

**Supplementary Information:**

**Efficient and Practical Synthesis of Unsymmetrical Disulfides via Base-Catalyzed Aerobic Oxidative Dehydrogenative Heterocoupling of Thiols**

Xu Qiu, Xiaoxue Yang, Yiqun Zhang, Song Song,\* and Ning Jiao.

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## General Remarks

$\text{Cs}_2\text{CO}_3$  (99.9%) and  $\text{K}_2\text{CO}_3$  (99.9%) were purchased from J&K Scientific and used as received. Other commercially available compounds were purchased from Alfa-Aesar Acros, Sigma-Aldrich, Beijing Chemical Works and J&K Scientific, Ltd. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. All reactions were conducted with test tube.  $^1\text{H}$ -NMR spectra were recorded on a Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were calibrated with  $\text{CDCl}_3$  ( $\delta = 7.26$  ppm).  $^{13}\text{C}$ -NMR spectra were obtained by using the same NMR spectrometers and were calibrated with  $\text{CDCl}_3$  ( $\delta = 77.16$  ppm).  $^{19}\text{F}$ -NMR spectra were obtained by using the same NMR spectrometers and were calibrated with  $\text{CDCl}_3$ . HR-ESIMS spectra were measured on a Fourier Transform Ion Cyclotron Resonance Mass spectrometer (APEX IV, Bruker). HR-EI-MS spectra were recorded on a GCT-MS Micromass UK spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

## General procedure

### Typical procedure for the $\text{K}_2\text{CO}_3$ -catalyzed aerobic CDC reaction of aryl thiols with alkyl thiols

$\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) was added to a 25 mL tube with a magnetic bar, MeCN (1 mL), aryl thiols **1** (0.2 mmol) and alkyl thiols **2** (0.2 mmol) were added and then the mixture was stirred at 30°C under air and monitored by TLC. The solution was diluted with ethyl acetate (10 mL), and evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford product **3**.

### Typical procedure for the $\text{Cs}_2\text{CO}_3$ -catalyzed aerobic CDC reaction of alkyl thiols

$\text{Cs}_2\text{CO}_3$  (0.04 mmol, 13 mg) was added to a 25 mL tube with a magnetic bar. MeCN (1 mL), alkyl thiols **2** (0.2 mmol) and alkyl thiols **2'** (0.2 mmol) were added and then the mixture was stirred at 60°C under air and monitored by TLC. After cooling down to room temperature, the solution was diluted with ethyl acetate (10 mL), and evaporate under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the product **5**.

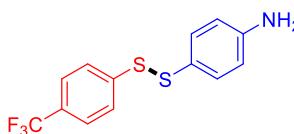
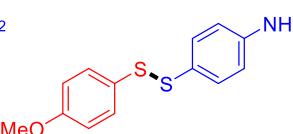
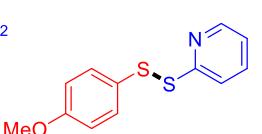
### Typical procedure for the $\text{M}_2\text{CO}_3$ -catalyzed aerobic CDC reaction of thiols

For Aryl thiols:  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) was added to a 25 mL tube with a magnetic bar. MeCN (1 mL) and aryl thiols **1** (0.4 mmol) were added and then the mixture was stirred at 30°C under air and monitored by TLC. The solution was diluted with ethyl acetate (10 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford product **4**.

For Alkyl thiols:  $\text{Cs}_2\text{CO}_3$  (0.08 mmol, 26.1 mg) was added to a 25 mL tube with a magnetic bar, MeCN (1 mL) and alkyl thiols **2** (0.4 mmol) were added and then the mixture was stirred at 60°C under air and monitored by TLC. After cooling down to

room temperature, the solution was diluted with ethyl acetate (10 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford product **6**.

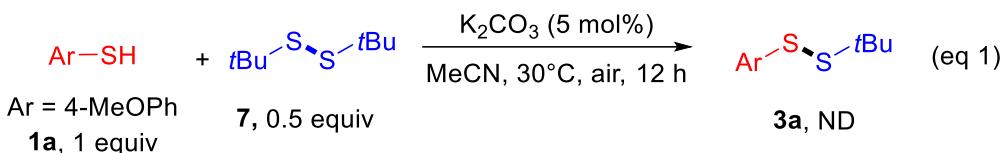
Table S1. The synthesis of unsymmetrical di-aryl disulfides

$\text{Ar}^1\text{-SH}$ 1 (1 equiv)	$\text{Ar}^2\text{-SH}$ 1' (1 equiv)	$\xrightarrow[\text{MeCN, 30 } ^\circ\text{C, air, 3h}]{\text{K}_2\text{CO}_3 \text{ (5 mol\%)}}$	$\text{Ar}^1\text{-S-S-Ar}^2$ 8
			
<b>8a, 60%</b>	<b>8b, 53%</b>	<b>8c, 41%</b>	

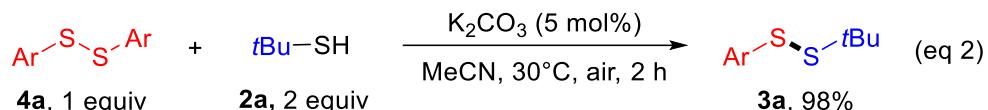
**Typical procedure for the  $\text{K}_2\text{CO}_3$ -catalyzed aerobic CDC reaction of aryl thiols**

$\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) was added to a 25 mL tube with a magnetic bar, MeCN (1 mL), aryl thiols **1** (0.2 mmol) and aryl thiols **1'** (0.2 mmol) were added and then the mixture was stirred at 30°C under air and monitored by TLC. The solution was diluted with ethyl acetate (10 mL), and evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford product **8**.

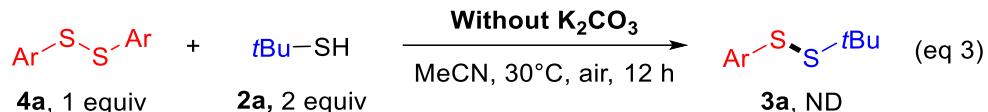
## Mechanism Studies



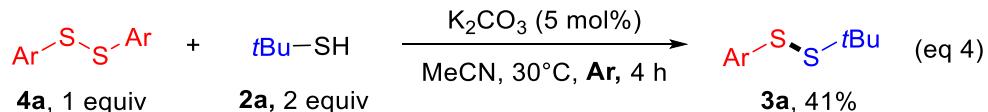
The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), 2-methylpropane-2-thiol **7** (0.1 mmol, 17.8 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 12 h, the desired product **3a** was not detected by  $^1\text{H-NMR}$  and TLC.



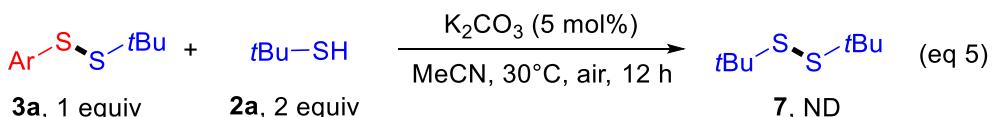
The reaction of 1,2-bis(4-methoxyphenyl)disulfane **4a** (0.1 mmol, 27.8 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 2 h, 98% yield of **3a** was detected by  $^1\text{H-NMR}$  with 1,1,2,2-tetrachloroethane (0.2 mmol, 33.6 mg) as internal standard.



The reaction of 1,2-bis(4-methoxyphenyl)disulfane **4a** (0.1 mmol, 27.8 mg) and 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 12 h, the desired product **3a** was not detected by  $^1\text{H-NMR}$  and TLC.



The reaction of 1,2-bis(4-methoxyphenyl)disulfane **4a** (0.1 mmol, 27.8 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under Ar at 30 °C for 4 h, 41% yield of **3a** was detected by  $^1\text{H-NMR}$  with 1,1,2,2-tetrachloroethane (0.2 mmol, 33.6 mg) as internal standard.

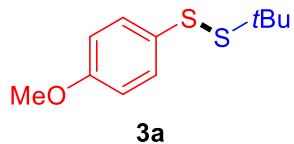


The reaction of 1-(tert-butyl)-2-(4-methoxyphenyl)disulfane **3a** (0.1 mmol, 22.8 mg),

2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 12 h, the desired product **7** was not detected by  $^1\text{H-NMR}$  and TLC.

## Analytical data for products

### **1-(tert-butyl)-2-(4-methoxyphenyl)disulfane (3a)<sup>[1]</sup>**



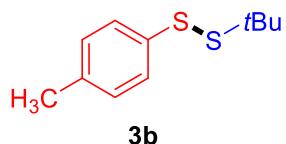
The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 1 h, afforded 42.5 mg (93%) of **3a** as colorless oil.

Gram-scale experiments: The reaction of 4-methoxybenzenethiol **1a** (10 mmol, 1.40 g), 2-methylpropane-2-thiol **2a** (10 mmol, 902 mg), K<sub>2</sub>CO<sub>3</sub> (0.25 mmol, 34.5 mg) in CH<sub>3</sub>CN (10 mL) under air at 30 °C for 8 h, afforded 1.88 g (83%) of **3a** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.51 – 7.47 (m, 2H), 6.86 – 6.82 (m, 2H), 3.79 (s, 3H), 1.29 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 158.9, 130.3, 129.8, 114.4, 55.4, 49.0, 29.9.

### **1-(tert-butyl)-2-(p-tolyl)disulfane (3b)<sup>[1]</sup>**

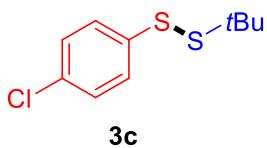


The reaction of 4-methylbenzenethiol **1b** (0.2 mmol, 24.8 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 3 h, afforded 40.0 mg (94%) of **3b** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.46 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 1.31 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 136.3, 135.4, 129.5, 127.4, 49.1, 29.9, 21.0.

### **1-(tert-butyl)-2-(4-chlorophenyl)disulfane (3c)<sup>[1]</sup>**

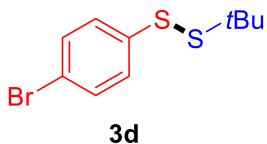


The reaction of 4-chlorobenzenethiol **1c** (0.2 mmol, 28.9 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 8 h, afforded 45.3 mg (97%) of **3c** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.51 – 7.46 (m, 2H), 7.28 – 7.23 (m, 2H), 1.30 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 137.5, 132.1, 128.8, 128.1, 49.4, 29.8.

### 1-(4-bromophenyl)-2-(tert-butyl)disulfane (**3d**)<sup>[1]</sup>

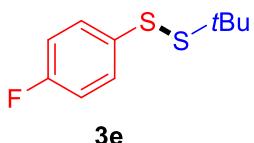


The reaction of 4-bromobenzenethiol **1d** (0.2 mmol, 37.8 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 7 h, afforded 50.1 mg (90%) of **3d** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.46 – 7.37 (m, 4H), 1.30 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2, 131.7, 128.3, 119.9, 49.5, 29.8.

### 1-(tert-butyl)-2-(4-fluorophenyl)disulfane (**3e**)



The reaction of 4-fluorobenzenethiol **1e** (0.2 mmol, 25.6 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 6 h, afforded 31.8 mg (73%) of **3e** as colorless oil.

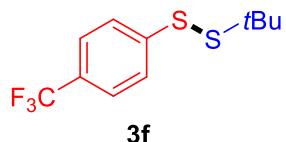
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.57 – 7.49 (m, 2H), 7.03 – 6.95 (m, 2H), 1.30 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  = 161.8 (d,  $^1J_{\text{C-F}} = 246.0$  Hz), 134.0 (d,  $^4J_{\text{C-F}} = 3.2$  Hz), 129.3 (d,  $^3J_{\text{C-F}} = 8.0$  Hz), 115.8 (d,  $^2J_{\text{C-F}} = 22.2$  Hz), 49.3, 29.8.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -116.0.

HRMS (EI) exact mass calc'd for C<sub>10</sub>H<sub>13</sub>S<sub>2</sub>F ([M]<sup>+</sup>): 216.0443; found m/z: 216.0441.

### 1-(tert-butyl)-2-(4-(trifluoromethyl)phenyl)disulfane (3f)



The reaction of 4-(trifluoromethyl)benzenethiol **1f** (0.2 mmol, 35.6 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 36 h, afforded 40.1 mg (75%) of **3f** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.70 – 7.62 (m, 2H), 7.57 – 7.50 (m, 2H), 1.32 (s, 9H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ = 143.9, 128.2 (q, <sup>2</sup>J<sub>C-F</sub> = 32.6 Hz), 126.0, 125.6 (q, <sup>3</sup>J<sub>C-F</sub> = 3.8 Hz), 124.1 (q, <sup>1</sup>J<sub>C-F</sub> = 272.7 Hz), 49.7, 29.8.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -62.3.

HRMS (EI) exact mass calc'd for C<sub>11</sub>H<sub>13</sub>S<sub>2</sub>F<sub>3</sub> ([M]<sup>+</sup>): 266.0411; found m/z: 266.0408.

### 4-(tert-butyldisulfaneyl)phenol (3g)



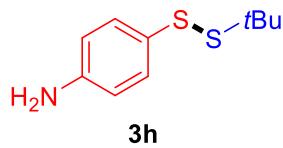
The reaction of 4-mercaptophenol **1g** (0.2 mmol, 25.2 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.21 mmol, 29.0 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 2 h, afforded 41.2 mg (96%) of **3g** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.51 – 7.36 (m, 2H), 6.85 – 6.72 (m, 2H), 5.40 (s, 1H), 1.29 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 154.9, 130.5, 130.0, 116.0, 49.0, 29.9.

HRMS (EI) exact mass calc'd for C<sub>10</sub>H<sub>14</sub>OS<sub>2</sub> ([M]<sup>+</sup>): 214.0486; found m/z: 214.0490.

### 4-(tert-butyldisulfaneyl)aniline (3h)



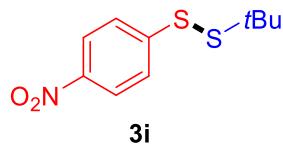
The reaction of 4-aminobenzenethiol **1h** (0.2 mmol, 25.0 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 2 h, afforded 40.9 mg (96%) of **3h** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  = 7.46 – 7.29 (m, 2H), 6.67 – 6.52 (m, 2H), 3.70 (s, 2H), 1.30 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 146.0, 131.4, 126.9, 115.5, 48.8, 30.0.

HRMS (ESI) exact mass calc'd for  $\text{C}_{10}\text{H}_{16}\text{NS}_2$  ( $[\text{M}+\text{H}]^+$ ): 214.0724; found m/z: 214.0715.

### 1-(tert-butyl)-2-(4-nitrophenyl)disulfane (**3i**)<sup>[1]</sup>

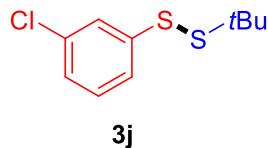


The reaction of 4-nitrobenzenethiol **1i** (0.2 mmol, 31.0 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 12 h, afforded 37.0 mg (76%) of **3i** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  = 8.18 – 8.10 (m, 2H), 7.73 – 7.65 (m, 2H), 1.33 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 148.4, 146.0, 125.8, 123.8, 50.2, 29.8.

### 1-(tert-butyl)-2-(3-chlorophenyl)disulfane (**3j**)

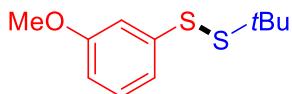


The reaction of 3-chlorobenzenethiol **1j** (0.2 mmol, 28.9 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 5 h, afforded 43.4 mg (93%) of **3j** as white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.56 (t, *J* = 1.9 Hz, 1H), 7.41 – 7.39 (m, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.15 – 7.12 (m, 1H), 1.31 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 141.0, 134.8, 129.7, 126.3, 126.2, 124.5, 49.5, 29.8. HRMS (EI) exact mass calc'd for C<sub>10</sub>H<sub>13</sub>S<sub>2</sub>Cl ([M]<sup>+</sup>): 232.0147; found m/z: 232.0144.

### 1-(tert-butyl)-2-(3-methoxyphenyl)disulfane (3k)



**3k**

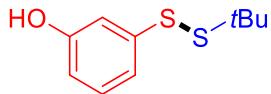
The reaction of 3-methoxybenzenethiol **1k** (0.2 mmol, 28.0 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 2 h, afforded 39.5 mg (87%) of **3k** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.20 (t, *J* = 7.9 Hz, 1H), 7.17 – 7.14 (m, 1H), 7.13 – 7.11 (m, 1H), 6.70 – 6.63 (m, 1H), 3.82 (s, 3H), 1.32 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 159.9, 140.2, 129.5, 118.9, 112.2, 111.8, 55.3, 49.2, 29.9.

HRMS (EI) exact mass calc'd for C<sub>12</sub>H<sub>16</sub>OS<sub>2</sub> ([M]<sup>+</sup>): 228.0643; found m/z: 228.0640.

### 3-(tert-butyldisulfaneyl)phenol (3l)



**3l**

The reaction of 3-mercaptophenol **1l** (0.2 mmol, 25.2 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.21 mmol, 29.0 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 2 h, afforded 38.6 mg (90%) of **3l** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.18 – 7.12 (m, 1H), 7.12 – 7.07 (m, 2H), 6.66 – 6.63 (m, 1H), 5.05 (s, 1H), 1.31 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 155.9, 140.5, 129.8, 119.0, 113.4, 113.3, 49.3, 29.8.

HRMS (EI) exact mass calc'd for C<sub>10</sub>H<sub>14</sub>OS<sub>2</sub> ([M]<sup>+</sup>): 214.0486; found m/z: 214.0488.

**1-(tert-butyl)-2-(2-methoxyphenyl)disulfane (3m)**



**3m**

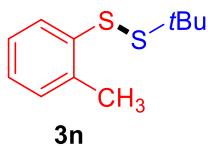
The reaction of 2-methoxybenzenethiol **1m** (0.2 mmol, 28.0 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 2 h, afforded 44.2 mg (97%) of **3m** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.77 (dd, *J* = 7.8 Hz, 1.7 Hz, 1H), 7.18 – 7.14 (m, 1H), 6.99 – 6.94 (m, 1H), 6.83 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H), 3.90 (s, 3H), 1.33 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 156.1, 127.2, 127.1, 126.5, 121.0, 110.5, 55.9, 48.9, 29.9.

HRMS (EI) exact mass calc'd for  $\text{C}_{11}\text{H}_{16}\text{OS}_2$  ( $[\text{M}]^+$ ): 228.0643; found m/z: 228.0645.

**1-(tert-butyl)-2-(o-tolyl)disulfane (3n)<sup>[2]</sup>**



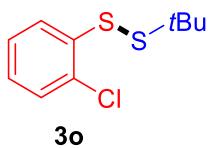
**3n**

The reaction of 2-methylbenzenethiol **1n** (0.2 mmol, 24.8 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 2 h, afforded 35.8 mg (84%) of **3n** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.79 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.21 – 7.10 (m, 1H), 7.15 – 7.07 (m, 2H), 2.45 (s, 3H), 1.32 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 137.2, 135.9, 130.1, 127.2, 126.3, 126.2, 49.1, 29.9, 19.9.

**1-(tert-butyl)-2-(2-chlorophenyl)disulfane (3o)**



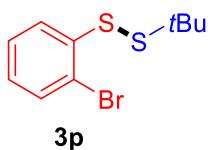
The reaction of 2-chlorobenzenethiol **1o** (0.2 mmol, 28.9 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $K_2CO_3$  (0.01 mmol, 1.4 mg) in  $CH_3CN$  (1 mL) under air at 30 °C for 24 h, afforded 39.7 mg (85%) of **3o** as colorless oil.

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.85 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.30 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.13 – 7.09 (m, 1H), 1.33 (s, 9H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 137.3, 131.3, 129.4, 127.6, 126.9, 49.5, 29.8.

HRMS (EI) exact mass calc'd for  $C_{10}H_{13}S_2Cl$  ( $[M]^+$ ): 232.0147; found m/z: 232.0145.

### 1-(2-bromophenyl)-2-(tert-butyl)disulfane (**3p**)<sup>[2]</sup>

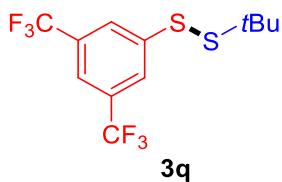


The reaction of 2-bromobenzenethiol **1p** (0.2 mmol, 37.8 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $K_2CO_3$  (0.01 mmol, 1.4 mg) in  $CH_3CN$  (1 mL) under air at 30 °C for 7 h, afforded 50.0 mg (90%) of **3p** as colorless oil.

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.84 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.48 (dd, *J* = 7.9 Hz, 1.3 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.07 – 7.00 (m, 1H), 1.33 (s, 9H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 139.1, 132.6, 127.5, 127.2, 120.8, 49.6, 29.9.

### 1-(3,5-bis(trifluoromethyl)phenyl)-2-(tert-butyl)disulfane (**3q**)



The reaction of 2-bromobenzenethiol **3q** (0.2 mmol, 49.2 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $K_2CO_3$  (0.01 mmol, 1.4 mg) in  $CH_3CN$  (1 mL) under air at 60 °C for 8 h, afforded 48.3 mg (73%) of **3q** as colorless oil.

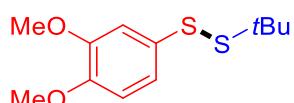
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 8.03 – 8.00 (m, 2H), 7.66 – 7.64 (m, 1H), 1.33 (s, 9H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ = 142.7, 132.1 (q, <sup>2</sup>*J*<sub>C-F</sub>=33.5), 125.8, 123.1 (q, <sup>1</sup>*J*<sub>C-F</sub>= 273.0), 120.7 – 119.6 (m), 50.2, 29.7.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -63.1.

HRMS (EI) exact mass calc'd for C<sub>12</sub>H<sub>12</sub>F<sub>6</sub>S<sub>2</sub> ([M]<sup>+</sup>): 334.0285; found m/z: 334.0283.

**1-(tert-butyl)-2-(3,4-dimethoxyphenyl)disulfane (3r)**



**3r**

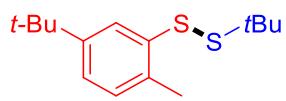
The reaction of 4-methoxy-3-(trifluoromethyl)benzenethiol **1r** (0.2 mmol, 41.6 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 2 h, afforded 50.1 mg (97%) of **3r** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.17 – 7.04 (m, 2H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 1.30 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 149.2, 148.4, 130.1, 120.8, 111.8, 111.4, 56.0, 55.9, 49.0, 29.9.

HRMS (EI) exact mass calc'd for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub> ([M]<sup>+</sup>): 258.0748; found m/z: 258.0750.

**1-(tert-butyl)-2-(5-(tert-butyl)-2-methylphenyl)disulfane (3s)**



**3s**

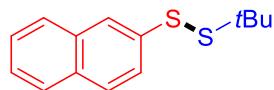
The reaction of 5-(tert-butyl)-2-methylbenzenethiol **1s** (0.2 mmol, 36.6 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 3 h, afforded 51.8 mg (93%) of **3s** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.88 (d, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 7.9 Hz, 2.0 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 2.41 (s, 3H), 1.34 (s, 9H), 1.33 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 149.2, 136.2, 132.9, 129.8, 124.2, 123.1, 48.9, 34.8, 31.4, 30.0, 19.2.

HRMS (EI) exact mass calc'd for C<sub>15</sub>H<sub>24</sub>S<sub>2</sub> ([M]<sup>+</sup>): 268.1319; found m/z: 268.1317.

**1-(tert-butyl)-2-(naphthalen-2-yl)disulfane (3t)<sup>[2]</sup>**



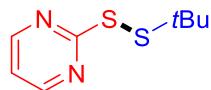
**3t**

The reaction of naphthalene-2-thiol **1t** (0.2 mmol, 36.0 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 5 h, afforded 48.7 mg (98%) of **3t** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 8.03 (d, *J* = 1.9 Hz, 1H), 7.84 – 7.75 (m, 3H), 7.69 (dd, *J* = 8.7 Hz, 1.9 Hz, 1H), 7.58 – 7.36 (m, 2H), 1.35 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 136.2, 133.5, 132.1, 128.5, 127.8, 127.2, 126.6, 125.8, 125.2, 125.1, 49.4, 29.9.

**2-(tert-butyldisulfaneyl)pyrimidine (3u)<sup>[1]</sup>**



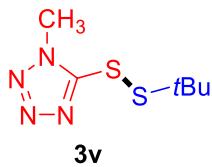
**3u**

The reaction of pyrimidine-2-thiol **1u** (0.2 mmol, 40.0 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 60 °C for 48 h, afforded 30.1 mg (75%) of **3u** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 8.58 (d, *J* = 4.8 Hz, 2H), 7.05 (t, *J* = 4.8 Hz, 1H), 1.34 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 172.3, 157.7, 117.8, 49.1, 29.7.

**5-(tert-butyldisulfaneyl)-1-methyl-1H-tetrazole (3v)<sup>[1]</sup>**

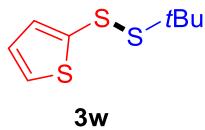


The reaction of 1-methyl-1H-tetrazole-5-thiol **1v** (0.2 mmol, 23.2 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 24 h, afforded 24.6 mg (60%) of **3v** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 4.11 (s, 3H), 1.35 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 153.5, 50.5, 34.6, 29.6.

### 2-(tert-butyldisulfaneyl)thiophene (**3w**)<sup>[3]</sup>



The reaction of thiophene-2-thiol **1w** (0.2 mmol, 23.2 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 2 h, afforded 39.6 mg (97%) of **3w** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.33 (dd, *J* = 5.3 Hz, 1.3 Hz, 1H), 7.21 (dd, *J* = 3.6 Hz, 1.3 Hz, 1H), 6.93 (dd, *J* = 5.3 Hz, 3.6 Hz, 1H), 1.37 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 139.3, 132.6, 129.5, 127.3, 49.0, 30.0.

### 2-(tert-butyldisulfaneyl)pyridine (**3x**)<sup>[1]</sup>

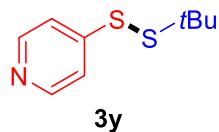


The reaction of pyridine-2-thiol **1x** (0.2 mmol, 22.2 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 24 h, afforded 16.0 mg (40%) of **3x** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 8.44 – 8.41 (m, 1H), 7.80 – 7.77 (m, 1H), 7.63 – 7.59 (m, 1H), 7.06 – 7.02 (m, 1H), 1.33 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 161.7, 149.2, 136.8, 120.3, 119.6, 49.3, 29.8.

**4-(tert-butyldisulfaneyl)pyridine (3y)<sup>[2]</sup>**

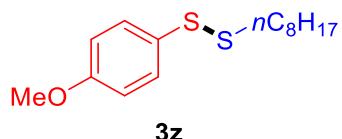


The reaction of pyridine-4-thiol **1y** (0.2 mmol, 22.2 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 24 h, afforded 19.4 mg (49%) of **3y** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 8.45 – 8.43 (m, 2H), 7.49 – 7.46 (m, 2H), 1.32 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 150.3, 149.3, 120.1, 49.8, 29.8.

**1-(4-methoxyphenyl)-2-octyldisulfane (3z)<sup>[4]</sup>**

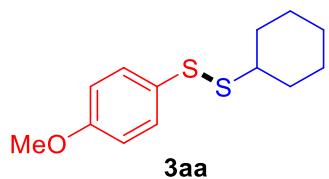


The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), octane-1-thiol **2b** (0.3 mmol, 43.8 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 2 h, afforded 43.4 mg (71%) of **3z** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.51 – 7.44 (m, 2H), 6.89 – 6.82 (m, 2H), 3.80 (d, *J* = 1.6 Hz, 3H), 2.73 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.34 – 1.20 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 159.5, 131.6, 128.6, 114.6, 55.4, 38.9, 31.8, 29.1, 28.7, 28.5, 22.6, 14.1.

**1-cyclohexyl-2-(4-methoxyphenyl)disulfane (3aa)<sup>[5]</sup>**



The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), cyclohexanethiol **2c** (0.3 mmol, 34.9 mg),  $K_2CO_3$  (0.01 mmol, 1.4 mg) in  $CH_3CN$  (1 mL) under air at 30 °C for 2 h, afforded 40.4 mg (71%) of **3aa** as colorless oil.

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.54 – 7.40 (m, 2H), 6.91 – 6.83 (m, 2H), 3.80 (s, 3H), 2.81 – 2.79 (m, 1H), 2.07 – 1.97 (m, 2H), 1.82 – 1.70 (m, 2H), 1.47 – 1.08 (m, 6H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 159.1, 130.7, 129.4, 114.5, 55.4, 49.7, 32.6, 26.0, 25.7.

### **1-benzyl-2-(4-methoxyphenyl)disulfane (**3ab**)<sup>[6]</sup>**

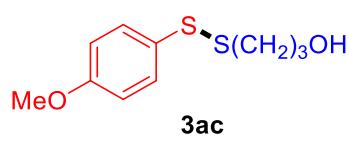


The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), phenylmethanethiol **2d** (0.2 mmol, 24.8 mg),  $K_2CO_3$  (0.01 mmol, 1.4 mg) in  $CH_3CN$  (1 mL) under air at 30 °C for 2 h, afforded 25.4 mg (48%) of **3ab** as white solid.

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.55 – 7.37 (m, 2H), 7.34 – 7.24 (m, 5H), 6.91 – 6.69 (m, 2H), 3.97 (s, 2H), 3.83 (s, 3H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 159.6, 136.8, 132.0, 129.4, 128.5, 128.0, 127.5, 114.6, 55.4, 43.3.

### **3-((4-methoxyphenyl)disulfaneyl)propan-1-ol (**3ac**)**



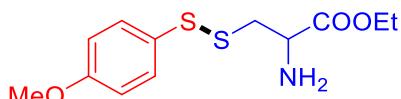
The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), 3-mercaptopropan-1-ol **2e** (0.3 mmol, 27.7 mg),  $K_2CO_3$  (0.01 mmol, 1.4 mg) in  $CH_3CN$  (1 mL) under air at 30 °C for 2 h, afforded 30.8 mg (67%) of **3ac** as colorless oil.

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.52 – 7.45 (m, 2H), 6.90 – 6.82 (m, 2H), 3.80 (s, 3H), 3.71 (t,  $J$ =6.1, 2H), 2.84 (t,  $J$ =7.1, 2H), 2.00 – 1.90 (m, 2H), 1.43 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.7, 132.0, 128.2, 114.7, 61.1, 55.4, 35.0, 31.4.

HRMS (EI) exact mass calc'd for  $\text{C}_{10}\text{H}_{14}\text{O}_2\text{S}_2$  ( $[\text{M}]^+$ ): 230.0435; found m/z: 230.0432.

### ethyl S-((4-methoxyphenyl)thio)cysteinate (3ad)



**3ad**

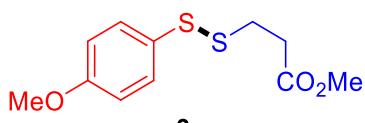
The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), L-Cysteine ethyl ester hydrochloride **2f** (0.3 mmol, 55.7 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 2 h, afforded 29.7 mg (52%) of **3ad** as colorless iol.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.49 (d,  $J$  = 8.8 Hz, 2H), 6.86 (d,  $J$  = 8.8 Hz, 2H), 4.18 (q,  $J$  = 7.1 Hz, 2H), 3.81 – 3.78 (m, 4H), 3.14 (dd,  $J$  = 13.6 Hz, 4.4 Hz, 1H), 2.87 (dd,  $J$  = 13.6 Hz, 8.1 Hz, 1H), 1.68 (s, 2H), 1.27 (t,  $J$  = 7.1 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 173.7, 160.0, 132.6, 127.6, 114.8, 61.3, 55.4, 53.4, 43.6, 14.2.

HRMS (ESI) exact mass calc'd for  $\text{C}_{12}\text{H}_{18}\text{NO}_3\text{S}_2$  ( $[\text{M}+\text{H}]^+$ ): 288.0728; found m/z: 288.0730.

### methyl 3-((4-methoxyphenyl)disulfaneyl)propanoate (3ae)



**3ae**

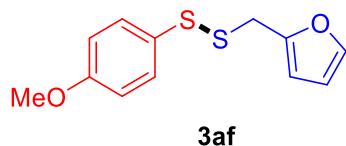
The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), methyl 3-mercaptopropanoate **2g** (0.3 mmol, 36.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 2 h, afforded 34.7 mg (67%) of **3ae** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.51 – 7.43 (m, 2H), 6.94 – 6.83 (m, 2H), 3.80 (s, 3H), 3.68 (s, 3H), 2.95 (t,  $J$  = 7.3 Hz, 2H), 2.74 (t,  $J$  = 7.3 Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 172.2, 159.8, 132.0, 127.8, 114.8, 55.4, 51.8, 33.6, 33.0.

HRMS (EI) exact mass calc'd for  $\text{C}_{11}\text{H}_{14}\text{O}_3\text{S}_2$  ( $[\text{M}]^+$ ): 258.0384 ; found m/z: 258.0380.

**2-(((4-methoxyphenyl)disulfaneyl)methyl)furan (3af)**



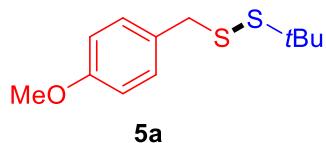
The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), furan-2-ylmethanethiol **2h** (0.2 mmol, 22.8 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 2 h, afforded 30.4 mg (60%) of **3af** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.42 – 7.35 (m, 2H), 7.32 (dd,  $J$  = 2.0 Hz, 0.9 Hz, 1H), 6.89 – 6.77 (m, 2H), 6.35 – 6.19 (m, 2H), 3.95 (s, 2H), 3.80 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.6, 150.1, 142.5, 131.9, 127.8, 114.6, 110.6, 109.1, 55.4, 35.5.

HRMS (ESI) exact mass calc'd for  $\text{C}_{12}\text{H}_{13}\text{O}_2\text{S}_2$  ( $[\text{M}+\text{H}]^+$ ): 253.0357; found m/z: 253.0351.

**1-(tert-butyl)-2-(4-methoxybenzyl)disulfane (5a)**



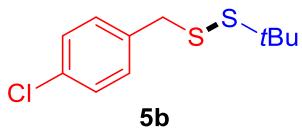
The reaction of 4-methoxyphenylmethanethiol **2i** (0.2 mmol, 30.8 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{Cs}_2\text{CO}_3$  (0.04 mmol, 13.0 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 60 °C for 8 h, afforded 46.1 mg (95%) of **5a** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.24 (d,  $J$  = 8.6 Hz, 2H), 6.86 (d,  $J$  = 8.6 Hz, 2H), 3.91 (s, 2H), 3.80 (s, 3H), 1.35(s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.0, 130.4, 129.4, 114.0, 55.3, 48.0, 45.2, 30.1.

HRMS (EI) exact mass calc'd for  $\text{C}_{12}\text{H}_{18}\text{OS}_2$  ( $[\text{M}]^+$ ): 242.0799; found m/z: 242.0796.

**1-(tert-butyl)-2-(4-chlorobenzyl)disulfane (5b)**



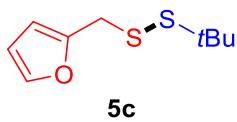
The reaction of 4-chlorophenylmethanethiol **2j** (0.2 mmol, 31.7 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{Cs}_2\text{CO}_3$  (0.04 mmol, 13.0 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 60 °C for 8 h, afforded 46.0 mg (93%) of **5b** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.32 – 7.27 (m, 2H), 7.26 – 7.20 (m, 2H), 3.88 (s, 2H), 1.34 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 136.0, 133.2, 130.6, 128.7, 48.2, 44.8, 30.0.

HRMS (EI) exact mass calc'd for  $\text{C}_{11}\text{H}_{15}\text{S}_2\text{Cl}$  ( $[\text{M}]^+$ ): 246.0304; found m/z: 246.0307.

### 2-((tert-butyldisulfaneyl)methyl)furan (5c)



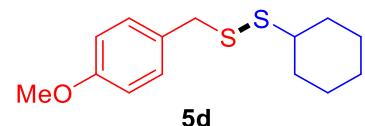
The reaction of furan-2-ylmethanethiol **2h** (0.2 mmol, 22.8 mg), 2-methylpropane-2-thiol **2a** (0.2 mmol, 18.0 mg),  $\text{Cs}_2\text{CO}_3$  (0.04 mmol, 13.0 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 60 °C for 8 h, afforded 36.4 mg (90%) of **5c** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.37 (dd,  $J$  = 1.9 Hz, 0.9 Hz, 1H), 6.31 (dd,  $J$  = 3.3 Hz, 1.9 Hz, 1H), 6.26 – 6.22 (m, 1H), 3.94 (s, 2H), 1.32 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 150.7, 142.4, 110.6, 108.5, 48.1, 37.8, 29.9.

HRMS (ESI) exact mass calc'd for  $\text{C}_9\text{H}_{15}\text{OS}_2$  ( $[\text{M}+\text{H}]^+$ ): 203.0564; found m/z: 203.0569.

### 1-cyclohexyl-2-(4-methoxybenzyl)disulfane (5d)



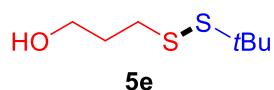
The reaction of 4-methoxyphenylmethanethiol **2i** (0.2 mmol, 30.8 mg), cyclohexanethiol **2c** (0.2 mmol, 23.2 mg),  $\text{Cs}_2\text{CO}_3$  (0.04 mmol, 13.0 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 60 °C for 8 h, afforded 22.0 mg (41%) of **5d** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.26 – 7.20 (m, 2H), 6.88 – 6.82 (m, 2H), 3.86 (s, 2H), 3.80 (s, 3H), 2.47-2.43 (m, 1H), 1.99-1.93 (m, 2H), 1.80 – 1.70 (m, 2H), 1.35 – 1.16 (m, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 159.0, 130.4, 129.6, 113.9, 55.3, 49.4, 44.2, 32.8, 26.1, 25.6.

HRMS (EI) exact mass calc'd for C<sub>14</sub>H<sub>20</sub>OS<sub>2</sub> ([M]<sup>+</sup>): 268.0956; found m/z: 268.0956.

### 3-(tert-butyldisulfaneyl)propan-1-ol (**5e**)



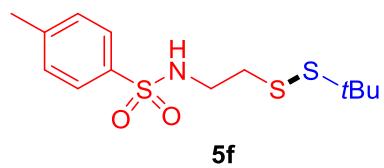
The reaction of 3-mercaptopropan-1-ol **2e** (0.2 mmol, 18.4 mg), 2-methylpropane-2-thiol **2c** (0.2 mmol, 18.0 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.04 mmol, 13.0 mg) in CH<sub>3</sub>CN (1 mL) under air at 60 °C for 8 h, afforded 22.7 mg (63%) of **5e** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  = 3.75 (t, *J* = 6.1 Hz, 2H), 2.81 (t, *J* = 7.1 Hz, 2H), 1.93 (tt, *J* = 7.1 Hz, 6.1 Hz, 2H), 1.53 (s, 1H), 1.33 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 61.1, 47.9, 37.0, 32.0, 30.0.

HRMS (ESI) exact mass calc'd for C<sub>7</sub>H<sub>17</sub>OS<sub>2</sub> ([M+H]<sup>+</sup>): 181.0721; found m/z: 181.0713.

### N-(2-(tert-butyldisulfaneyl)ethyl)-4-methylbenzenesulfonamide (**5f**)



The reaction of 2-aminoethane-1-thiol **2k** (0.2 mmol, 15.4 mg), 2-methylpropane-2-thiol **2c** (0.2 mmol, 18.0 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.04 mmol, 13.0 mg) in CH<sub>3</sub>CN (1 mL) under air at 60 °C for 8 h, after cooling to room temperature, Tosyl chloride (0.4 mmol, 76.3 mg) was added and stirred for 2 hours at room temperature, the solution was diluted with ethyl acetate (10 mL), and evaporate under vacuum. The crude reaction mixture

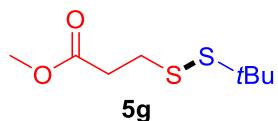
was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afforded 36.1 mg (57%) of **5f** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.79 – 7.70 (m, 2H), 7.35 – 7.28 (m, 2H), 4.97 (t, *J* = 6.2 Hz, 1H), 3.26 (td, *J* = 6.2 Hz, 6.4 Hz, 2H), 2.70 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 1.27 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 143.6, 136.9, 129.8, 127.1, 48.2, 41.8, 39.1, 29.8, 21.5.

HRMS (ESI) exact mass calc'd for C<sub>13</sub>H<sub>22</sub>NO<sub>2</sub>S<sub>3</sub> ([M+H]<sup>+</sup>): 320.0813; found m/z: 320.0802.

### **methyl 3-(tert-butyldisulfaneyl)propanoate (5g)**



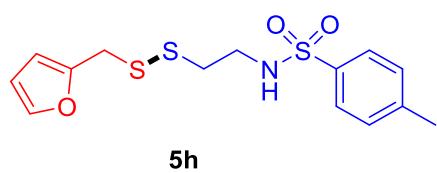
The reaction of methyl 3-mercaptopropanoate **2g** (0.2 mmol, 24.0 mg), 2-methylpropane-2-thiol **2c** (0.2 mmol, 18.0 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.04 mmol, 13.0 mg) in CH<sub>3</sub>CN (1 mL) under air at 60 °C for 8 h, afforded 26.0 mg (63%) of **5g** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  = 3.69 (s, 3H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 1.33 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.3, 51.8, 48.0, 34.9, 34.1, 29.9.

HRMS (EI) exact mass calc'd for C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub> ([M]+): 208.0592; found m/z: 208.0589.

### **N-(2-((furan-2-ylmethyl)disulfaneyl)ethyl)-4-methylbenzenesulfonamide (5h)**



The reaction of furan-2-ylmethanethiol **2h** (0.2 mmol, 22.8 mg), 2-aminoethane-1-thiol **2k** (0.2 mmol, 15.4 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.04 mmol, 13.0 mg) in CH<sub>3</sub>CN (1 mL) under air at

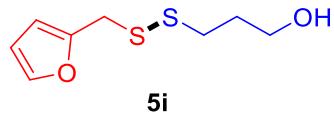
60 °C for 8 h, after cooling to room temperature, Tosyl chloride (0.4 mmol, 76.3 mg) was added and stirred for 2 hours at room temperature, the solution was diluted with ethyl acetate (10 mL), and evaporate under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afforded 34.2 mg (50%) of **5h** as white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.74 (d, *J* = 8.2 Hz, 2H), 7.35 (dd, *J* = 1.9 Hz, 0.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.31 (dd, *J* = 3.2 Hz, 1.9 Hz, 1H), 6.24 (dd, *J* = 3.2 Hz, 0.8 Hz, 1H), 4.88 (t, *J* = 6.2 Hz, 1H), 3.81 (s, 2H), 3.16 (t, *J* = 6.2 Hz, 2H), 2.45 – 2.40 (m, 5H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 149.9, 143.6, 142.6, 136.9, 129.8, 127.1, 110.9, 109.2, 41.3, 37.5, 35.5, 21.5.

HRMS (ESI) exact mass calc'd for C<sub>14</sub>H<sub>18</sub>NO<sub>3</sub>S<sub>3</sub> ([M+H]<sup>+</sup>): 344.0449; found m/z: 344.0442.

### 3-((furan-2-ylmethyl)disulfaneyl)propan-1-ol (**5i**)



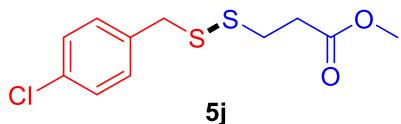
The reaction of furan-2-ylmethanethiol **2h** (0.2 mmol, 22.8 mg), 3-mercaptopropan-1-ol **2e** (0.2 mmol, 18.4 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.04 mmol, 13.0 mg) in CH<sub>3</sub>CN (1 mL) under air at 60 °C for 8 h, afforded 19.0 mg (47%) of **5i** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.39 (dd, *J* = 1.9 Hz, 0.9 Hz, 1H), 6.33 (dd, *J* = 3.3 Hz, 1.9 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 3.90 (s, 2H), 3.69 (t, *J* = 5.0 Hz, 2H), 2.53 (t, *J* = 7.1 Hz, 2H), 1.88 – 1.82 (m, 2H), 1.46 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 150.4, 142.5, 110.8, 108.9, 61.1, 35.9, 34.9, 31.7.

HRMS (ESI) exact mass calc'd for C<sub>8</sub>H<sub>13</sub>O<sub>2</sub>S<sub>2</sub> ([M+H]<sup>+</sup>): 205.0357; found m/z: 205.0348.

### methyl 3-((4-chlorobenzyl)disulfaneyl)propanoate (**5j**)

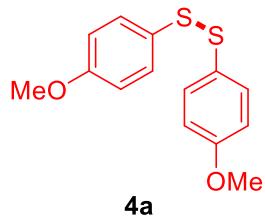


The reaction of (4-chlorophenyl)methanethiol **2j** (0.2 mmol, 31.7 mg), methyl 3-mercaptopropanoate **2g** (0.2 mmol, 24.0 mg),  $\text{Cs}_2\text{CO}_3$  (0.04 mmol, 13.0 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 60 °C for 8 h, afforded 19.5 mg (44%) of **5j** as white solid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.30 (d,  $J$  = 8.6 Hz, 2H), 7.25 (d,  $J$  = 8.5 Hz, 2H), 3.85 (s, 2H), 3.69 (s, 3H), 2.67 (t,  $J$  = 6.4 Hz, 2H), 2.63 (t,  $J$  = 6.4 Hz, 2H).  
 $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 172.1, 135.9, 133.4, 130.6, 128.7, 51.9, 42.7, 33.8, 32.9.

HRMS (ESI) exact mass calc'd for  $\text{C}_{11}\text{H}_{14}\text{ClO}_2\text{S}_2$  ( $[\text{M}+\text{H}]^+$ ): 277.0124; found m/z: 277.115.

### 1,2-bis(4-methoxyphenyl)disulfane (**4a**)<sup>[7]</sup>



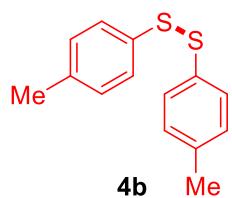
The reaction of 4-methoxybenzenethiol **1a** (0.4 mmol, 56.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 5 h, afforded 54.0 mg (97%) of **4a** as yellow solid.

Gram-scale experiments: The reaction of 4-methoxybenzenethiol **1a** (20 mmol, 2.80 g),  $\text{K}_2\text{CO}_3$  (0.5 mmol, 69 mg) in  $\text{CH}_3\text{CN}$  (10 mL) under air at 30 °C for 8 h, afforded 2.76 g (99%) of **4a**.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.41 (d,  $J$  = 8.8 Hz, 4H), 6.84 (d,  $J$  = 8.8 Hz, 4H), 3.80 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.9, 132.7, 128.5, 114.7, 55.4.

### 1,2-di-p-tolyldisulfane (**4b**)<sup>[7]</sup>

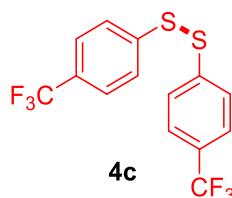


The reaction of 4-methylbenzenethiol **1b** (0.4 mmol, 49.7 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 1 h, afforded 48.8mg (99%) of **4b** as white solid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.40 (d,  $J$  = 8.1 Hz, 4H), 7.12 (d,  $J$  = 8.1 Hz, 4H), 2.34 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  = 137.5, 134.0, 129.8, 128.6, 21.1.

### 1,2-bis(4-(trifluoromethyl)phenyl)disulfane (**4c**)<sup>[7]</sup>



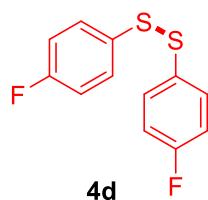
The reaction 4-(trifluoromethyl)benzenethiol **1f** (0.4 mmol, 71.3 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 12 h, afforded 51.8 mg (93%) of **4c** as white solid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.63 – 7.53 (m, 8H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  = 140.8, 129.4 (q,  $^2J_{\text{C-F}}=32.9$  Hz), 126.6, 126.1 (q,  $J$  = 3.8 Hz), 123.8 (q,  $^1J_{\text{C-F}}=272.0$  Hz).

$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  = -62.6.

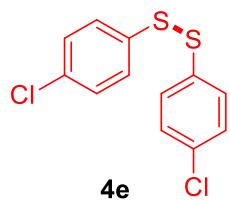
### 1,2-bis(4-fluorophenyl)disulfane (**4d**)<sup>[8]</sup>



The reaction 4-fluorobenzenethiol **1f** (0.4 mmol, 51.3 mg),  $K_2CO_3$  (0.01 mmol, 1.4 mg) in  $CH_3CN$  (1 mL) under air at 30 °C for 8 h, afforded 44.3 mg (87%) of **4c** as colorless oil.

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.50 – 7.40 (m, 4H), 7.06 – 6.96 (m, 4H).  
 $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  = 162.6 (d,  $^1J_{C-F}$ =248.1 Hz), 132.2 (d,  $^4J_{C-F}$ =3.3 Hz), 131.3 (d,  $^3J_{C-F}$ =8.4 Hz), 116.3 (d,  $^2J_{C-F}$ =22.2 Hz).  
 $^{19}F$  NMR (376 MHz, Chloroform-*d*)  $\delta$  = -113.5 (s, 2).

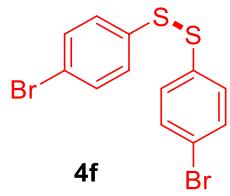
### 1,2-bis(4-chlorophenyl)disulfane (**4e**) <sup>[7]</sup>



The reaction 4-chlorobenzenethiol **1e** (0.4 mmol, 57.8 mg),  $K_2CO_3$  (0.01 mmol, 1.4 mg) in  $CH_3CN$  (1 mL) under air at 30 °C for 8 h, afforded 55.7 mg (97%) of **4e** as white solid.

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.45 – 7.36 (m, 4H), 7.31 – 7.23 (m, 4H).  
 $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 135.2, 133.7, 129.4, 129.3.

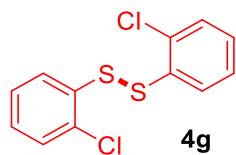
### 1,2-bis(4-bromophenyl)disulfane(**4f**) <sup>[8]</sup>



The reaction 4-bromobenzenethiol **1d** (0.4 mmol, 75.6 mg),  $K_2CO_3$  (0.01 mmol, 1.4 mg) in  $CH_3CN$  (1 mL) under air at 30 °C for 8 h, afforded 73.8 mg (98%) of **4f** as light yellow solid.

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.46 – 7.39 (m, 4H), 7.37 – 7.30 (m, 4H).  
 $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 135.8, 132.3, 129.4, 121.6.

### 1,2-bis(2-chlorophenyl)disulfane (**4g**)<sup>[7]</sup>

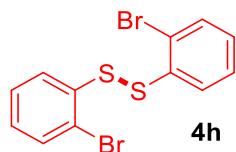


The reaction 2-chlorobenzenethiol **1o** (0.4 mmol, 57.8 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 12 h, afforded 54.1 mg (94%) of **4g** as white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.54 (dd, *J* = 7.9 Hz, 1.4 Hz, 4H), 7.27 – 7.25(m, 2H), 7.12 – 7.04 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 136.2, 132.9, 128.2, 128.0, 127.0, 121.1.

### 1,2-bis(2-bromophenyl)disulfane (**4h**)<sup>[9]</sup>

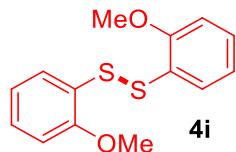


The reaction 2-bromobenzenethiol **1p** (0.4 mmol, 75.6 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 4 h, afforded 70.2 mg (93%) of **4h** as white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.57 (dd, *J* = 7.9 Hz, 1.7 Hz, 2H), 7.37 (dd, *J* = 7.9 Hz, 1.5 Hz, 2H), 7.18 – 7.14(m, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 134.4, 131.9, 129.7, 127.8, 127.6, 127.2.

### 1,2-bis(2-methoxyphenyl)disulfane (**4i**)<sup>[7]</sup>

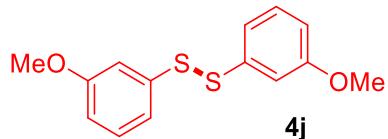


The reaction 2-methoxybenzenethiol **1m** (0.4 mmol, 56.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 4 h, afforded 55.2 mg (99%) of **4i** as white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.55 (dd, *J* = 7.8 Hz, 1.6 Hz, 2H), 7.22 – 7.18 (m, 2H), 6.94 – 6.92 (m, 2H), 6.86 (dd, *J* = 8.1 Hz, 1.1 Hz, 2H), 3.90 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 156.6, 127.8, 127.6, 124.6, 121.4, 110.6, 55.9.

**1,2-bis(3-methoxyphenyl)disulfane (4j)** <sup>[7]</sup>

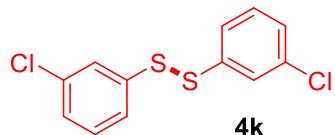


The reaction 3-methoxybenzenethiol **1k** (0.4 mmol, 56.0 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 4 h, afforded 51.0 mg (92%) of **4j** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.22 (dd, *J* = 8.6 Hz, 7.4 Hz, 2H), 7.12 – 7.05 (m, 4H), 6.80 – 6.74 (m, 2H), 3.77 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 160.1, 138.3, 129.9, 119.6, 113.2, 112.6, 55.3.

**1,2-bis(3-chlorophenyl)disulfane (4k)** <sup>[10]</sup>

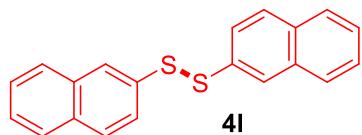


The reaction 3-chlorobzenethiol **1j** (0.4 mmol, 57.8 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 18 h, afforded 53.3 mg (93%) of **4k** as light yellow solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.48 (t, *J* = 1.7 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.28 – 7.17 (m, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.4, 135.1, 130.2, 127.6, 127.0, 125.4.

**1,2-di(naphthalen-2-yl)disulfane (4l)** <sup>[8]</sup>



The reaction naphthalene-2-thiol **1t** (0.4 mmol, 64.1 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 5 h, afforded 63.2mg (99%) of **4l** as light yellow solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 8.01 (d, *J* = 1.9 Hz, 2H), 7.80 (dd, *J* = 9.1 Hz, 3.0 Hz, 4H), 7.77 – 7.71 (m, 2H), 7.64 (dd, *J* = 8.7 Hz, 2.0 Hz, 2H), 7.51 – 7.42 (m, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 134.3, 133.5, 132.5, 129.0, 127.8, 127.5, 126.8, 126.6, 126.3, 125.7.

**1,2-di(pyridin-2-yl)disulfane (4m)** <sup>[9]</sup>

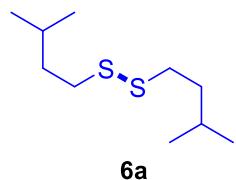


The reaction pyridine-2-thiol **1x** (0.4 mmol, 44.5 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.08 mmol, 26.1 mg) in CH<sub>3</sub>CN (1 mL) under air at 60 °C for 24 h, afforded 37.6 mg (85%) of **4l** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 8.45 (d, *J* = 4.8 Hz, 2H), 7.59 (d, *J* = 5.9 Hz, 4H), 7.14 – 7.01 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 159.0, 149.6, 137.4, 121.1, 119.7.

**1,2-diisopentyldisulfane (6a)** <sup>[11]</sup>

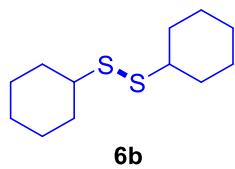


The reaction 3-methylbutane-1-thiol **2h** (0.4 mmol, 41.7 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.08 mmol, 26.1 mg) in CH<sub>3</sub>CN (1 mL) under air at 60 °C for 8 h, afforded 36.1 mg (87%) of **6a** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 2.73 – 2.65 (t, *J* = 13.0 Hz, 4H), 1.70 – 1.64 (m, 2H), 1.59 – 1.50 (m, 4H), 0.91 (d, *J* = 6.5 Hz, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 38.3, 37.3, 27.2, 22.3.

**1,2-dicyclohexyldisulfane (6b)** <sup>[10]</sup>



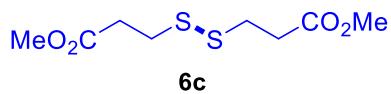
The reaction cyclohexanethiol **2c** (0.4 mmol, 46.5 mg),  $\text{Cs}_2\text{CO}_3$  (0.08 mmol, 26.1 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 60 °C for 8 h, afforded 38.1 mg (83%) of **6b** as colorless oil.

Gram-scale experiments: The reaction cyclohexanethiol **2c** (20 mmol, 2.32 g),  $\text{Cs}_2\text{CO}_3$  (4 mmol, 1.30 g) in  $\text{CH}_3\text{CN}$  (10 mL) under air at 60 °C for 16 h, afforded 1.95 mg (85%) of **6b** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 2.70 – 2.67 (m, 2H), 2.12 – 1.99 (m, 4H), 1.82 – 1.74 (m, 4H), 1.69 – 1.60 (m, 2H), 1.40 – 1.15 (m, 10H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 50.0, 32.9, 26.1, 25.7.

#### **dimethyl 3,3'-disulfanediyldipropionate (6c)** <sup>[12]</sup>

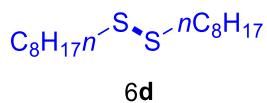


The reaction methyl 3-mercaptopropanoate **2g** (0.4 mmol, 48.1 mg),  $\text{Cs}_2\text{CO}_3$  (0.08 mmol, 26.1 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 60 °C for 8 h, afforded 36.9 mg (77%) of **6c** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 3.66 (s, 6H), 2.87 (t,  $J$  = 7.2 Hz, 4H), 2.69 (t,  $J$  = 7.2 Hz, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 172.1, 51.9, 33.9, 33.1.

#### **1,2-dioctyldisulfane (6d)** <sup>[13]</sup>

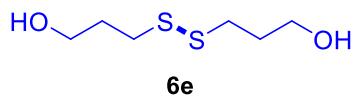


The reaction octane-1-thiol **2b** (0.4 mmol, 58.5 mg),  $\text{Cs}_2\text{CO}_3$  (0.08 mmol, 26.1 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 60 °C for 8 h, afforded 51.5 mg (89%) of **6d** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 2.73 – 2.62 (m, 4H), 1.69 – 1.65 (m, 4H), 1.40 – 1.22 (m, 20H), 0.92 – 0.84 (m, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 39.2, 31.8, 29.25, 29.22, 29.20, 28.6, 22.7, 14.1.

**3,3'-disulfanediylbis(propan-1-ol) (6e) [14]**

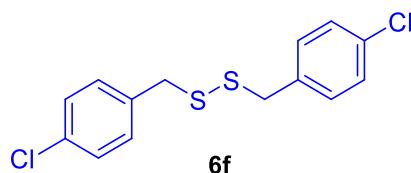


The reaction 3-mercaptopropan-1-ol **2e** (0.4 mmol, 36.8 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.08 mmol, 26.1 mg) in CH<sub>3</sub>CN (1 mL) under air at 60 °C for 8 h, afforded 27.1 mg (74%) of **6e** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 3.74 (t, *J* = 6.1 Hz, 4H), 2.81 (t, *J* = 7.1 Hz, 4H), 2.14 (s, 2H), 1.94 (tt, *J* = 7.1 Hz, 6.1 Hz, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 61.0, 35.2, 31.8.

**1,2-bis(4-chlorobenzyl)disulfane (6f) [15]**

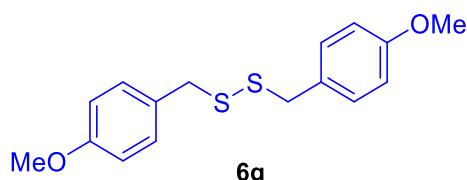


The reaction (4-chlorophenyl)methanethiol **2j** (0.4 mmol, 63.0 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.08 mmol, 26.1 mg) in CH<sub>3</sub>CN (1 mL) under air at 60 °C for 4 h, afforded 59.4 mg (94%) of **6f** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ = 7.33 – 7.27 (m, 4H), 7.18 – 7.12 (m, 4H), 3.58 (s, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.8, 133.4, 130.7, 128.7, 42.5.

**1,2-bis(4-methoxybenzyl)disulfane (6g) [16]**

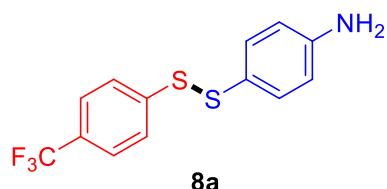


The reaction (4-methoxyphenyl)methanethiol **2i** (0.4 mmol, 61.3 mg),  $\text{Cs}_2\text{CO}_3$  (0.08 mmol, 26.1 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 60 °C for 4 h, afforded 60.7 mg (99%) of **6g** as pink crystal.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.22 – 7.13 (m, 4H), 6.91 – 6.83 (m, 4H), 3.81 (s, 6H), 3.61 (s, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.1, 130.5, 129.4, 113.9, 55.3, 42.8.

**4-((4-(trifluoromethyl)phenyl)disulfaneyl)aniline (8a)**



The reaction of 4-(trifluoromethyl)benzenethiol **1f** (0.2 mmol, 35.6 mg), 4-aminobenzenethiol **1h** (0.2 mmol, 25.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 3 h, afforded 36.0 mg (60%) of **8a** as colorless oil.

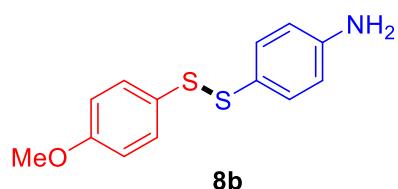
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.66 (d,  $J$  = 8.2 Hz, 2H), 7.58 (d,  $J$  = 8.3 Hz, 2H), 7.33 (d,  $J$  = 8.6 Hz, 2H), 6.61 (d,  $J$  = 8.6 Hz, 2H), 4.06 – 3.60 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  147.5, 142.8, 133.0, 128.7 (q,  $^2J_{C-F}$  = 32.5 Hz), 127.2, 125.8 (q,  $^3J_{C-F}$  = 3.9 Hz), 124.1 (q,  $^1J_{C-F}$  = 271.8 Hz), 123.9, 115.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.38 (s, 3F).

HRMS (ESI) exact mass calc'd for  $\text{C}_{13}\text{H}_{11}\text{F}_3\text{NS}_2$  ( $[\text{M}+\text{H}]^+$ ): 302.0285; found m/z: 302.0283.

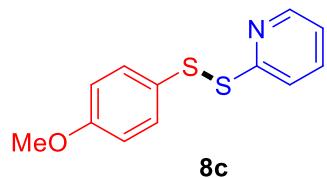
**4-((4-methoxyphenyl)disulfaneyl)aniline (8b) <sup>[17]</sup>**



The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), 4-aminobenzenethiol **1h** (0.2 mmol, 25.0 mg),  $\text{K}_2\text{CO}_3$  (0.01 mmol, 1.4 mg) in  $\text{CH}_3\text{CN}$  (1 mL) under air at 30 °C for 3 h, afforded 27.7 mg (53%) of **8b** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.80 (s, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.9, 147.2, 133.7, 133.0, 128.8, 125.4, 115.4, 114.6, 55.4.

**2-((4-methoxyphenyl)disulfaneyl)pyridine (8c)** <sup>[17]</sup>



The reaction of 4-methoxybenzenethiol **1a** (0.2 mmol, 28.0 mg), pyridine-2-thiol **1x** (0.2 mmol, 22.2 mg), K<sub>2</sub>CO<sub>3</sub> (0.01 mmol, 1.4 mg) in CH<sub>3</sub>CN (1 mL) under air at 30 °C for 3 h, afforded 20.3 mg (41%) of **8c** as colorless oil.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.49 – 8.45 (m, 1H), 7.75 – 7.67 (m, 1H), 7.67 – 7.57 (m, 1H), 7.53 – 7.44 (m, 2H), 7.11 – 7.05 (m, 1H), 6.88 – 6.75 (m, 2H), 3.77 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.1, 159.8, 149.6, 137.2, 131.4, 127.2, 120.8, 119.8, 114.8, 55.4.

