

## Supporting Information

# Copper-Catalyzed C(sp<sup>2</sup>)-S Coupling Reactions for the Synthesis of Aryl Dithiocarbamates with Thiuram Disulfide Reagents

Zhi-Bing Dong,<sup>a,b\*</sup> Xing Liu,<sup>a</sup> and Carsten Bolm<sup>b\*</sup>

<sup>a</sup> School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430205, China. Email: [dz04982@wit.edu.cn](mailto:dz04982@wit.edu.cn)

<sup>b</sup> Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, D-52056 Aachen, Germany. Email: [carsten.bolm@oc.rwth-aachen.de](mailto:carsten.bolm@oc.rwth-aachen.de)

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## General

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise stated. Yields refer to isolated compounds estimated to be >95% pure as determined by  $^1\text{H}$  NMR and capillary GC analysis. NMR spectra were recorded on a Bruker AM400 or Bruker AM 300 NMR instrument in  $\text{CDCl}_3$  using TMS as an internal standard. Chemical shifts are given in ppm and coupling constants ( $J$ ) are given in Hz. Melting points were determined on the Kofler micro melting point apparatus and were not corrected. High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT 95Q or Finnigan 90 mass instrument (ESI). TLC was performed using aluminum plates coated with  $\text{SiO}_2$  (Merck 60, F-254) and visualized with UV light at 254 nm. Column chromatography was performed on silica gel with PE-EtOAc as the eluent.

## Typical procedure for the preparation of dithiocarbamates **2** (TP)

The thiuram reagent (**1**, 2.0 mmol), the aryl iodide (**3**, 3.0 mmol),  $\text{Cu}_2\text{O}$  (42.9 mg, 0.3 mmol, 10 mol %), and  $\text{Cs}_2\text{CO}_3$  (1954.9 mg, 6 mmol) were added in a tube equipped with a septum and a magnetic stirring bar. Then, DMSO (5 mL) was added. The tube was sealed, and the mixture was stirred at 80 °C. (Note: Performing the reaction in open air led to a slower conversion.) After ca. 24 h the conversion of the starting material was complete (as revealed by TLC), and the reaction mixture was cooled to room temperature, quenched with a sat.  $\text{NH}_4\text{Cl}$  solution and subsequently extracted with ethyl acetate. The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated under vacuum. Product **2** was then purified by flash column chromatography.

## Analytical data of the products

### Dimethyl-dithiocarbamic acid phenyl ester (**2a**)

Following the TP, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to give **2a** as a white solid (496.5 mg, 84%). Mp: 95-95.7 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.49-7.45 (m, 5H), 3.56 (s, 3H), 3.50 (s, 3H);

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 197.6, 137.0, 131.7, 130.1, 129.1, 45.7, 42.0;

HRMS (ESI): calcd for  $\text{C}_9\text{H}_{11}\text{NS}_2$ , 197.0333; found: 197.0339.

#### **Dimethyl-dithiocarbamic acid 4-fluoro-phenyl ester (2b)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2b** as a white solid (567.6 mg, 88%). Mp: 91.7-92.7 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.44-7.39 (m, 2H), 7.14-7.09 (m, 2H), 3.53 (s, 3H) 3.48 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 197.4, 163.9 (d,  $J = 250$  Hz), 139.0 (d,  $J = 8$  Hz), 127.1 (d,  $J = 3$  Hz), 116.3 (d,  $J = 22$  Hz), 45.7, 41.9;

HRMS (ESI): calcd for  $\text{C}_9\text{H}_{10}\text{FNS}_2$ , 215.0239; found: 215.0234.

#### **Dimethyl-dithiocarbamic acid 4-chloro-phenyl ester (2c)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2c** as a white solid (616.7 mg, 89%). Mp: 100.9-101.4 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.41-7.36 (m, 4H), 3.53 (s, 3H), 3.47 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 196.7, 138.1, 136.5, 130.1, 129.3, 45.7, 41.9; HRMS (ESI): calcd for  $\text{C}_9\text{H}_{10}\text{ClNS}_2$ , 230.9943; found: 230.9949.

#### **Dimethyl-dithiocarbamic acid 2-chloro-phenyl ester (2d)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2d** as a gray solid (616.7 mg, 89%). Mp: 105-106.8 °C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.57-7.53 (m, 2H), 7.45-7.40 (m, 1H), 7.36-7.31 (m, 1H), 3.55 (s, 3H), 3.52 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 194.9, 140.5, 139.1, 131.7, 131.0, 130.2, 127.4, 45.6, 42.1; HRMS (ESI): calcd for  $\text{C}_9\text{H}_{10}\text{ClNS}_2$ , 230.9943; found: 230.9947.

**Dimethyl-dithiocarbamic acid 4-bromo-phenyl ester (2e)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2e** as a white solid (767.0 mg, 93%). Mp: 120-121.4 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.58 (s, 1H), 7.55 (s, 1H), 7.33 (s, 1H), 7.31 (s, 1H), 3.54 (s, 3H), 3.49 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 196.5, 138.4, 132.3, 130.7, 124.9, 45.7, 42.0; HRMS (ESI): calcd for C<sub>9</sub>H<sub>10</sub>BrNS<sub>2</sub>, 274.9438; found: 274.9445.

**Dimethyl-dithiocarbamic acid 4-nitro-phenyl ester (2f)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2f** as a white solid (580.8 mg, 80%). Mp: 153-154.5 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.29-8.24 (m, 2H), 7.67-7.63 (m, 2H), 3.56 (s, 3H), 3.53 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 194.5, 148.5, 139.5, 137.6, 123.8, 45.6, 42.2; HRMS (ESI): calcd for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>, 242.0184; found: 242.0189.

**Dimethyl-dithiocarbamic acid 2-nitro-phenyl ester (2g)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2g** as a white solid (500.9 mg, 69%). Mp: 124.5-125.8 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.00-7.97 (m, 1H), 7.67-7.60 (m, 3H), 3.53 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 193.9, 139.6, 132.6, 131.0, 126.5, 124.9, 45.6, 42.4; HRMS (ESI): calcd for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>, 242.0184; found: 242.0191.

**Dimethyl-dithiocarbamic acid 4-cyano-phenyl ester (2h)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2h** as a white solid (532.8 mg, 69%). Mp: 125-126 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.72-7.69 (m, 2H), 7.60-7.57 (m, 2H), 3.55 (s, 3H), 3.51 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 194.9, 137.4, 132.4,

118.2, 113.6, 45.6, 42.1; HRMS (ESI): calcd for  $C_{10}H_{10}N_2S_2$ , 222.0285; found: 222.0291.

**Dimethyl-dithiocarbamic acid 4-trifluoromethyl-phenyl ester (2i)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2i** as a white solid (667.8 mg, 84%). Mp: 85.2-86.2 °C.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.66 (d,  $J = 8.0$  Hz, 2H), 7.58 (d,  $J = 8.0$  Hz, 2H), 3.54 (s, 3H), 3.49 (s, 3H);  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 195.6, 137.1, 136.0 (d,  $J = 2$  Hz), 131.7 (d, 33 Hz), 125.8 (m,  $J = 4$  Hz), 123.8 (d,  $J = 271$  Hz), 45.6, 42.0; HRMS (ESI): calcd for  $C_{10}H_{10}F_3NS_2$ , 265.0207; found: 265.0211.

**Dimethyl-dithiocarbamic acid *p*-tolyl ester (2j)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2j** as a white solid (569.8 mg, 90%). Mp: 112.8-113.5 °C.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.33 (d,  $J = 8.0$  Hz, 2 H), 7.23 (d,  $J = 4.0$  Hz, 2 H), 3.51 (s, 3 H), 3.44 (s, 3H), 2.37 (s, 3H);  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 198.1, 140.4, 136.8, 130.0, 128.3, 45.7, 42.0; HRMS (ESI): calcd for  $C_{10}H_{13}NS_2$ , 211.0489; found: 211.0493.

**Dimethyl-dithiocarbamic acid 4-butyl-phenyl ester (2k)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2k** as a white solid (668.1 mg, 88%). Mp: 61-62 °C.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.36-7.34 (m, 2H), 7.25-7.23 (m, 2H), 3.54 (s, 3H), 3.48 (s, 3H), 2.65 (m, 2H), 1.65-1.58 (m, 2H), 1.39-1.33 (m, 2H), 0.92 (m, 3H);  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 198.1, 145.2, 136.7, 129.2, 128.4, 45.6, 41.9, 35.5, 33.2, 22.3, 13.9; HRMS (ESI): calcd for  $C_{13}H_{19}NS_2$ , 253.0959; found: 253.0962.

**Dimethyl-dithiocarbamic acid 2-methoxy-phenyl ester (2l)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2l** as a white solid (585.7 mg, 86%). Mp: 88-89.7 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.52-7.40 (m, 2H), 7.05-6.99 (m, 2H), 3.86 (s, 3H), 3.54 (s, 3H), 3.52 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 196.8, 160.5, 138.8, 132.4, 121.1, 119.8, 111.8, 56.2, 45.6, 42.0; HRMS (ESI): calcd for C<sub>10</sub>H<sub>13</sub>NOS<sub>2</sub>, 227.0439; found: 227.0446.

**Dimethyl-dithiocarbamic acid 4-methoxy-phenyl ester (2m)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1) to give **2m** as a white solid (572.1 mg, 84%). Mp: 97-99 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.37 (d, *J* = 4.0 Hz, 2H), 6.96 (d, *J* = 4.0 Hz, 2H), 3.83 (s, 3H), 3.54 (s, 3H), 3.48 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 198.7, 161.1, 138.4, 122.6, 114.7, 55.3, 45.8, 41.9; HRMS (ESI): calcd for C<sub>10</sub>H<sub>13</sub>NOS<sub>2</sub>, 227.0439; found: 227.0445.

**Dimethyl-dithiocarbamic acid 4-methoxy-2-nitro-phenyl ester (2n)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2n** as a white solid (669.1 mg, 82%). Mp: 115-117 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.54 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 3.0 Hz, 1H), 7.17-7.13 (m, 1H), 3.91 (s, 3H), 3.53 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 195.4, 161.5, 154.0, 141.0, 118.6, 116.7, 110.4, 56.0, 45.7, 42.2; HRMS (ESI): calcd for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>, 272.0289; found: 272.0294.

**Dimethyl-dithiocarbamic acid *o*-tolyl ester (2o)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2o** as a white solid (557.1 mg, 88%). Mp: 81.2-82 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.43-7.32 (m, 3H), 7.27-7.23 (m, 1H), 3.54 (s,

3H), 3.50 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 196.5, 143.8, 137.7, 131.1, 130.7, 130.7, 126.7, 45.5, 42.0, 20.9; HRMS (ESI): calcd for  $\text{C}_{10}\text{H}_{13}\text{NS}_2$ ; 211.0489; found: 211.0492.

#### **Dimethyl-dithiocarbamic acid 3,5-dimethyl-phenyl ester (2p)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2p** as a white solid (634.6 mg, 94%). Mp: 84.6-85.6 °C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.10 (s, 3H), 3.56 (s, 3H), 3.49 (s, 3H), 2.35 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 198.0, 138.6, 134.4, 131.9, 131.0, 45.6, 42.0, 21.2; HRMS (ESI): calcd for  $\text{C}_{11}\text{H}_{15}\text{NS}_2$ ; 225.0646; found: 225.0652.

#### **Dimethyl-dithiocarbamic acid naphthalen-1-yl ester (2q)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2q** as a yellow solid (600.3 mg, 81%). Mp: 150.8-152.8 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.25-8.23 (m, 1H), 7.99 (d,  $J = 8.0$  Hz, 1H), 7.88 (d,  $J = 4.0$  Hz, 1H), 7.74 (m, 1H), 8.24 (m, 1H), 7.56-7.49 (m, 3H), 3.61 (s, 3H), 3.55 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 196.5, 137.0, 135.0, 134.1, 131.4, 128.9, 128.6, 127.1, 126.2, 125.7, 125.7, 45.5, 42.1; HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{13}\text{NS}_2$ ; 247.0489; found: 247.0496.

#### **Dimethyl-dithiocarbamic acid phenanthren-9-yl ester (2r)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2r** as a yellow solid (846.6 mg, 95%). Mp: >175 °C, decomposed.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.73-8.69 (m, 2H), 8.33-8.31 (m, 1H), 8.09 (s, 1H), 7.91-7.88 (m, 1H), 7.73-7.59 (m, 4H), 3.64 (s, 3H), 3.57 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 196.4, 138.8, 132.4, 131.6, 131.5, 131.0, 130.1, 129.1, 128.2, 127.7, 127.1, 126.8, 126.7, 123.0, 122.7, 45.5, 42.1; HRMS (ESI): calcd for  $\text{C}_{17}\text{H}_{15}\text{NS}_2$ ; 297.0646; found: 297.0652.

**Dimethyl-dithiocarbamic acid thiophen-3-yl ester (2s)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2s** as a white solid (572.4 mg, 94%). Mp: 88-89 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.51-7.50 (m, 1H), 7.40-7.38 (m, 1H), 7.11-7.09 (m, 1H), 3.53 (s, 3H), 3.47 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 197.1, 133.5, 133.4, 126.9, 125.9, 45.7, 41.9; HRMS (ESI): calcd for C<sub>7</sub>H<sub>9</sub>NS<sub>3</sub>, 202.9897; found: 202.9906.

**Dimethyl-dithiocarbamic acid thiophen-2-yl ester (2t)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give **2t** as a white solid (572.4 mg, 94%). Mp: 94-95.2 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.63-7.62 (m, 1H), 7.24-7.22 (m, 1H), 7.14-7.12 (m, 1H), 3.54 (s, 3H), 3.48 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 197.3, 138.7, 133.4, 129.1, 127.8, 46.0, 41.7; HRMS (ESI): calcd for C<sub>7</sub>H<sub>9</sub>NS<sub>3</sub>, 202.9897; found: 202.9904.

**Dimethyl-dithiocarbamic acid pyridin-2-yl ester (2u)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) to give **2u** as a yellow solid (564.3 mg, 95%). Mp: 108.8-109.7 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.65 (s, 1H), 7.65-7.62 (m, 2H), 7.32 (s, 1H), 3.47 (s, 3H), 3.44 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 195.0, 153.8, 150.5, 137.2, 133.4, 127.6, 124.2, 45.2, 42.4; HRMS (ESI): calcd for C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>S<sub>2</sub>, 198.0285; found: 198.0291.

**Dimethyl-dithiocarbamic acid pyridin-3-yl ester (2v)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) to give **2v** as a brown solid (570.3 mg, 96%). Mp: 58-58.6 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.71 (s, 2H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.42 (s,

1H), 3.55 (s, 3H), 3.52 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 195.8, 156.4, 150.4, 144.4, 129.3, 124.0, 45.8, 42.0; HRMS (ESI): calcd for  $\text{C}_8\text{H}_{10}\text{N}_2\text{S}_2$ , 198.0285; found: 198.0292.

#### **Dimethyl-dithiocarbamic acid pyridin-4-yl ester (2w)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) to give **2w** as a brown solid (564.3 mg, 95%). Mp: 126.5-127 °C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.12 (s, 2H), 7.57 (s, 2H), 3.56 (s, 3H), 3.51 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 193.6, 149.3, 141.6, 127.5, 45.6, 42.3; HRMS (ESI): calcd for  $\text{C}_8\text{H}_{10}\text{N}_2\text{S}_2$ , 198.0285; found: 198.0295.

#### **Diethyl-dithiocarbamic acid phenyl ester (2x)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to give **2x** as a pale yellow oil (573.9 mg, 85%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.48 (d,  $J$  = 12.0 Hz, 5H), 4.03 (d,  $J$  = 4.0 Hz, 2H), 3.85 (d,  $J$  = 8.0 Hz, 2H), 1.39 (t,  $J$  = 4.0 Hz, 3H), 1.30 (d,  $J$  = 4.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 195.9, 137.2, 131.6, 130.0, 129.0, 49.9, 47.3, 12.8, 11.6; HRMS (ESI): calcd for  $\text{C}_{11}\text{H}_{15}\text{NS}_2$ , 225.0646; found: 225.0652.

