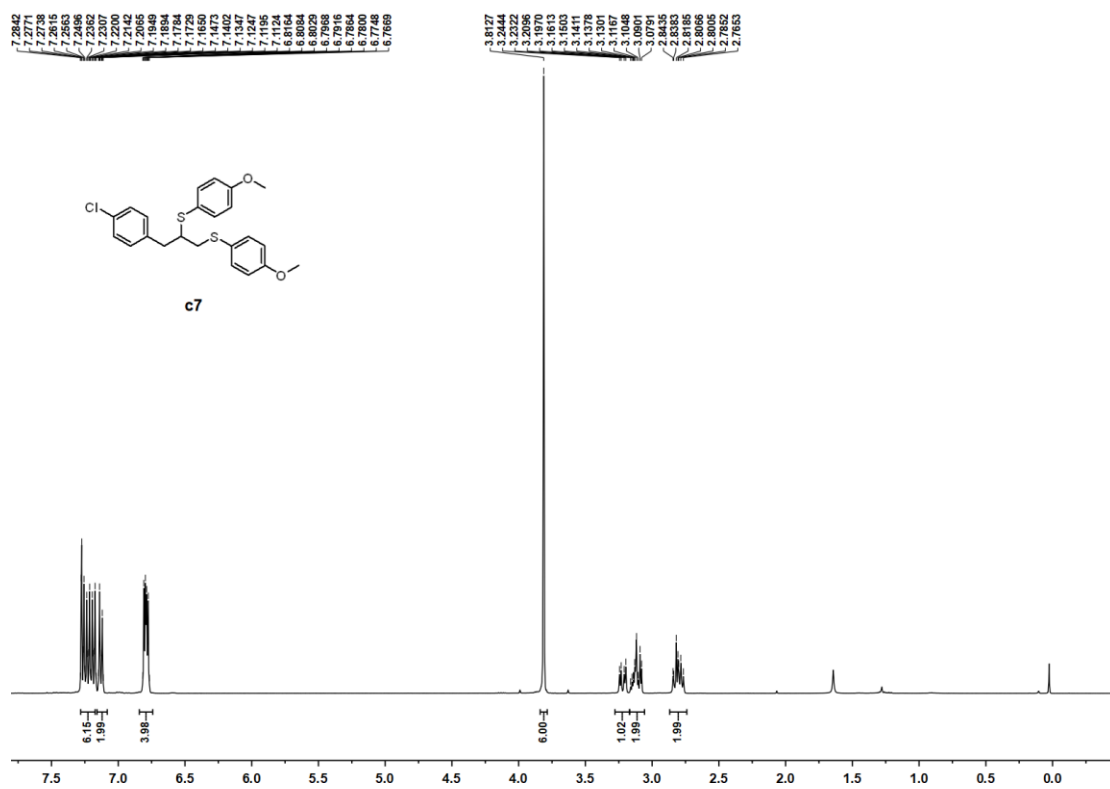
$^1\text{H}$  NMR spectra of compound **c6** in  $\text{CDCl}_3$  (400 MHz):



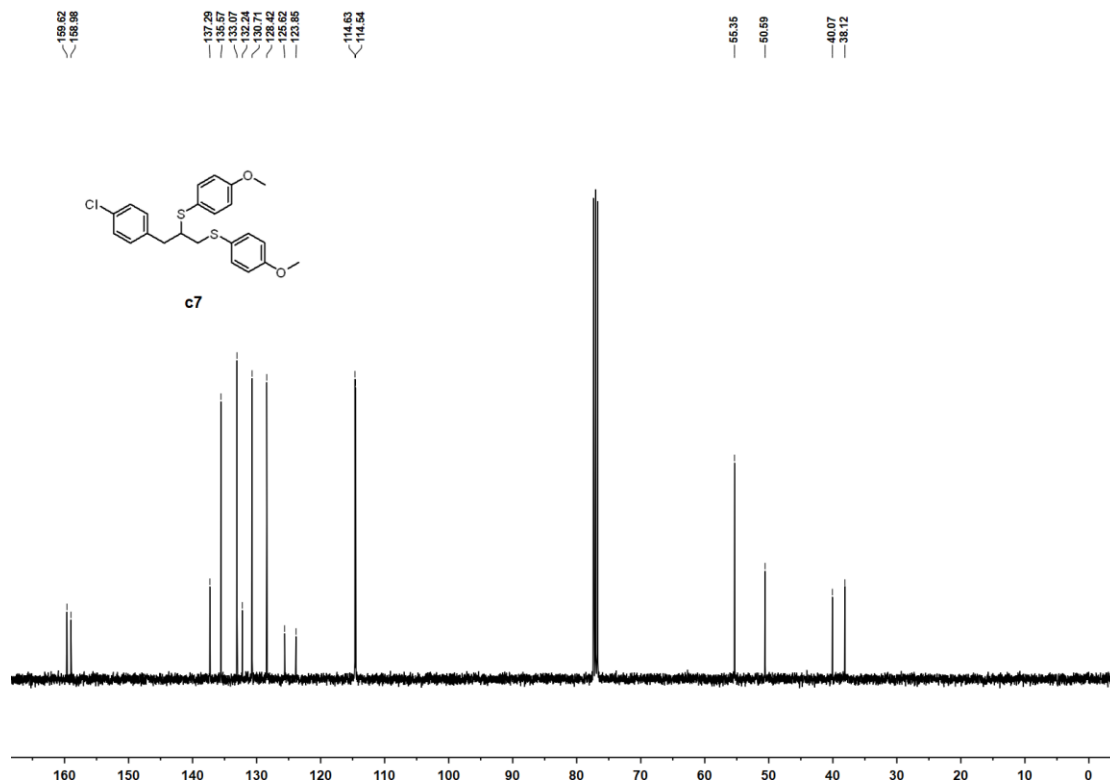
$^{13}\text{C}$  NMR spectra of compound **c6** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectra of compound **c7** in  $\text{CDCl}_3$  (400 MHz):

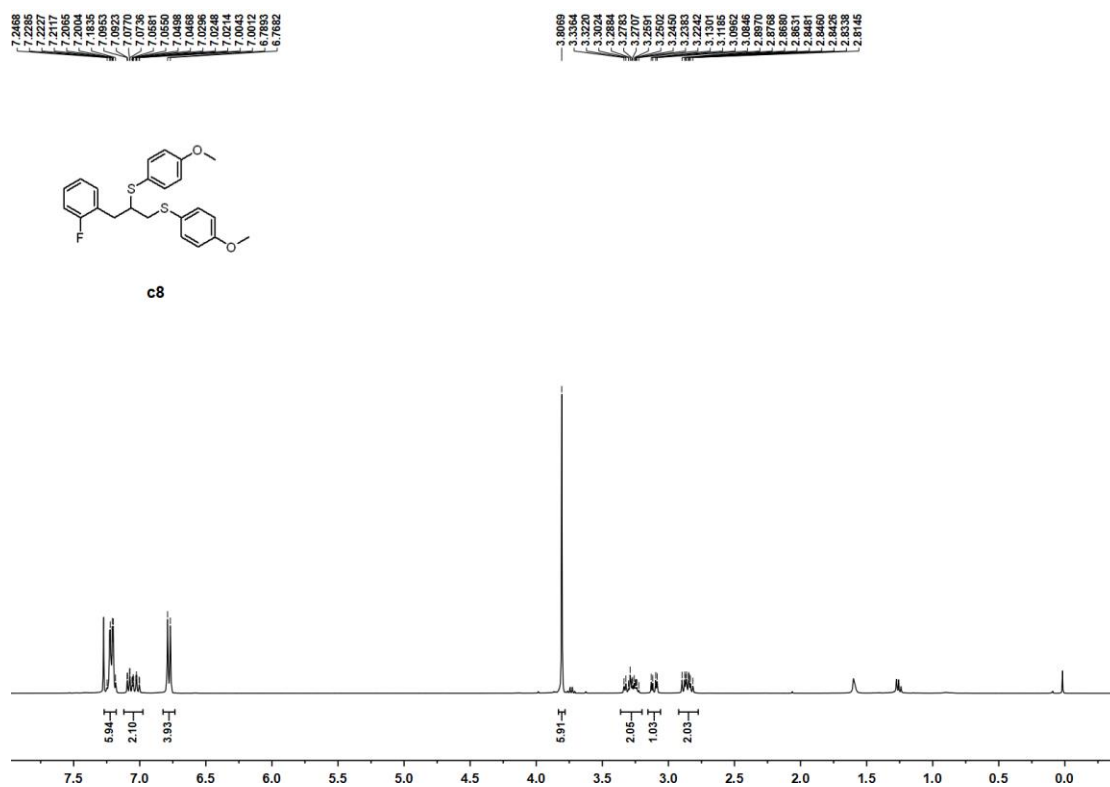


$^{13}\text{C}$  NMR spectra of compound **c7** in  $\text{CDCl}_3$  (101 MHz):

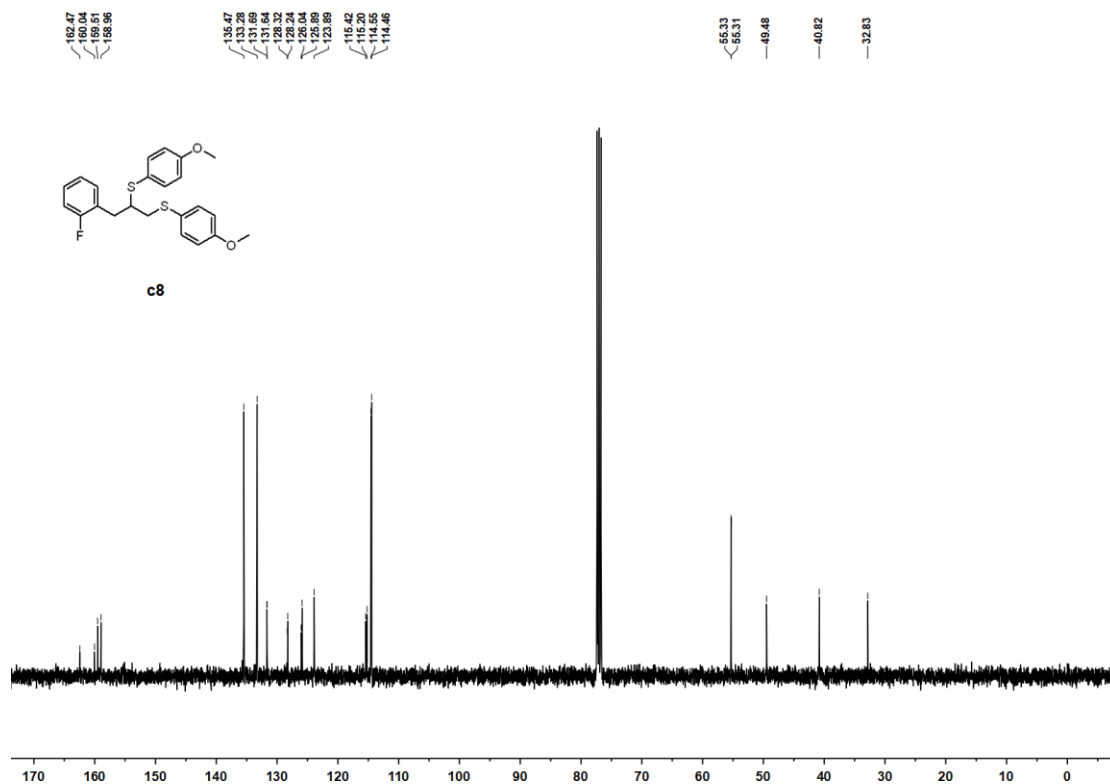




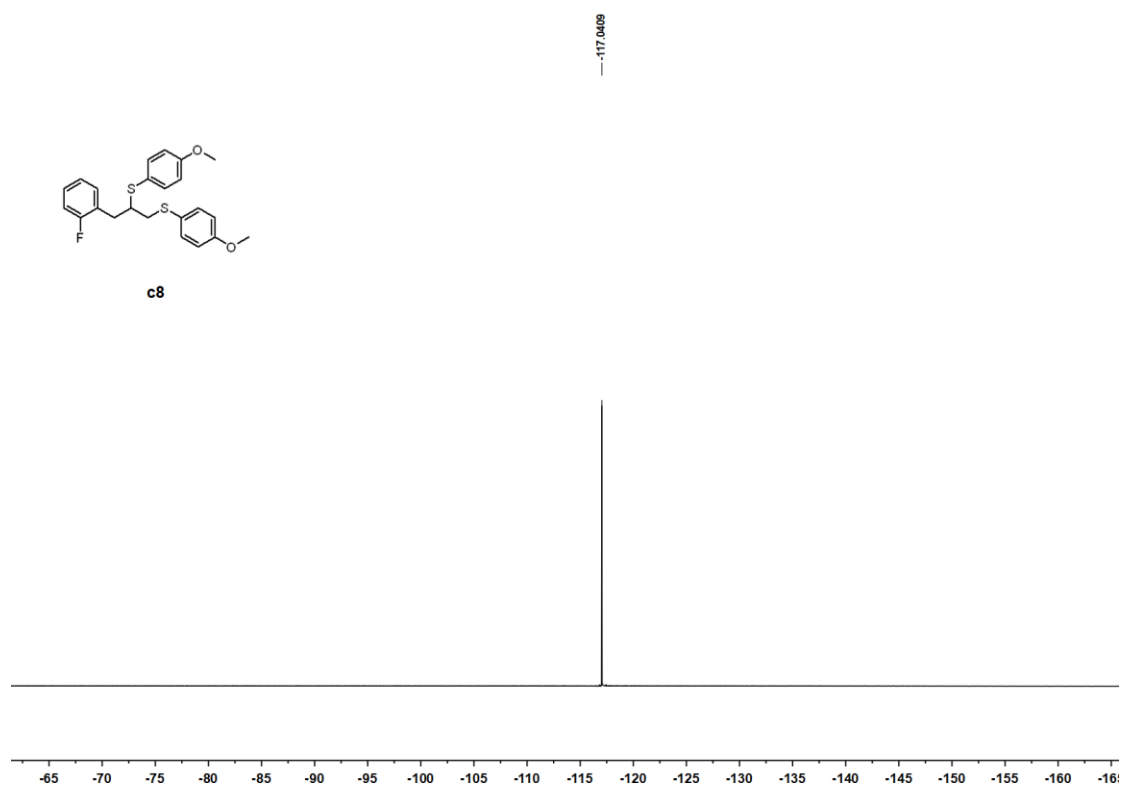
$^1\text{H}$  NMR spectra of compound **c8** in  $\text{CDCl}_3$  (400 MHz):



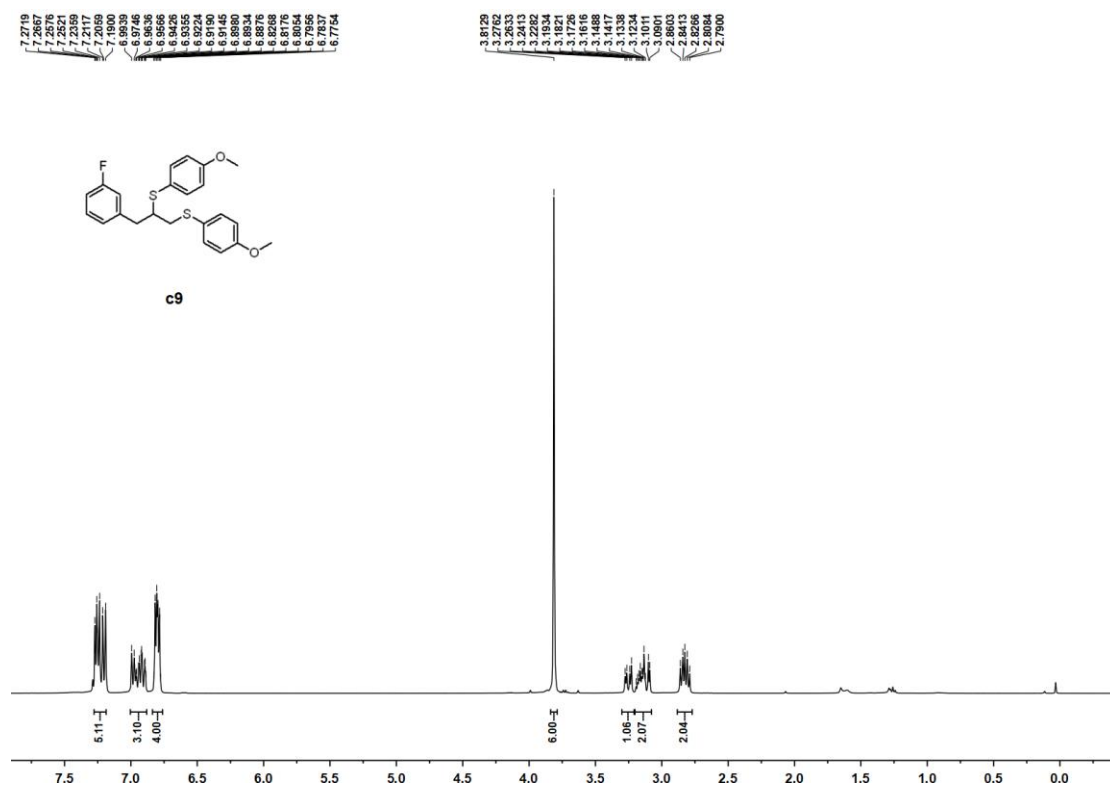
$^{13}\text{C}$  NMR spectra of compound **c8** in  $\text{CDCl}_3$  (101 MHz):



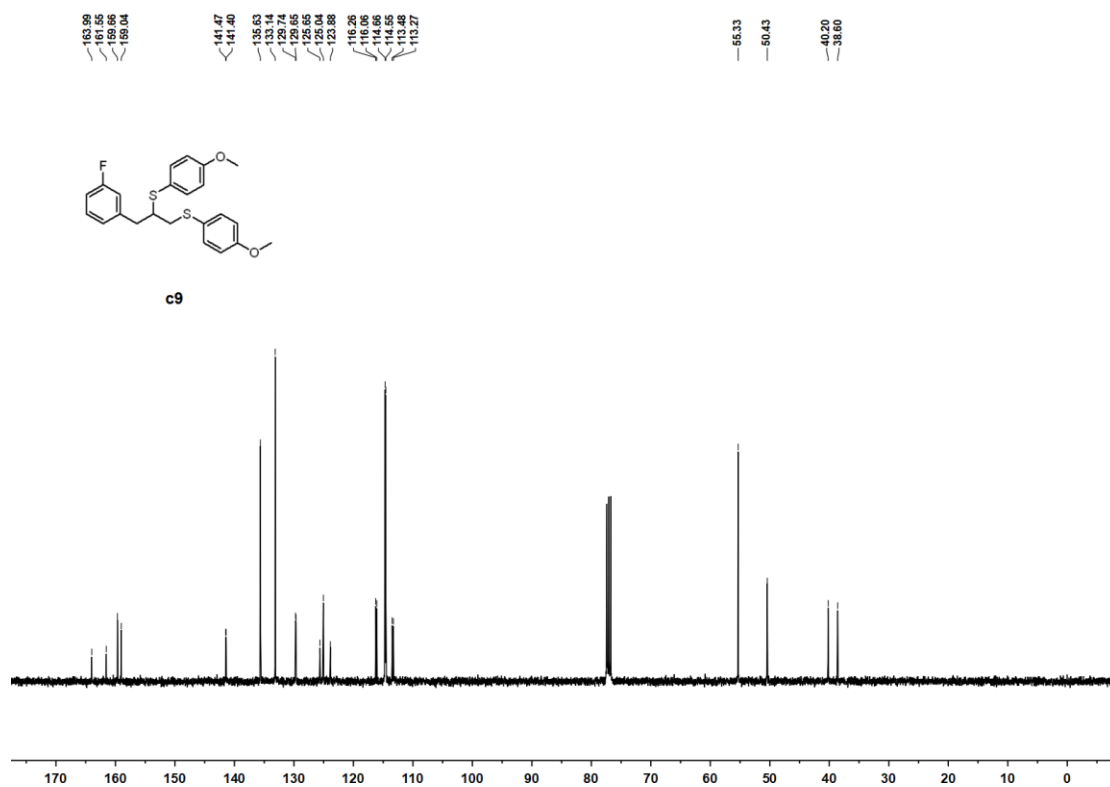
$^{19}\text{F}$  NMR spectra of compound **c8** in  $\text{CDCl}_3$  (376 MHz):



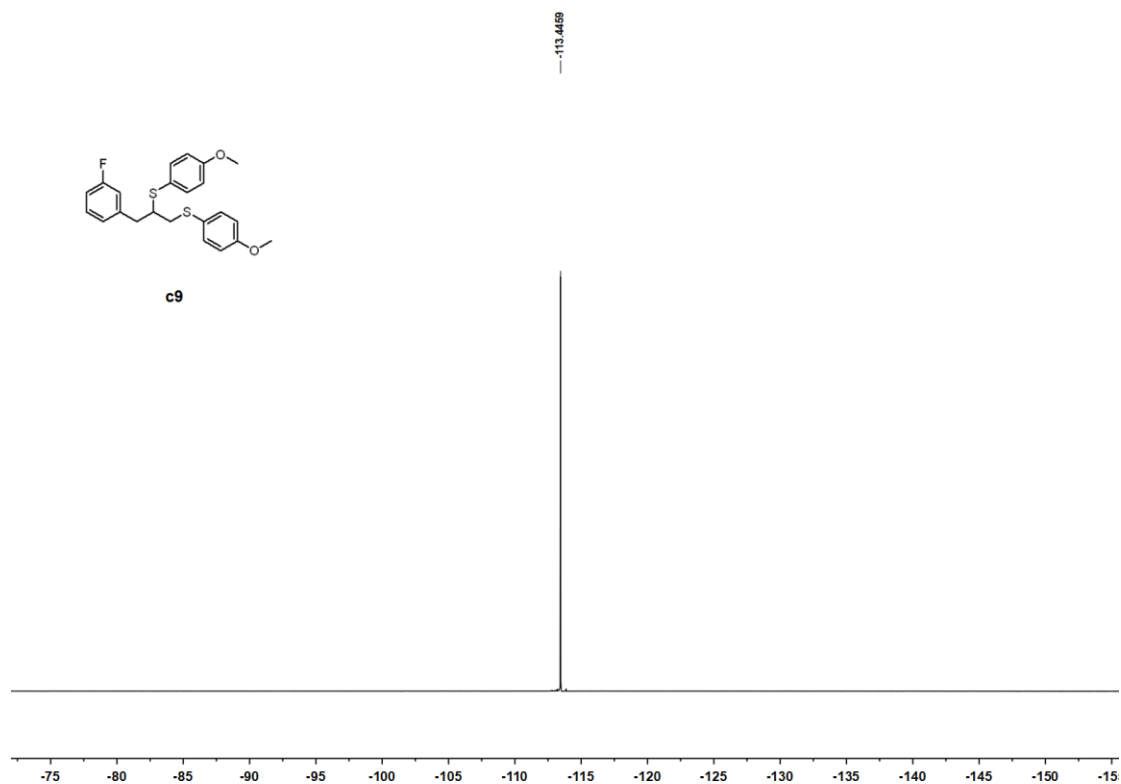
$^1\text{H}$  NMR spectra of compound **c9** in  $\text{CDCl}_3$  (400 MHz):



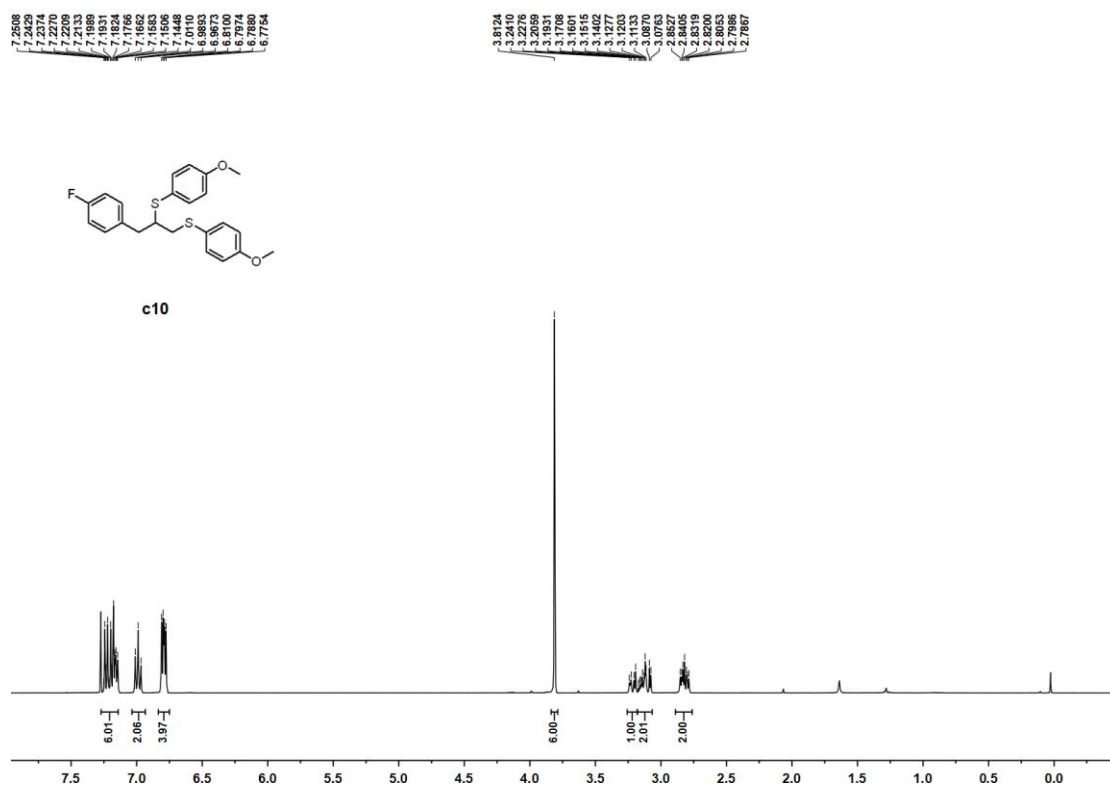
$^{13}\text{C}$  NMR spectra of compound **c9** in  $\text{CDCl}_3$  (101 MHz):



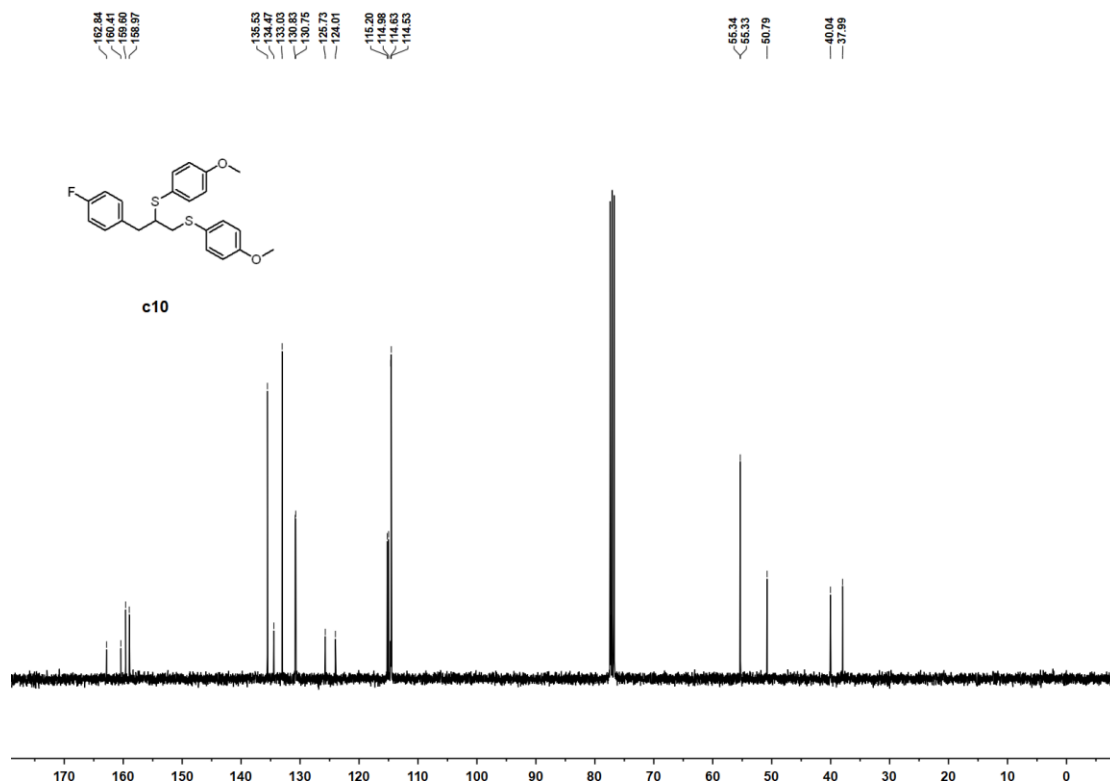
$^{19}\text{F}$  NMR spectra of compound **c9** in  $\text{CDCl}_3$  (376 MHz):



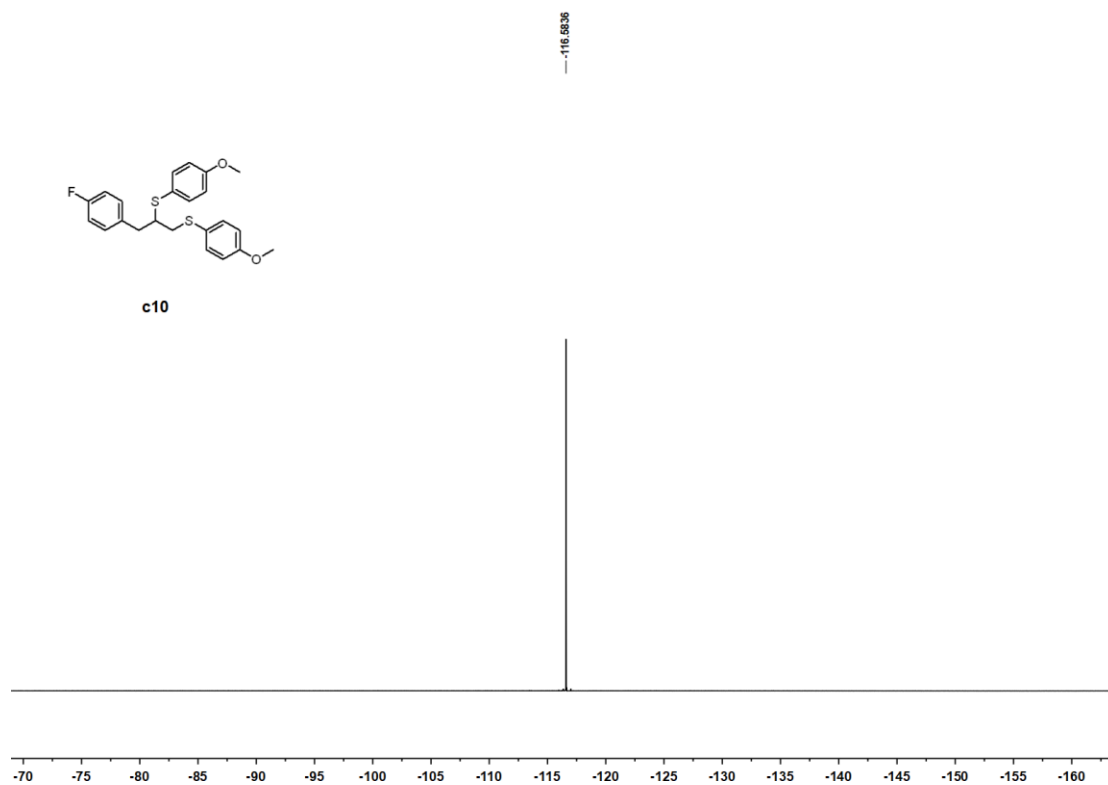
$^1\text{H}$  NMR spectra of compound **c10** in  $\text{CDCl}_3$  (400 MHz):



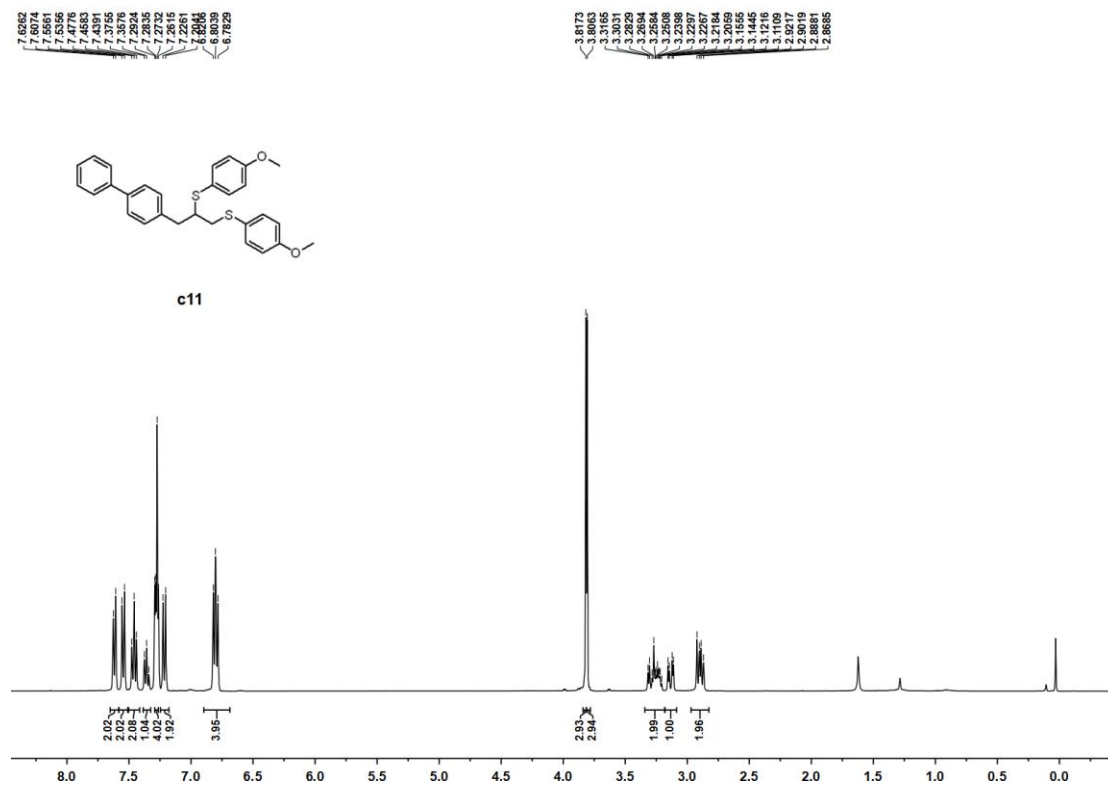
$^{13}\text{C}$  NMR spectra of compound **c10** in  $\text{CDCl}_3$  (101 MHz):