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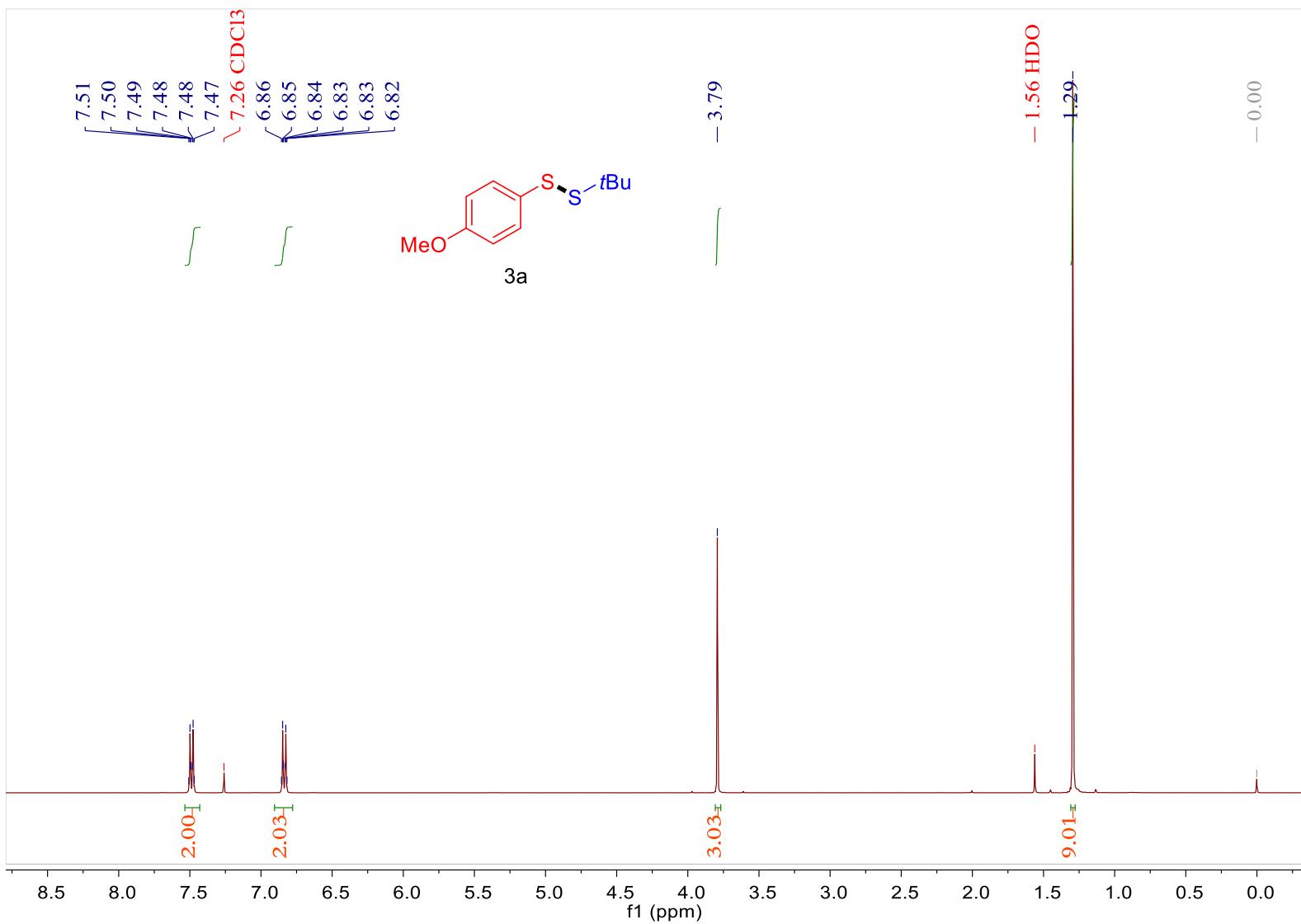
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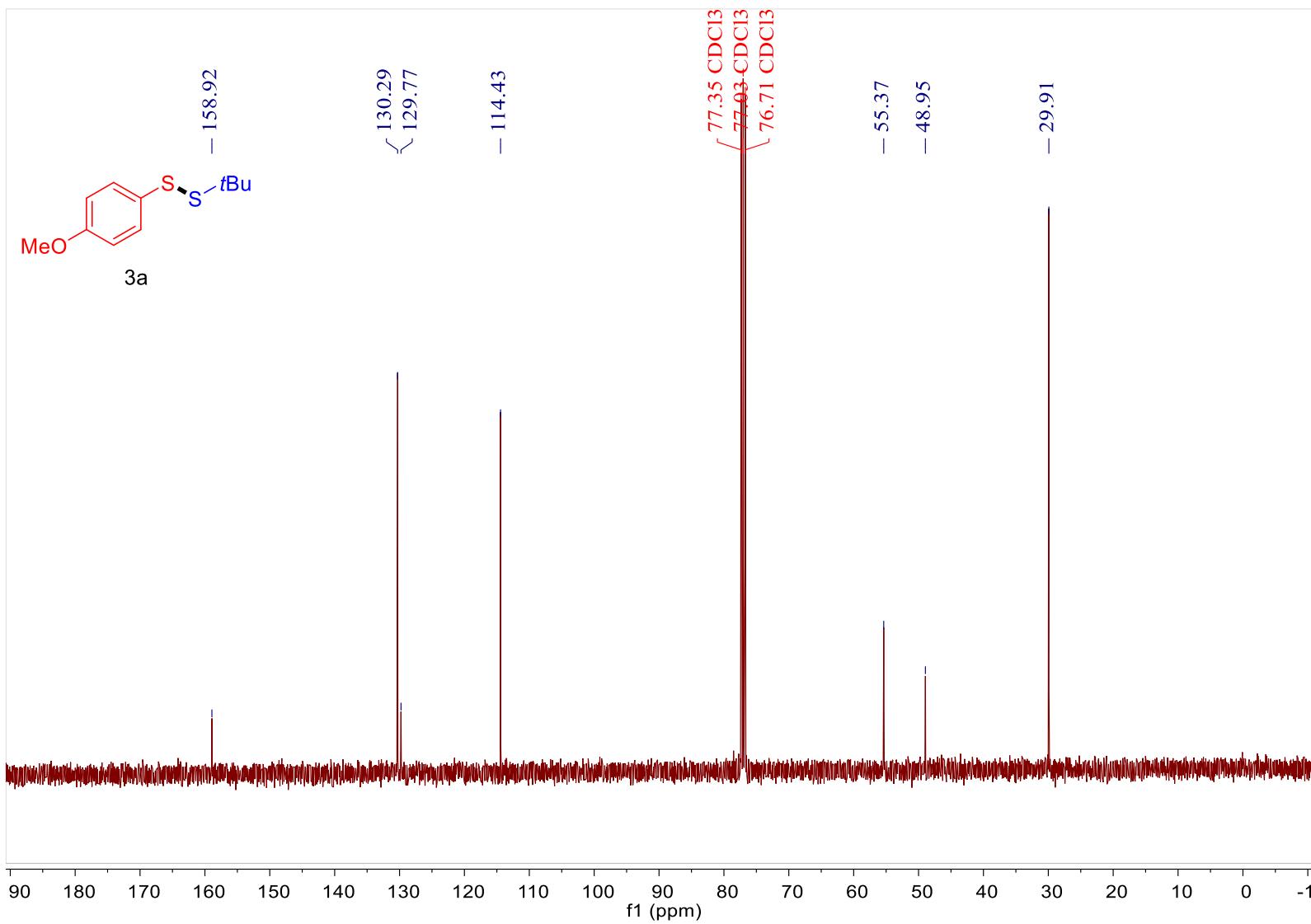
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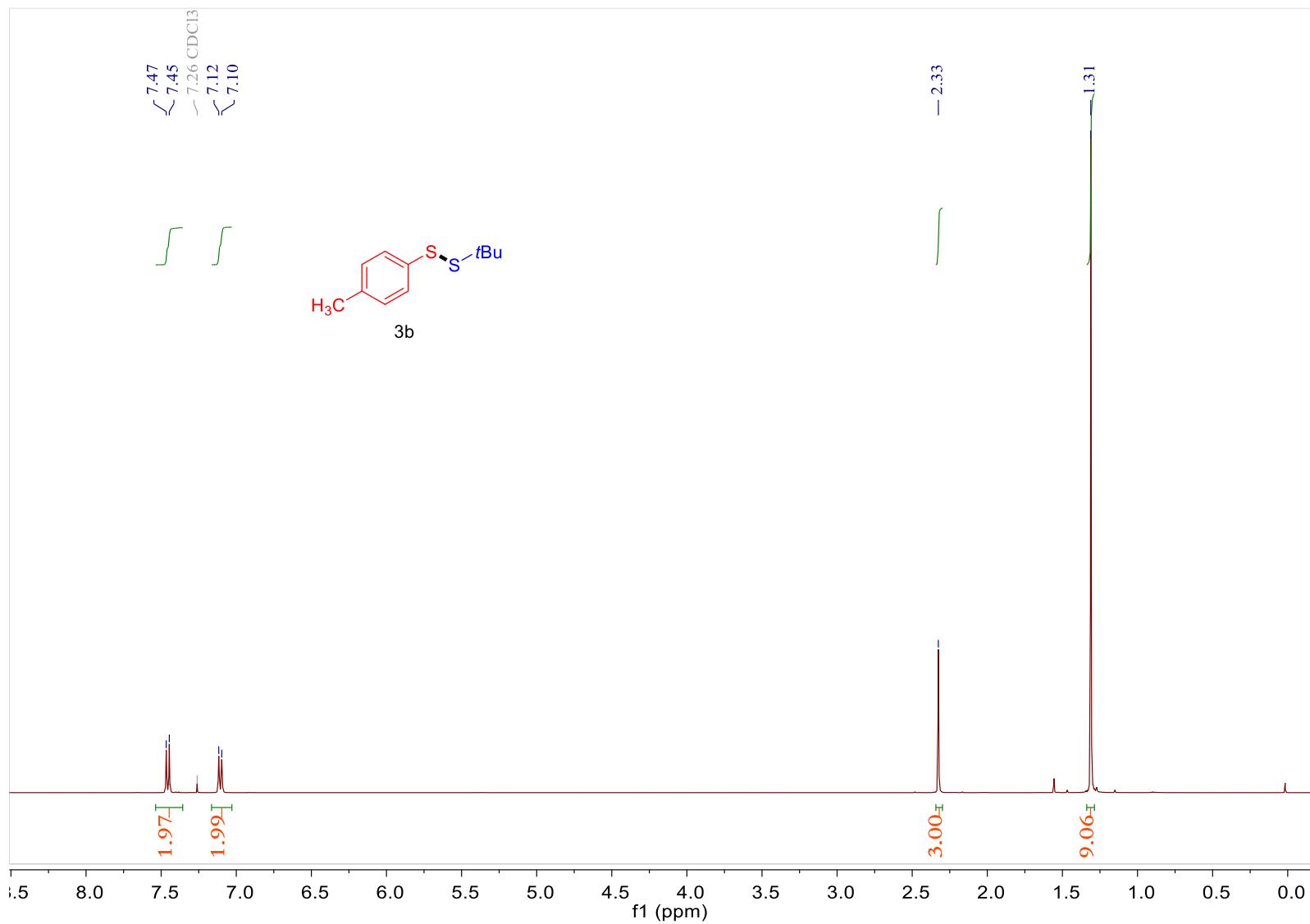
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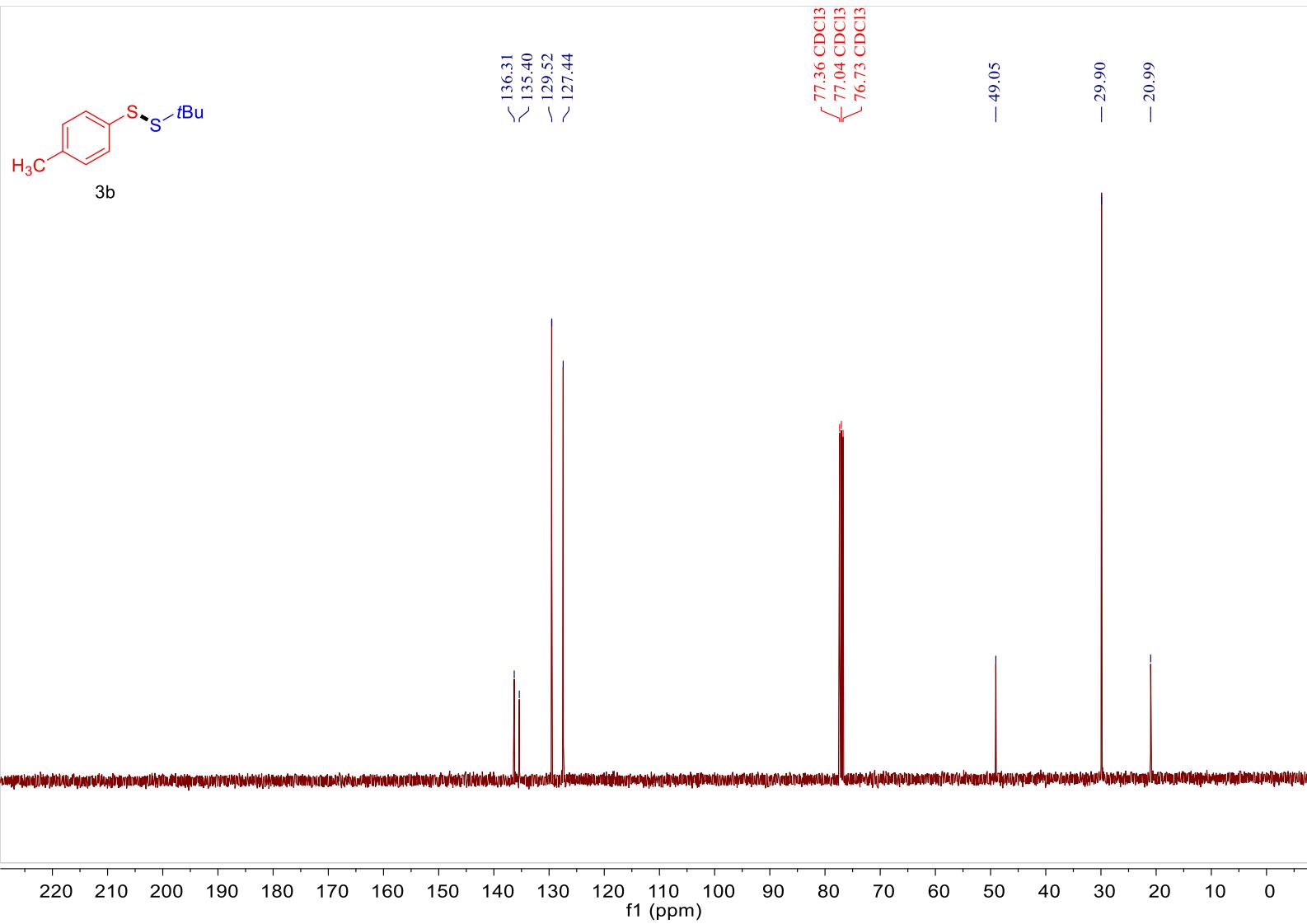
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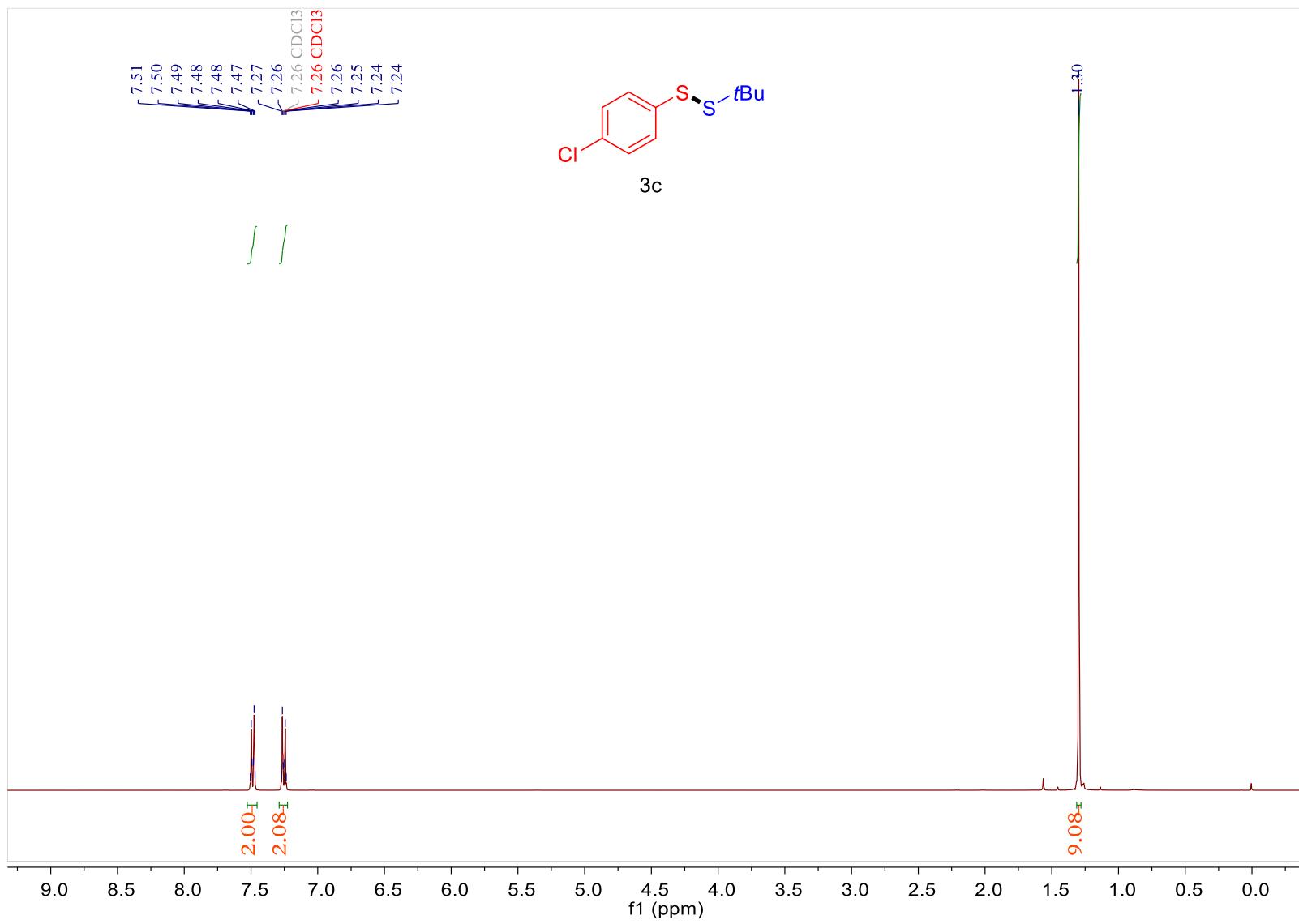
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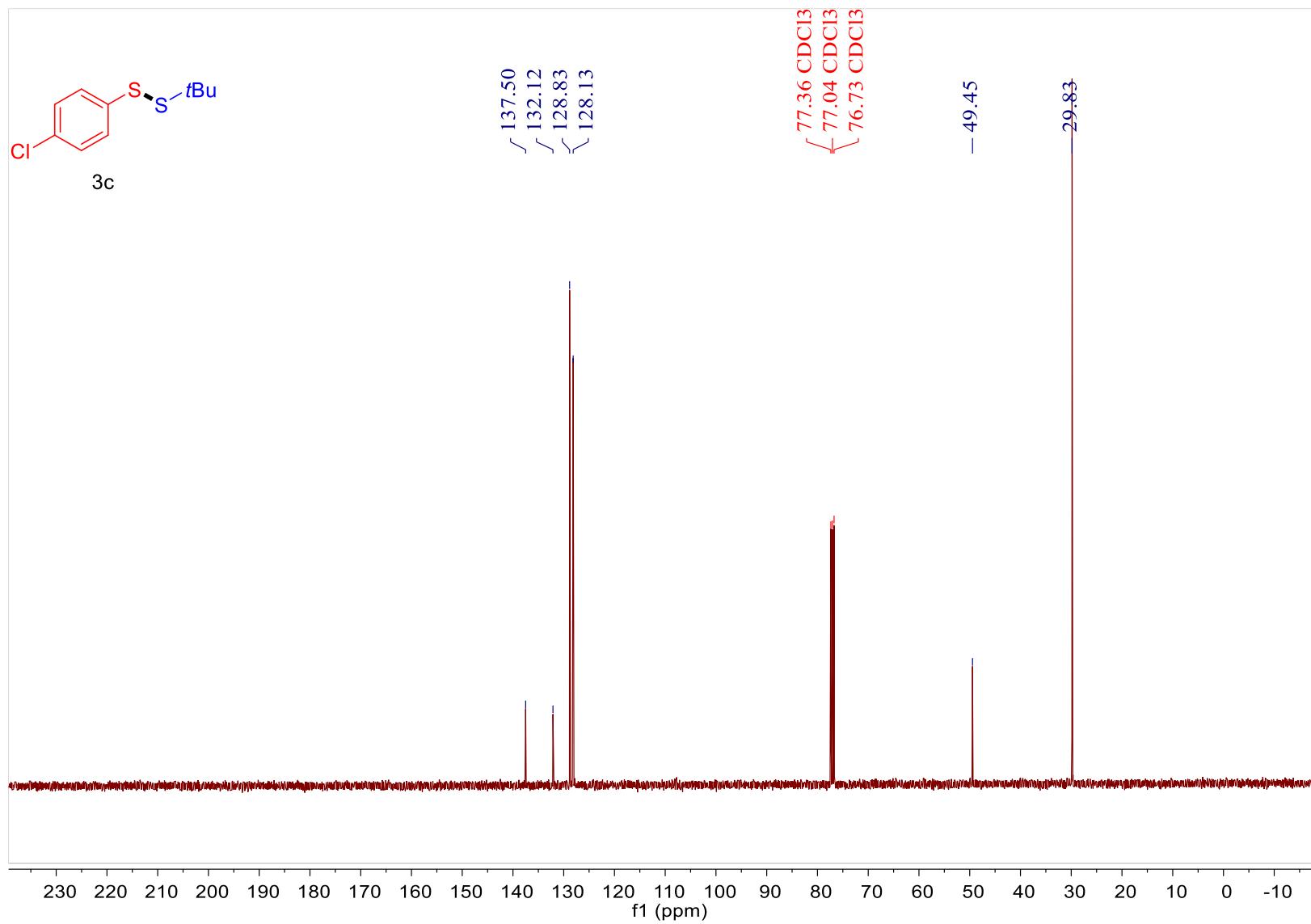