#### **Diethyl-dithiocarbamic acid *p*-tolyl ester (2y)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1) to give **2y** as a white solid (623.9 mg, 87%). Mp: 75-76 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.28 (d,  $J$  = 8.0 Hz, 2H), 7.16 (d,  $J$  = 4.0 Hz, 2H), 3.94 (d,  $J$  = 8.0 Hz, 2H), 3.77 (d,  $J$  = 4.0 Hz, 2H), 2.32 (s, 3H), 1.31 (t,  $J$  = 4.0 Hz, 3H), 1.20 (t,  $J$  = 4.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 196.5, 140.2, 137.0, 129.9, 128.1, 49.9, 47.2, 21.5, 12.7, 11.6; HRMS (ESI): calcd for  $\text{C}_{12}\text{H}_{17}\text{NS}_2$ , 239.0802; found: 239.0812.

**Diethyl-dithiocarbamic acid 4-methoxy-phenyl ester (2z)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1) to give **2z** as a white solid (627.4 mg, 82%). Mp: 73-75 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.23 (d,  $J = 8.0$  Hz, 2H), 6.80 (d,  $J = 8.0$  Hz, 2H), 3.87 (d,  $J = 8.0$  Hz, 2H), 3.68 (s, 5H), 1.24 (t,  $J = 8.0$  Hz, 3H), 1.13 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 197.1, 161.0, 138.6, 122.4, 114.6, 55.3, 50.0, 47.1, 12.7, 11.6; HRMS (ESI): calcd for  $\text{C}_{12}\text{H}_{17}\text{NOS}_2$ , 255.0752; found: 255.0759.

**Dibutyl-dithiocarbamic acid phenyl ester (2za)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to give **2za** as a brown oil (716.8 mg, 85%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.40-7.33 (m, 5H), 3.85 (t,  $J = 8.0$  Hz, 2H), 3.67 (t,  $J = 8.0$  Hz, 2H), 1.72-1.64 (m, 4H), 1.35-1.25 (m, 4H), 0.93 (t,  $J = 8.0$  Hz, 3H), 0.85 (t,  $J = 8.0$  Hz, 3 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 196.2, 137.1, 131.8, 129.9, 129.0, 55.3, 53.1, 29.6, 28.4, 20.2, 13.9, 13.8; HRMS (ESI): calcd for  $\text{C}_{15}\text{H}_{23}\text{NS}_2$ , 281.1272; found: 281.1278.

**Dibutyl-dithiocarbamic acid *p*-tolyl ester (2zb)**

Following the **TP**, the product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to give **2zb** as a brown oil (717.1 mg, 81%).

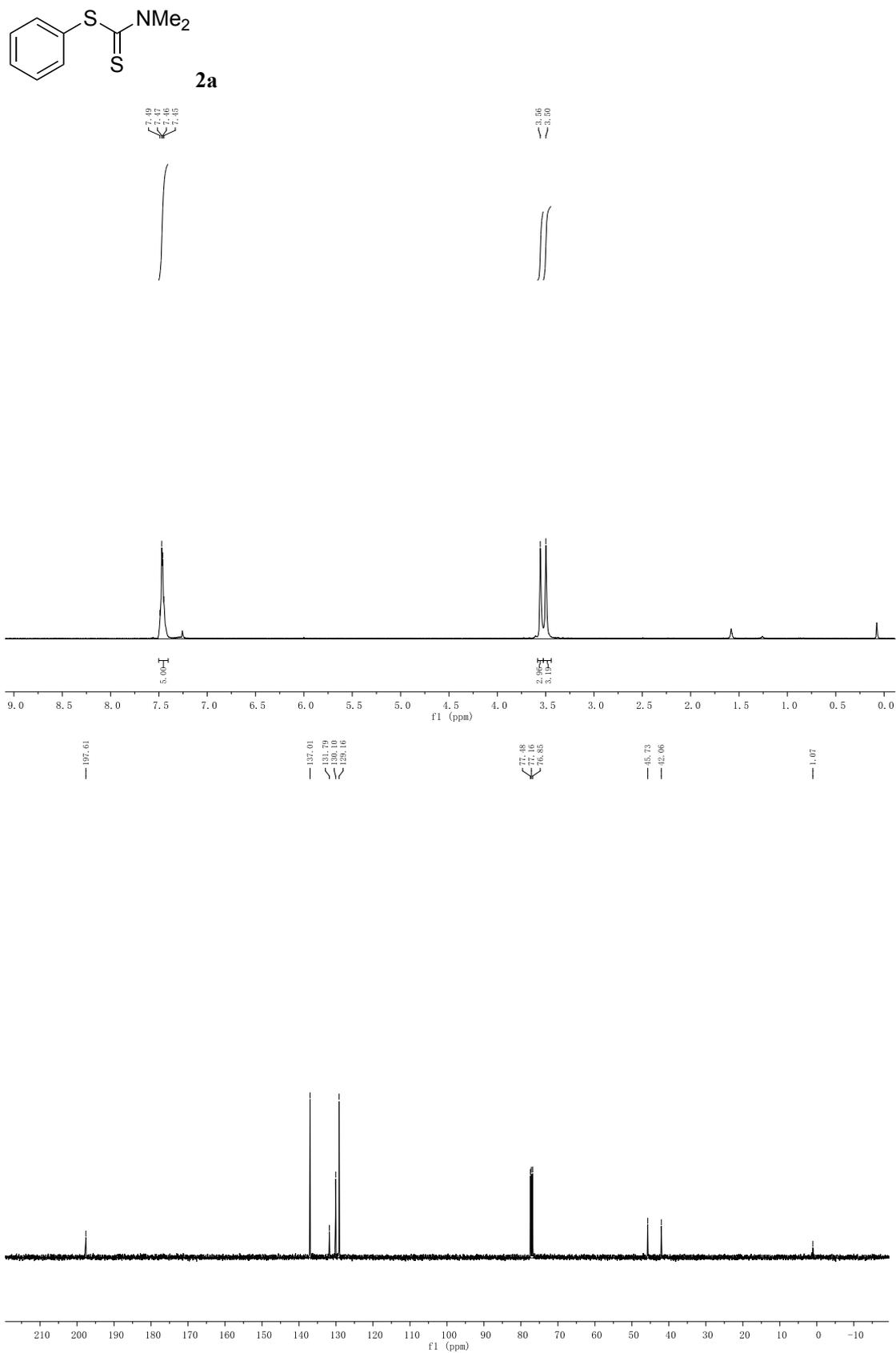
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.31 (d,  $J = 4.0$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 3.89 (t,  $J = 8.0$  Hz, 2H), 3.71 (t,  $J = 8.0$  Hz, 2H), 2.35 (s, 3H), 1.76-1.68 (m, 4H), 1.41-1.27 (m, 4H), 0.96 (t,  $J = 8.0$  Hz, 3H), 0.89 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 196.8, 140.1, 136.9, 129.9, 128.3, 55.4, 53.0, 29.6, 28.4, 21.5, 20.2, 13.9, 13.8; HRMS (ESI): calcd for  $\text{C}_{16}\text{H}_{25}\text{NS}_2$ , 295.1428; found: 295.1433.

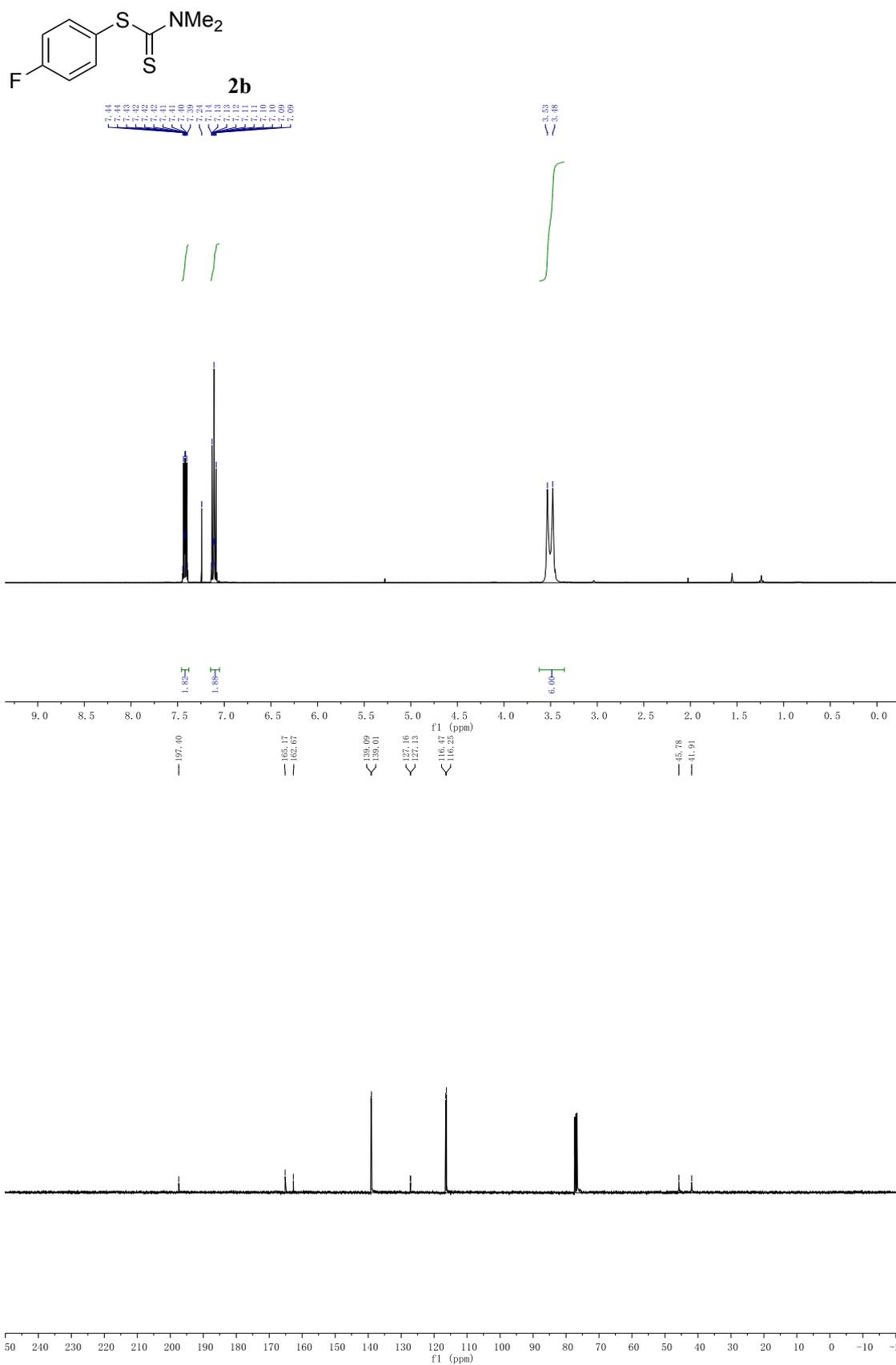
**Dibutyl-dithiocarbamic acid 4-methoxy-phenyl ester (2zc)**

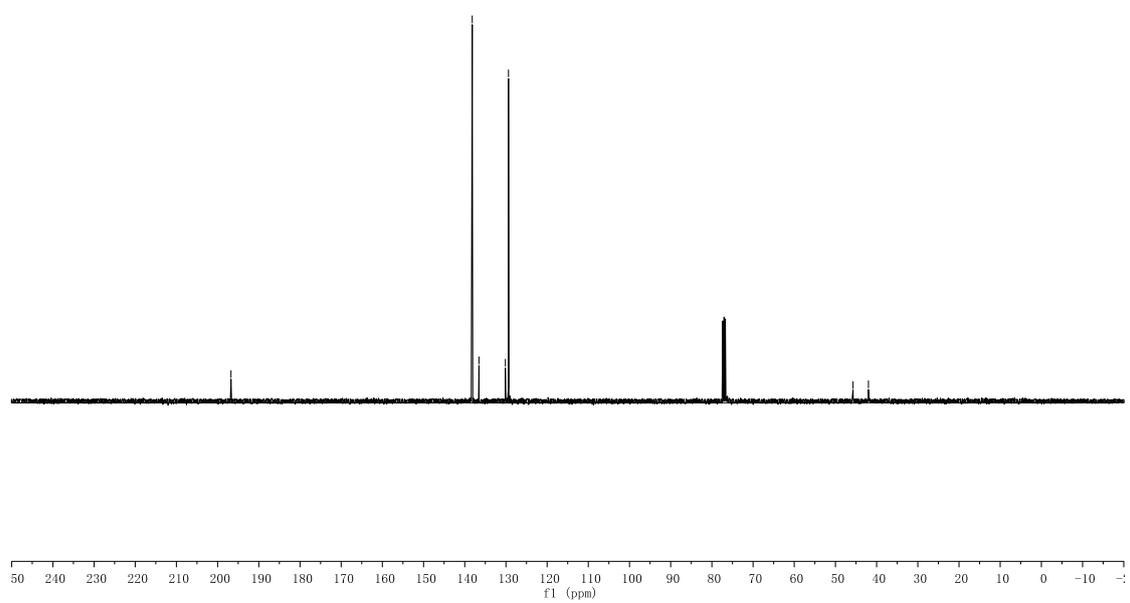
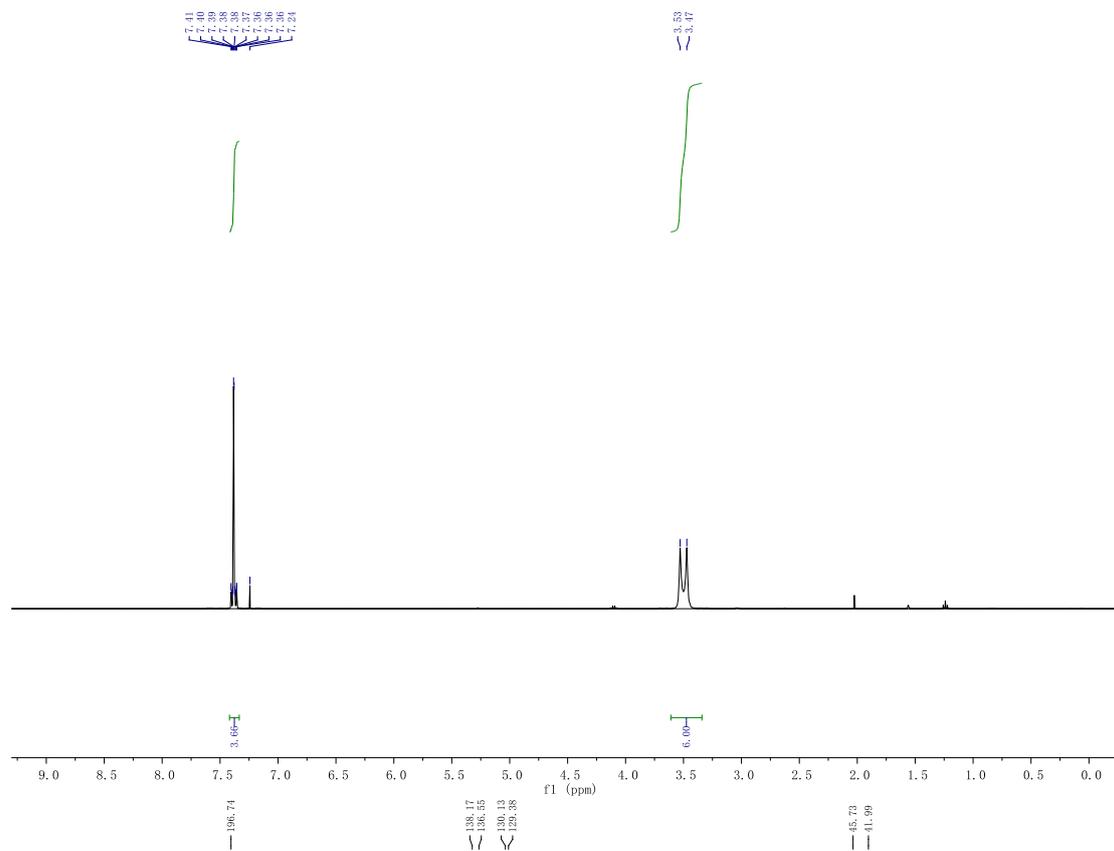
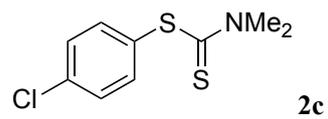
Following the **TP**, the product was purified by flash chromatography on silica gel