$^{19}\text{F}$  NMR spectra of compound **c10** in  $\text{CDCl}_3$  (376 MHz):

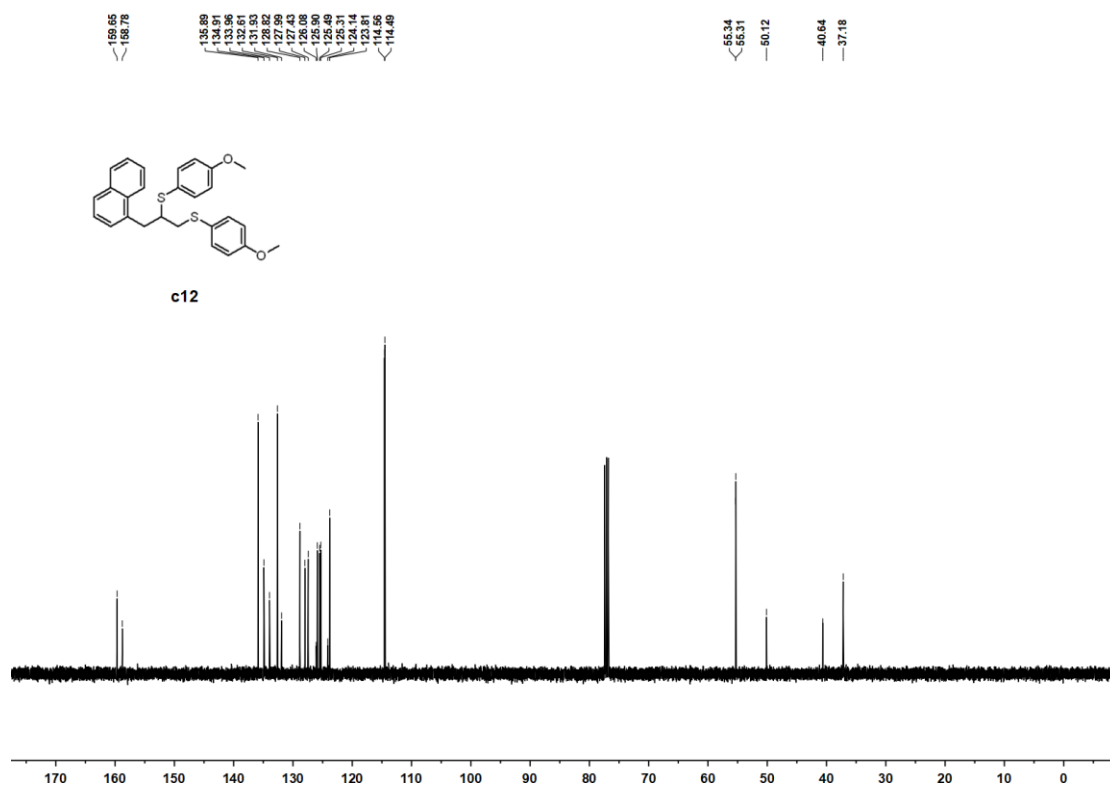


$^1\text{H}$  NMR spectra of compound **c11** in  $\text{CDCl}_3$  (400 MHz):

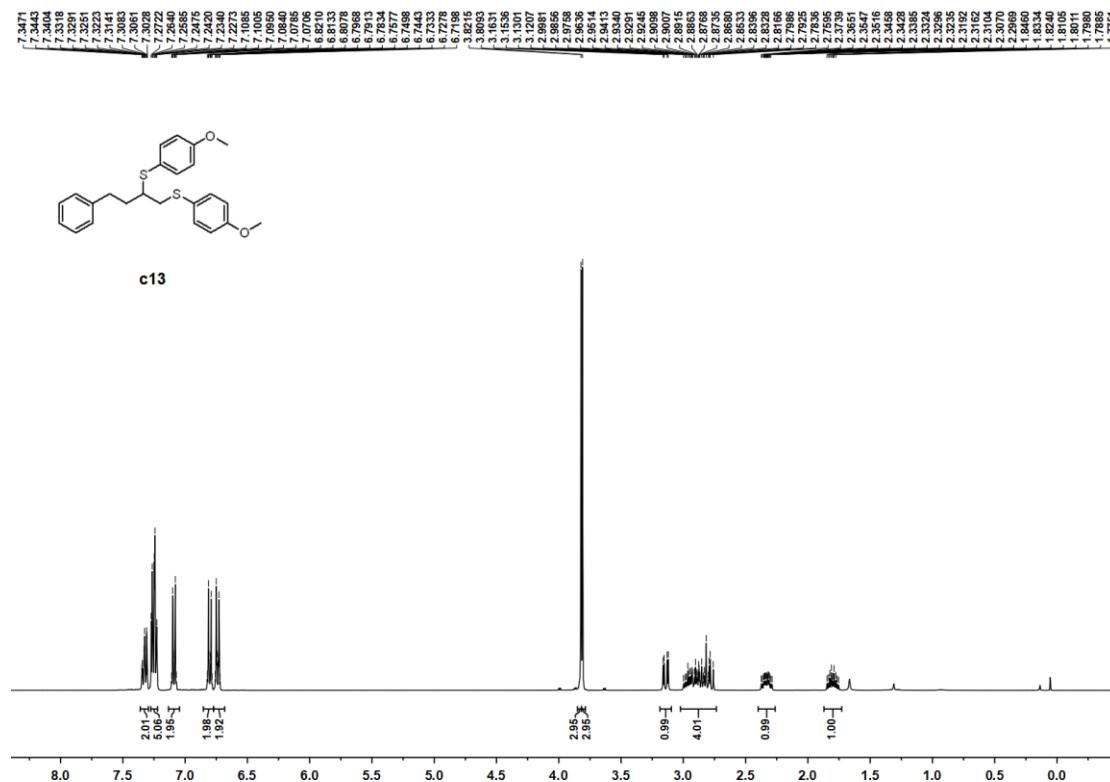




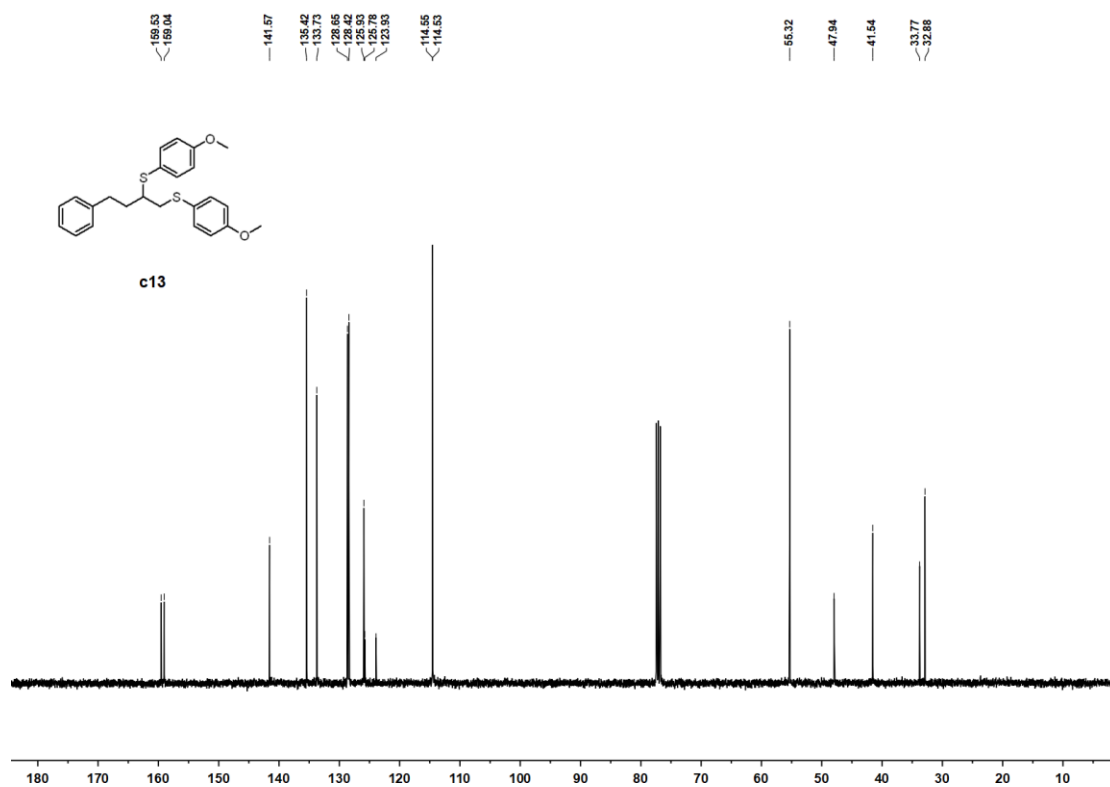
$^{13}\text{C}$  NMR spectra of compound **c12** in  $\text{CDCl}_3$  (101 MHz):



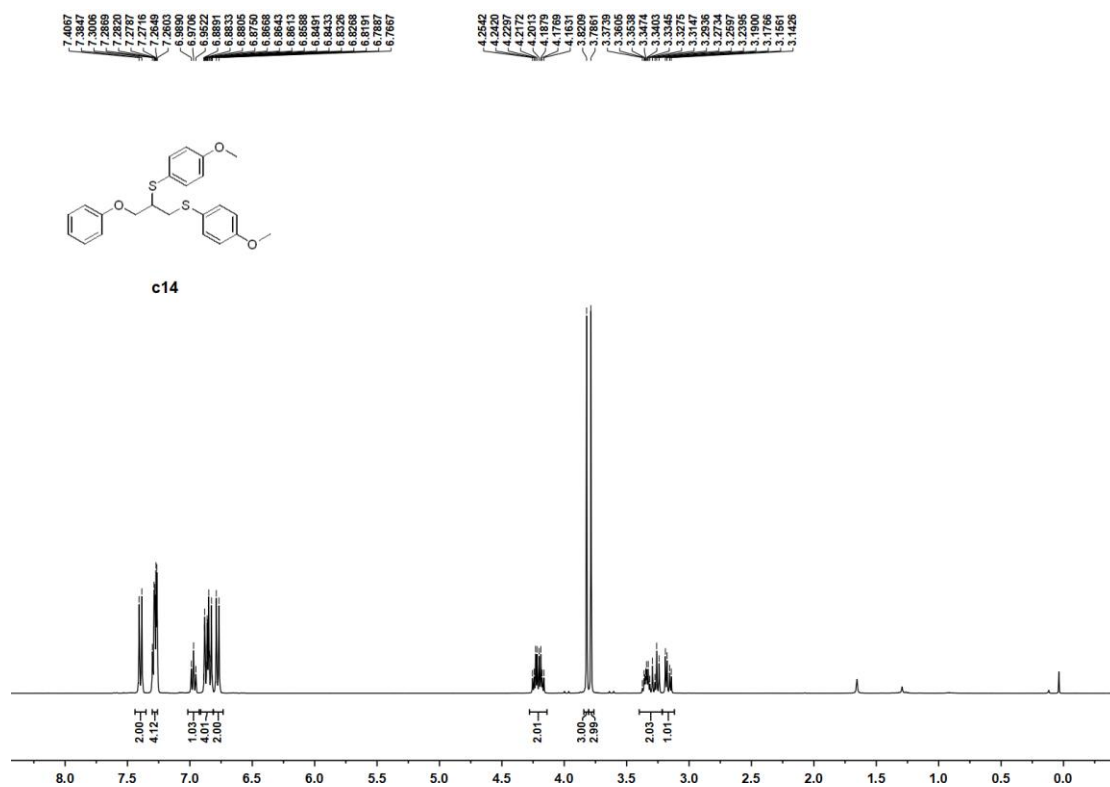
$^1\text{H}$  NMR spectra of compound **c13** in  $\text{CDCl}_3$  (400 MHz):



$^{13}\text{C}$  NMR spectra of compound **c13** in  $\text{CDCl}_3$  (101 MHz):

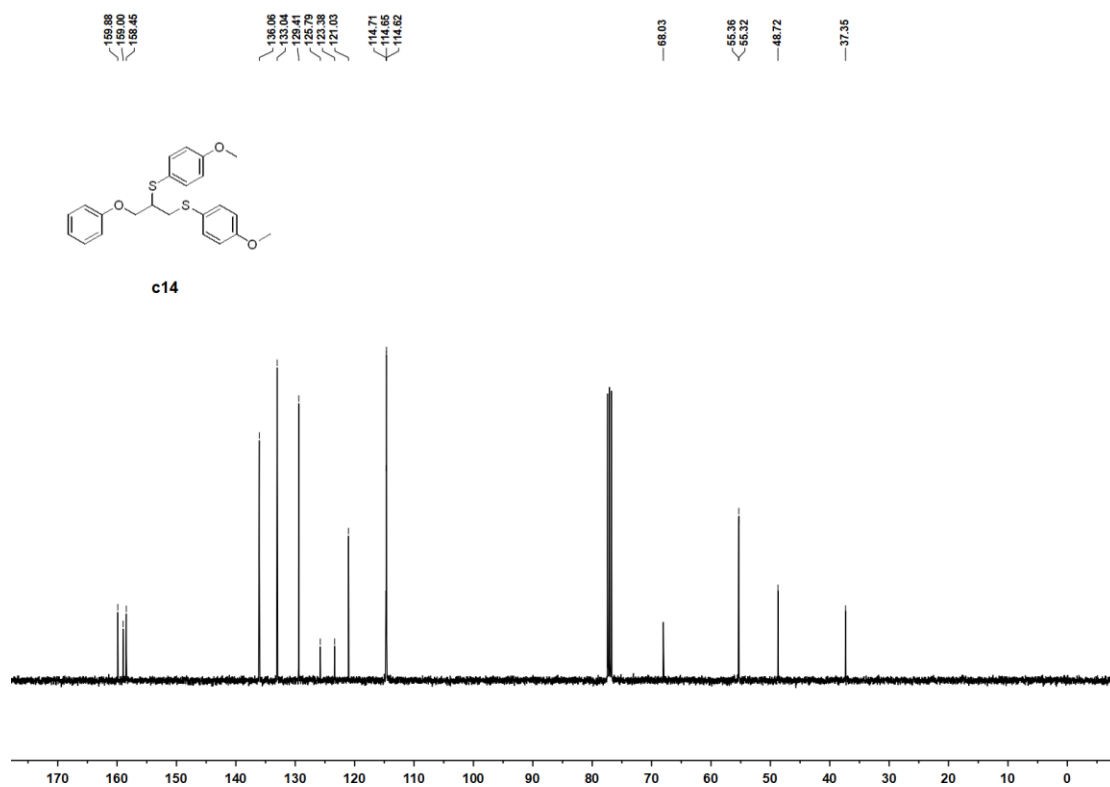


$^1\text{H}$  NMR spectra of compound **c14** in  $\text{CDCl}_3$  (400 MHz):

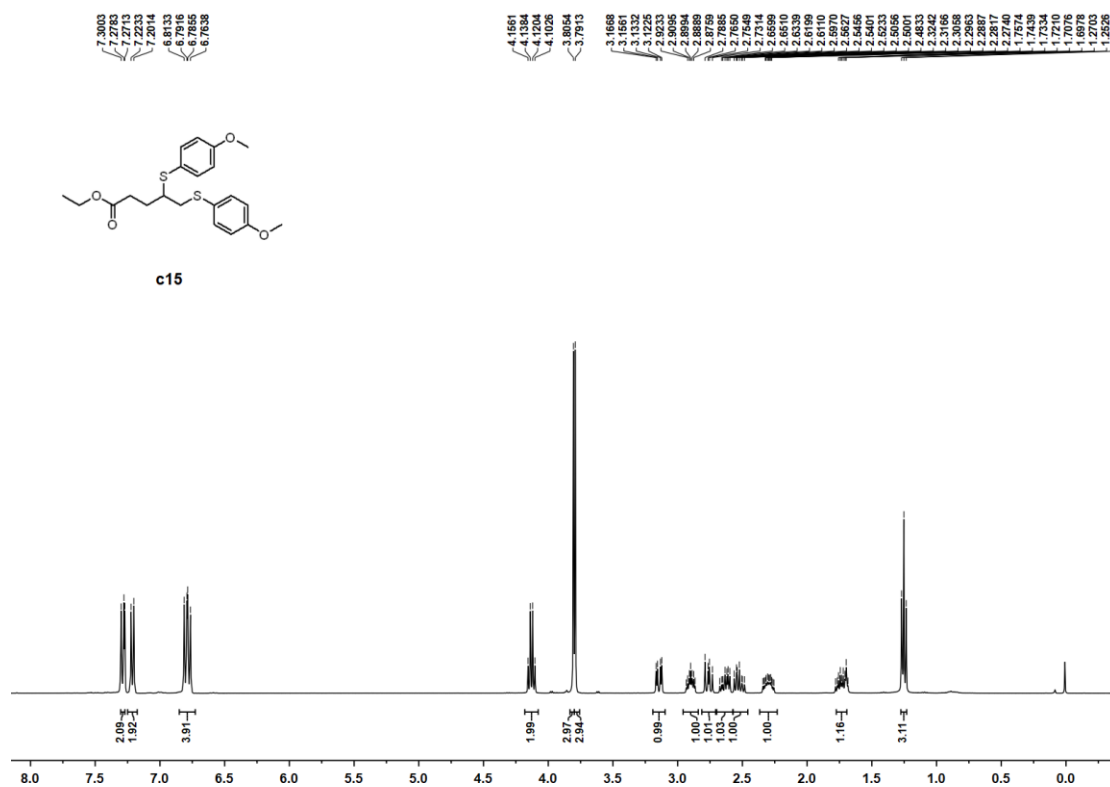




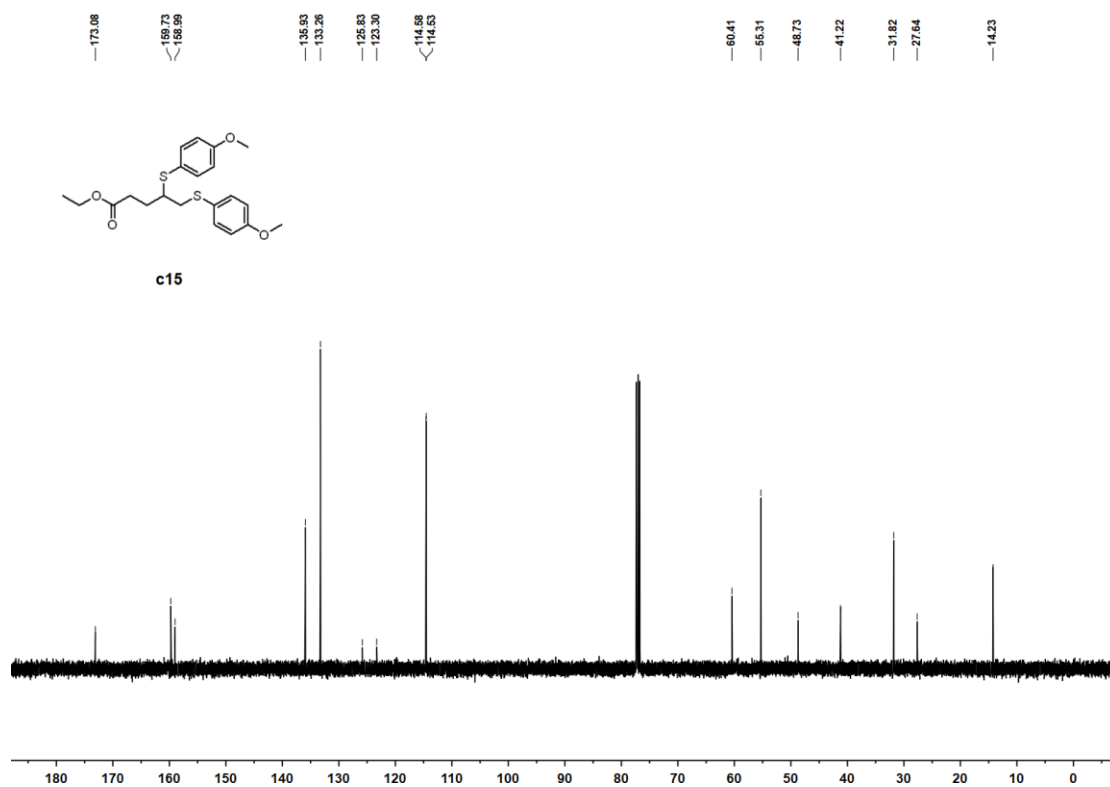
$^{13}\text{C}$  NMR spectra of compound **c14** in  $\text{CDCl}_3$  (101 MHz):



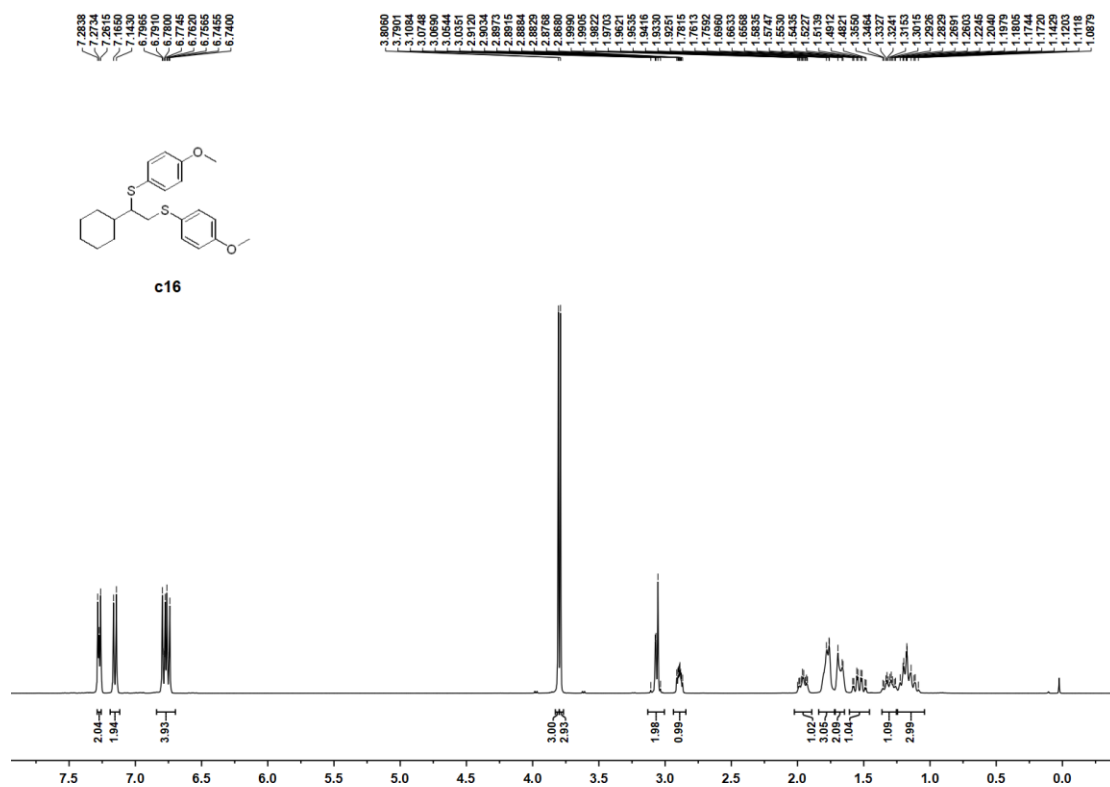
$^1\text{H}$  NMR spectra of compound **c15** in  $\text{CDCl}_3$  (400 MHz):



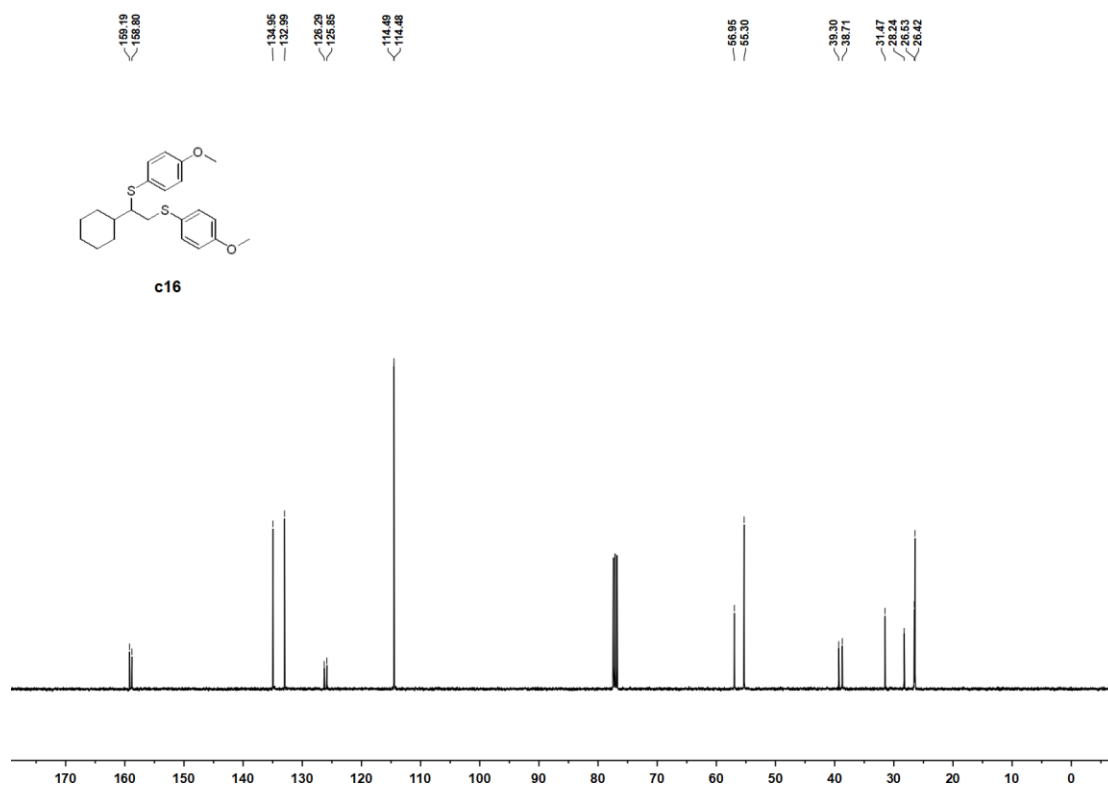
$^{13}\text{C}$  NMR spectra of compound **c15** in  $\text{CDCl}_3$  (101 MHz):



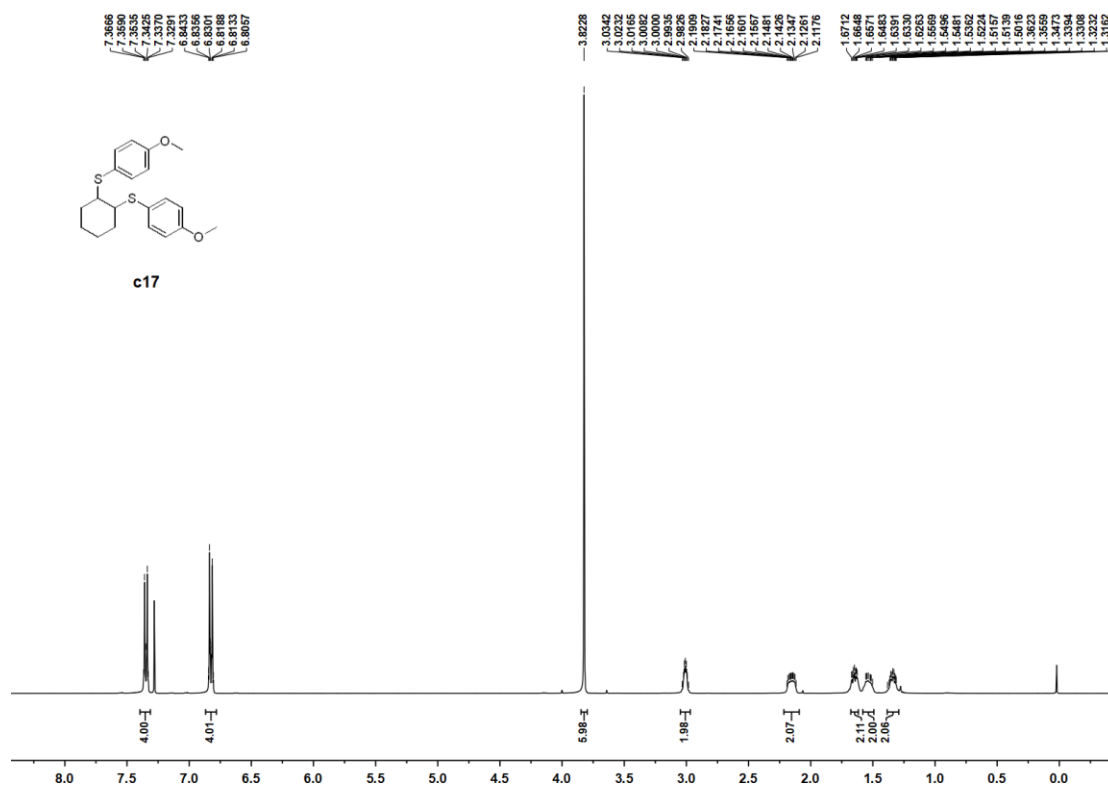
$^1\text{H}$  NMR spectra of compound **c16** in  $\text{CDCl}_3$  (400 MHz):



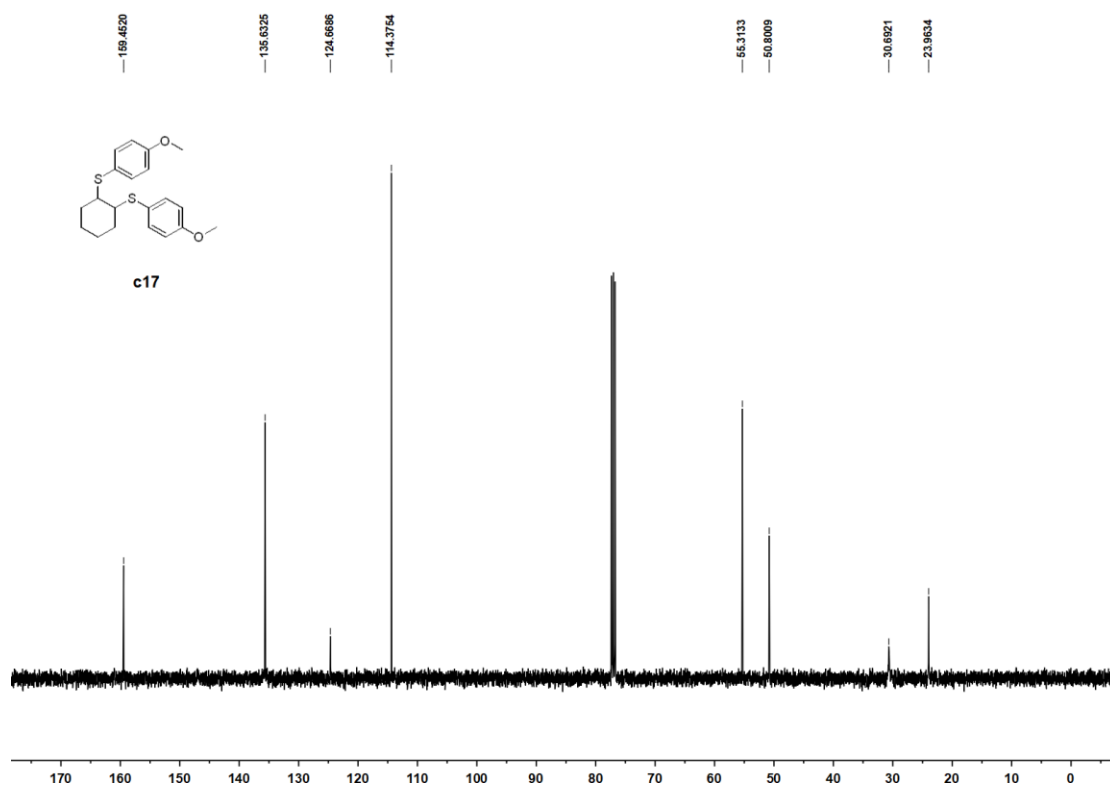
$^{13}\text{C}$  NMR spectra of compound **c16** in  $\text{CDCl}_3$  (101 MHz):