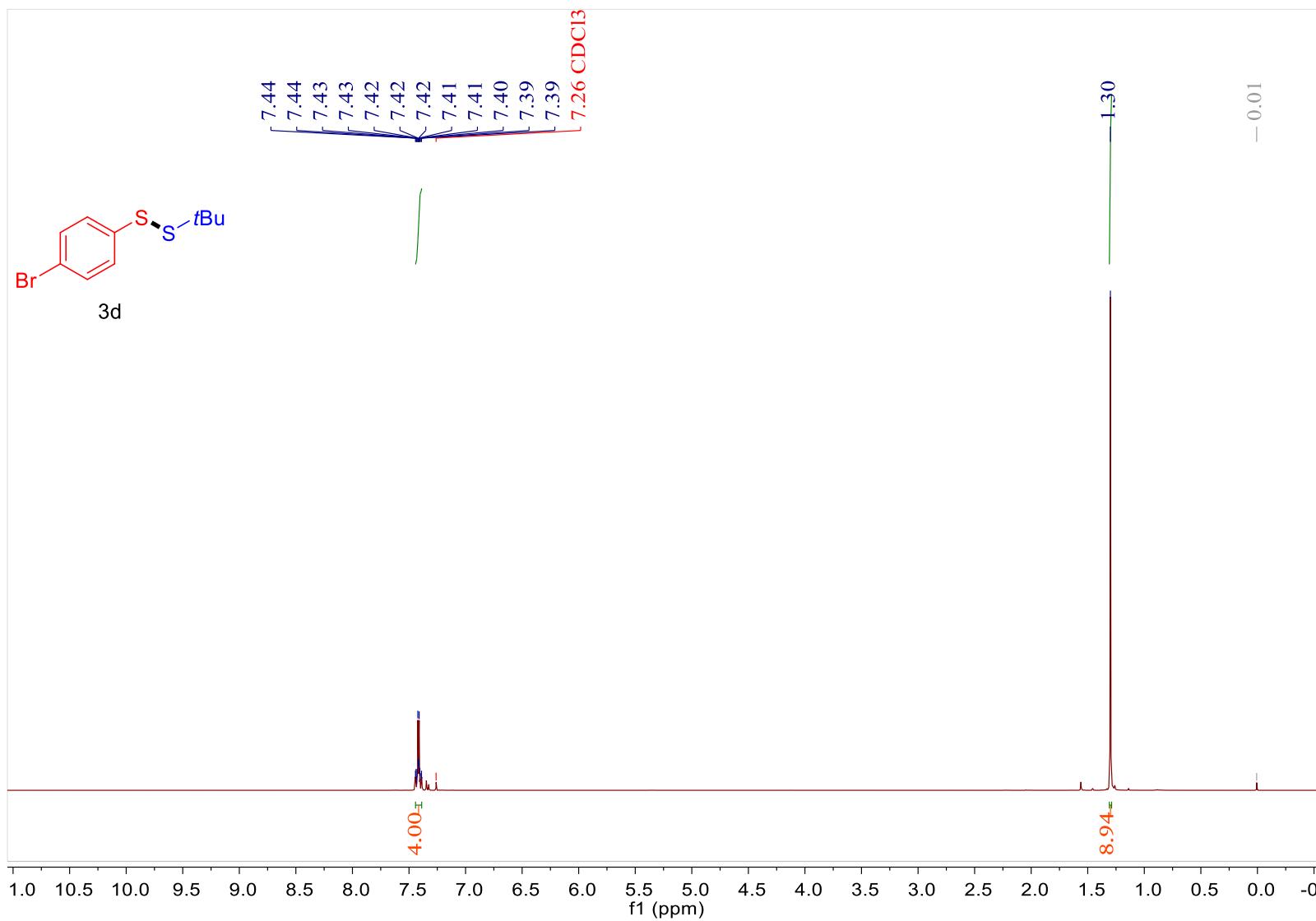


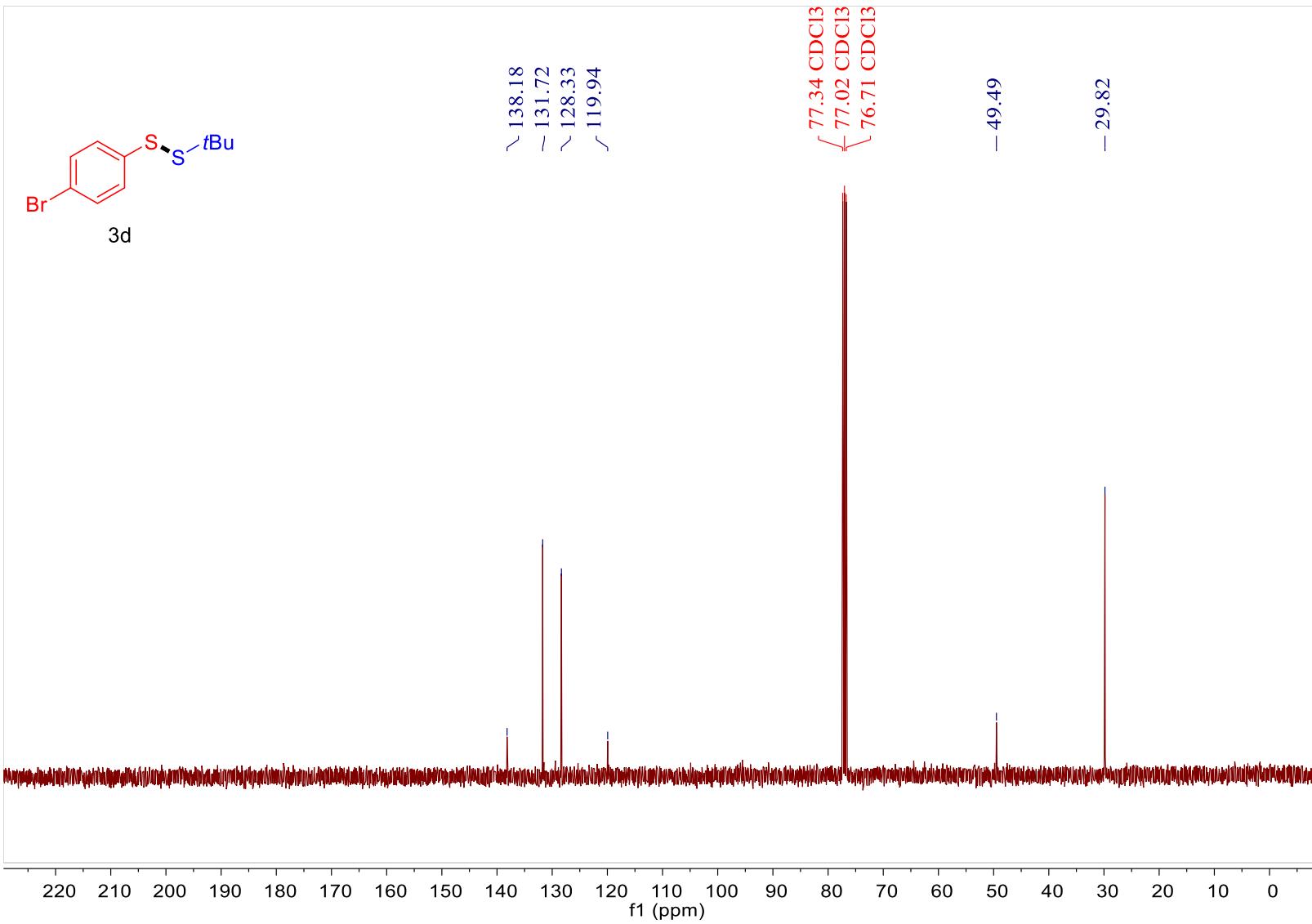


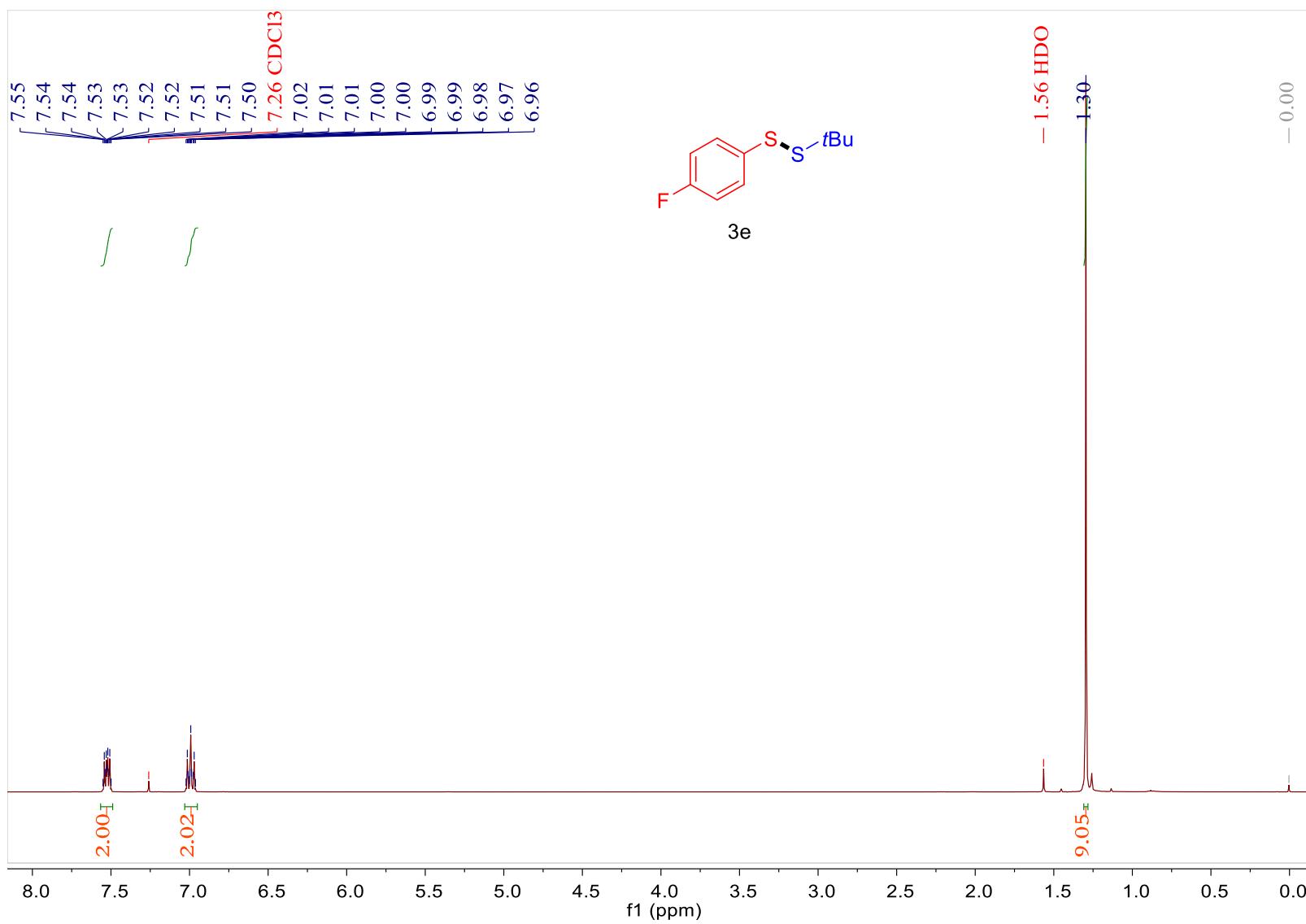


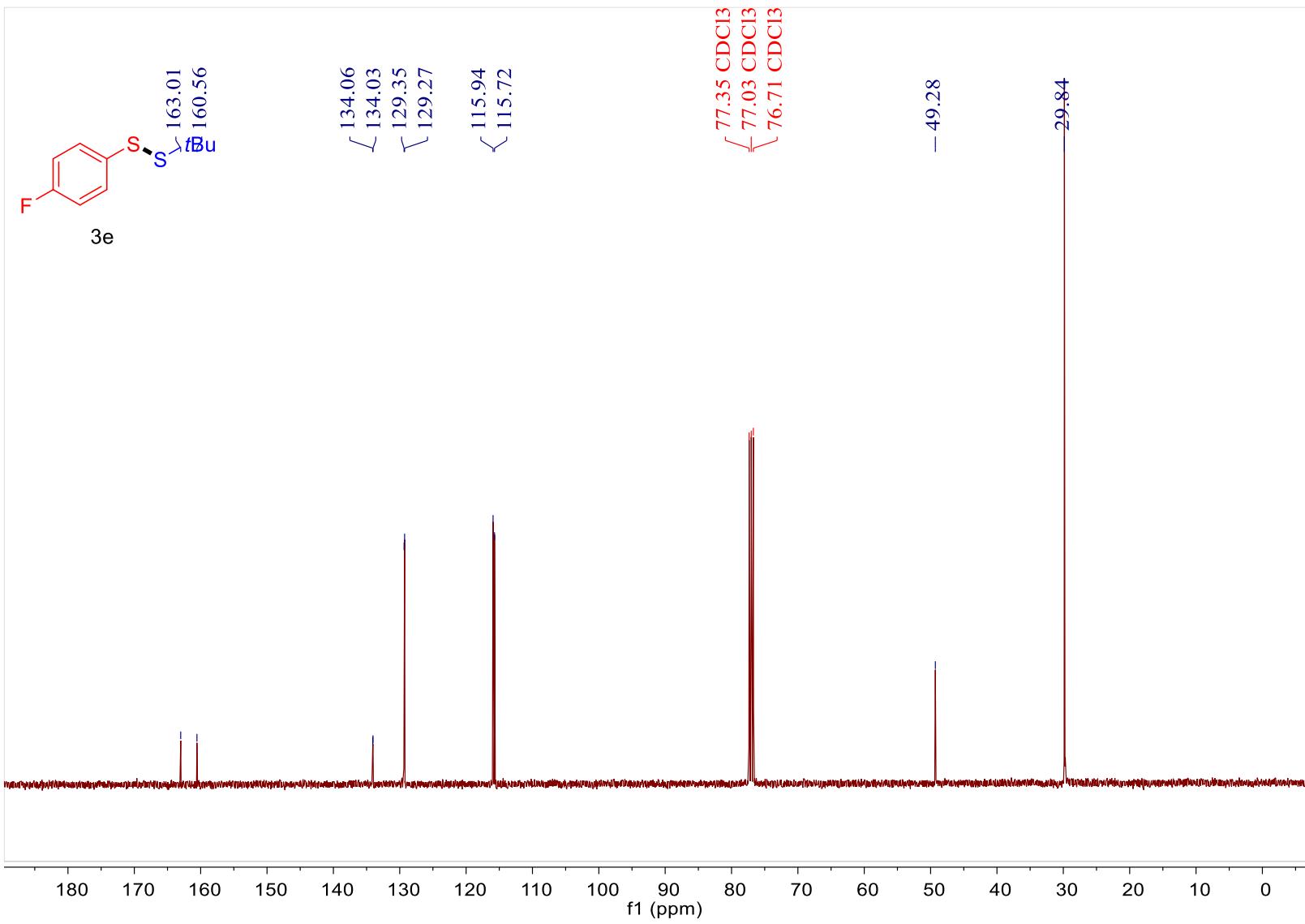


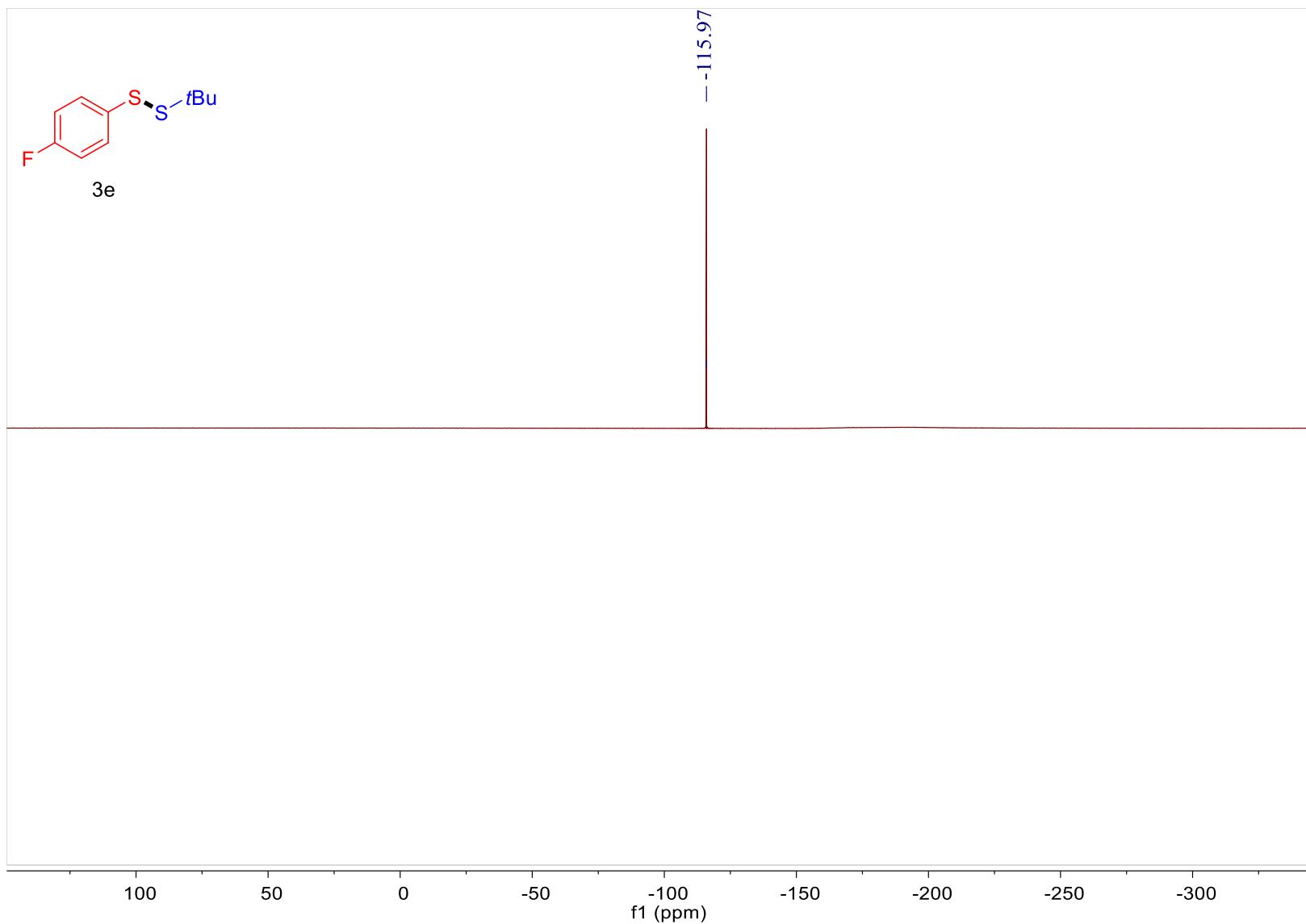


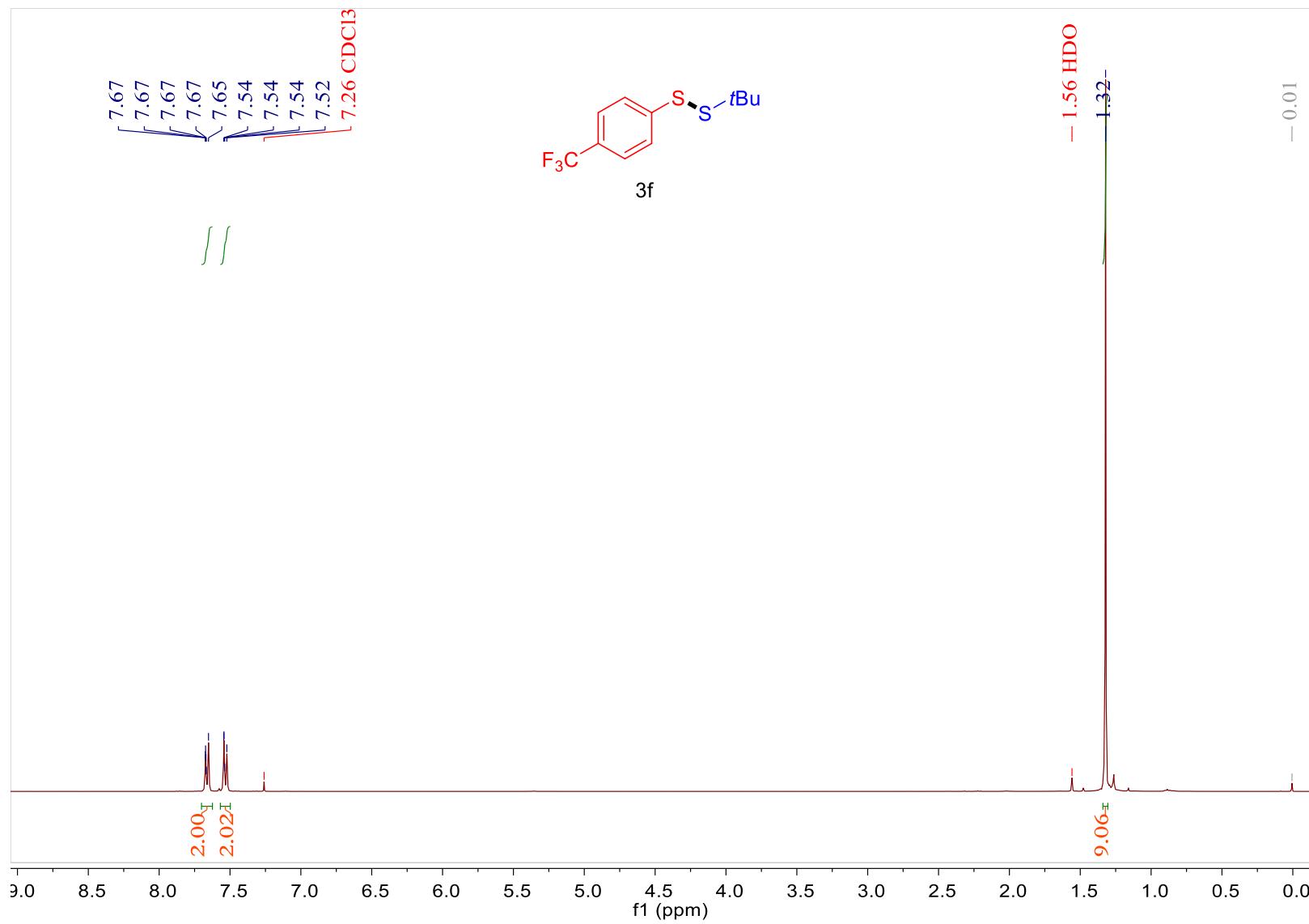


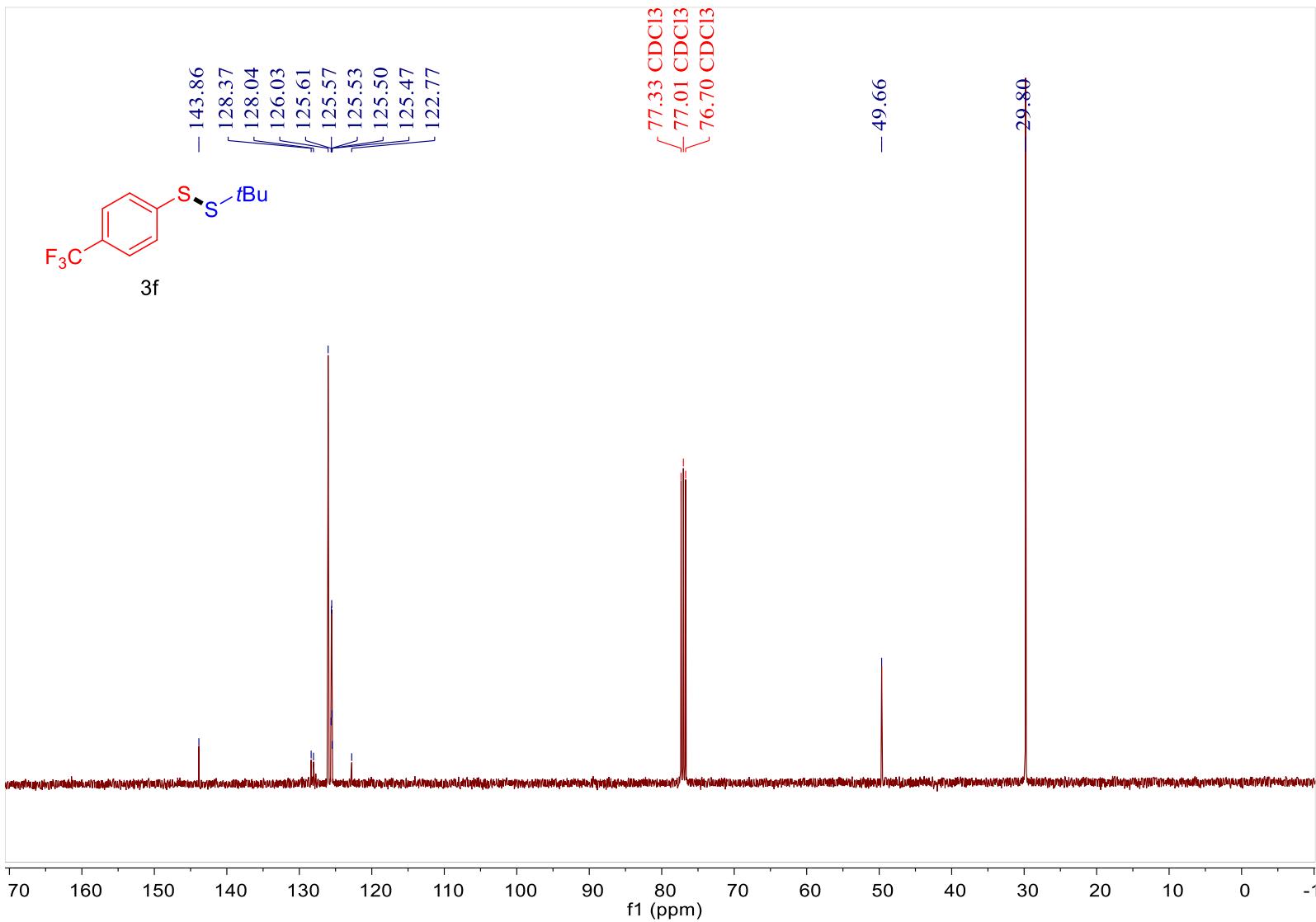


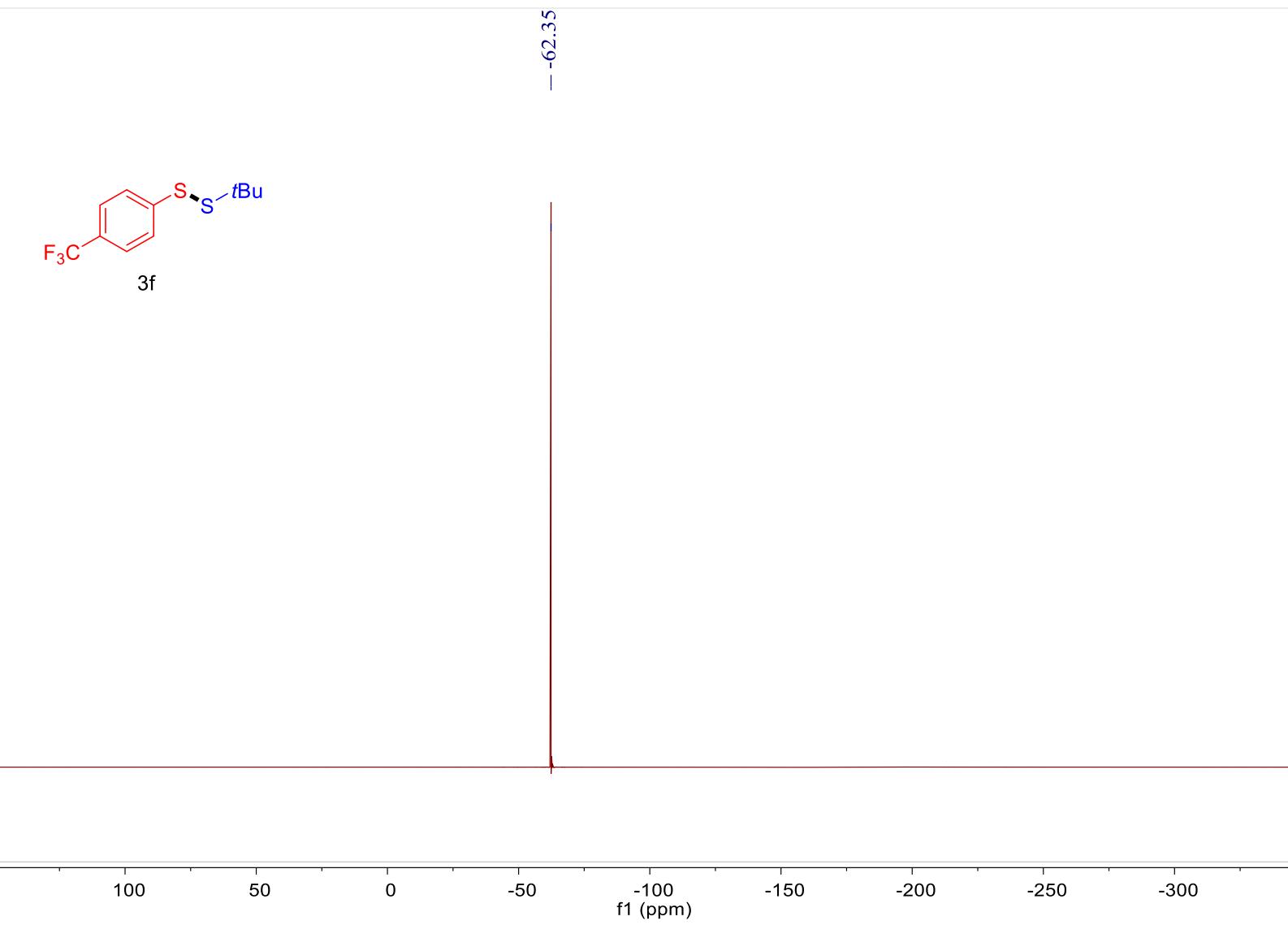


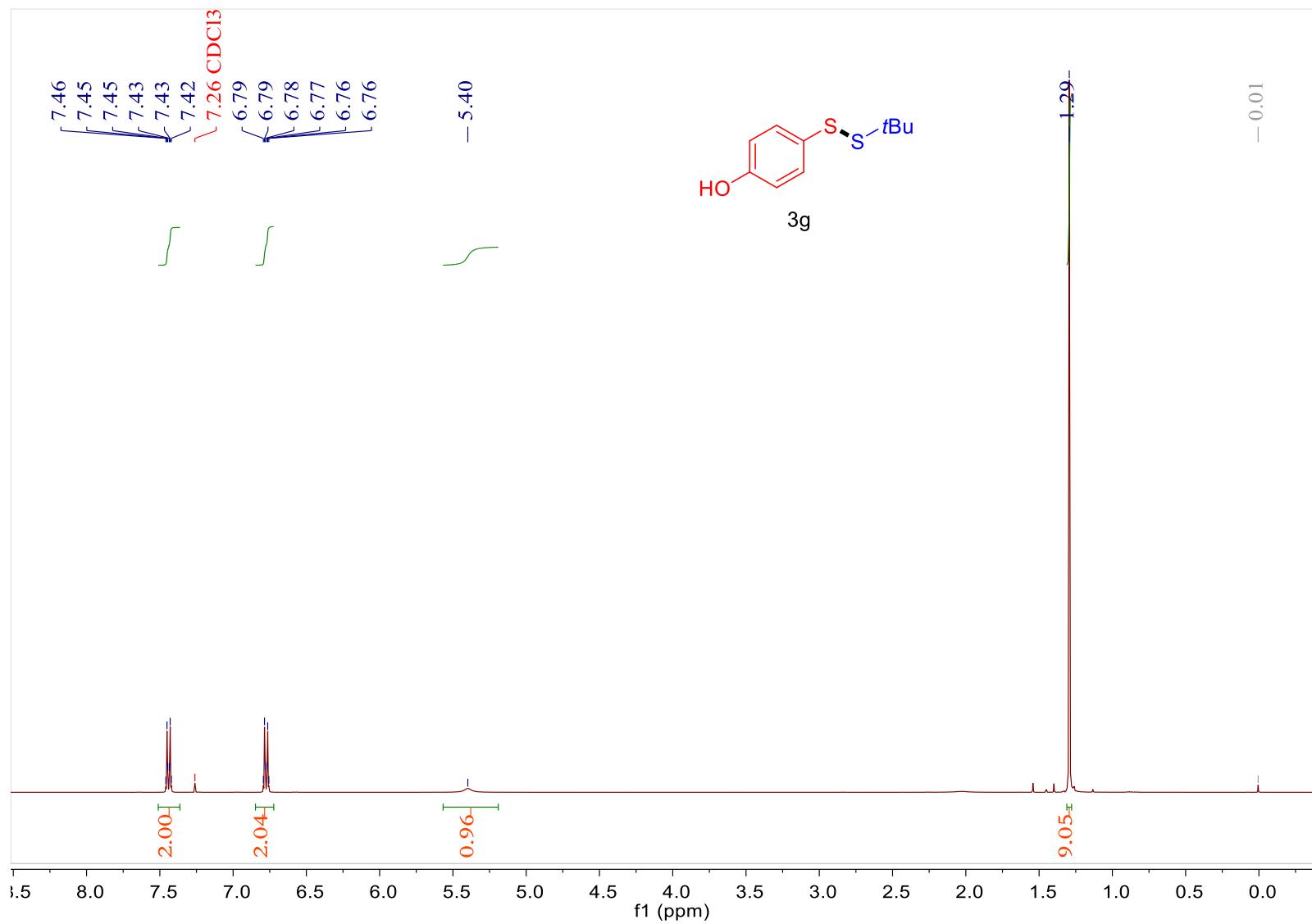


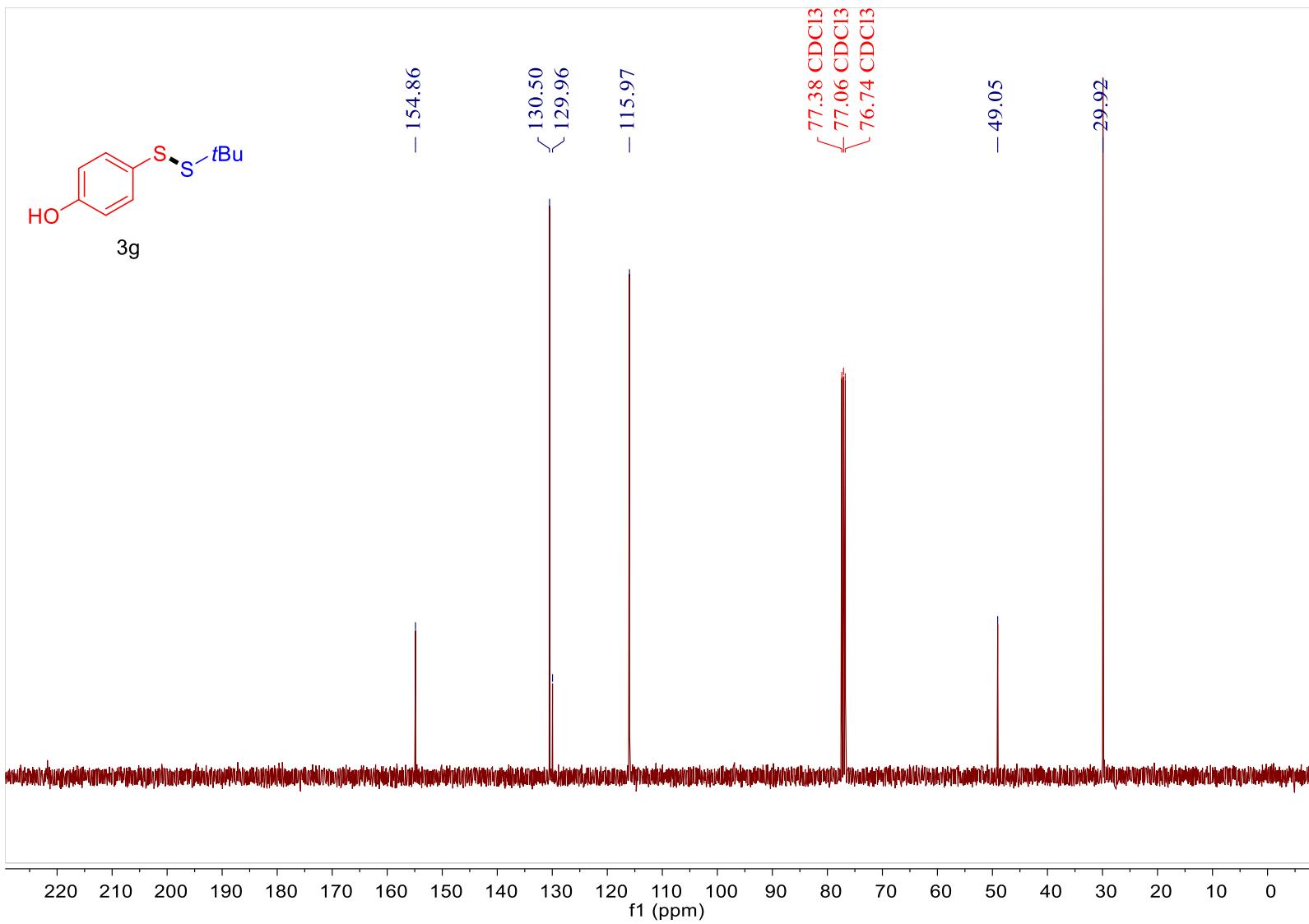


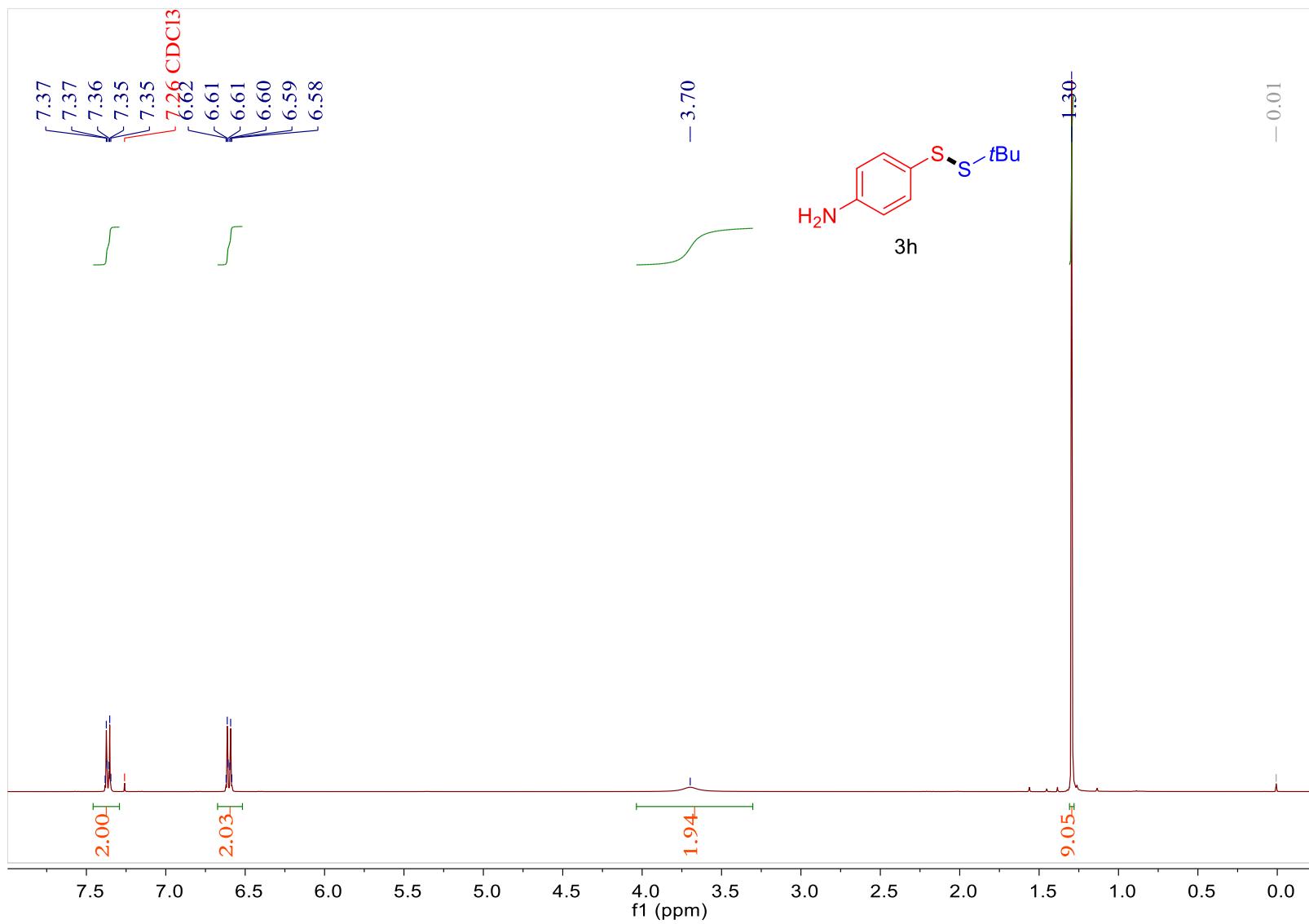


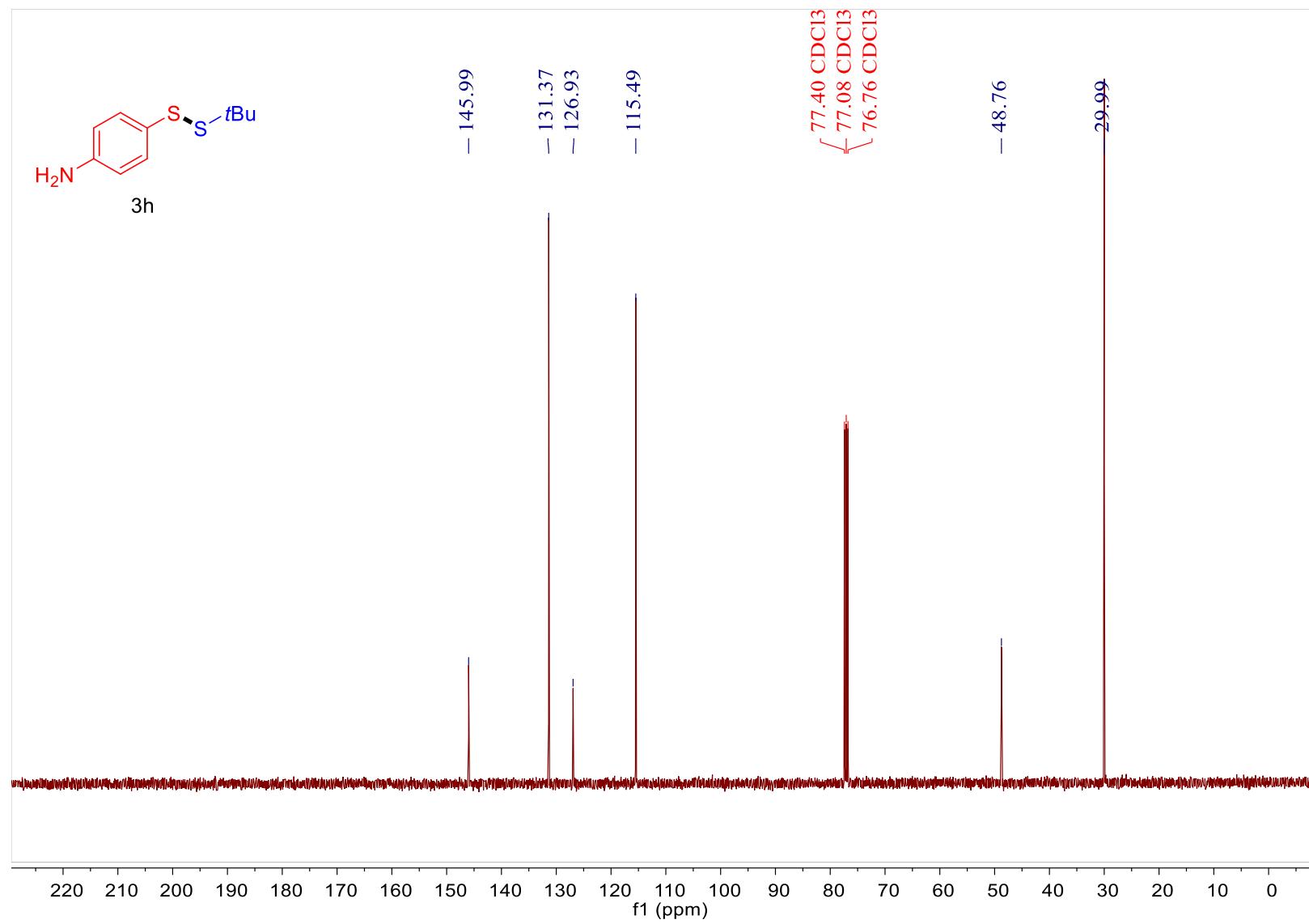


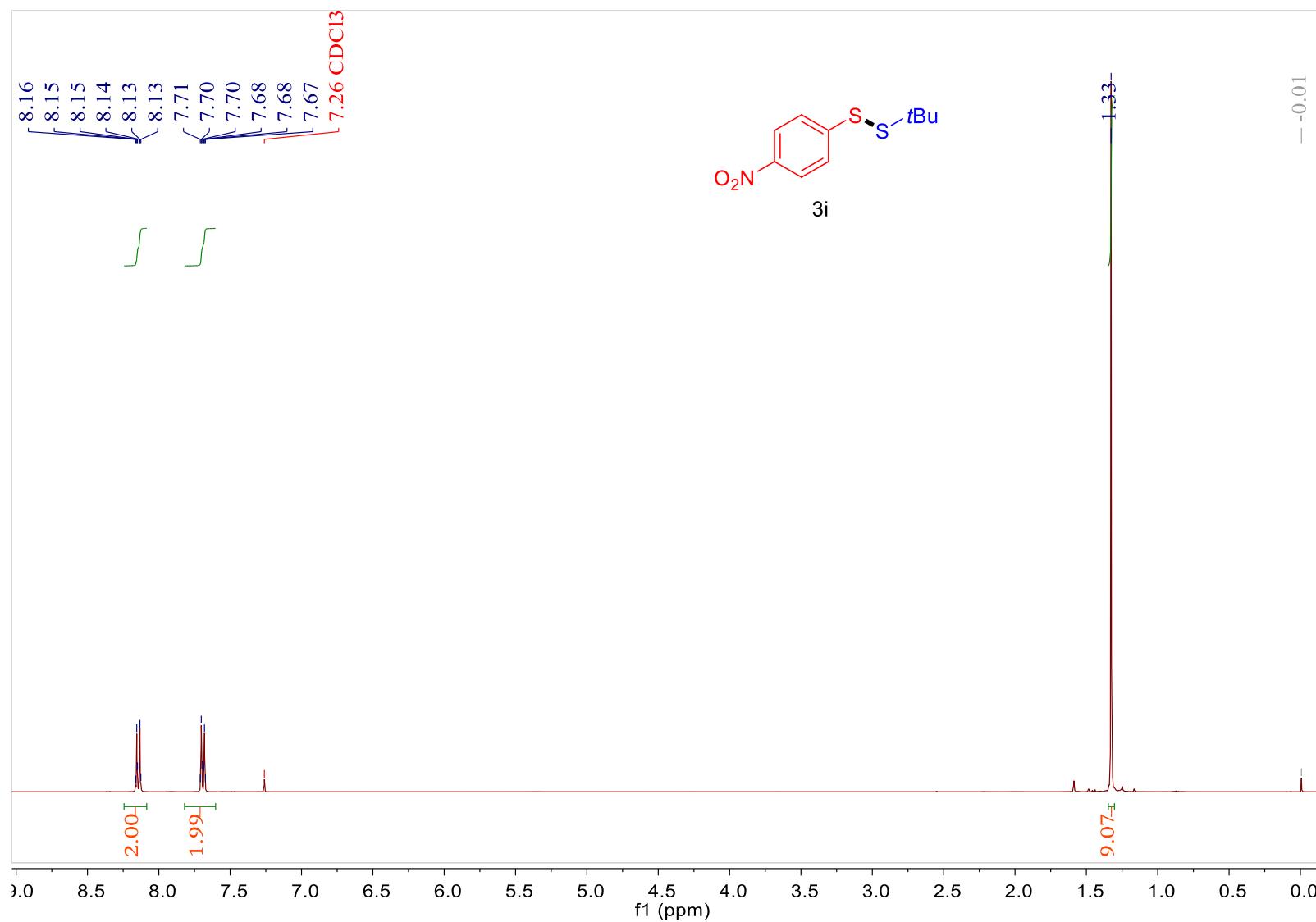


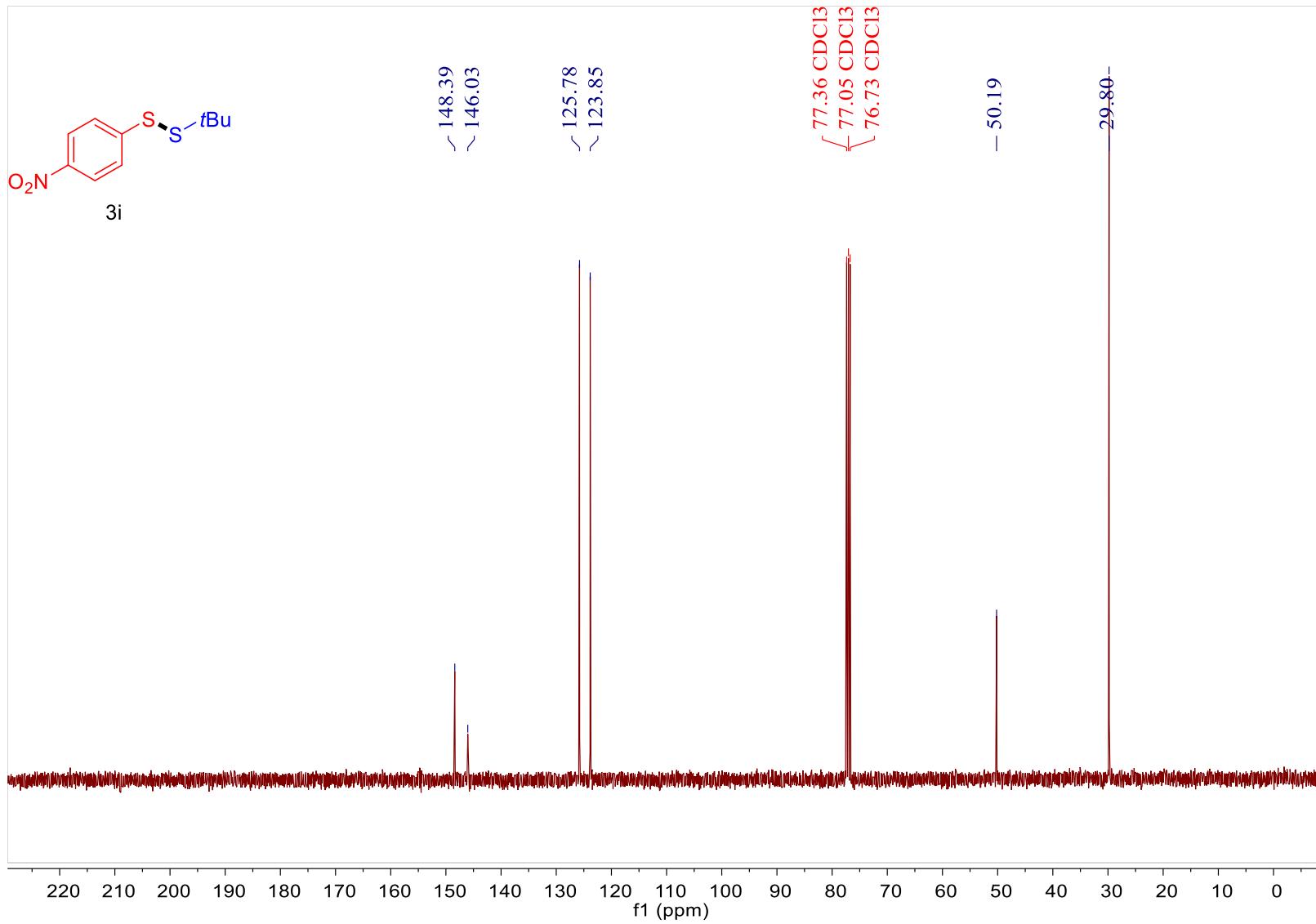


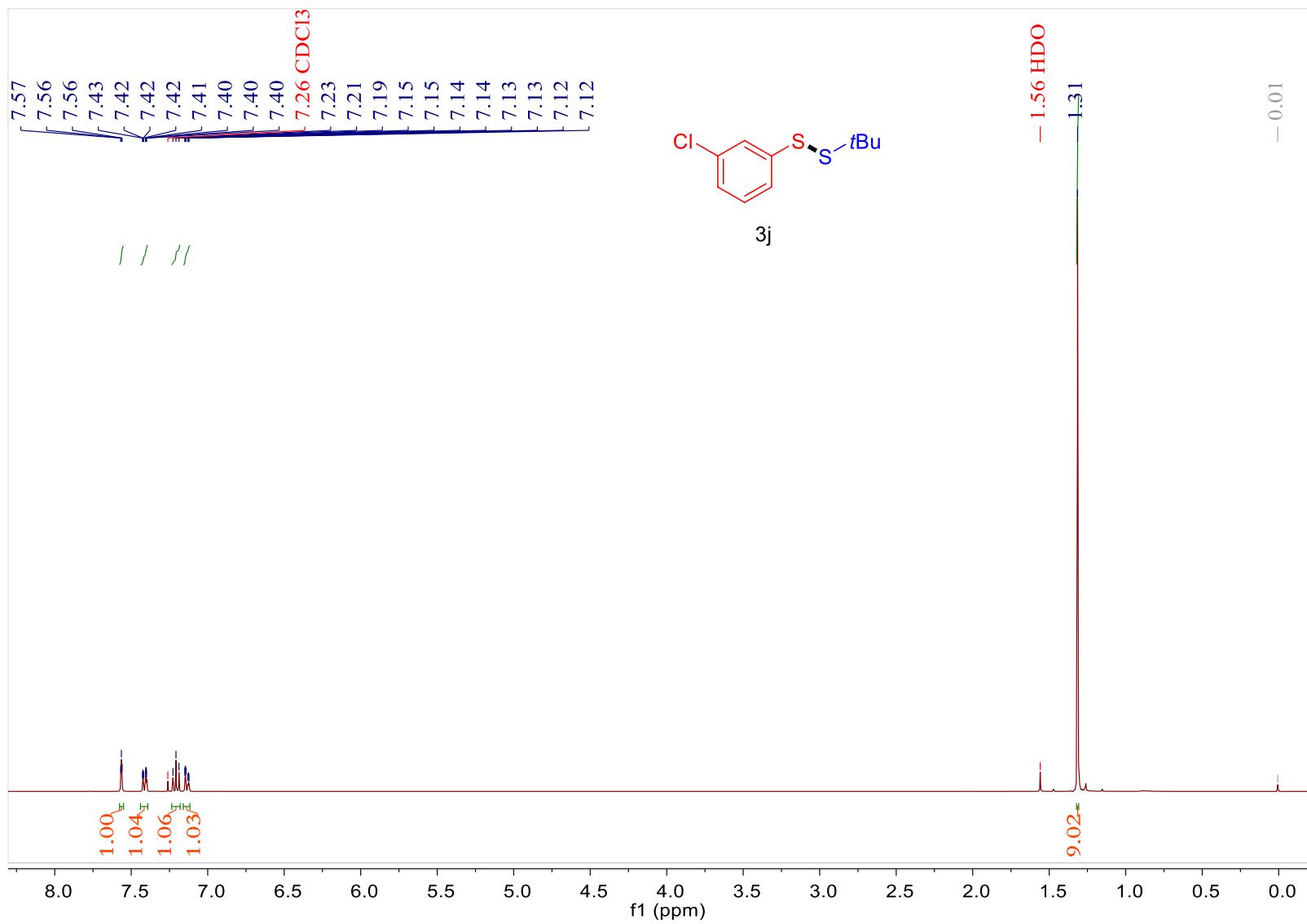


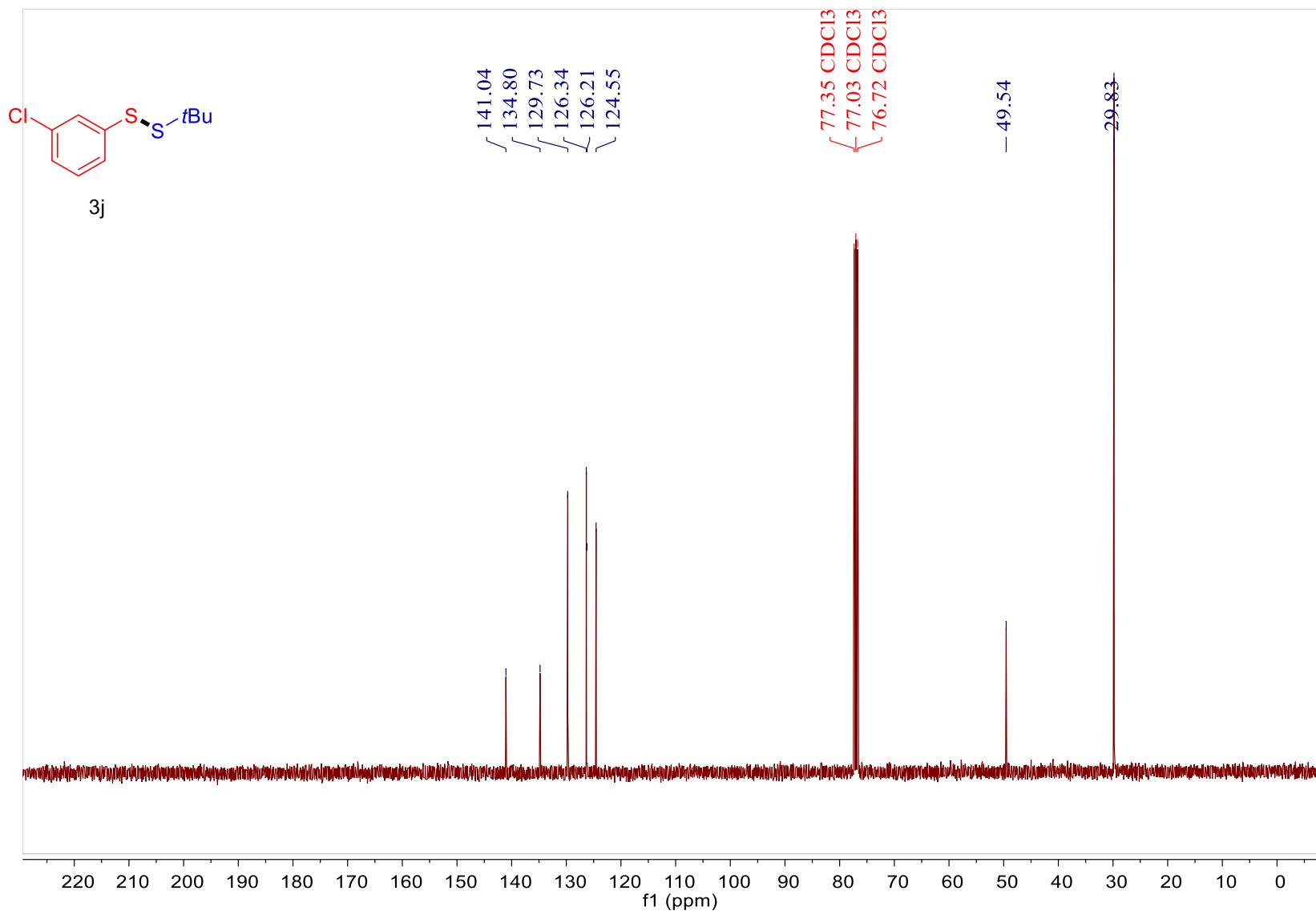


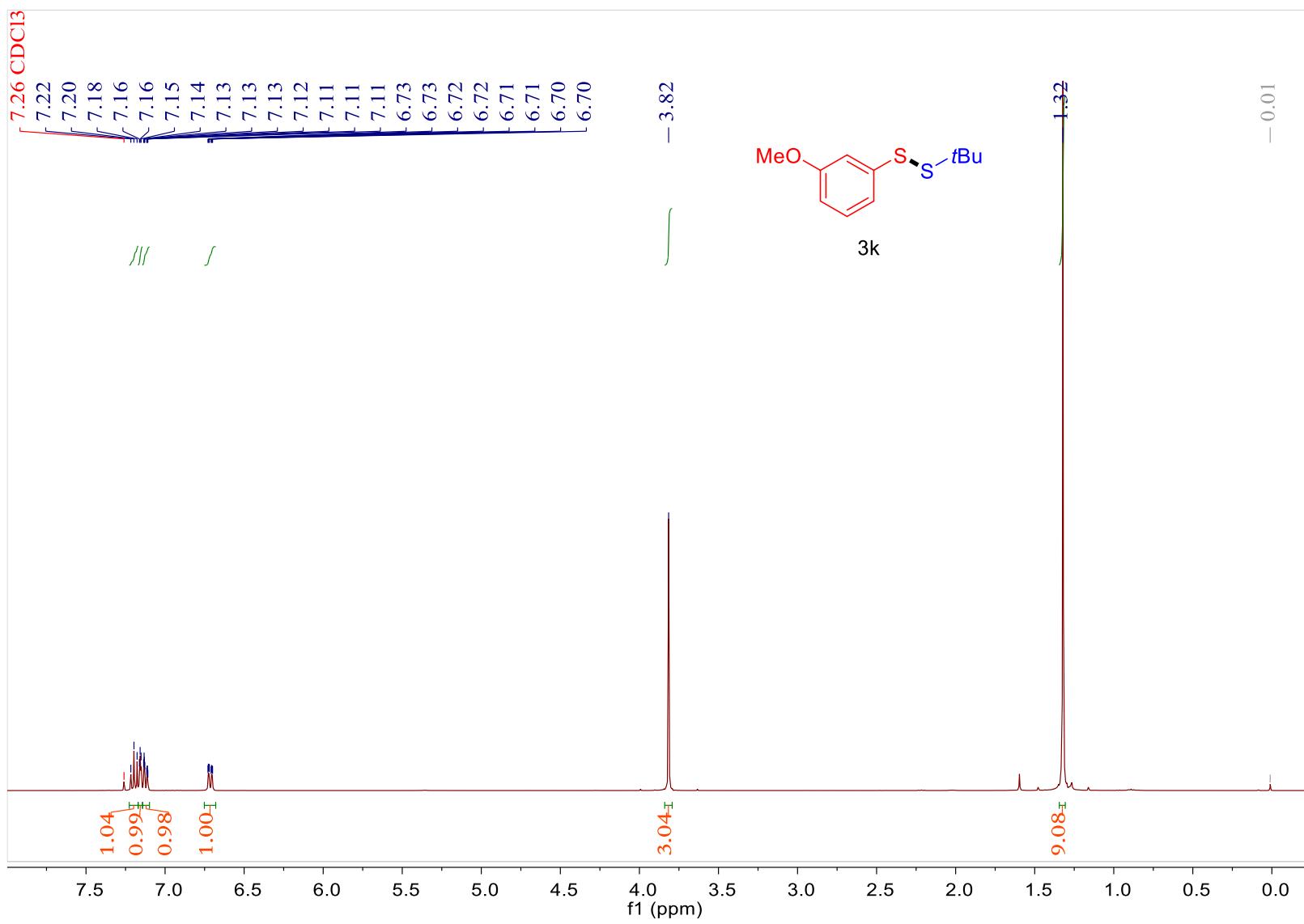


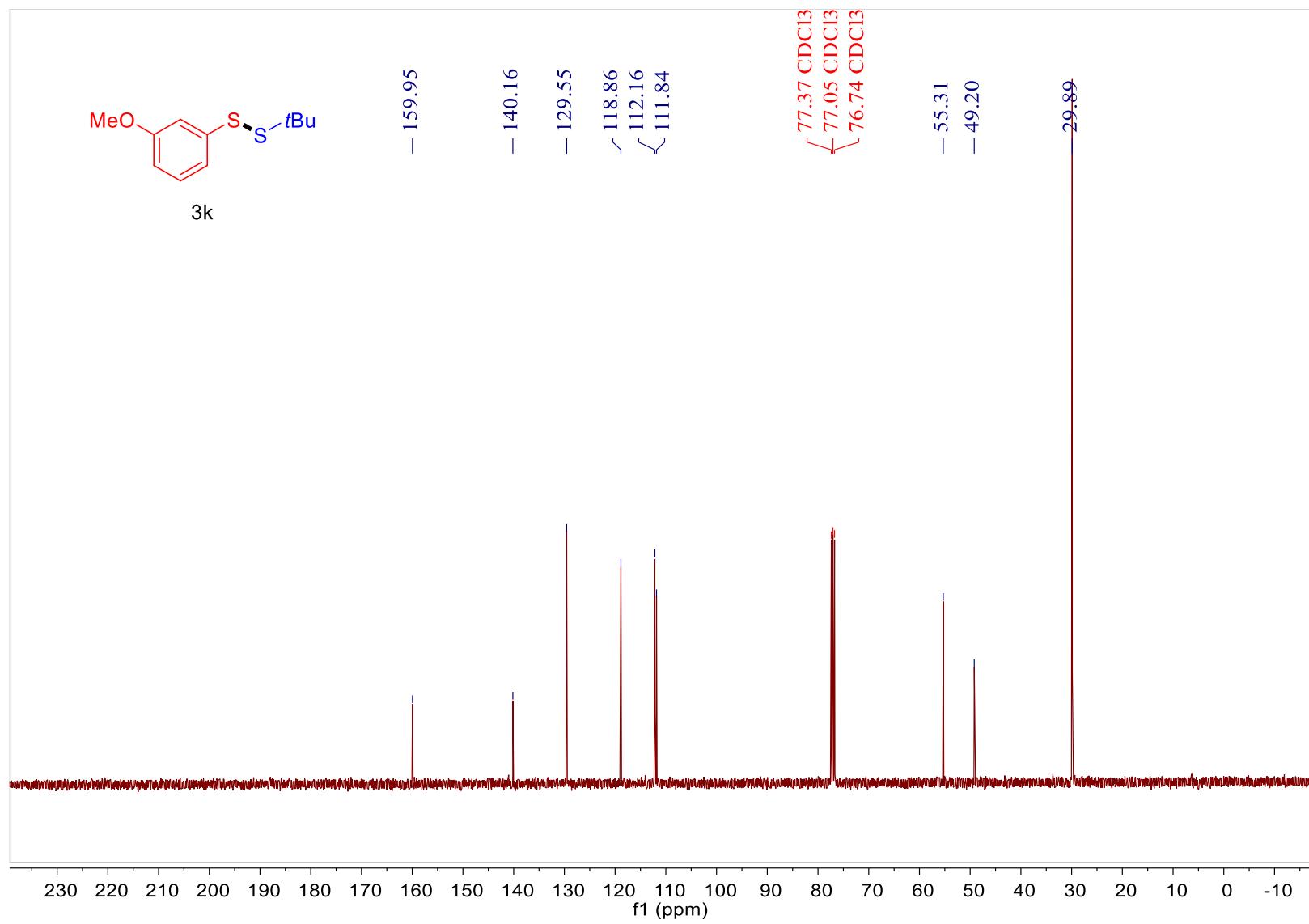


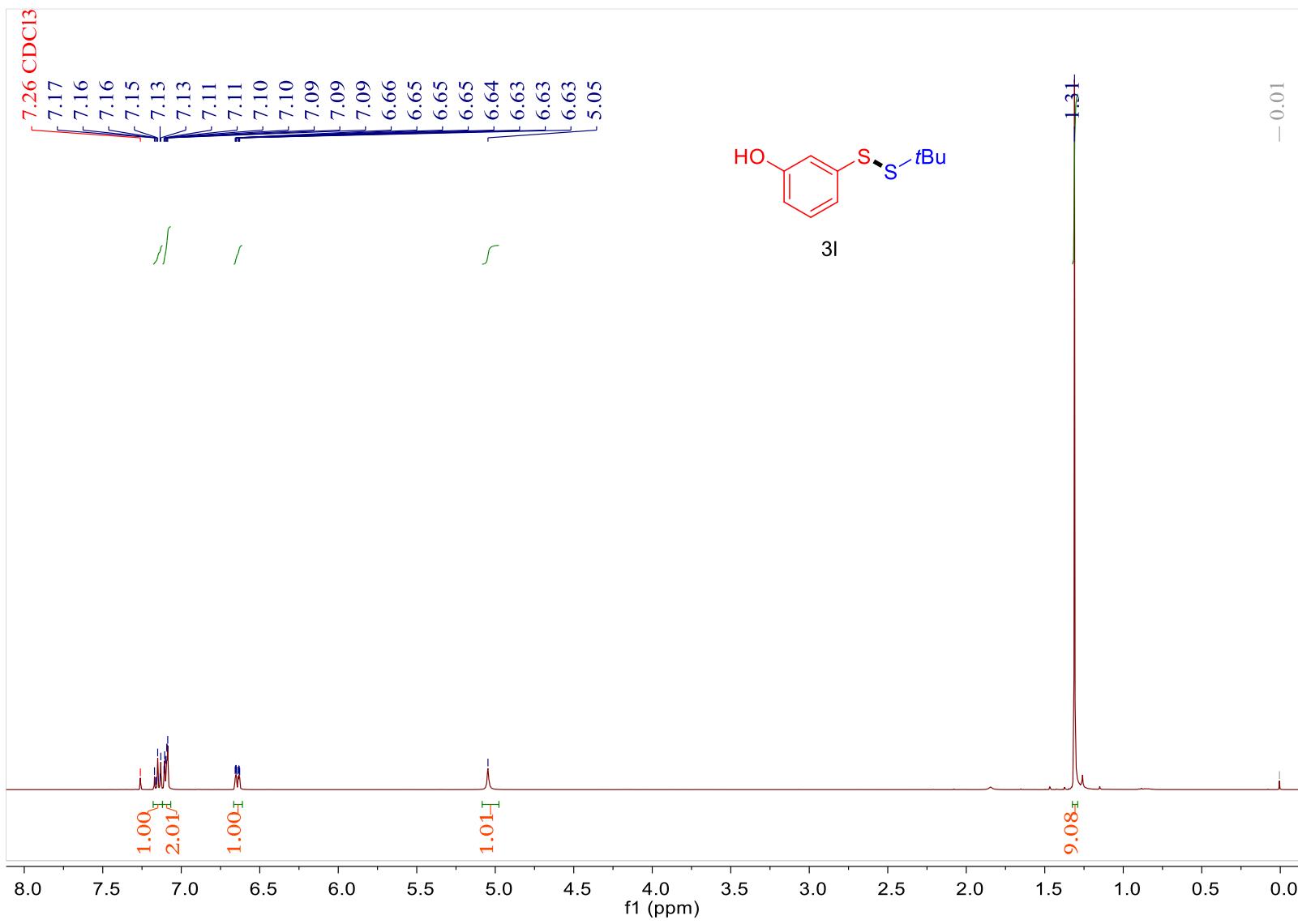