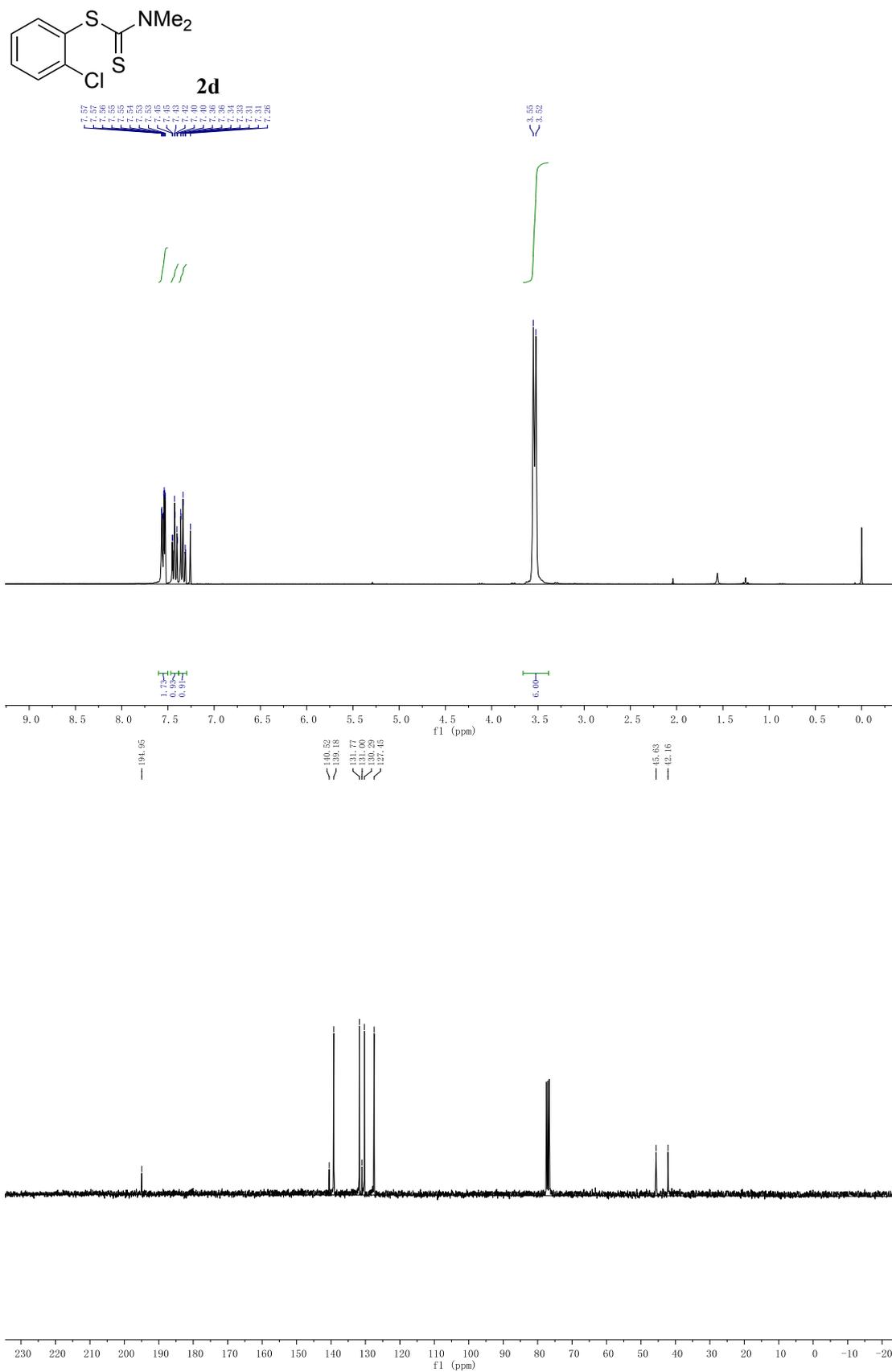
(eluent: petroleum ether/ethyl acetate = 20:1) to give **2zc** as a yellow oil (812.1 mg, 87%).

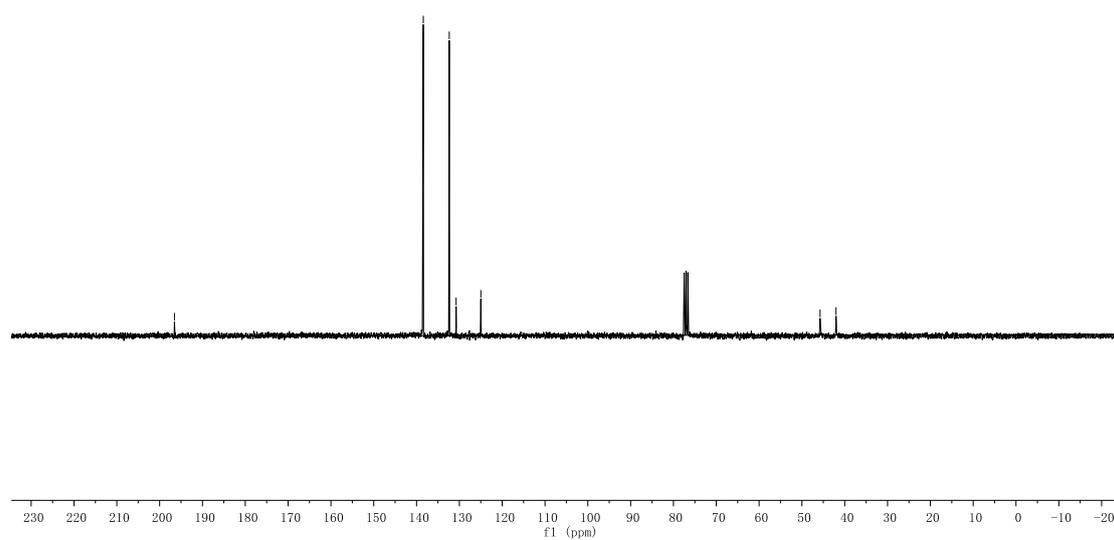
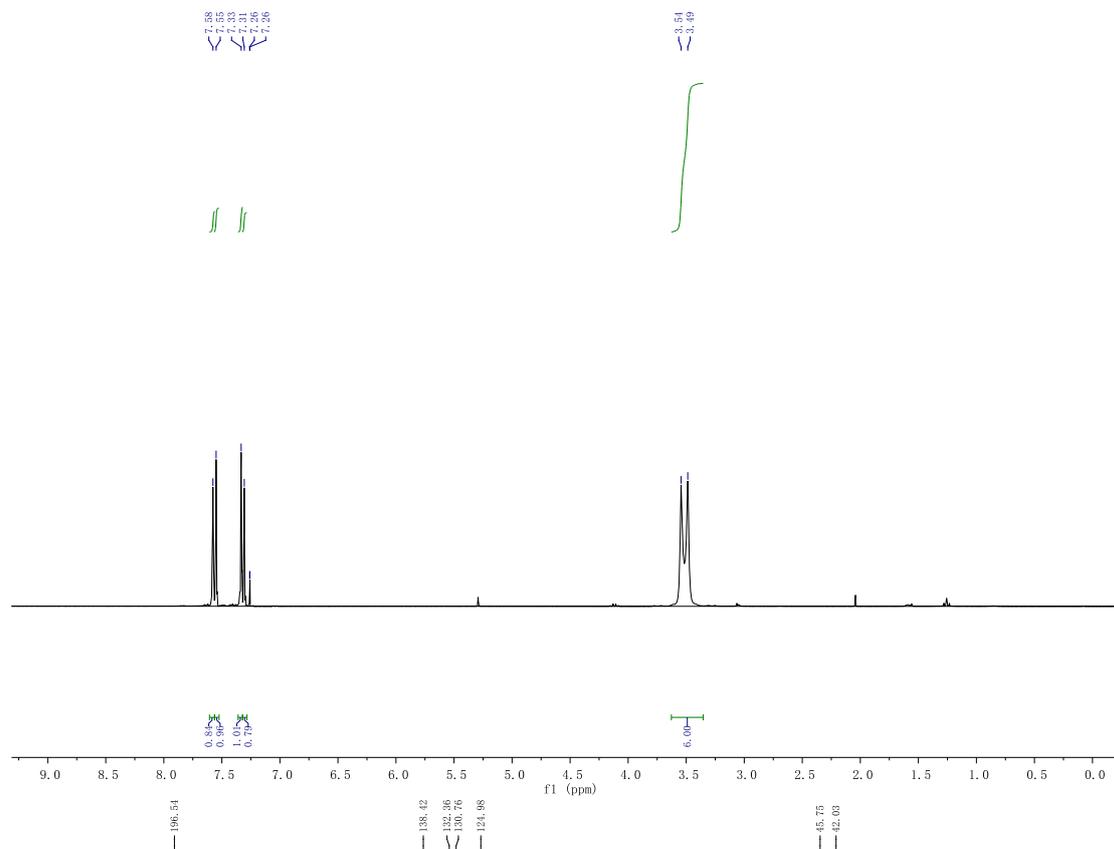
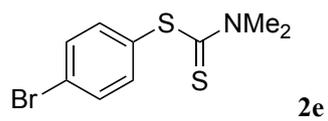
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.29 (d,  $J = 8.0$  Hz, 2H), 6.87 (d,  $J = 12.0$  Hz, 2H), 3.86 (s, 2H), 3.75 (s, 3 H), 3.69 (t,  $J = 8.0$  Hz, 2H), 1.76-1.72 (m, 4H), 1.38-1.23 (m, 4H), 0.93 (t,  $J = 8.0$  Hz, 3 ), 0.86 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 197.4, 161.0, 138.6, 122.6, 114.6, 55.5, 55.3, 52.9, 29.6, 28.4, 20.1, 13.9, 13.8; HRMS (ESI): calcd for  $\text{C}_{16}\text{H}_{25}\text{NOS}_2$ , 311.1378; found: 311.1382.

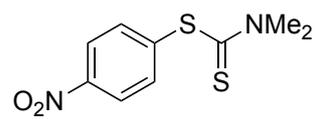
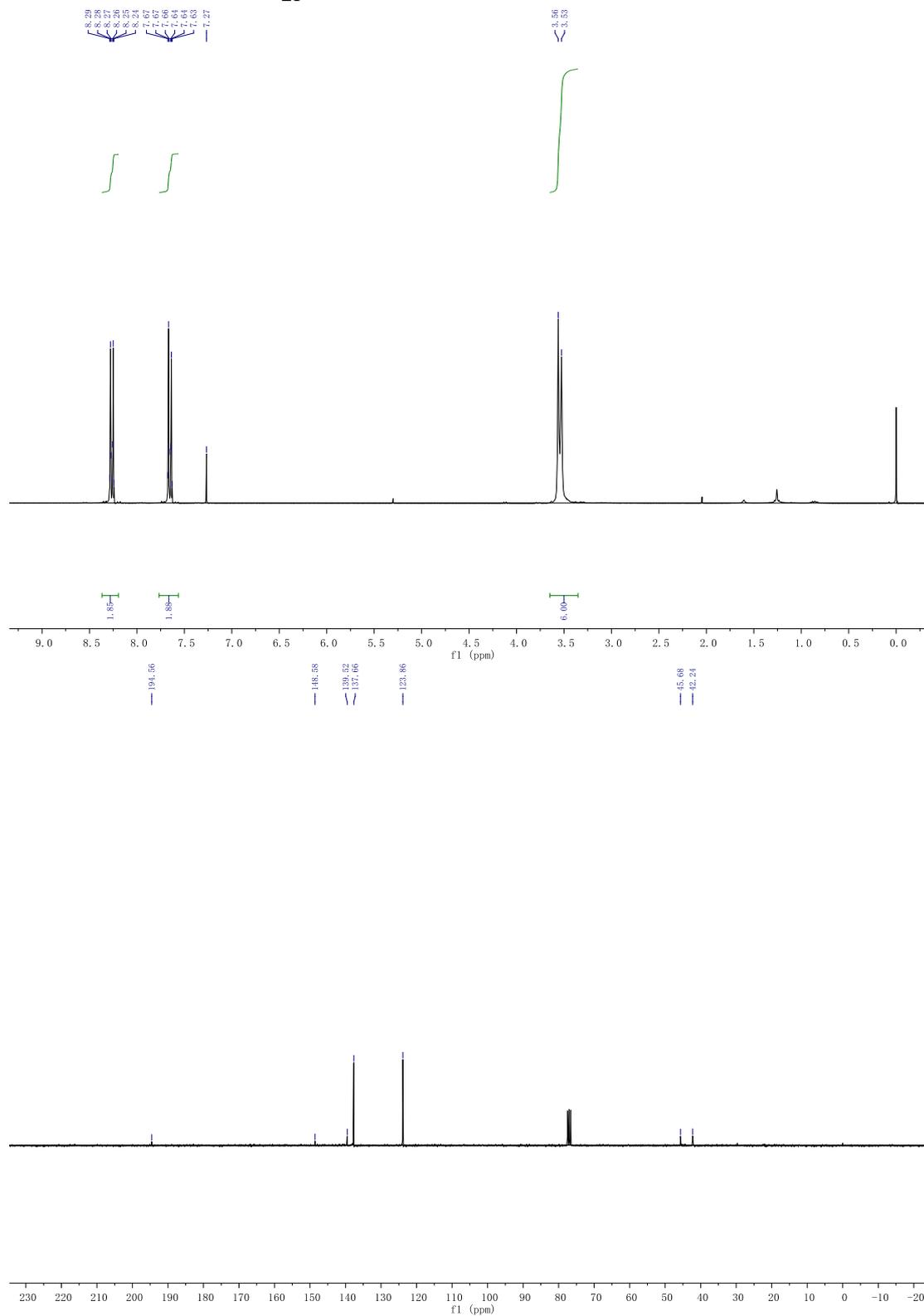
**$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the products**