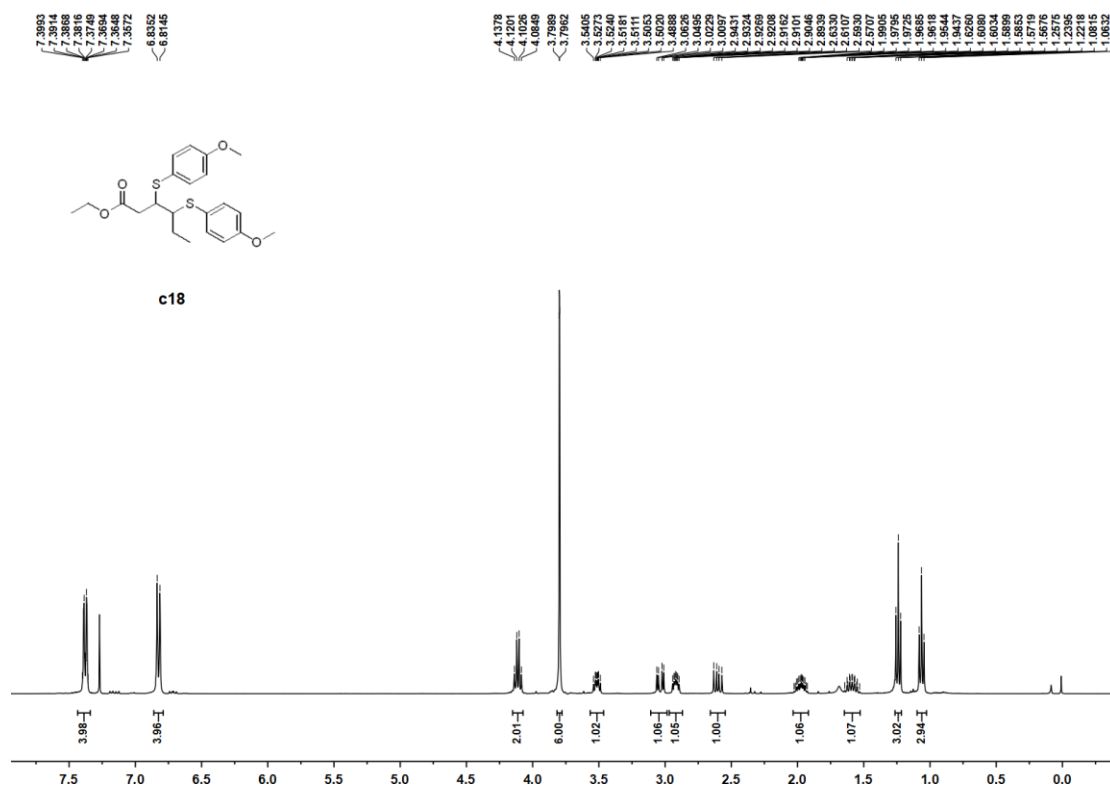
$^1\text{H}$  NMR spectra of compound **c17** in  $\text{CDCl}_3$  (400 MHz):



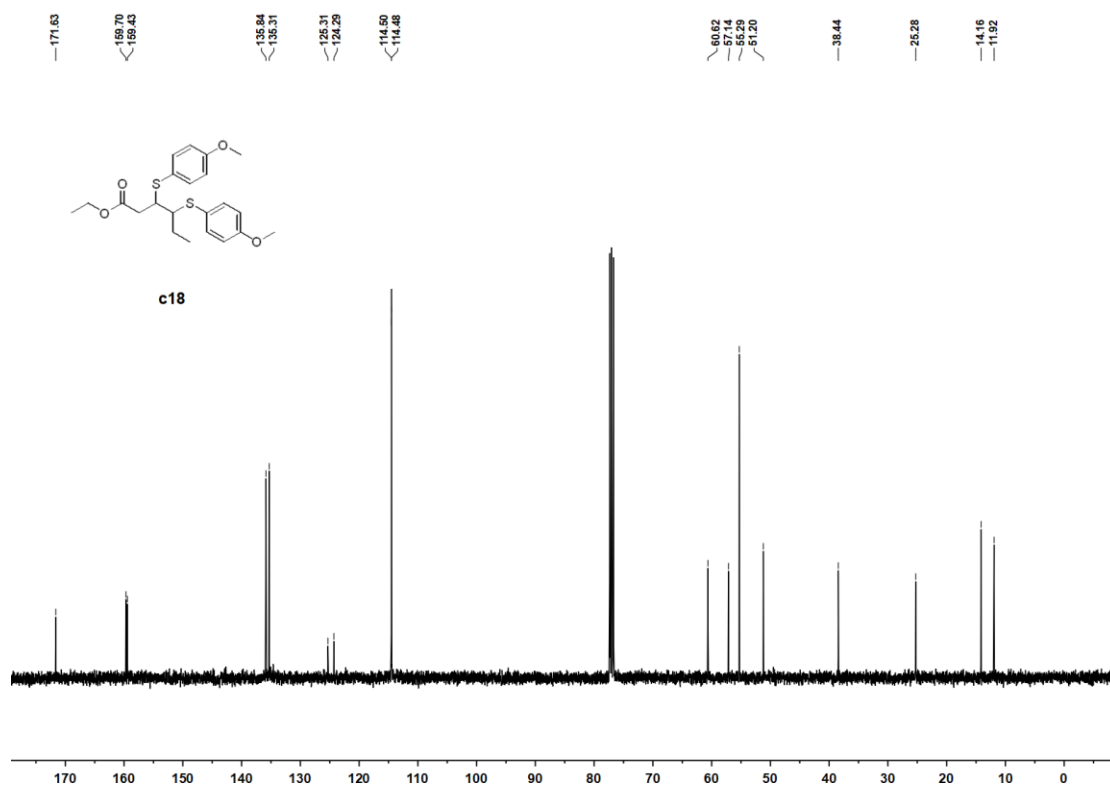
$^{13}\text{C}$  NMR spectra of compound **c17** in  $\text{CDCl}_3$  (101 MHz):



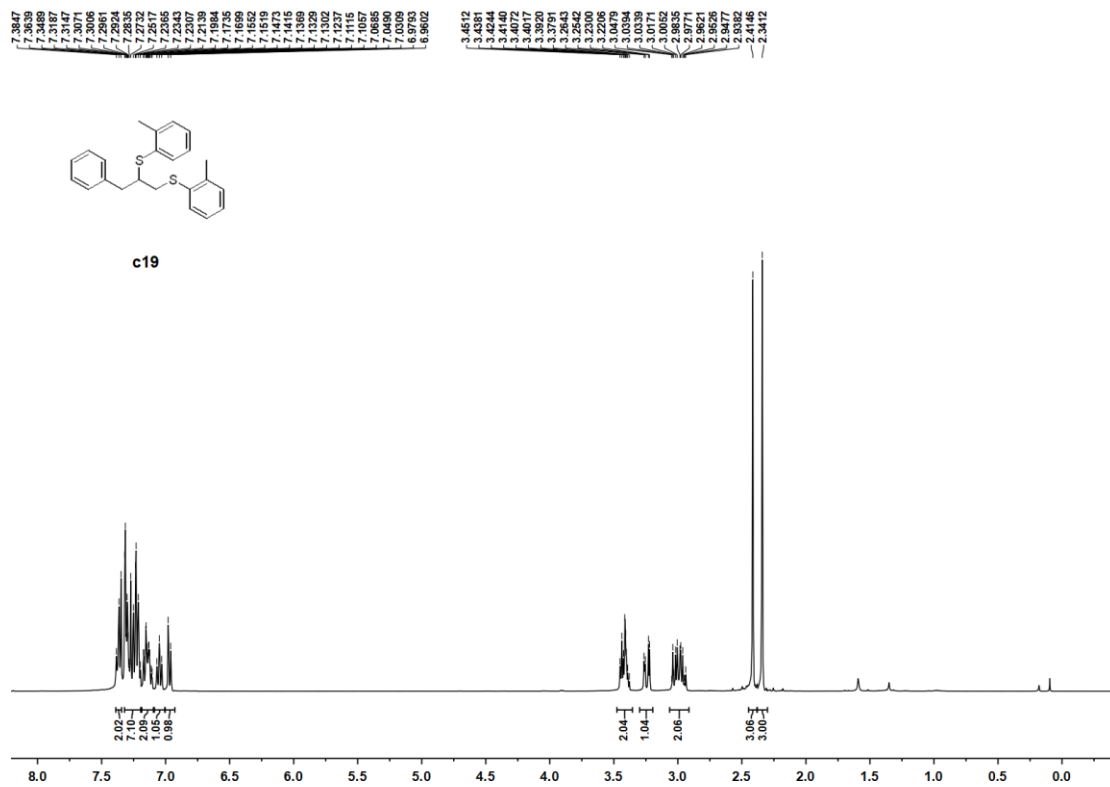
$^1\text{H}$  NMR spectra of compound **c18** in  $\text{CDCl}_3$  (400 MHz):



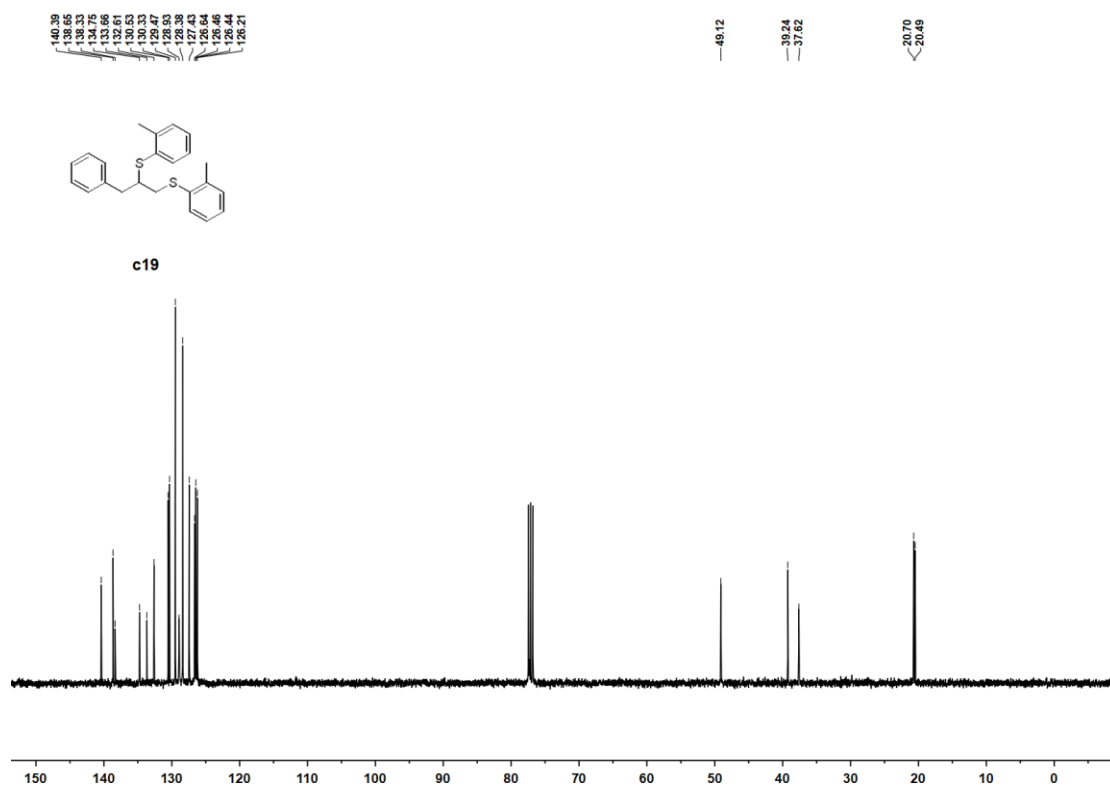
$^{13}\text{C}$  NMR spectra of compound **c18** in  $\text{CDCl}_3$  (101 MHz):



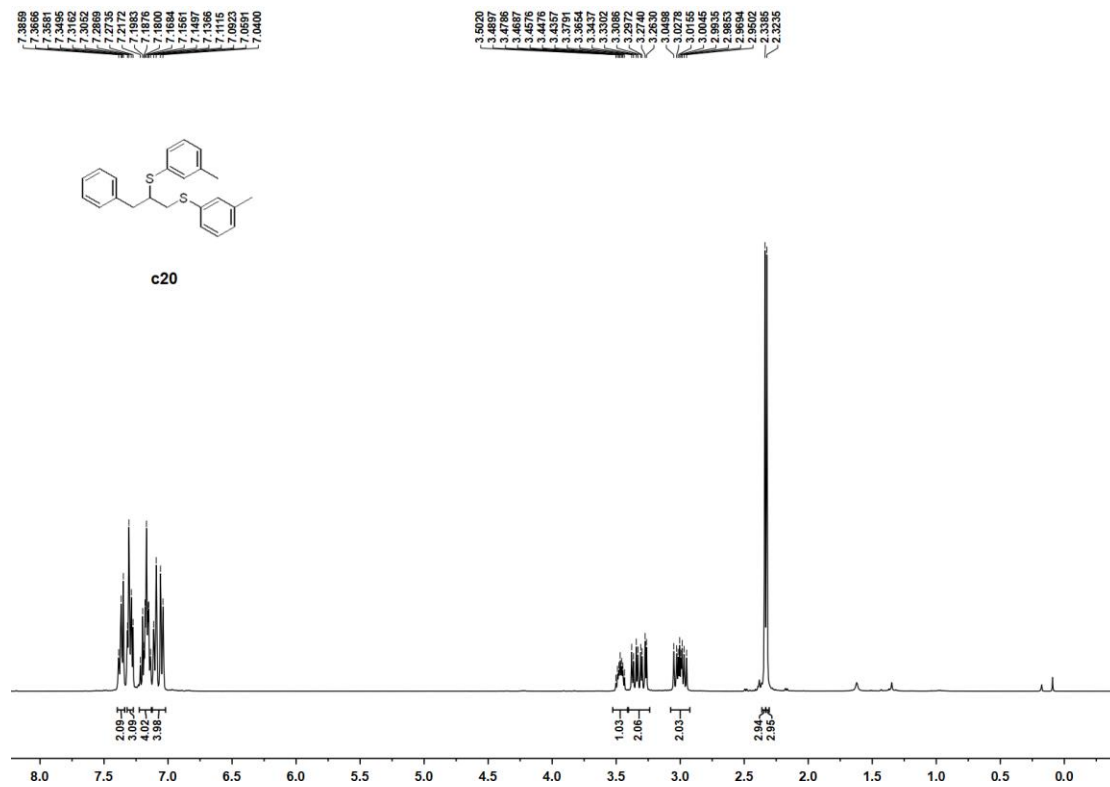
$^1\text{H}$  NMR spectra of compound **c19** in  $\text{CDCl}_3$  (400 MHz):



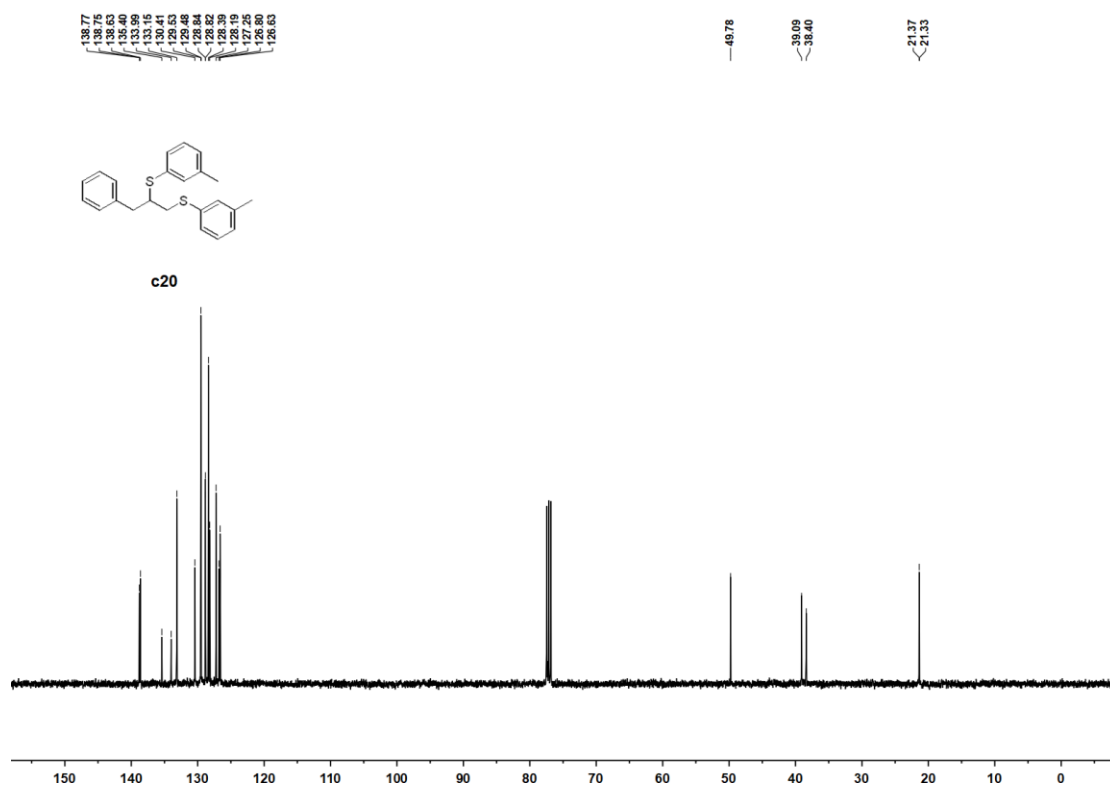
$^{13}\text{C}$  NMR spectra of compound **c19** in  $\text{CDCl}_3$  (101 MHz):



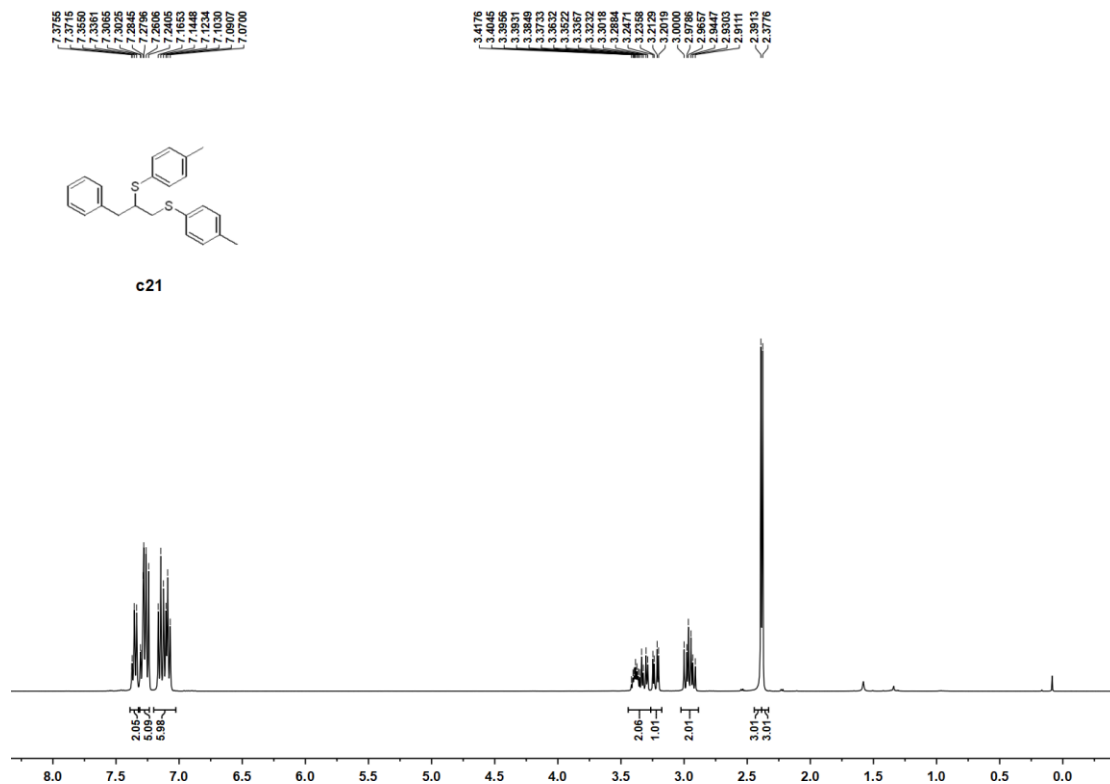
$^1\text{H}$  NMR spectra of compound **c20** in  $\text{CDCl}_3$  (400 MHz):



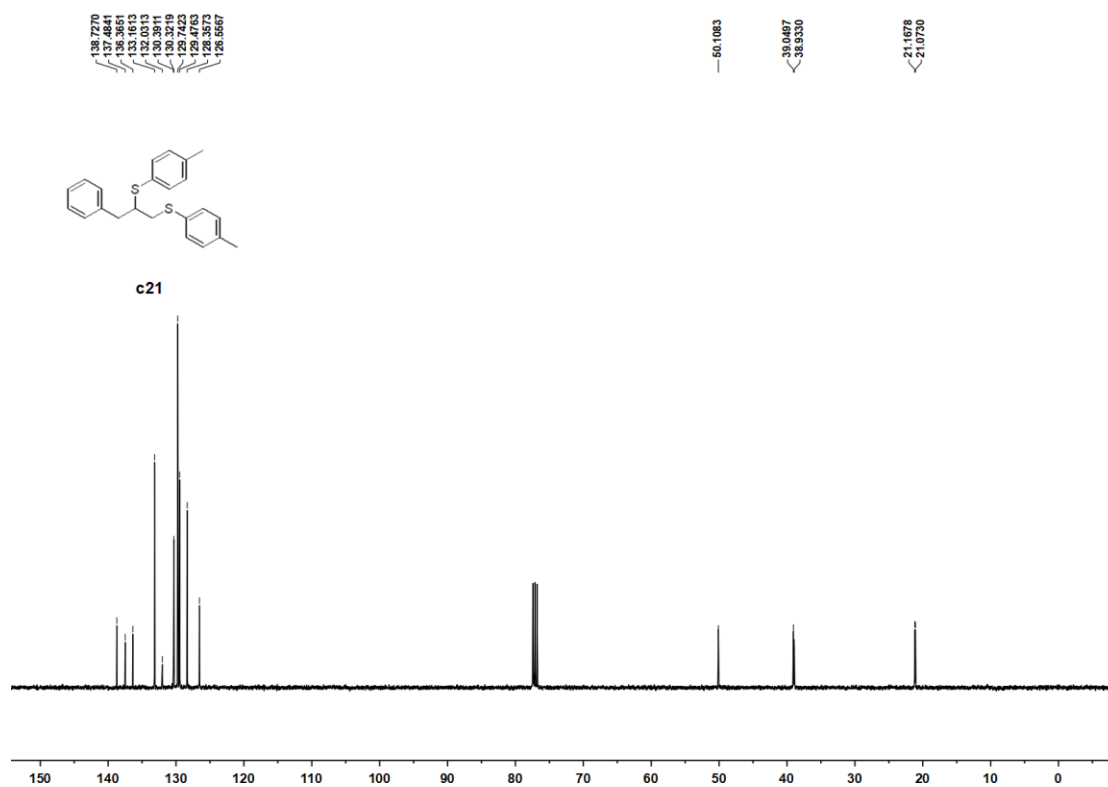
$^{13}\text{C}$  NMR spectra of compound **c20** in  $\text{CDCl}_3$  (101 MHz):



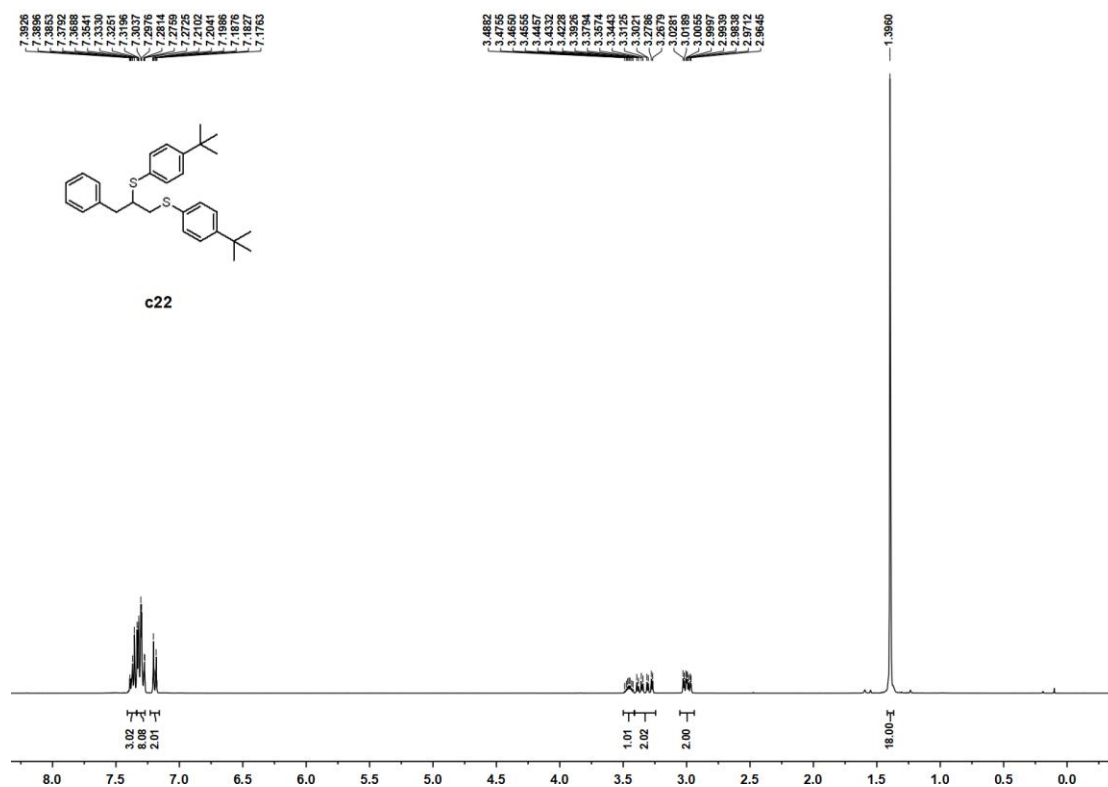
$^1\text{H}$  NMR spectra of compound **c21** in  $\text{CDCl}_3$  (400 MHz):



$^{13}\text{C}$  NMR spectra of compound **c21** in  $\text{CDCl}_3$  (101 MHz):

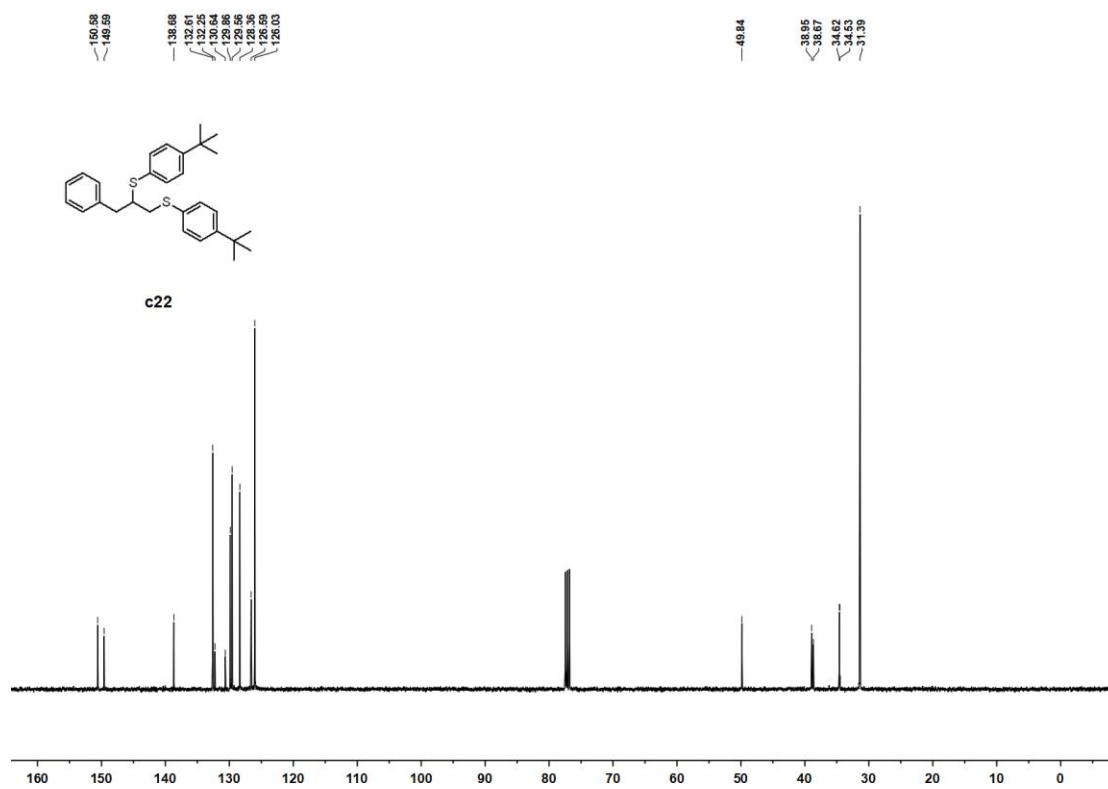


$^1\text{H}$  NMR spectra of compound **c22** in  $\text{CDCl}_3$  (400 MHz):

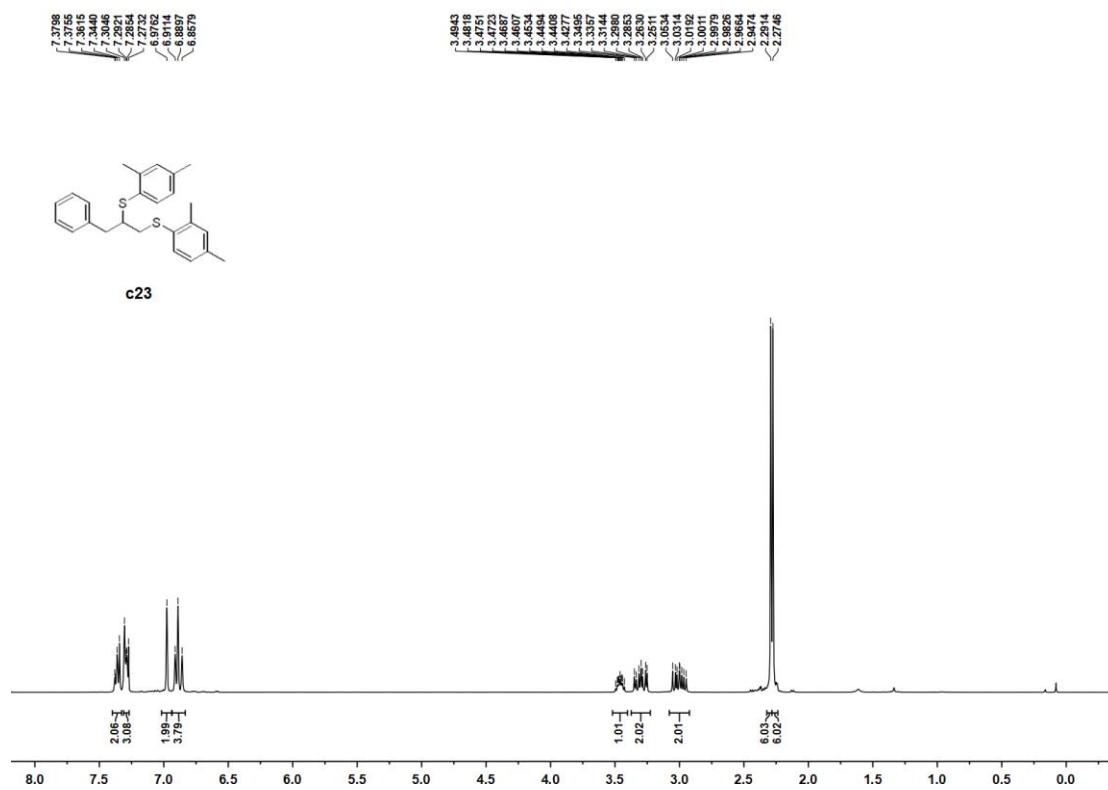




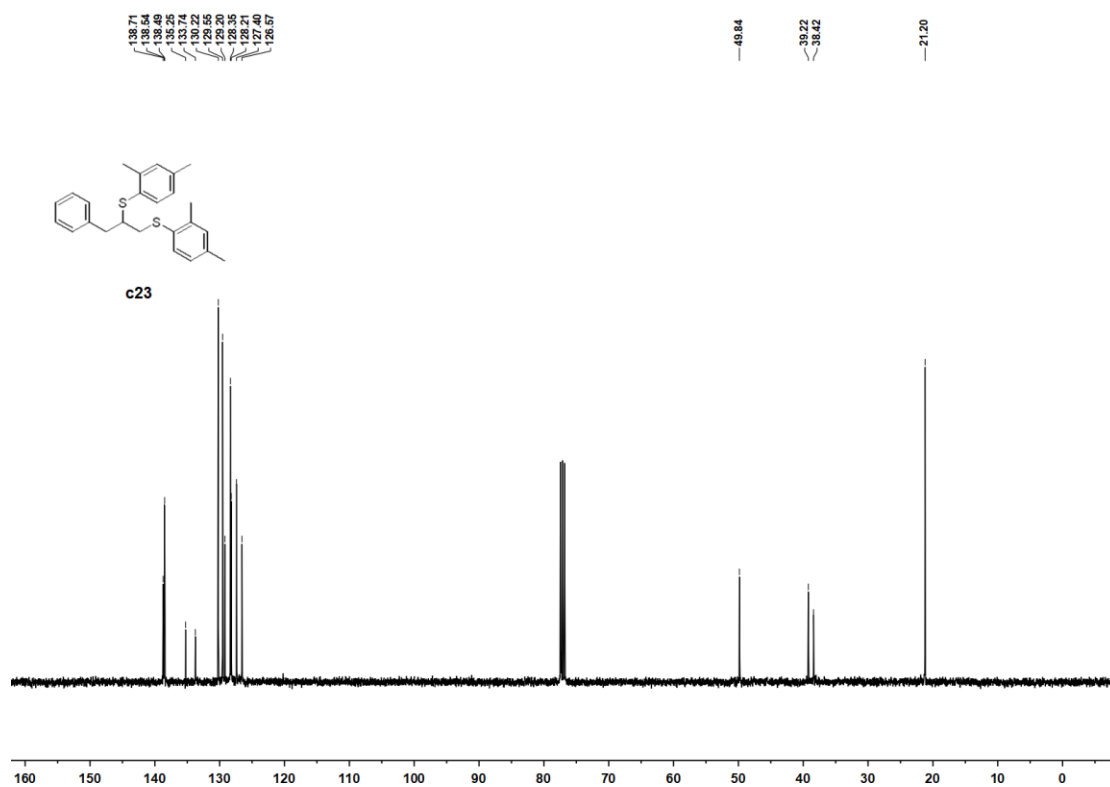
$^{13}\text{C}$  NMR spectra of compound **c22** in  $\text{CDCl}_3$  (101 MHz):