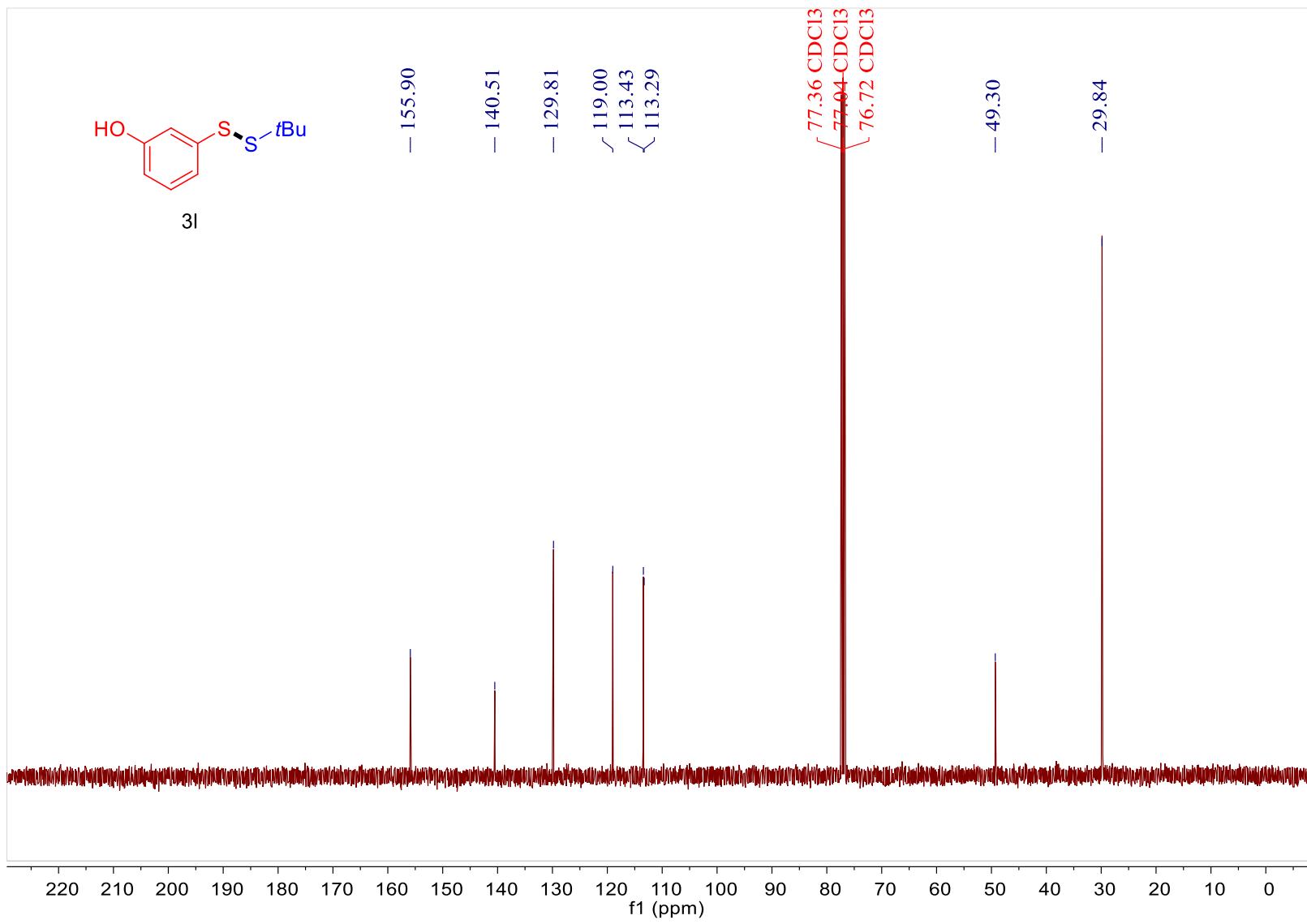


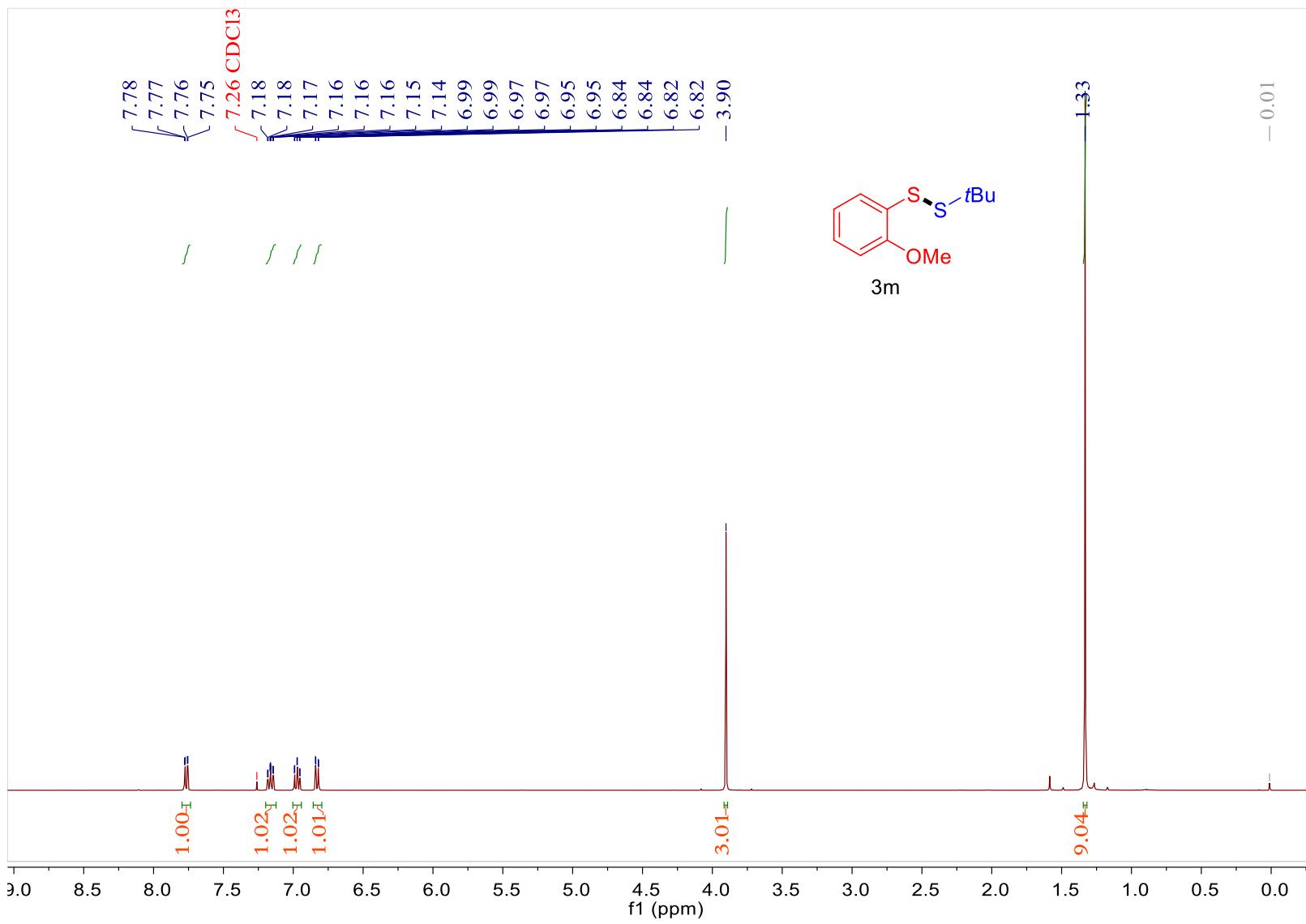


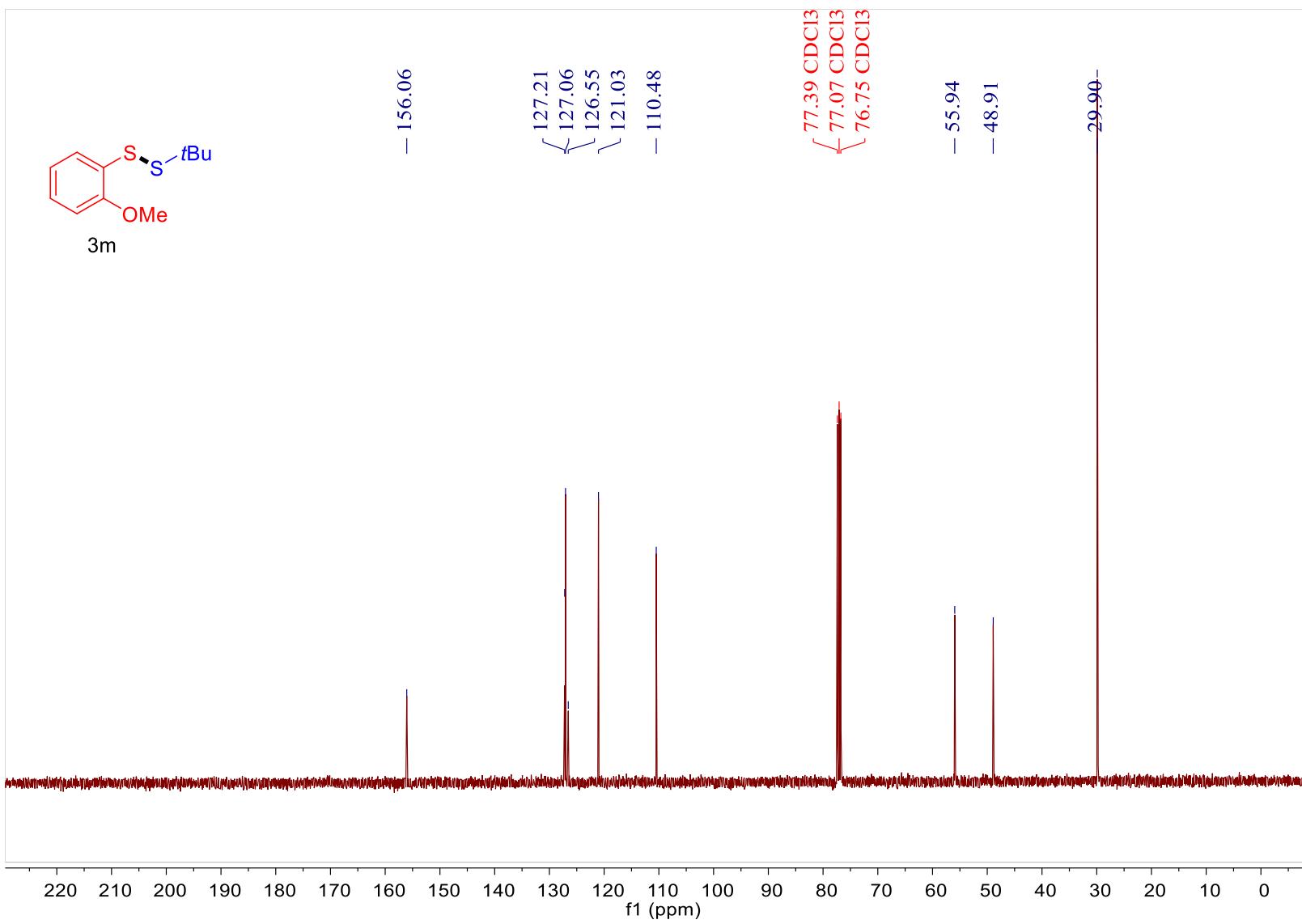


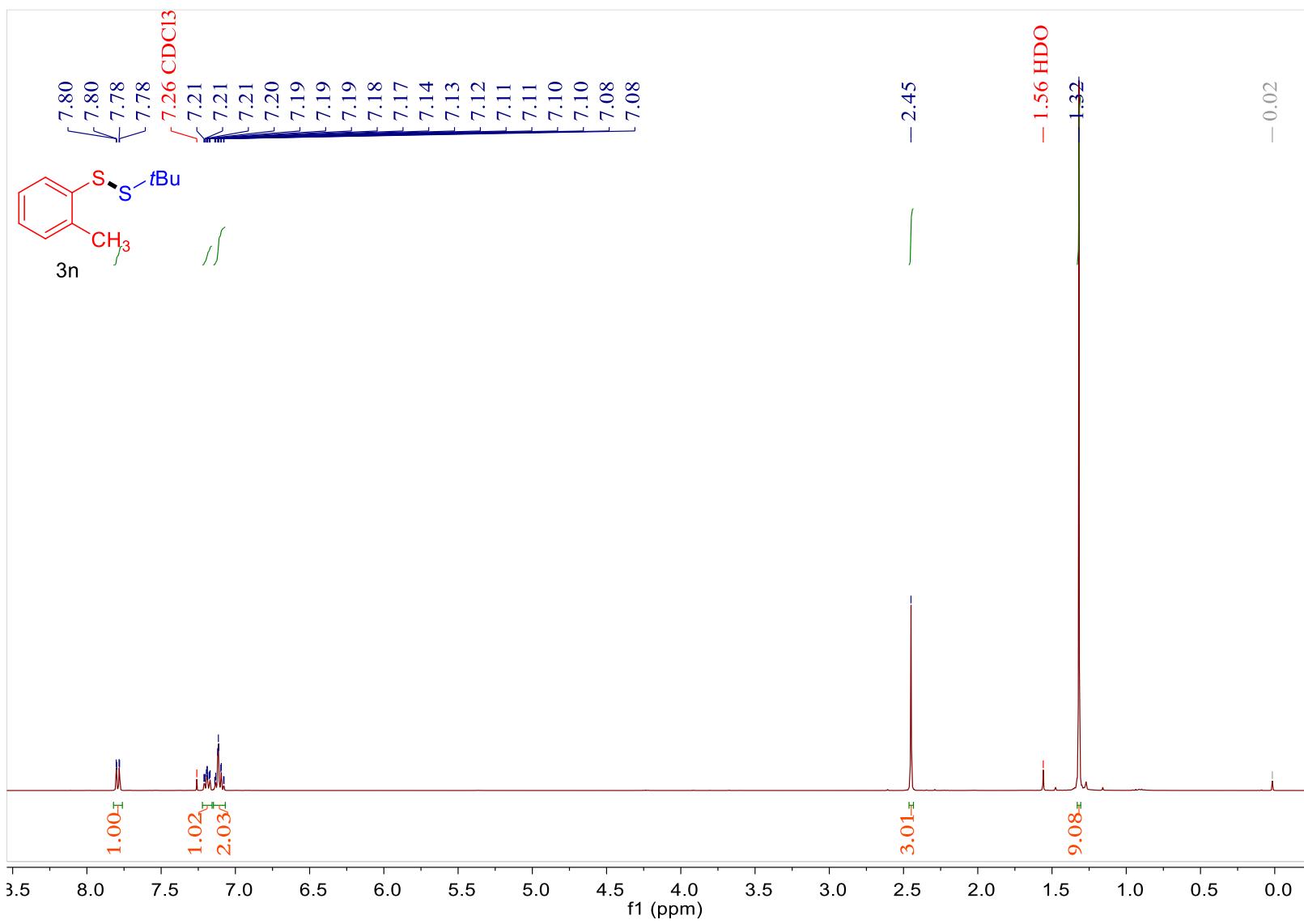


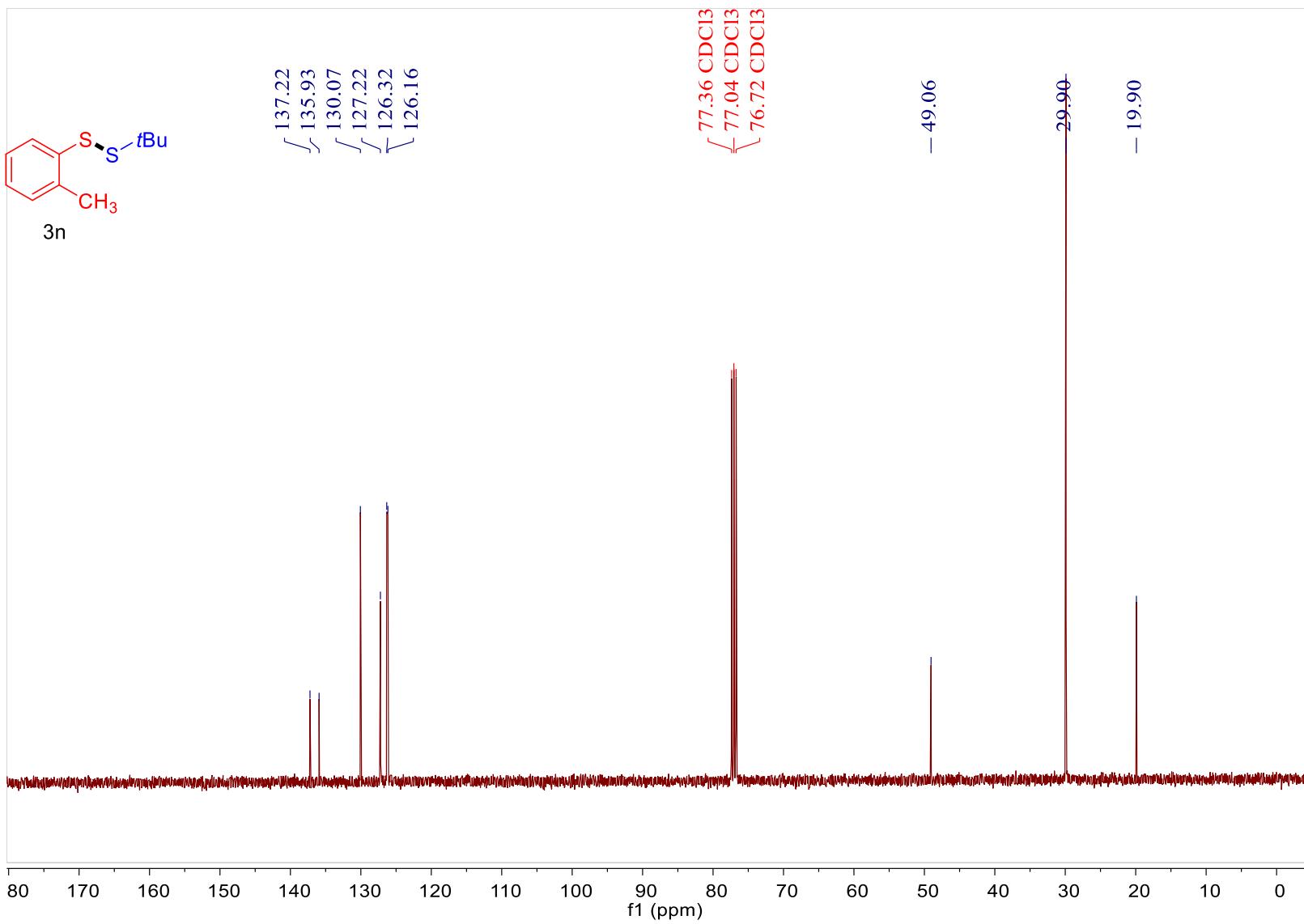


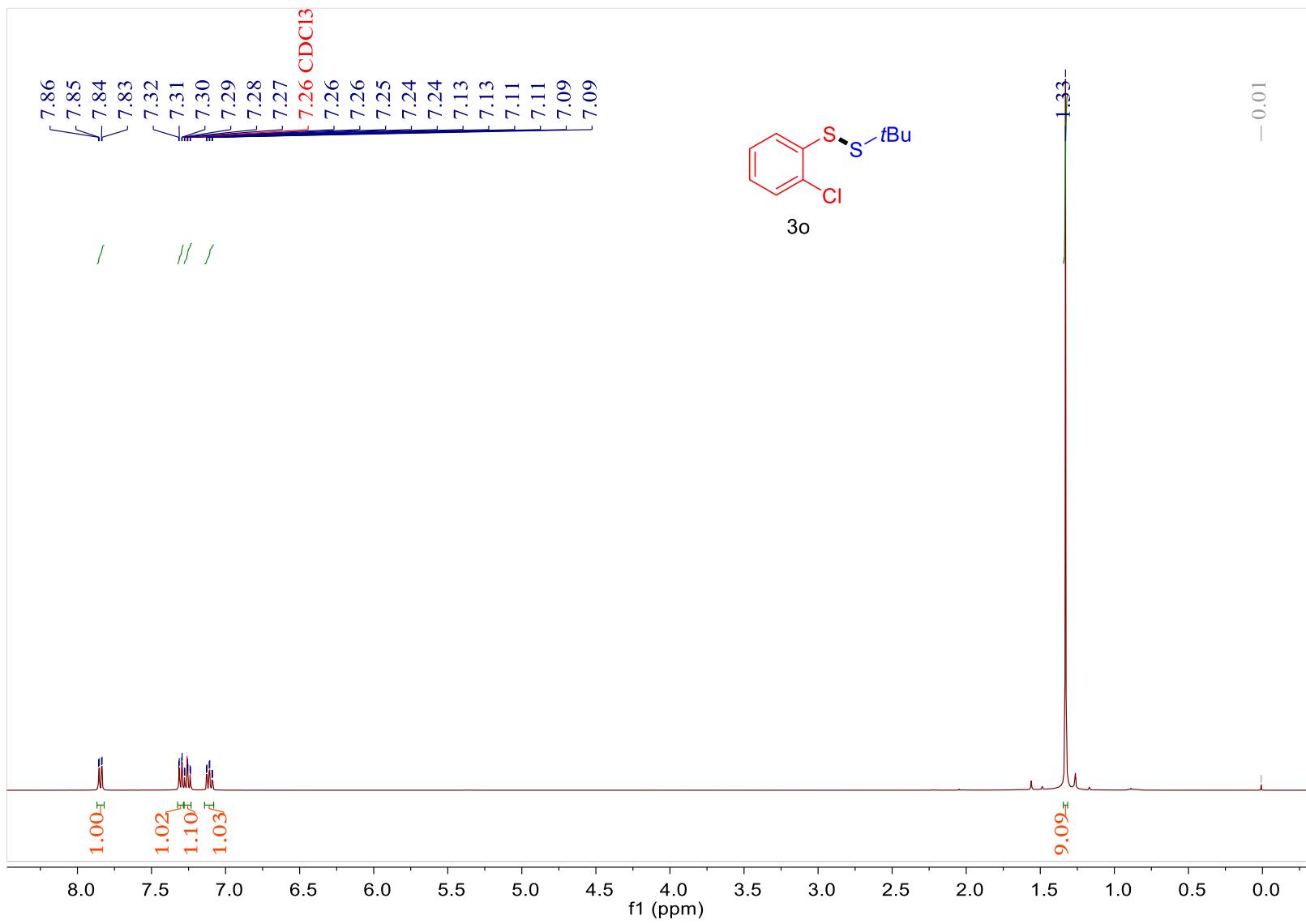


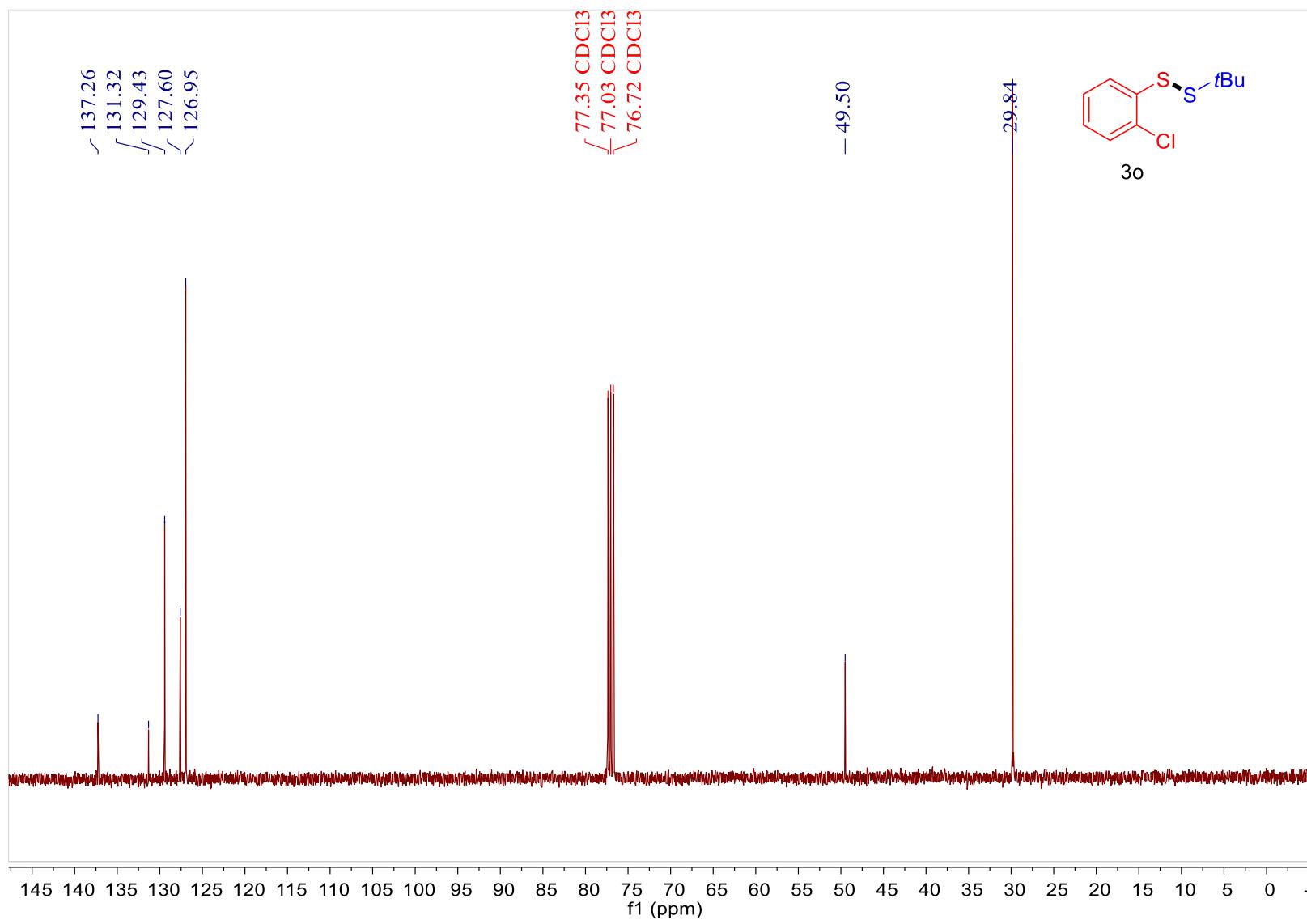


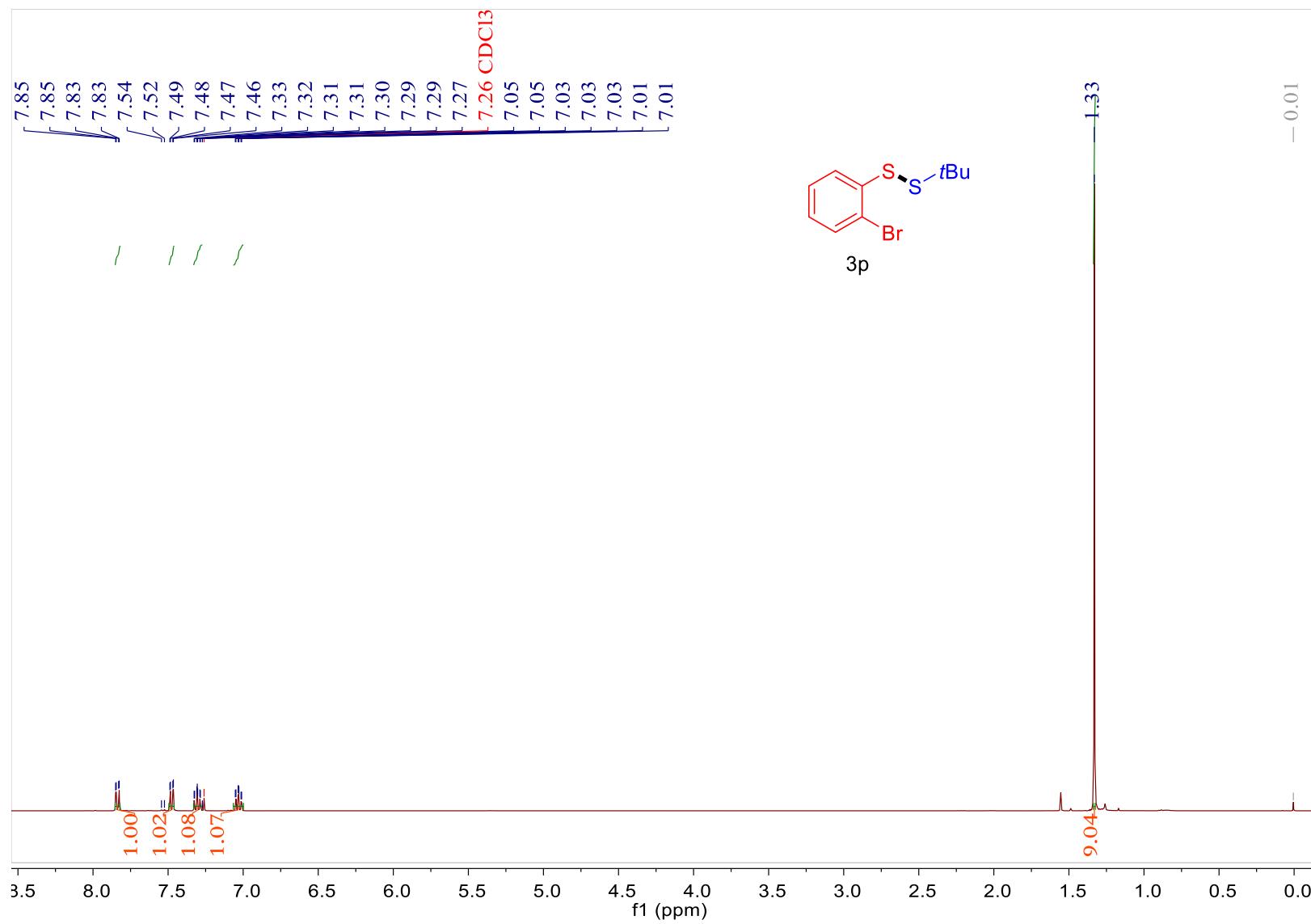


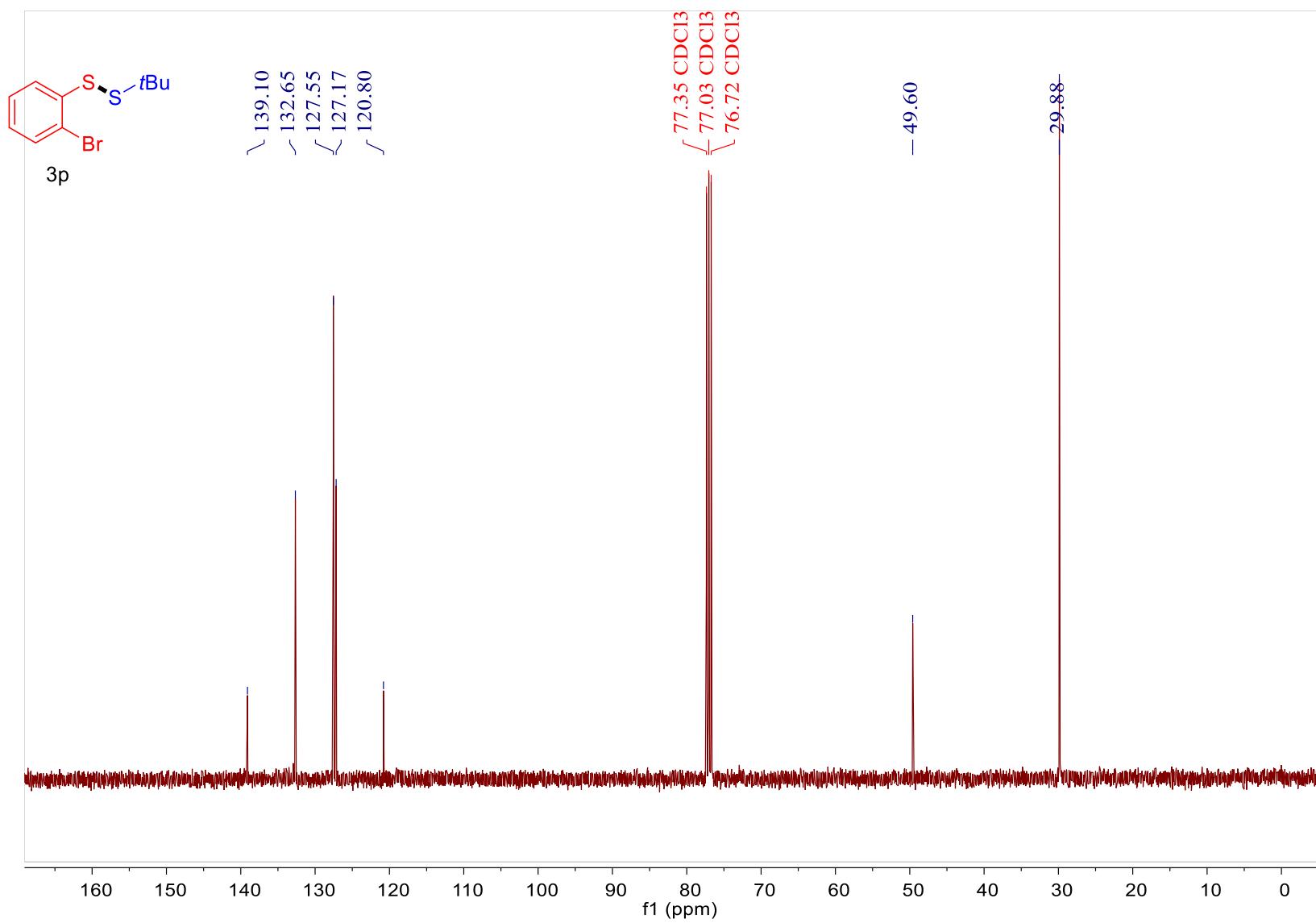


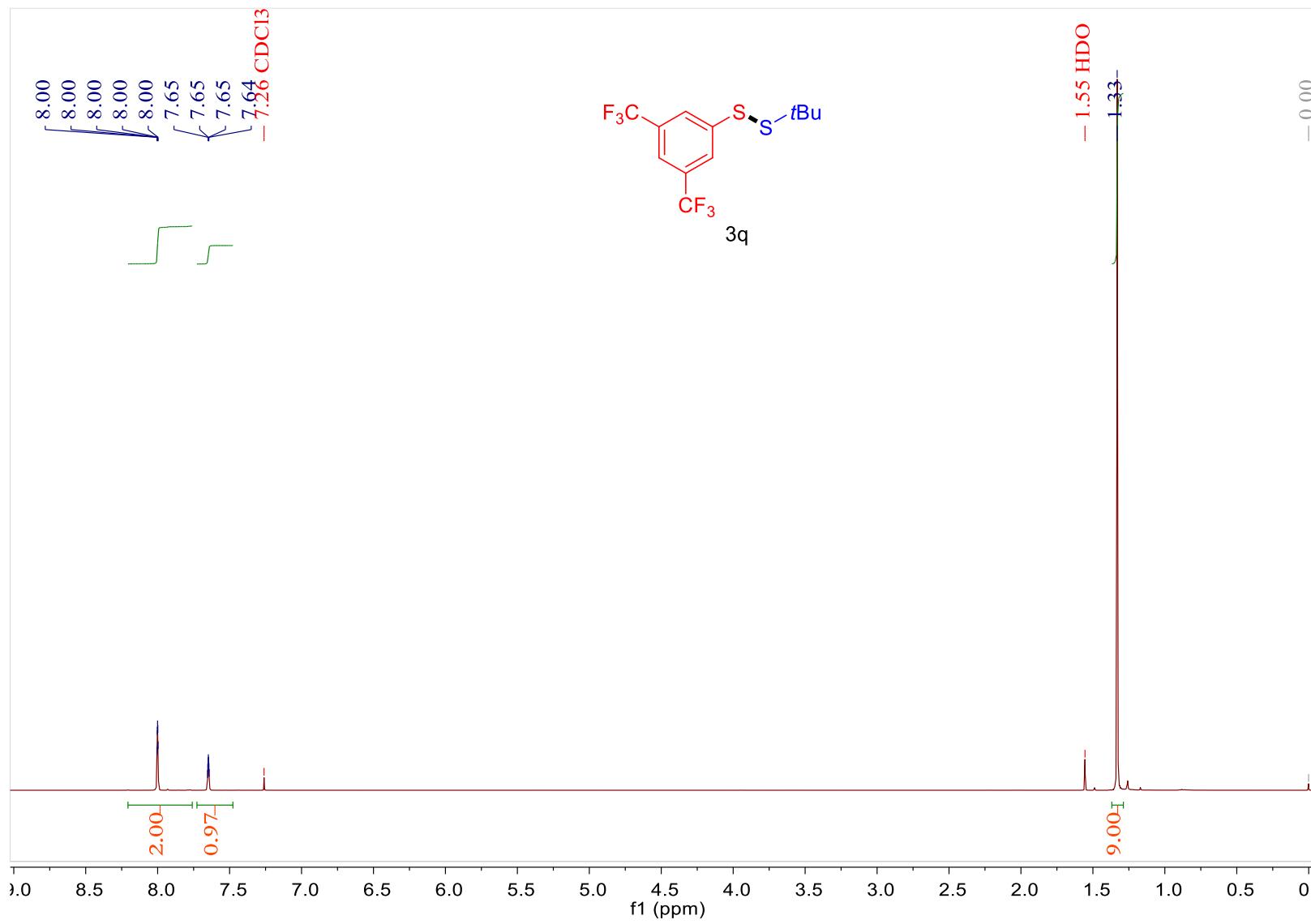




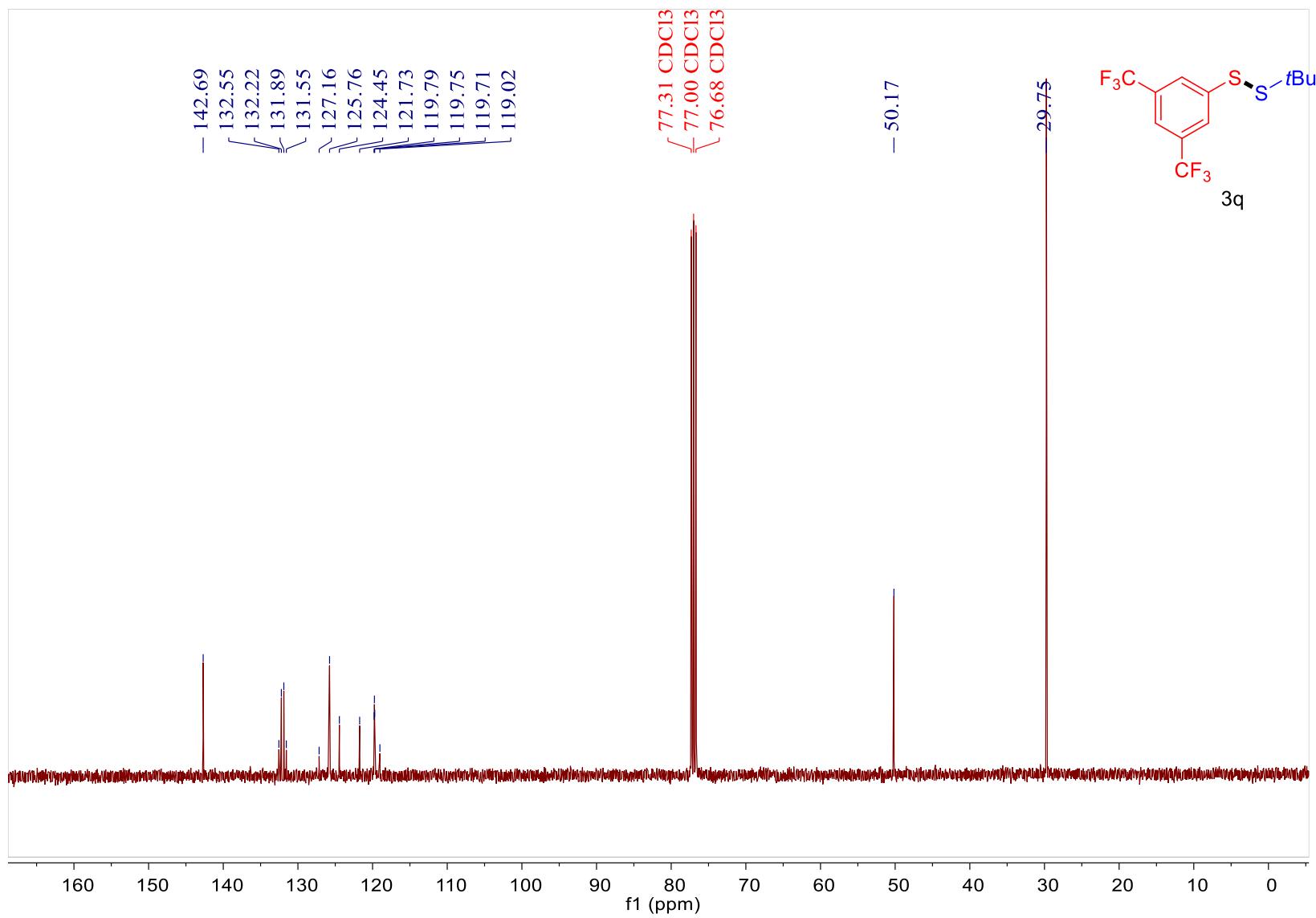




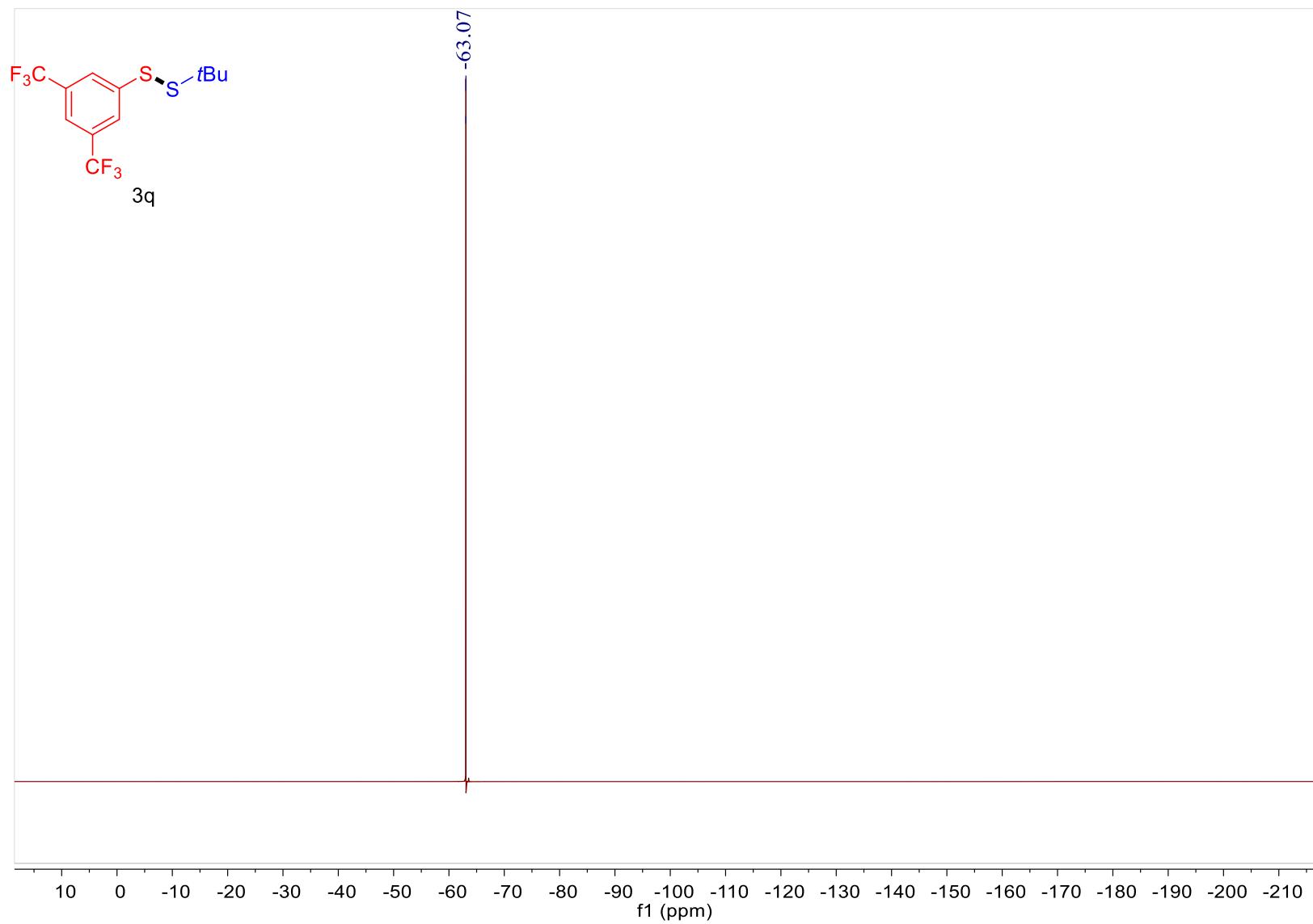


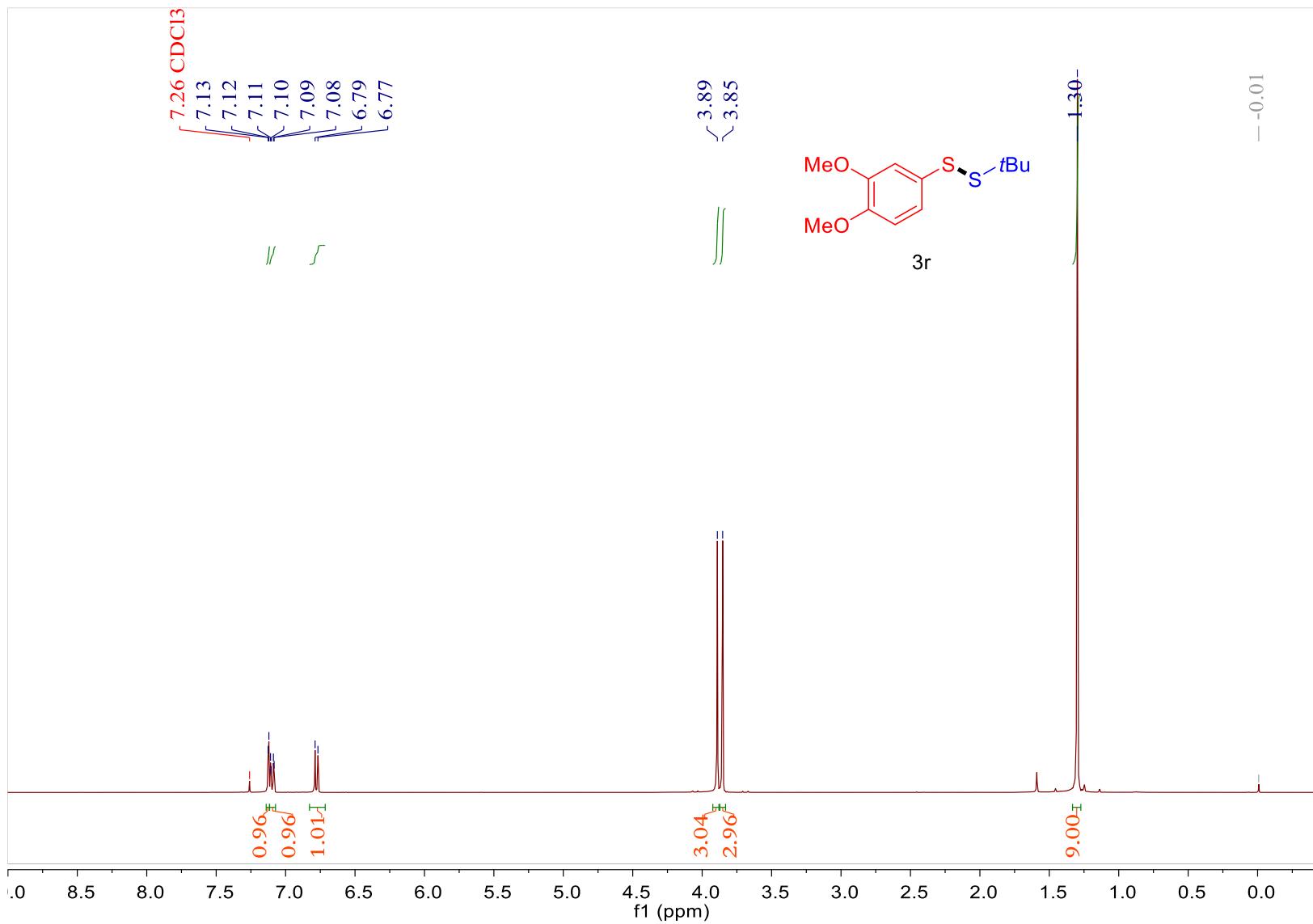


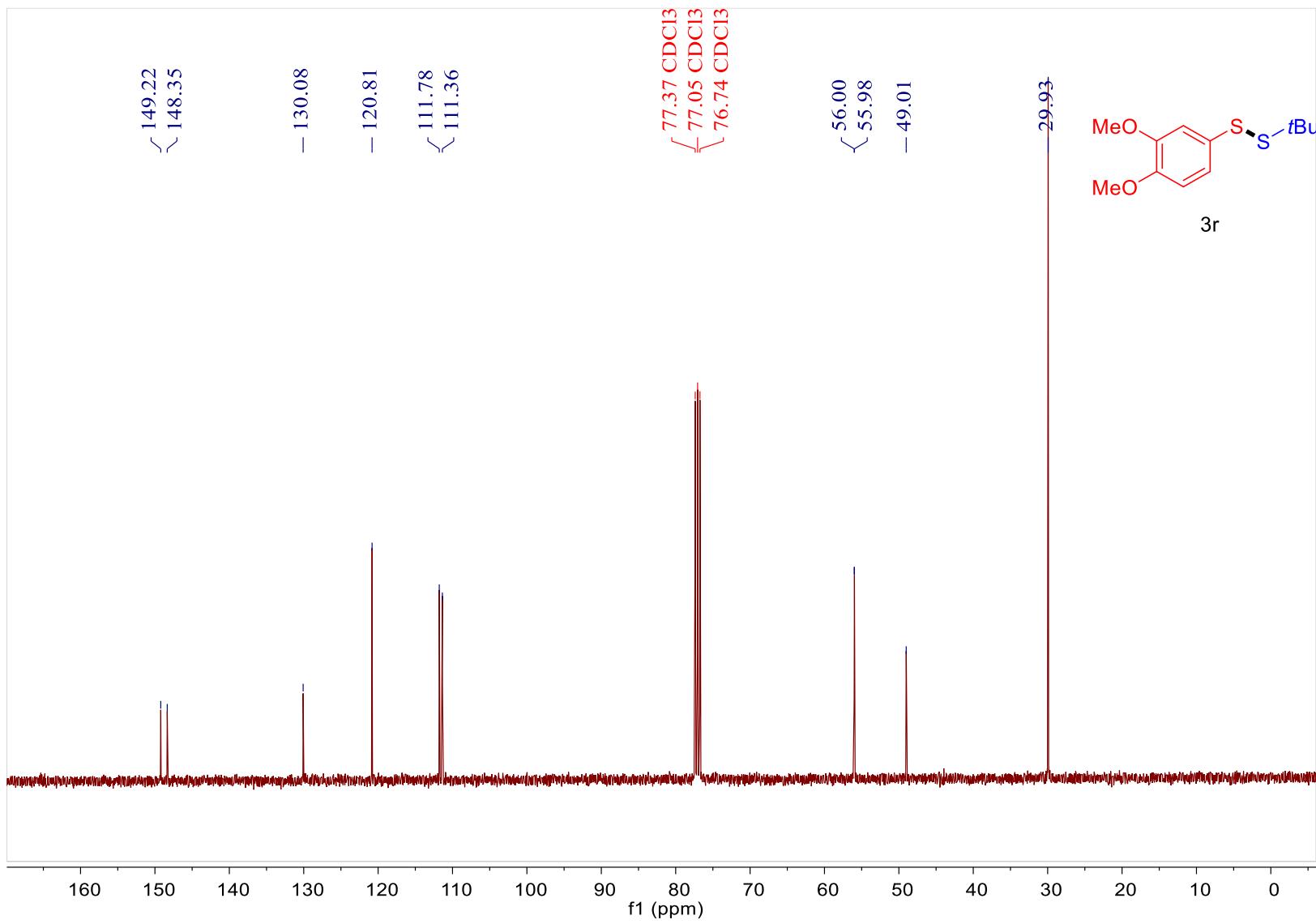
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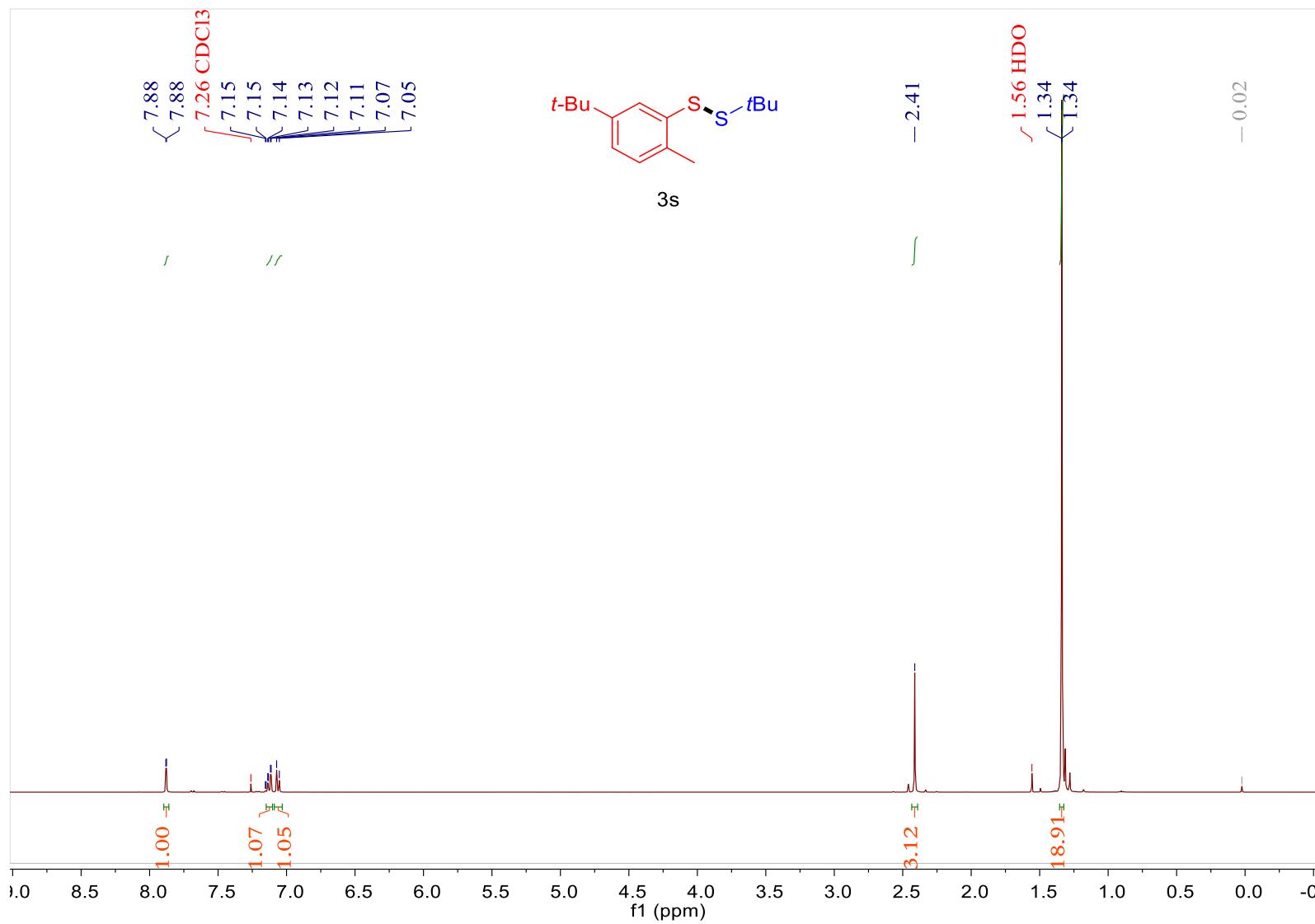


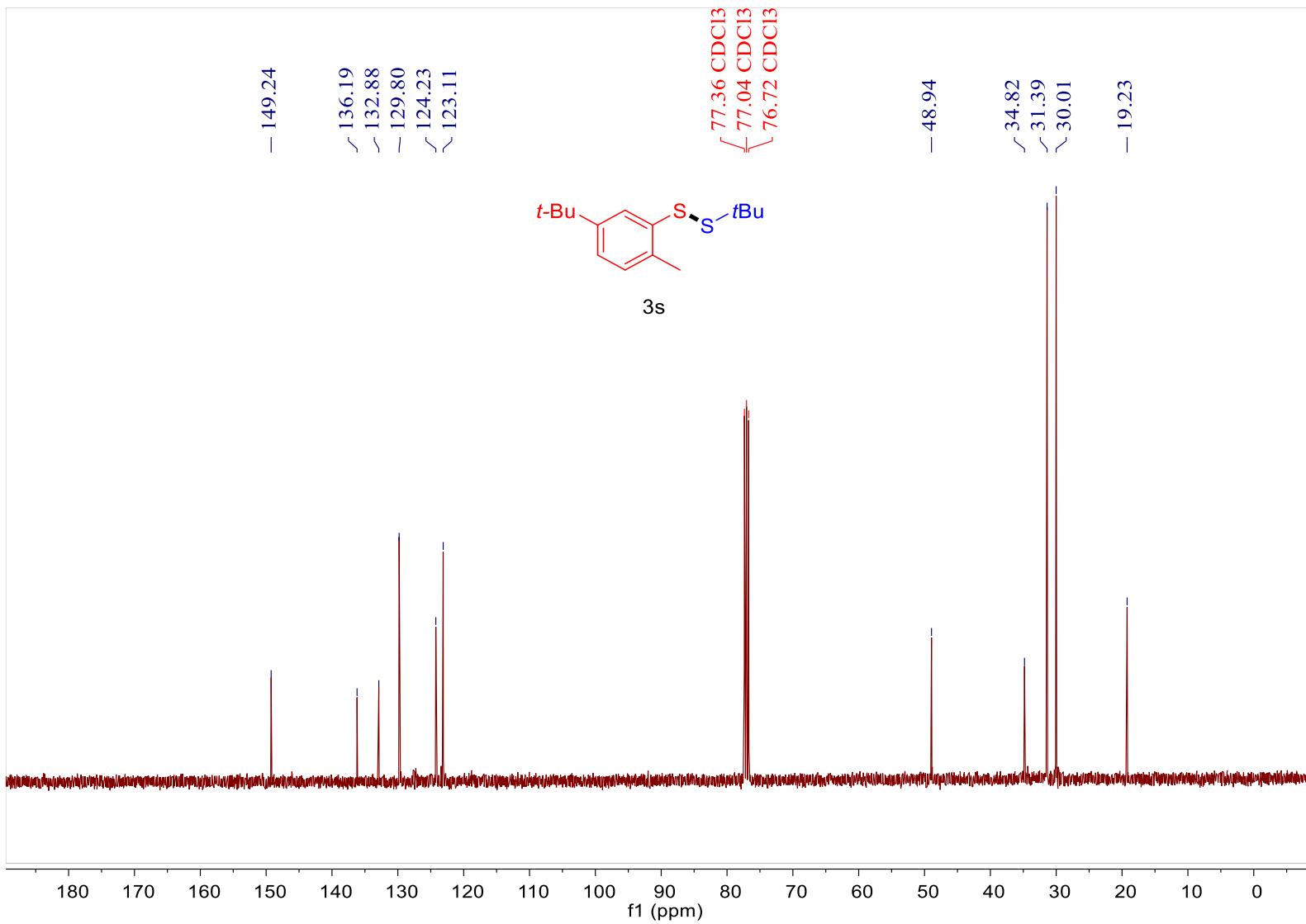
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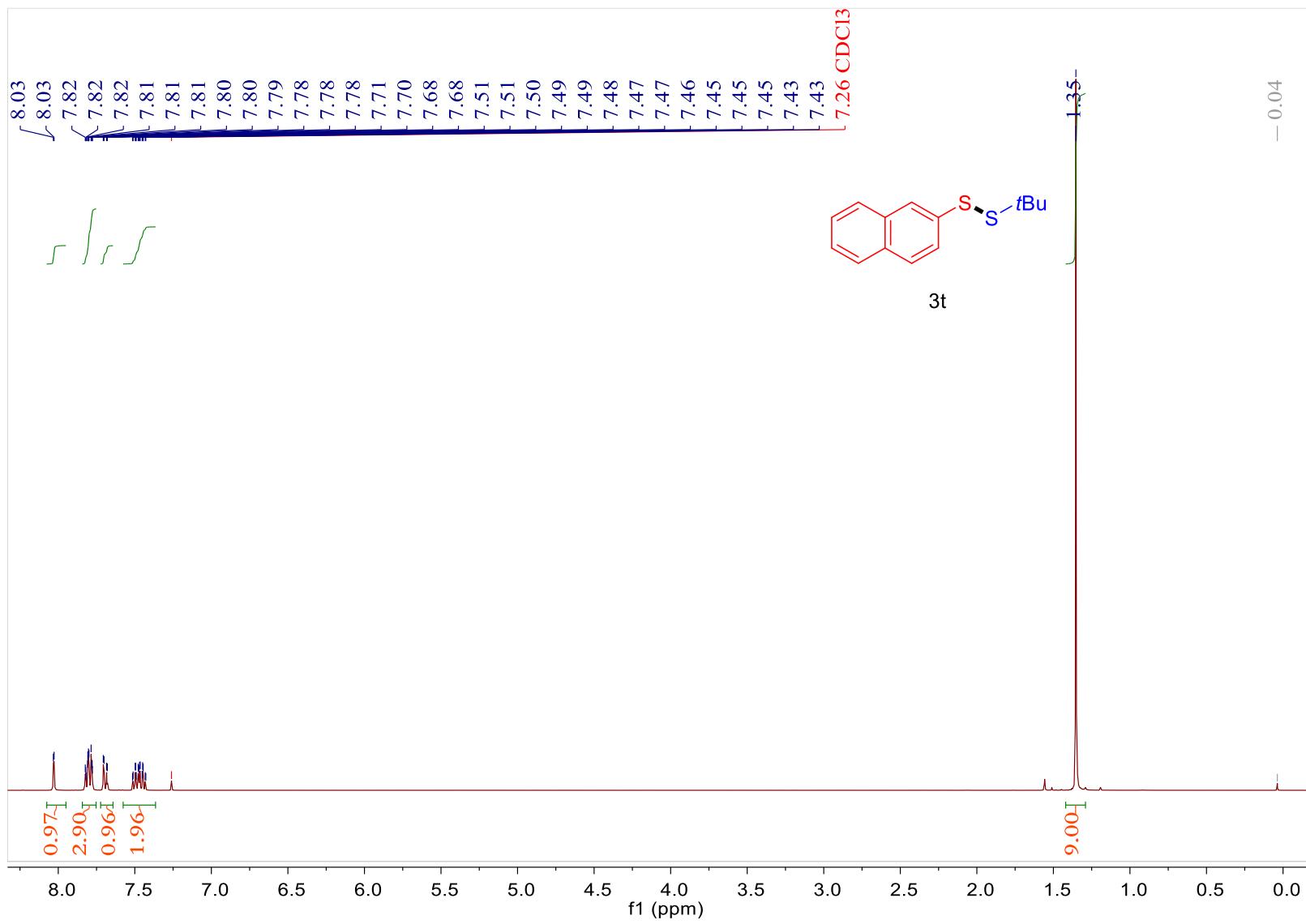