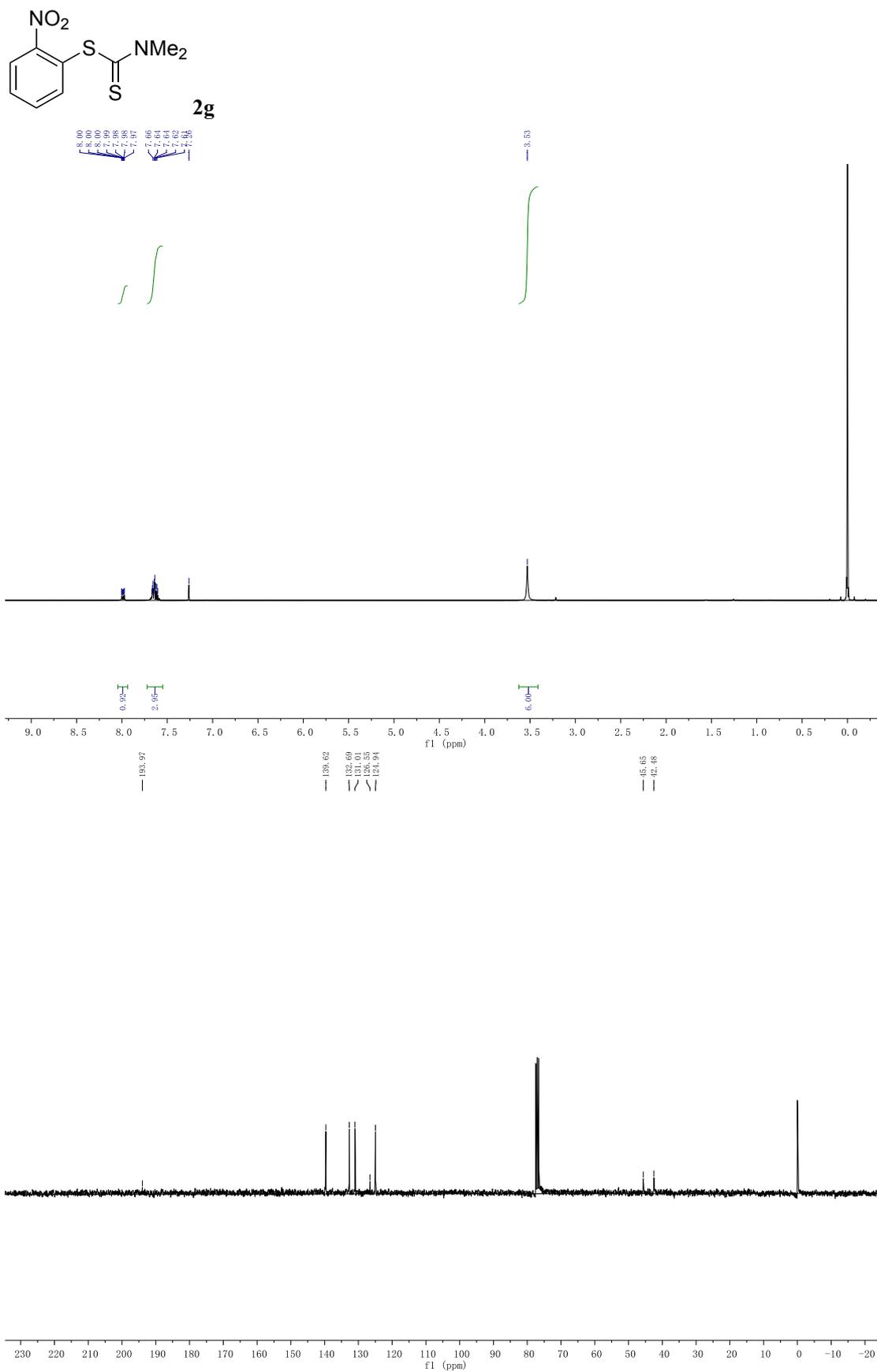


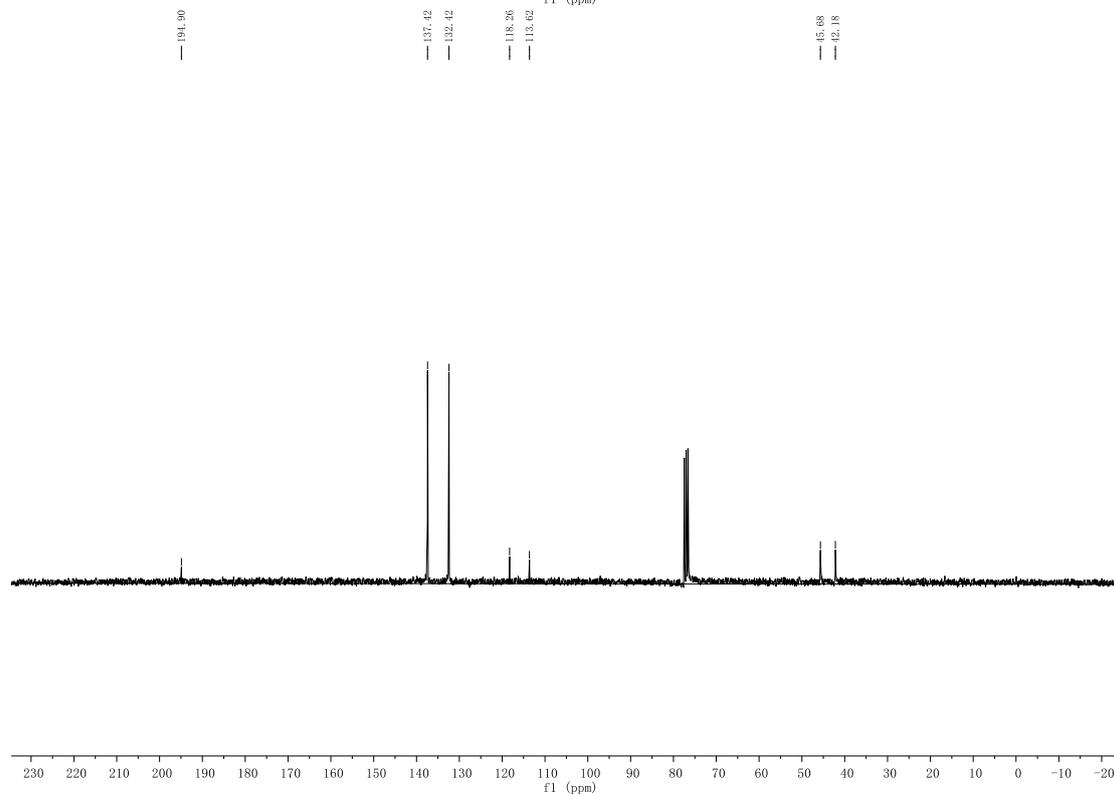
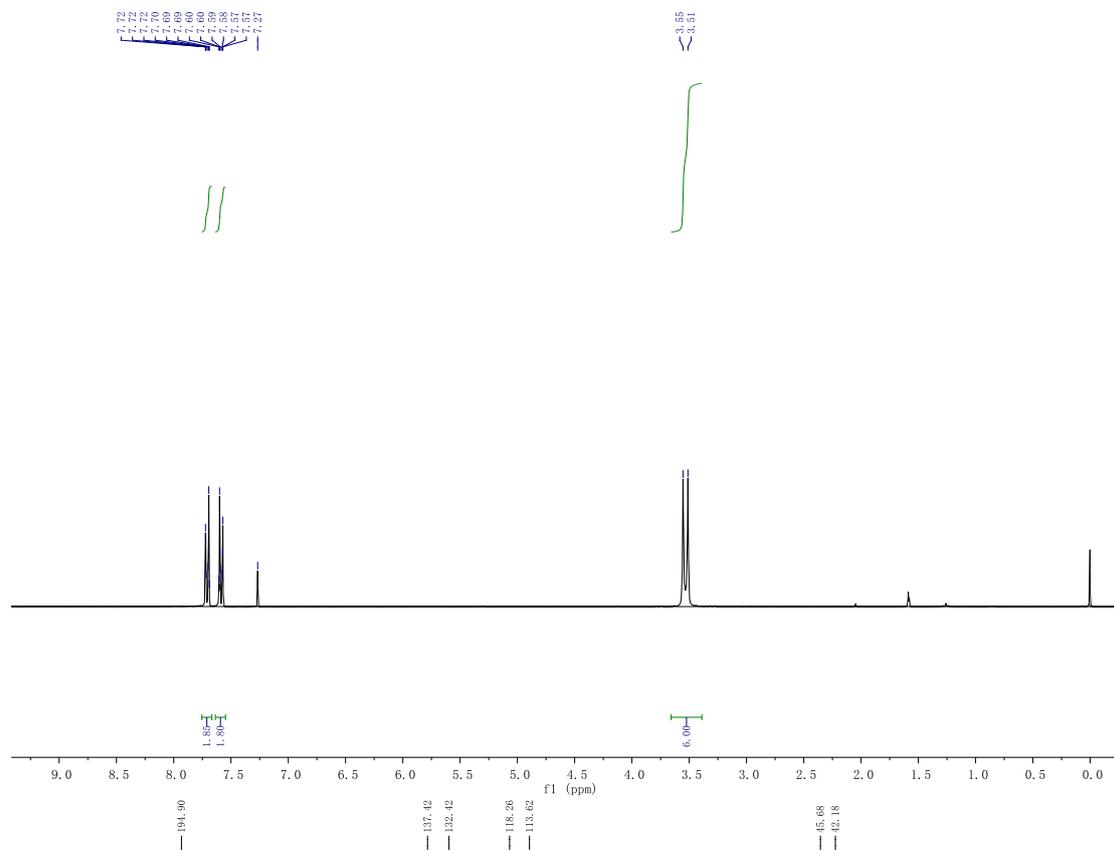
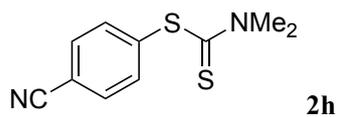




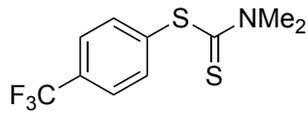


**2f**

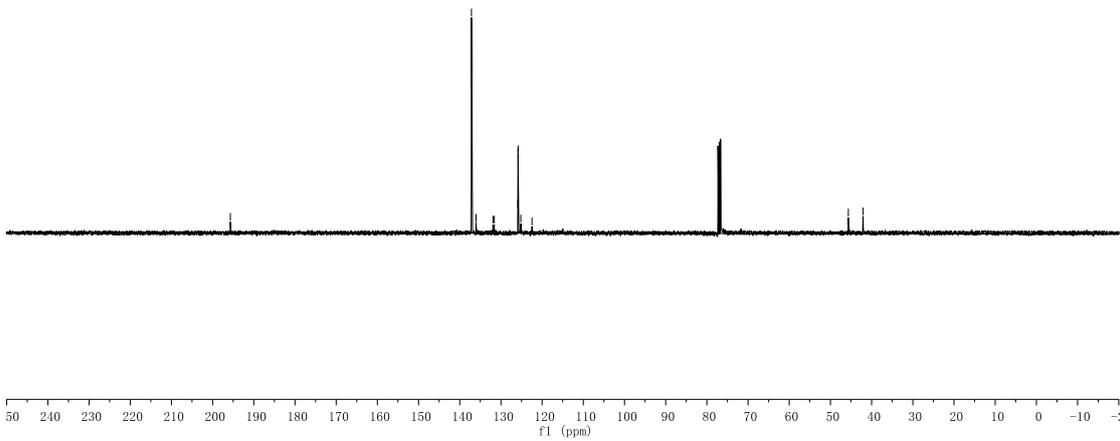
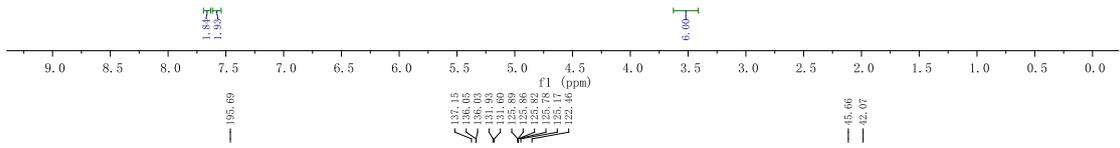
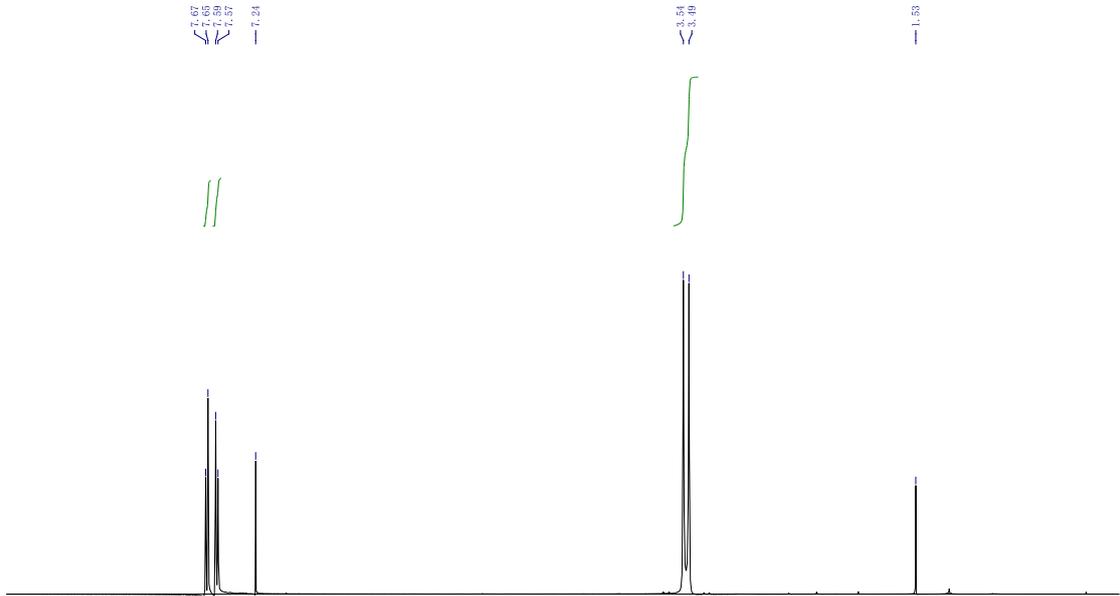


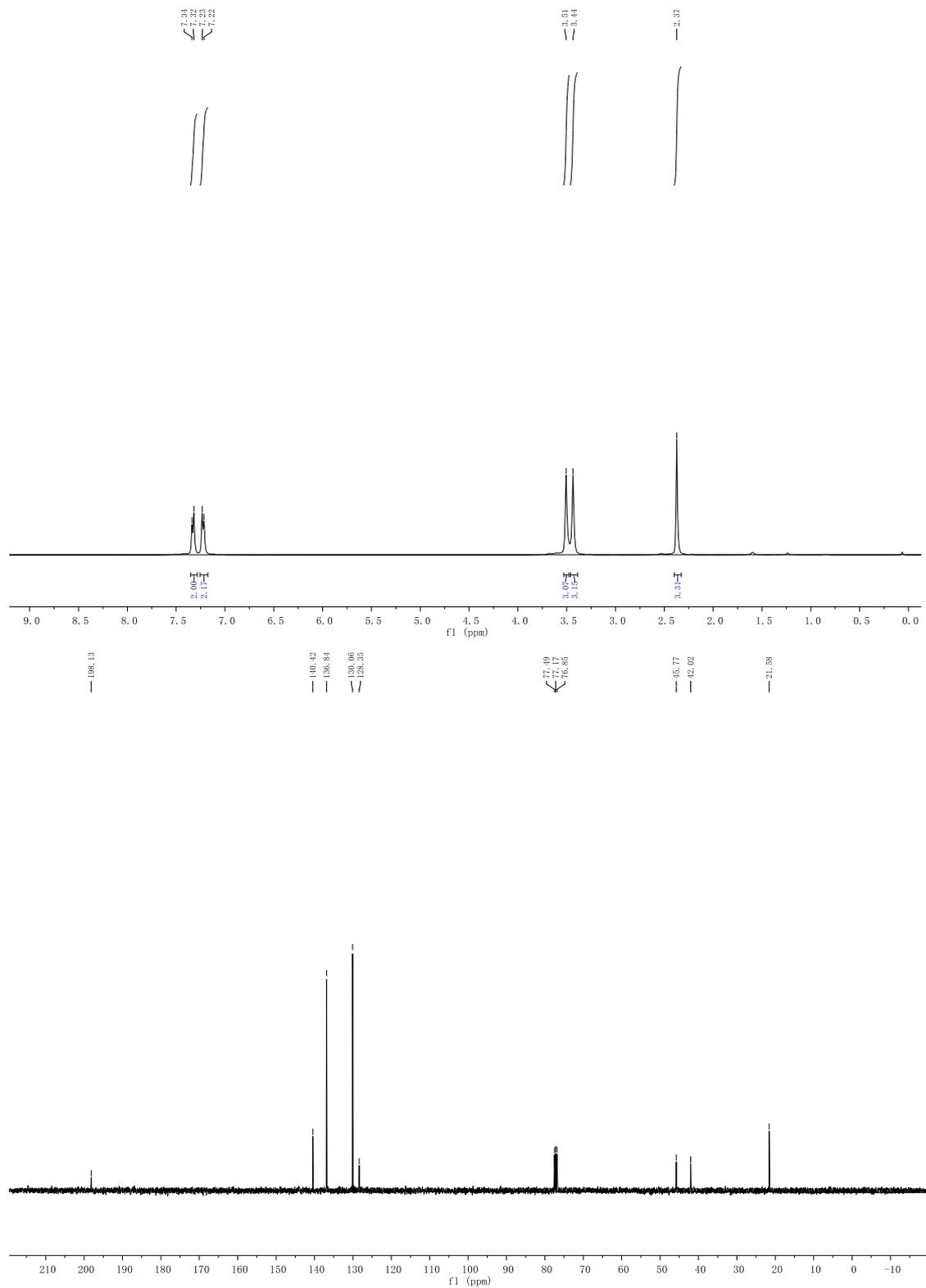
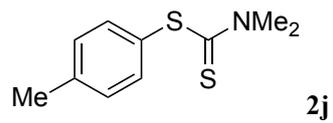