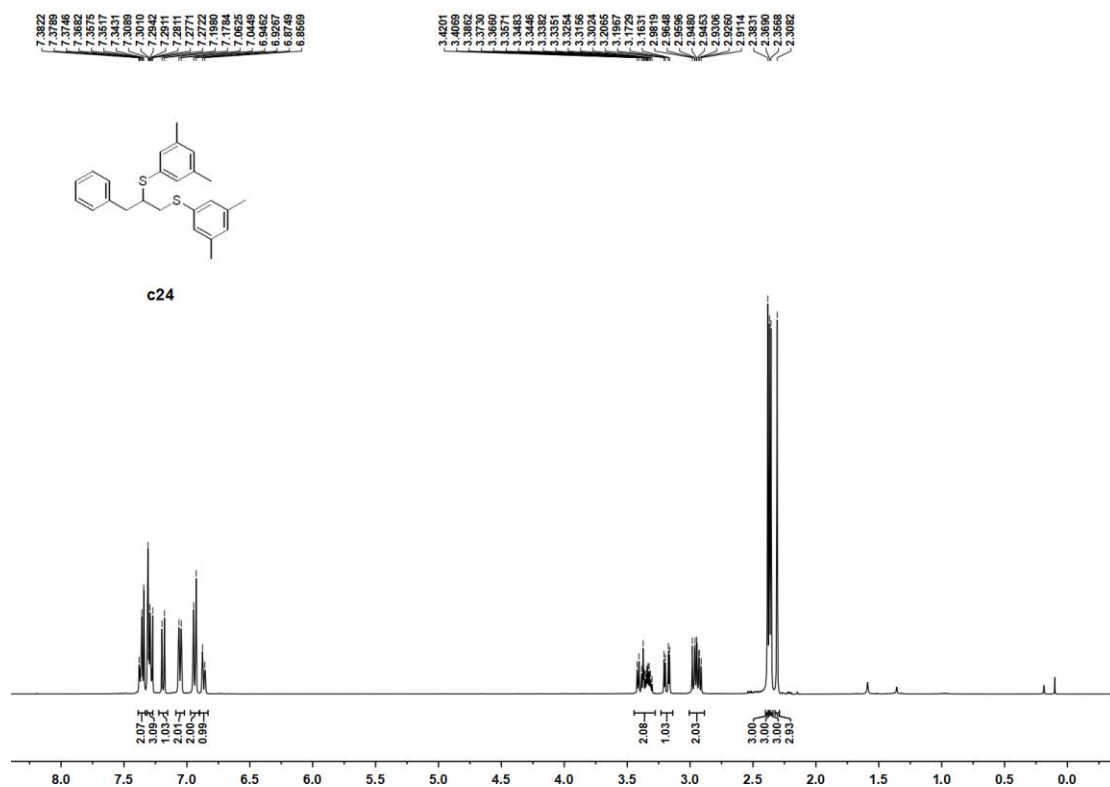
$^1\text{H}$  NMR spectra of compound **c23** in  $\text{CDCl}_3$  (400 MHz):



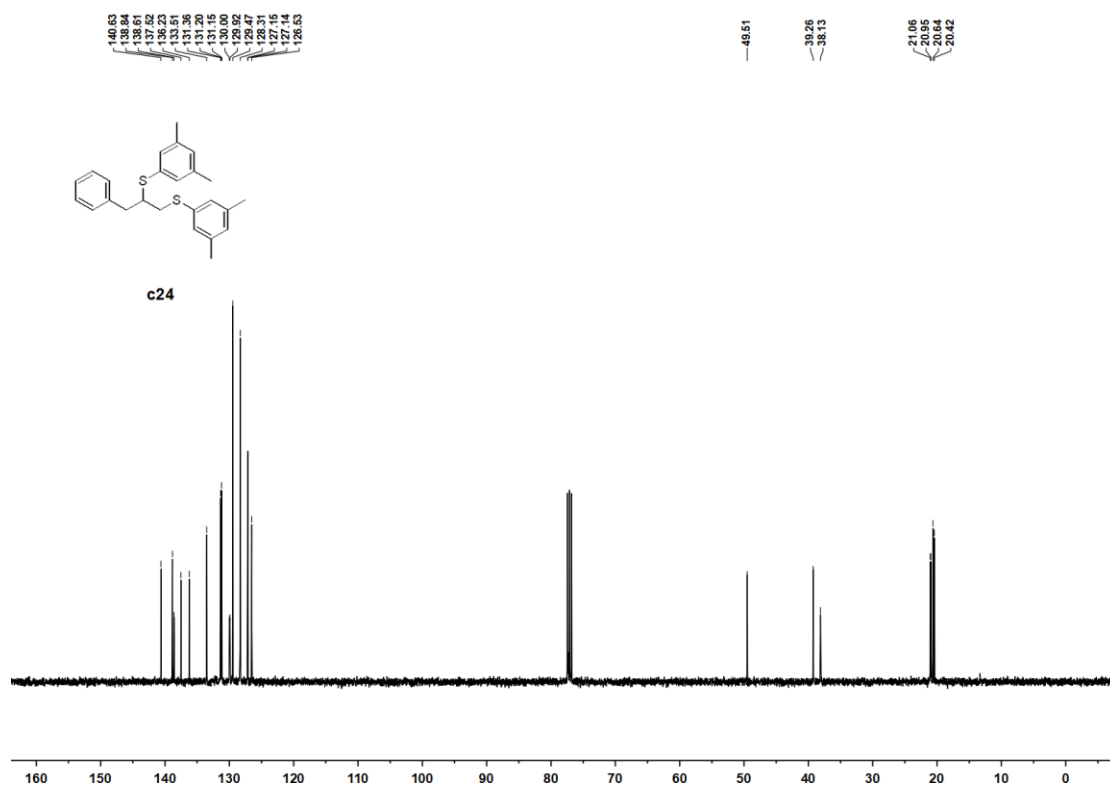
$^{13}\text{C}$  NMR spectra of compound **c23** in  $\text{CDCl}_3$  (101 MHz):



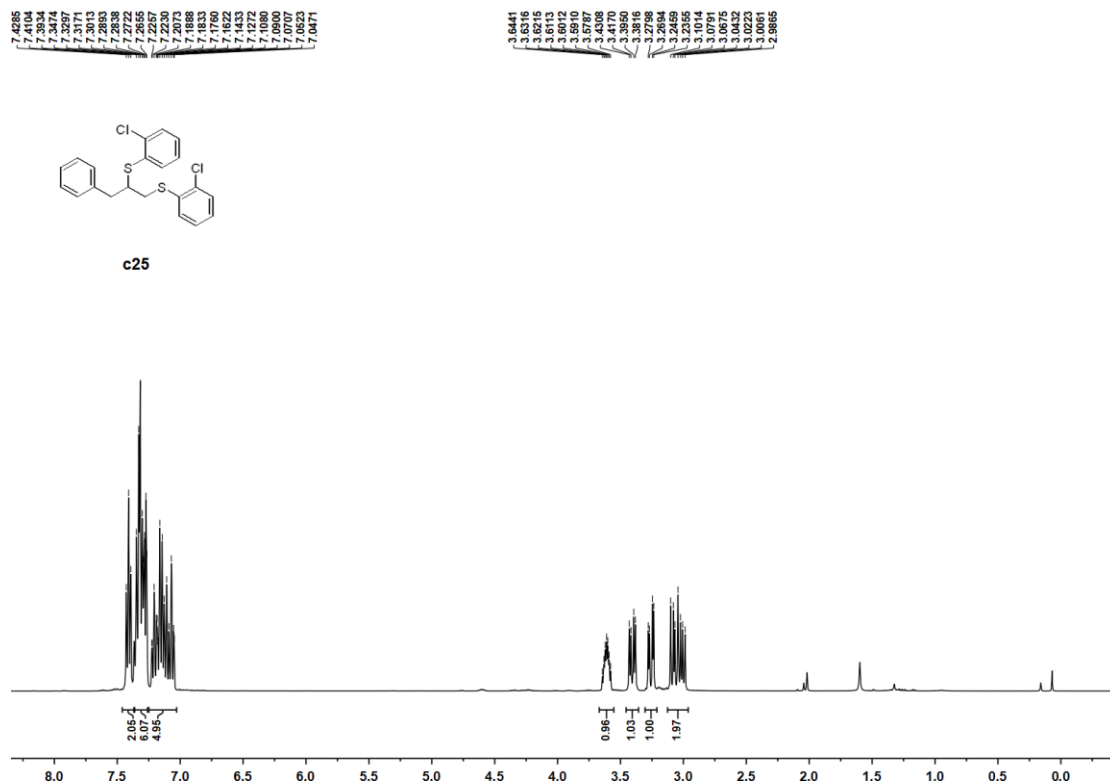
$^1\text{H}$  NMR spectra of compound **c24** in  $\text{CDCl}_3$  (400 MHz):



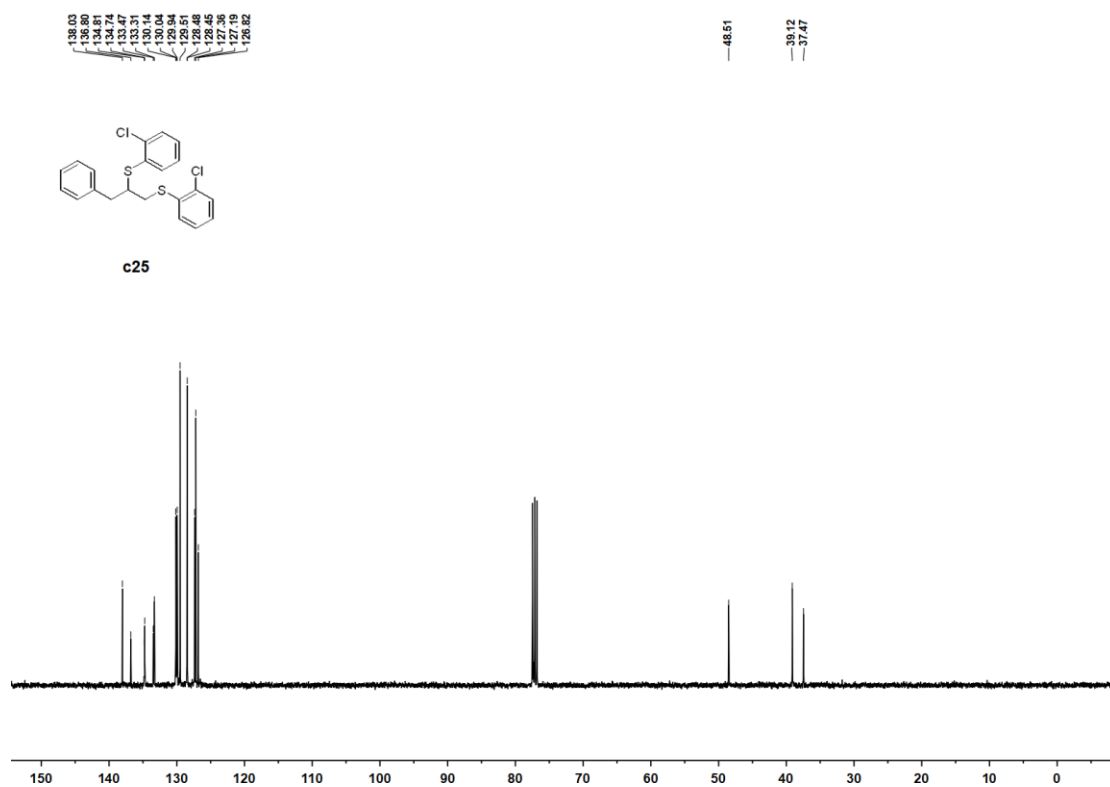
$^{13}\text{C}$  NMR spectra of compound **c24** in  $\text{CDCl}_3$  (101 MHz):



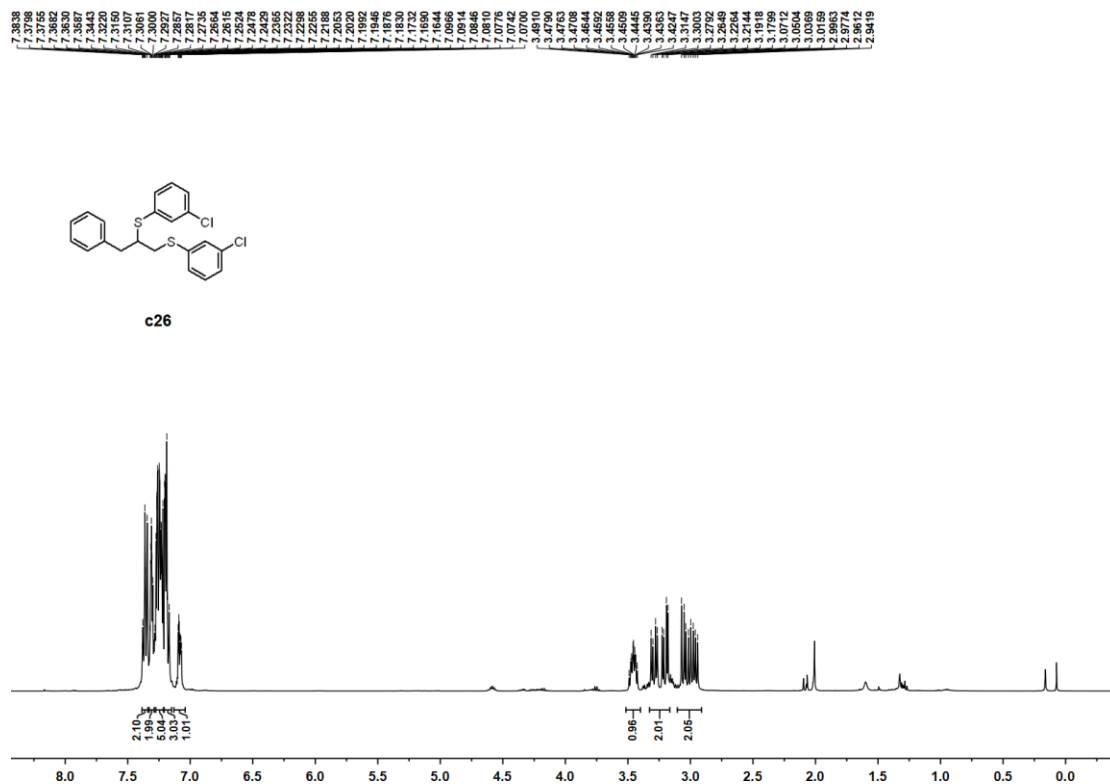
$^1\text{H}$  NMR spectra of compound **c25** in  $\text{CDCl}_3$  (400 MHz):



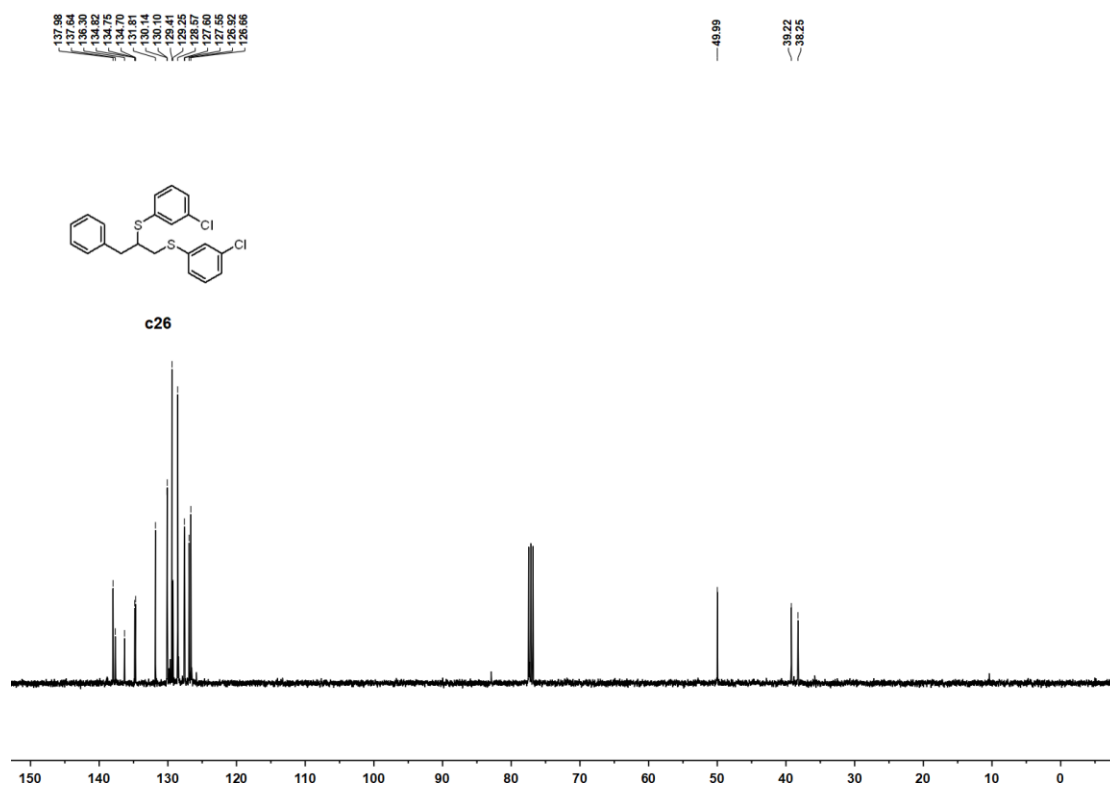
$^{13}\text{C}$  NMR spectra of compound **c25** in  $\text{CDCl}_3$  (101 MHz):



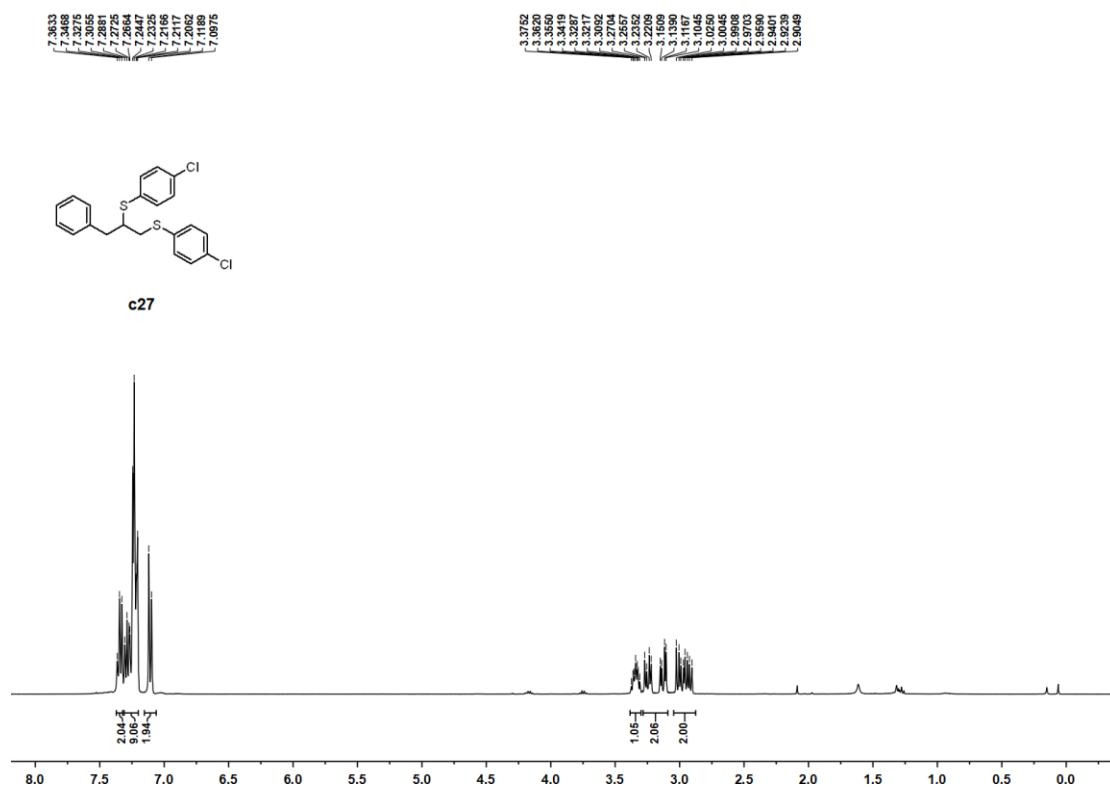
$^1\text{H}$  NMR spectra of compound **c26** in  $\text{CDCl}_3$  (400 MHz):



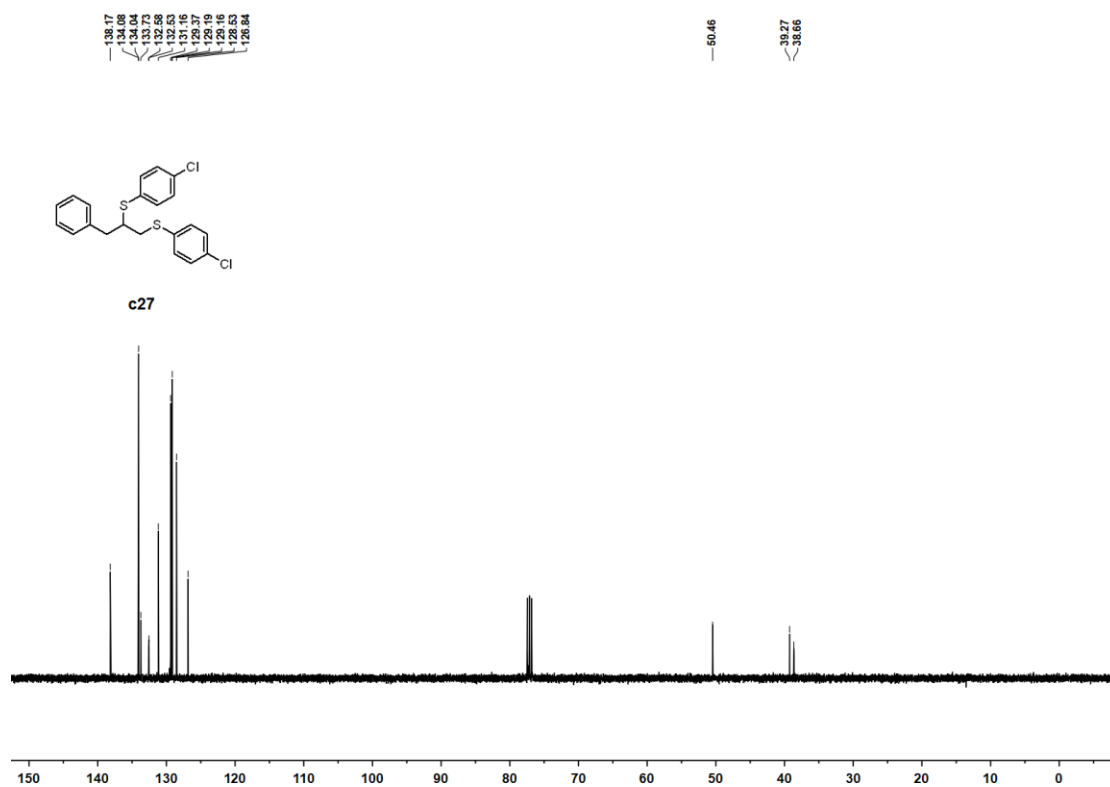
$^{13}\text{C}$  NMR spectra of compound **c26** in  $\text{CDCl}_3$  (101 MHz):



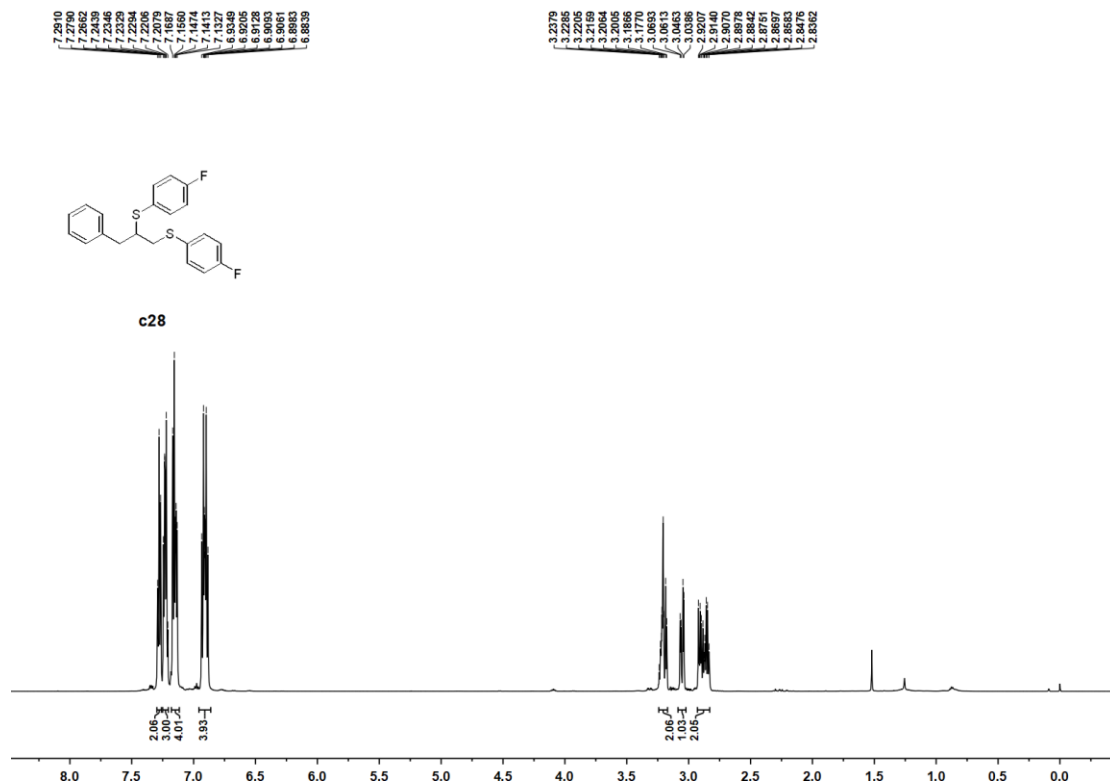
$^1\text{H}$  NMR spectra of compound **c27** in  $\text{CDCl}_3$  (400 MHz):



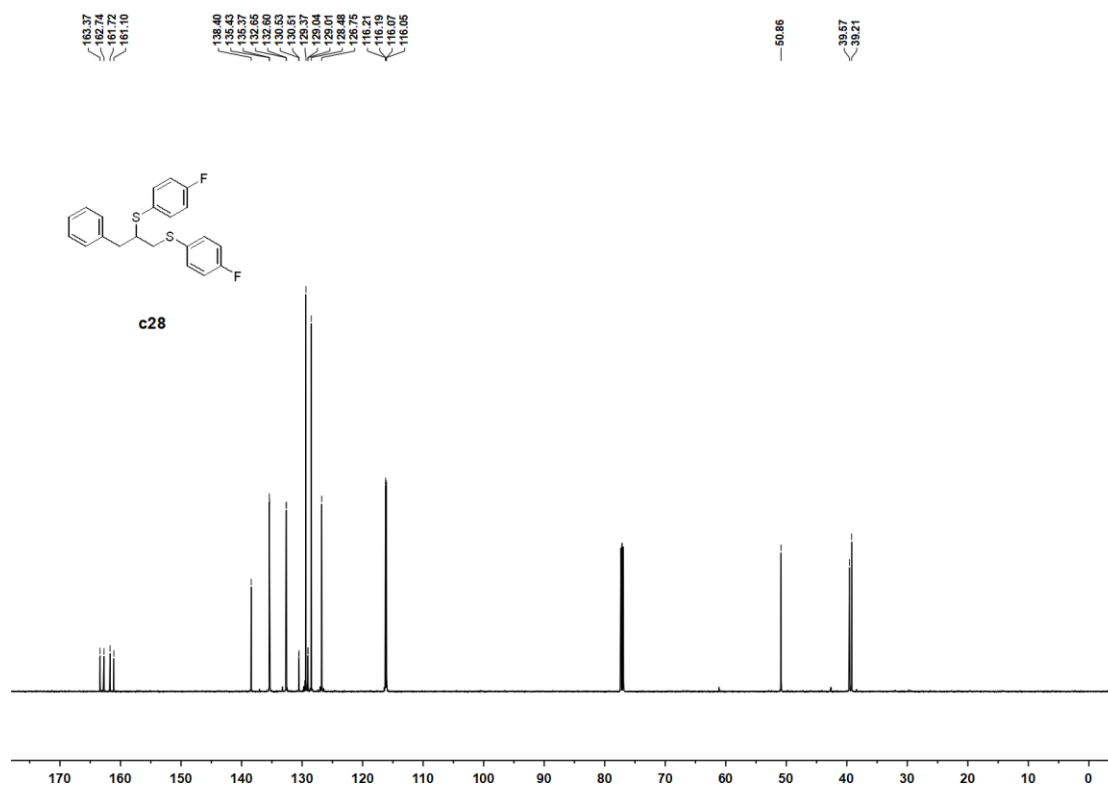
$^{13}\text{C}$  NMR spectra of compound **c27** in  $\text{CDCl}_3$  (101 MHz):



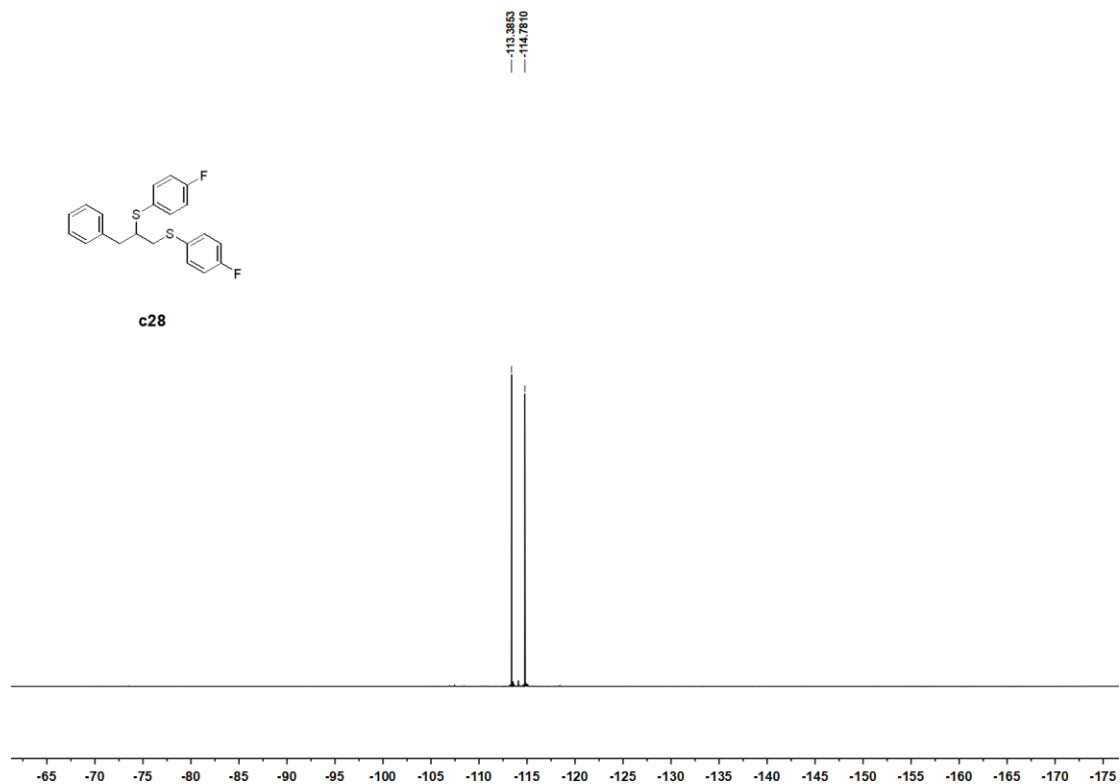
$^1\text{H}$  NMR spectra of compound **c28** in  $\text{CDCl}_3$  (600 MHz):