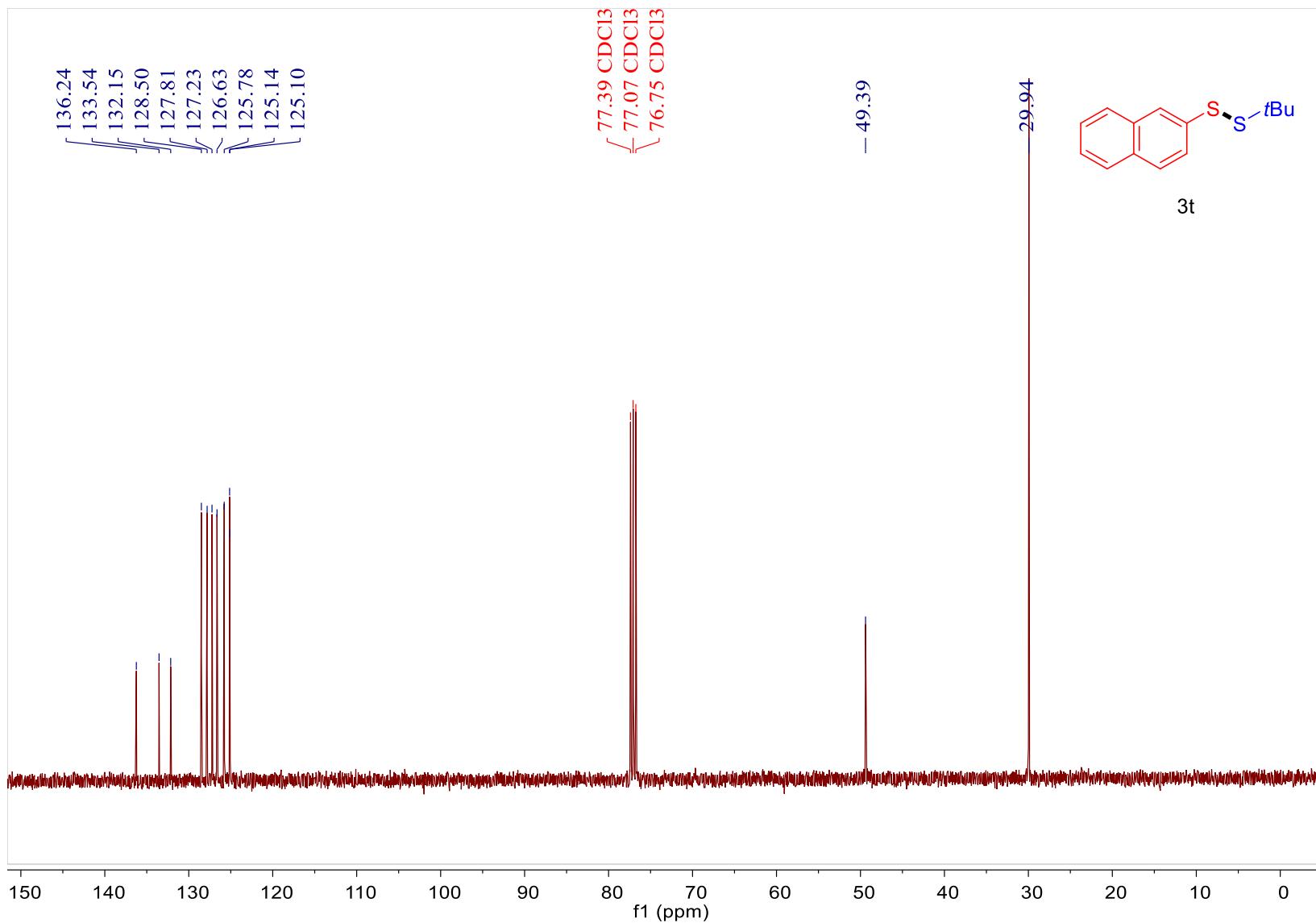


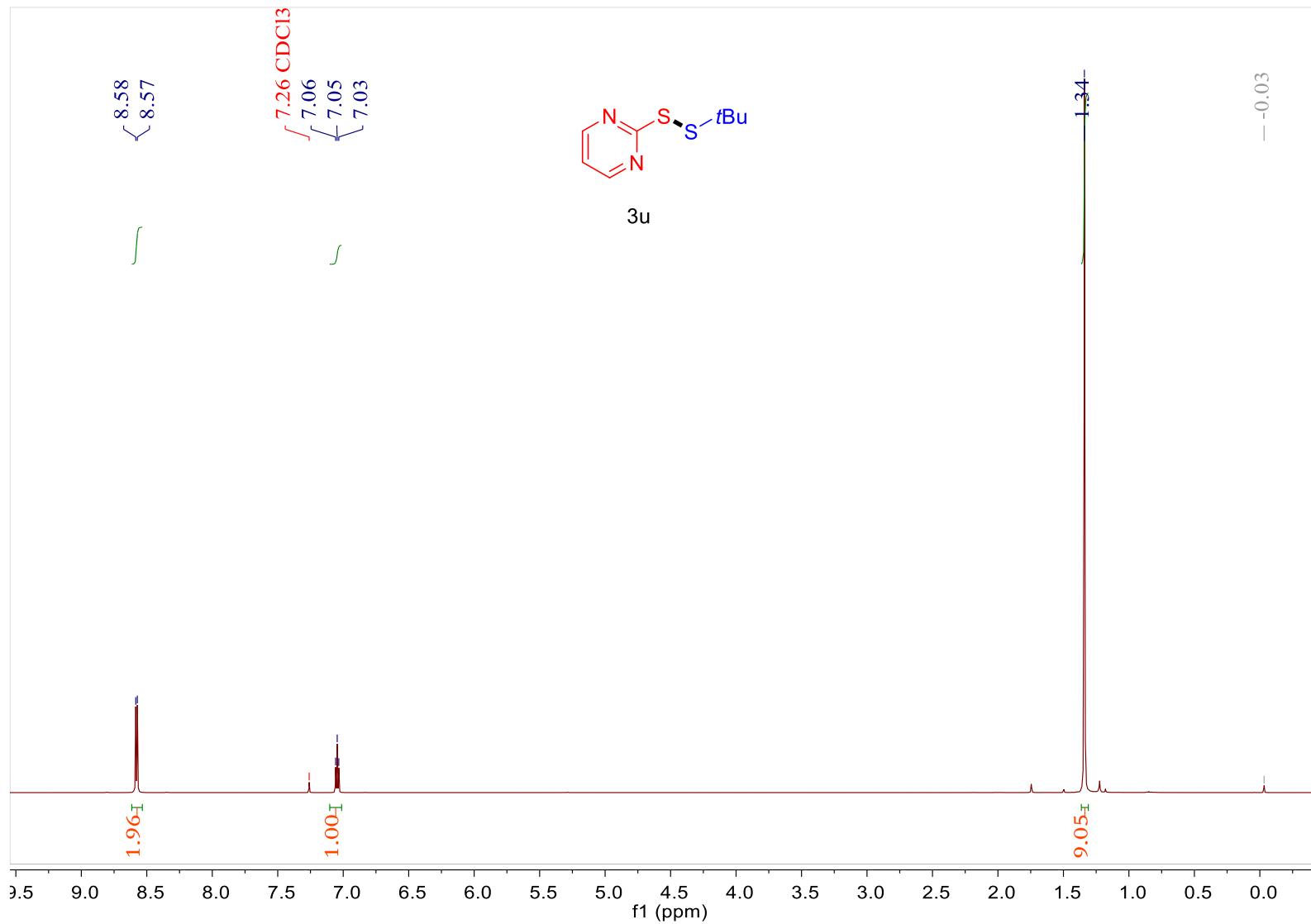


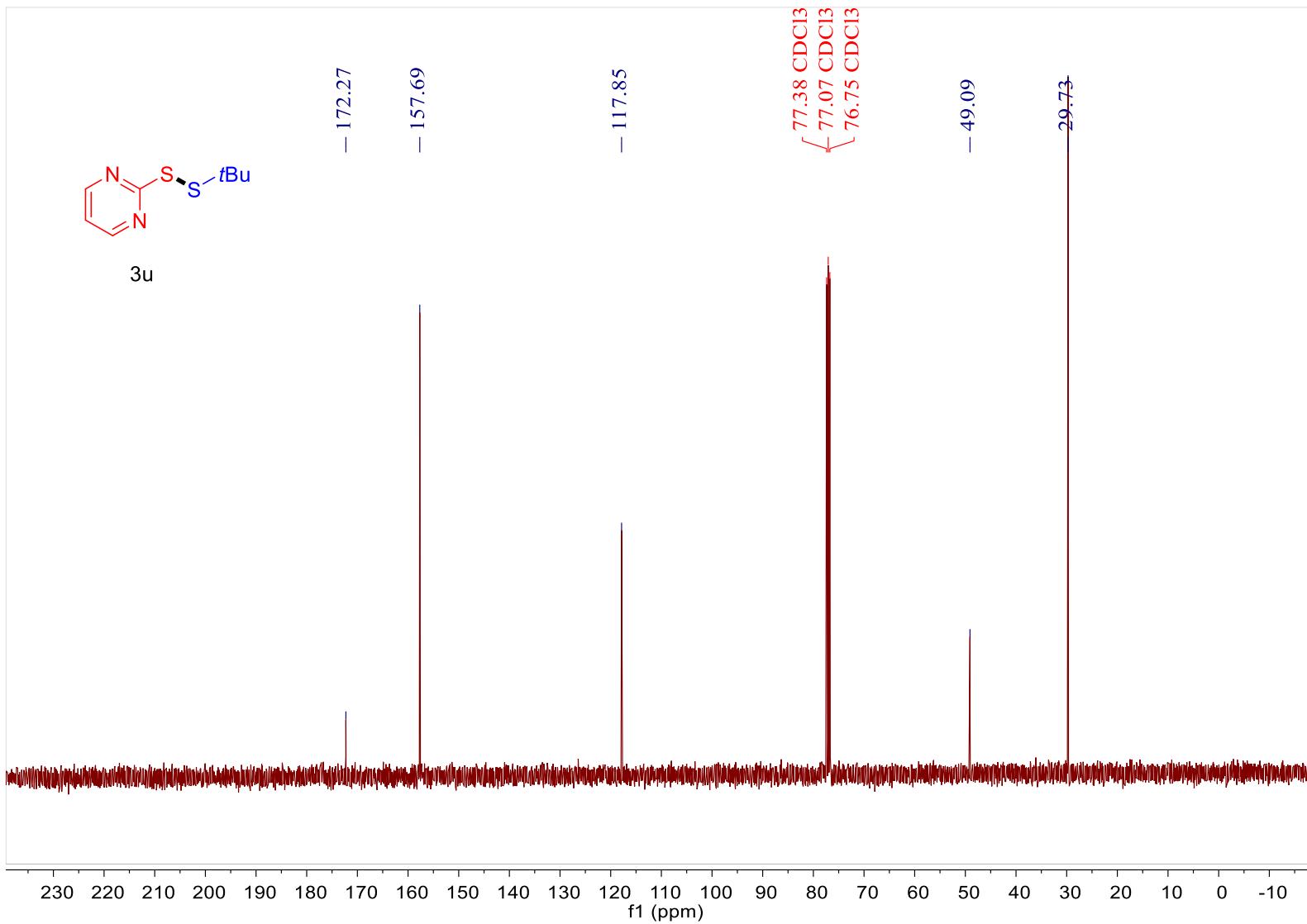


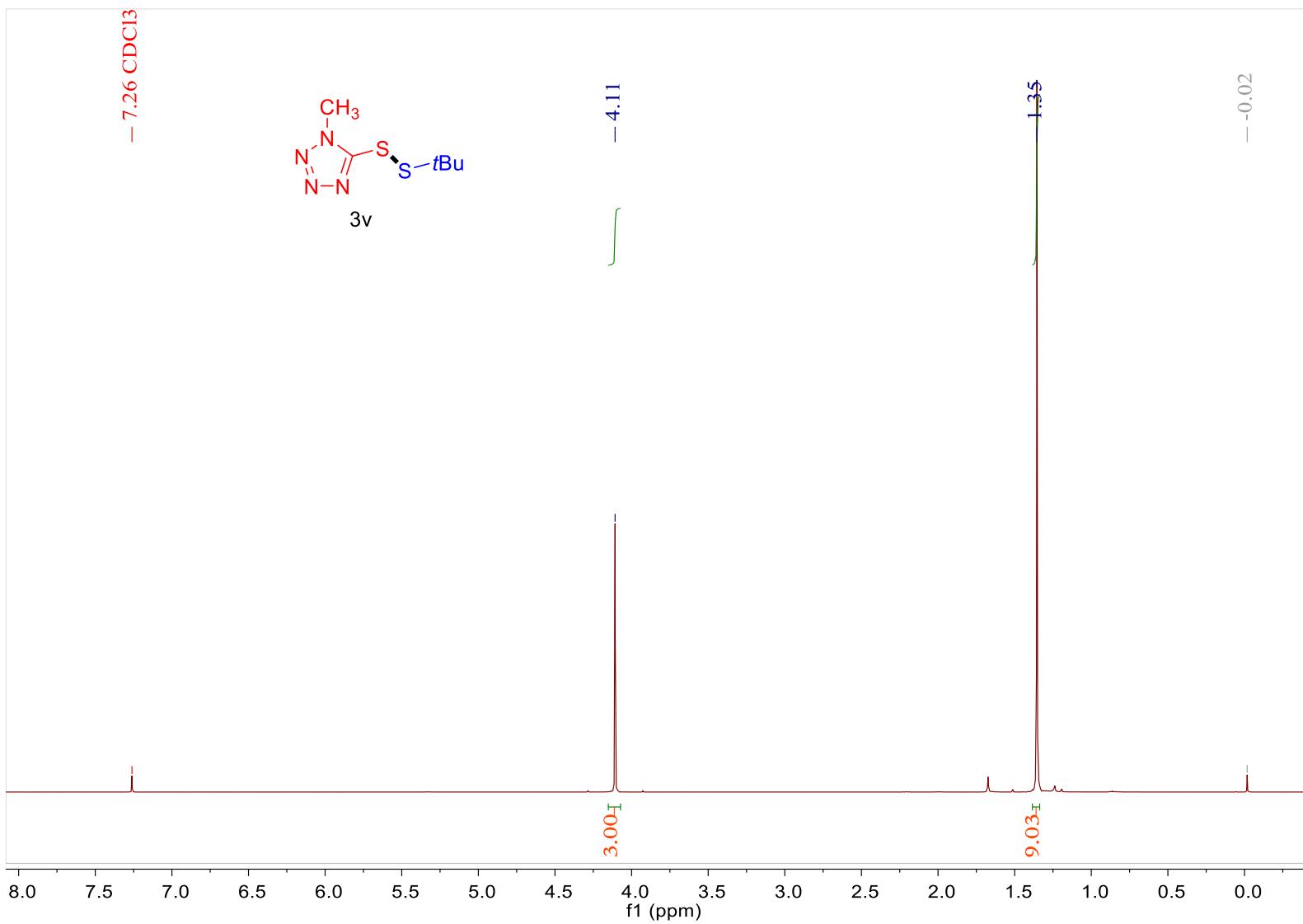


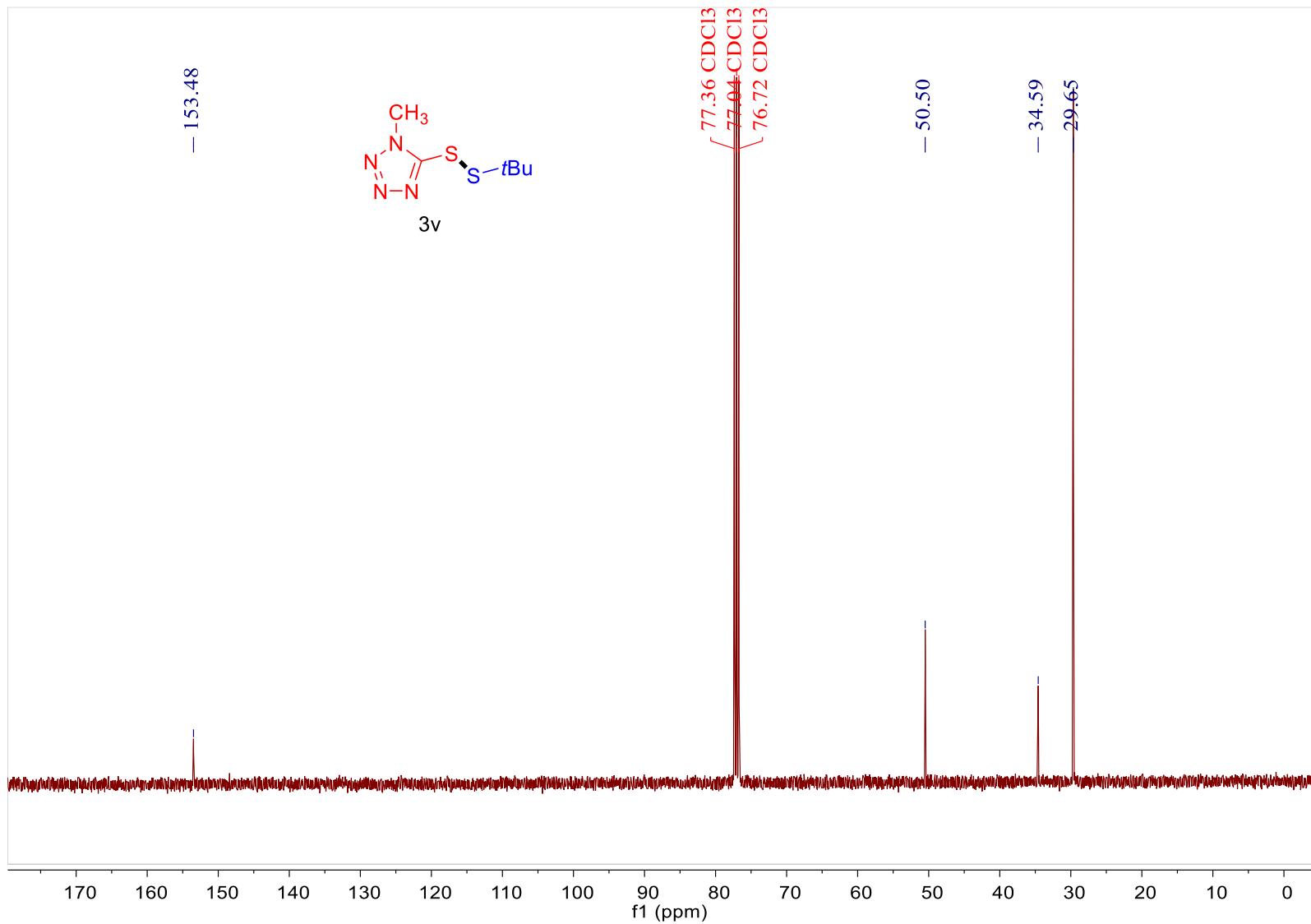


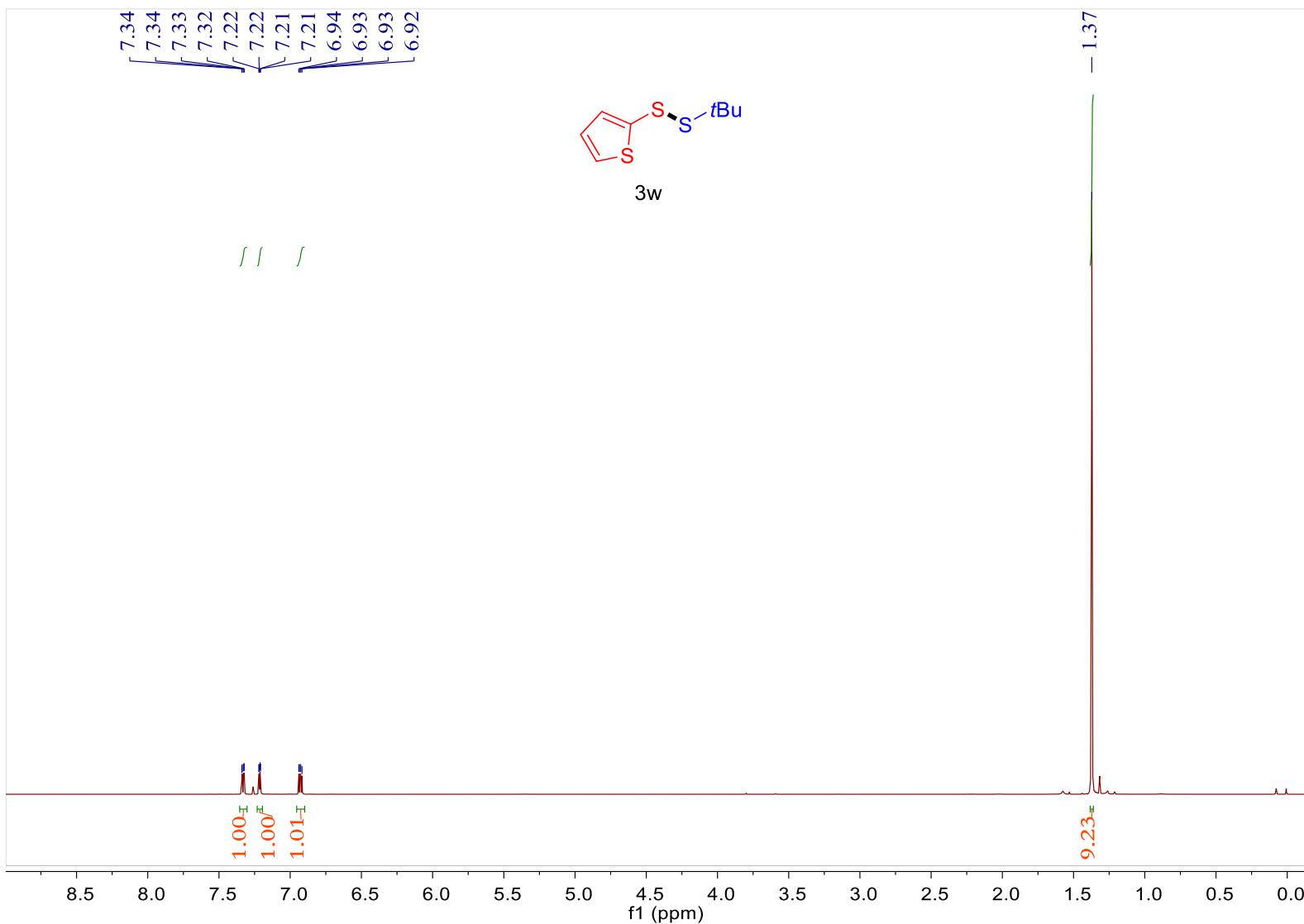


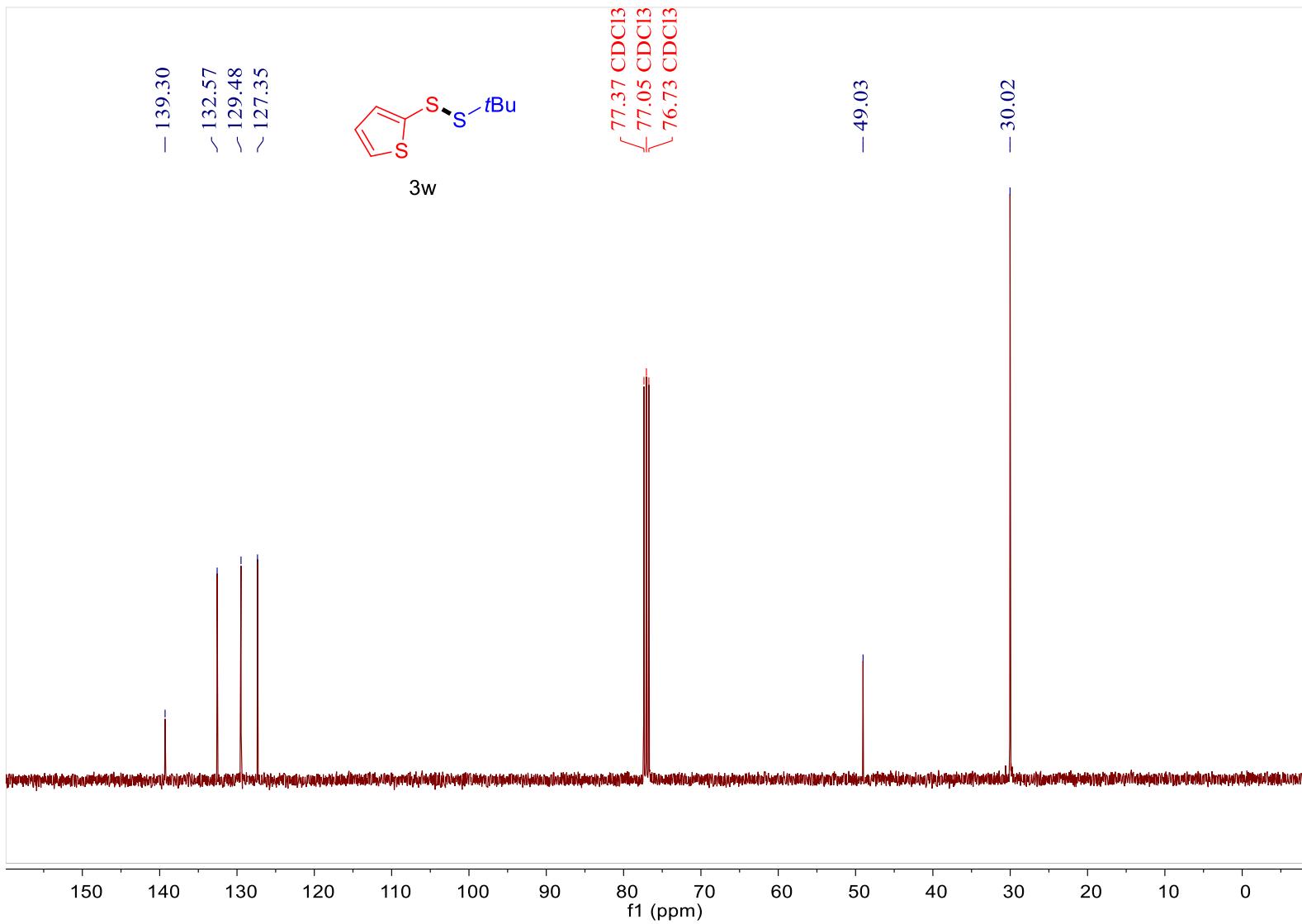


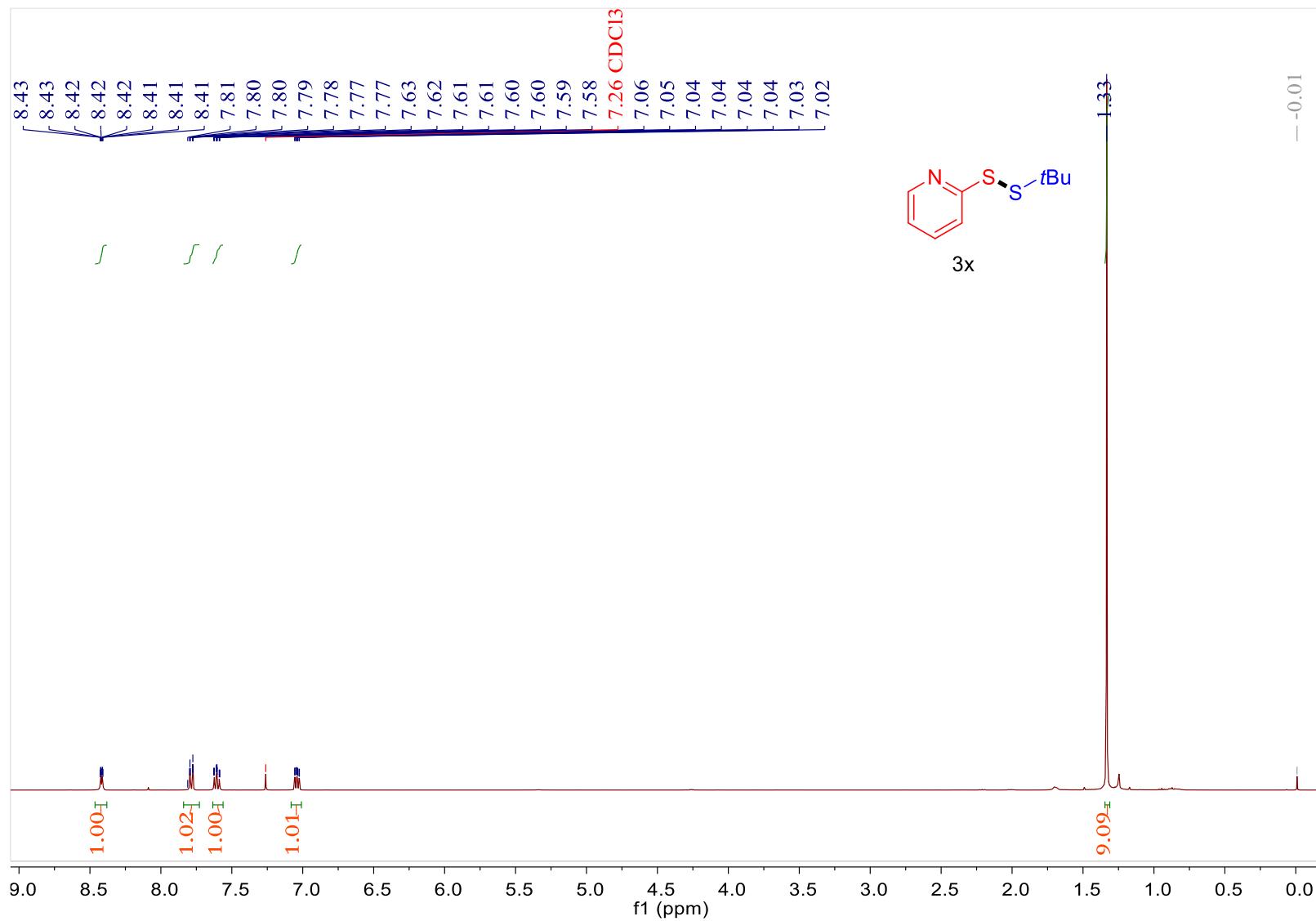


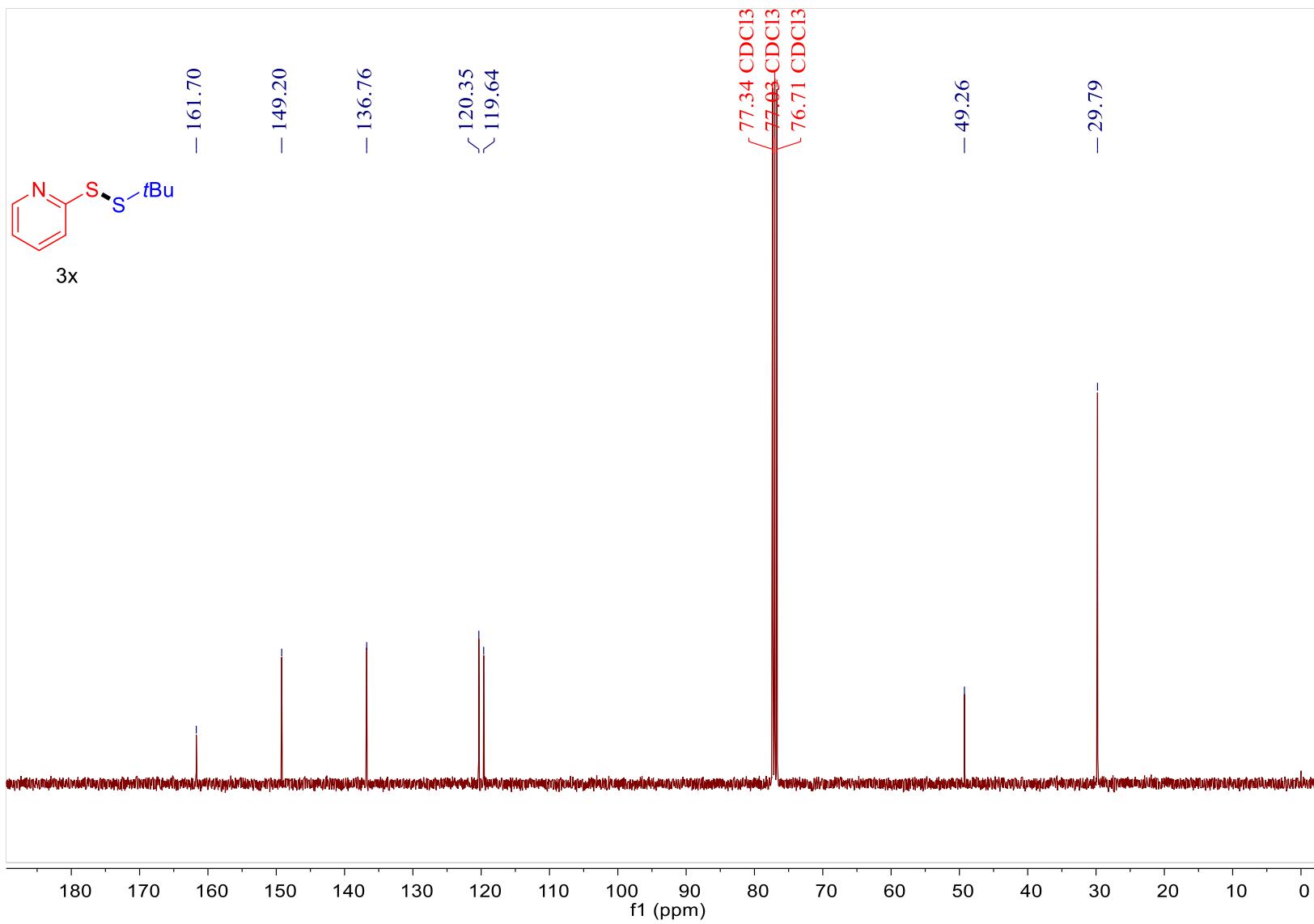


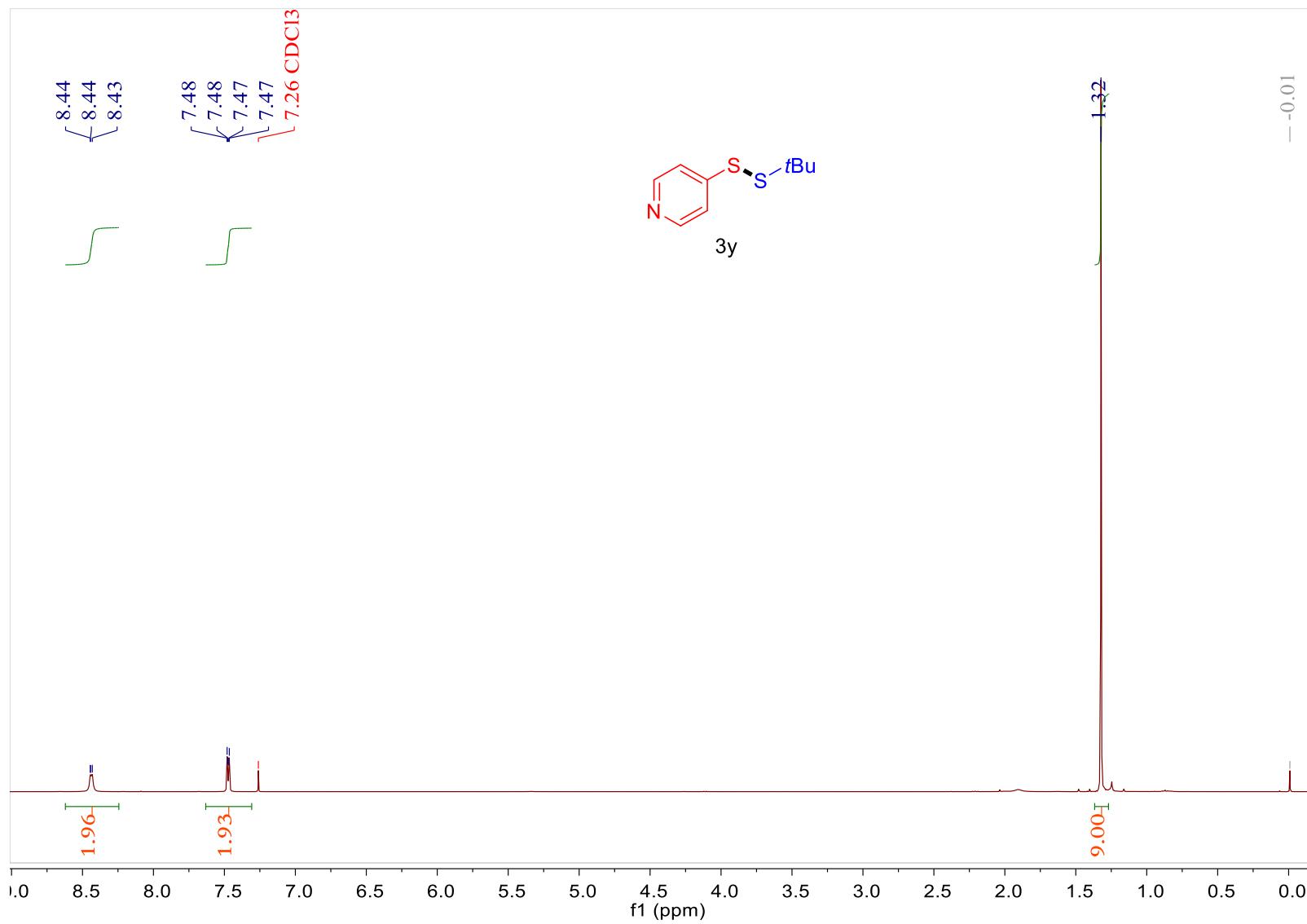


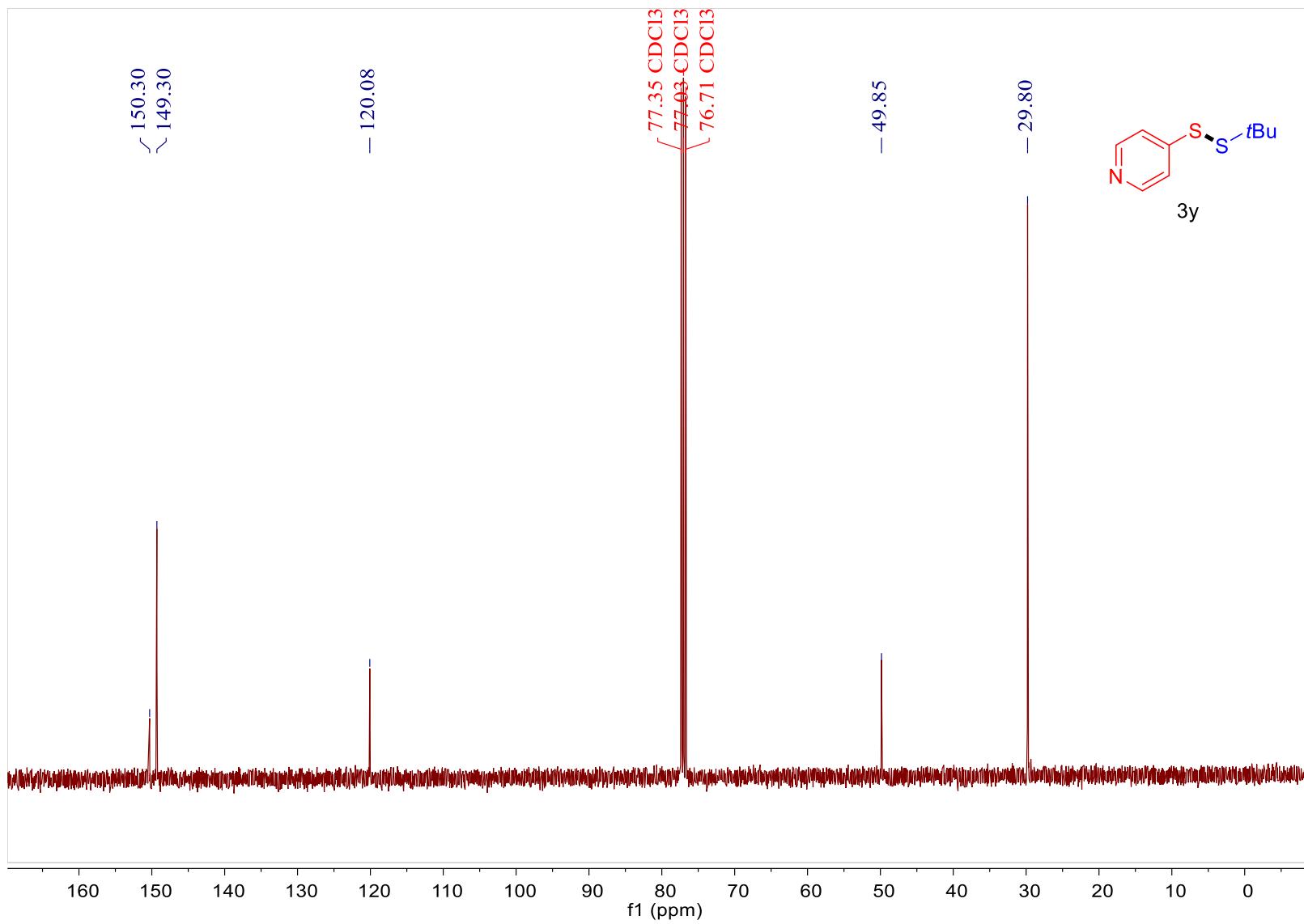


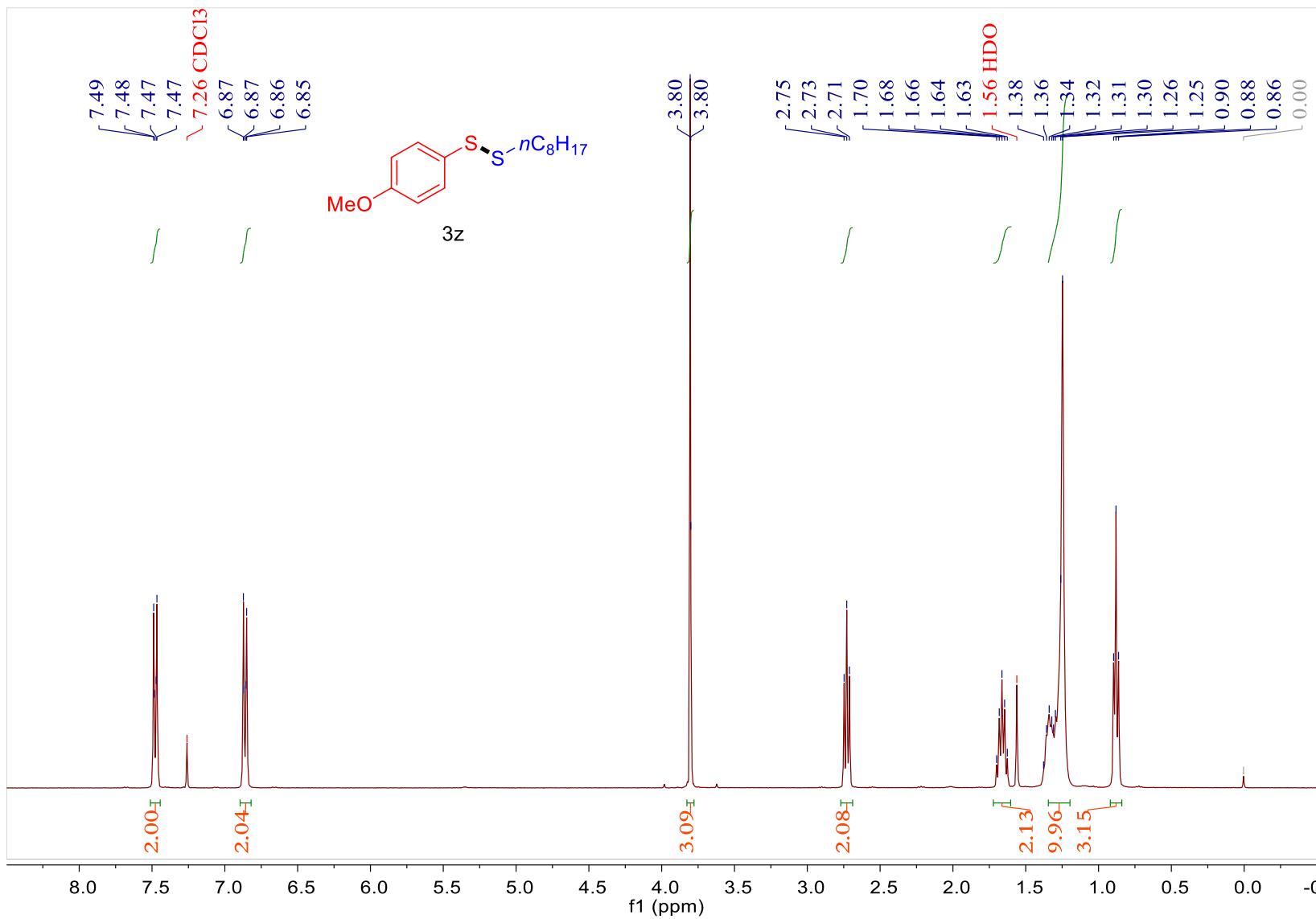


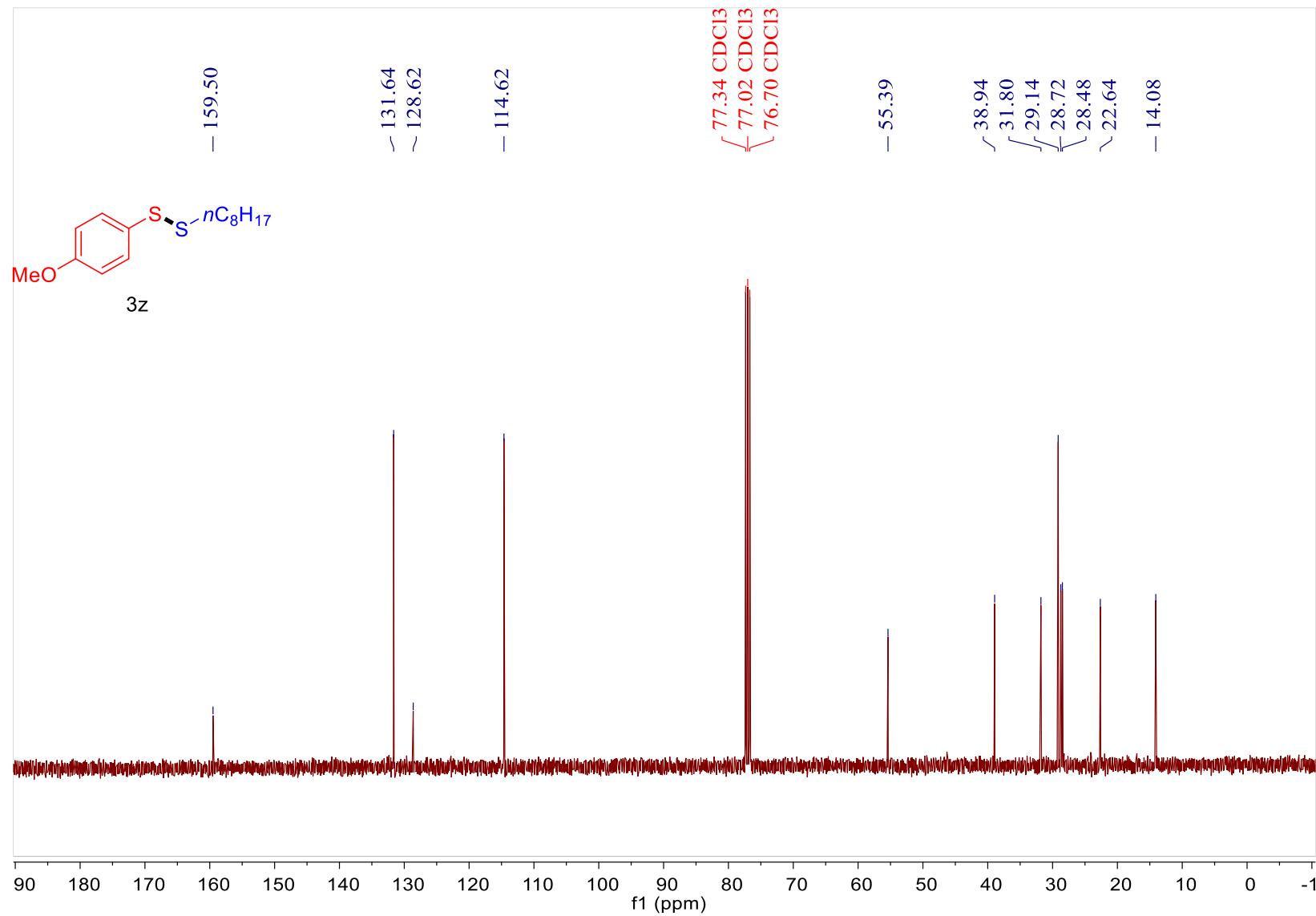


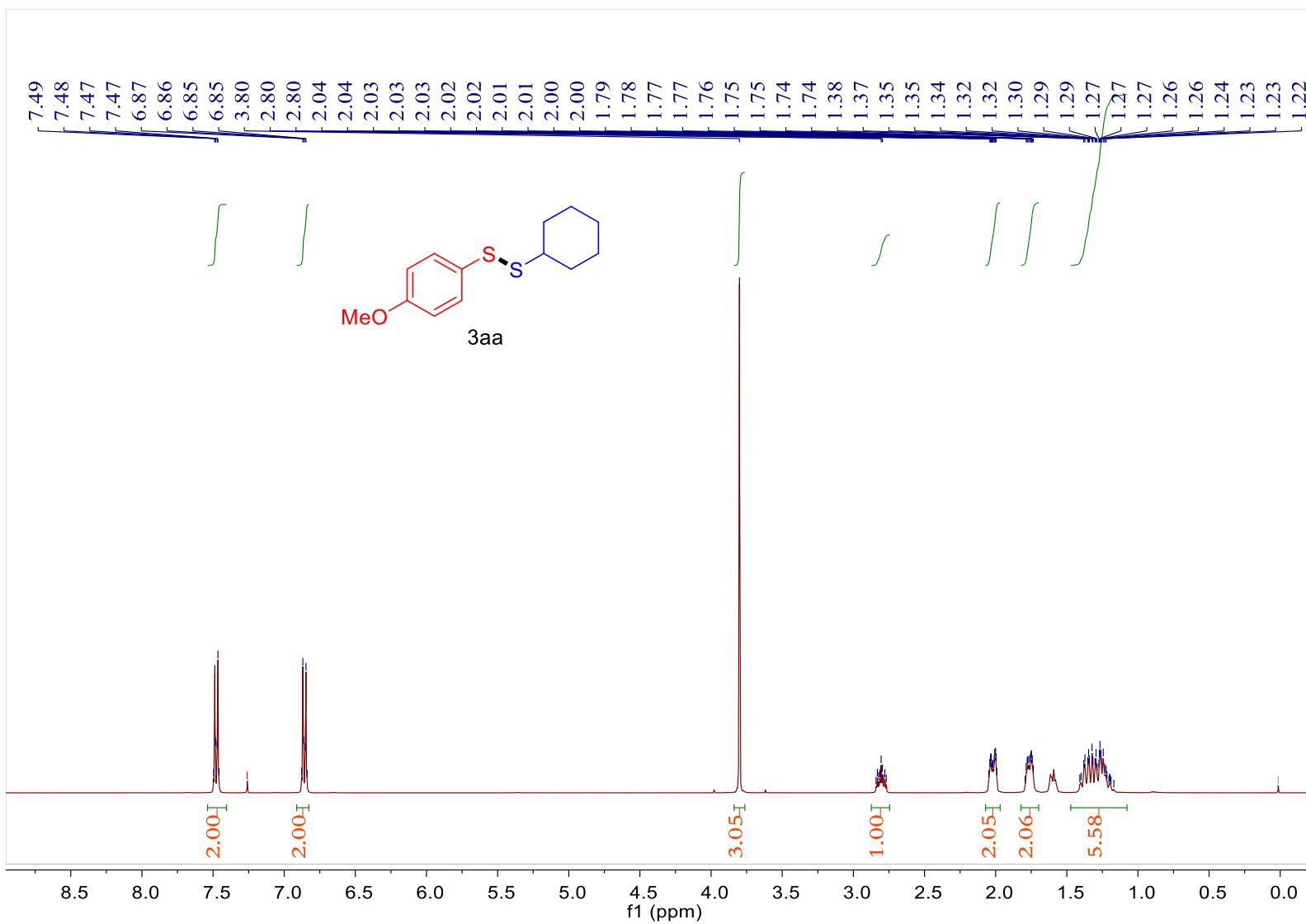


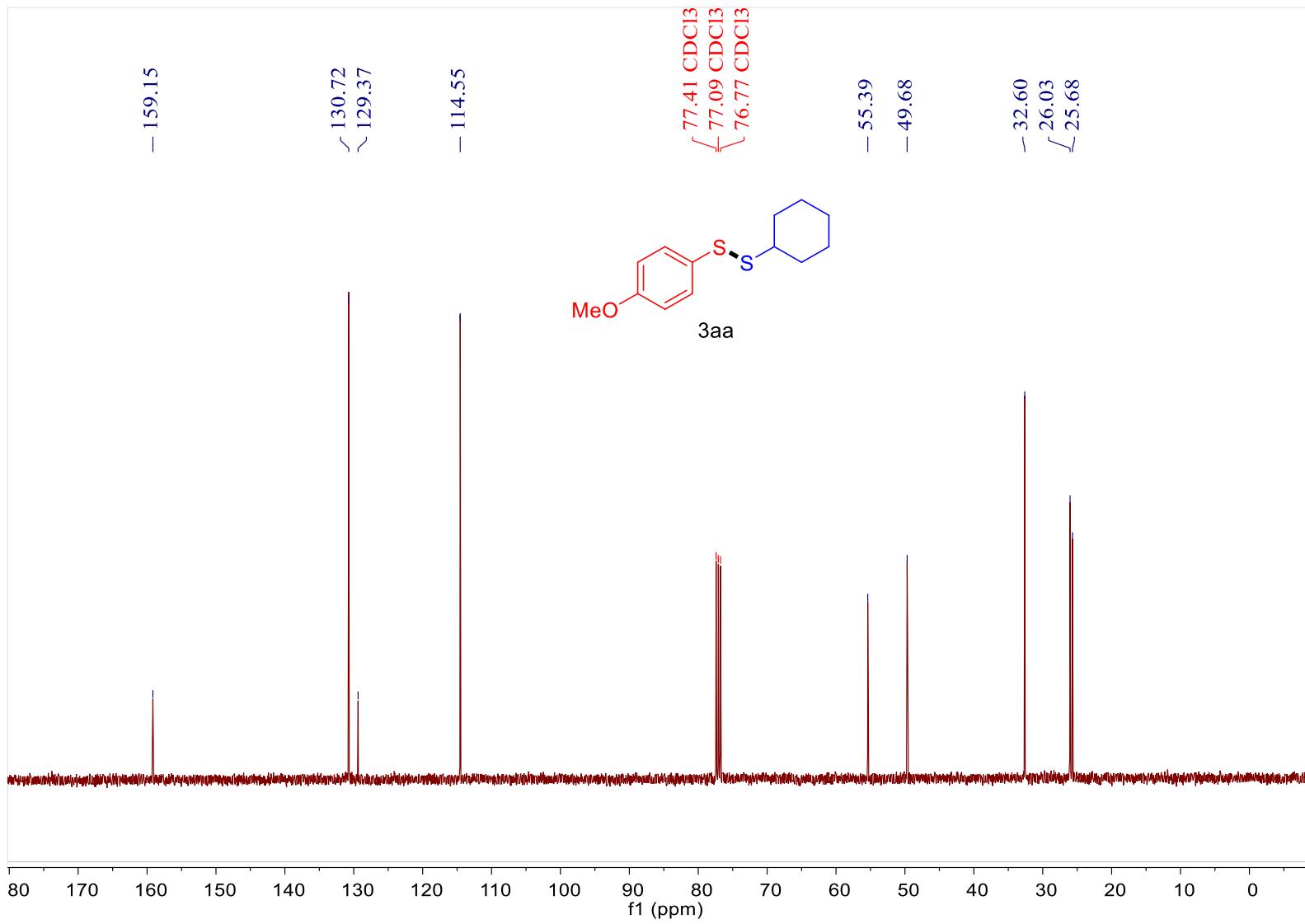


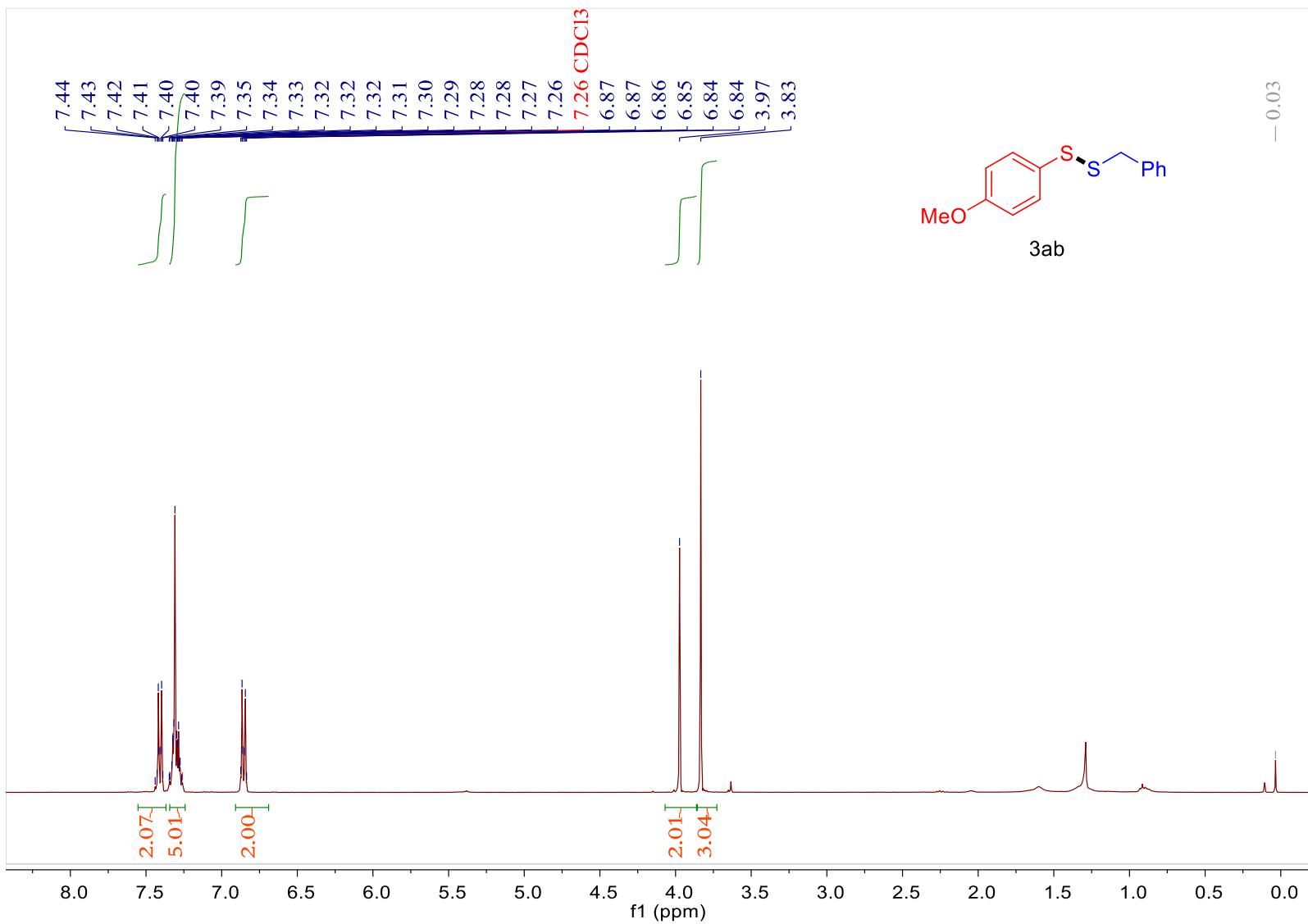


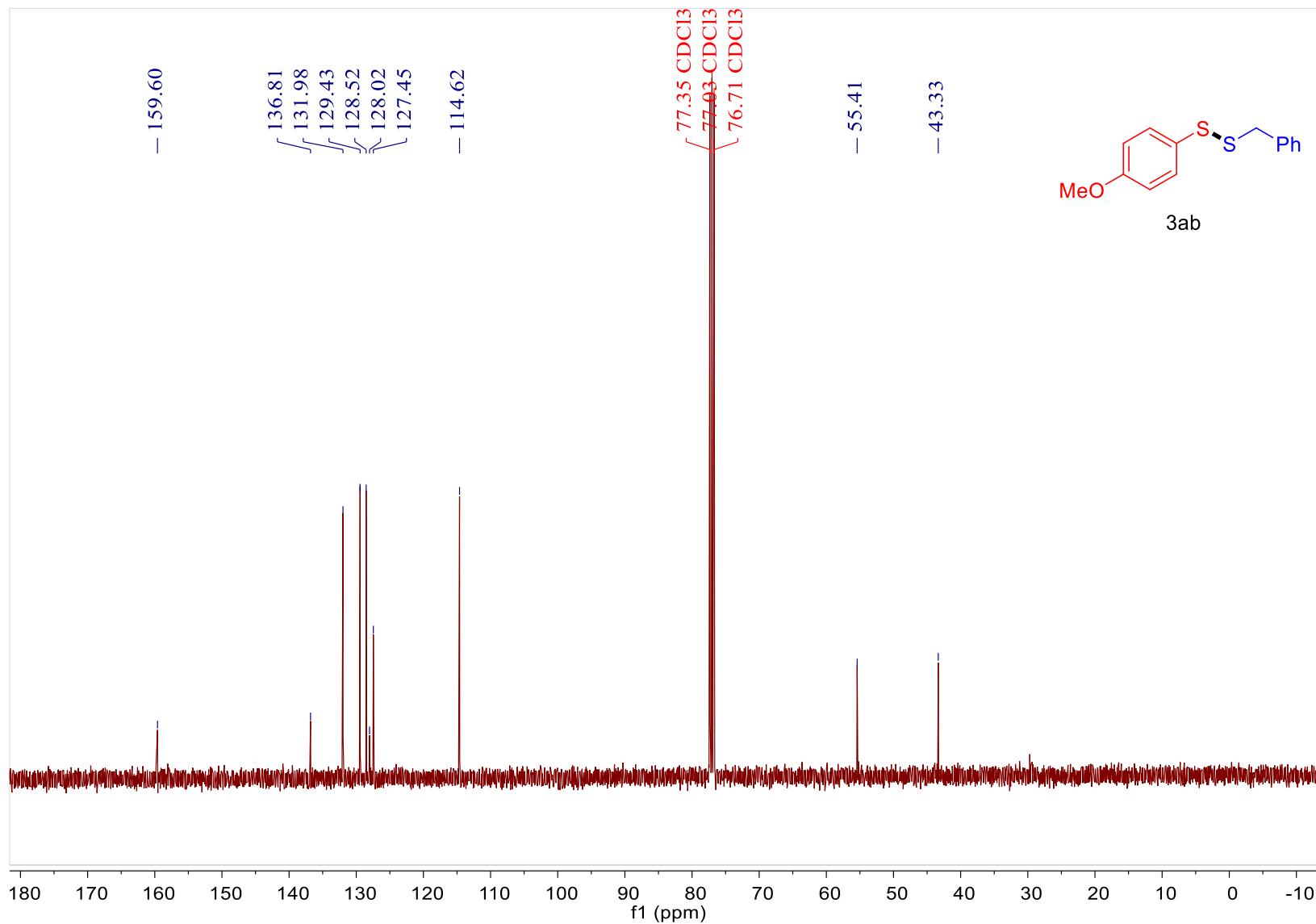


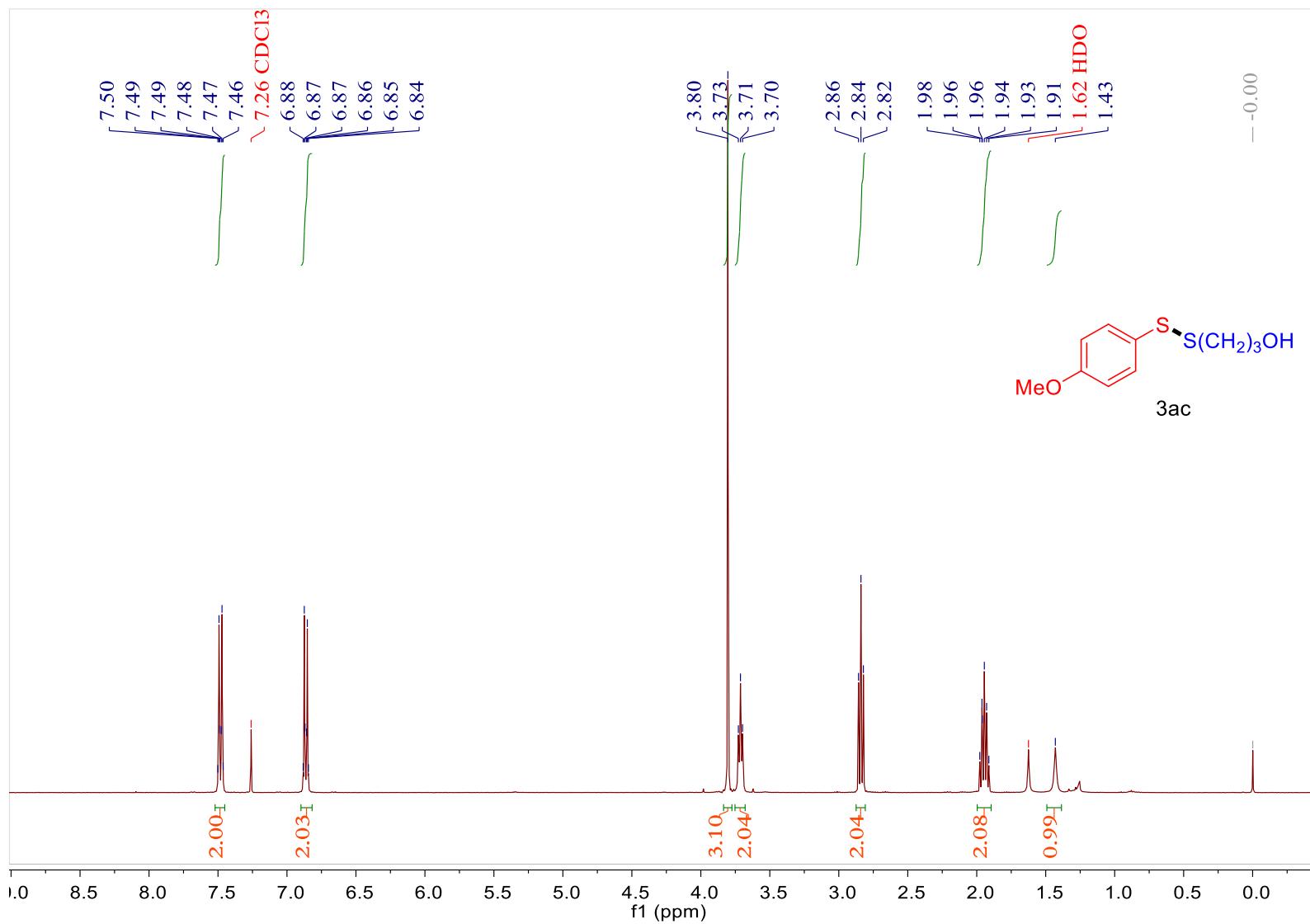


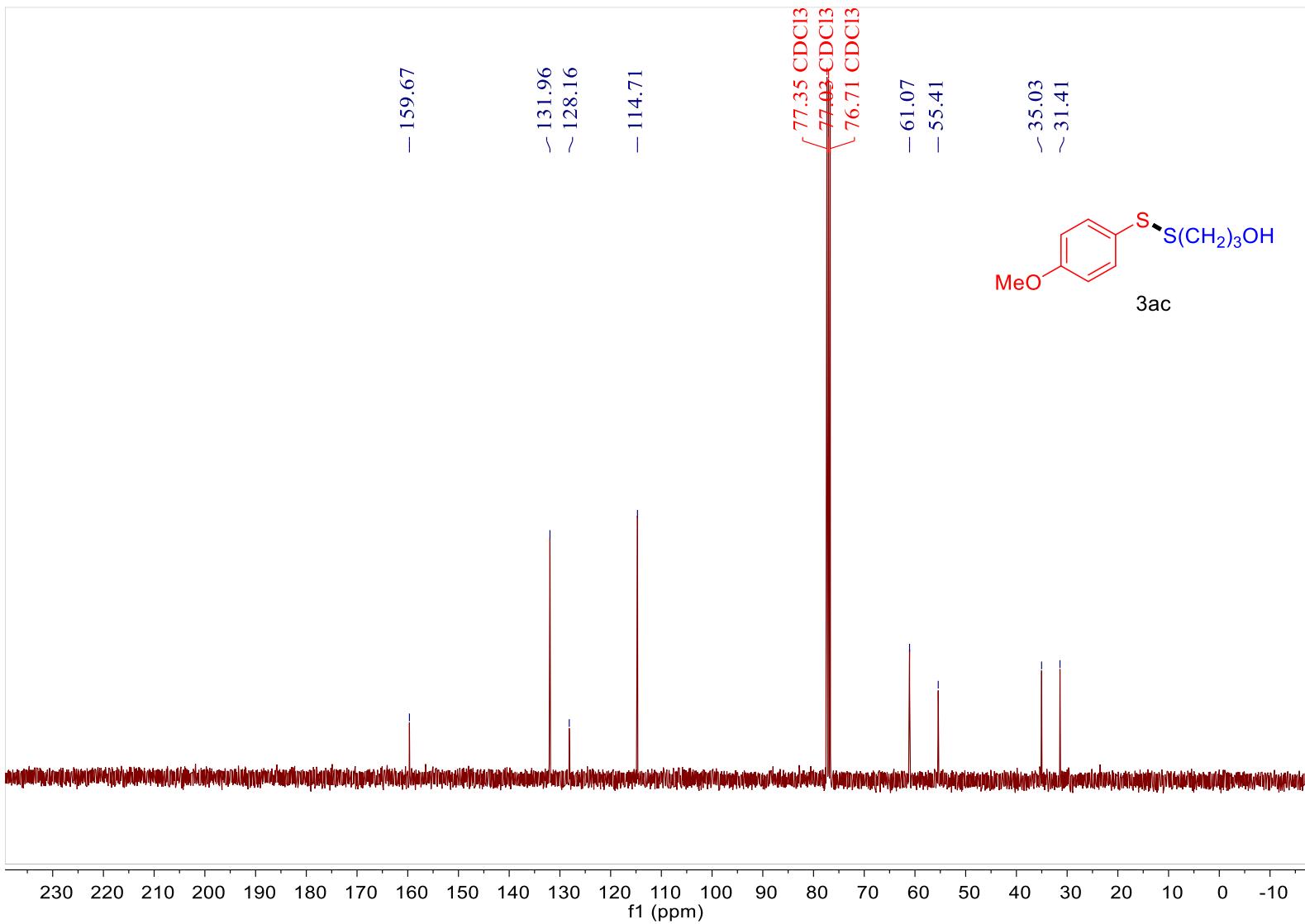


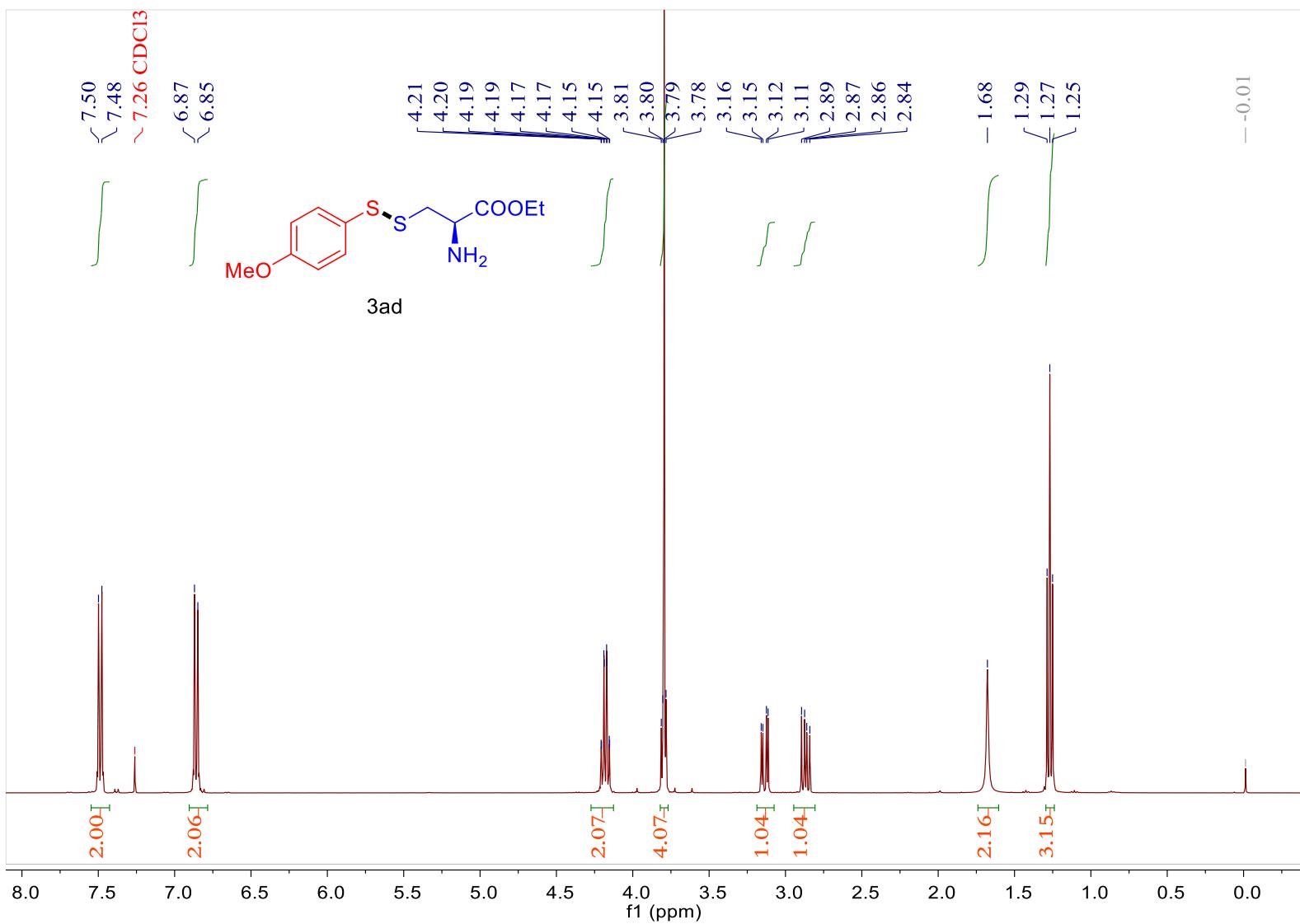


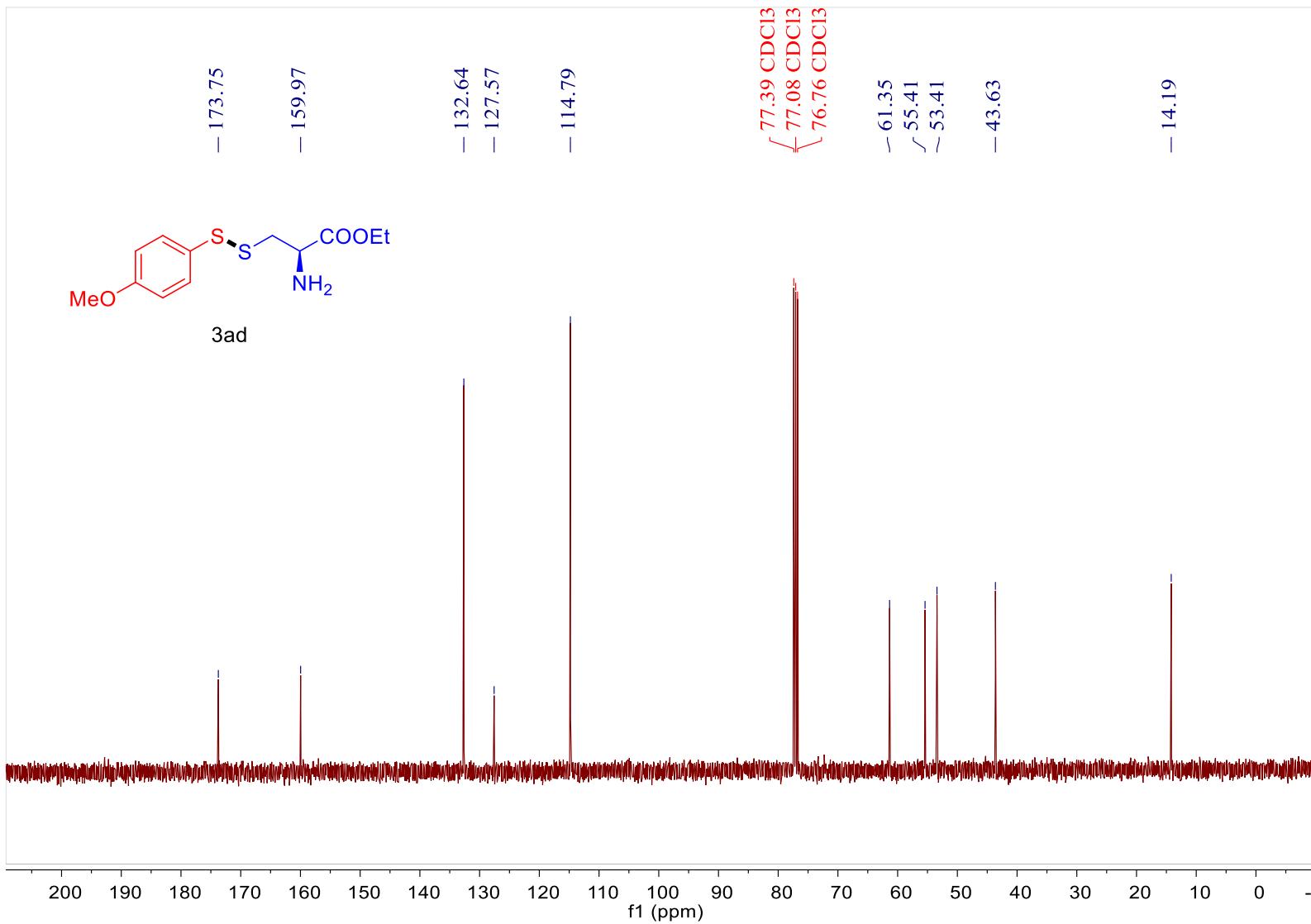


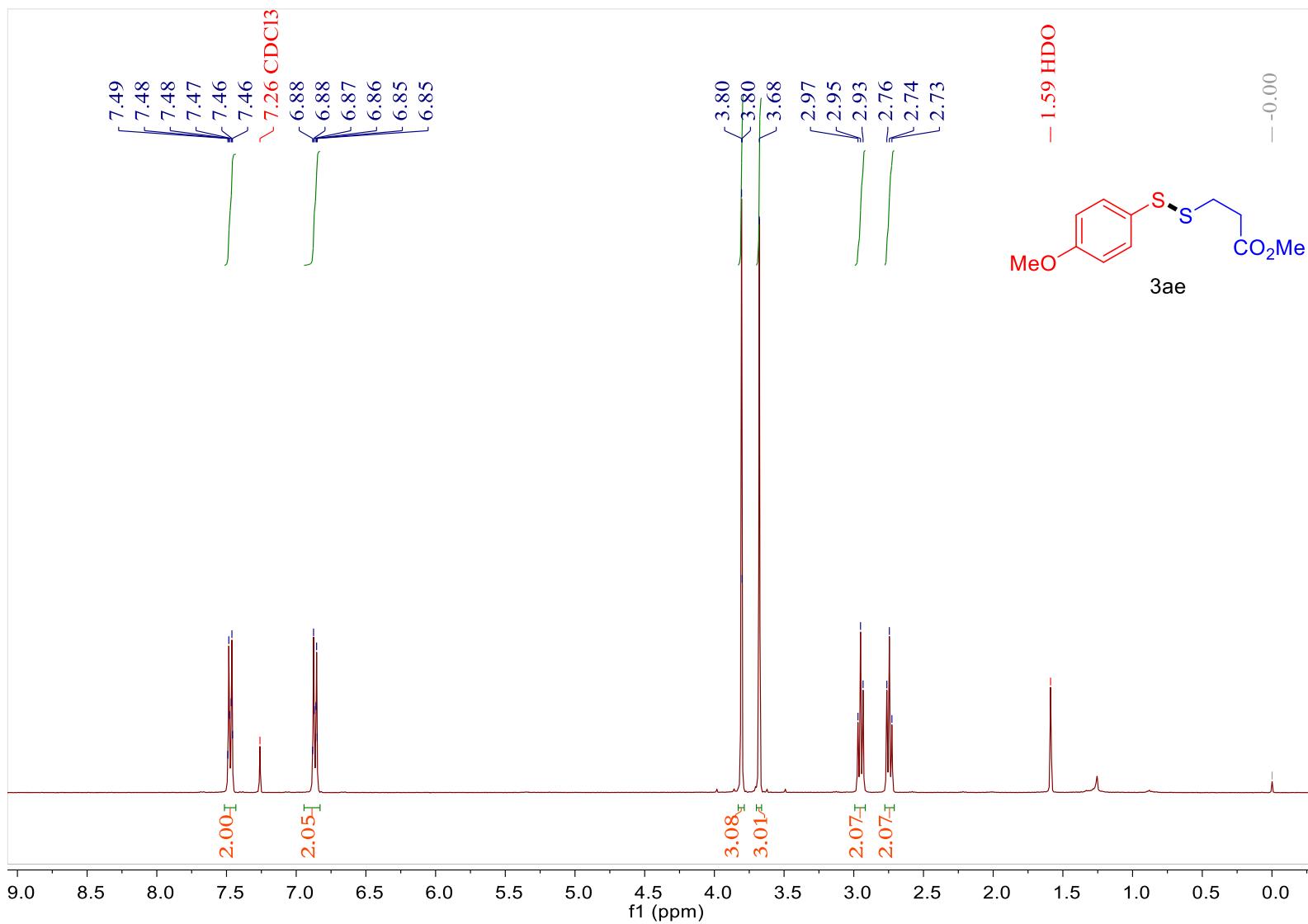


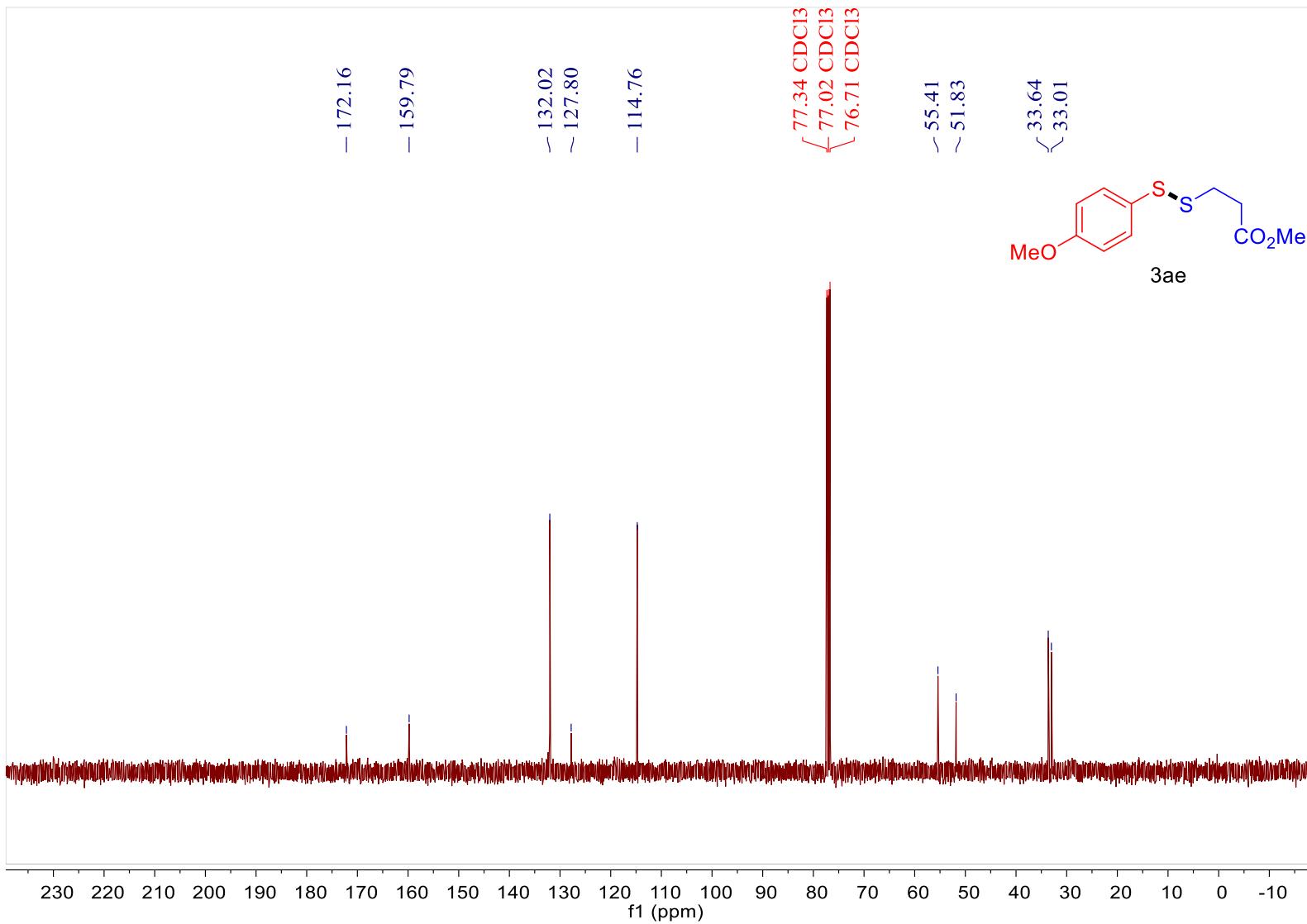




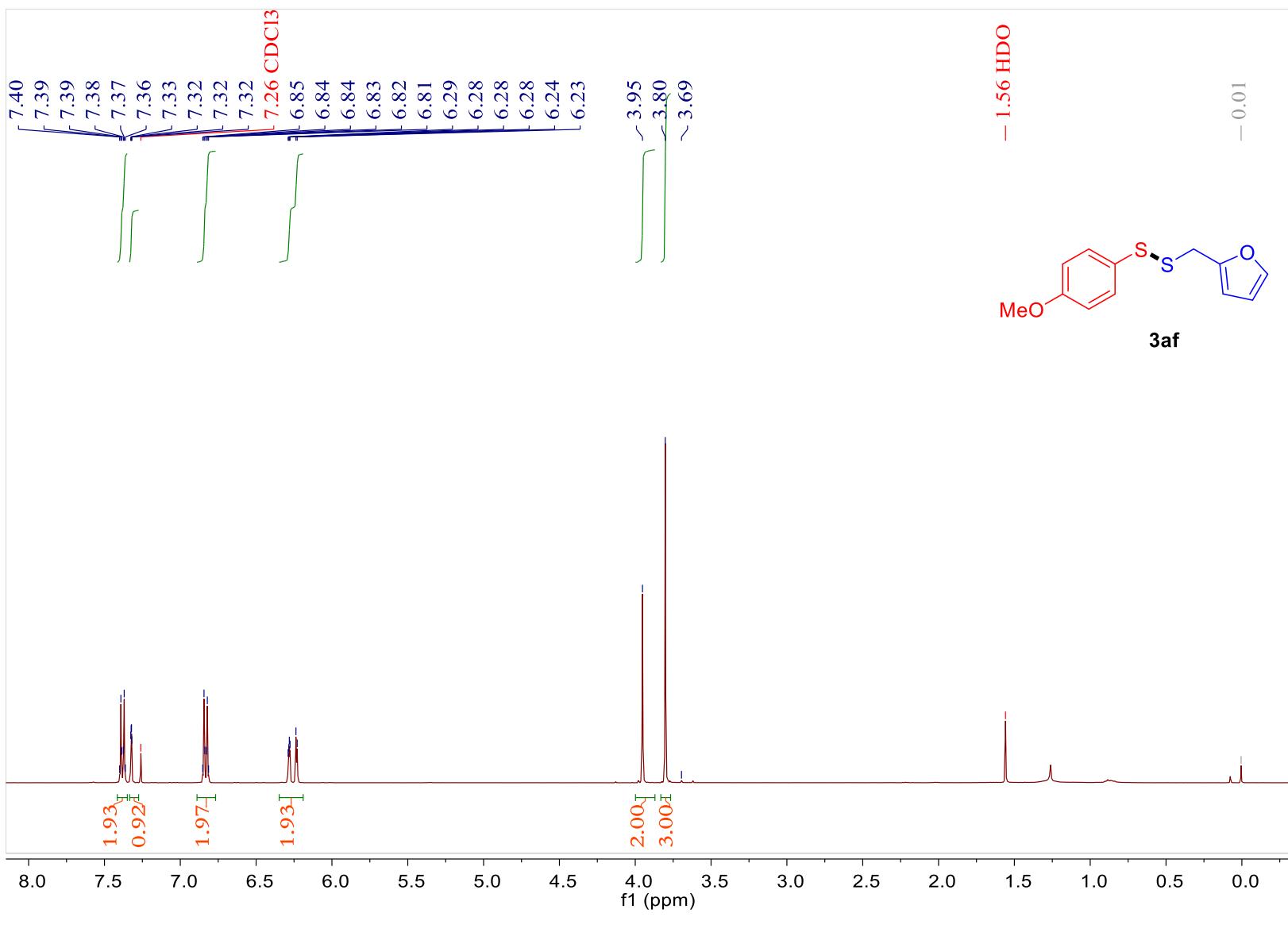




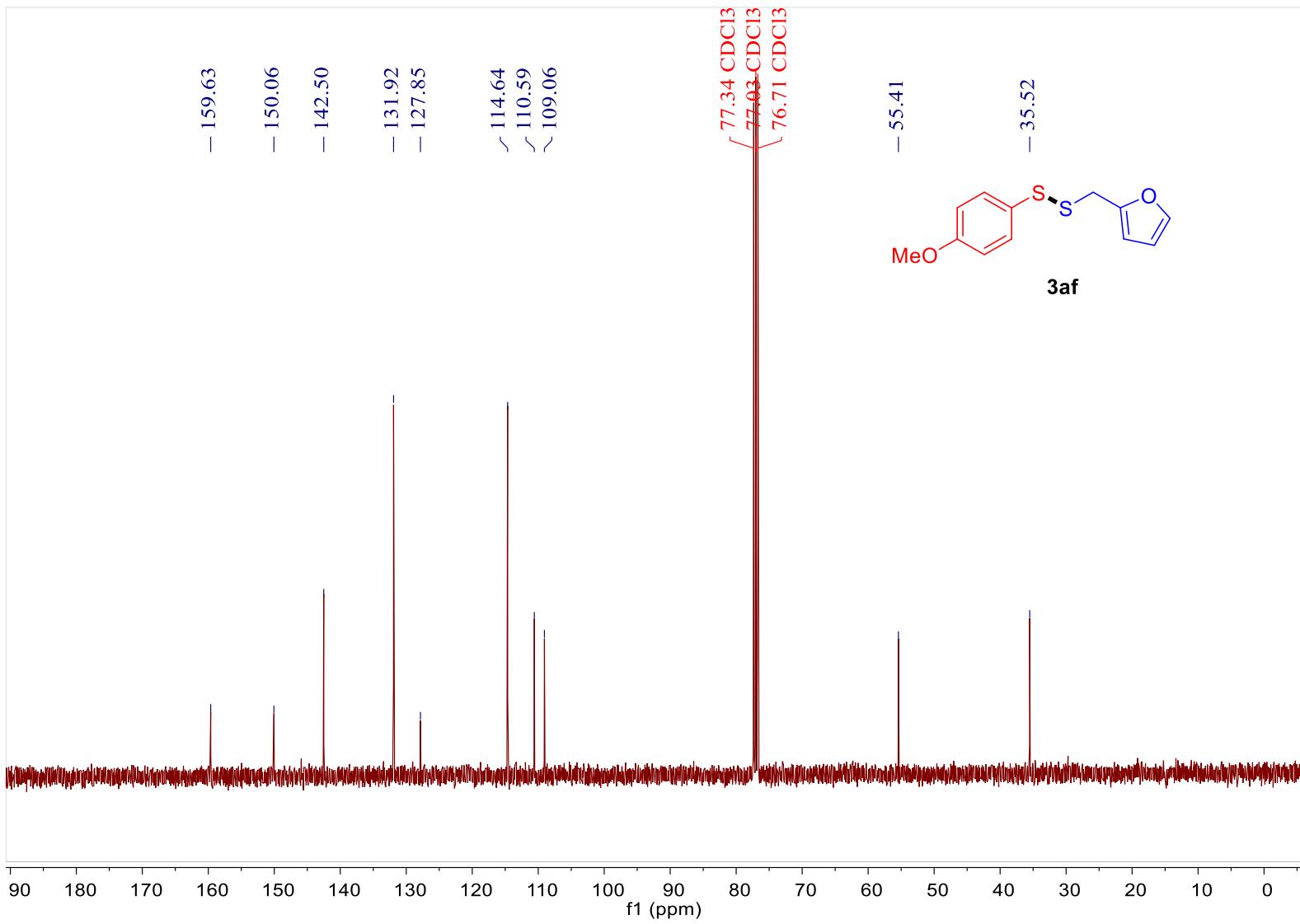


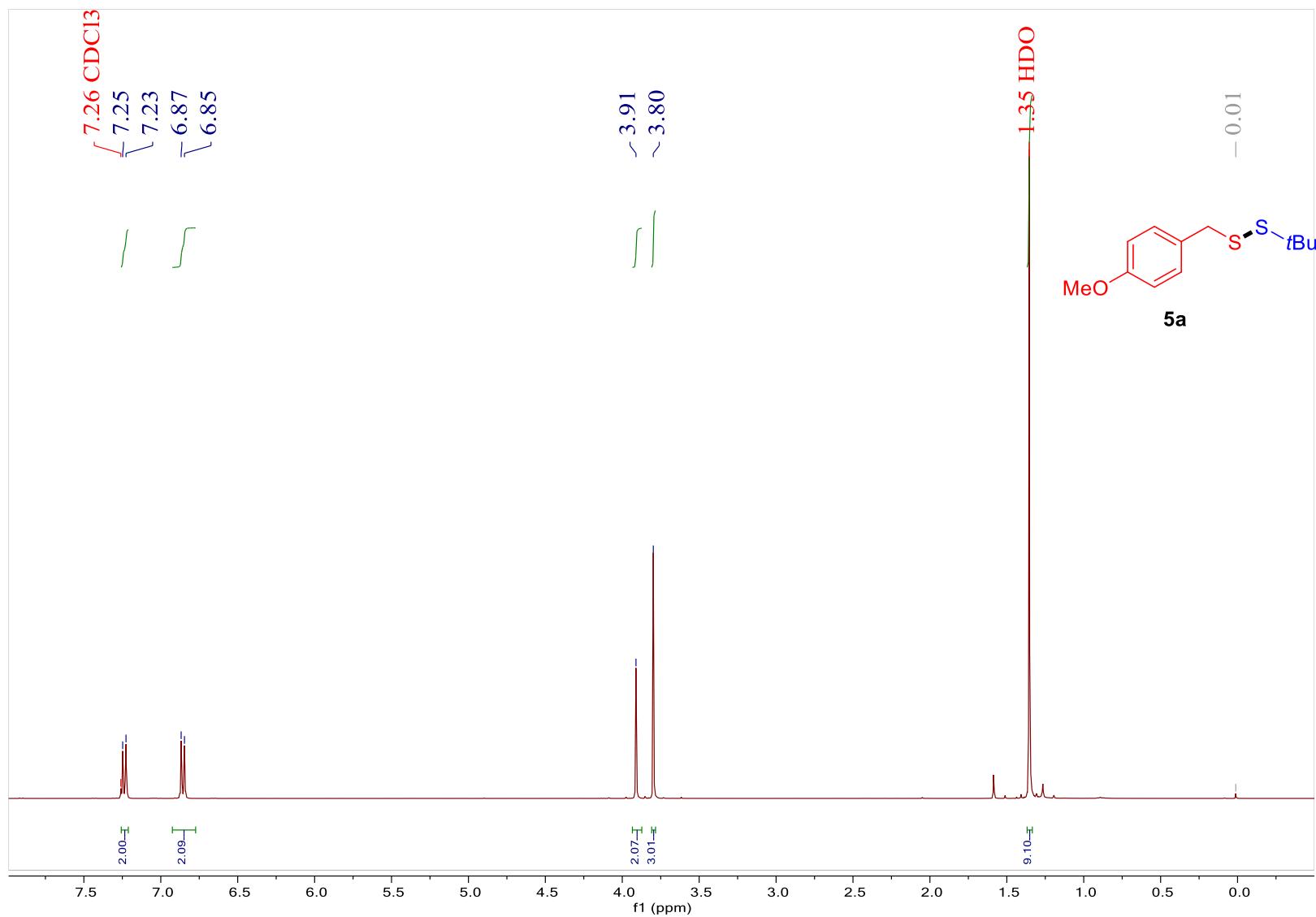


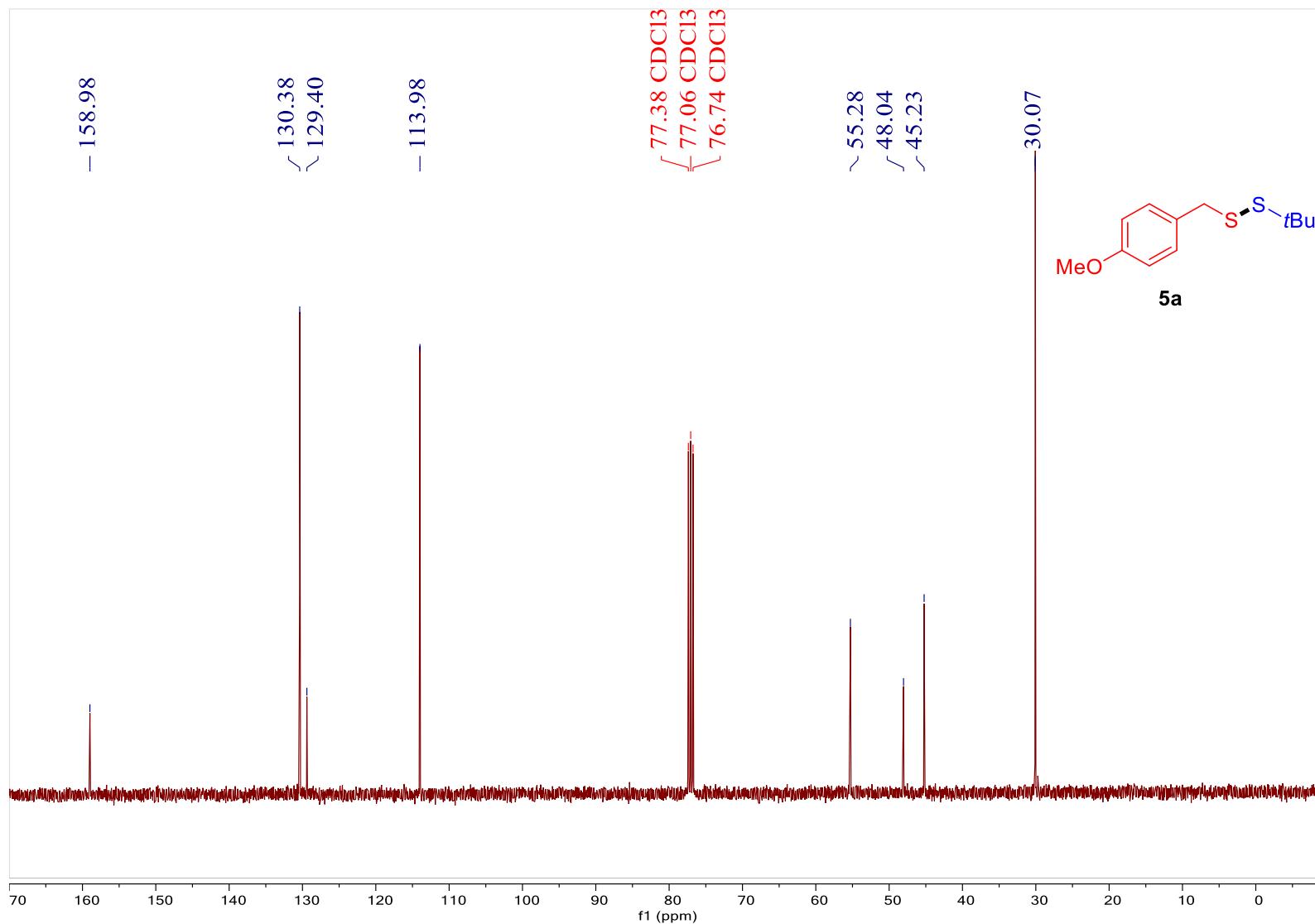
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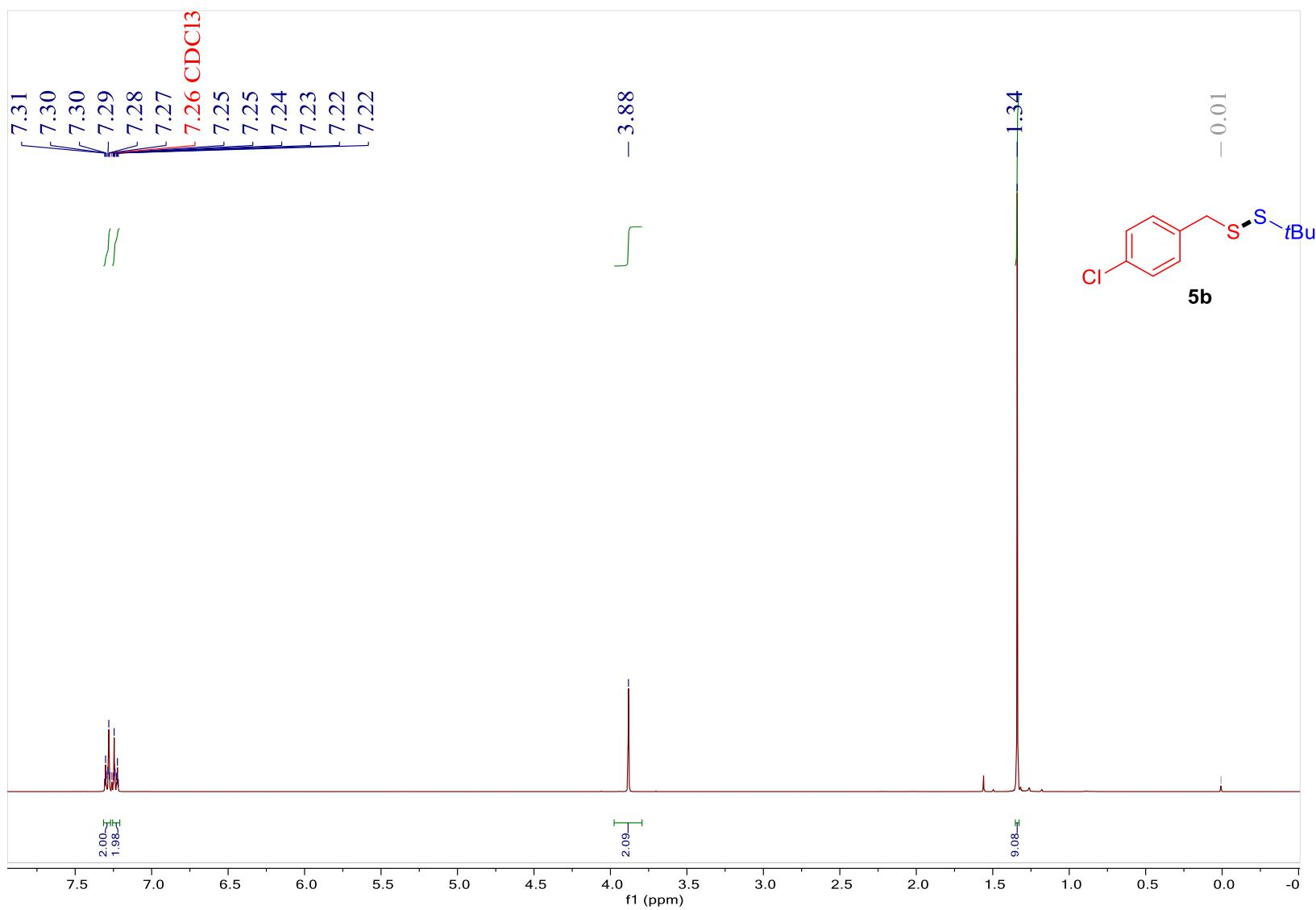