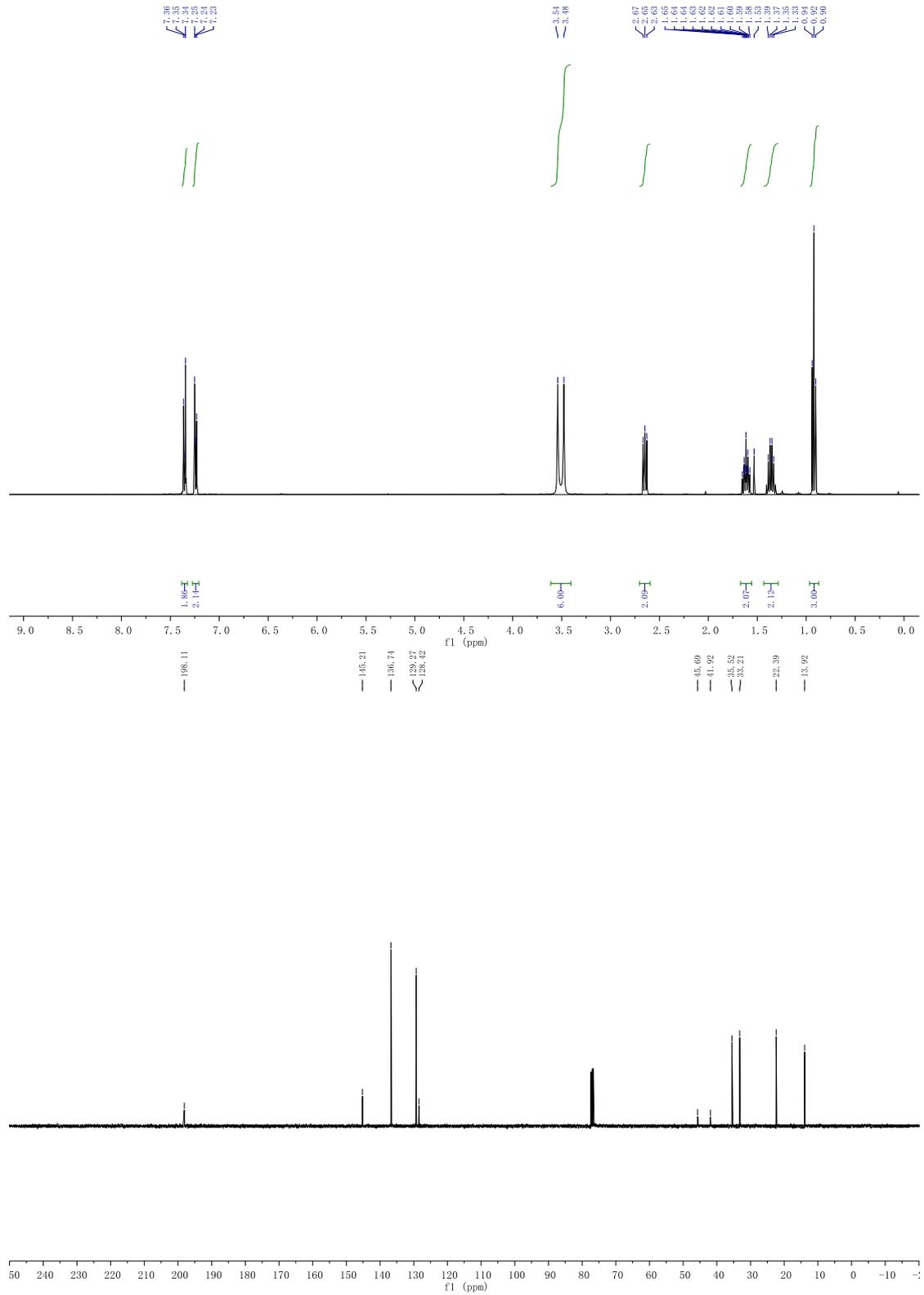
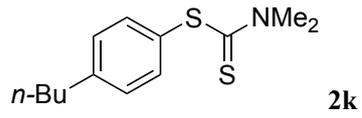
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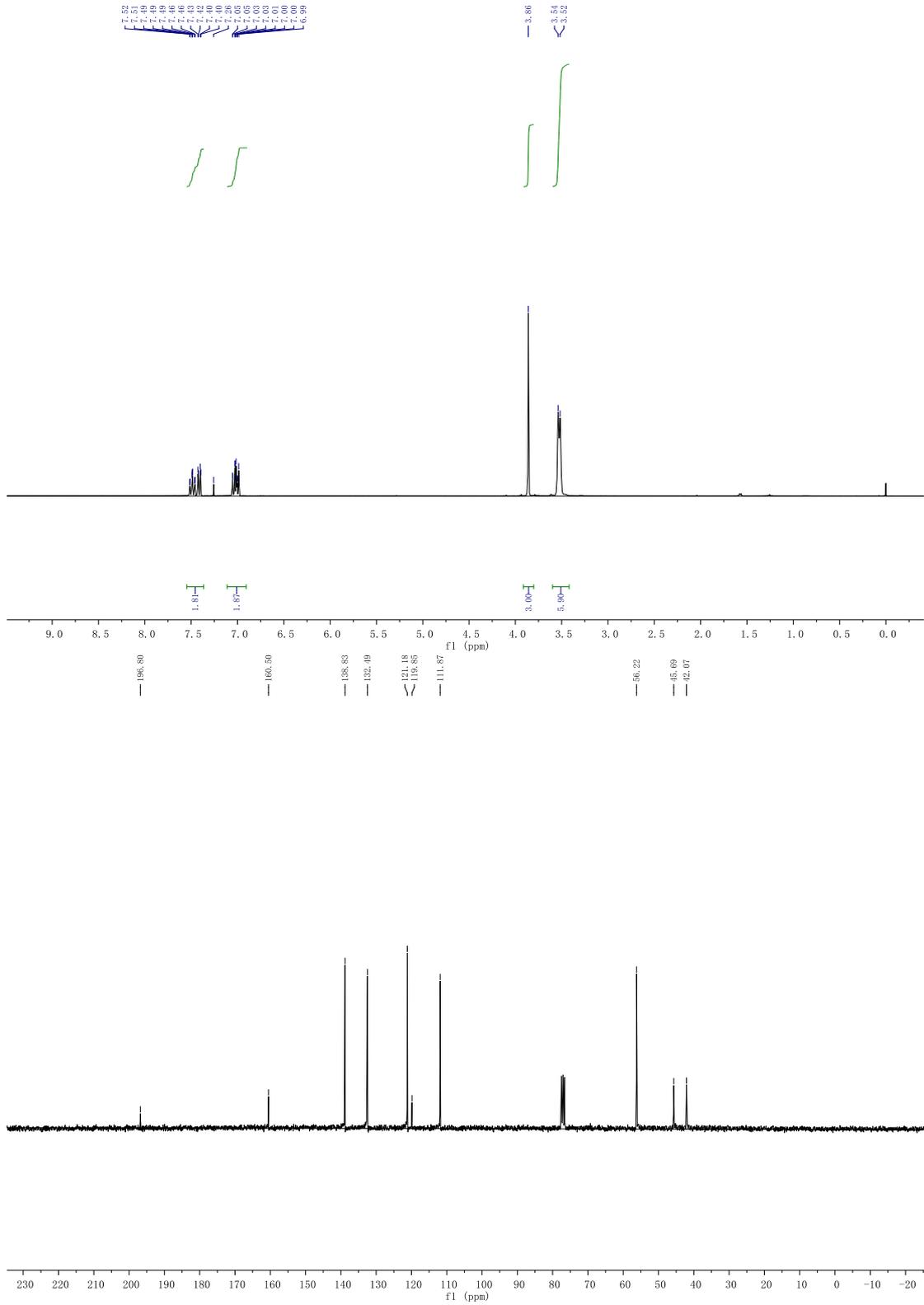
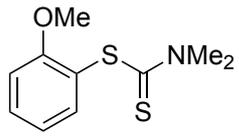


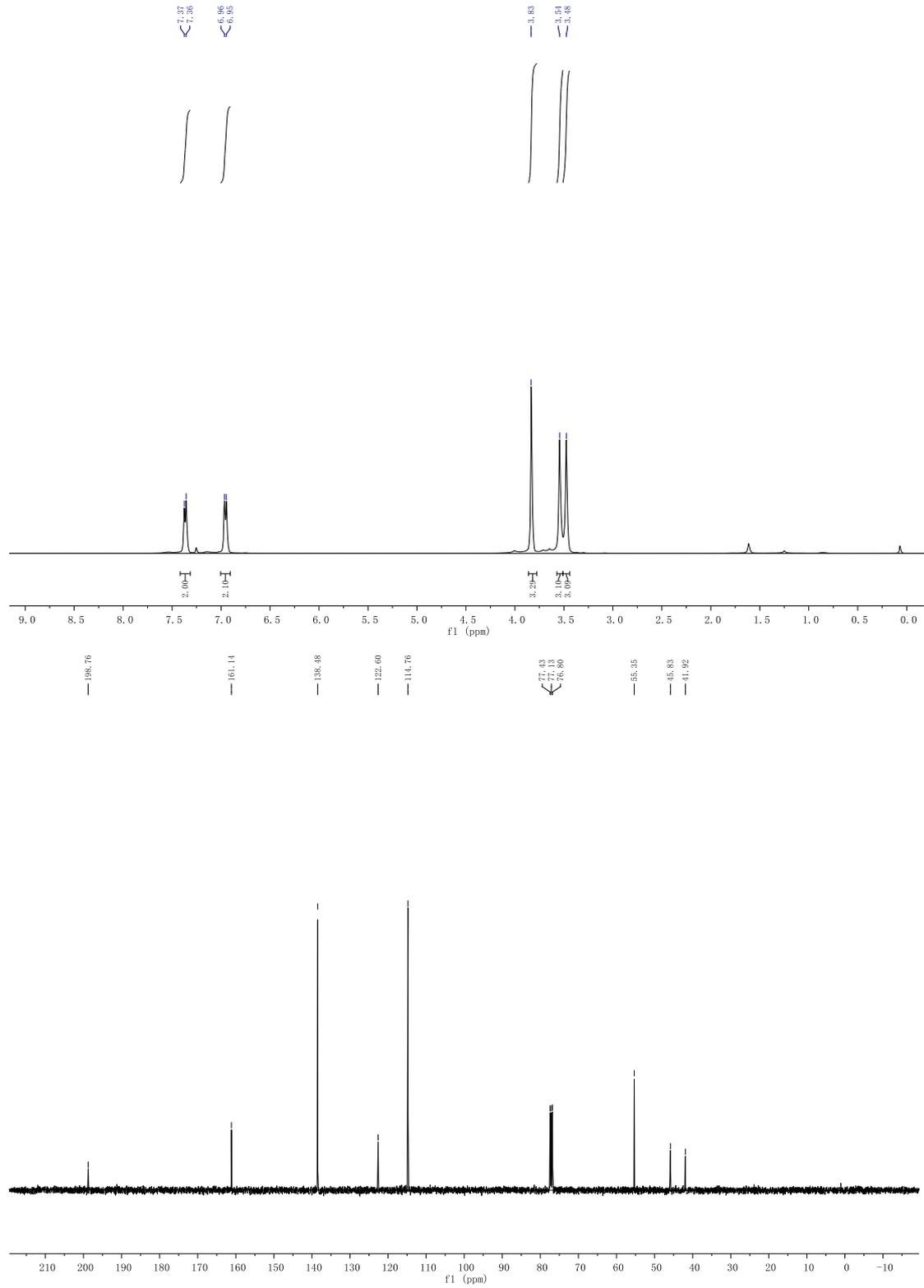
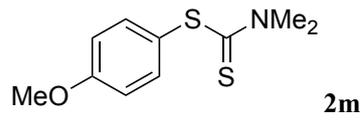
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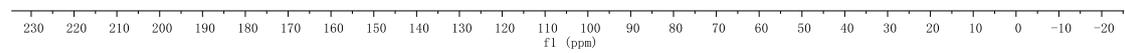
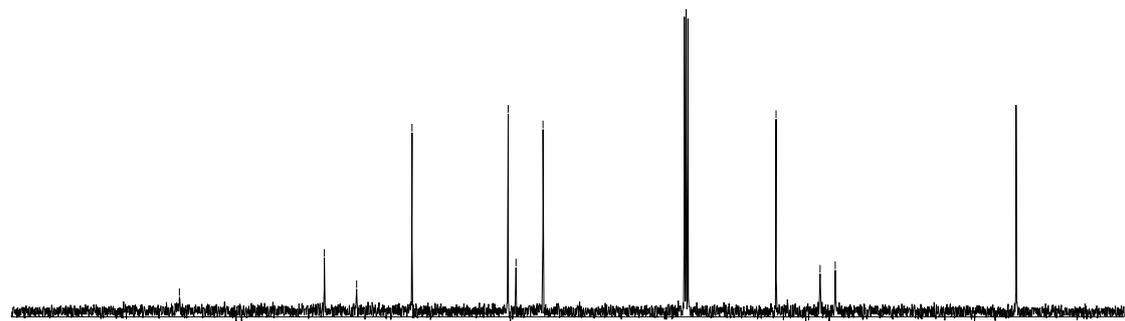
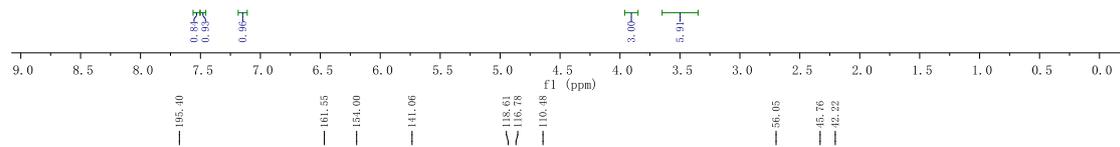
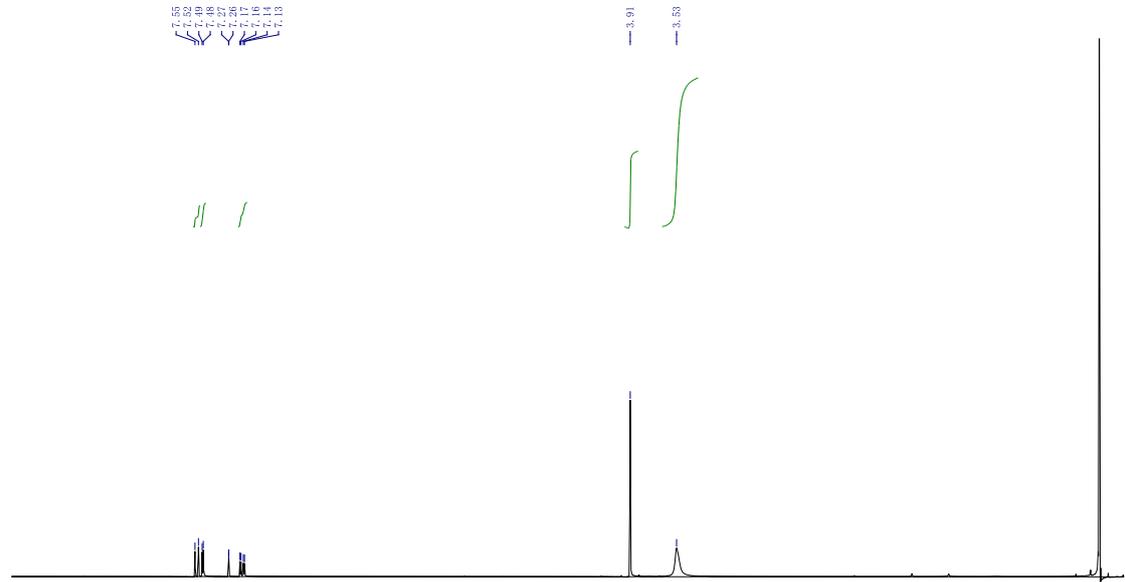