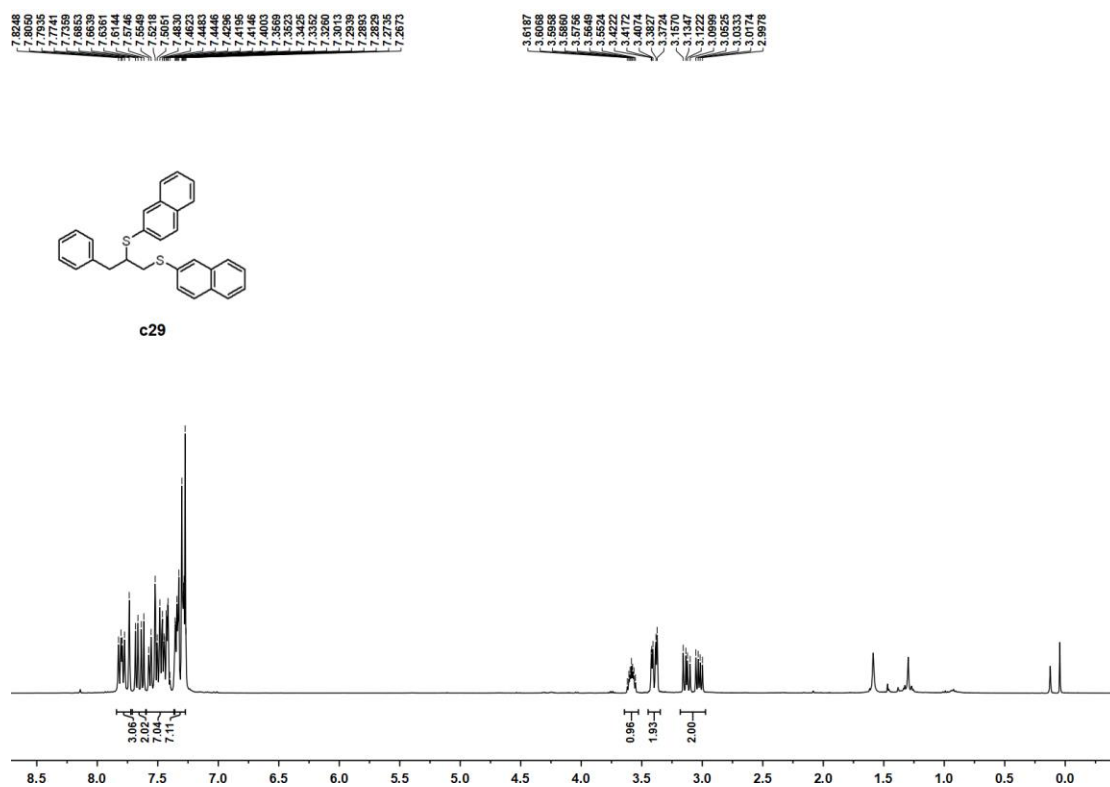
$^{13}\text{C}$  NMR spectra of compound **c28** in  $\text{CDCl}_3$  (151 MHz):



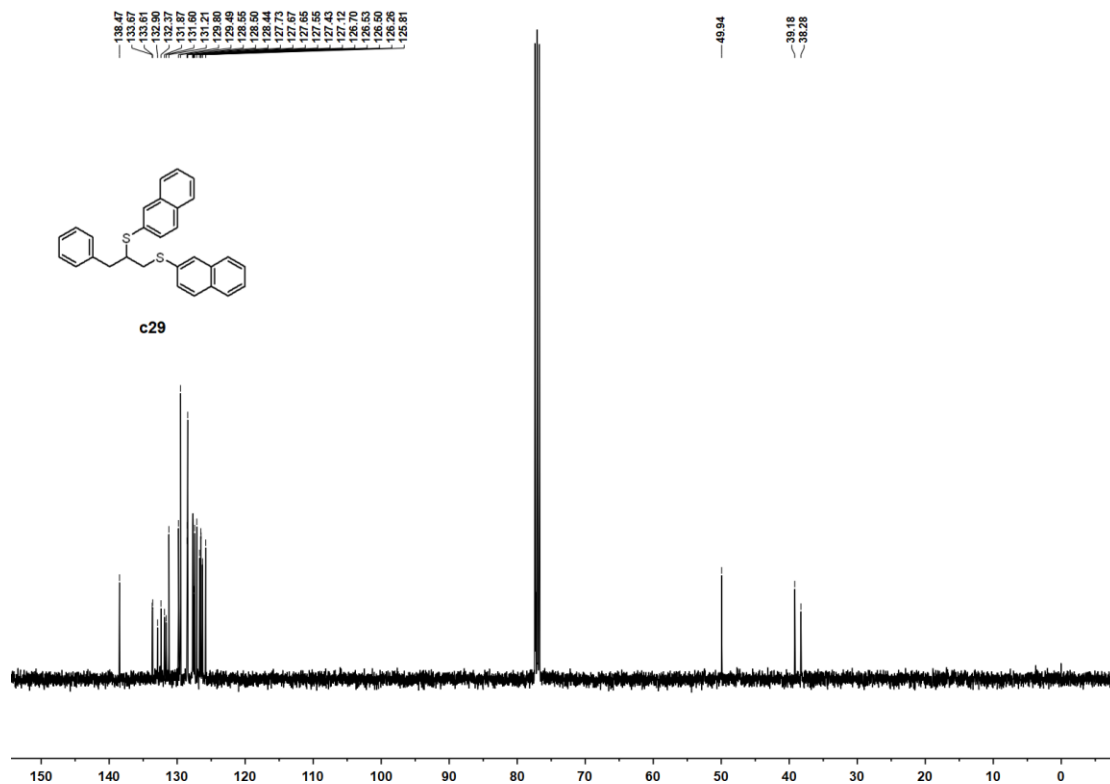
$^{19}\text{F}$  NMR spectra of compound **c28** in  $\text{CDCl}_3$  (565 MHz):



$^1\text{H}$  NMR spectra of compound **c29** in  $\text{CDCl}_3$  (400 MHz):

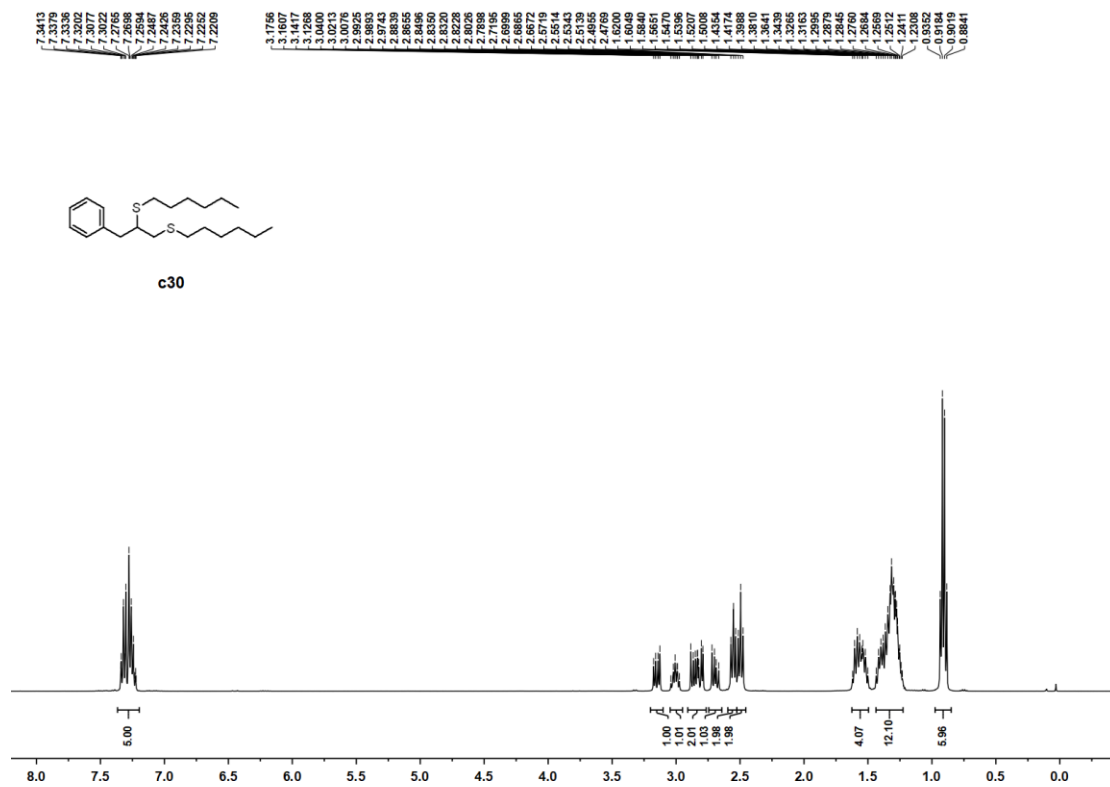


$^{13}\text{C}$  NMR spectra of compound **c29** in  $\text{CDCl}_3$  (101 MHz):

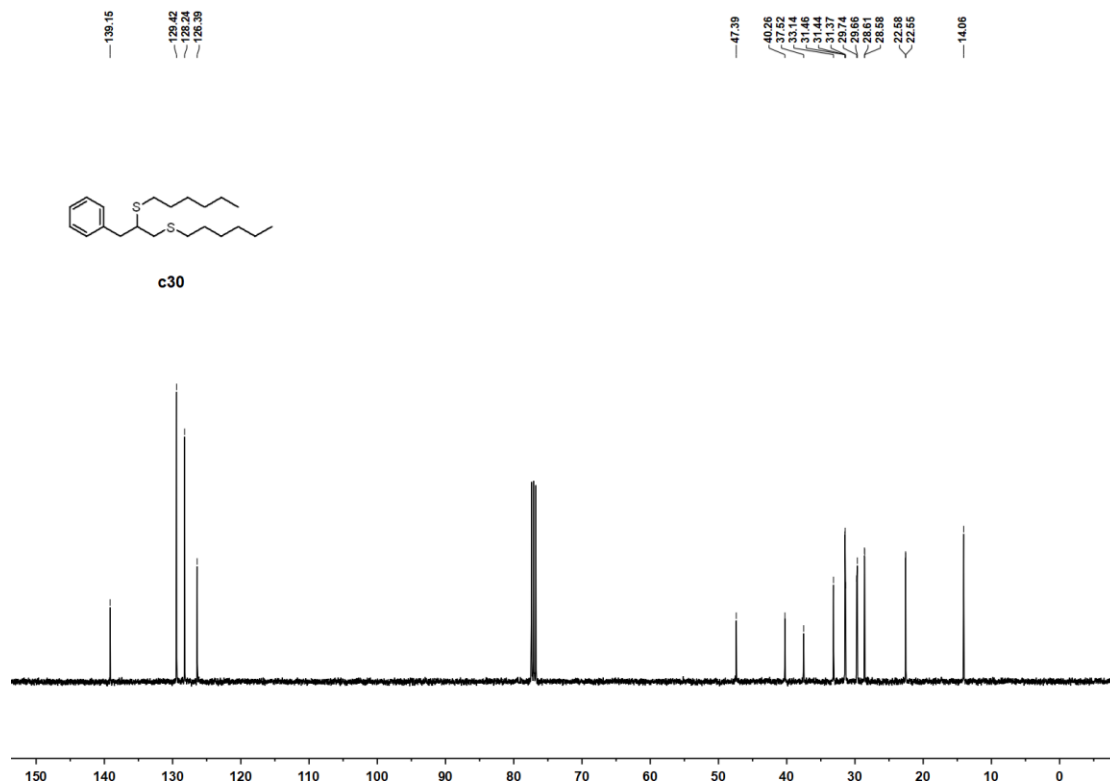




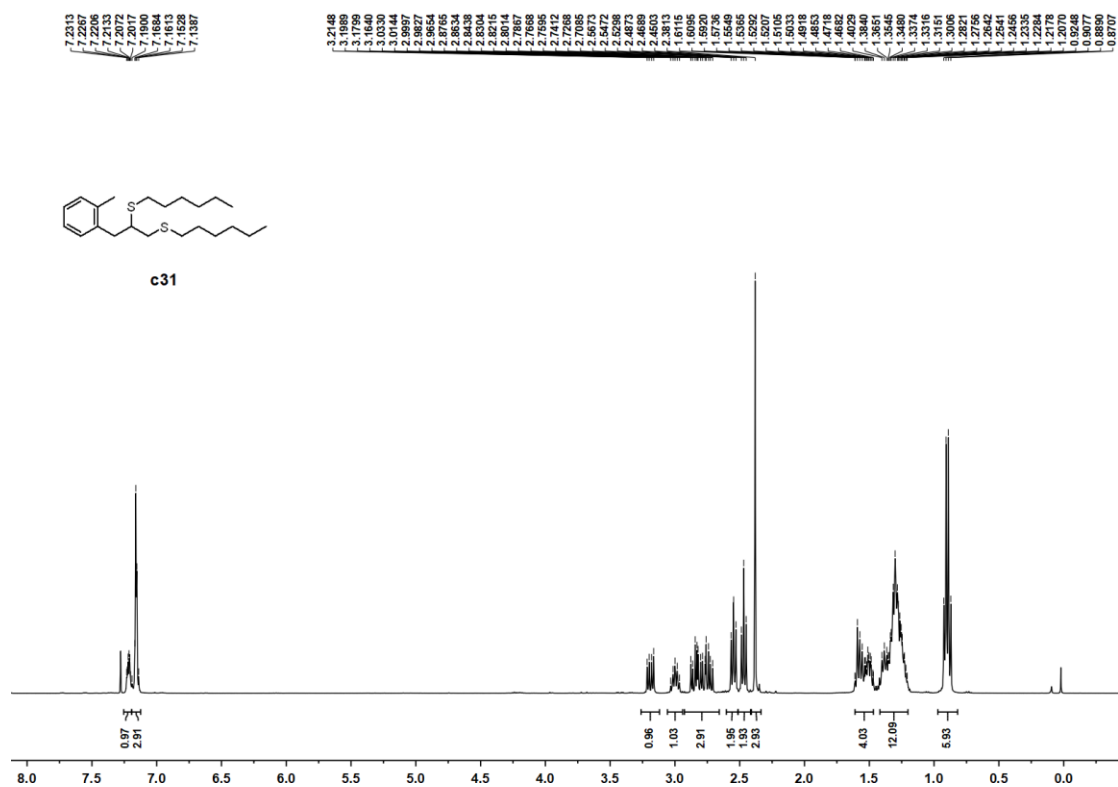
$^1\text{H}$  NMR spectra of compound **c30** in  $\text{CDCl}_3$  (400 MHz):



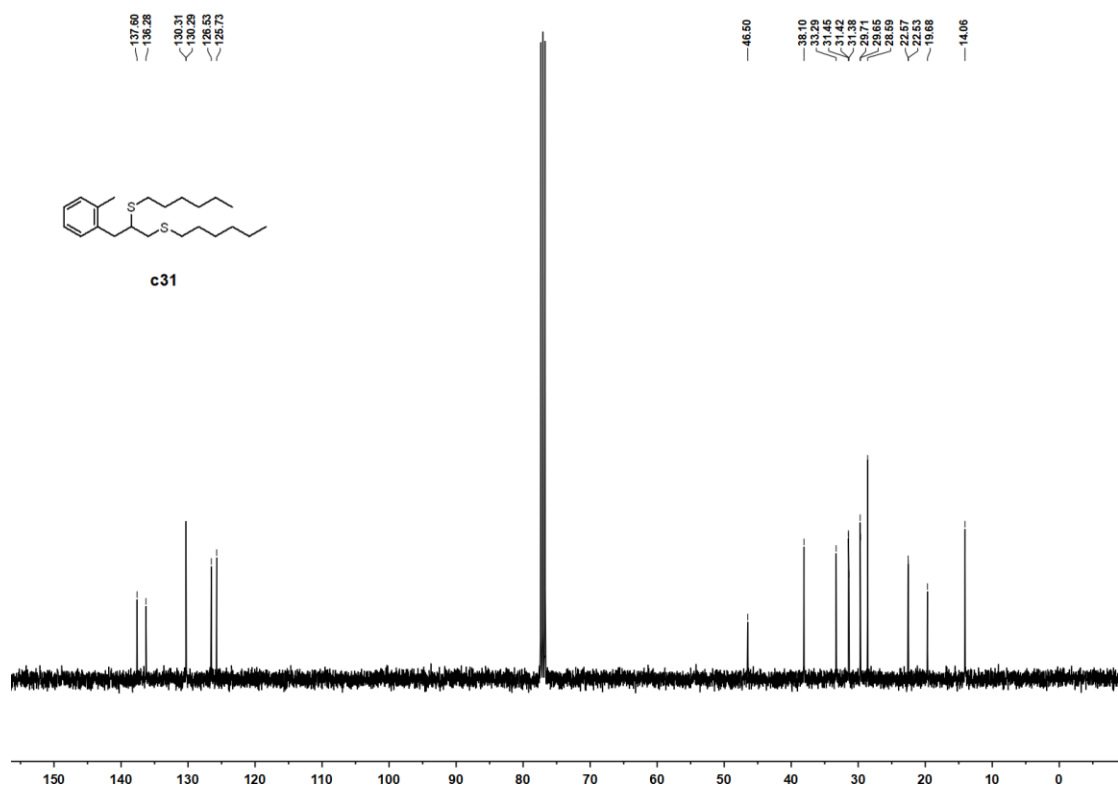
$^{13}\text{C}$  NMR spectra of compound **c30** in  $\text{CDCl}_3$  (101 MHz):



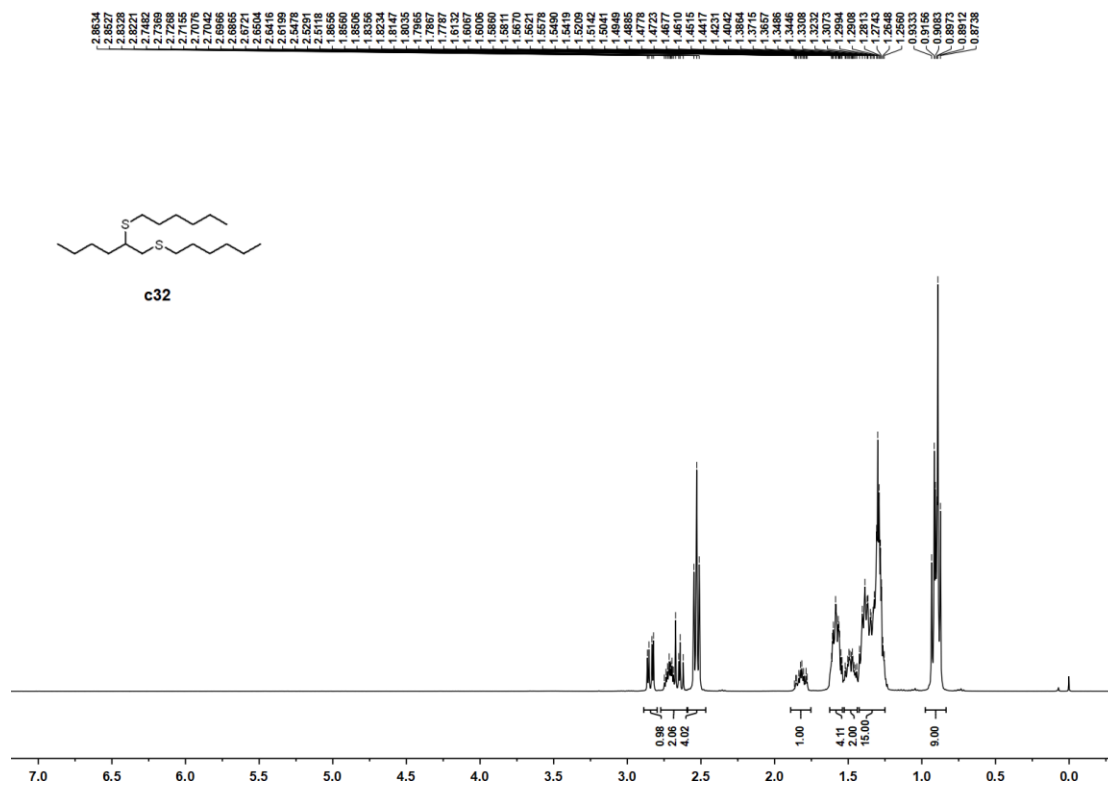
$^1\text{H}$  NMR spectra of compound **c31** in  $\text{CDCl}_3$  (400 MHz):



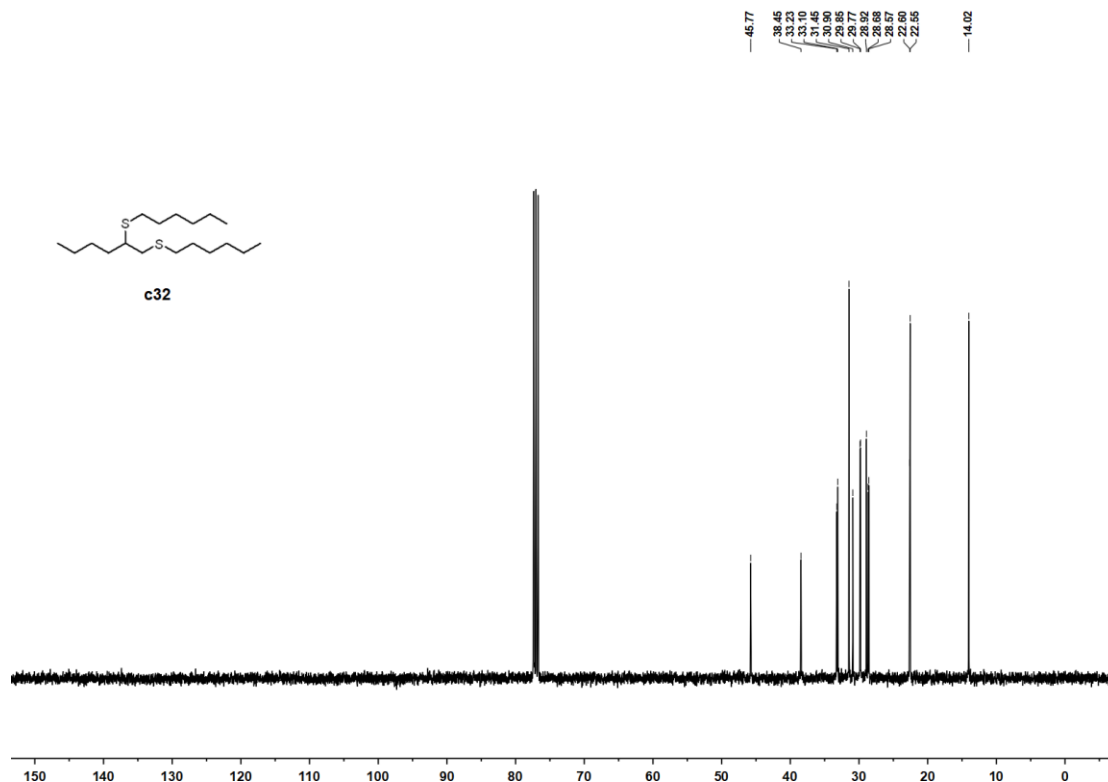
$^{13}\text{C}$  NMR spectra of compound **c31** in  $\text{CDCl}_3$  (101 MHz):



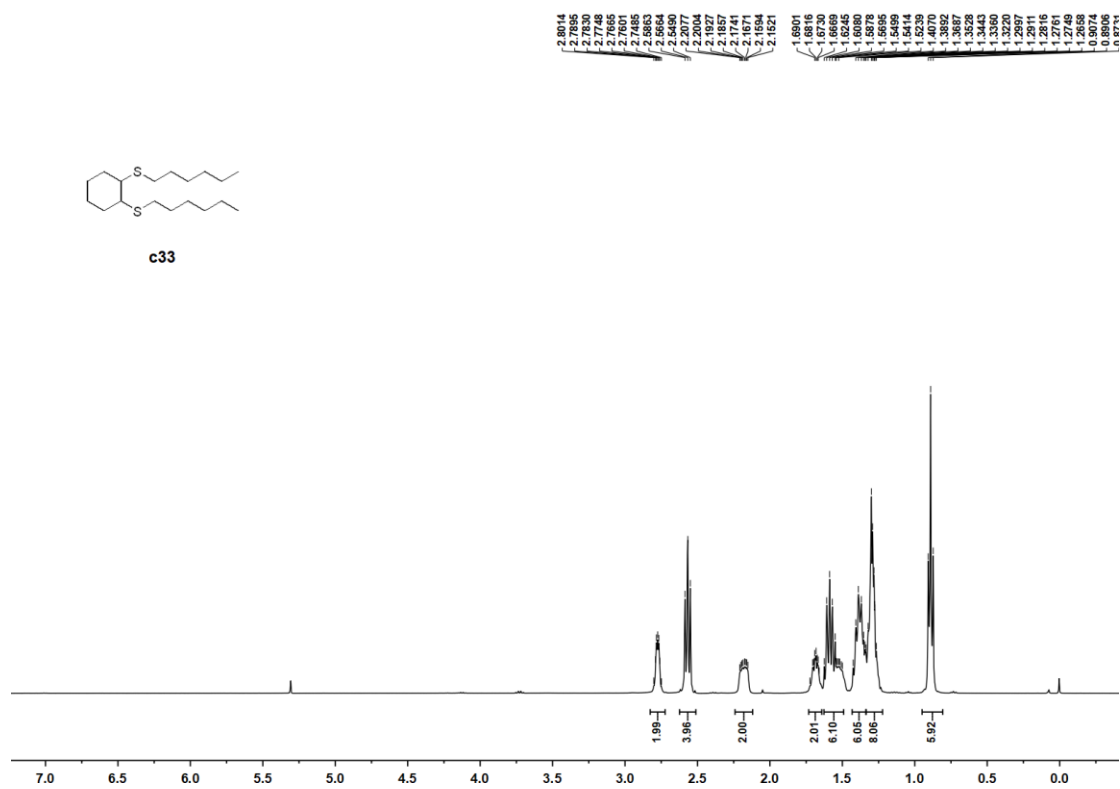
$^1\text{H}$  NMR spectra of compound **c32** in  $\text{CDCl}_3$  (400 MHz):



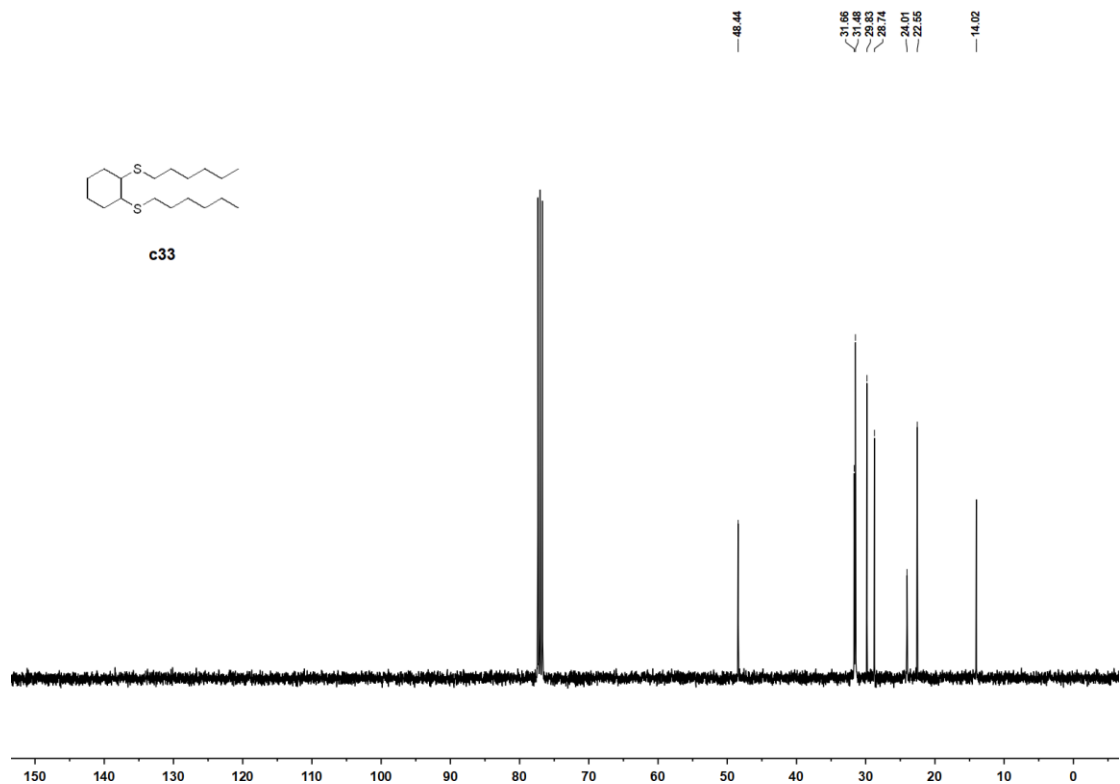
$^{13}\text{C}$  NMR spectra of compound **c32** in  $\text{CDCl}_3$  (101 MHz):



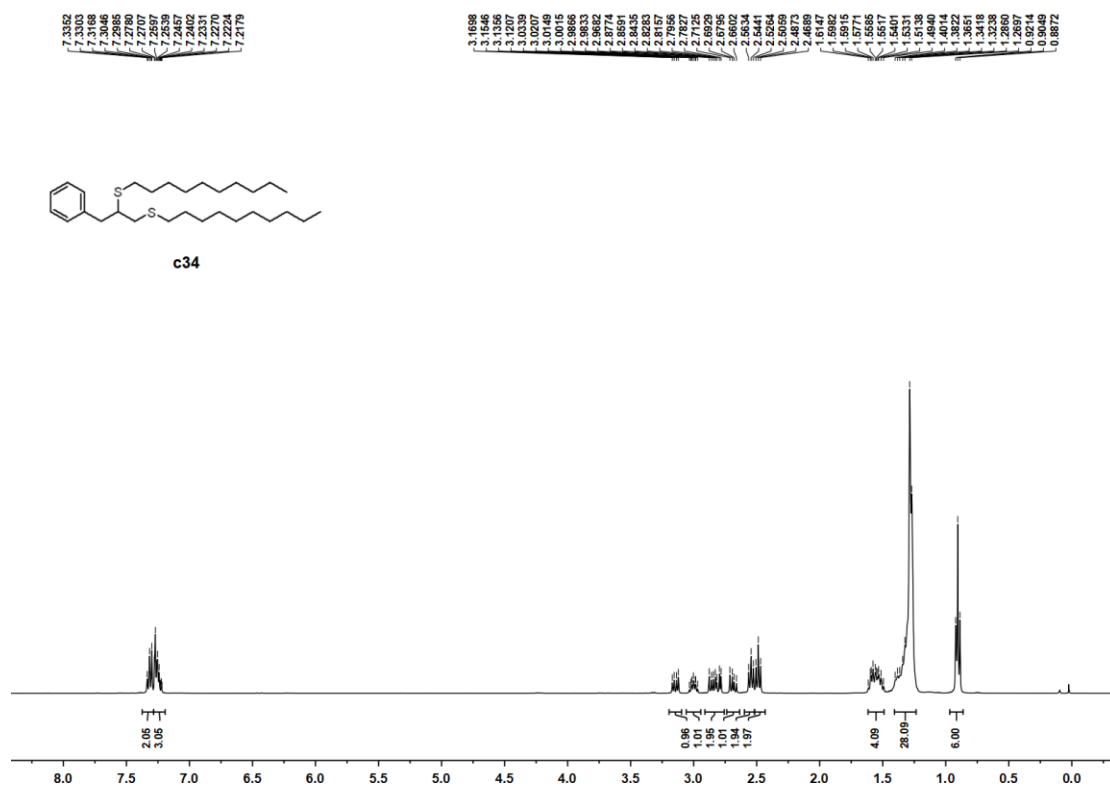
$^1\text{H}$  NMR spectra of compound **c33** in  $\text{CDCl}_3$  (400 MHz):



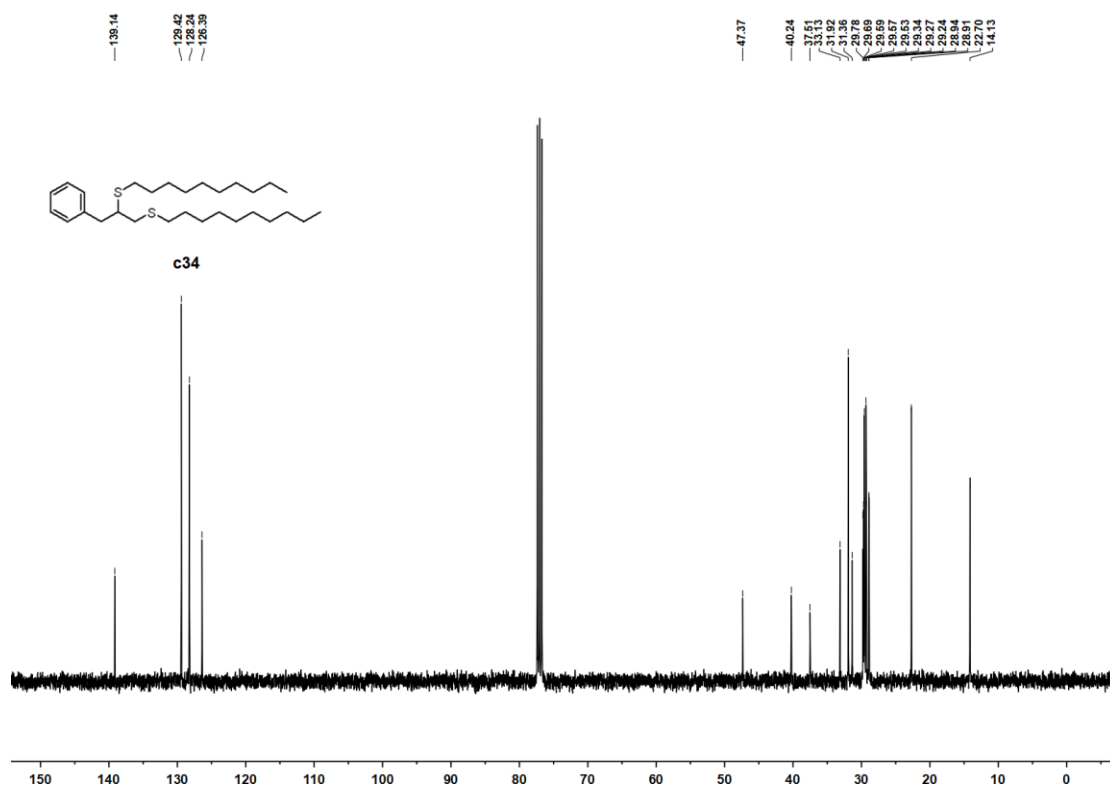
$^{13}\text{C}$  NMR spectra of compound **c33** in  $\text{CDCl}_3$  (101 MHz):