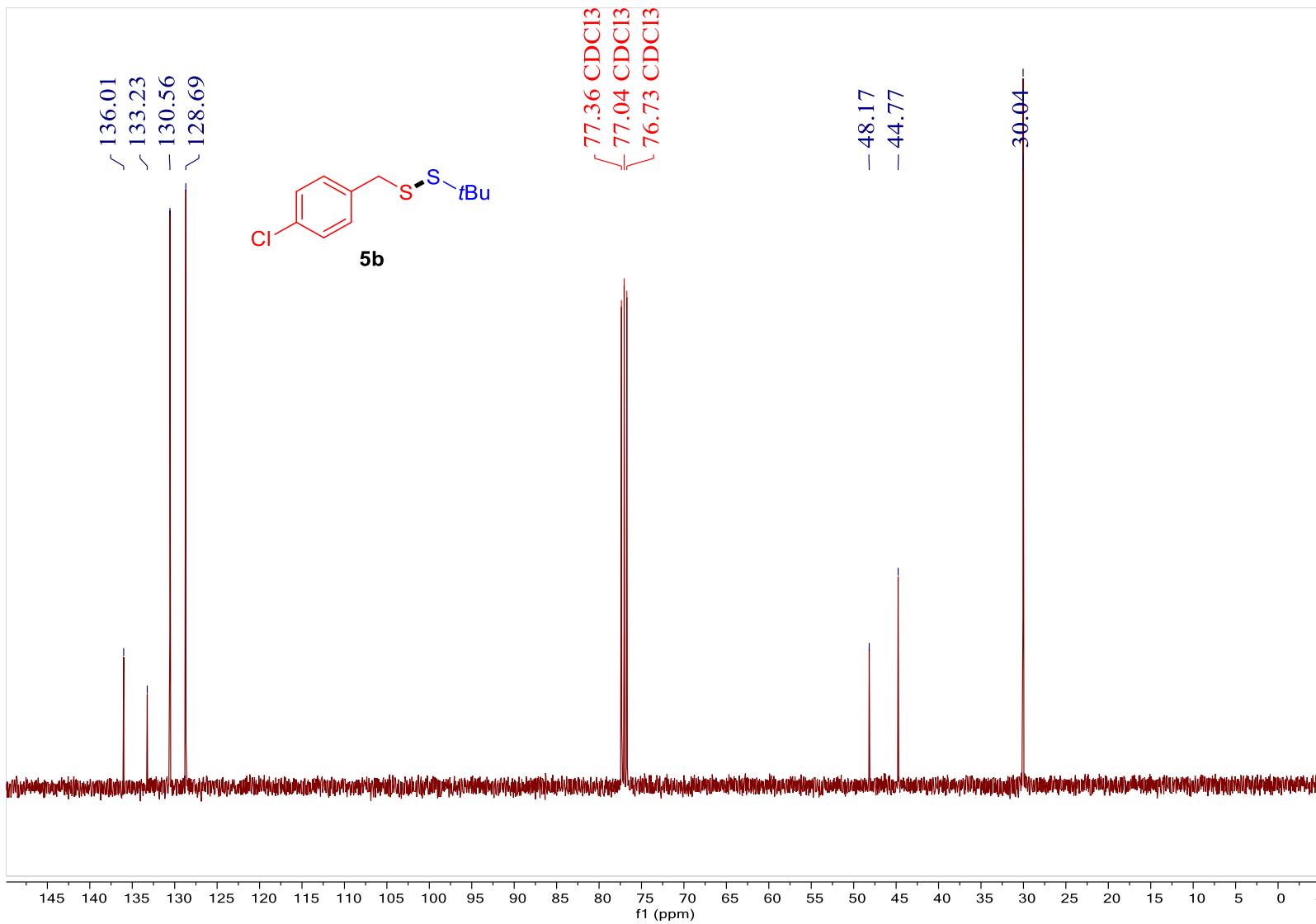
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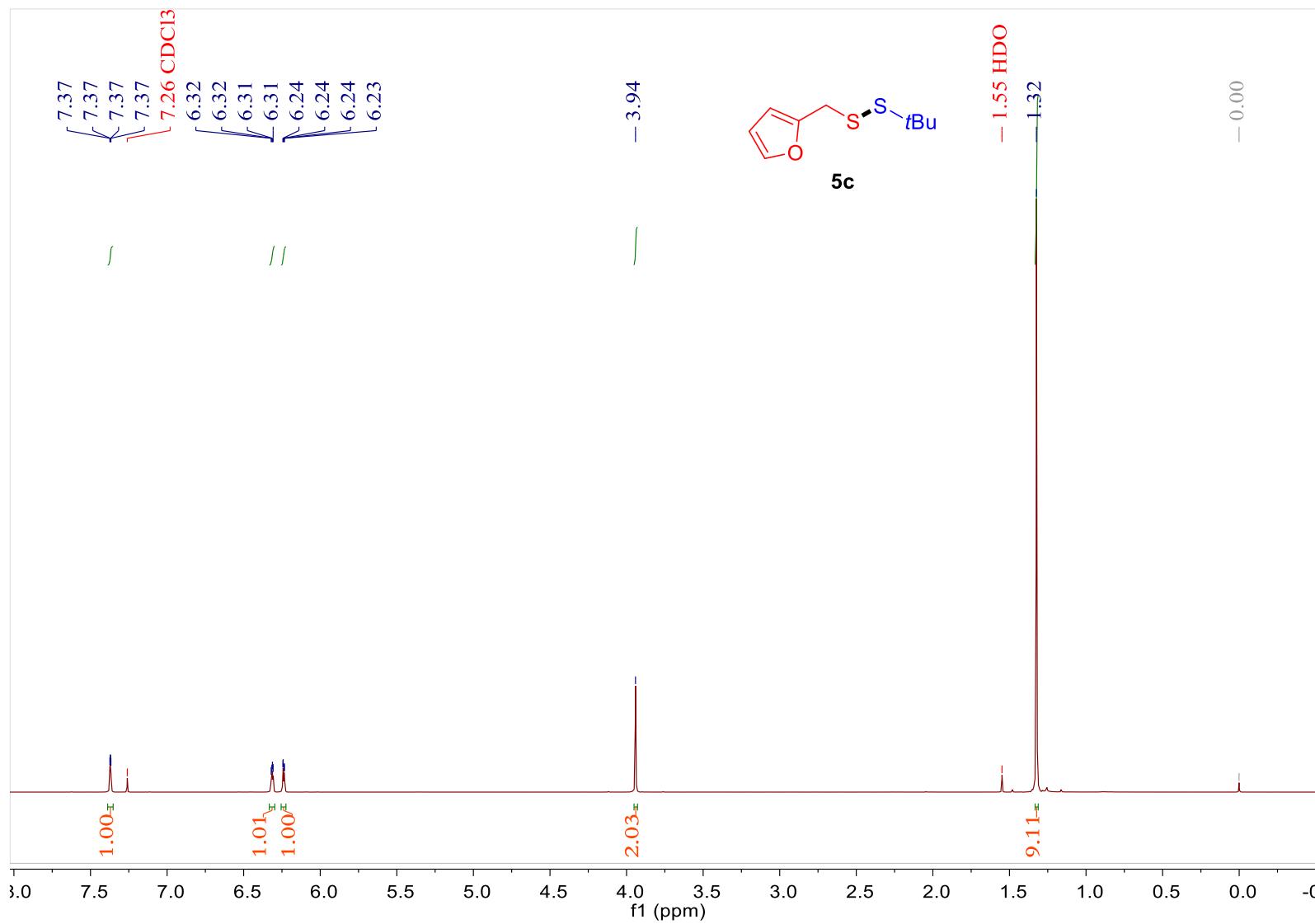


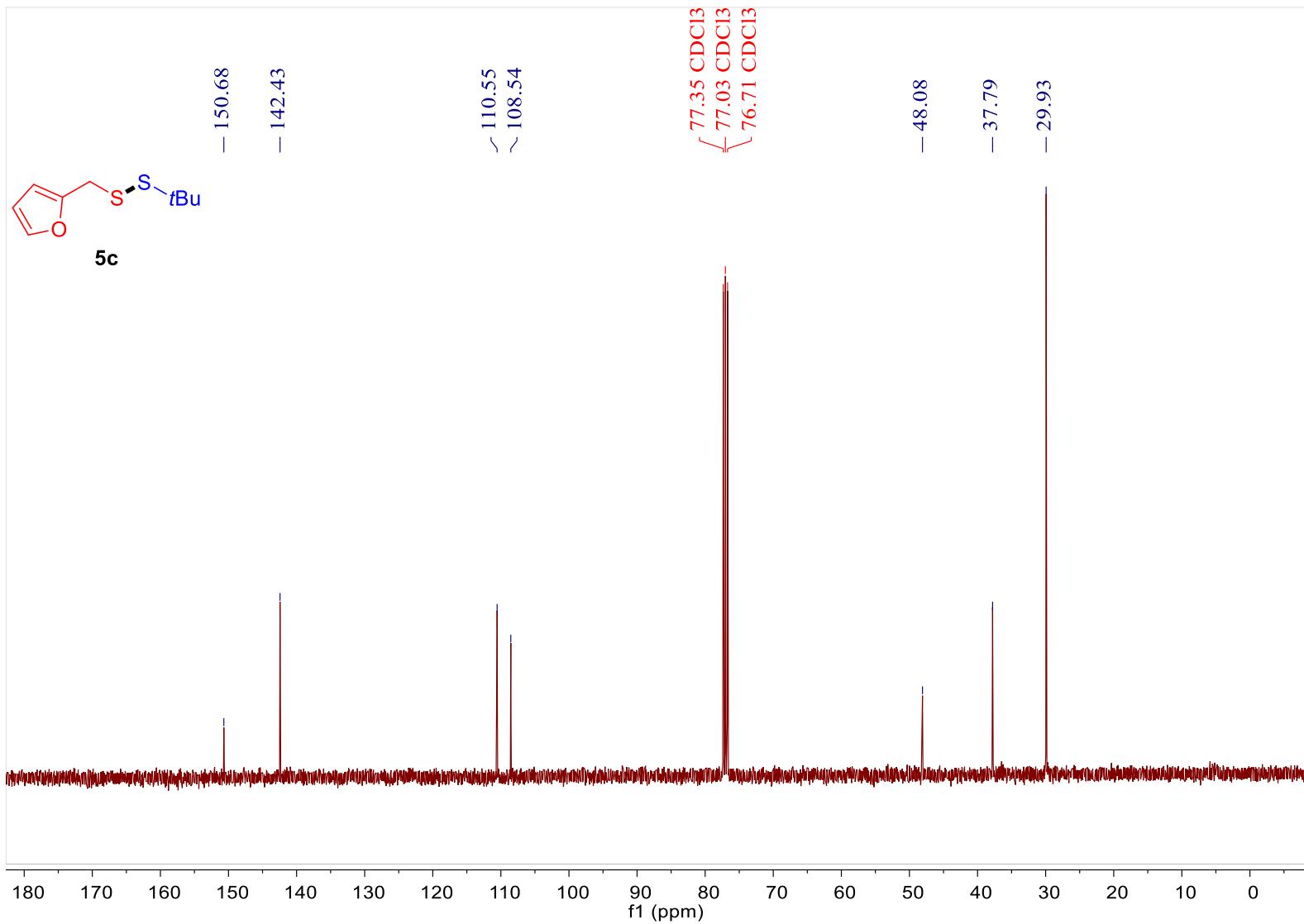


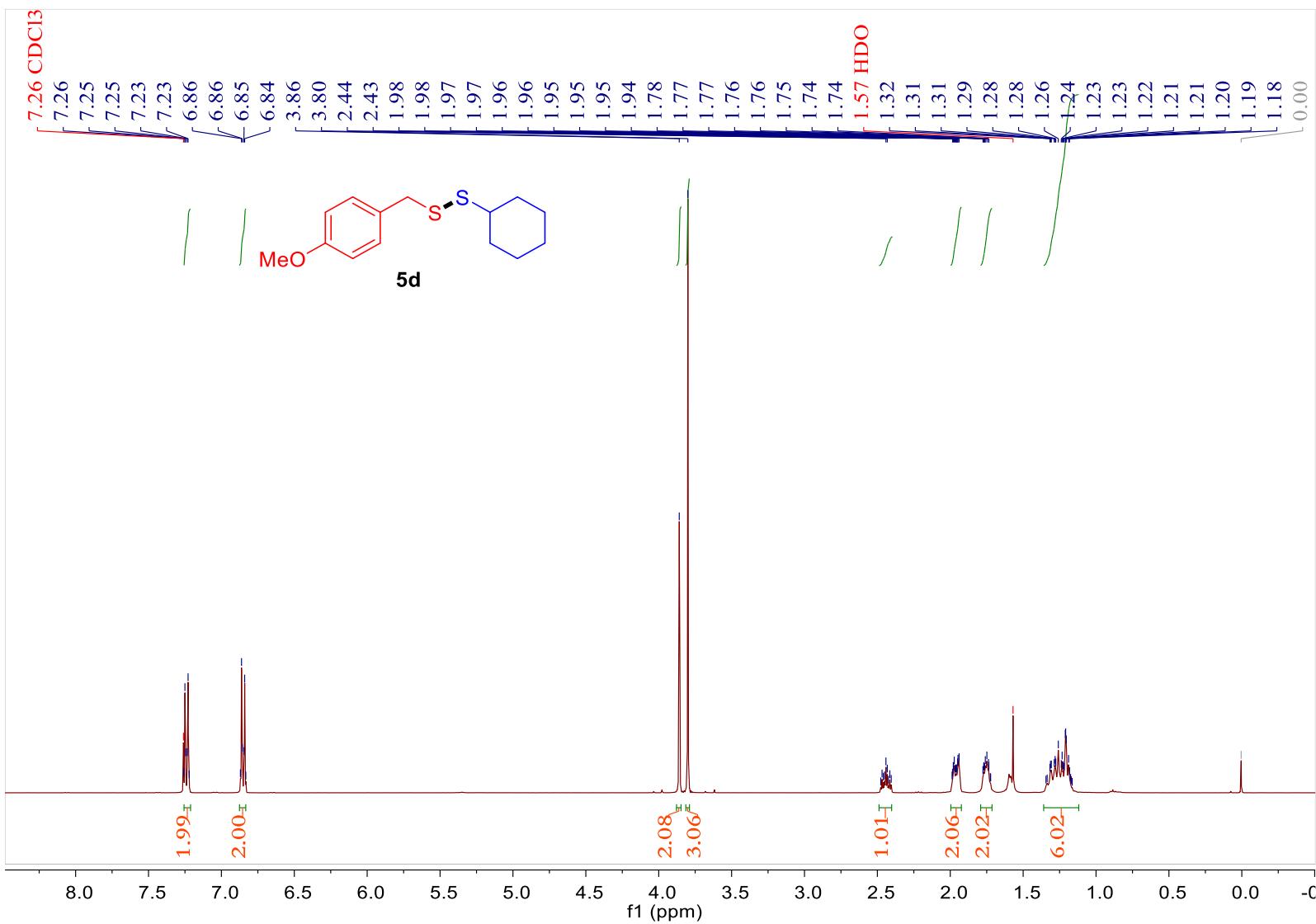


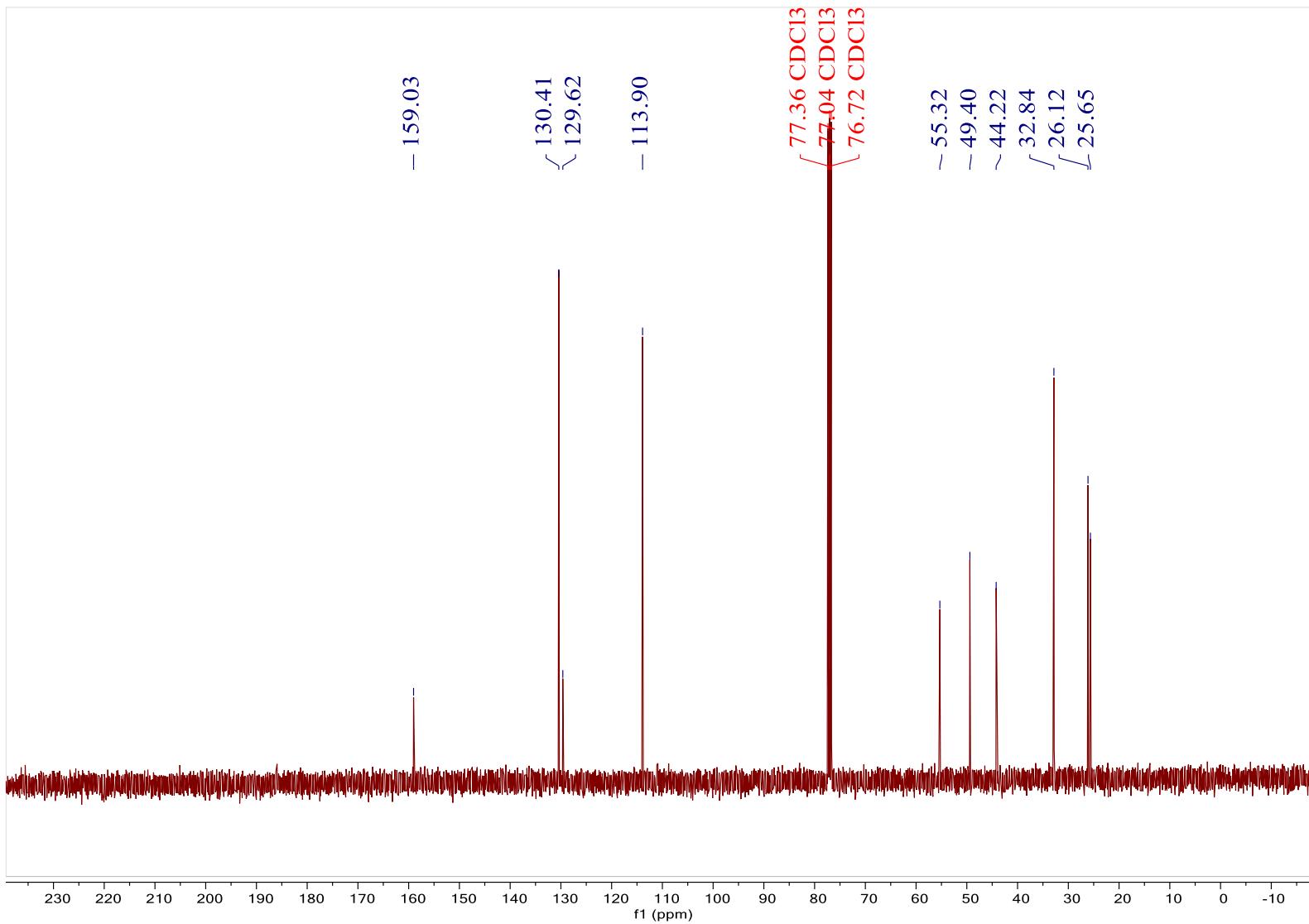






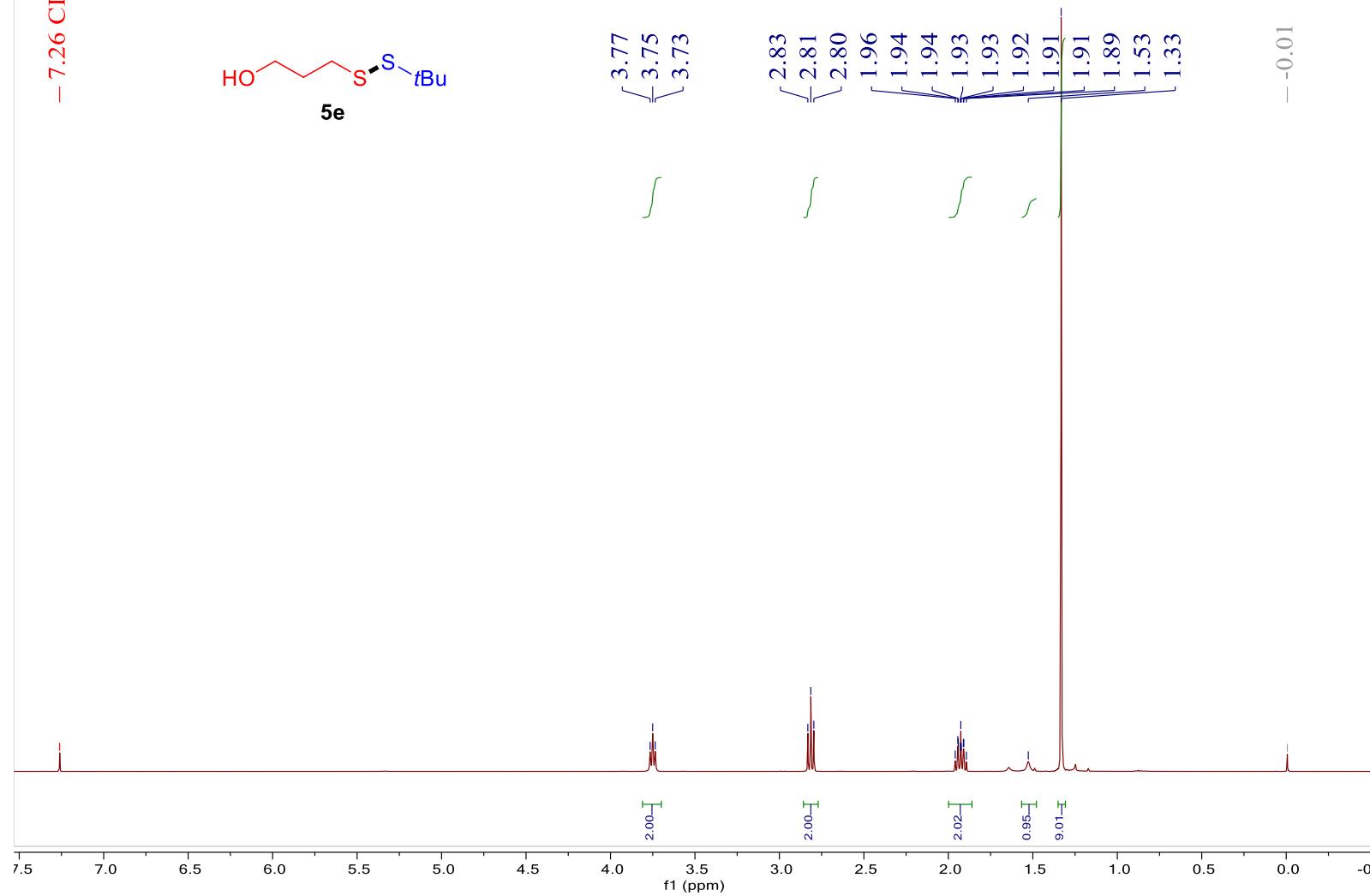
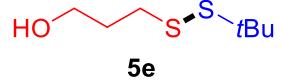


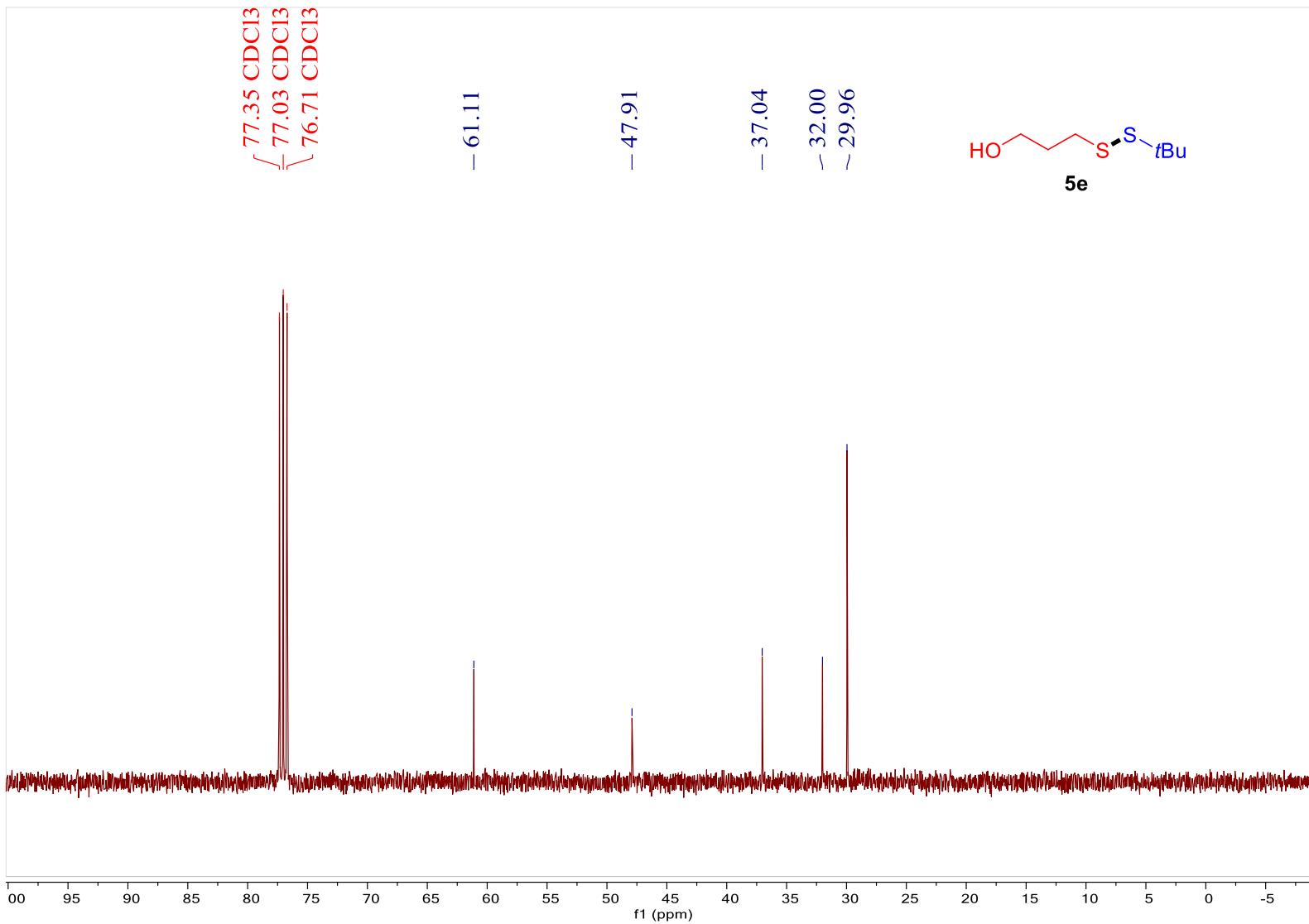


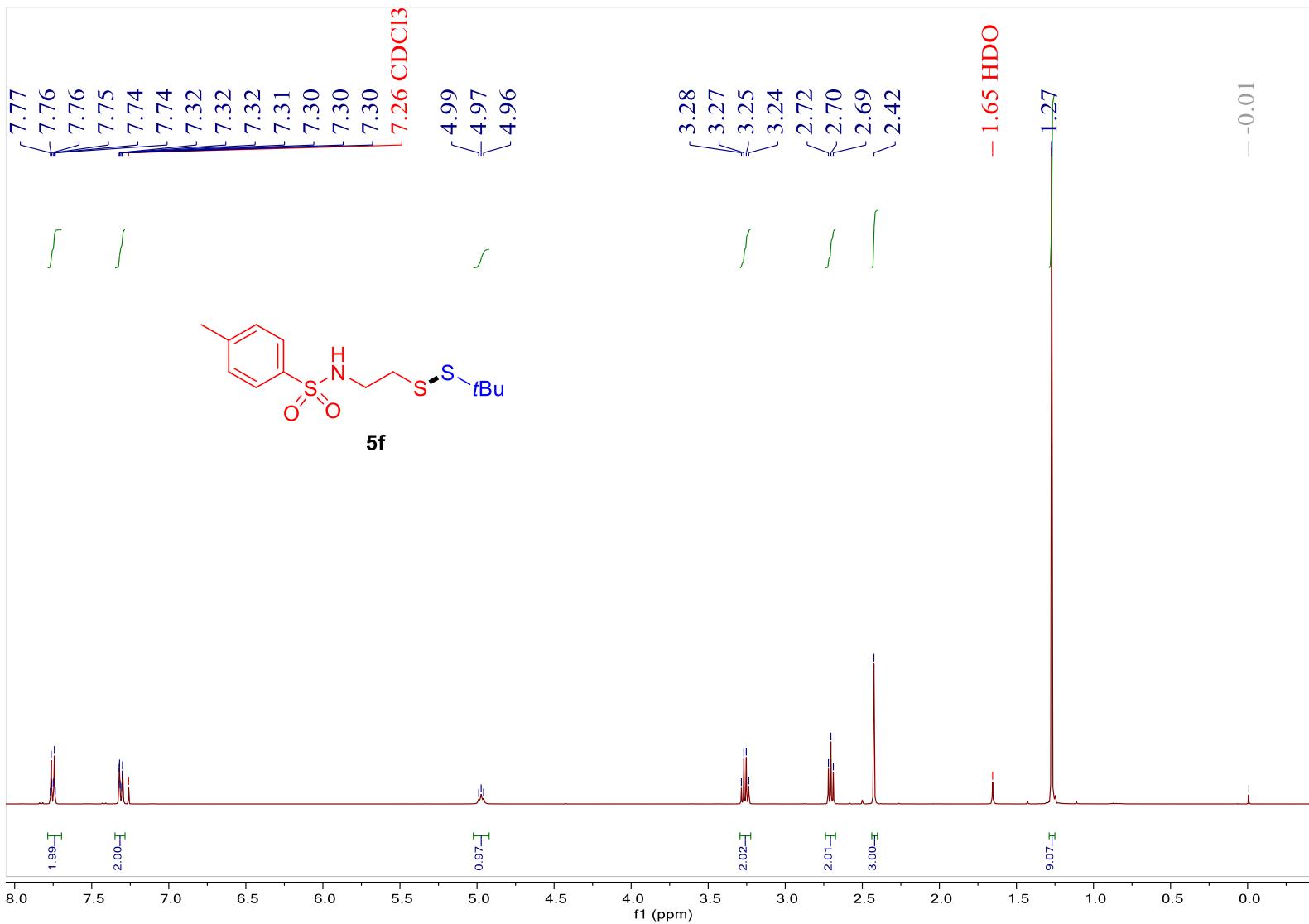


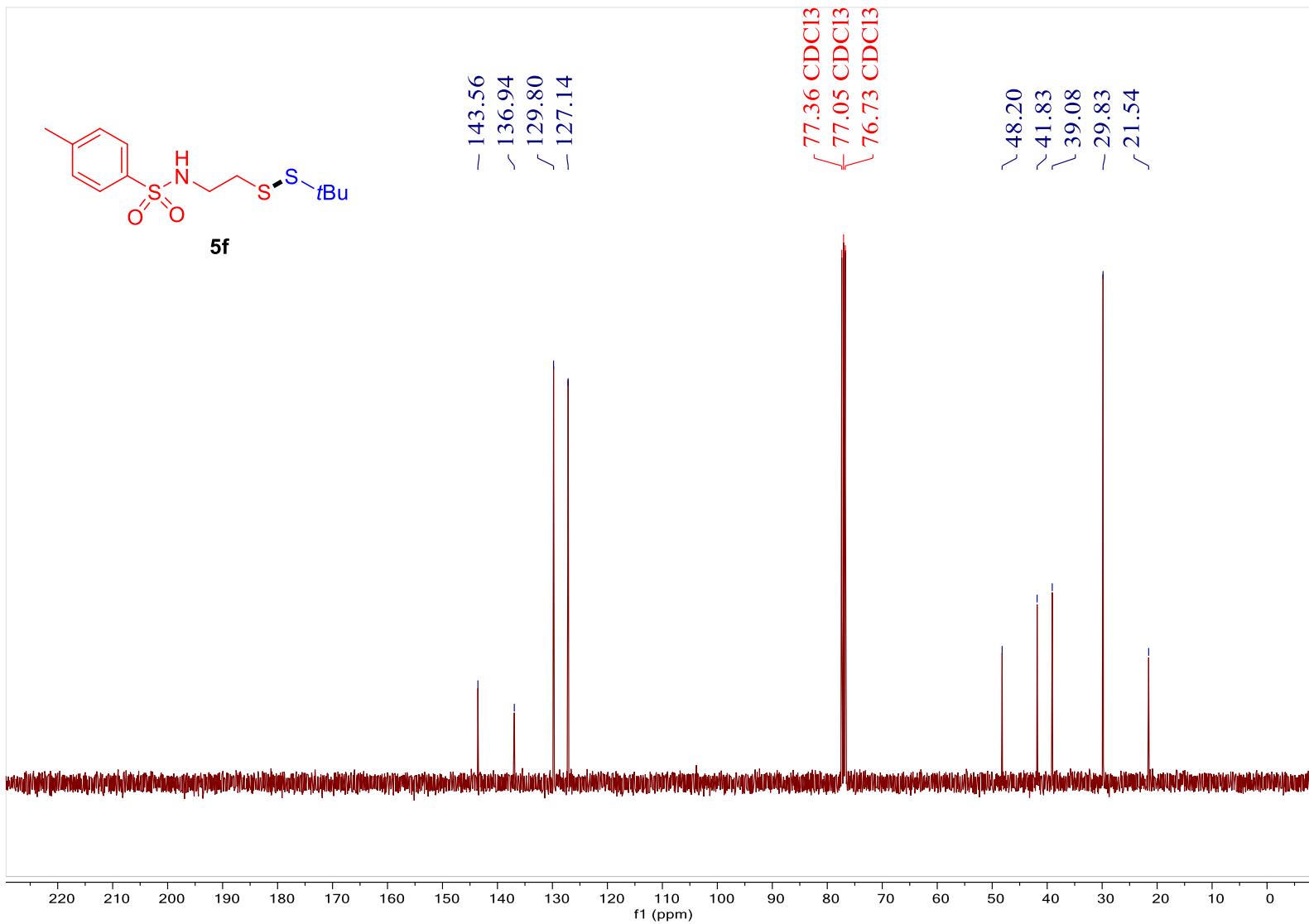
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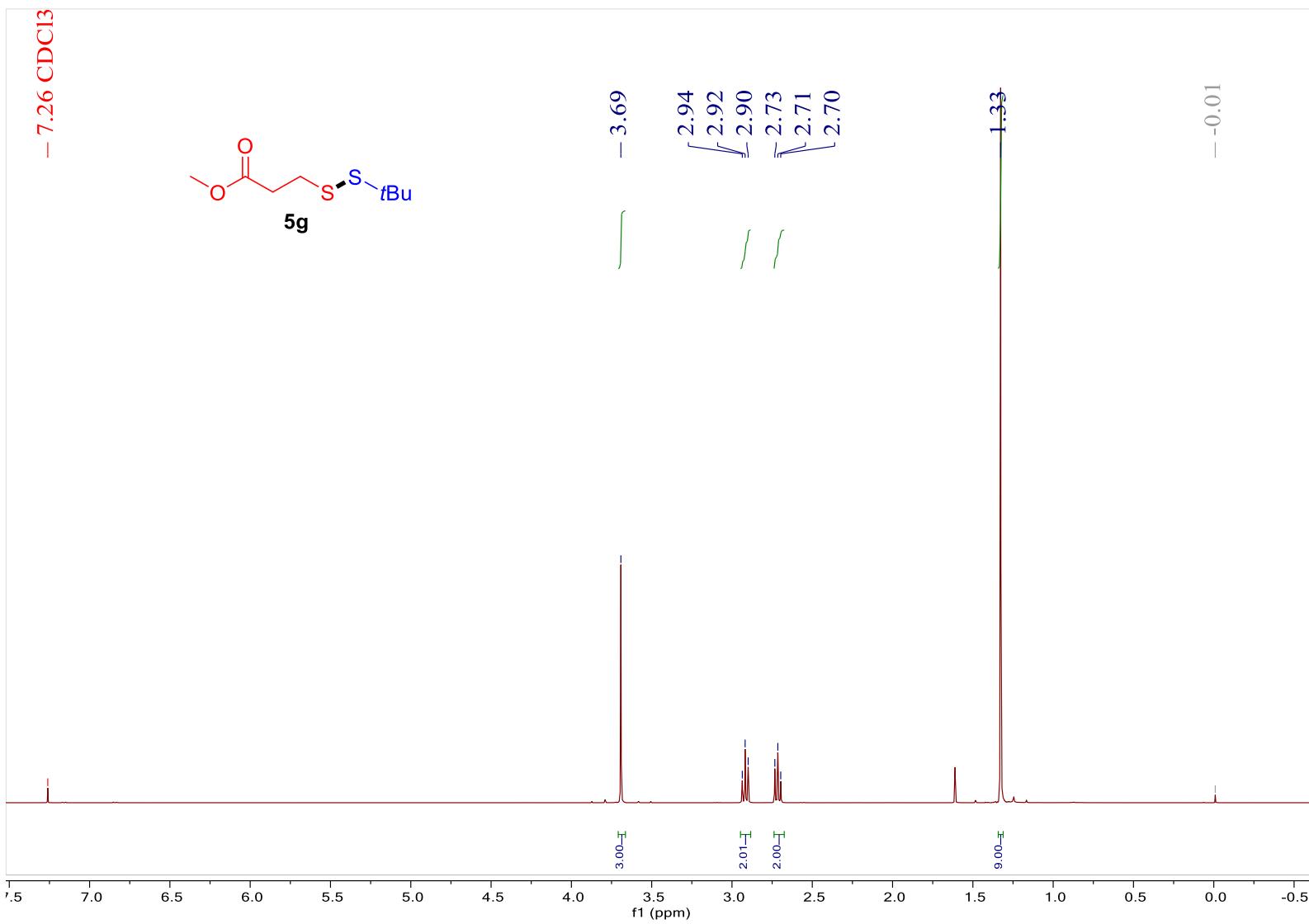
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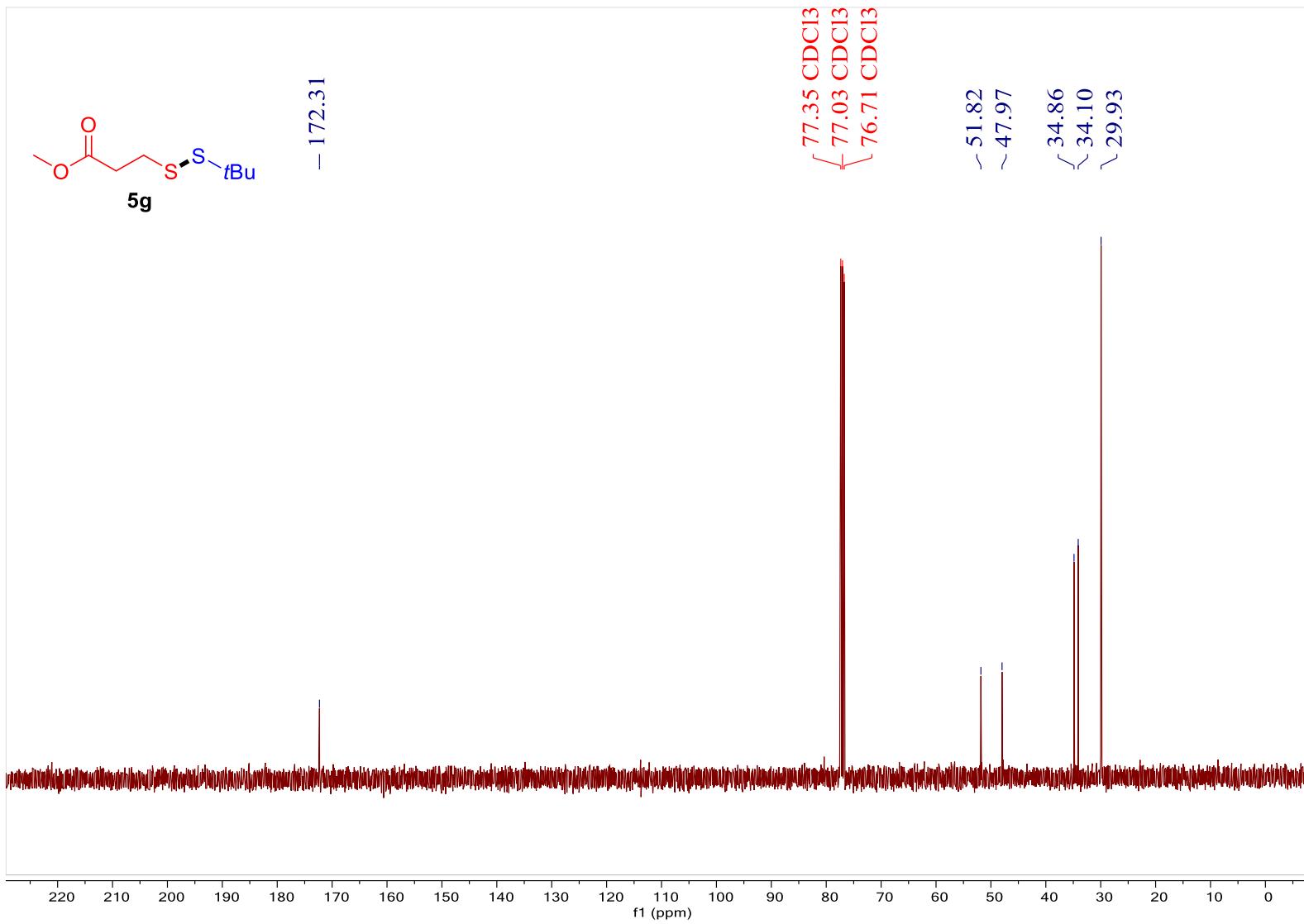