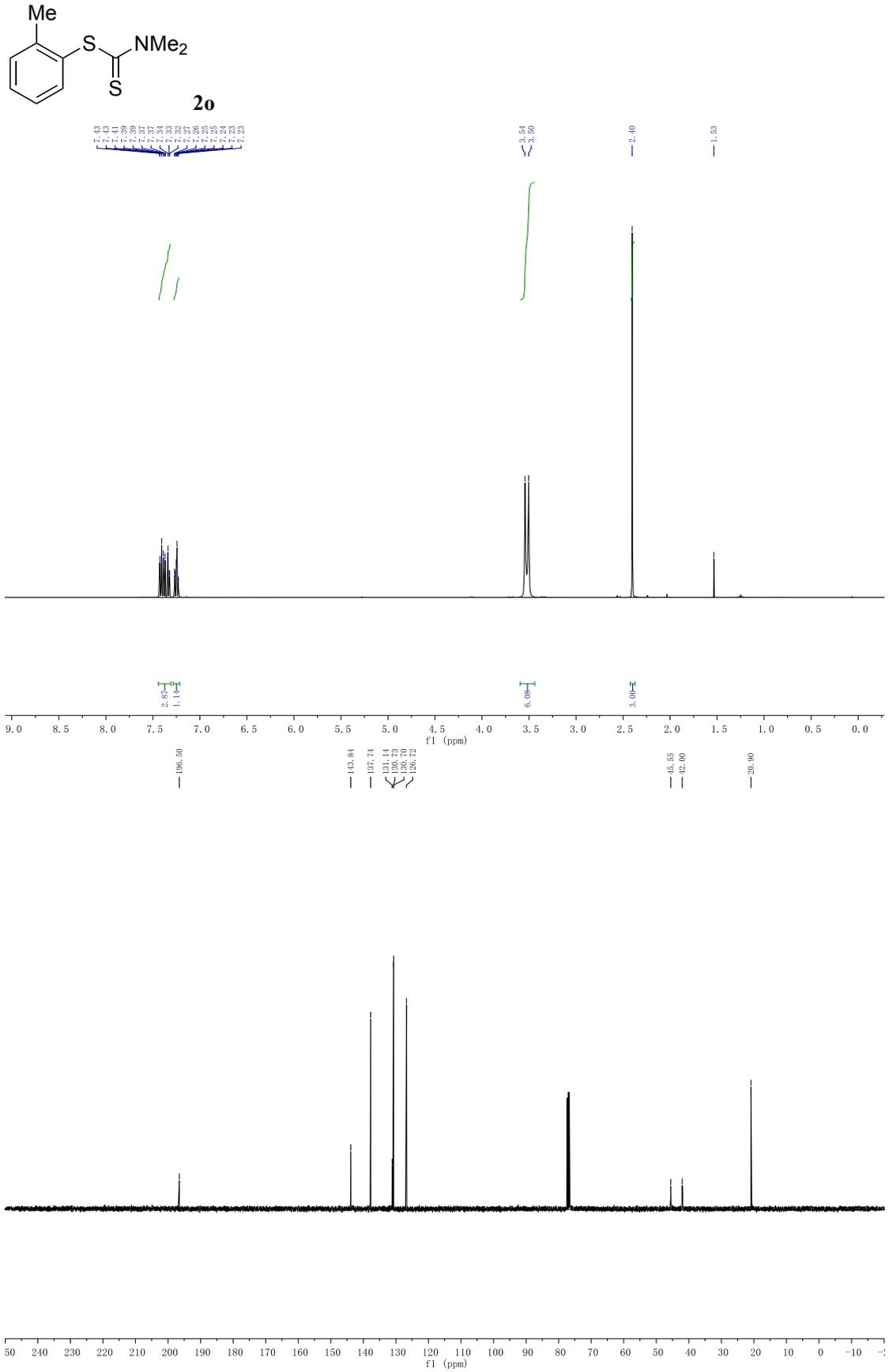


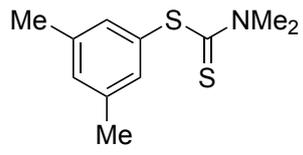




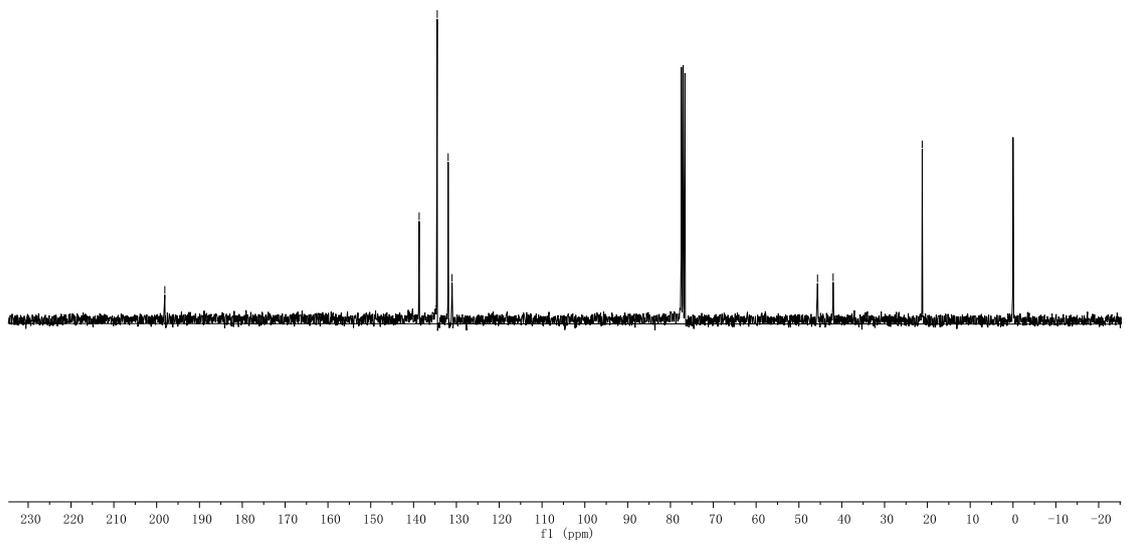
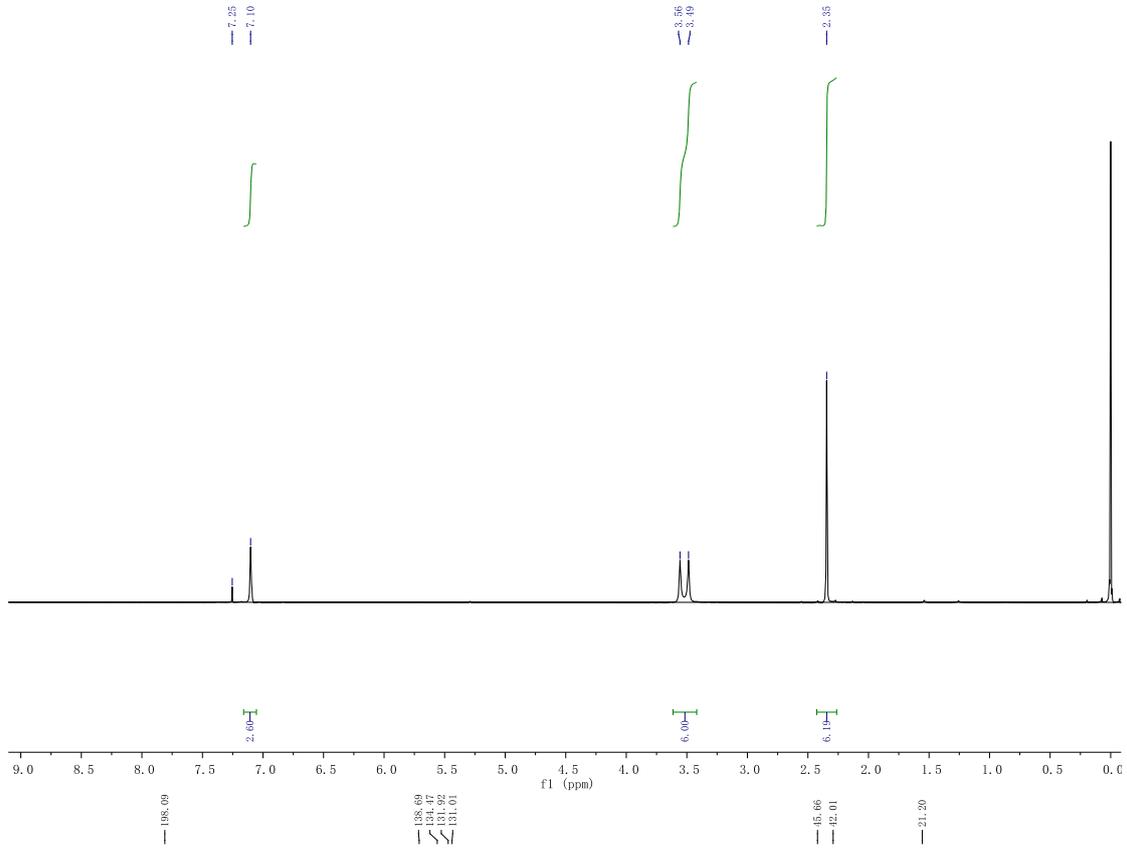