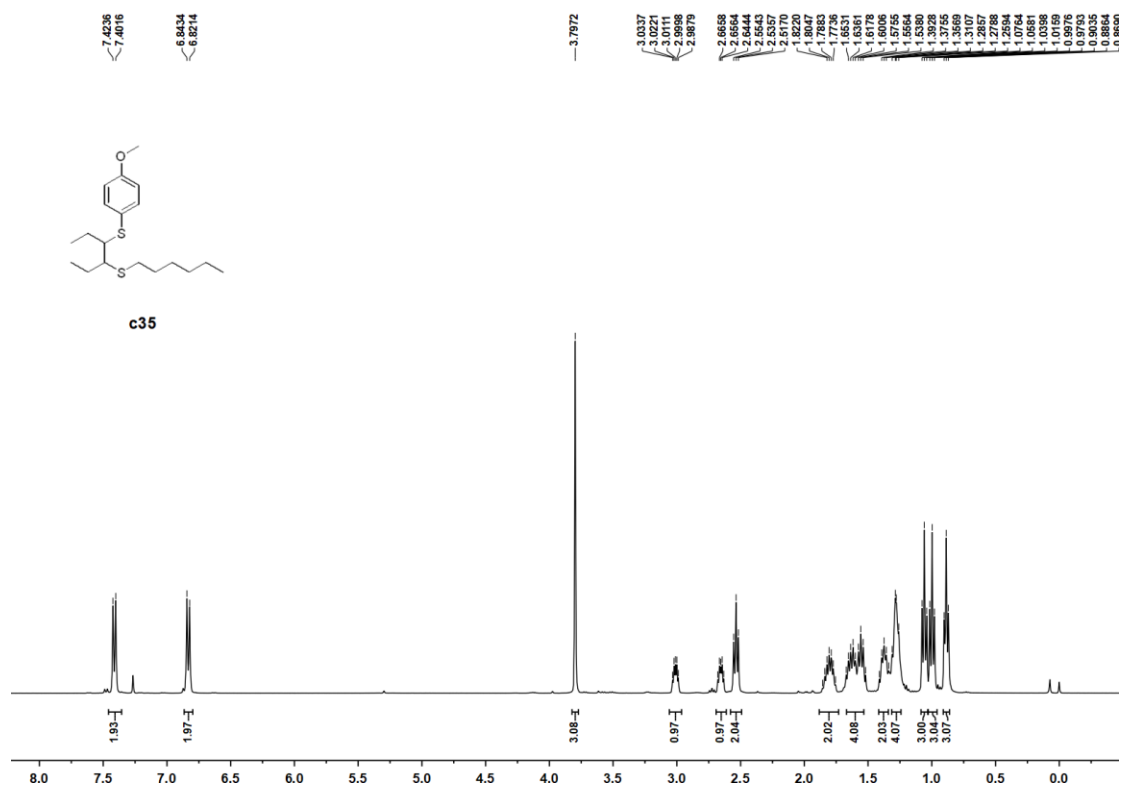
$^1\text{H}$  NMR spectra of compound **c34** in  $\text{CDCl}_3$  (400 MHz):



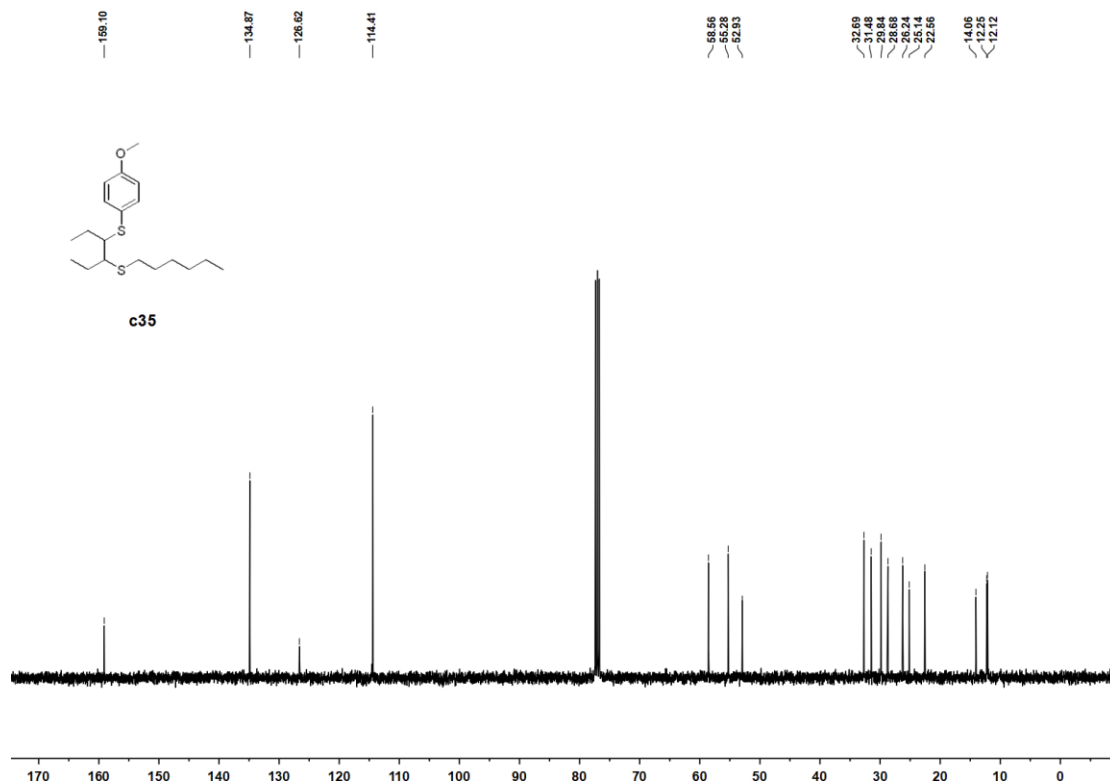
$^{13}\text{C}$  NMR spectra of compound **c34** in  $\text{CDCl}_3$  (101 MHz):



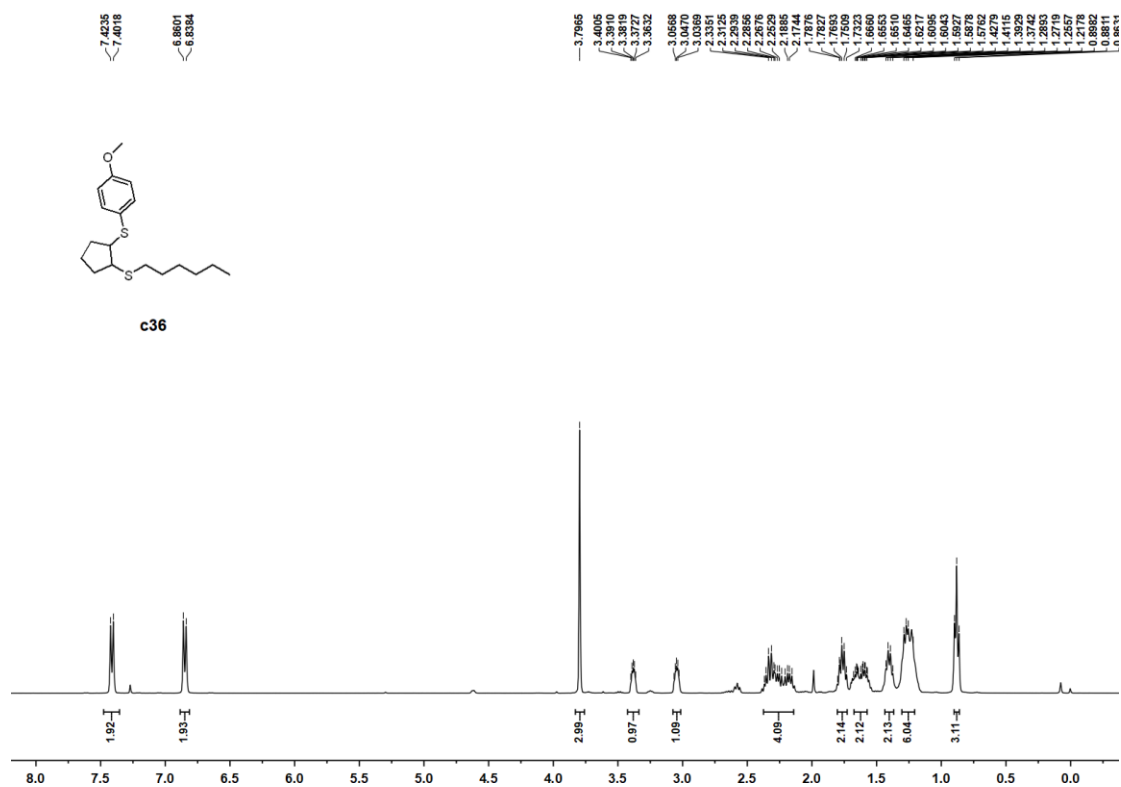
$^1\text{H}$  NMR spectra of compound **c35** in  $\text{CDCl}_3$  (400 MHz):



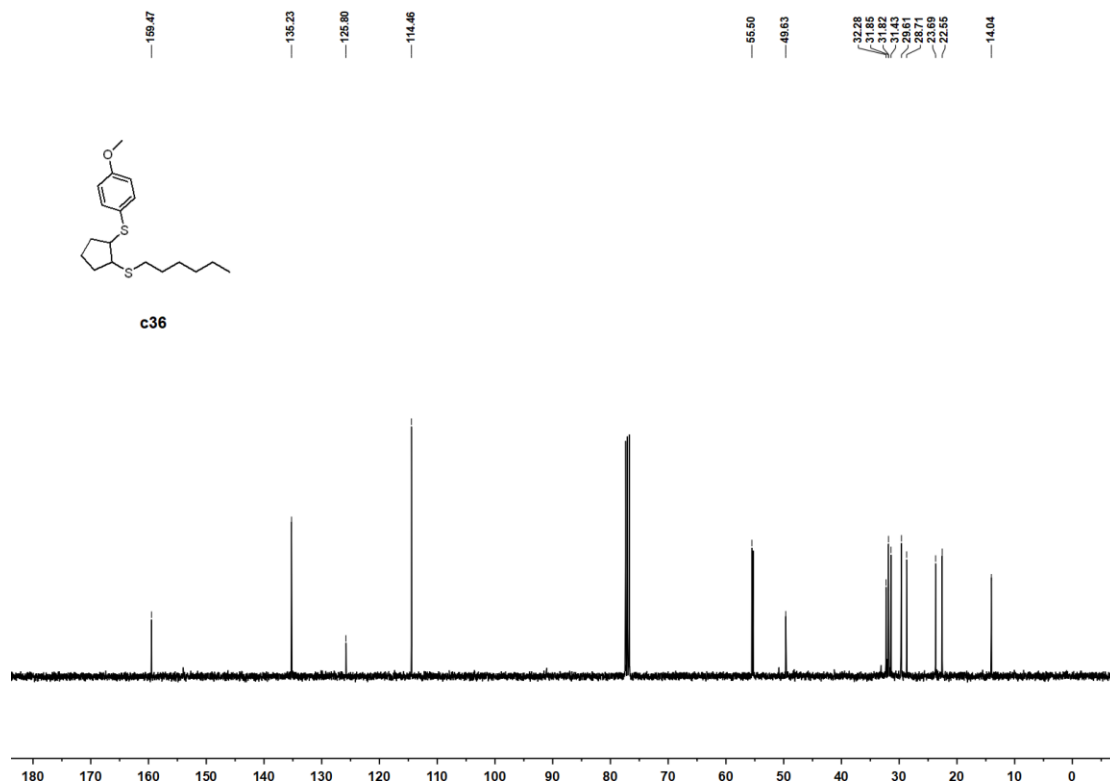
$^{13}\text{C}$  NMR spectra of compound **c35** in  $\text{CDCl}_3$  (101 MHz):



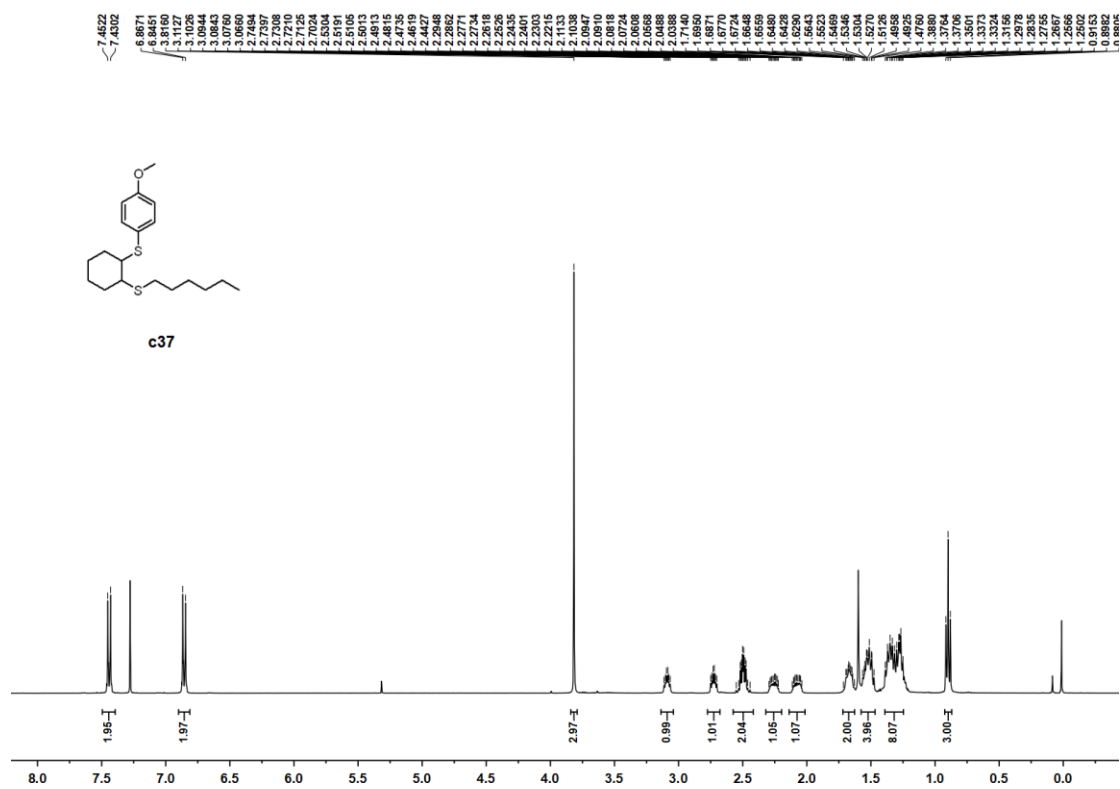
$^1\text{H}$  NMR spectra of compound **c36** in  $\text{CDCl}_3$  (400 MHz):



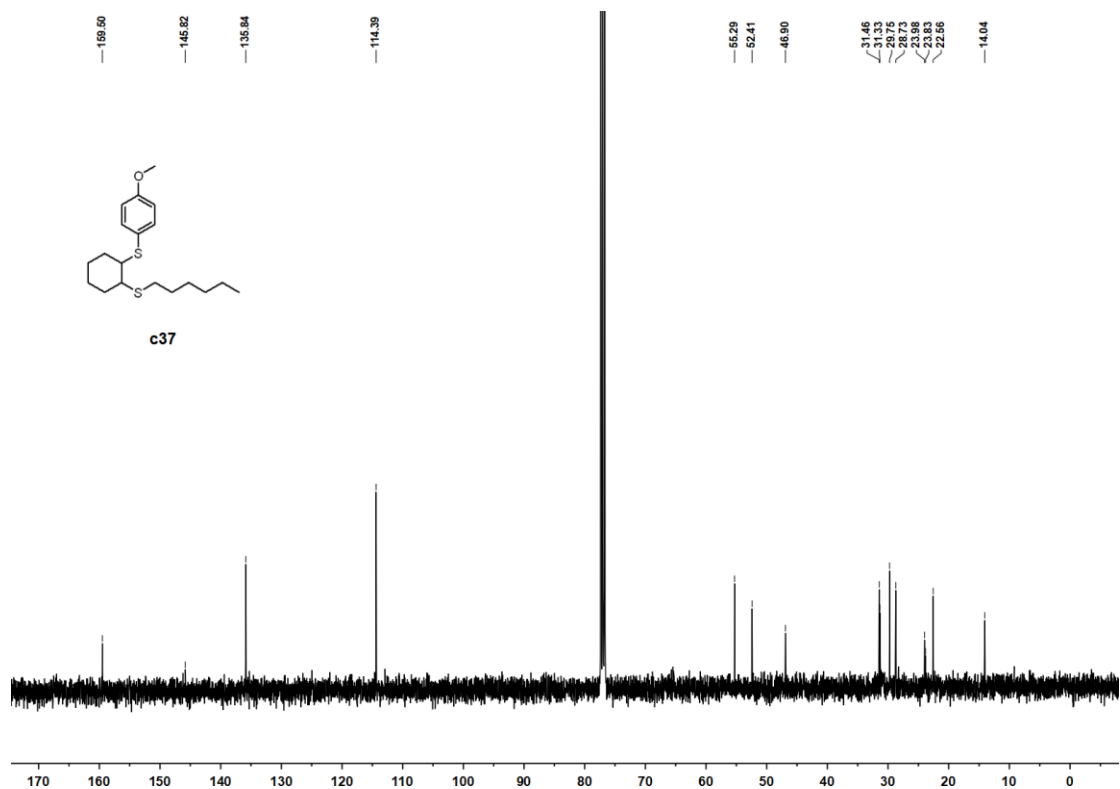
$^{13}\text{C}$  NMR spectra of compound **c36** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectra of compound **c37** in  $\text{CDCl}_3$  (400 MHz):

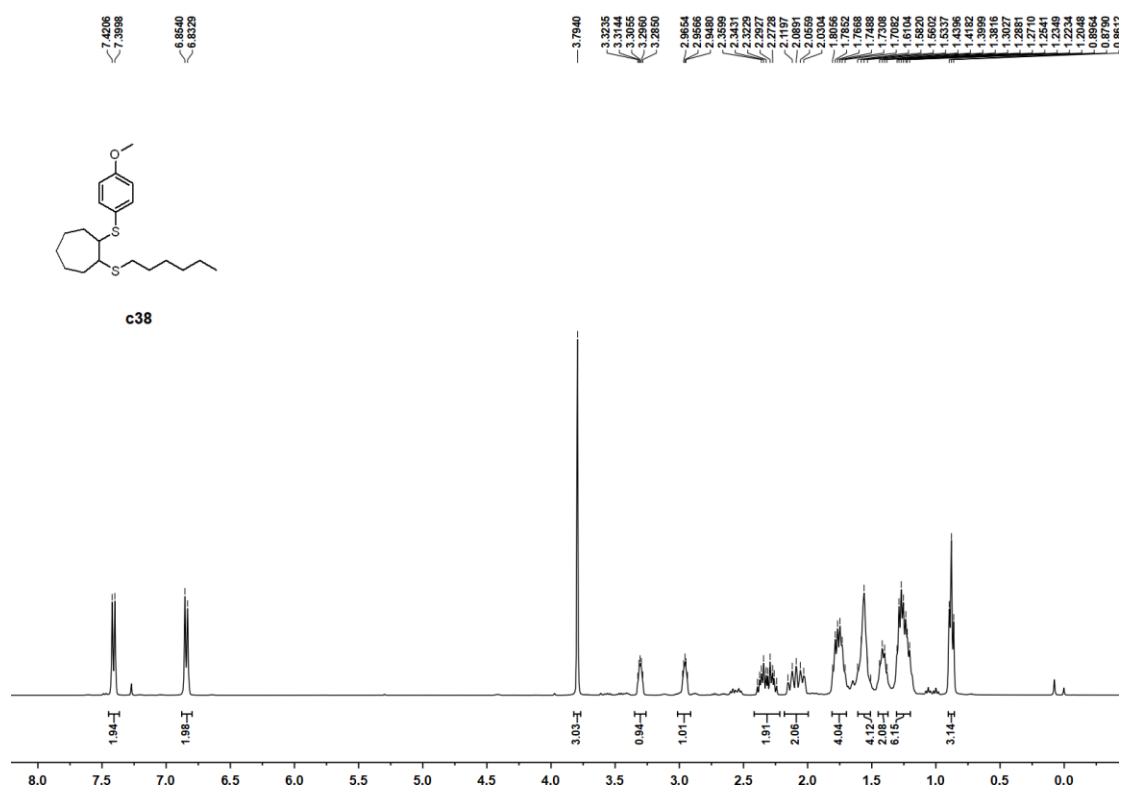


$^{13}\text{C}$  NMR spectra of compound **c37** in  $\text{CDCl}_3$  (101 MHz):

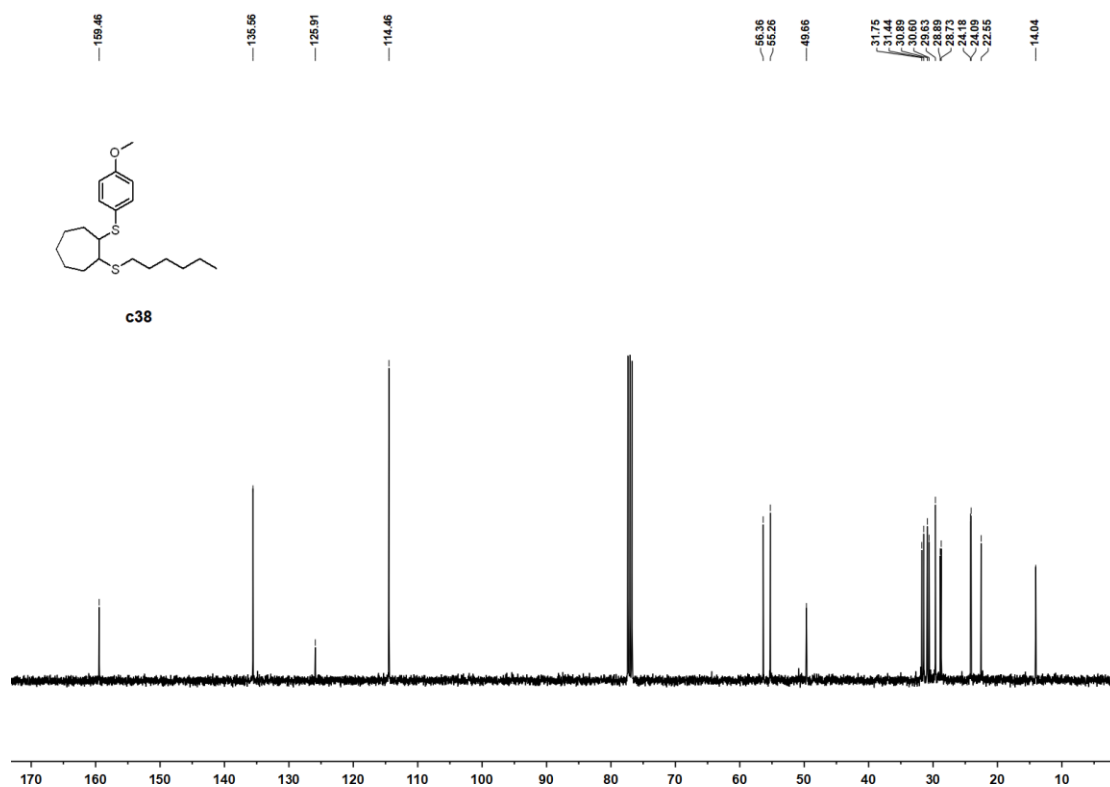




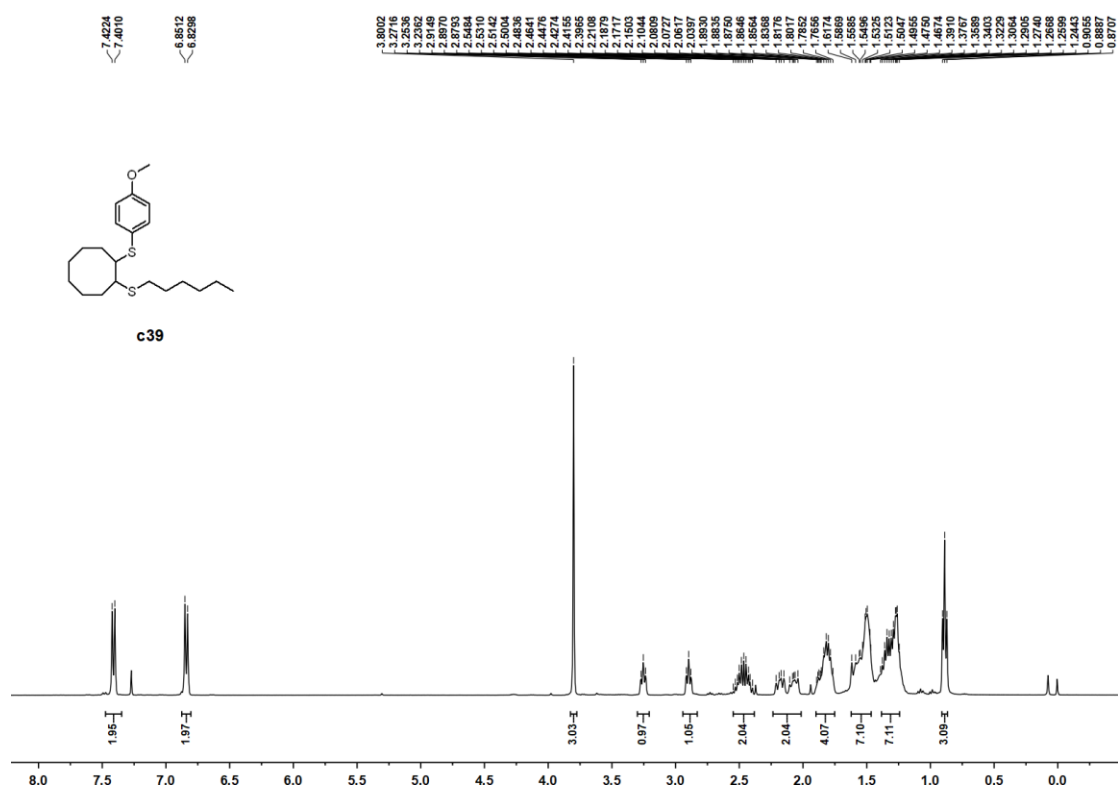
$^1\text{H}$  NMR spectra of compound **c38** in  $\text{CDCl}_3$  (400 MHz):



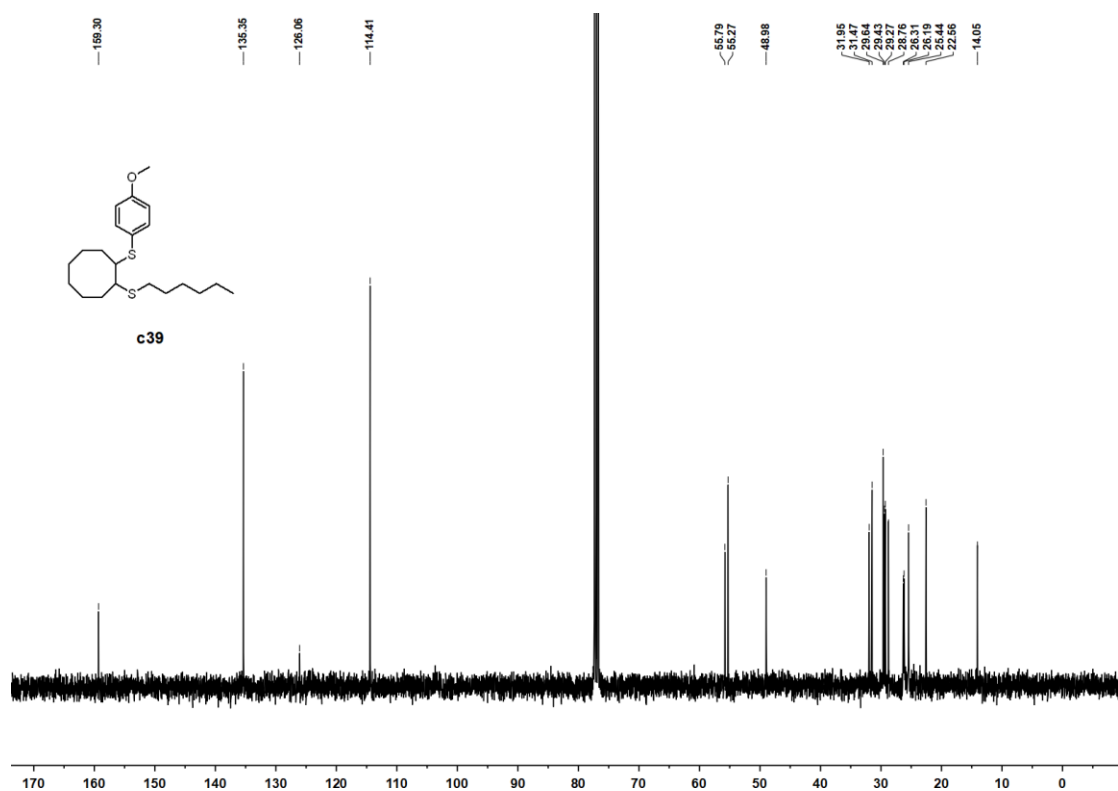
$^{13}\text{C}$  NMR spectra of compound **c38** in  $\text{CDCl}_3$  (101 MHz):



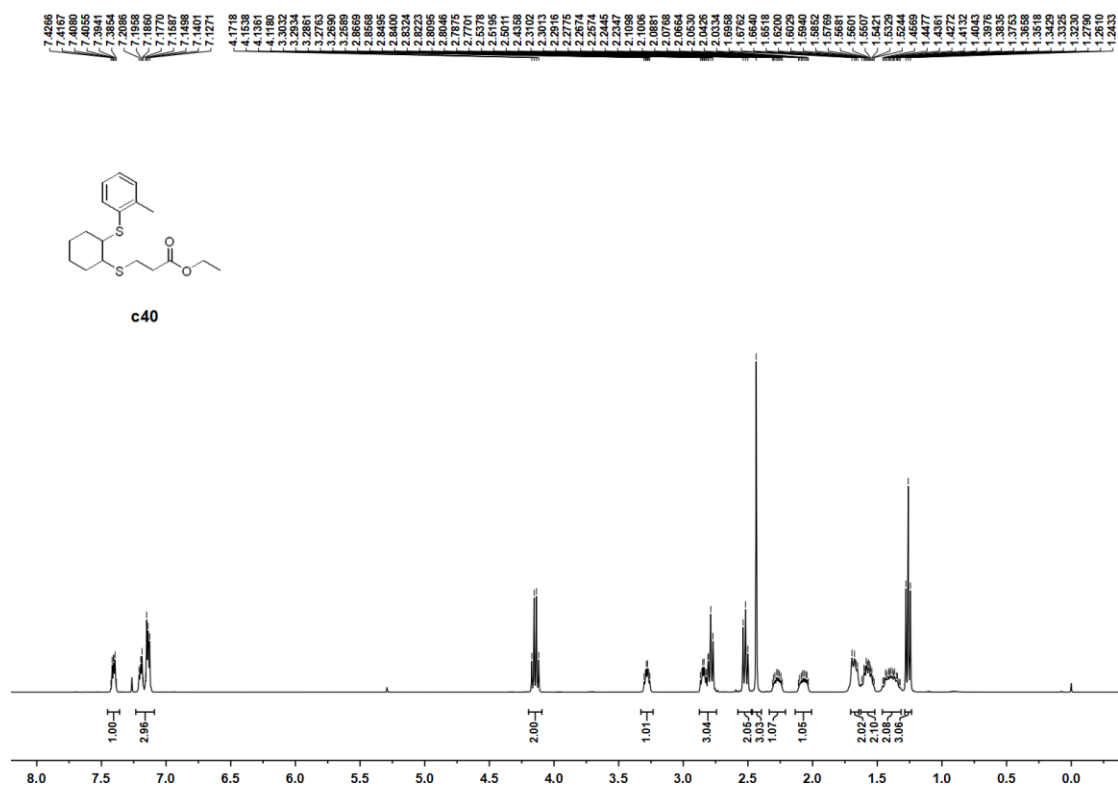
$^1\text{H}$  NMR spectra of compound **c39** in  $\text{CDCl}_3$  (400 MHz):