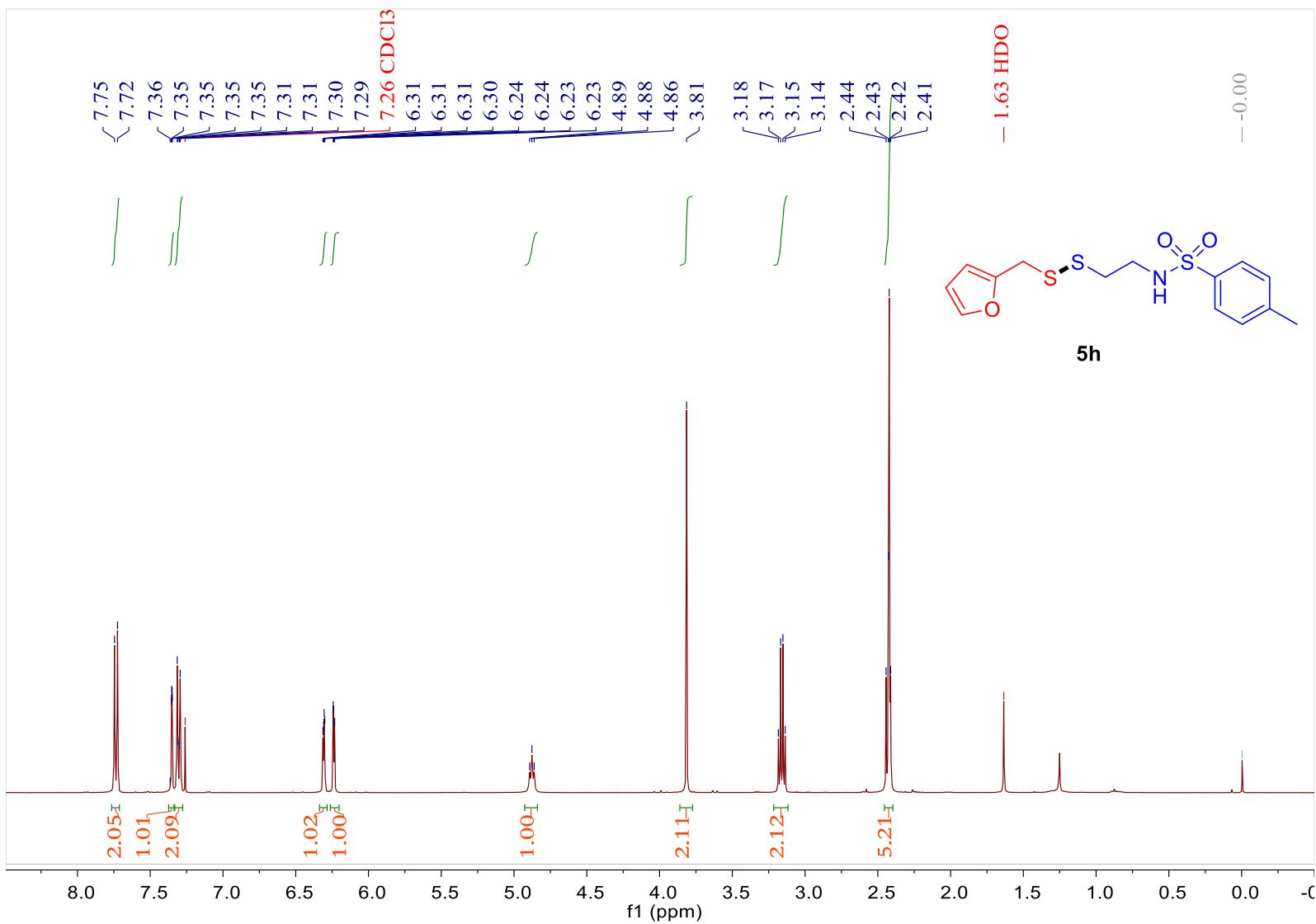


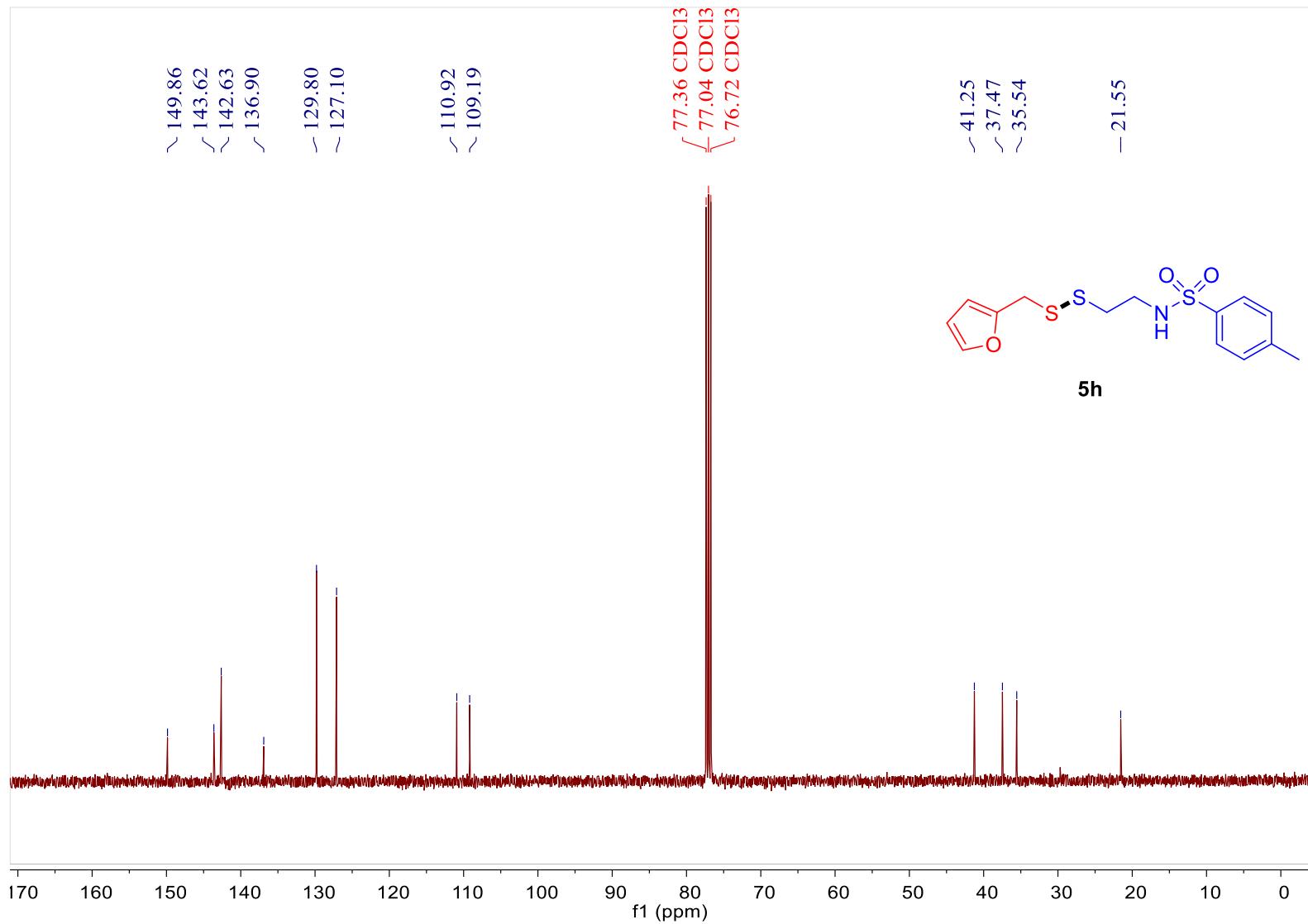


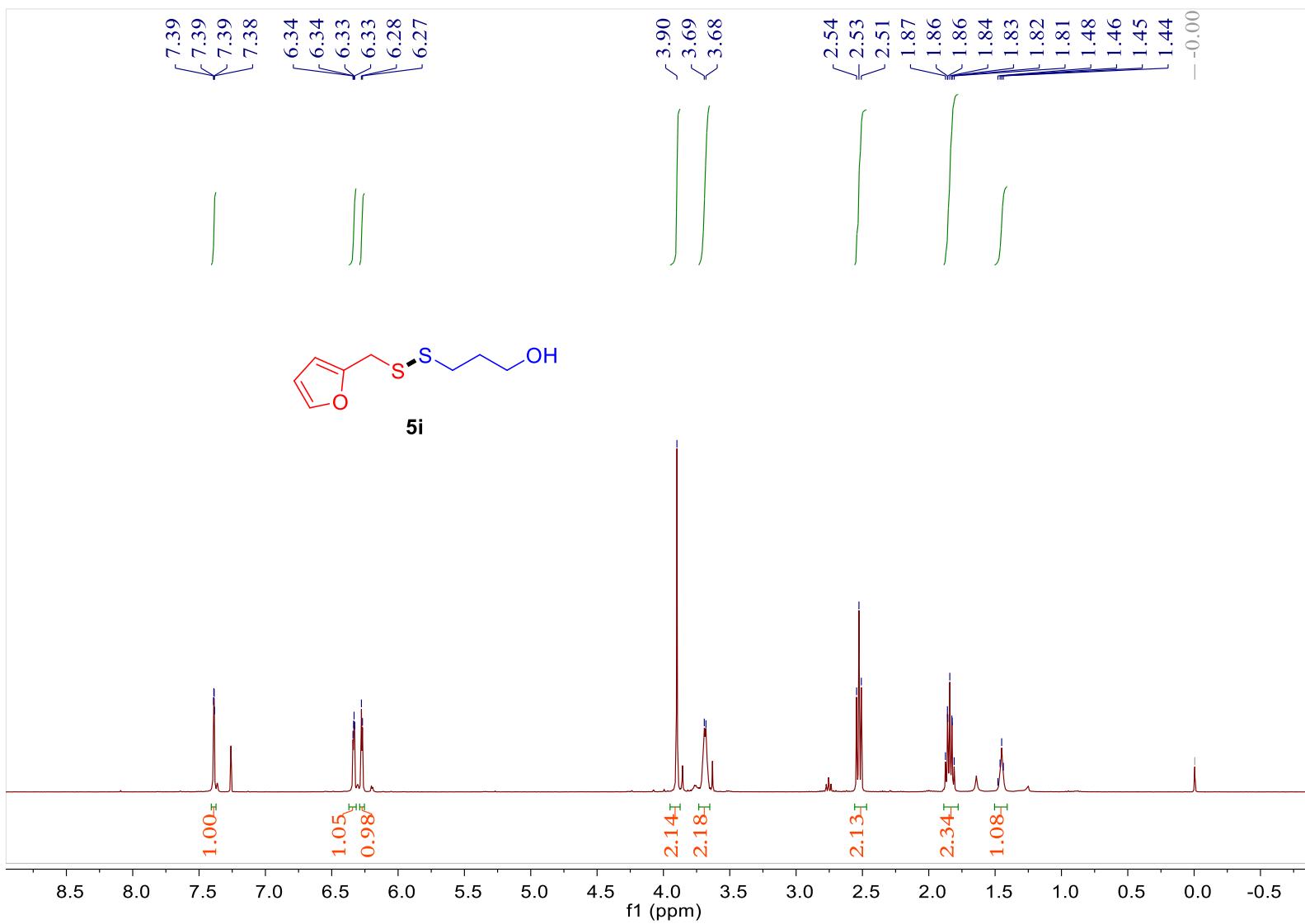


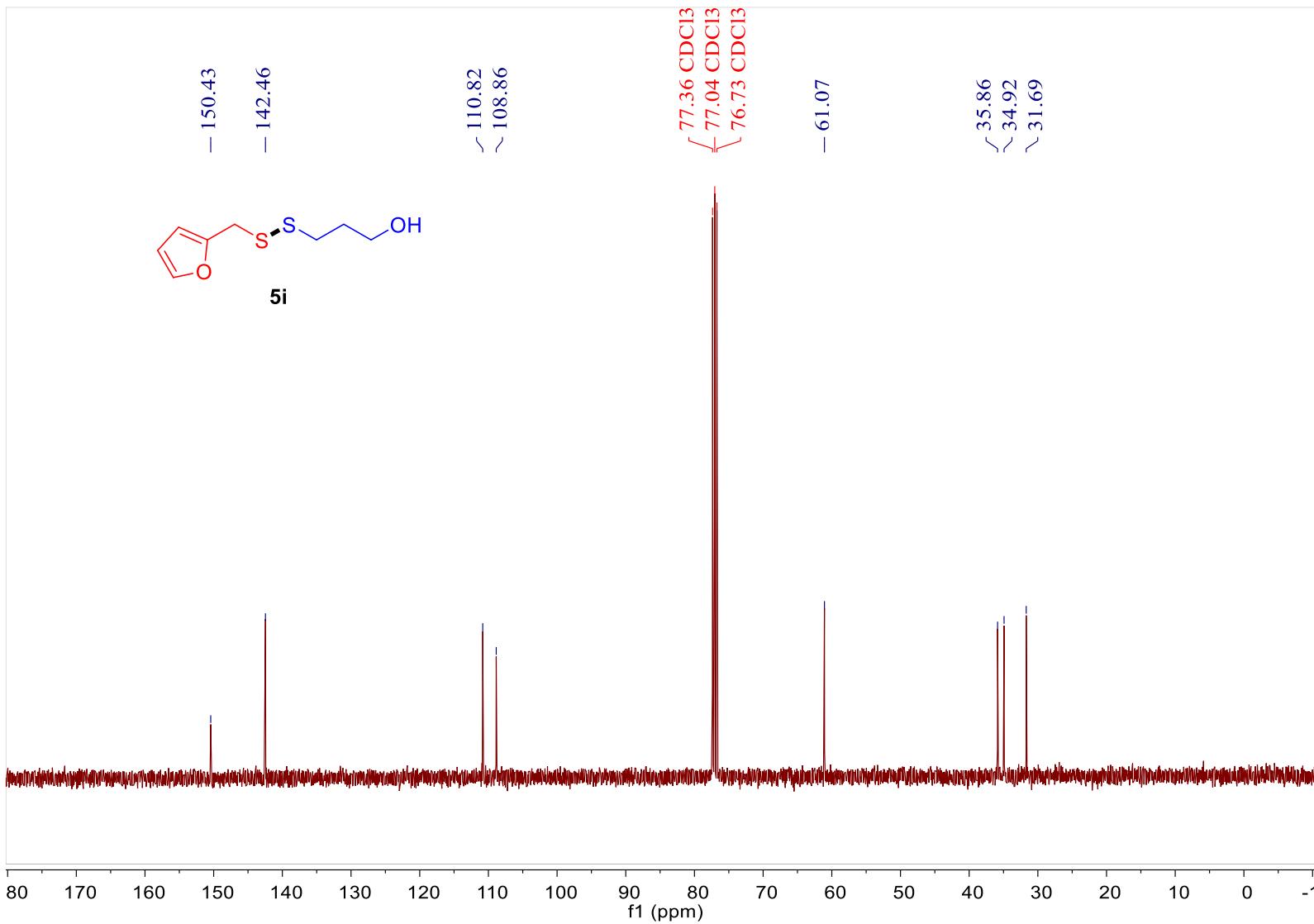


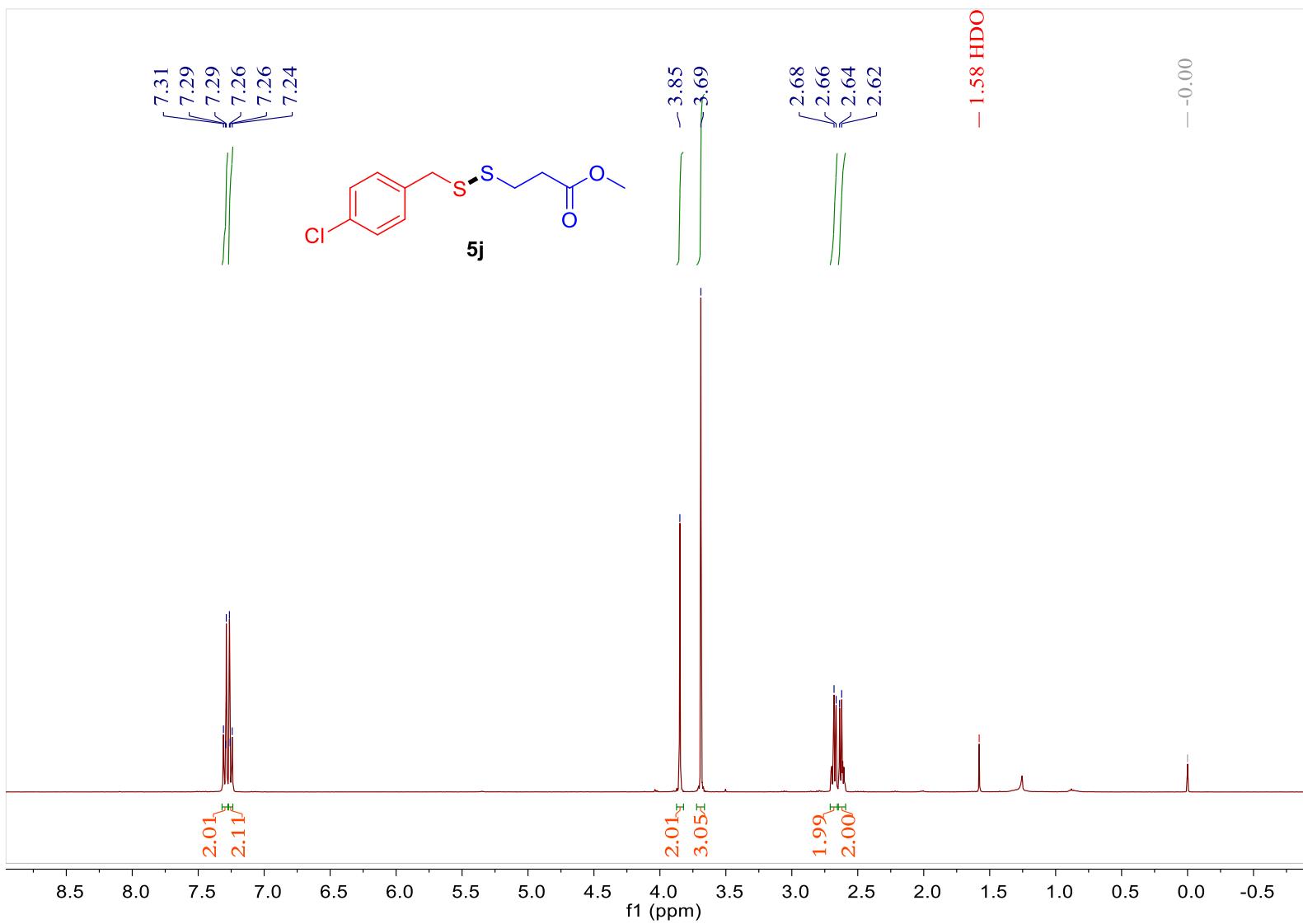


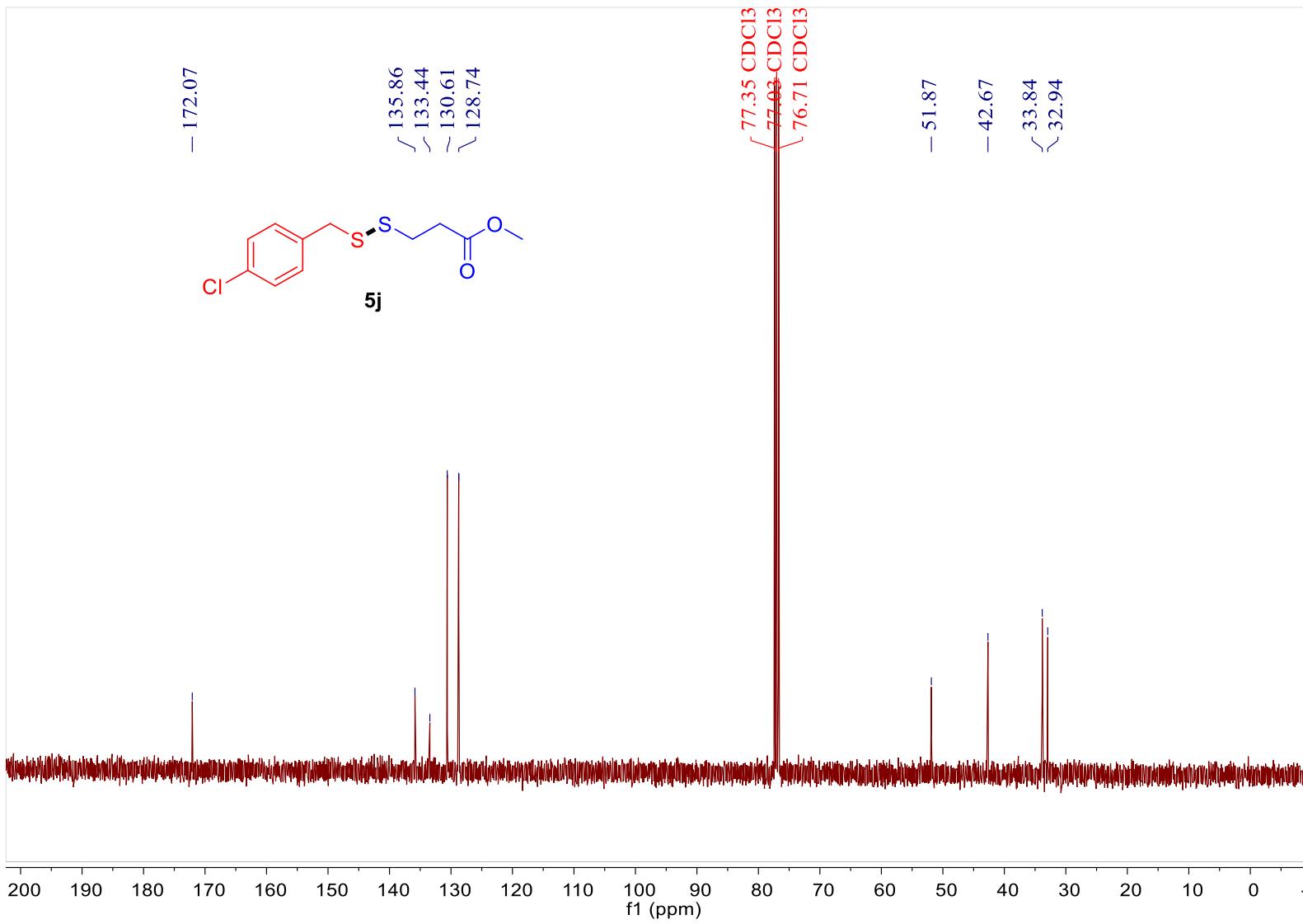


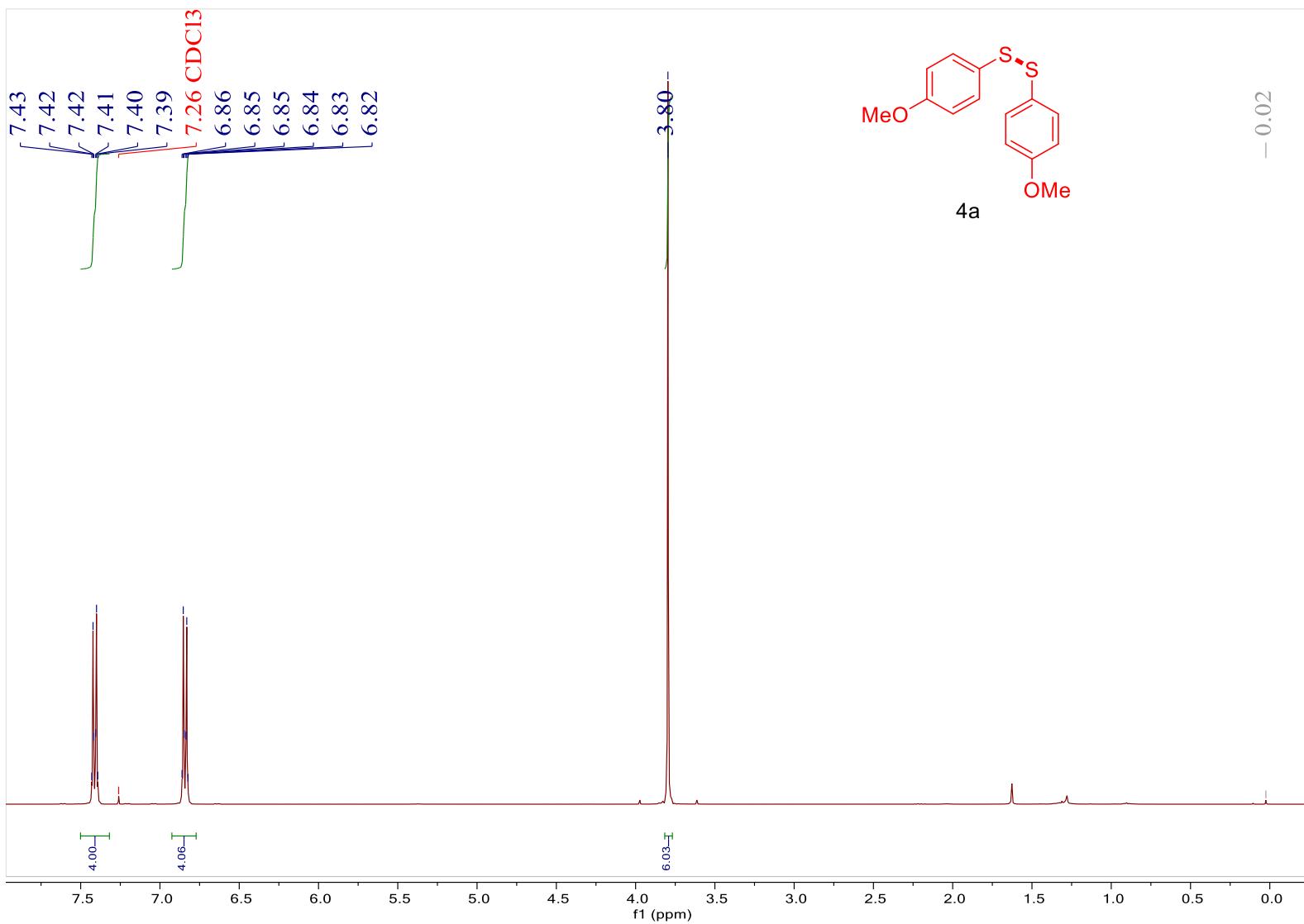


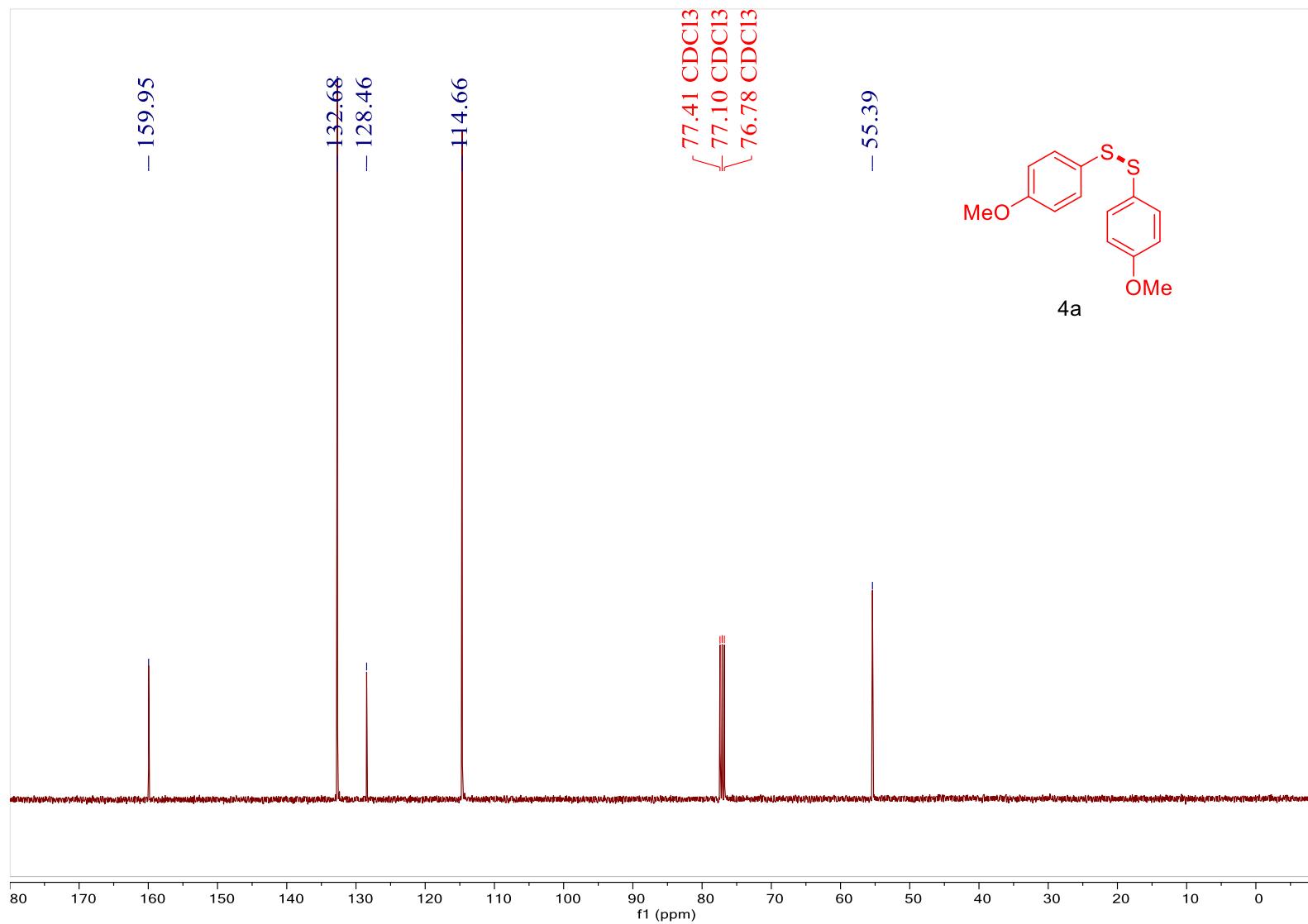


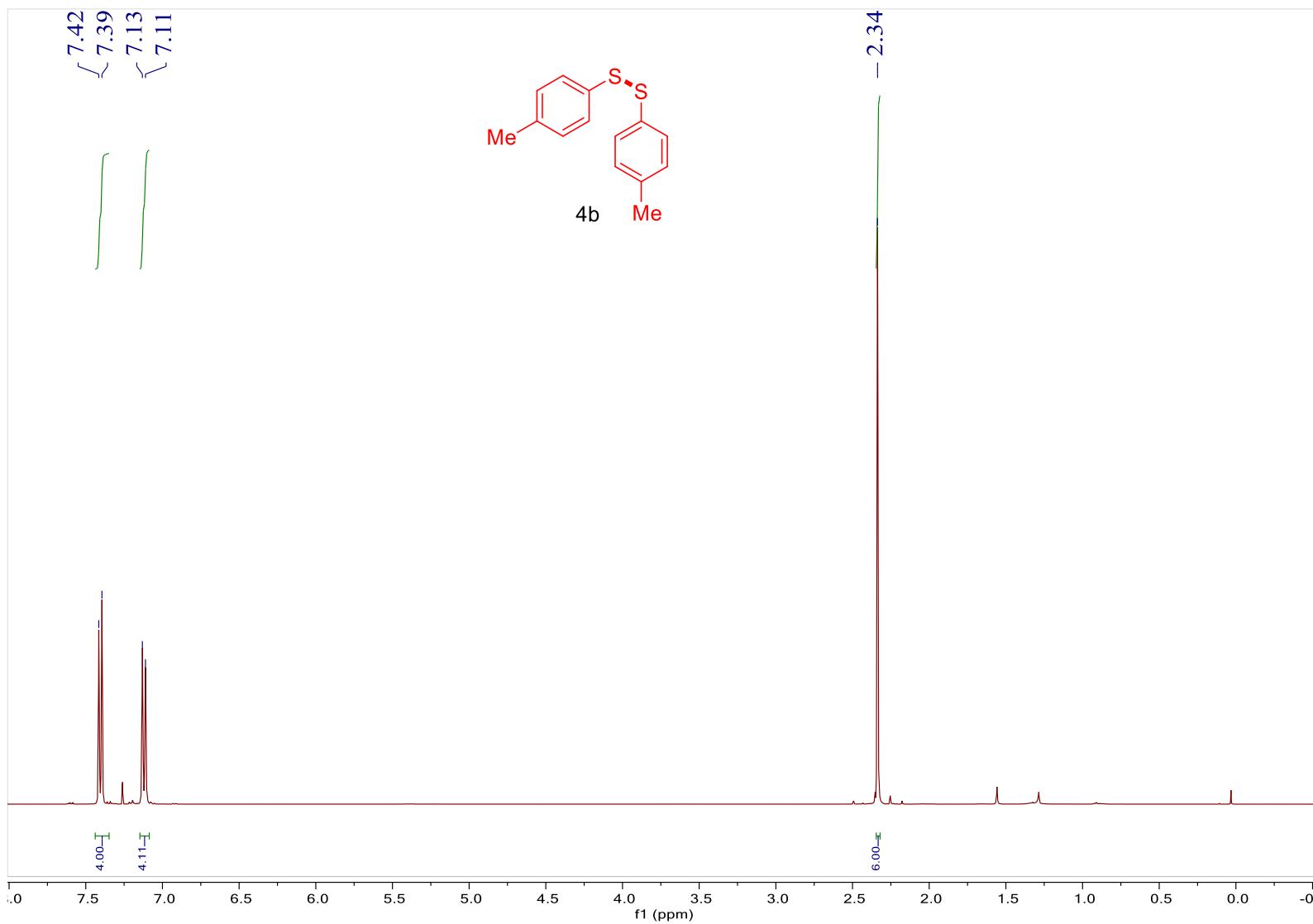


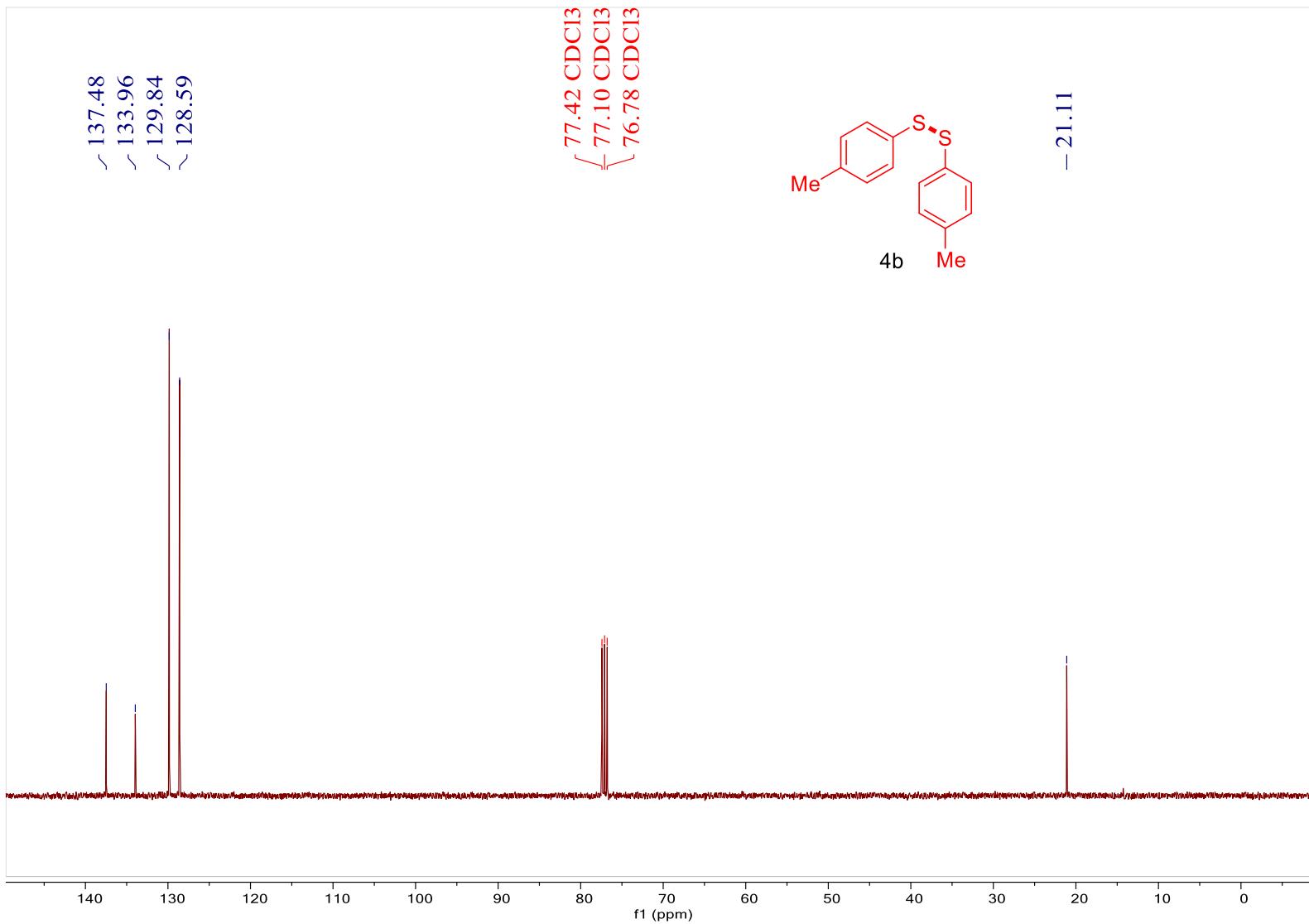


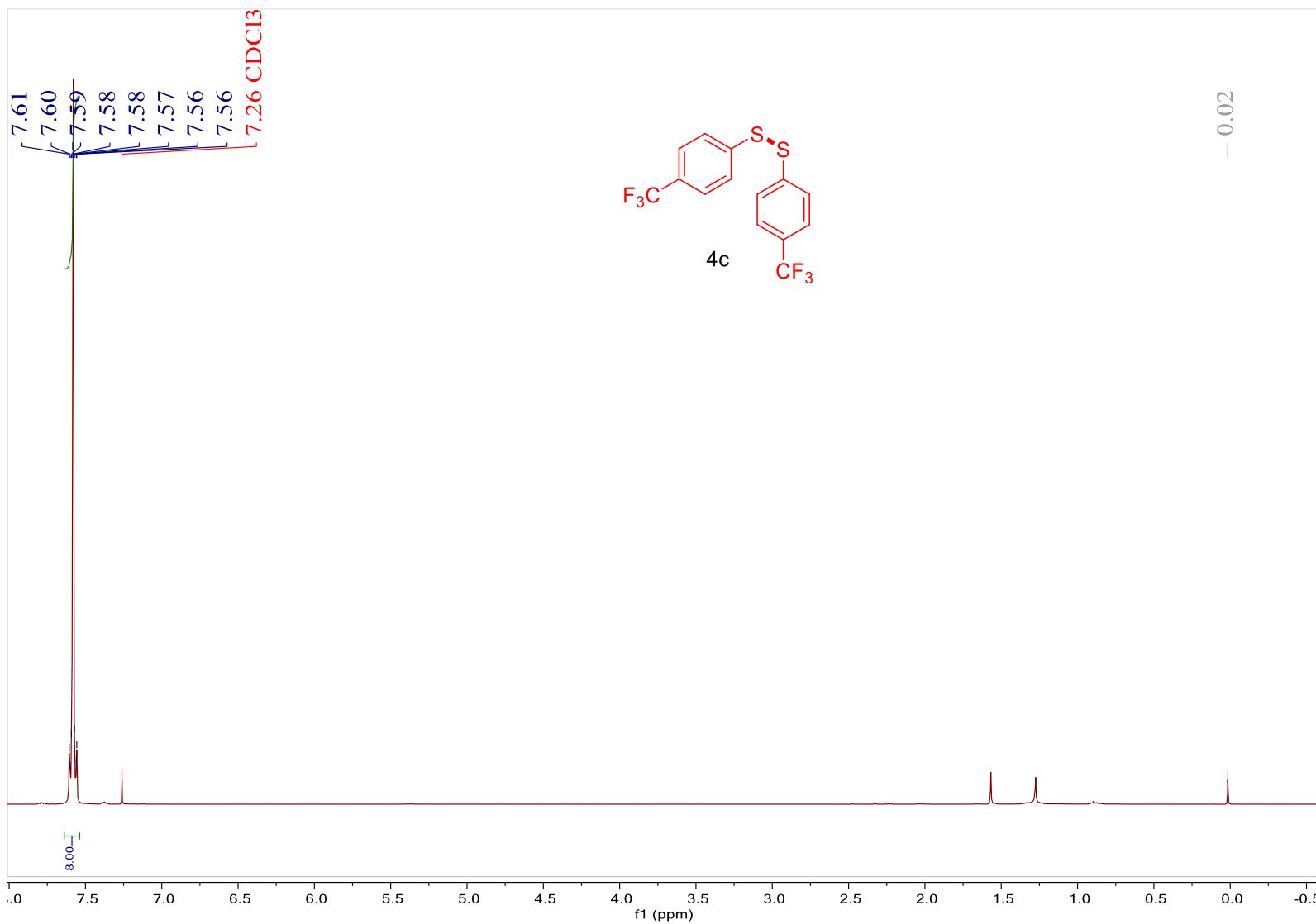


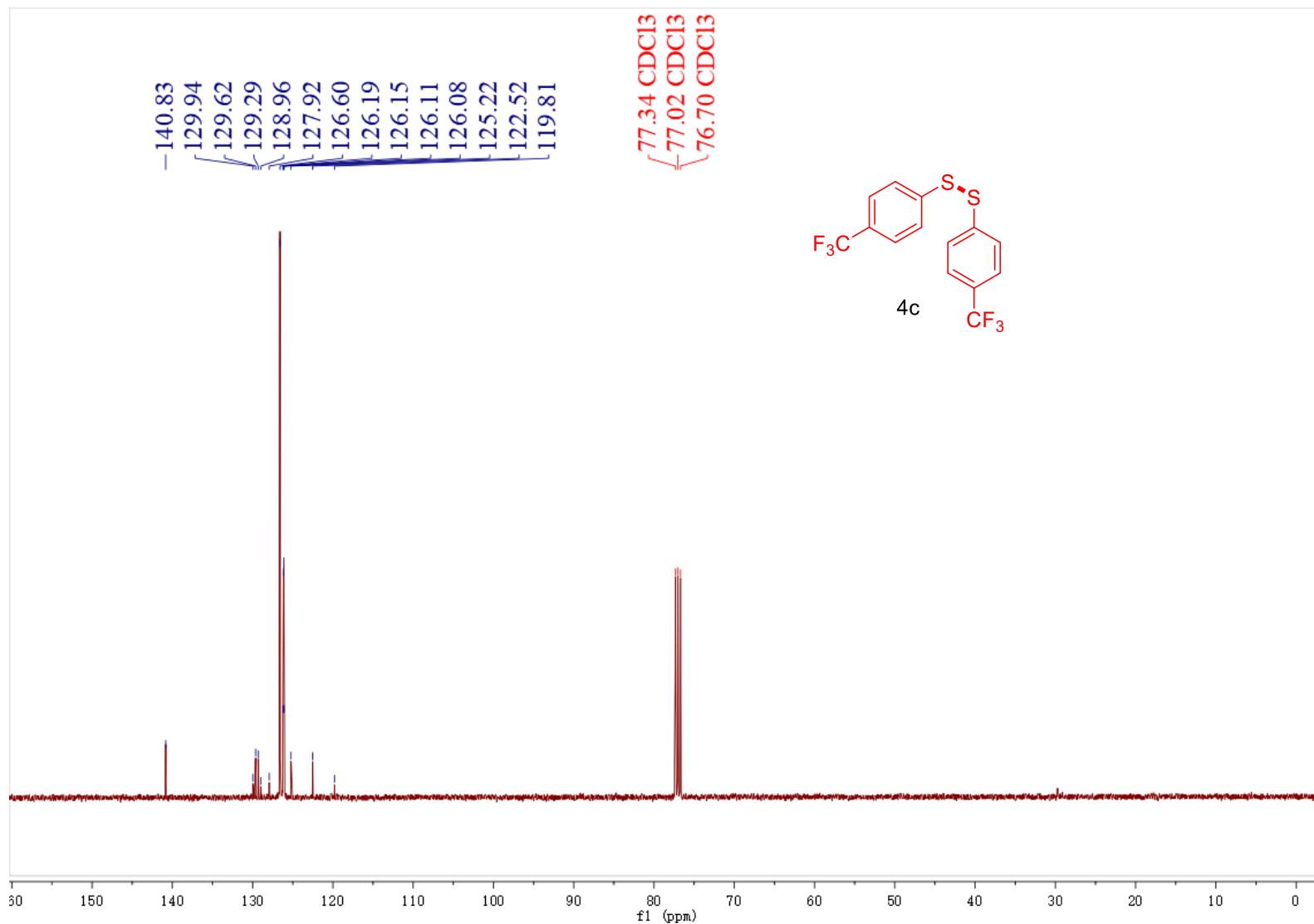


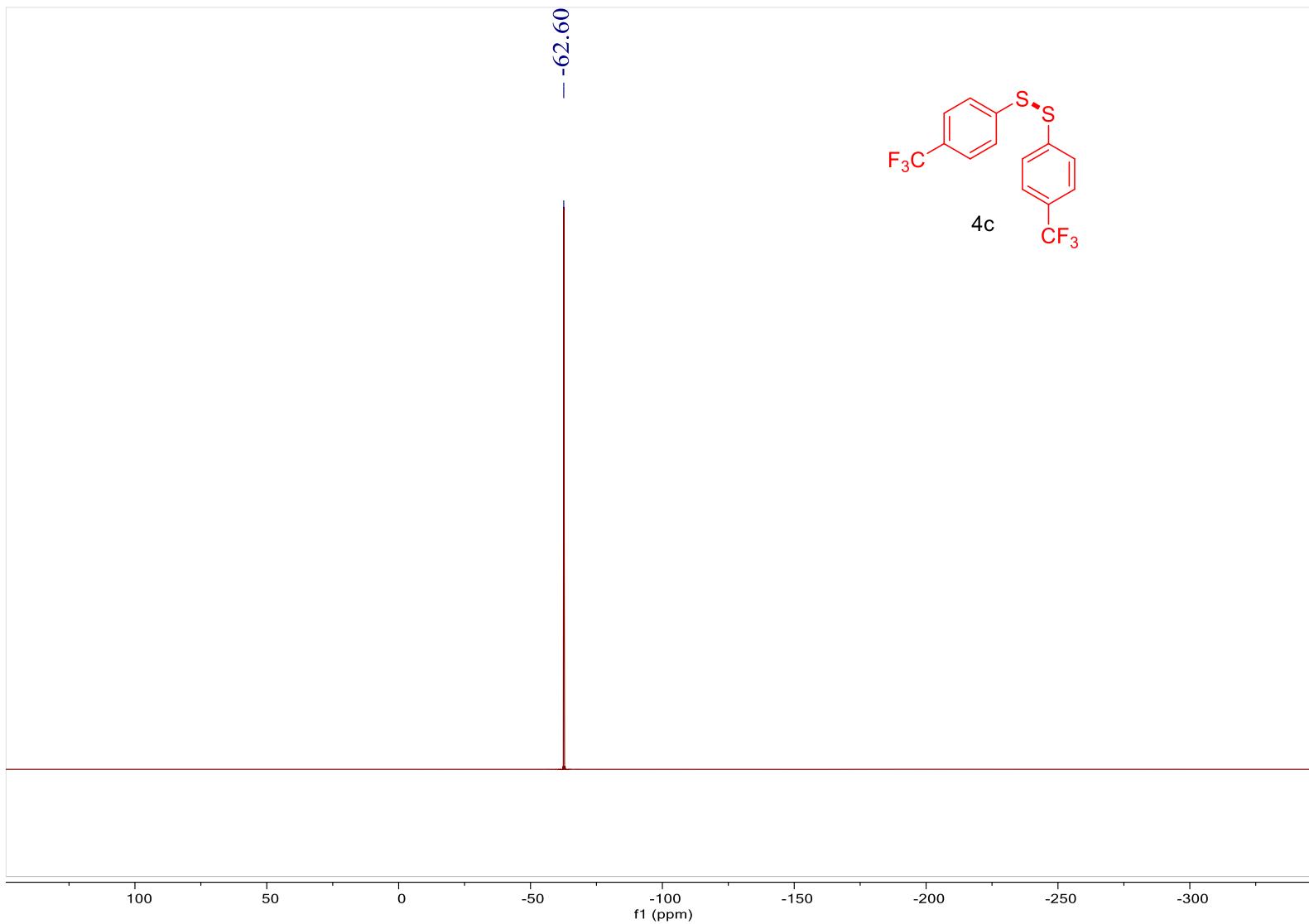


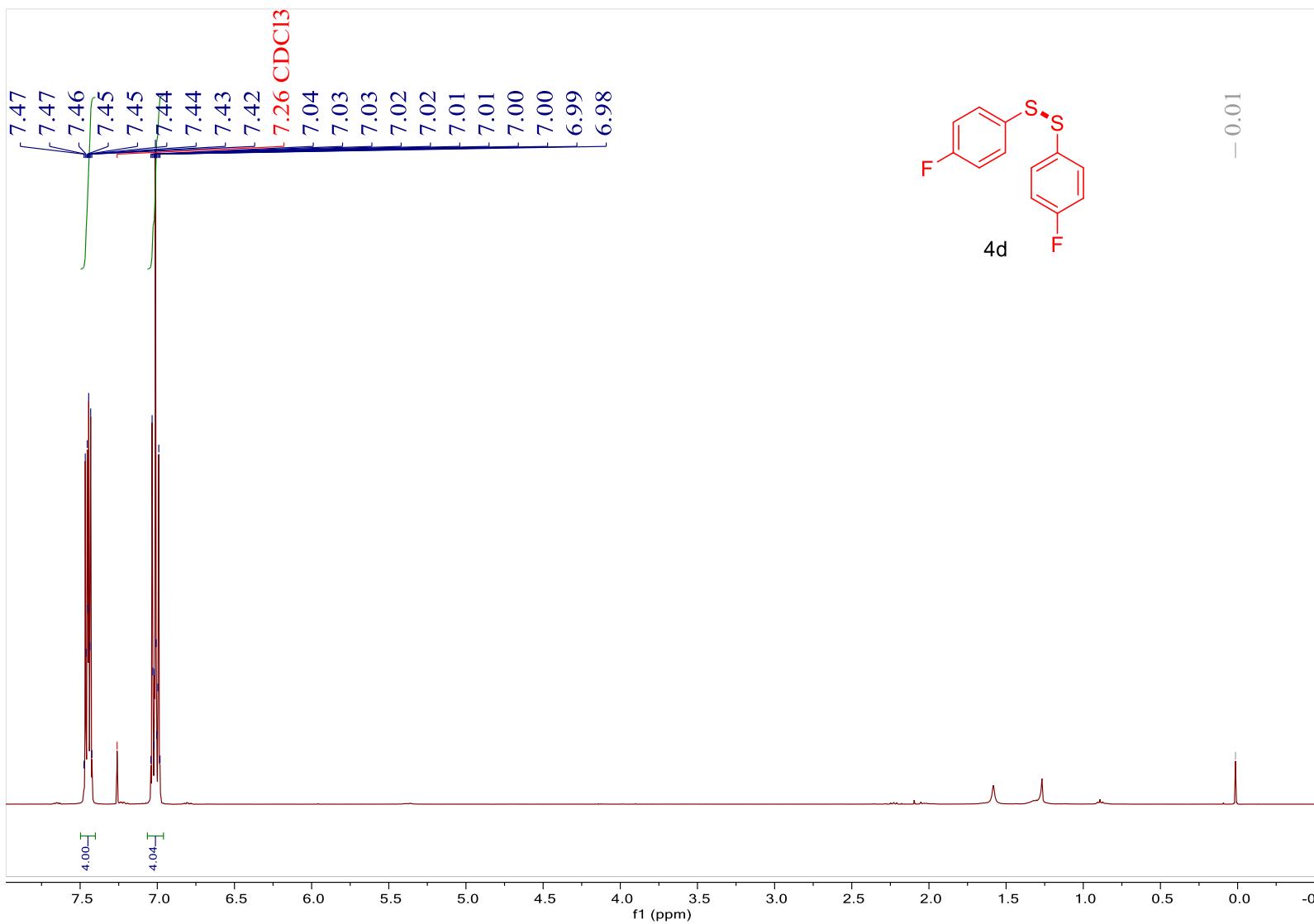


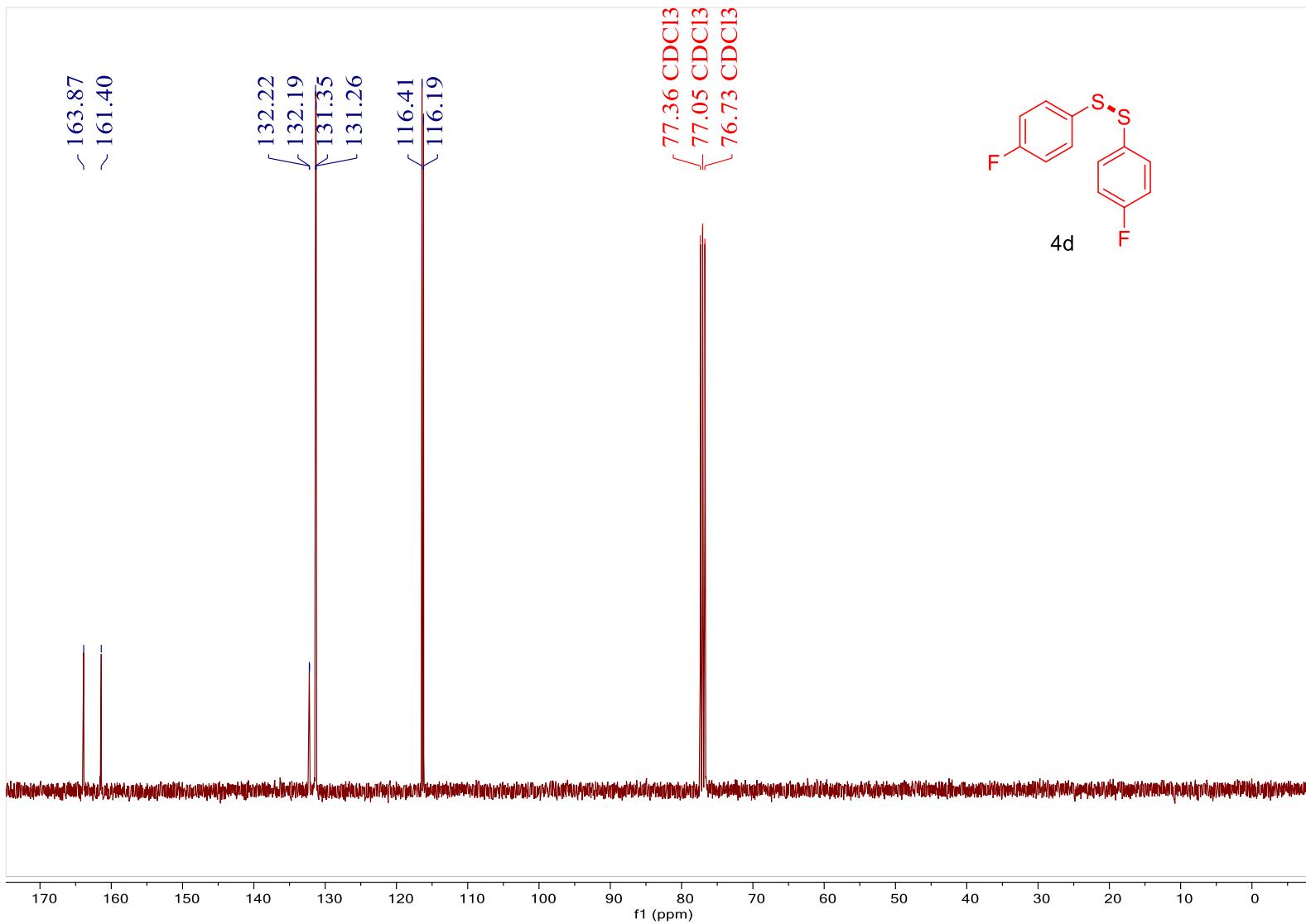


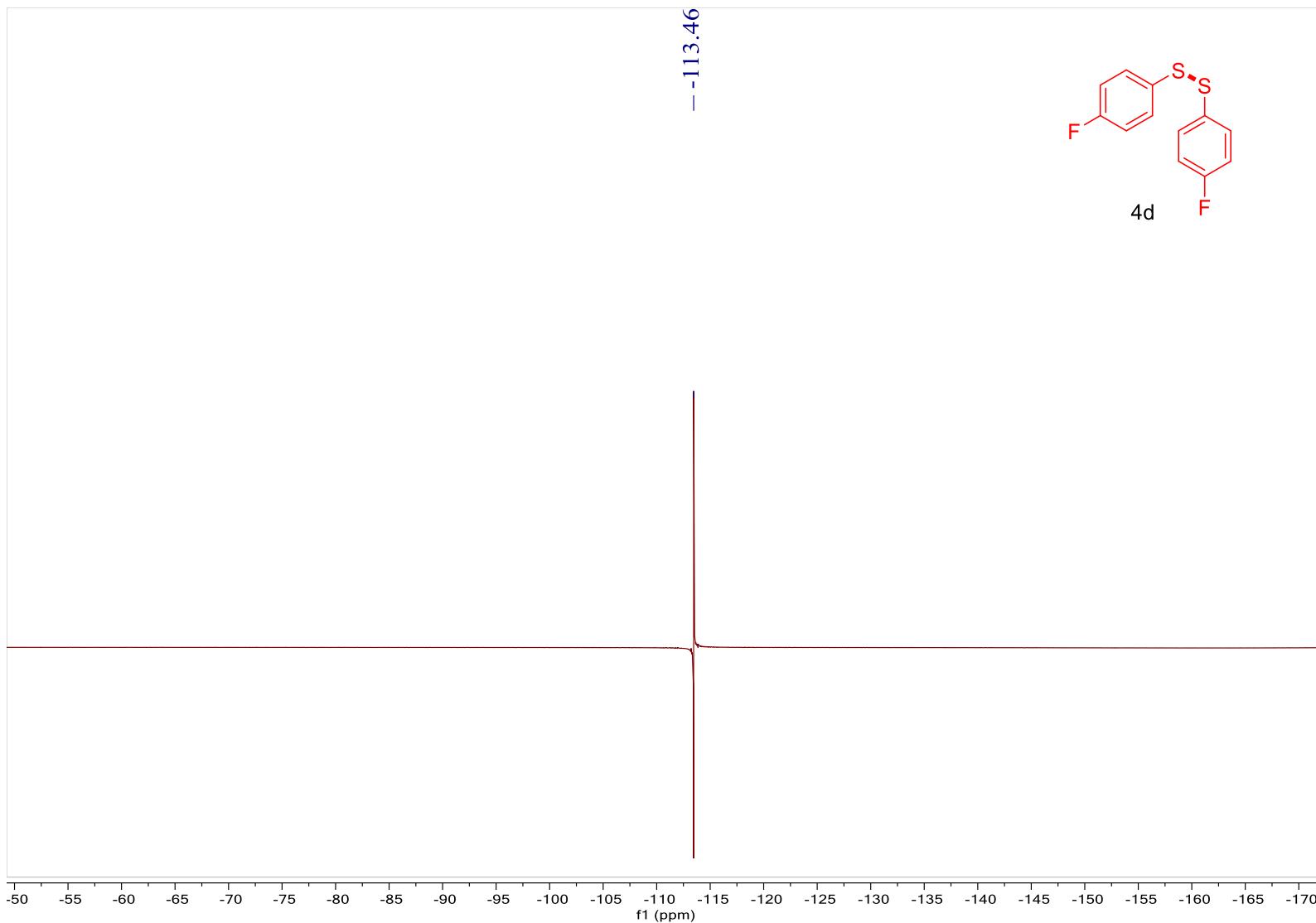


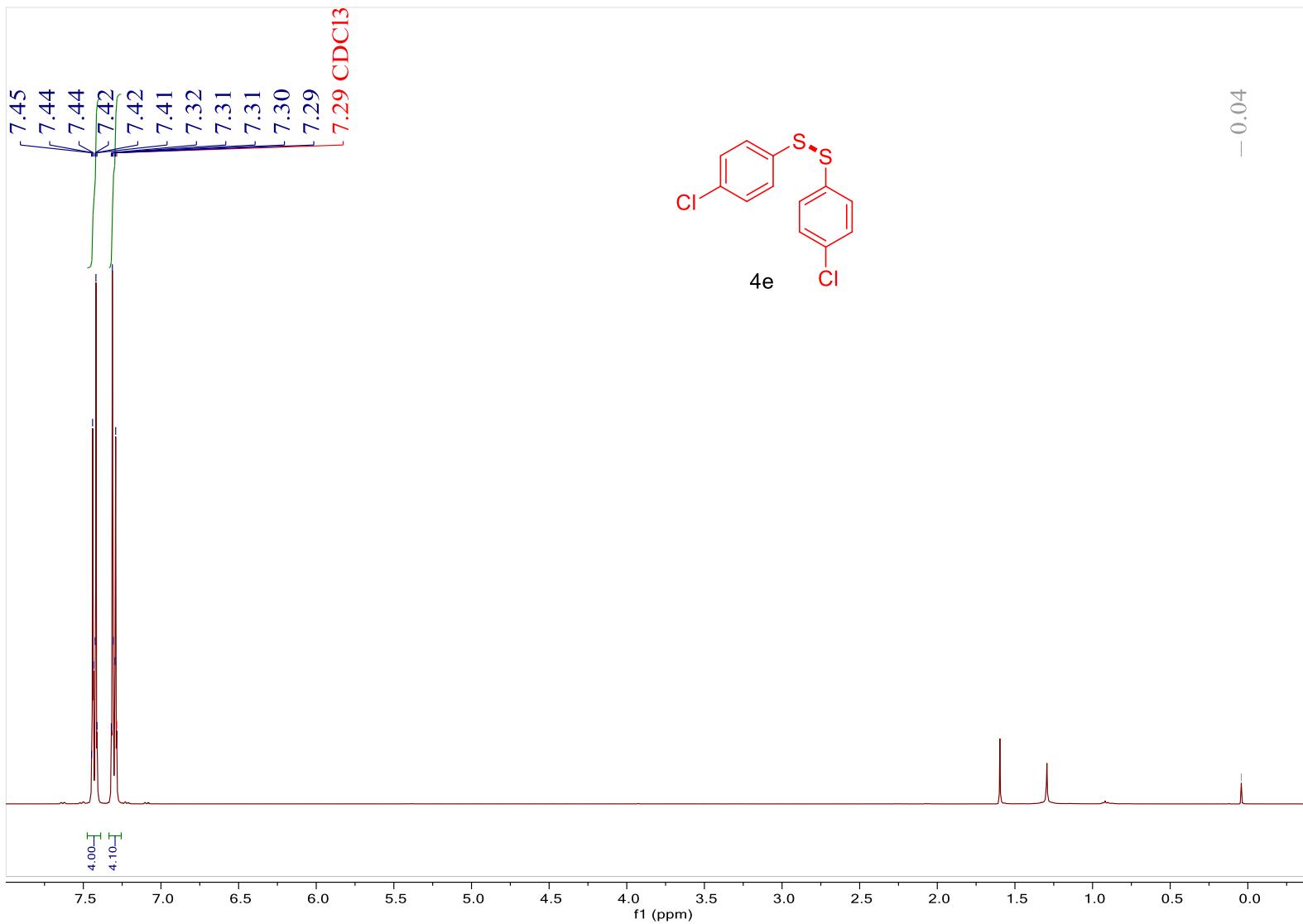


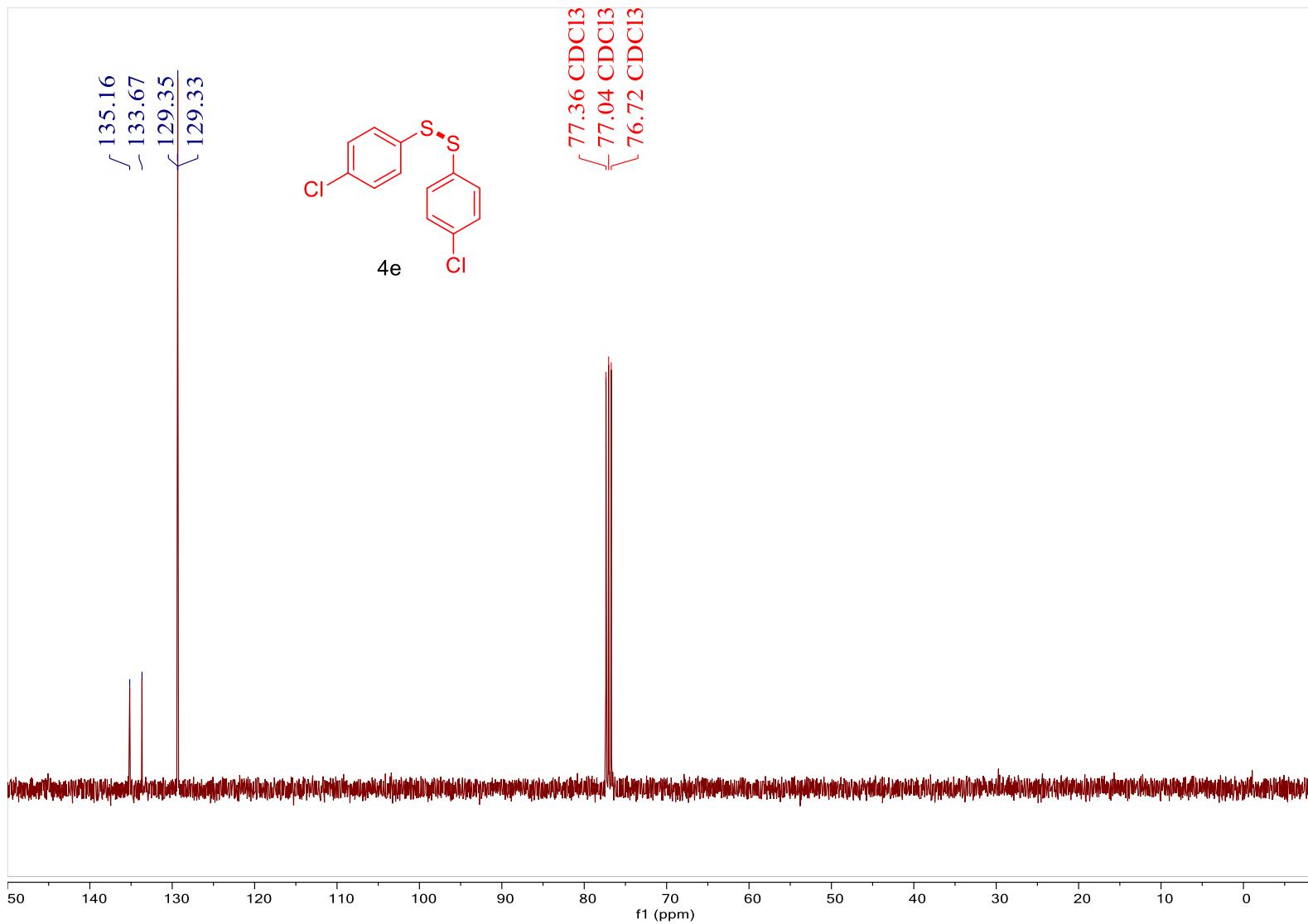


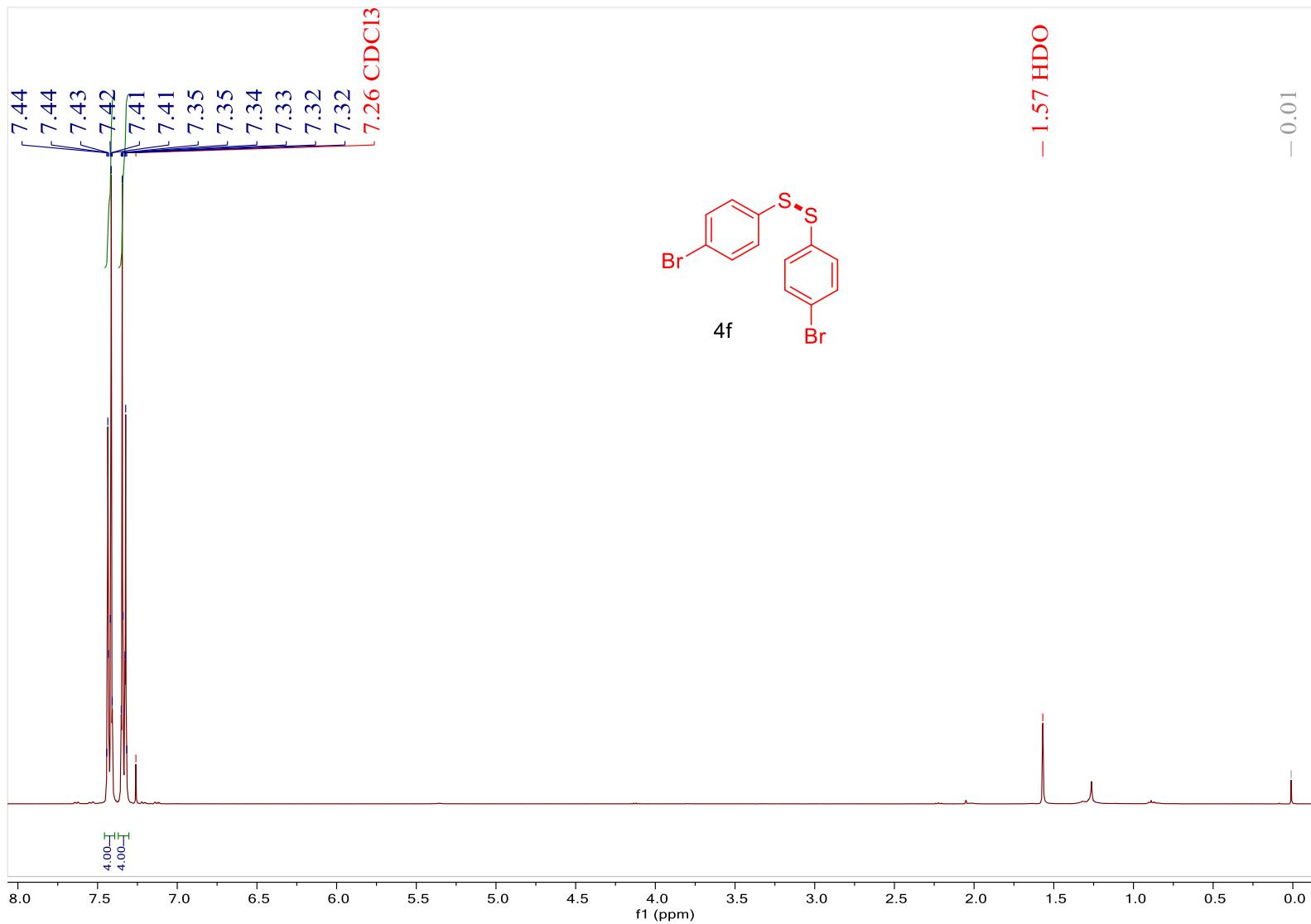


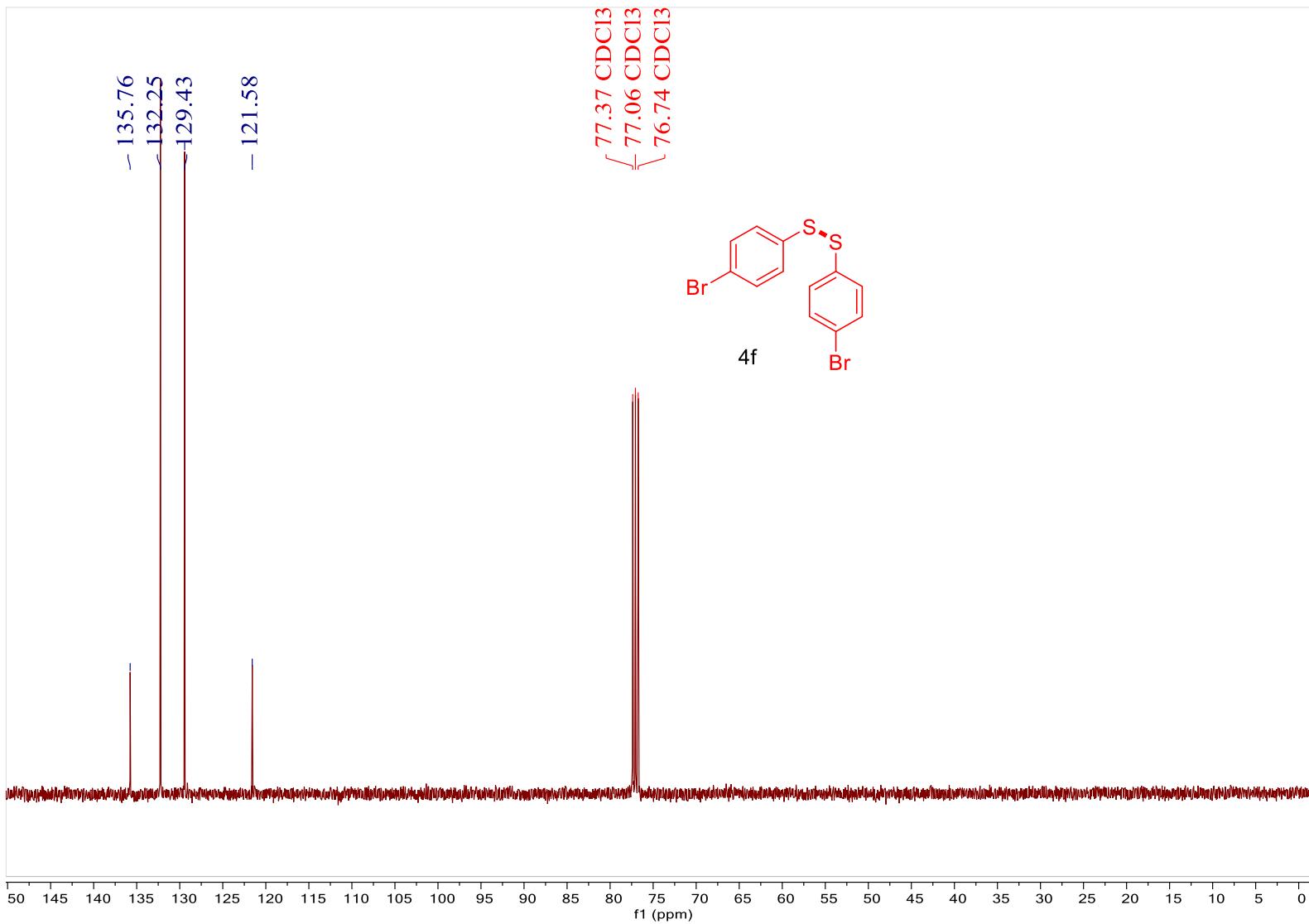


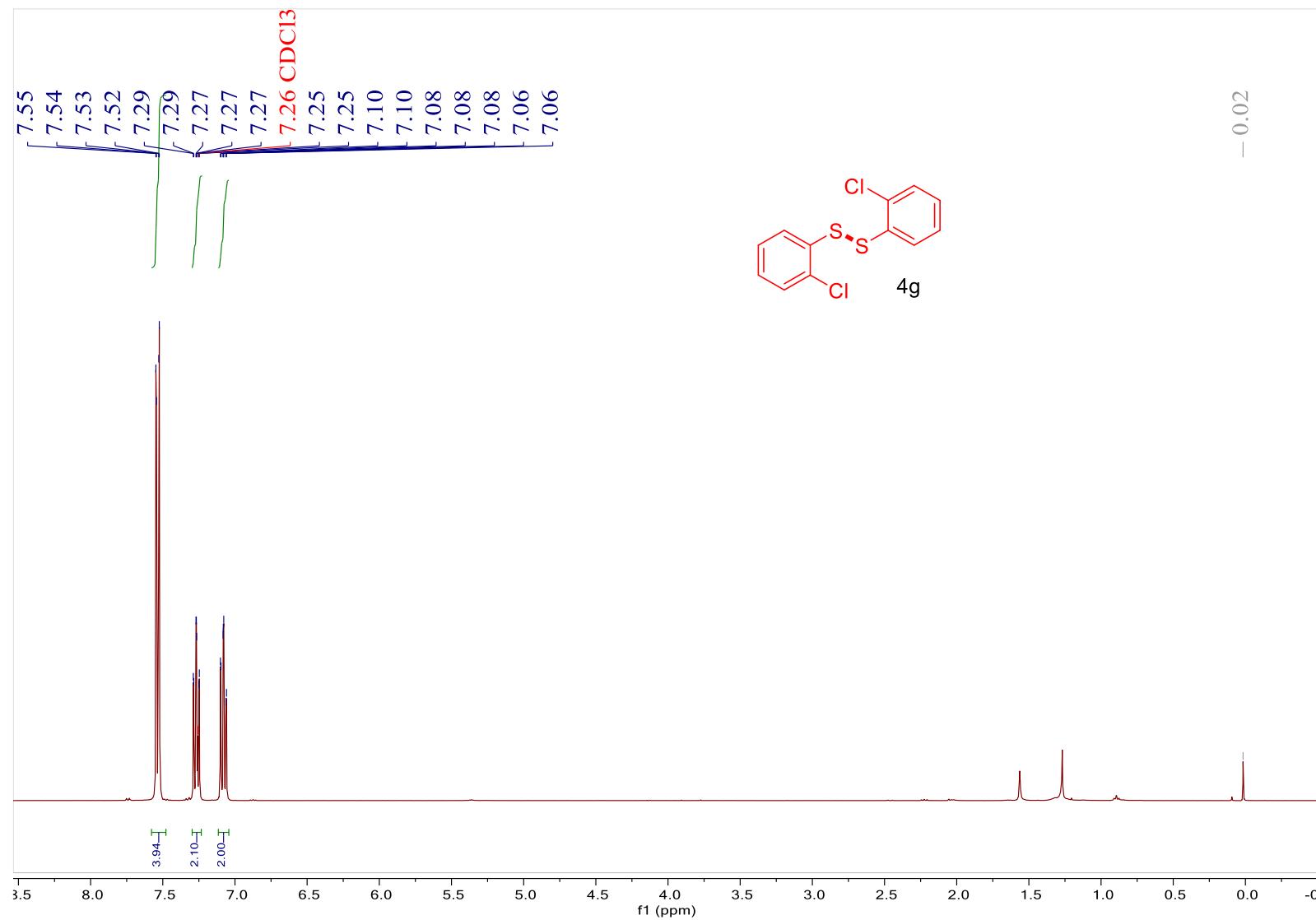