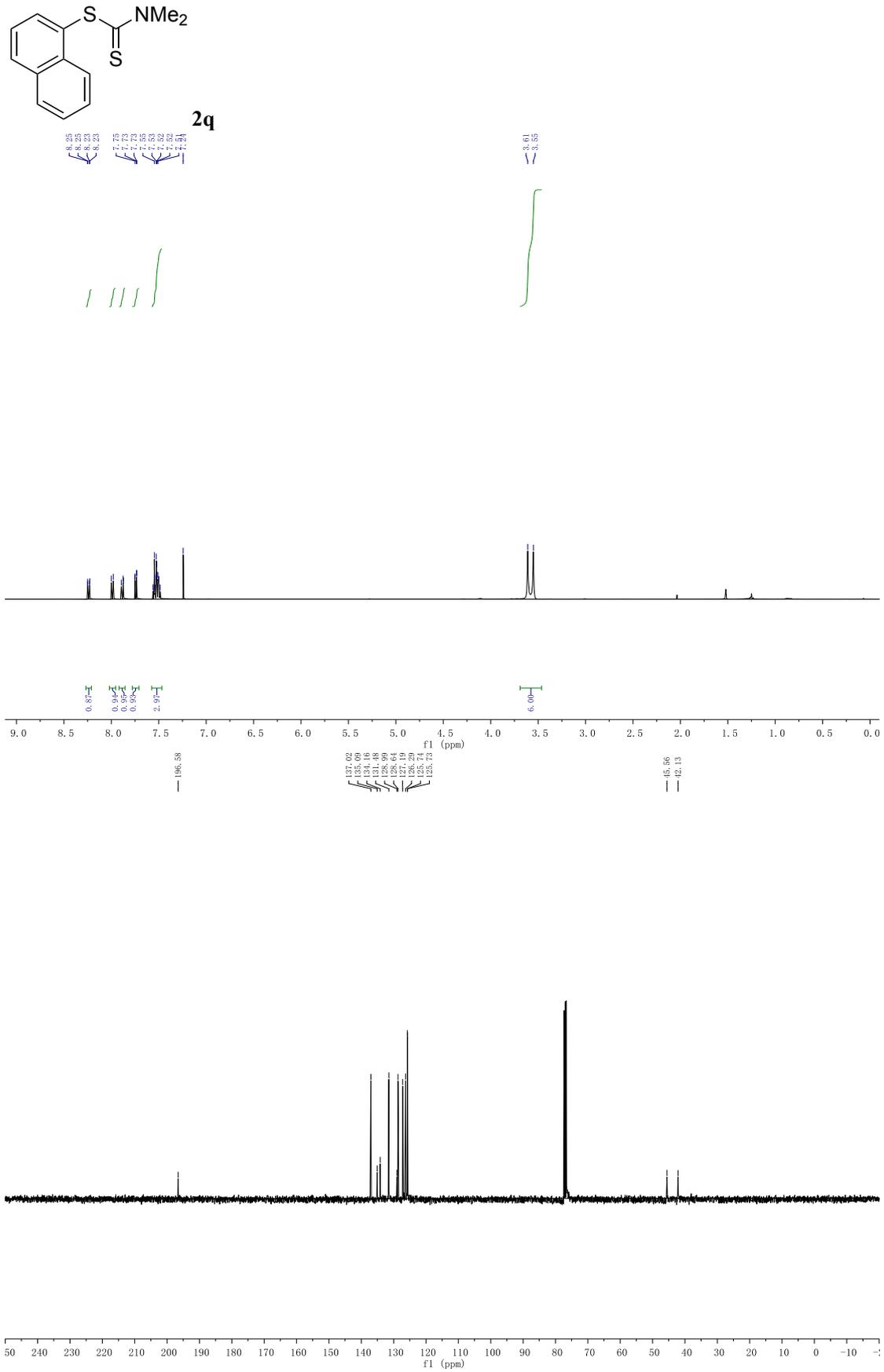


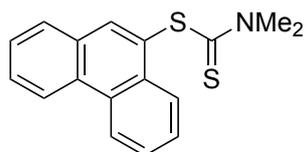




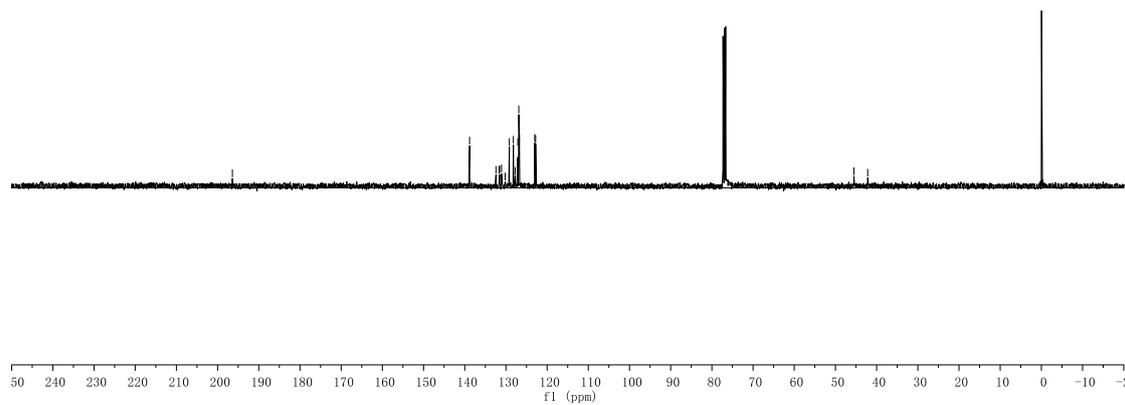
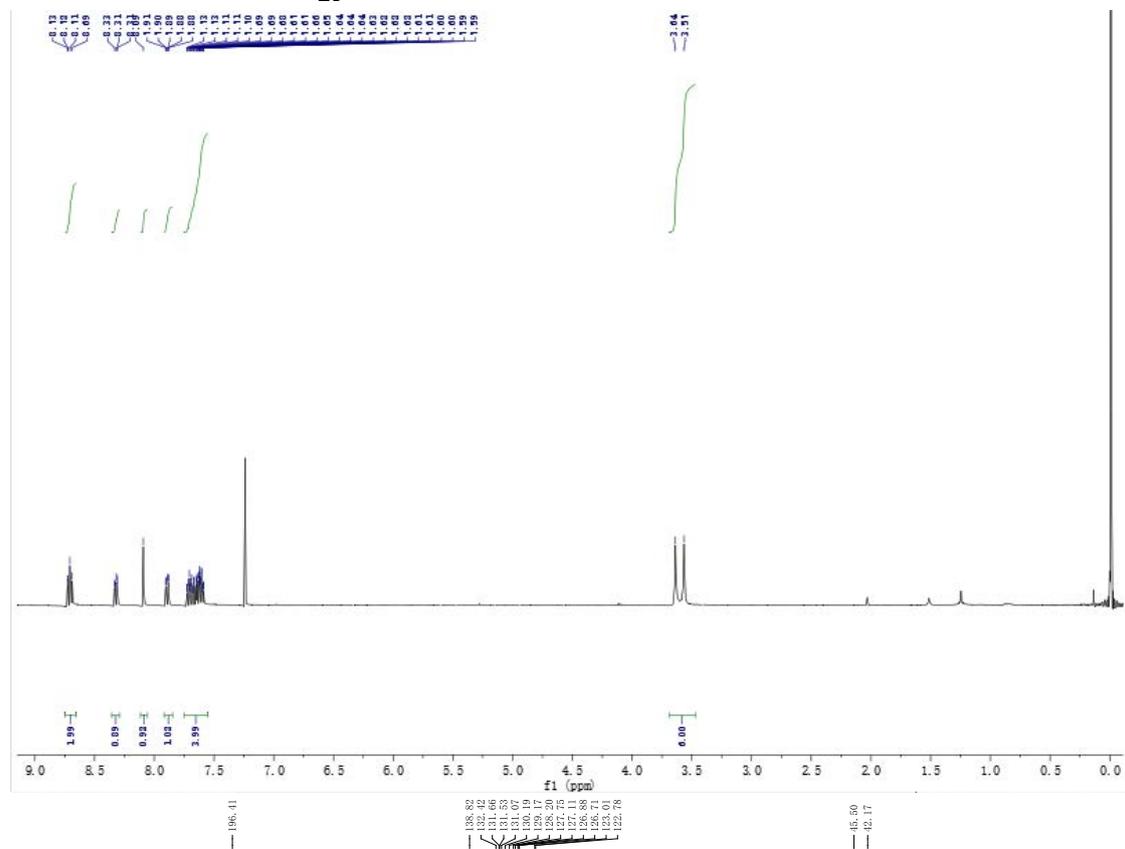
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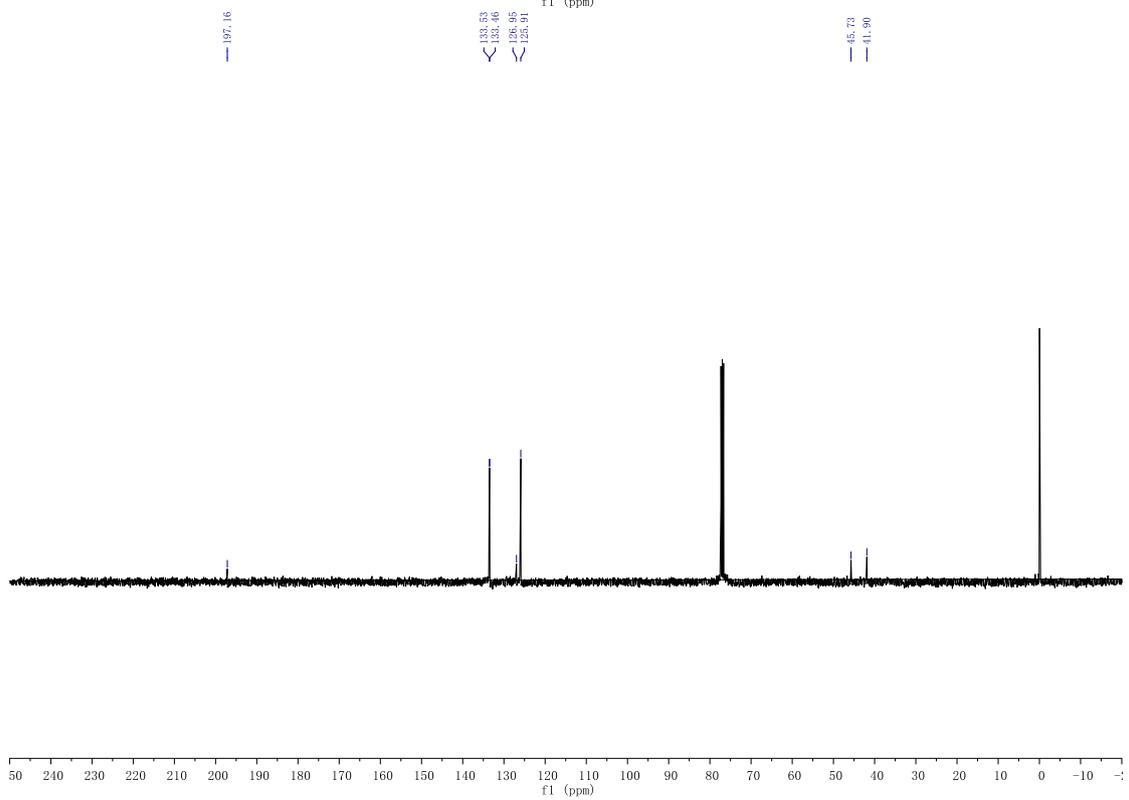
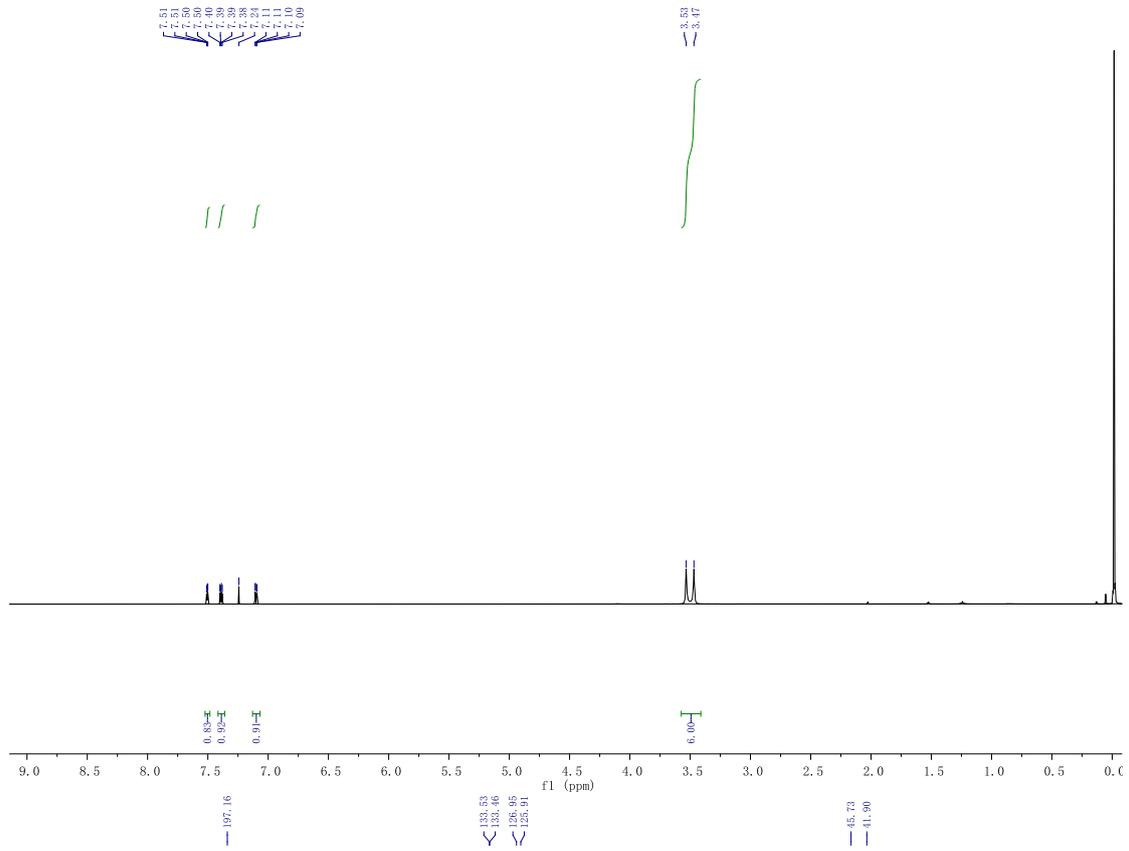
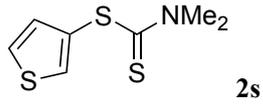


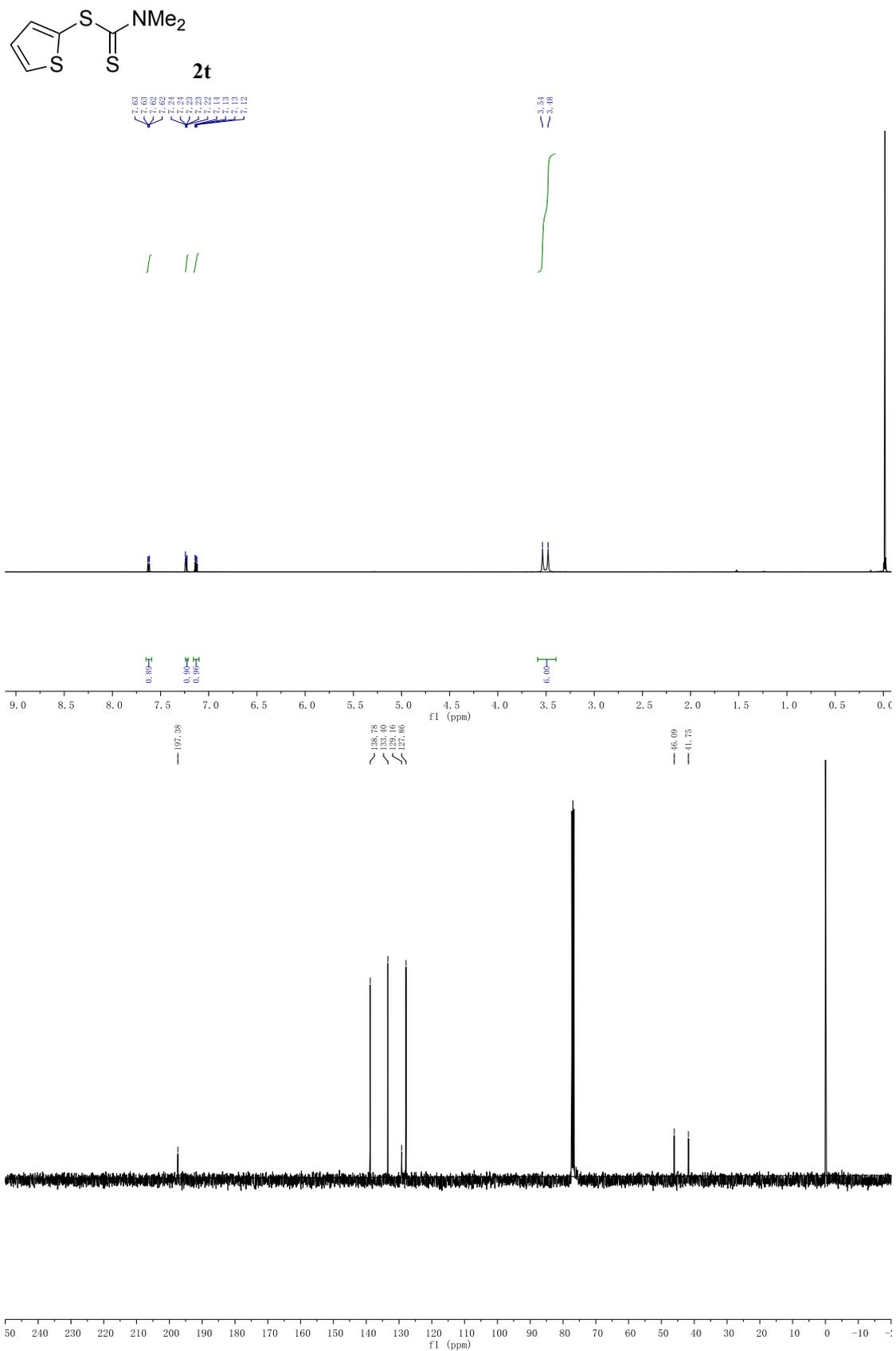


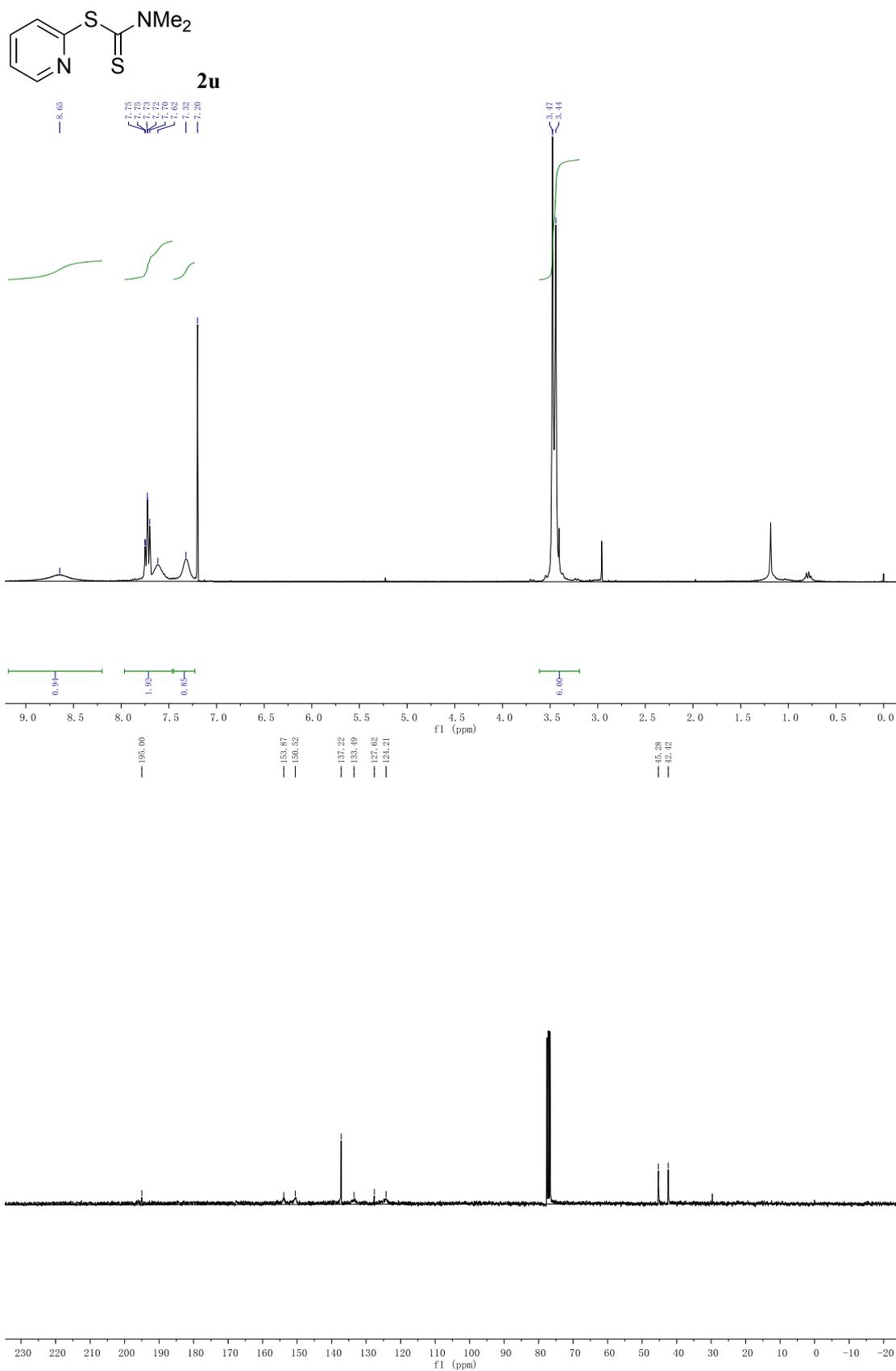
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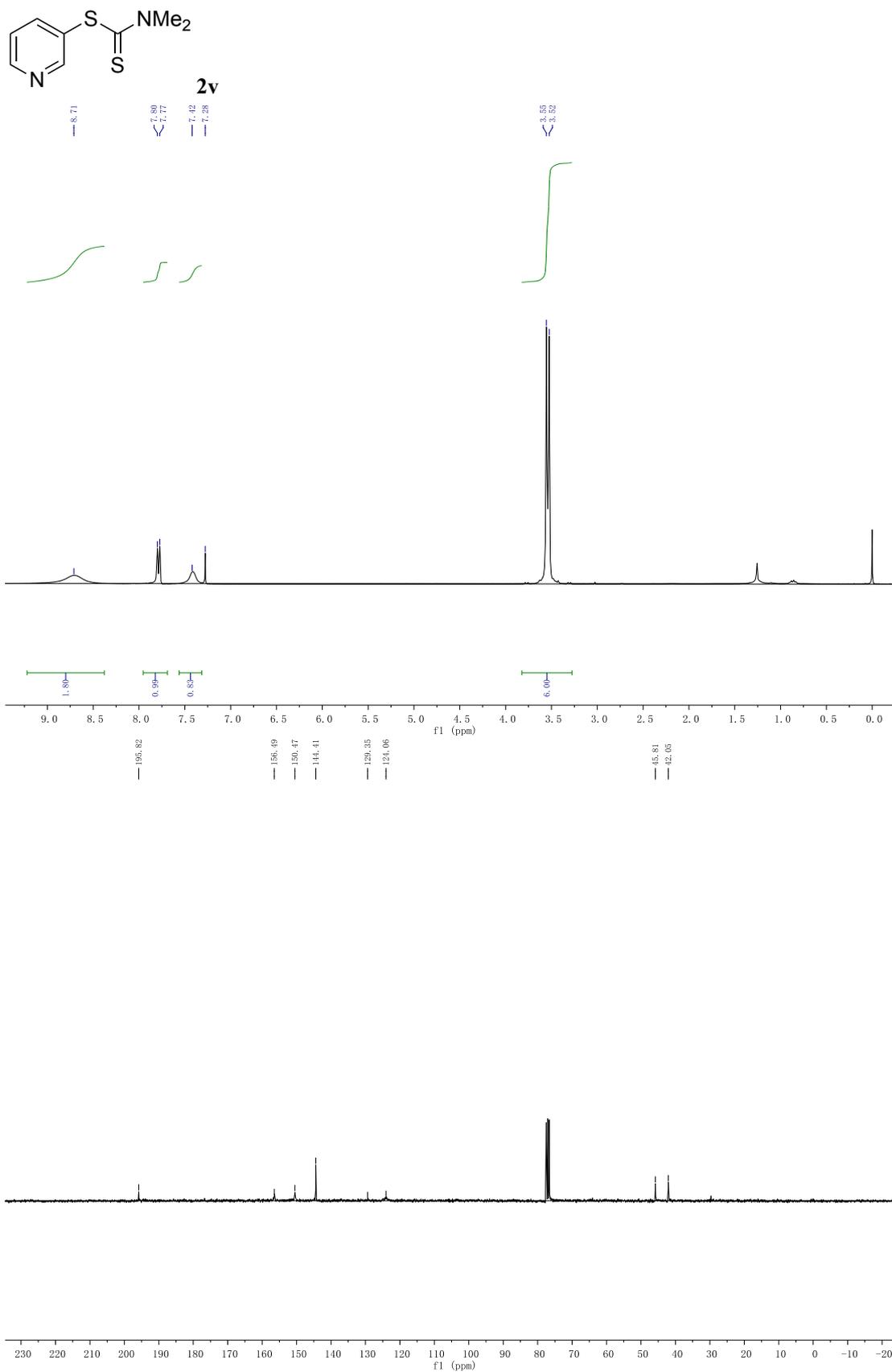