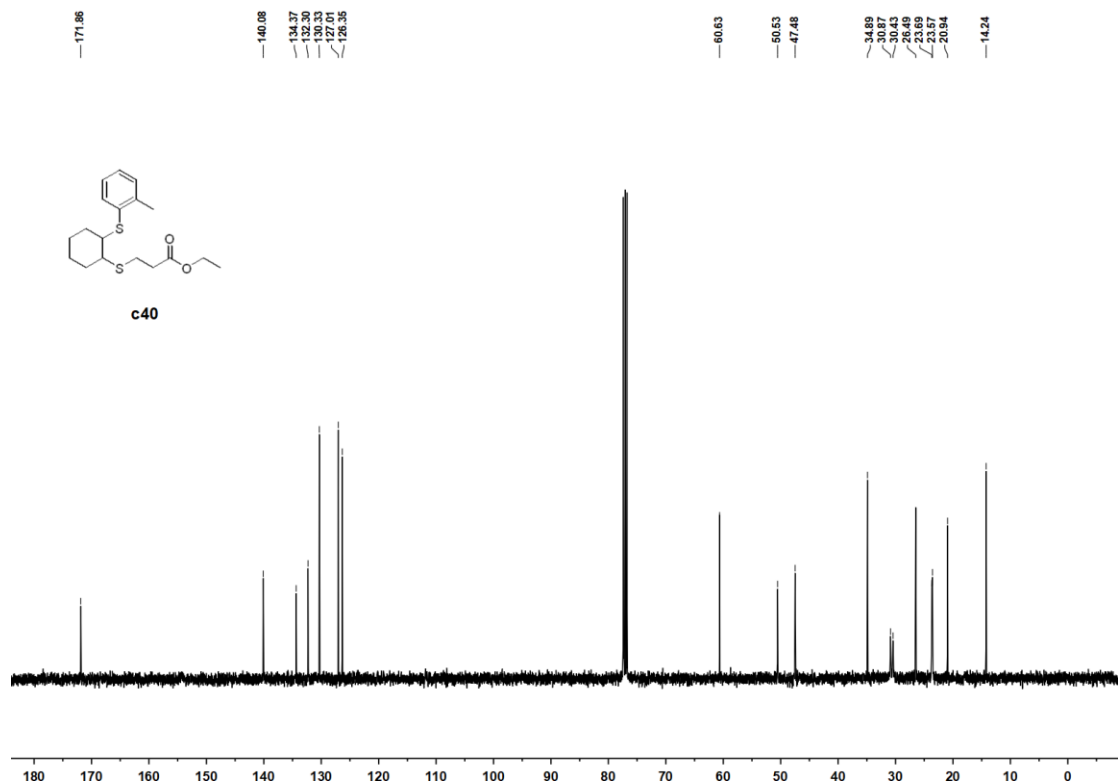
$^{13}\text{C}$  NMR spectra of compound **c39** in  $\text{CDCl}_3$  (101 MHz):



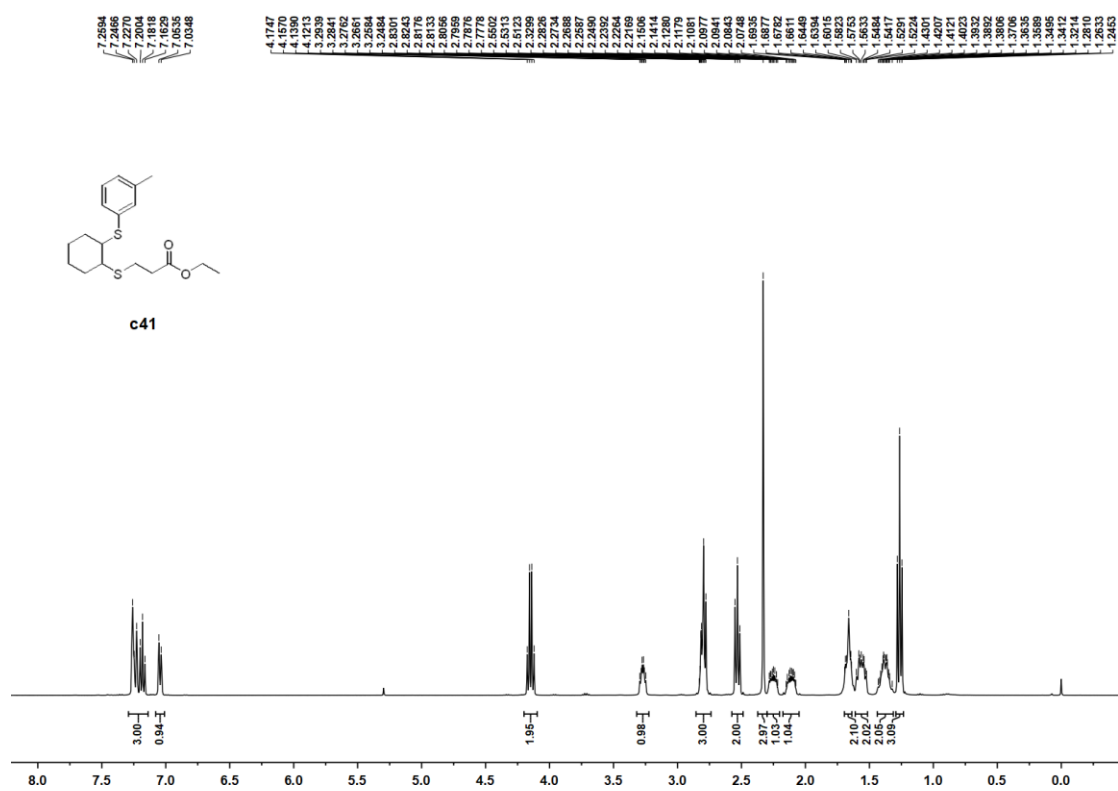
$^1\text{H}$  NMR spectra of compound **c40** in  $\text{CDCl}_3$  (400 MHz):



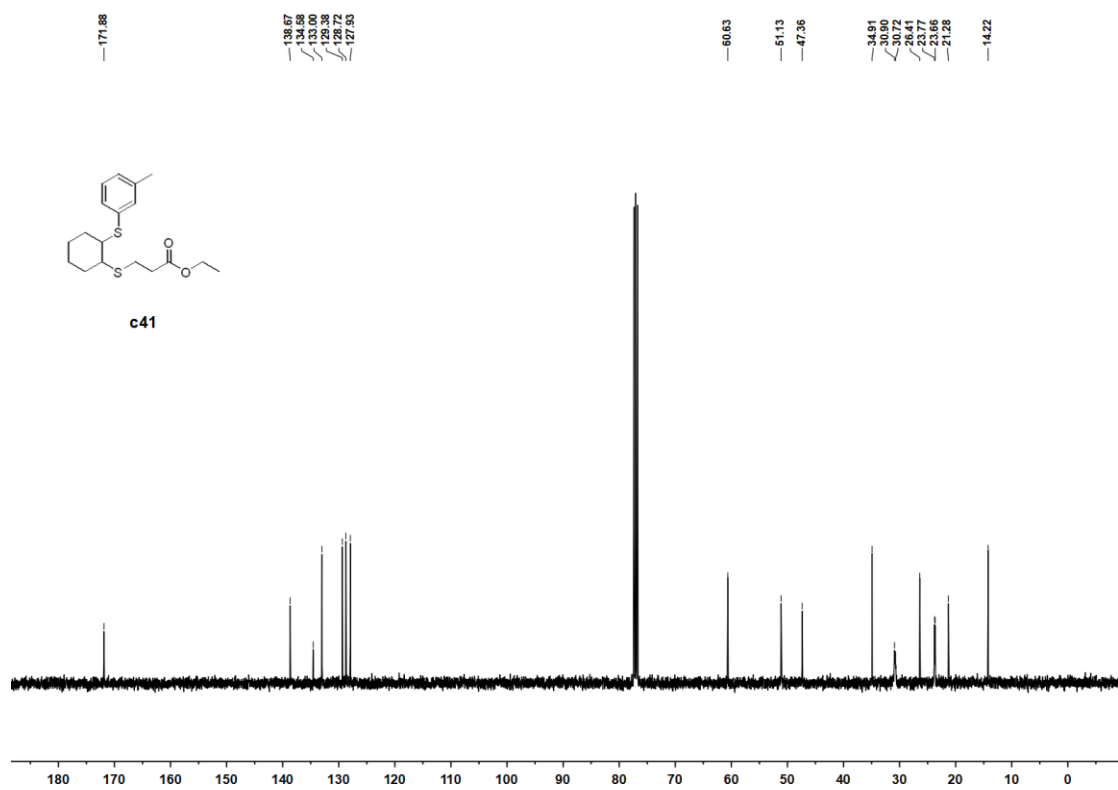
$^{13}\text{C}$  NMR spectra of compound **c40** in  $\text{CDCl}_3$  (101 MHz):



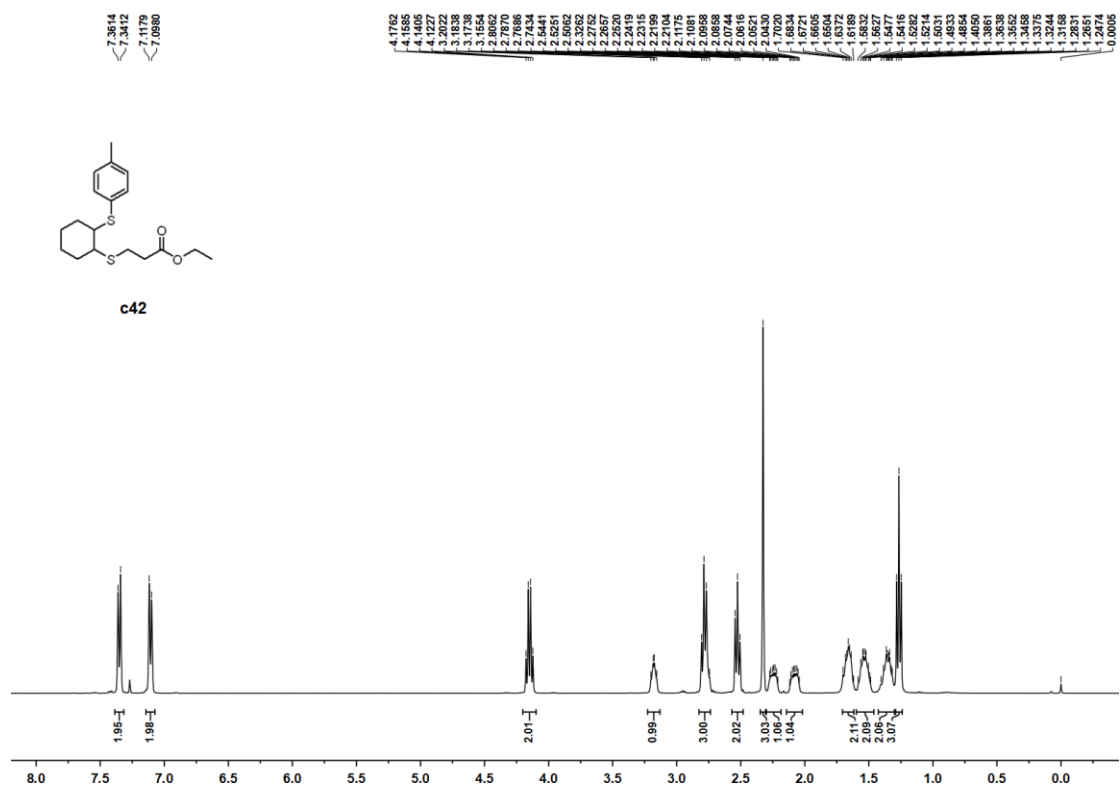
$^1\text{H}$  NMR spectra of compound **c41** in  $\text{CDCl}_3$  (400 MHz):



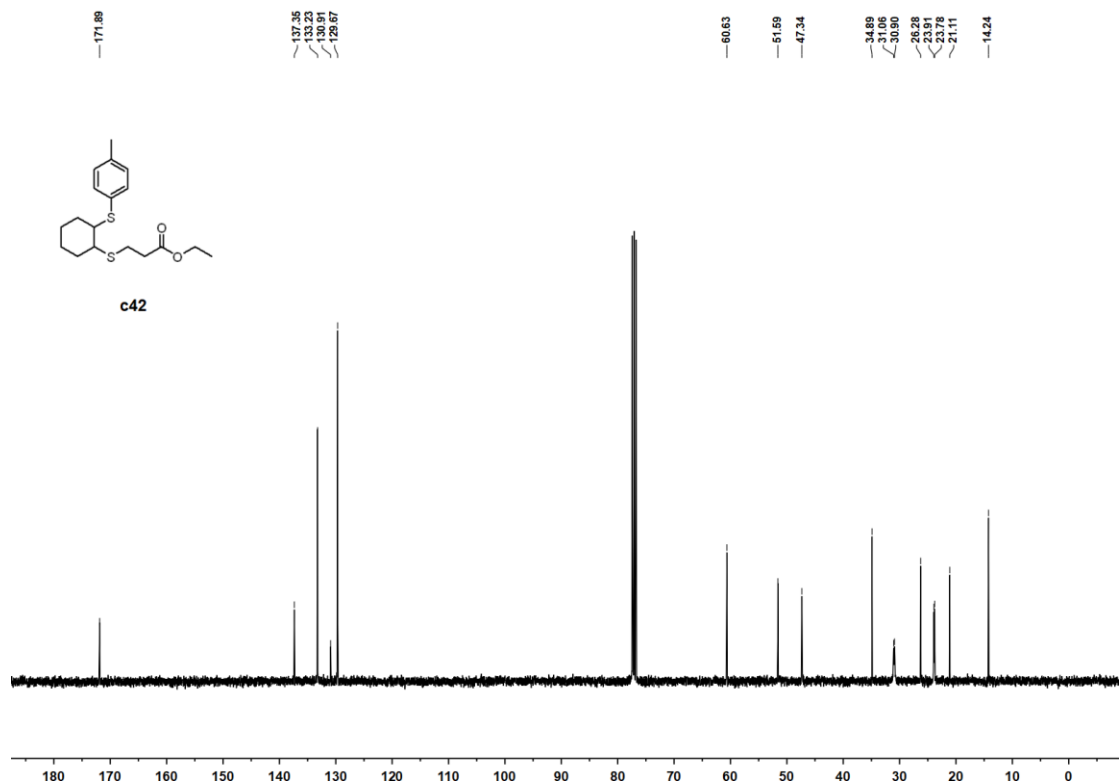
$^{13}\text{C}$  NMR spectra of compound **c41** in  $\text{CDCl}_3$  (101 MHz):



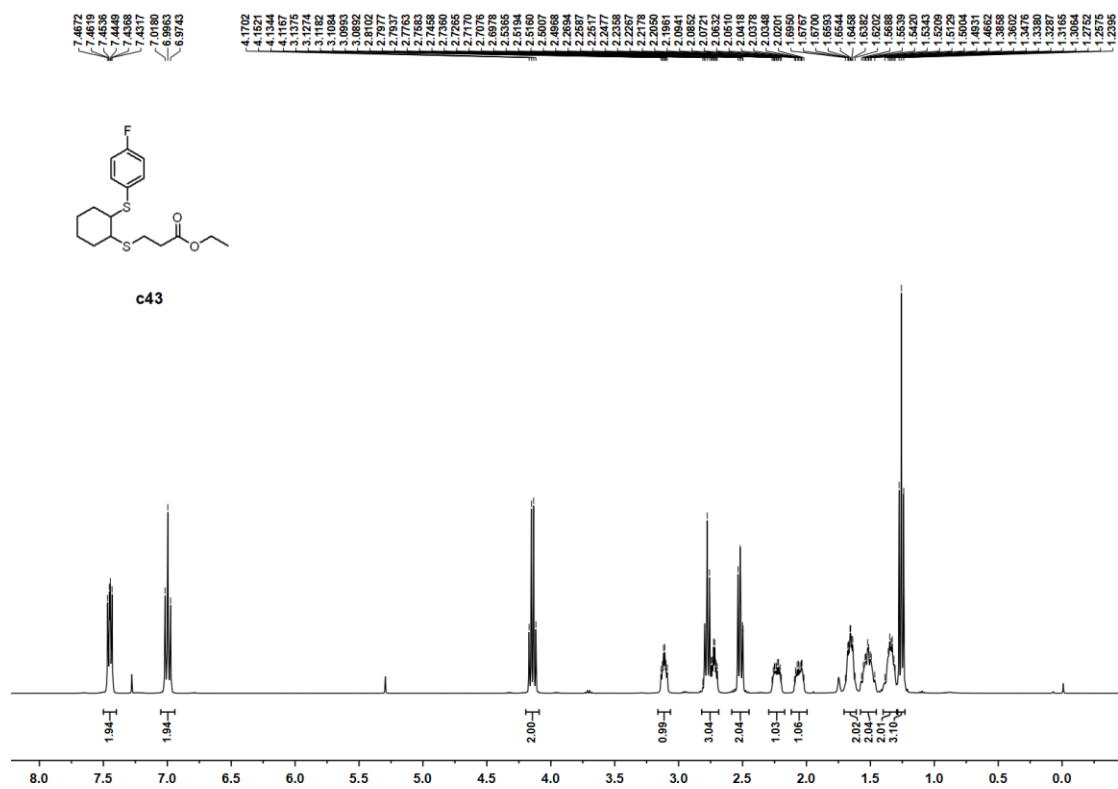
$^1\text{H}$  NMR spectra of compound **c42** in  $\text{CDCl}_3$  (400 MHz):



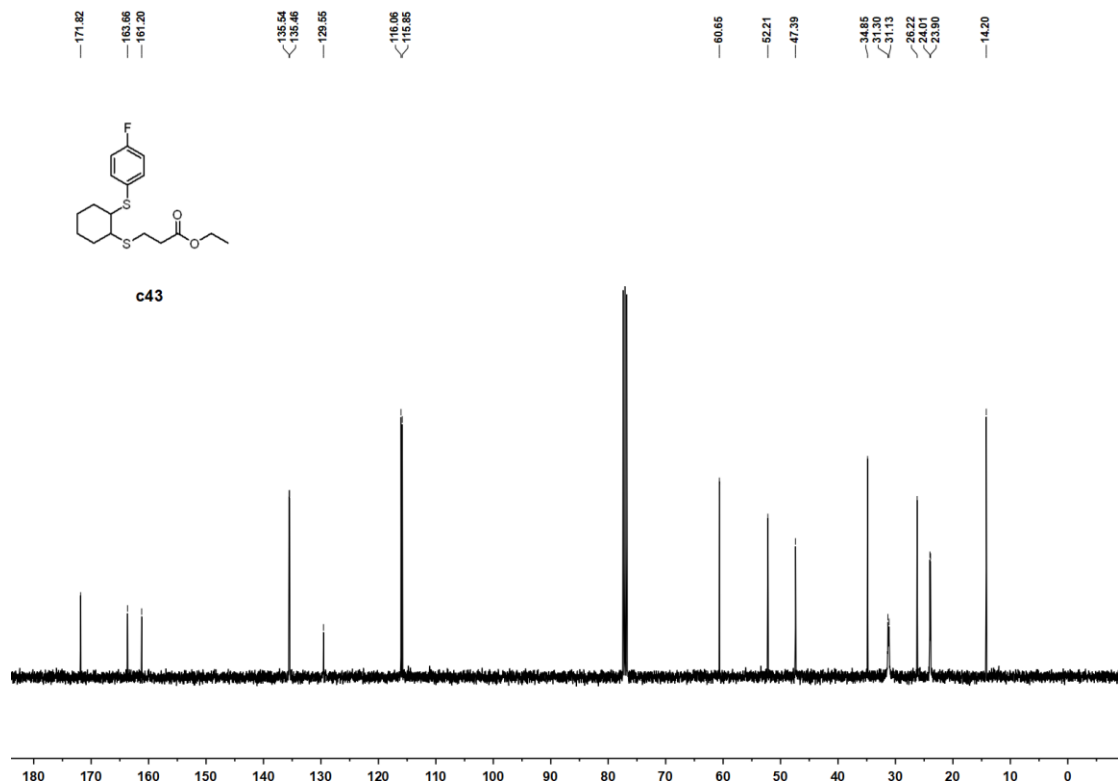
$^{13}\text{C}$  NMR spectra of compound **c42** in  $\text{CDCl}_3$  (101 MHz):



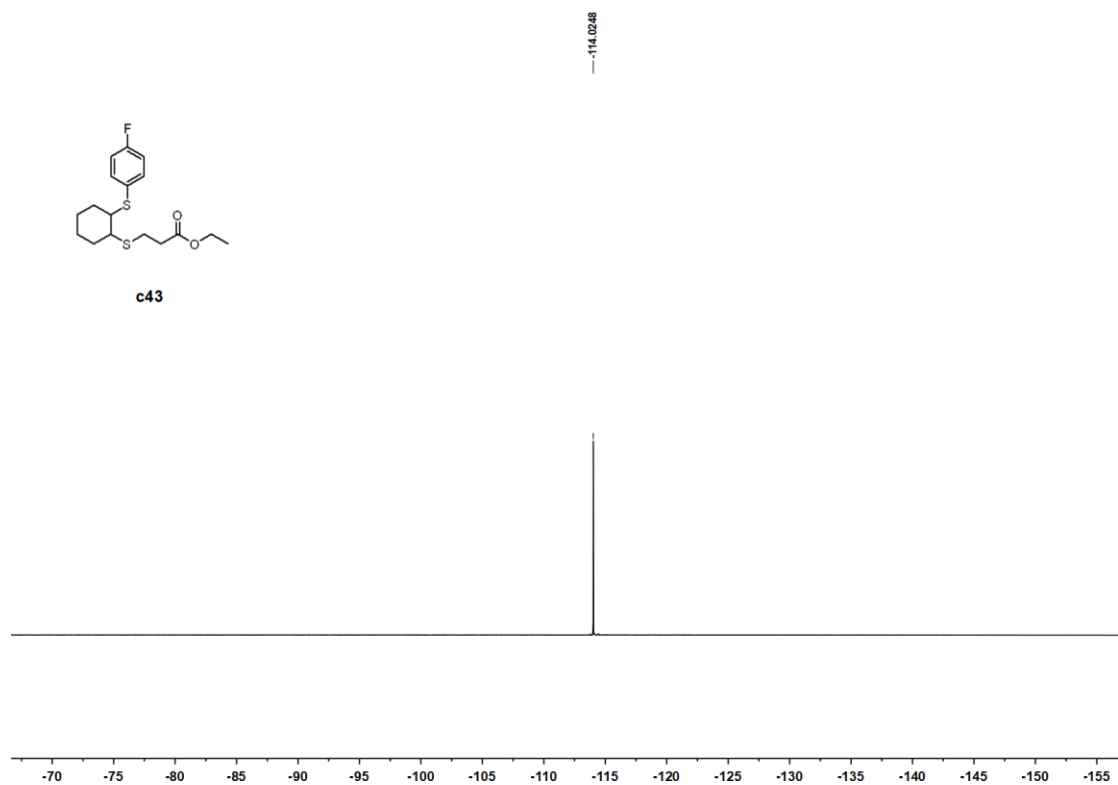
$^1\text{H}$  NMR spectra of compound **c43** in  $\text{CDCl}_3$  (400 MHz):



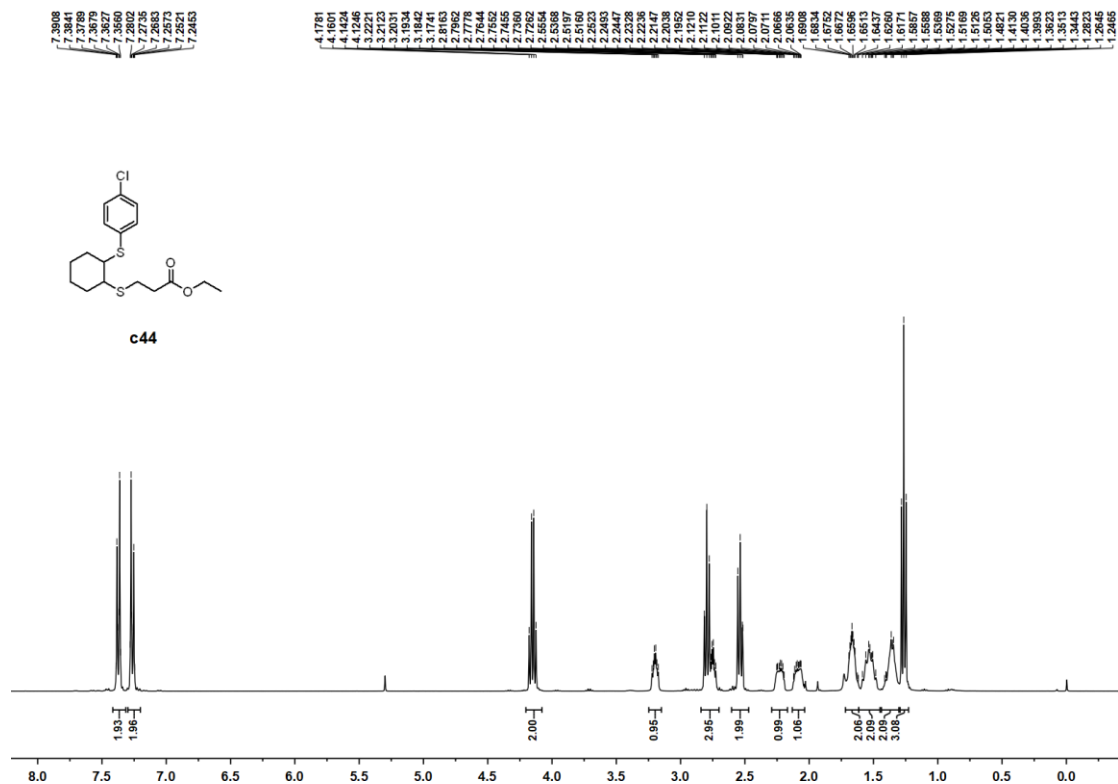
$^{13}\text{C}$  NMR spectra of compound **c43** in  $\text{CDCl}_3$  (101 MHz):



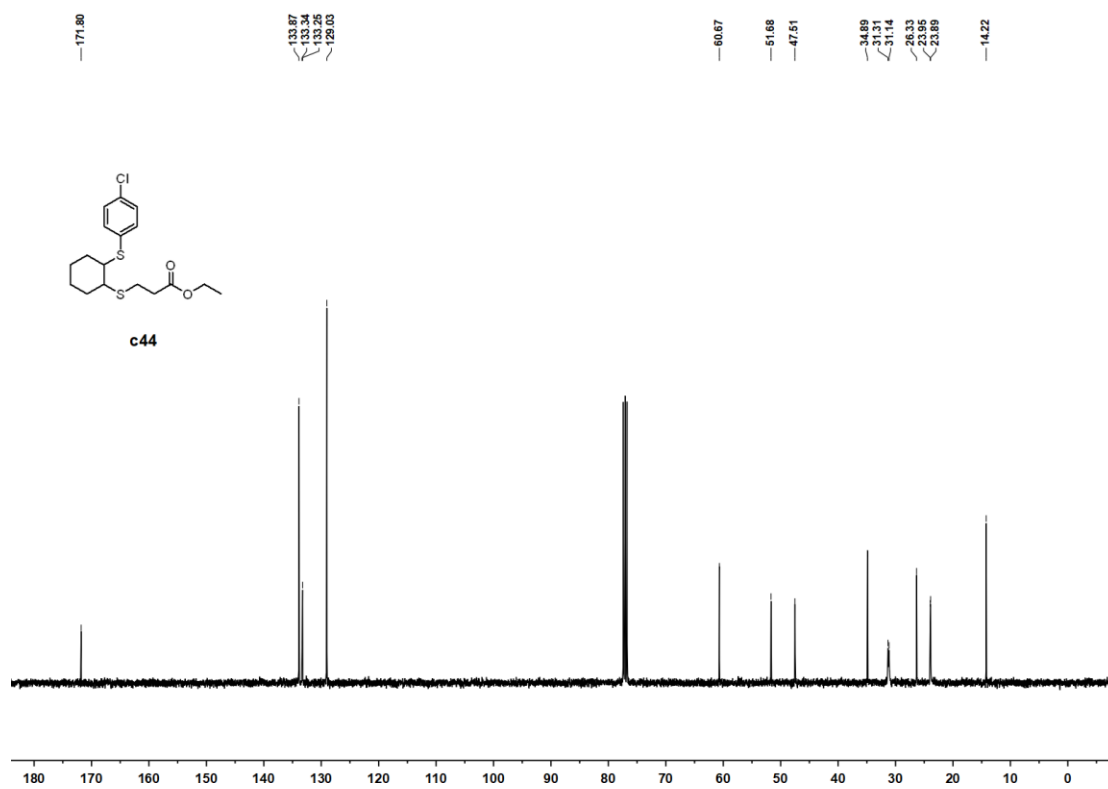
$^{19}\text{F}$  NMR spectra of compound **c43** in  $\text{CDCl}_3$  (376 MHz):



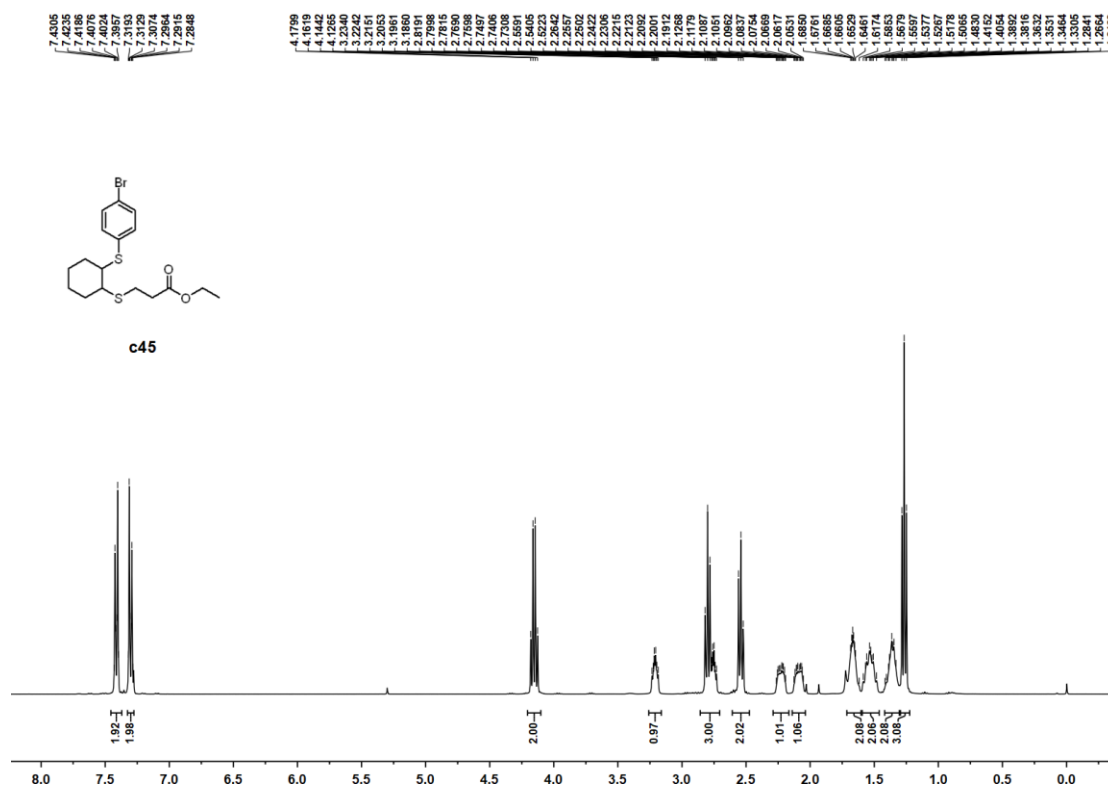
$^1\text{H}$  NMR spectra of compound **c44** in  $\text{CDCl}_3$  (400 MHz):



$^{13}\text{C}$  NMR spectra of compound **c44** in  $\text{CDCl}_3$  (101 MHz):

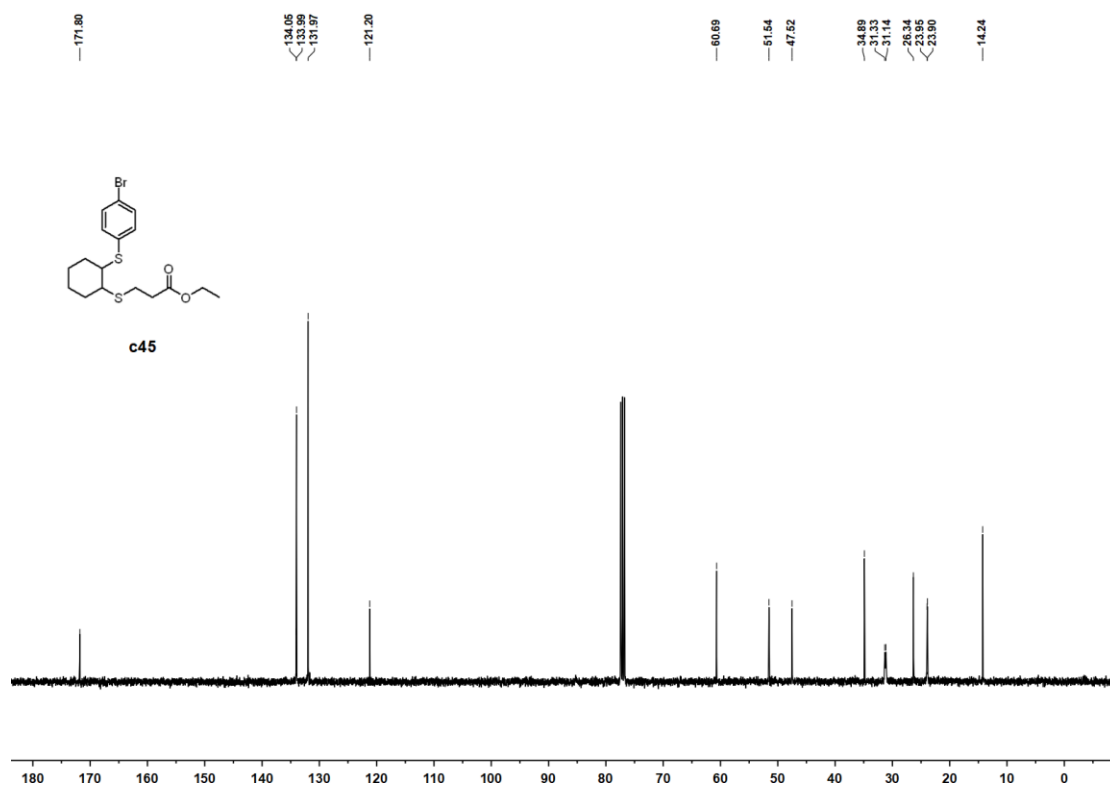


$^1\text{H}$  NMR spectra of compound **c45** in  $\text{CDCl}_3$  (400 MHz):