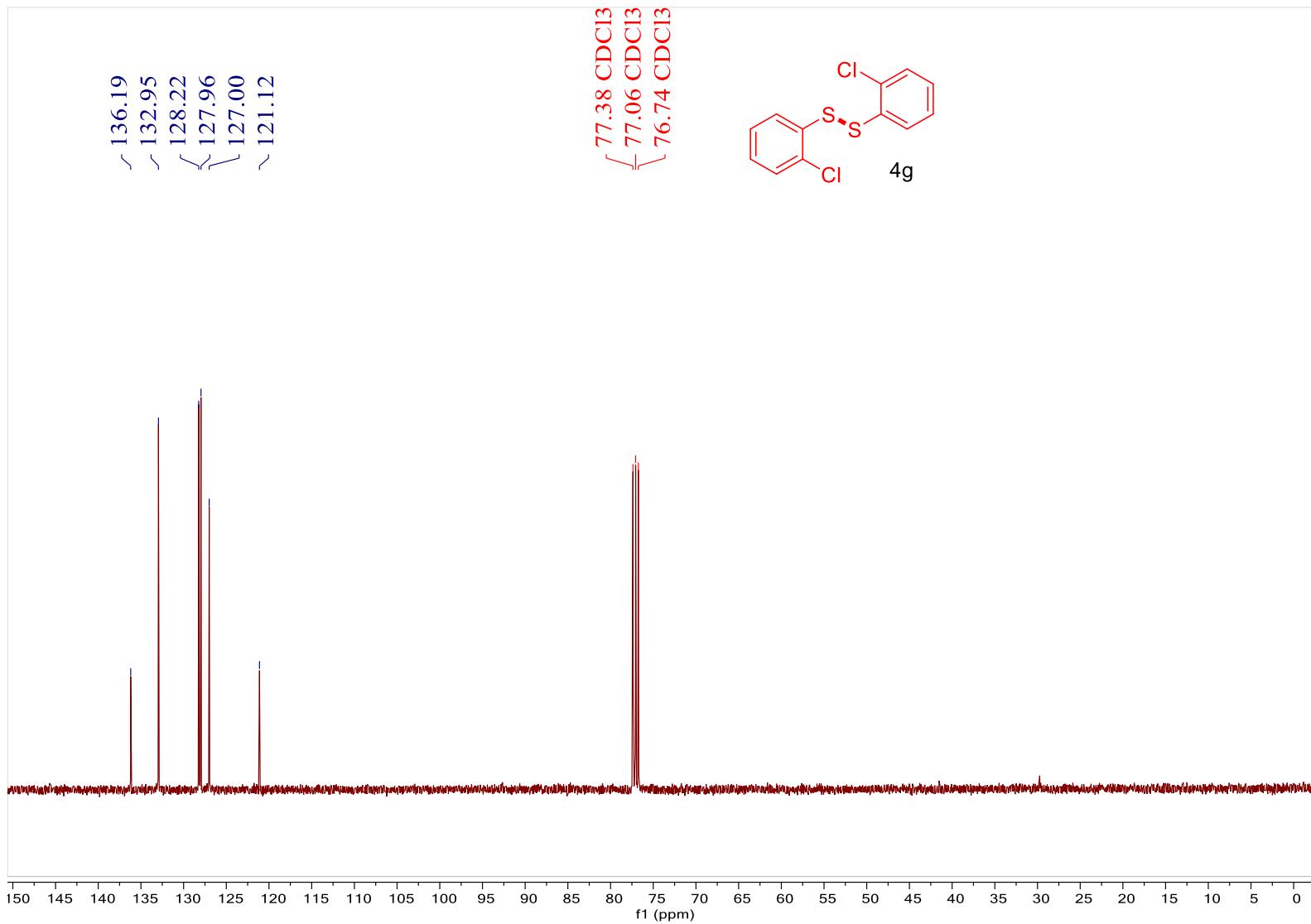


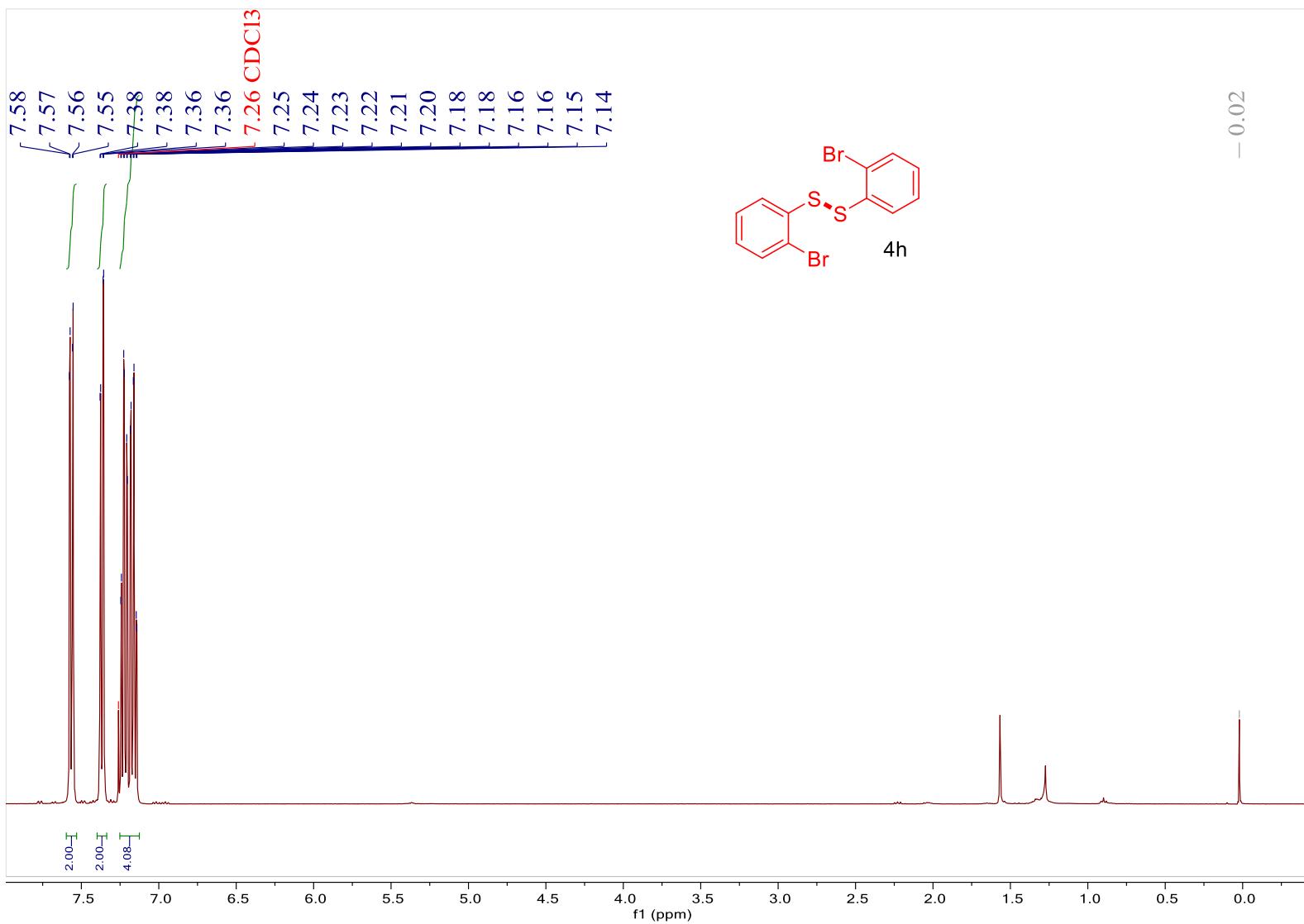


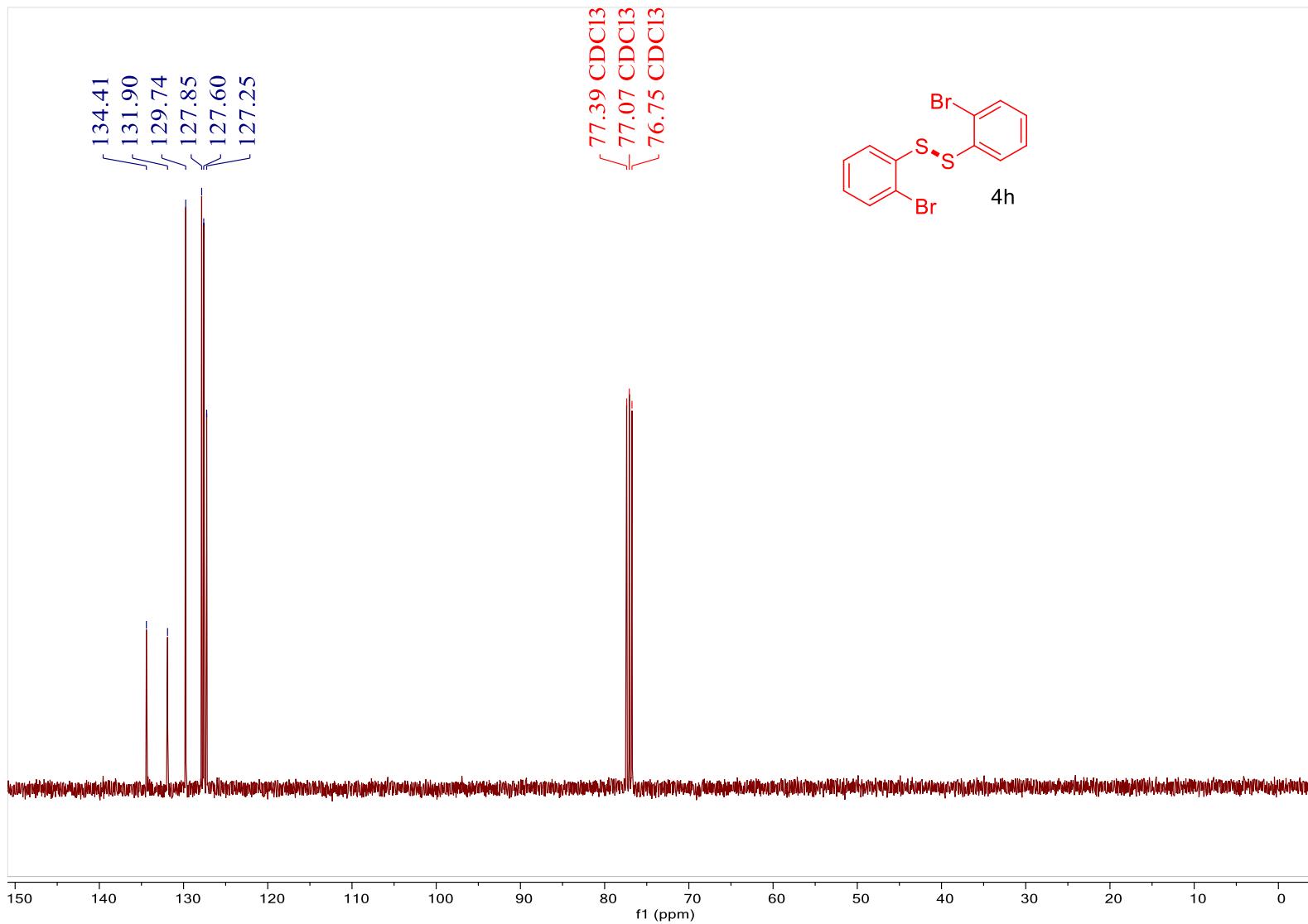




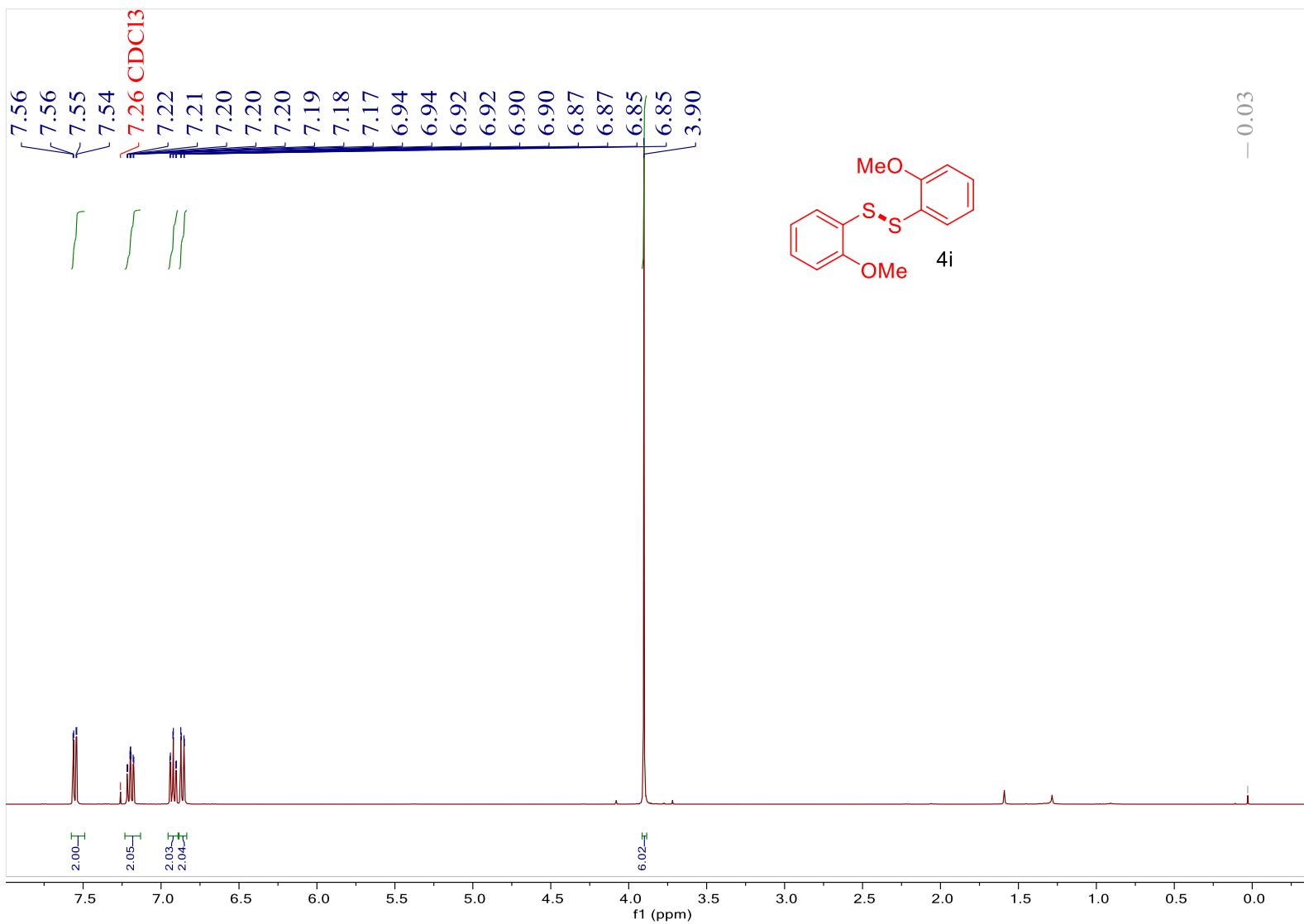
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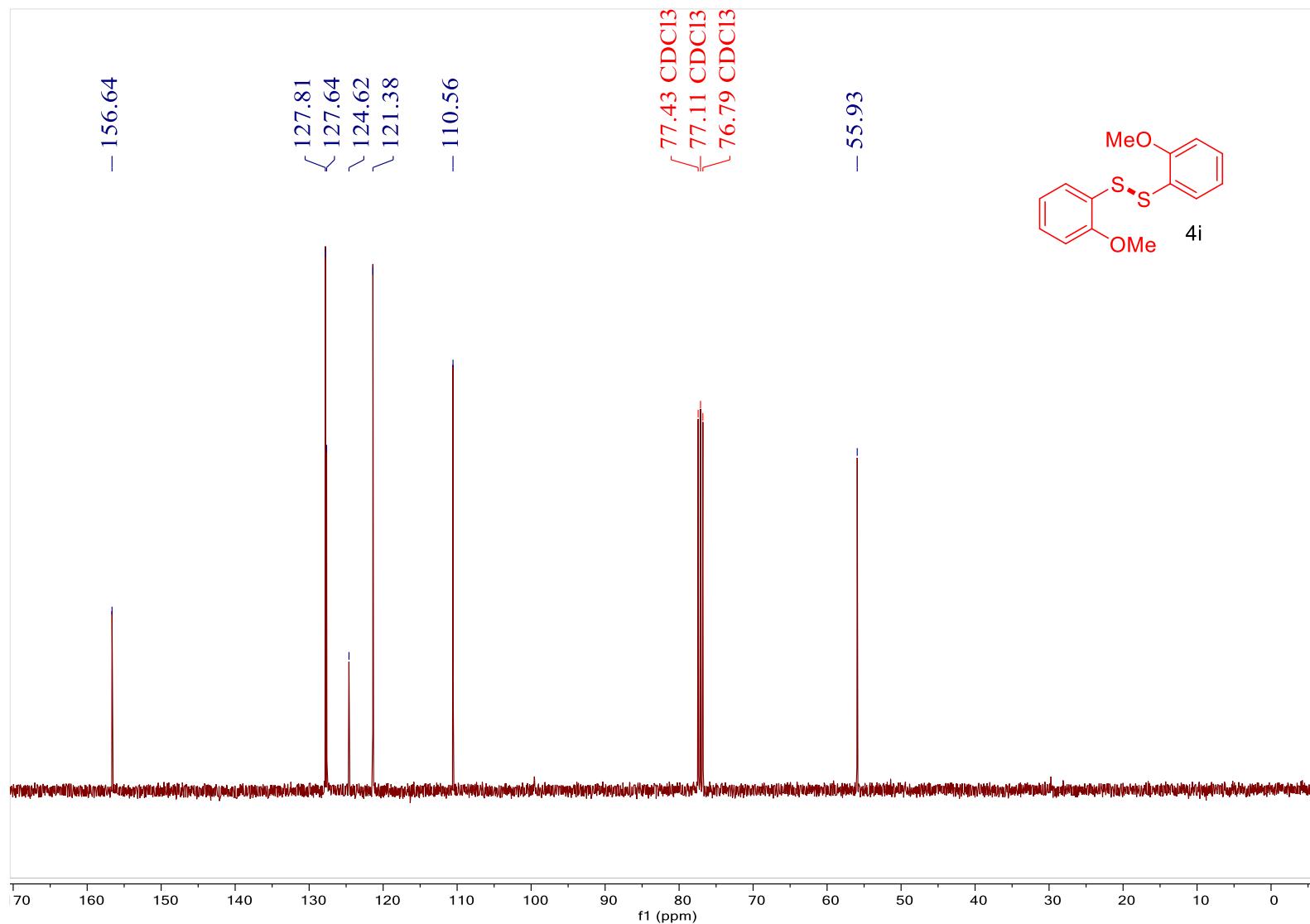


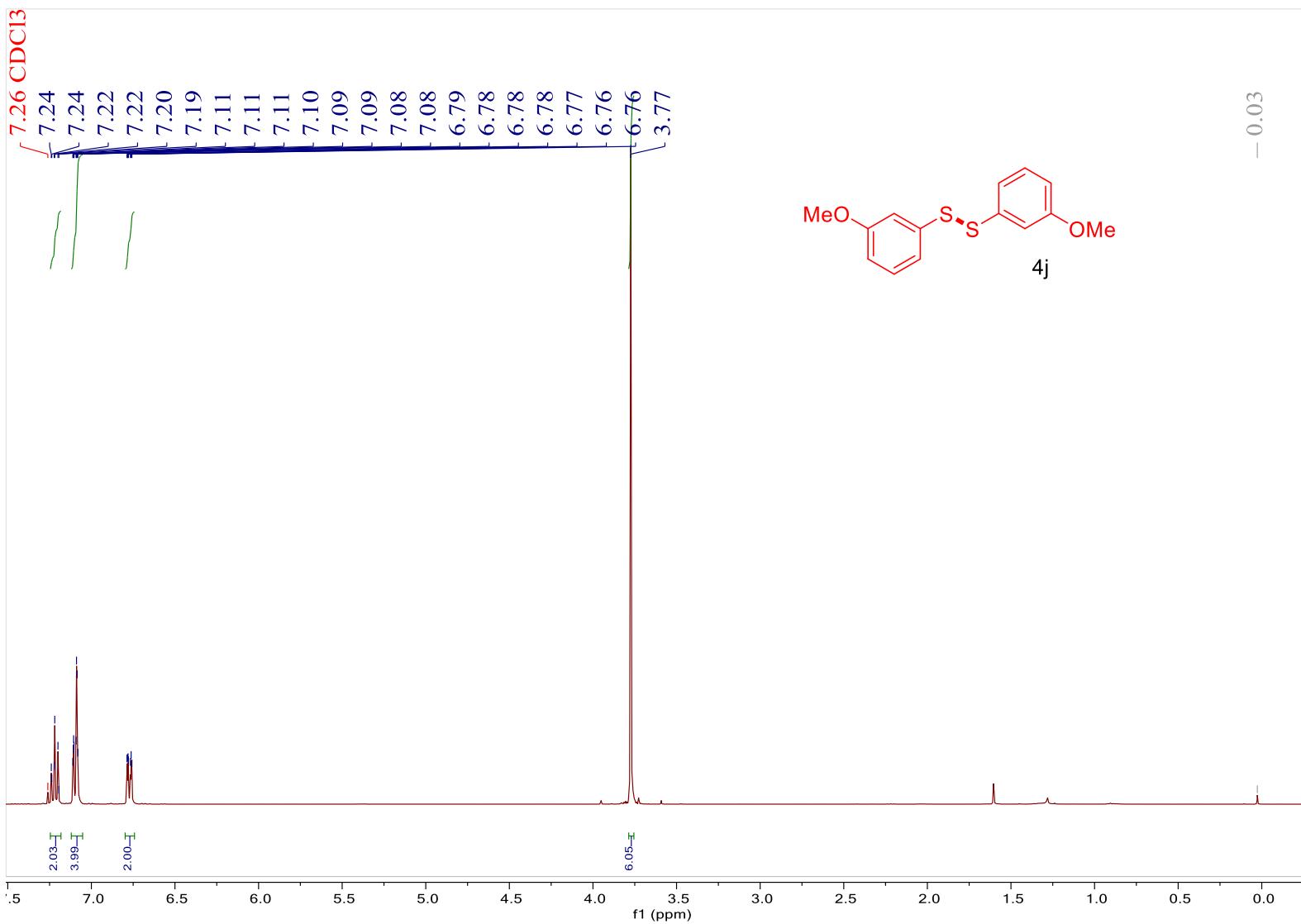


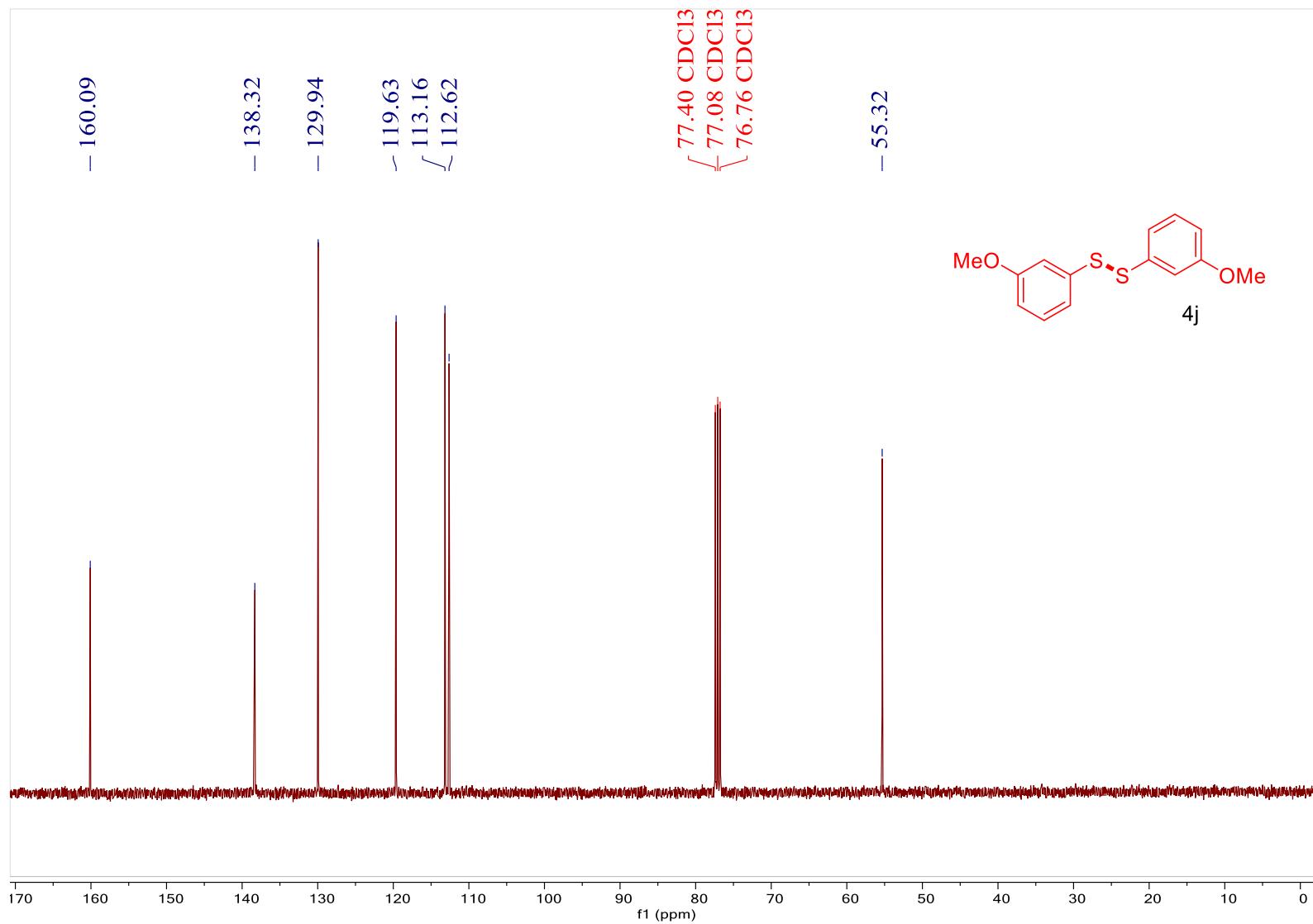


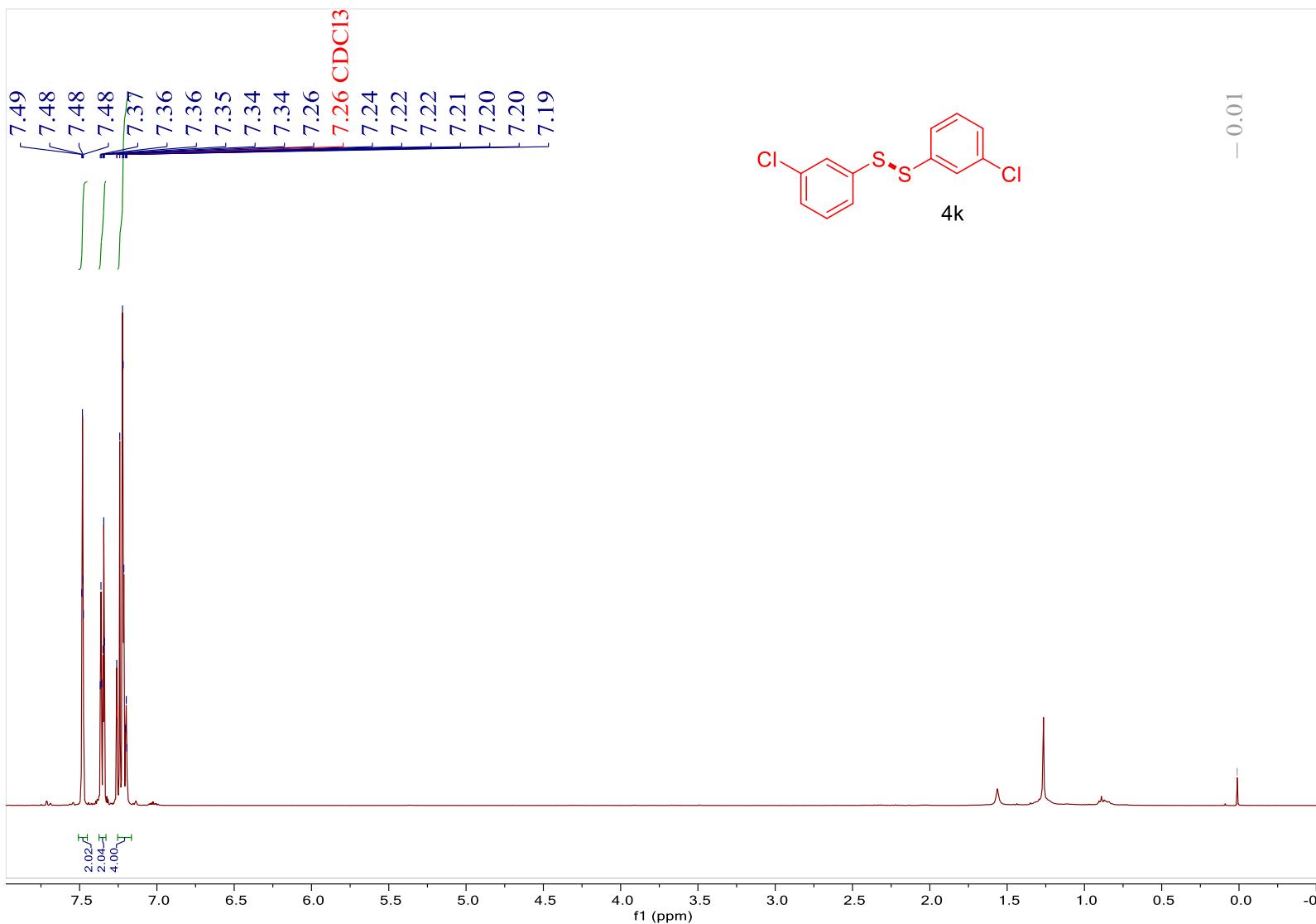
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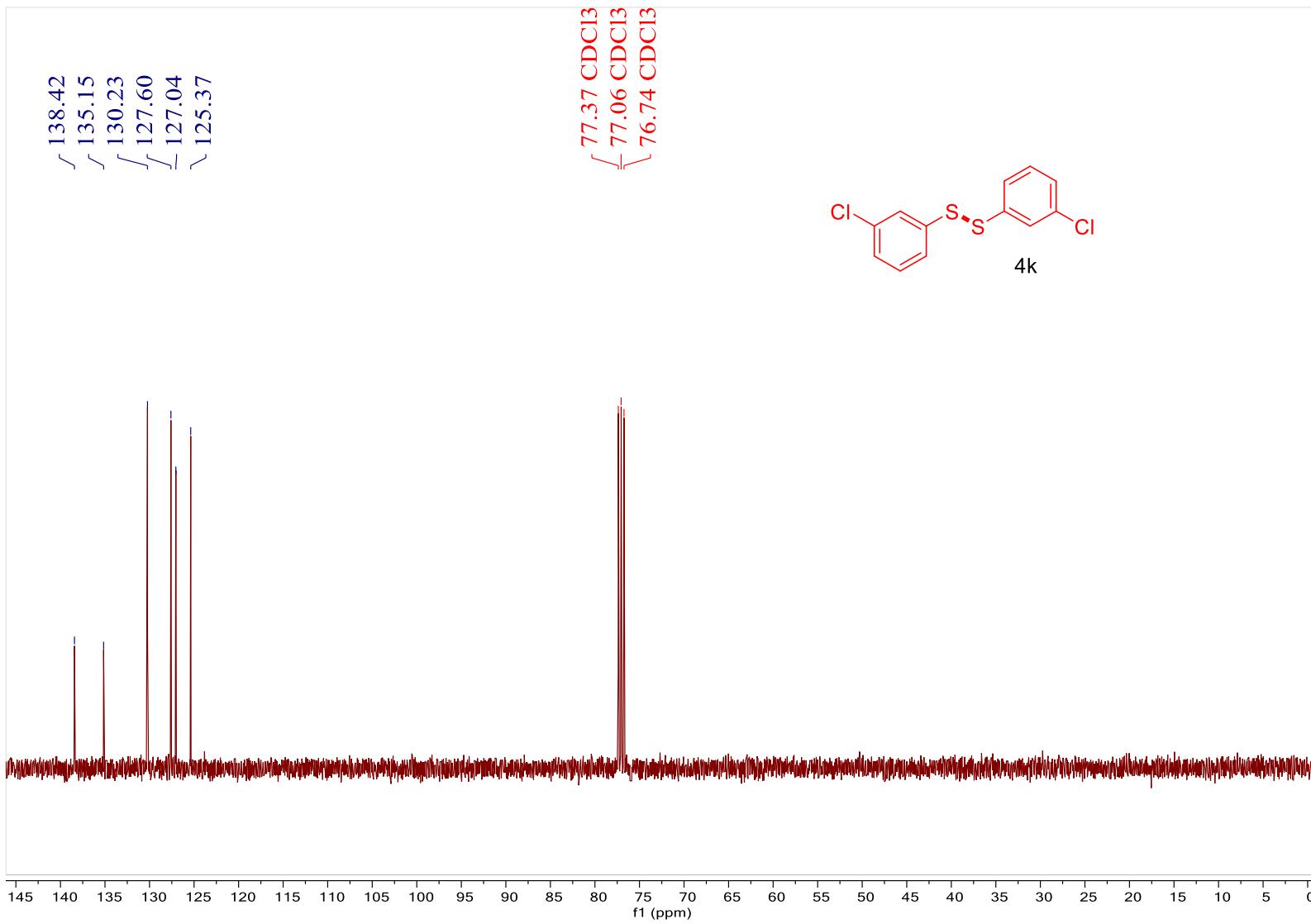


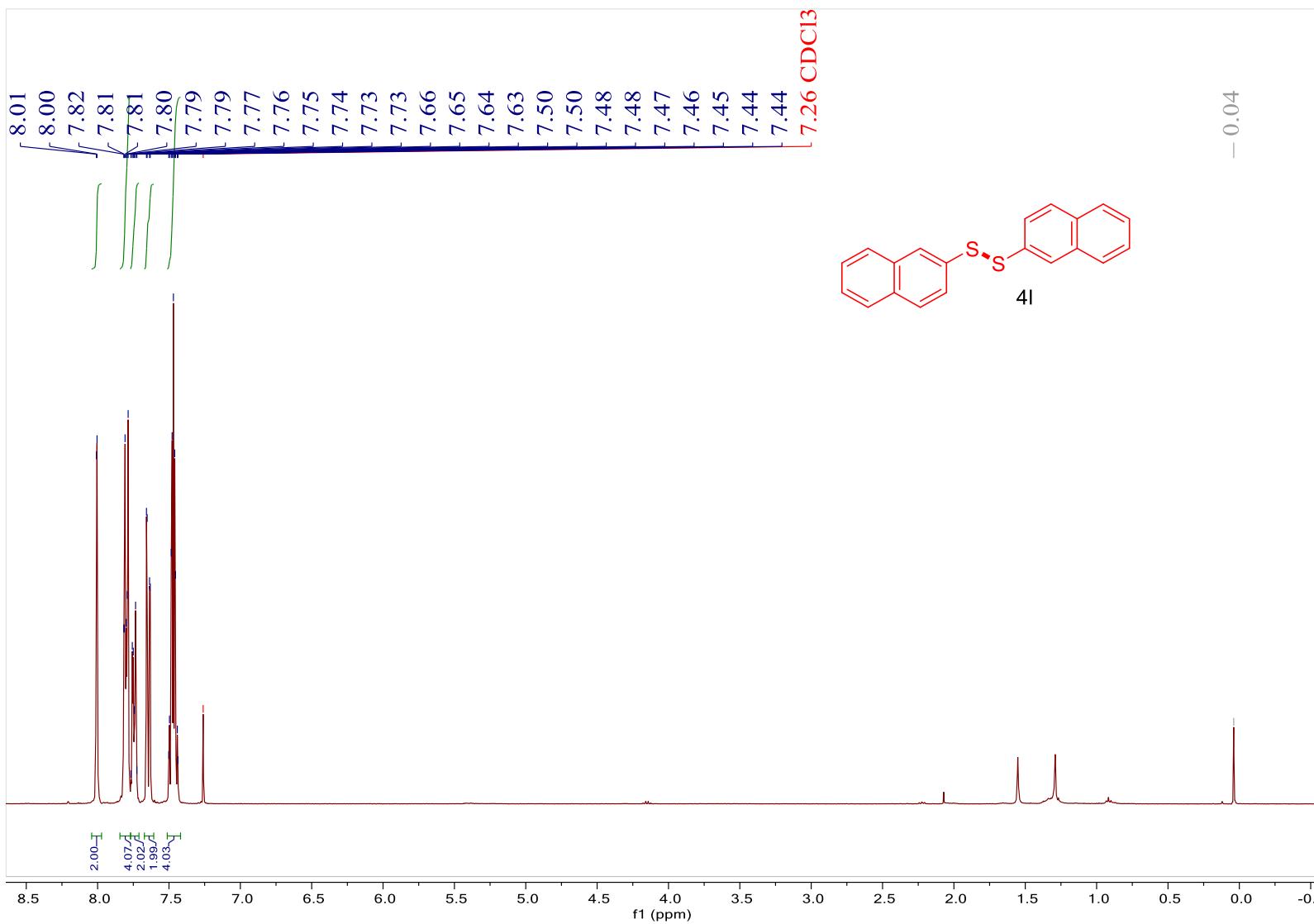


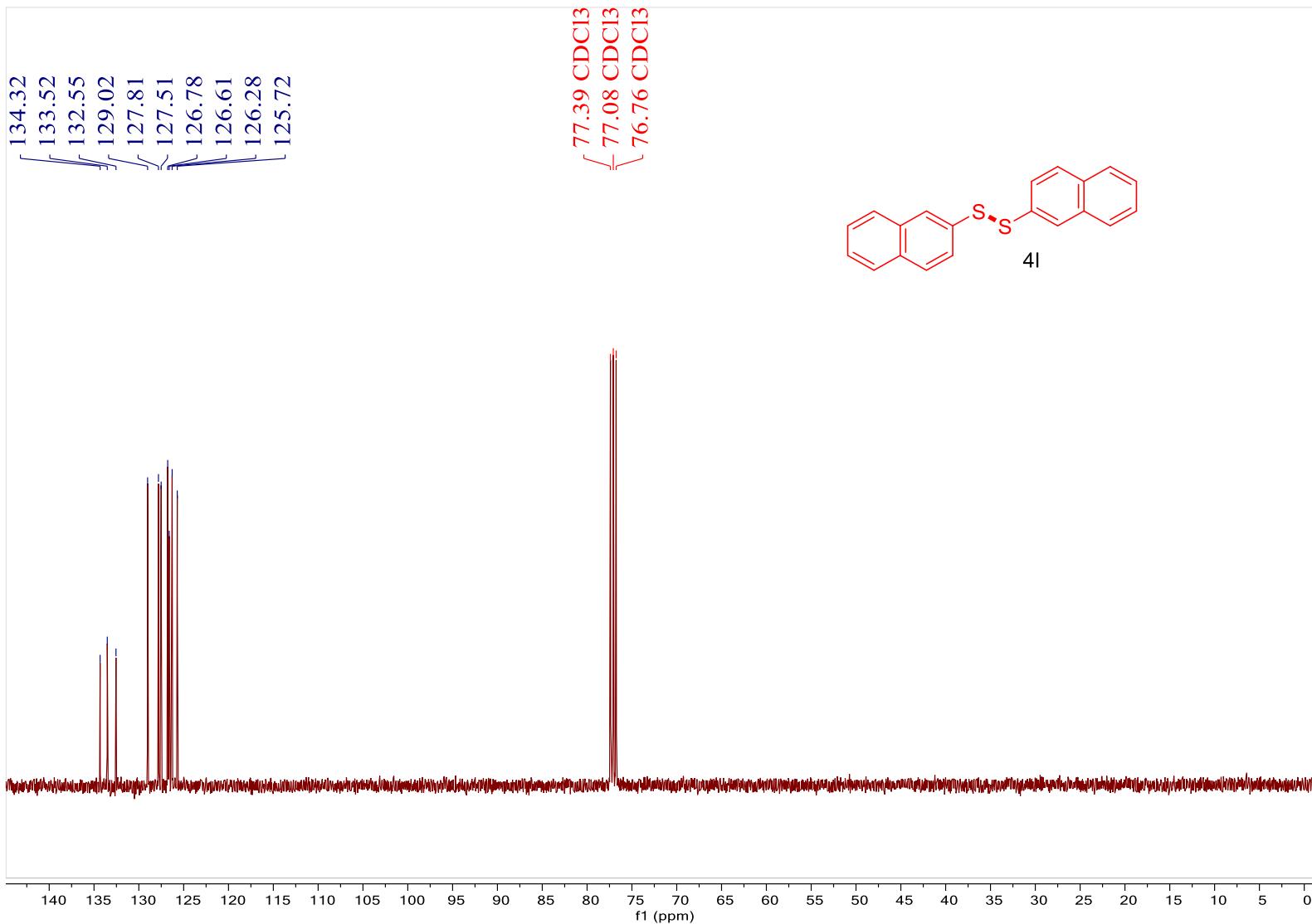


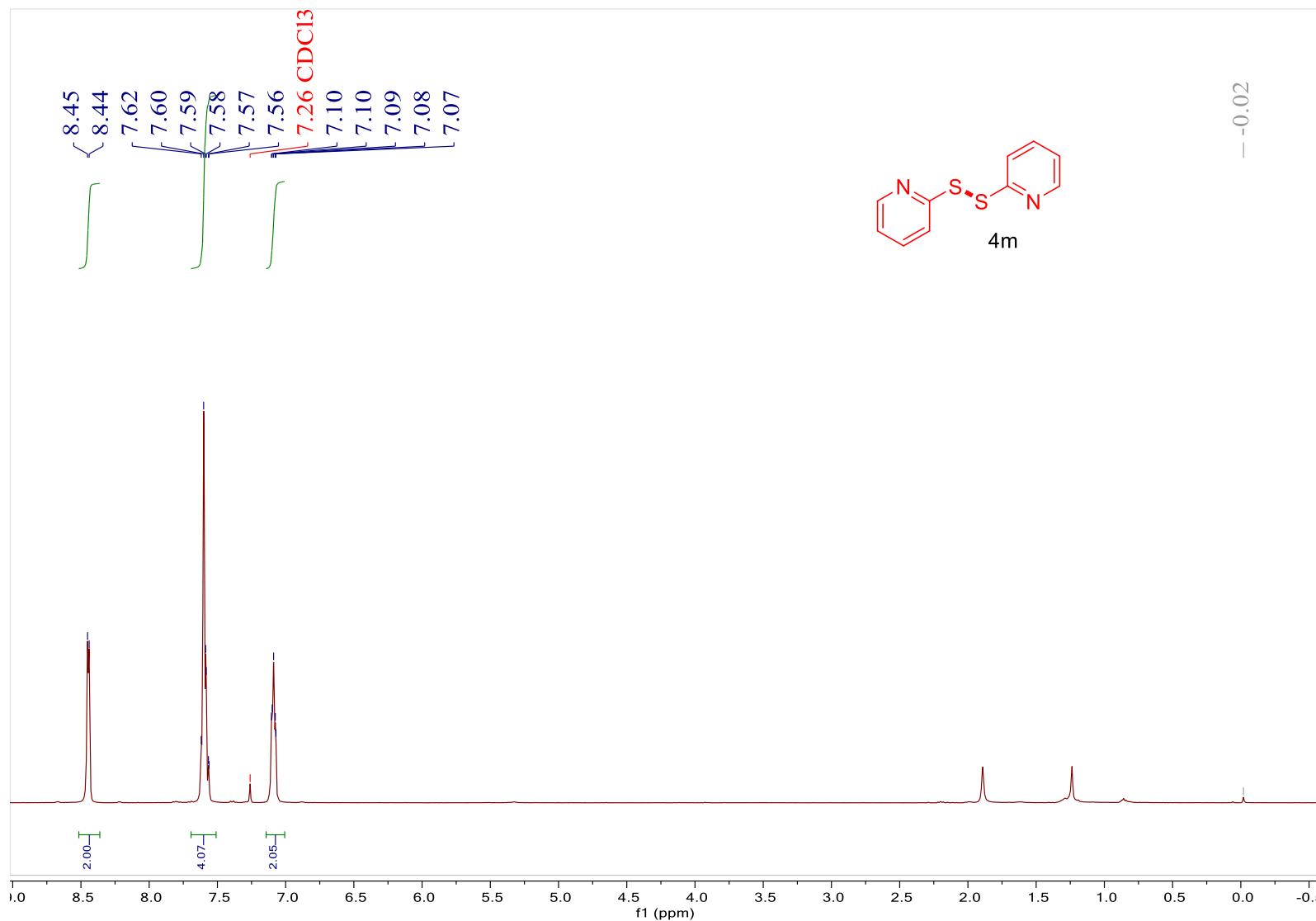


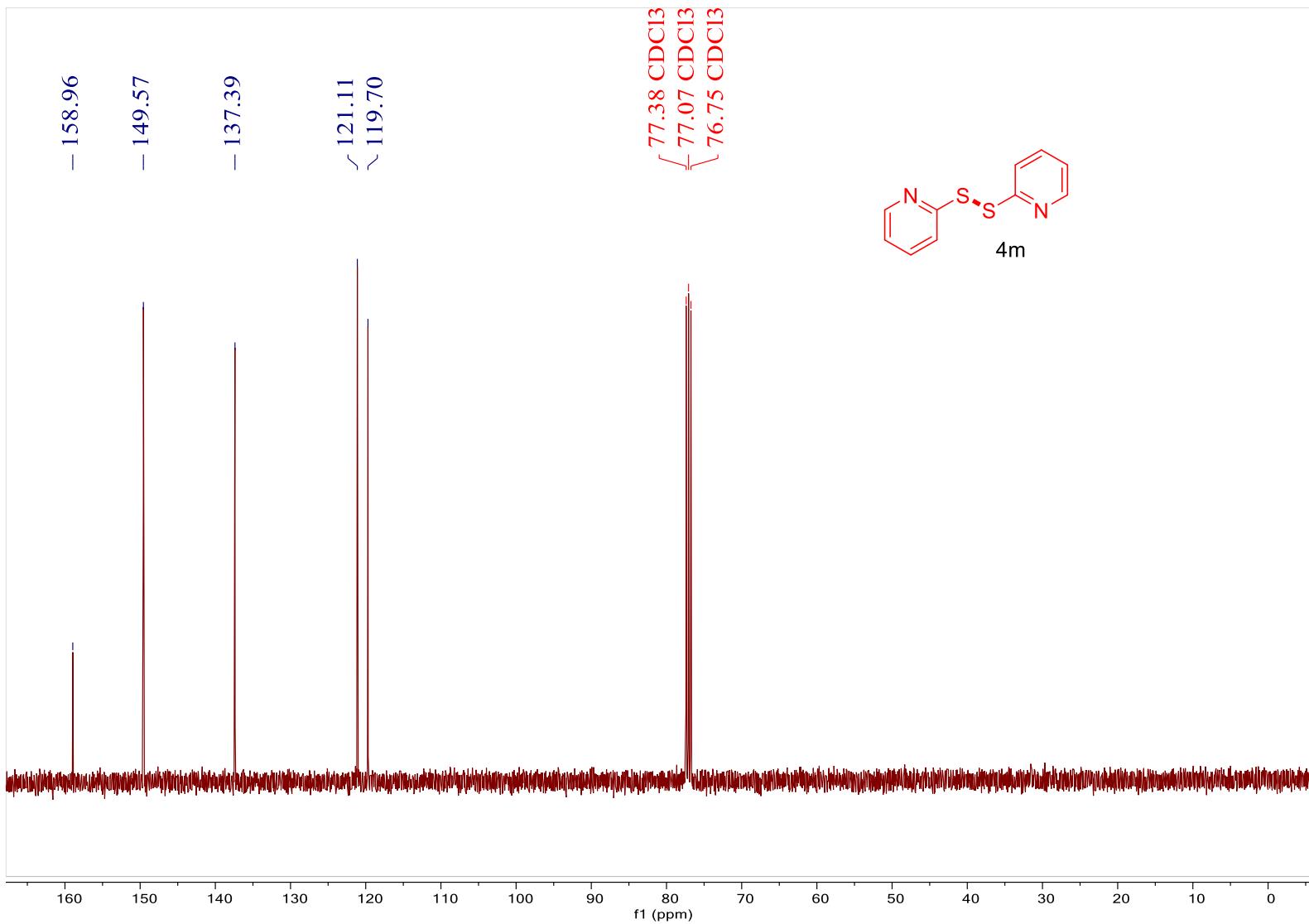


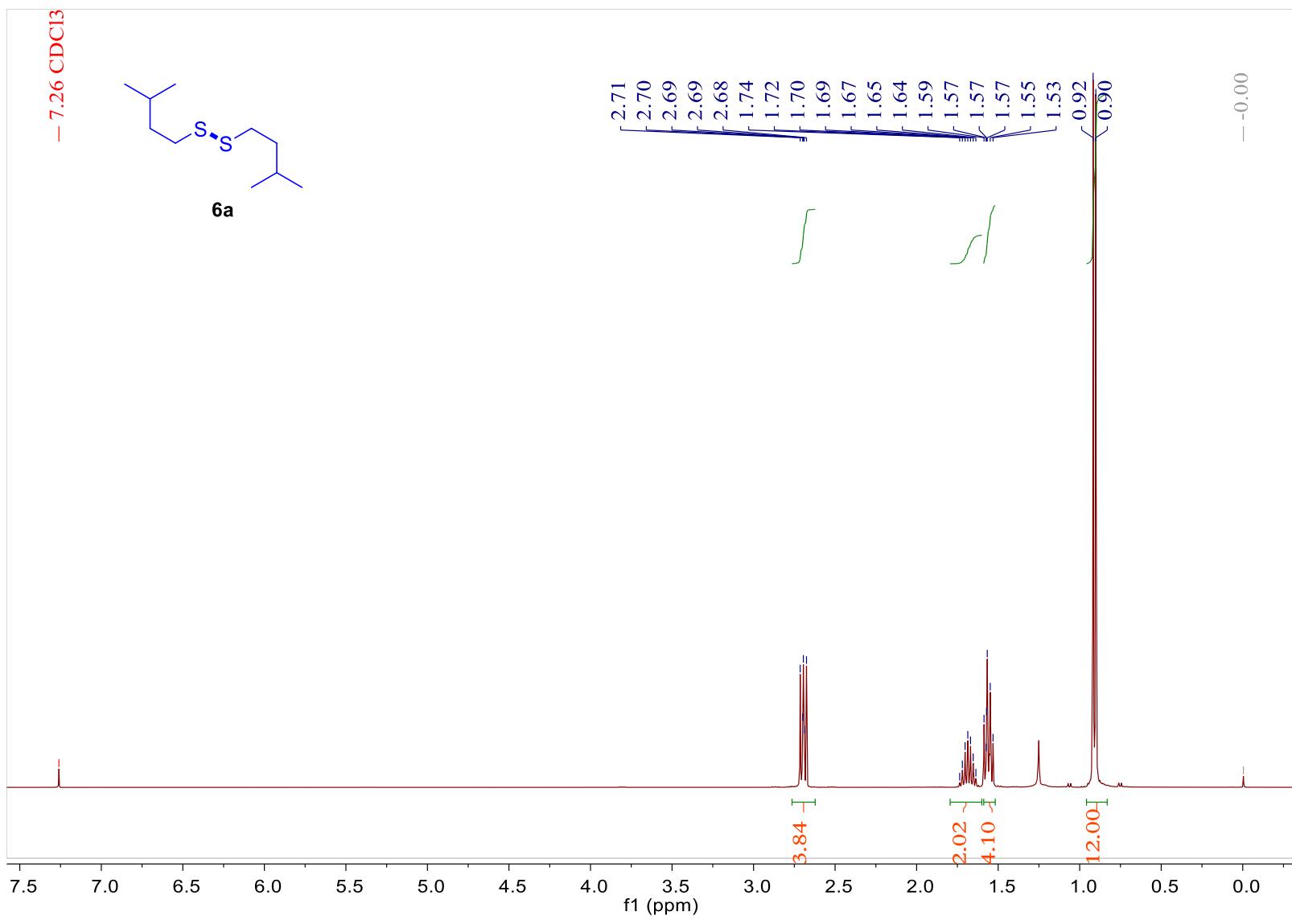


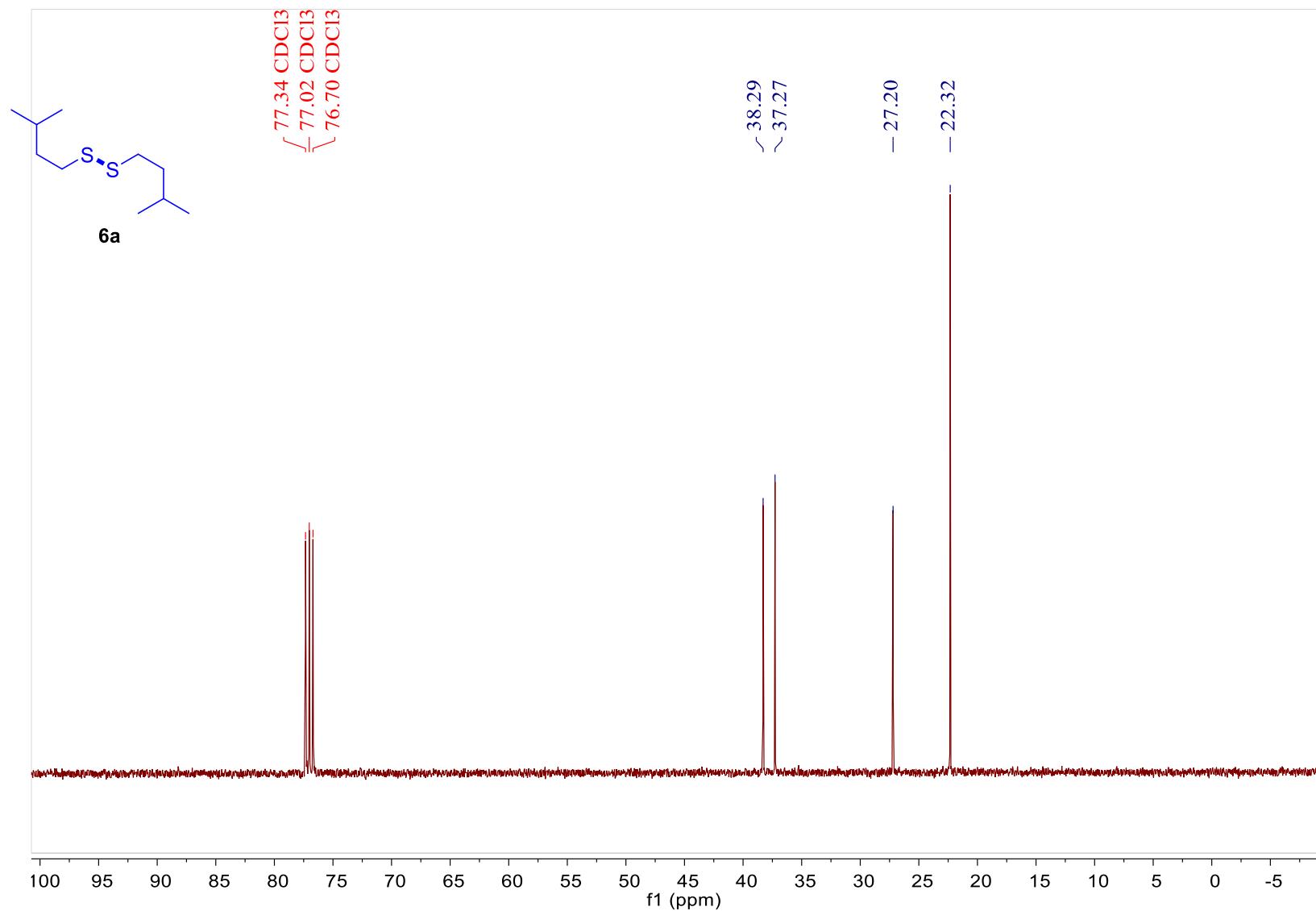






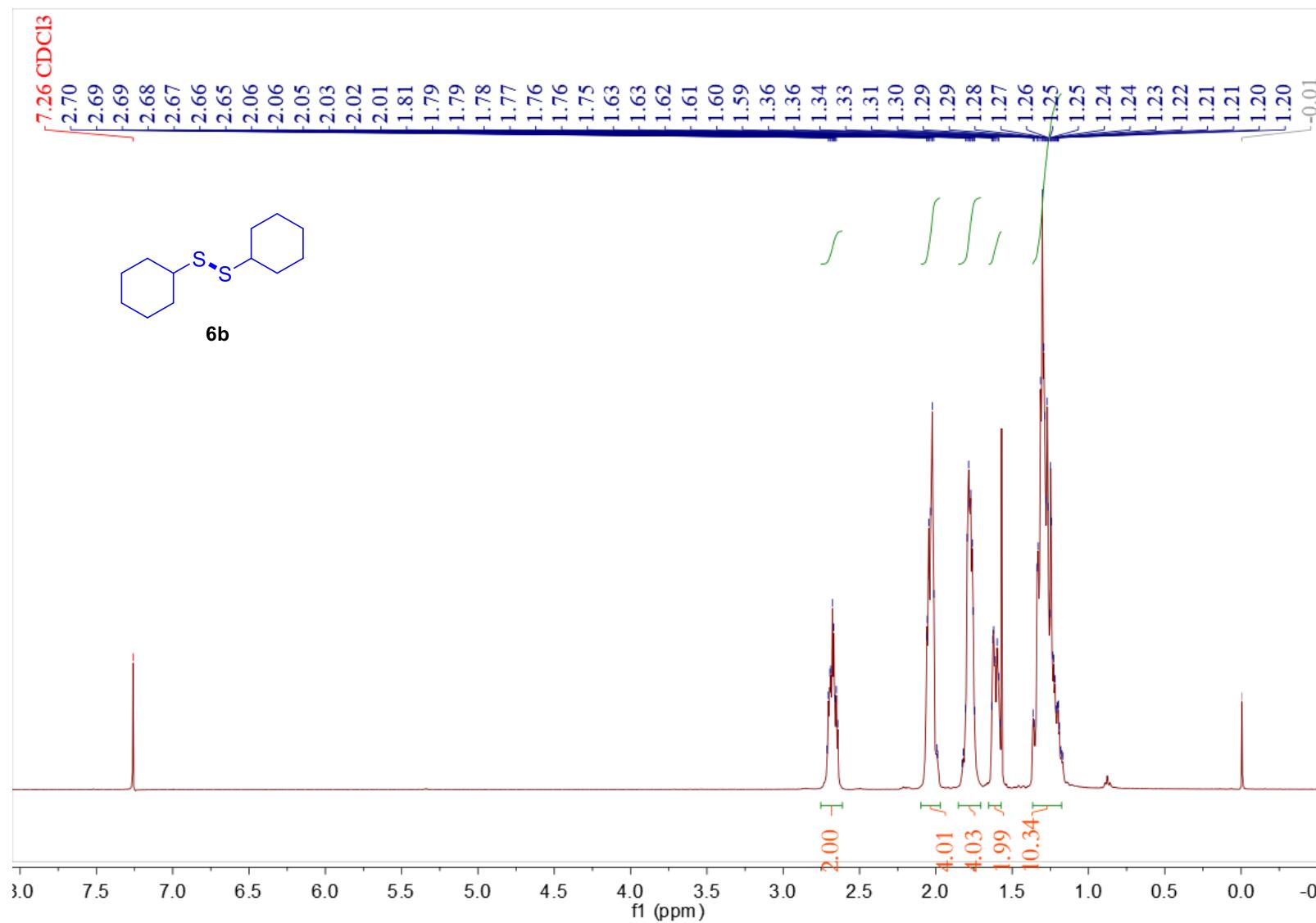


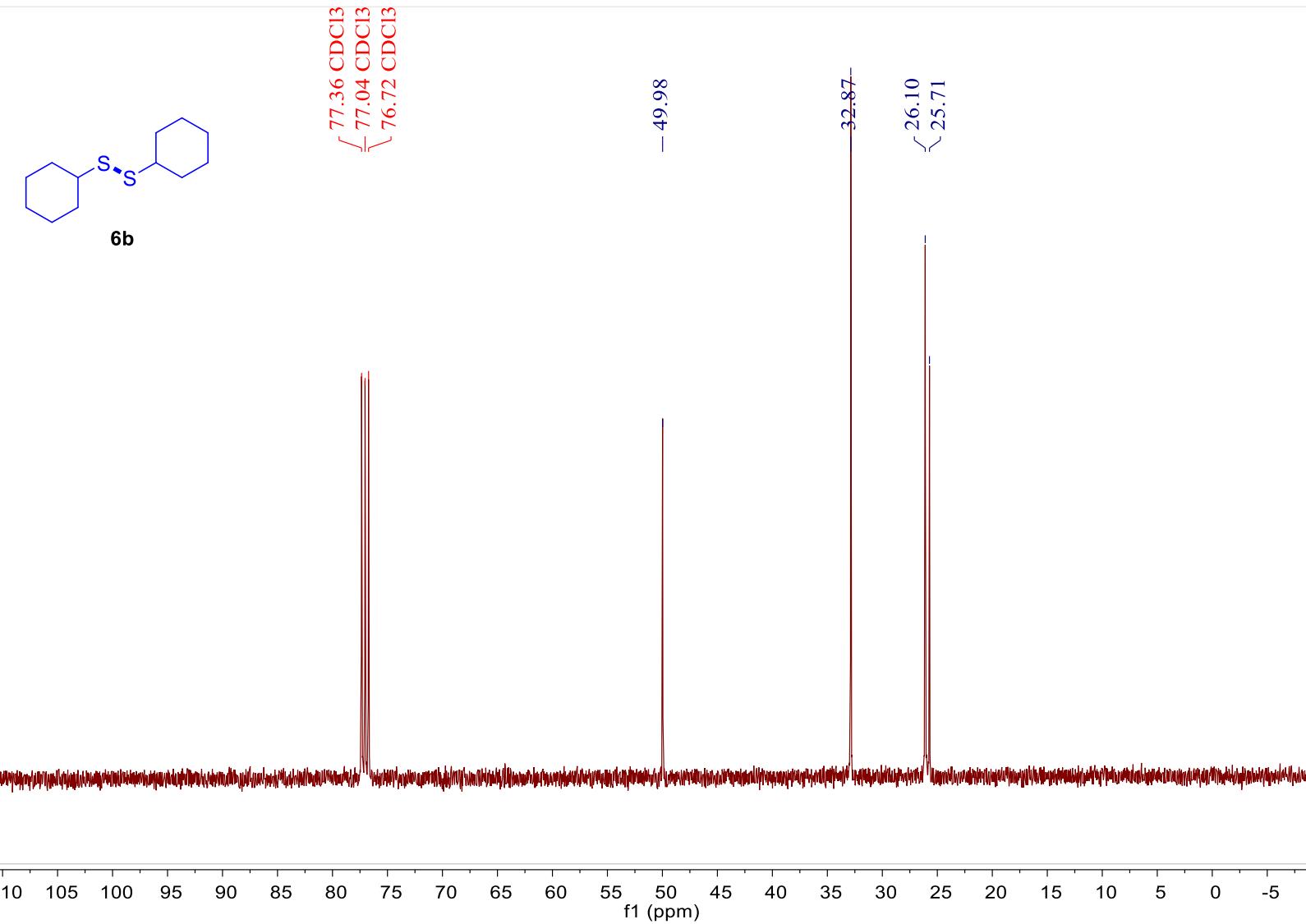






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