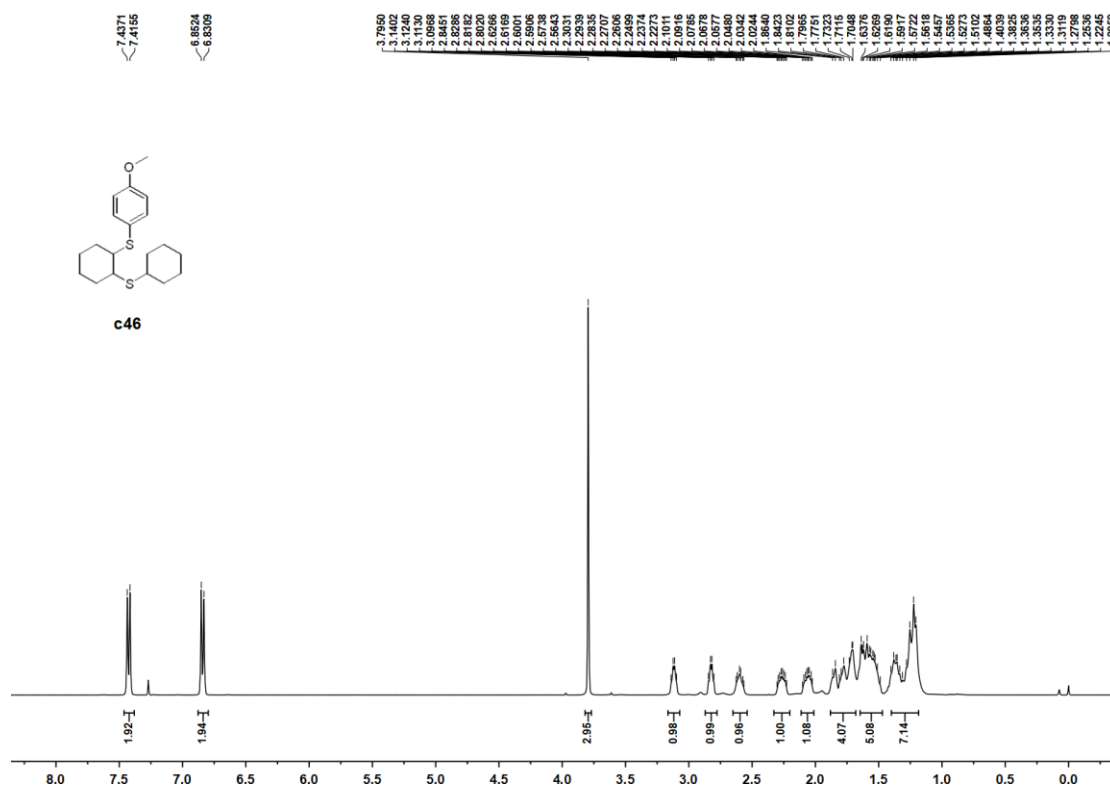




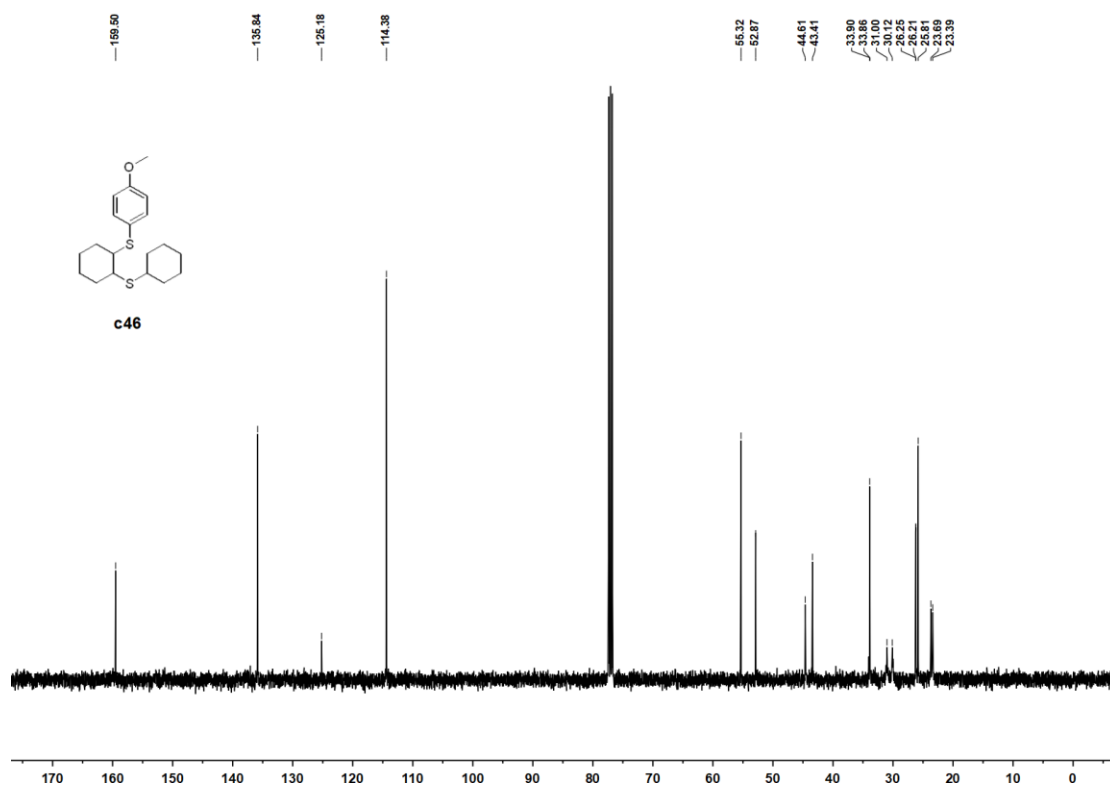
$^{13}\text{C}$  NMR spectra of compound **c45** in  $\text{CDCl}_3$  (101 MHz):



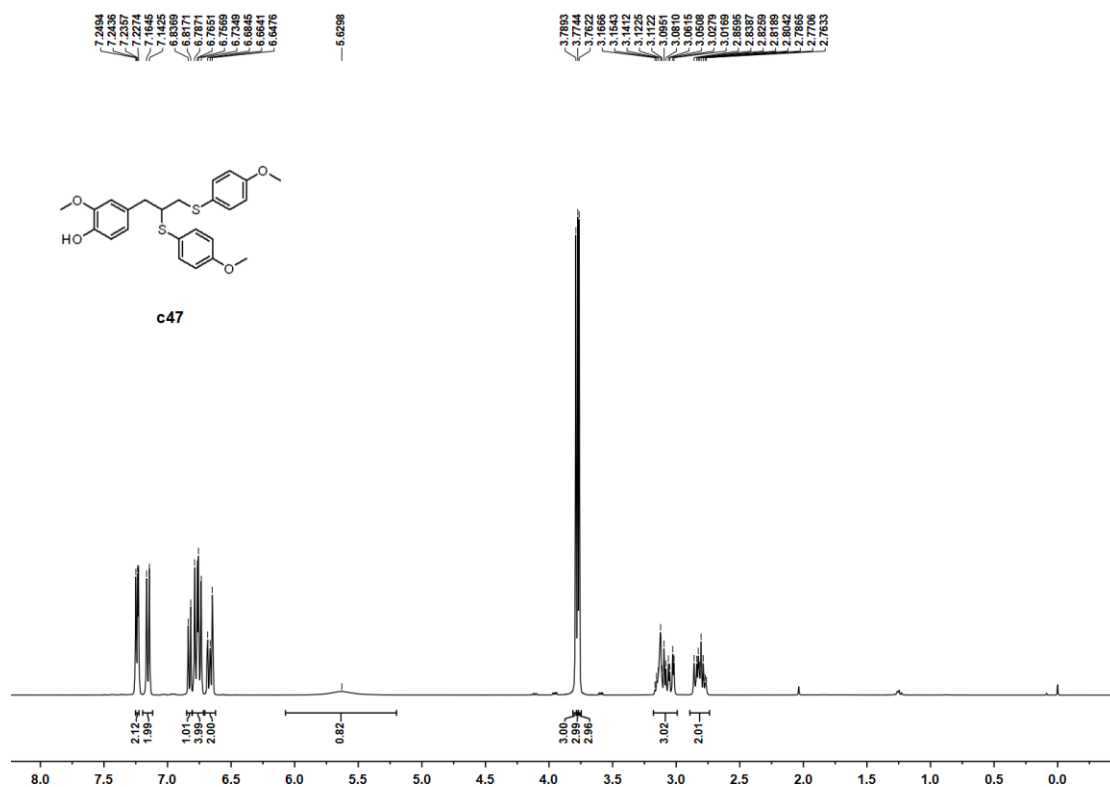
$^1\text{H}$  NMR spectra of compound **c46** in  $\text{CDCl}_3$  (400 MHz):



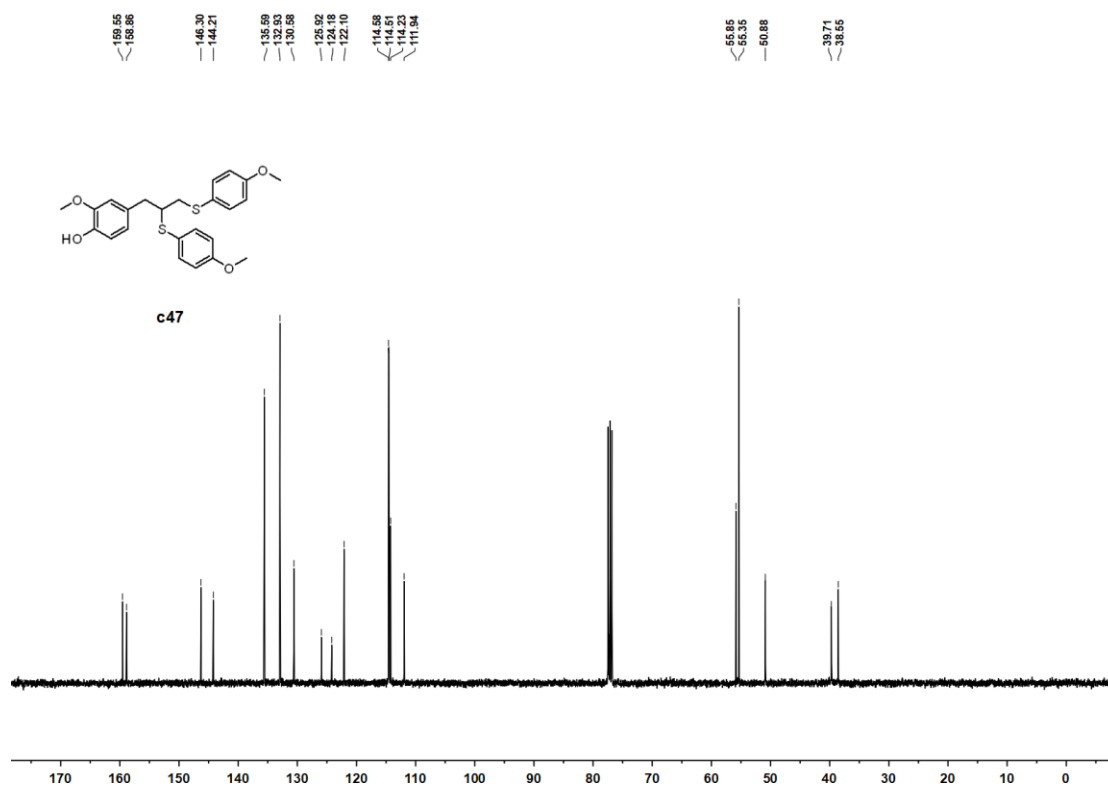
$^{13}\text{C}$  NMR spectra of compound **c46** in  $\text{CDCl}_3$  (101 MHz):



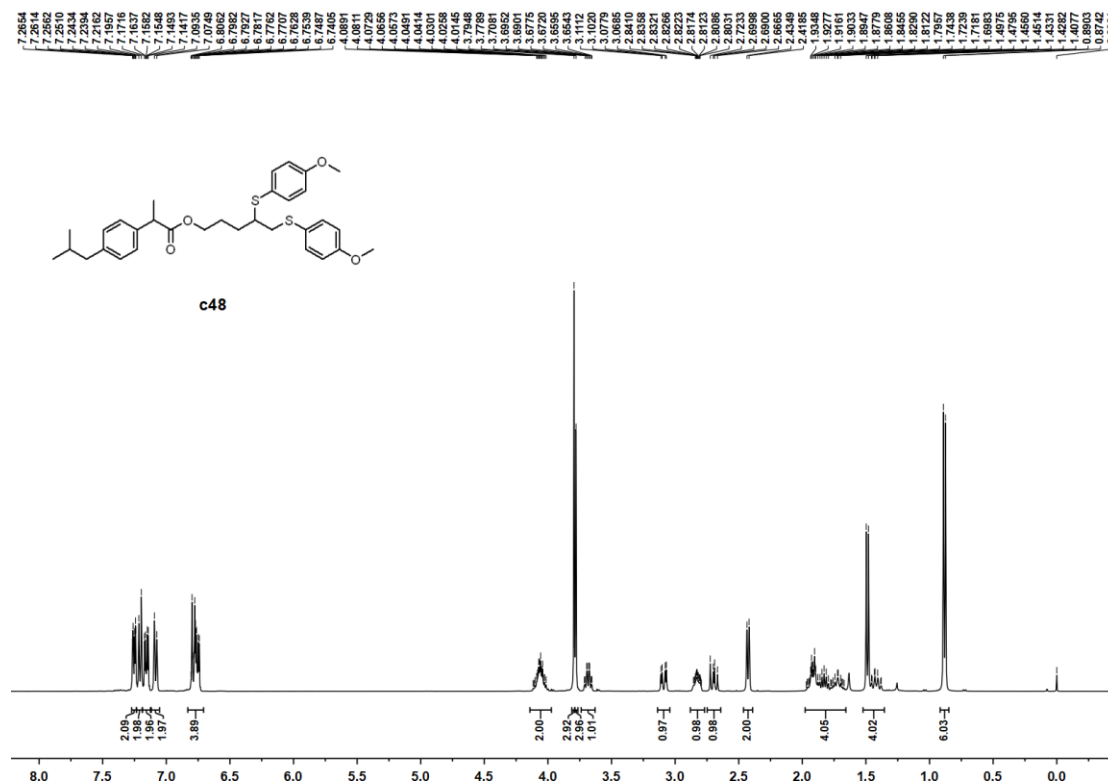
$^1\text{H}$  NMR spectra of compound **c47** in  $\text{CDCl}_3$  (400 MHz):



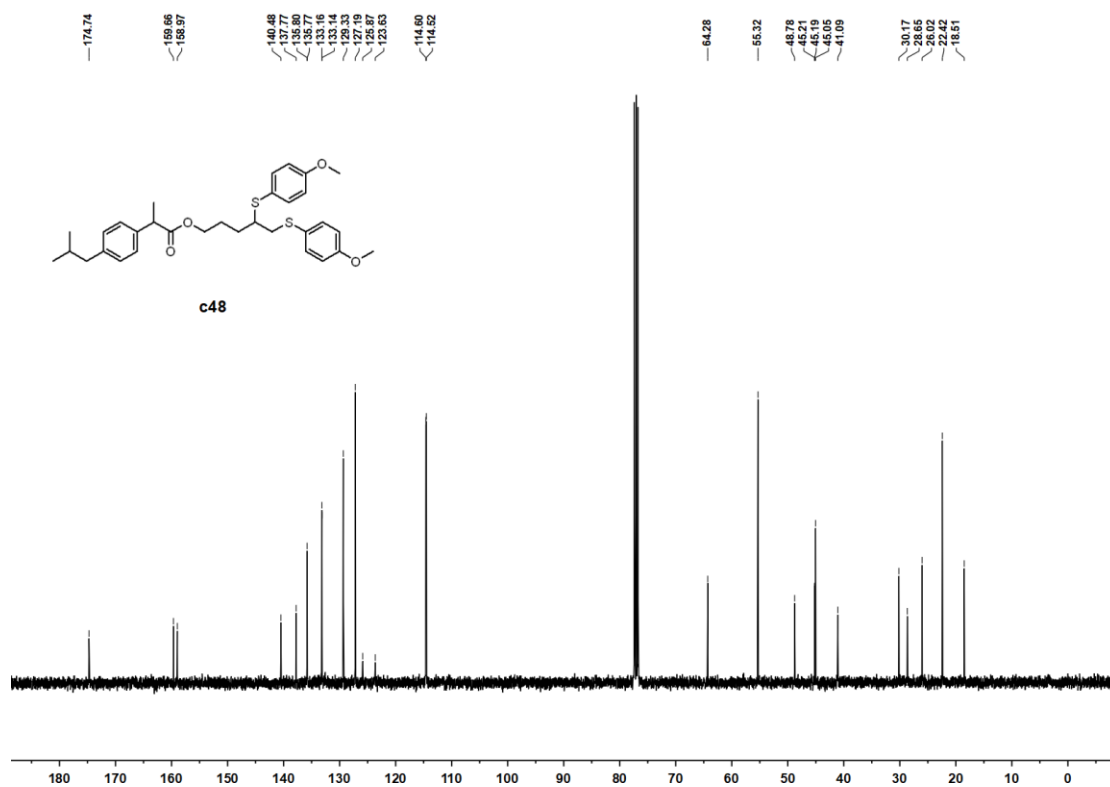
$^{13}\text{C}$  NMR spectra of compound **c47** in  $\text{CDCl}_3$  (101 MHz):



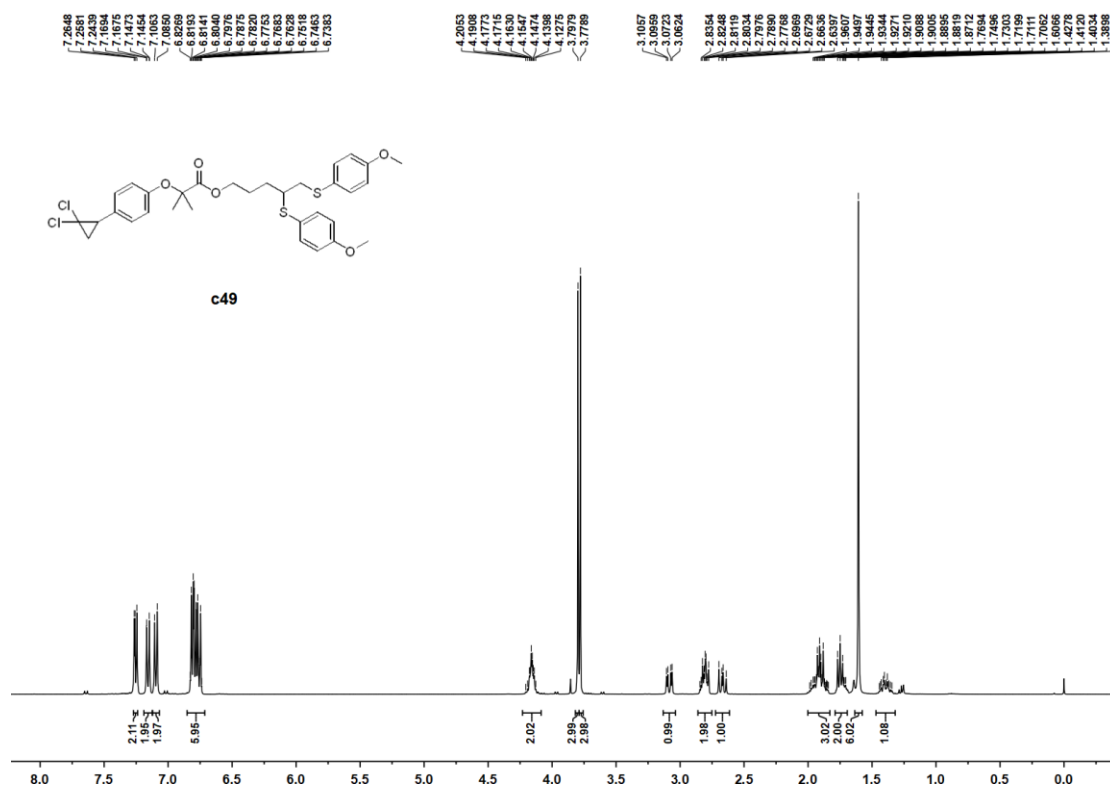
$^1\text{H}$  NMR spectra of compound **c48** in  $\text{CDCl}_3$  (400 MHz):



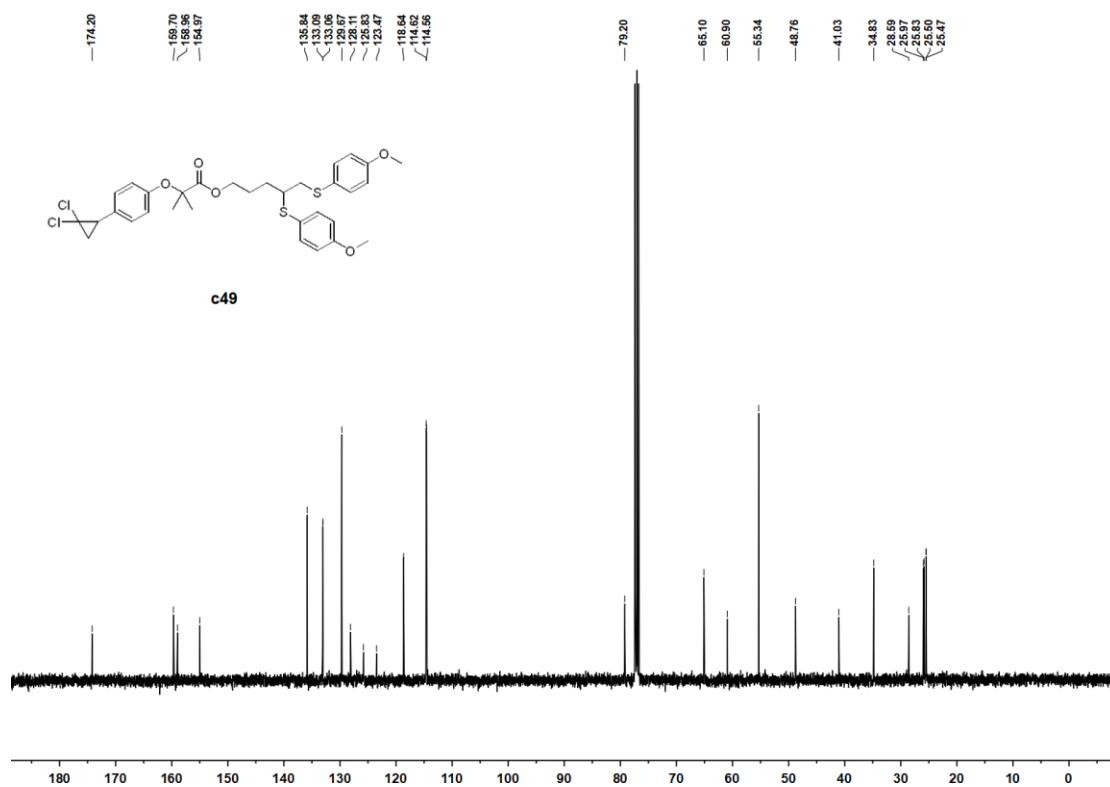
$^{13}\text{C}$  NMR spectra of compound **c48** in  $\text{CDCl}_3$  (101 MHz):



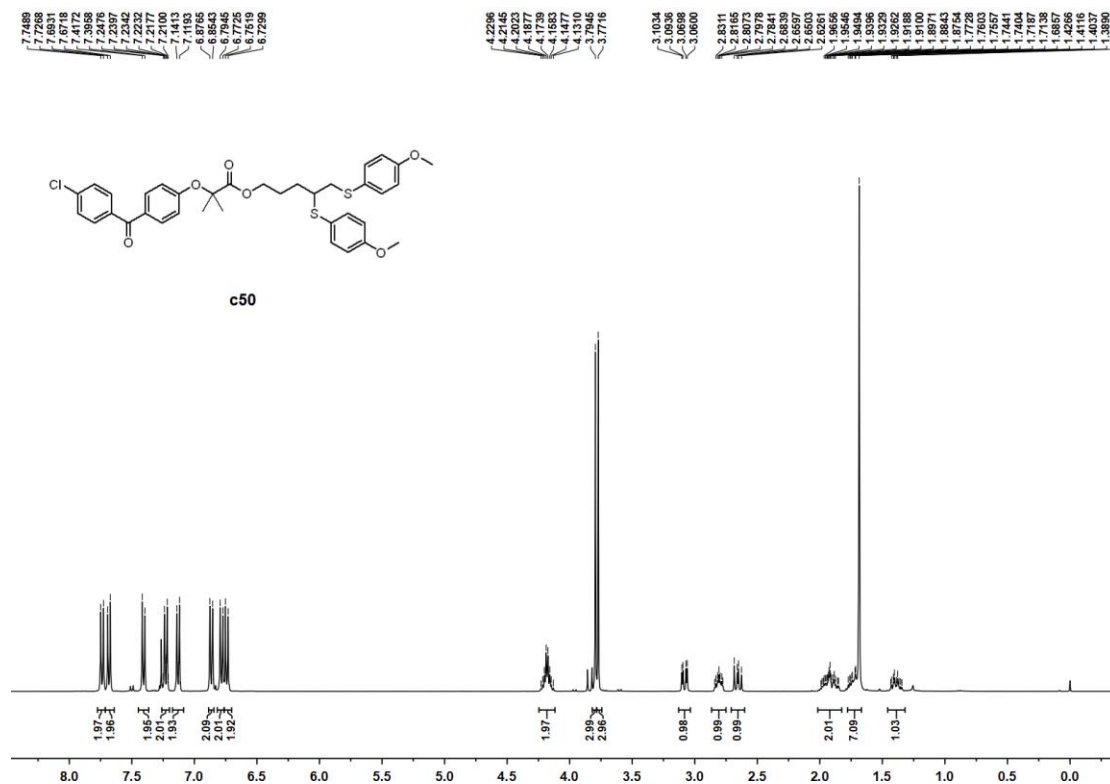
$^1\text{H}$  NMR spectra of compound **c49** in  $\text{CDCl}_3$  (400 MHz):



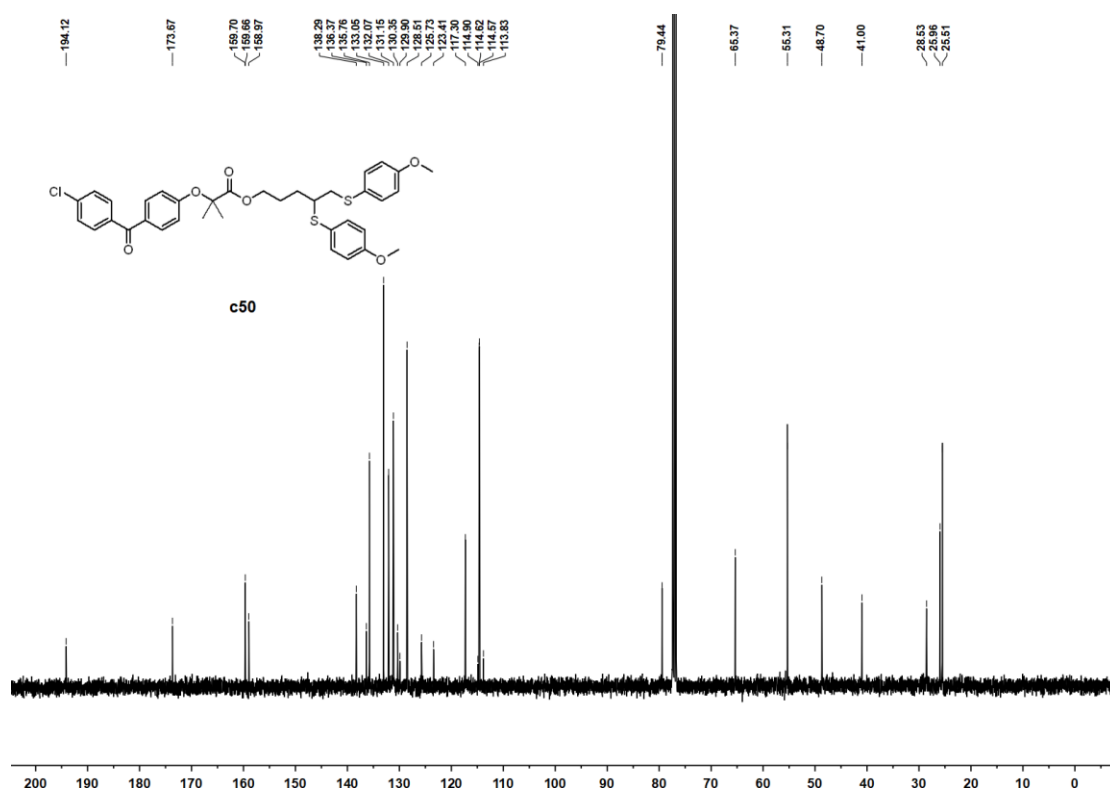
$^{13}\text{C}$  NMR spectra of compound **c49** in  $\text{CDCl}_3$  (101 MHz):



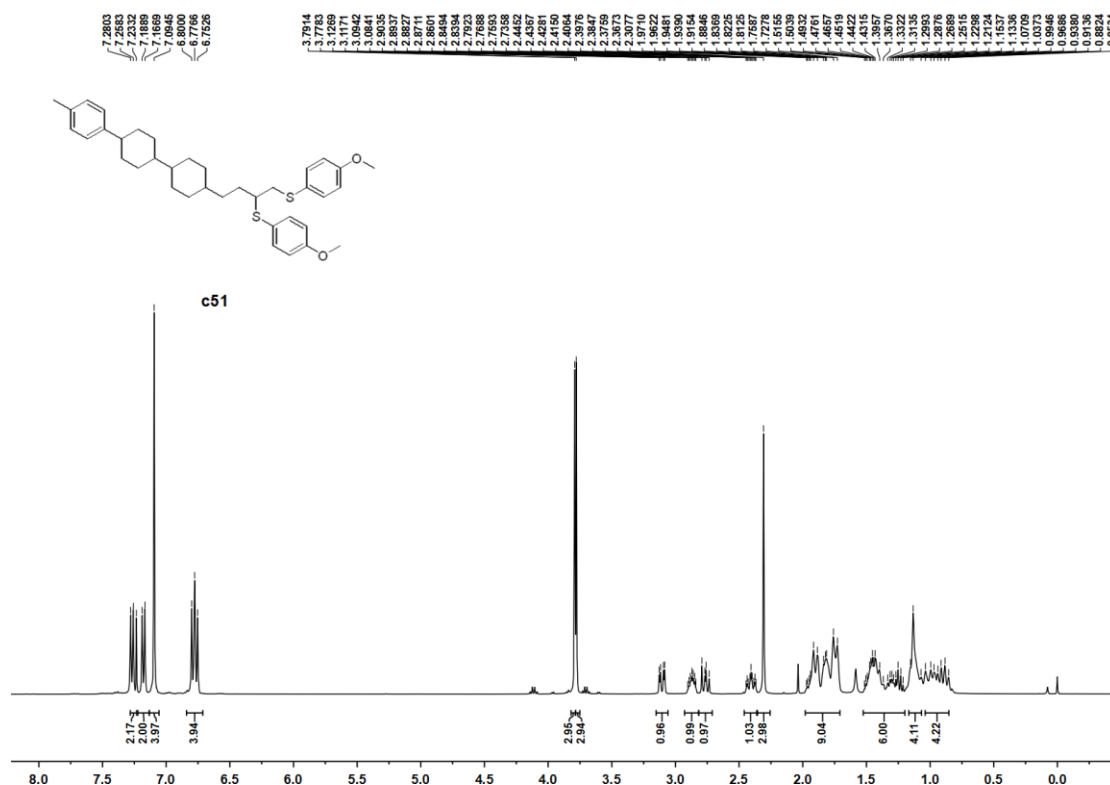
$^1\text{H}$  NMR spectra of compound **c50** in  $\text{CDCl}_3$  (400 MHz):



$^{13}\text{C}$  NMR spectra of compound **c50** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectra of compound **c51** in  $\text{CDCl}_3$  (400 MHz):



$^{13}\text{C}$  NMR spectra of compound **c51** in  $\text{CDCl}_3$  (101 MHz):