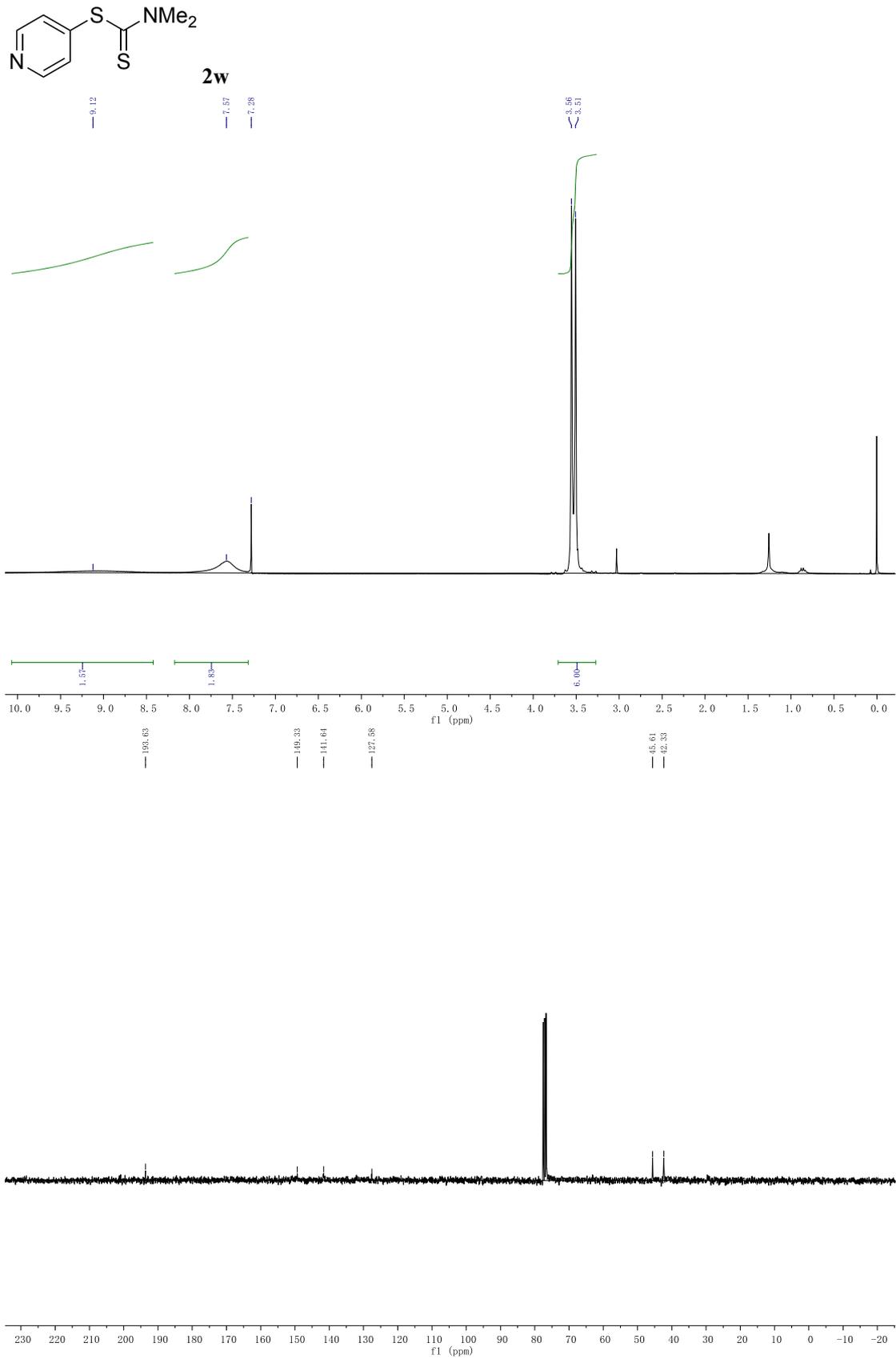
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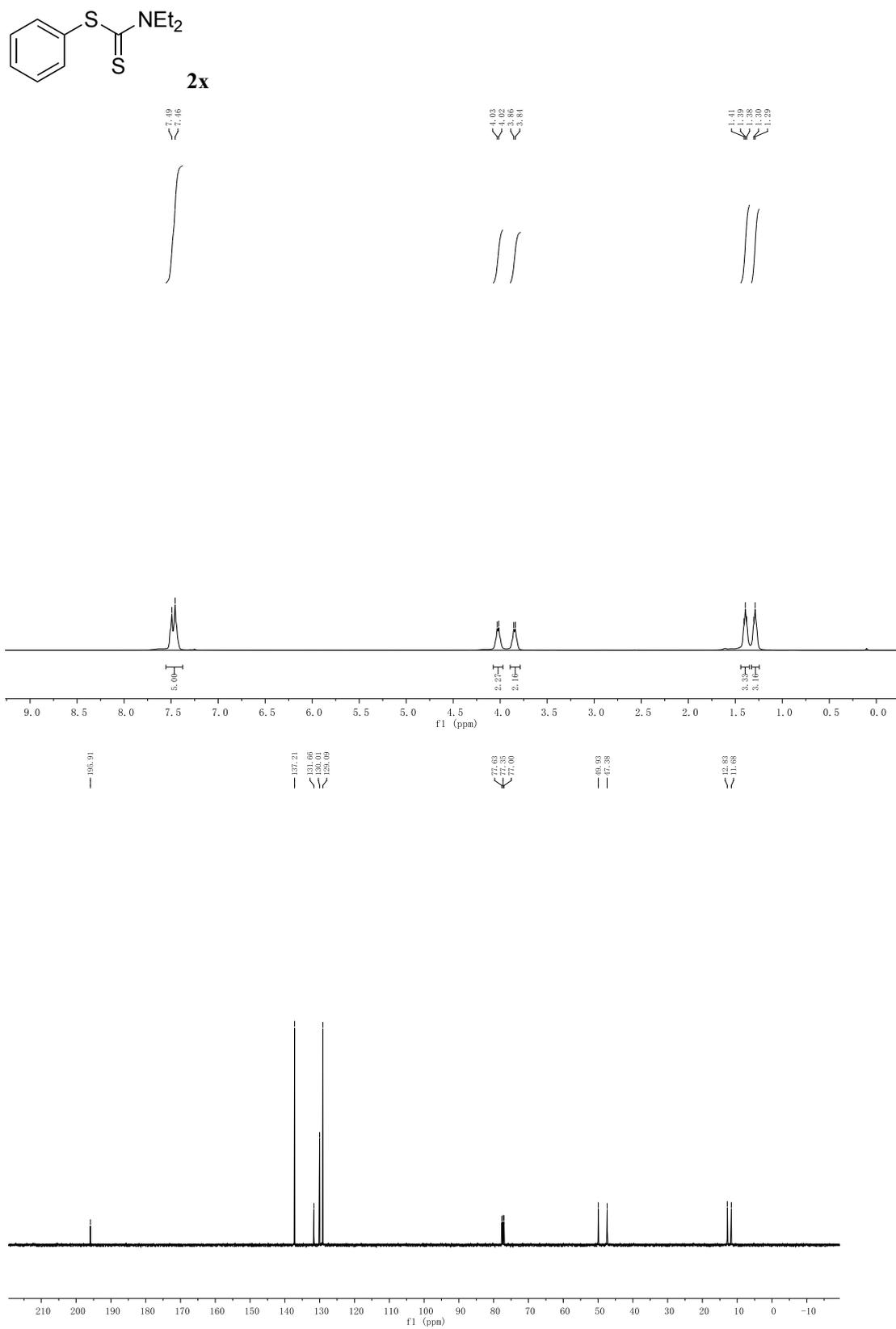


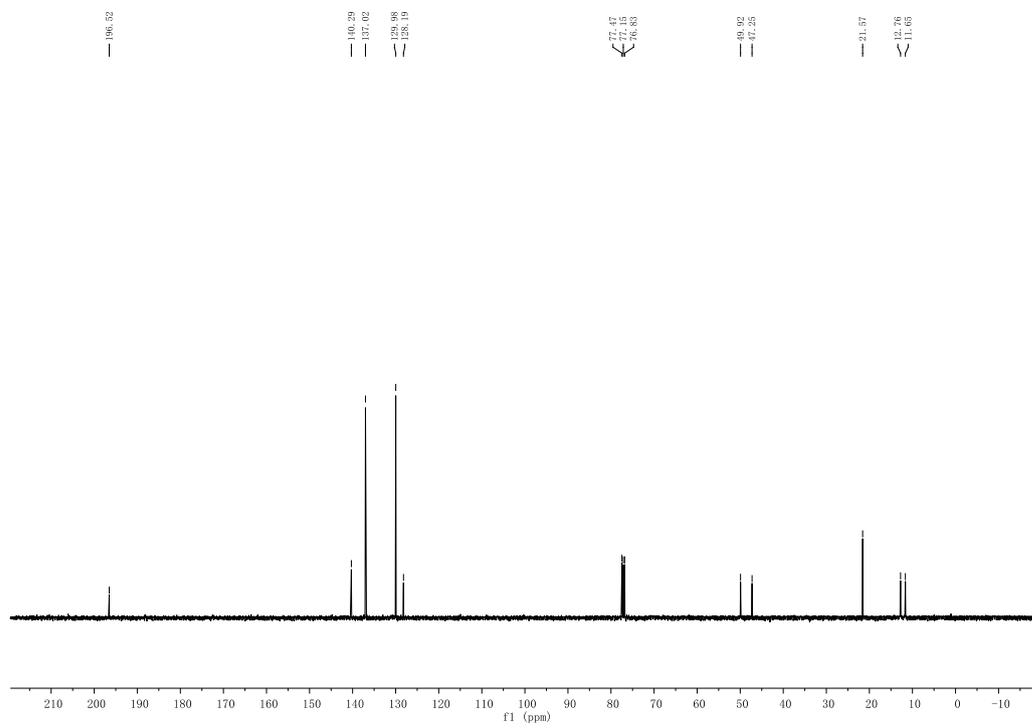
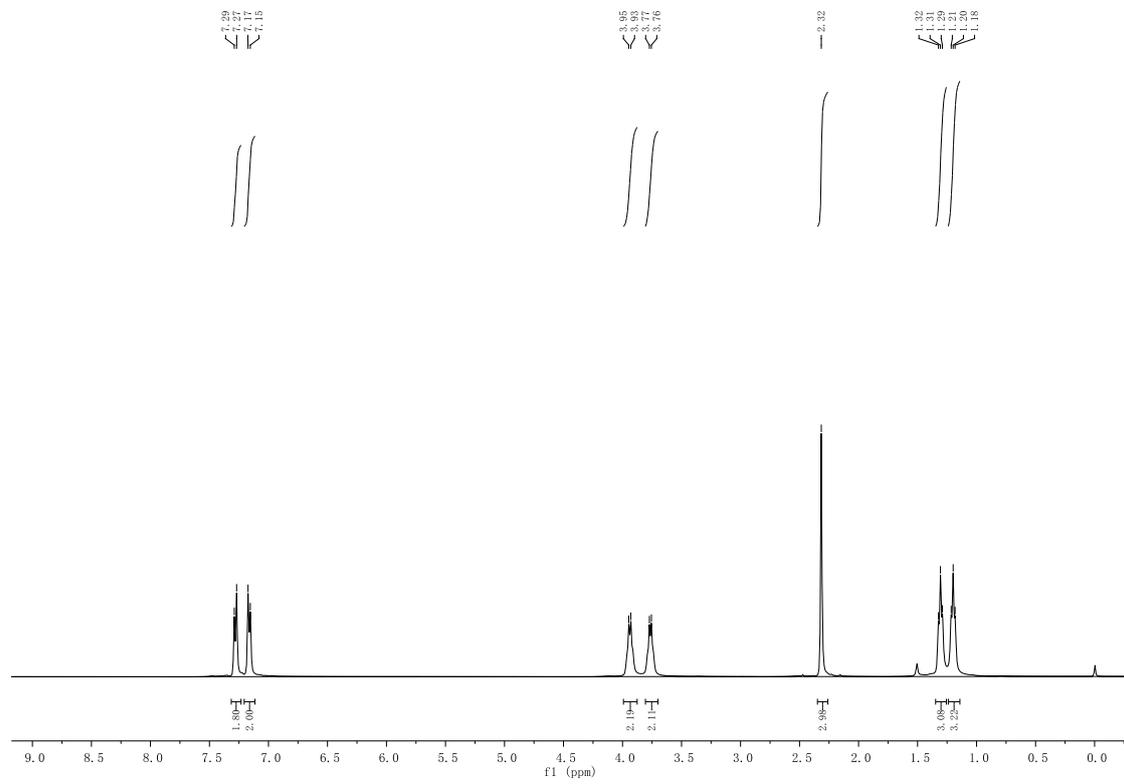
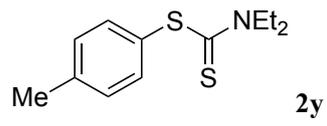


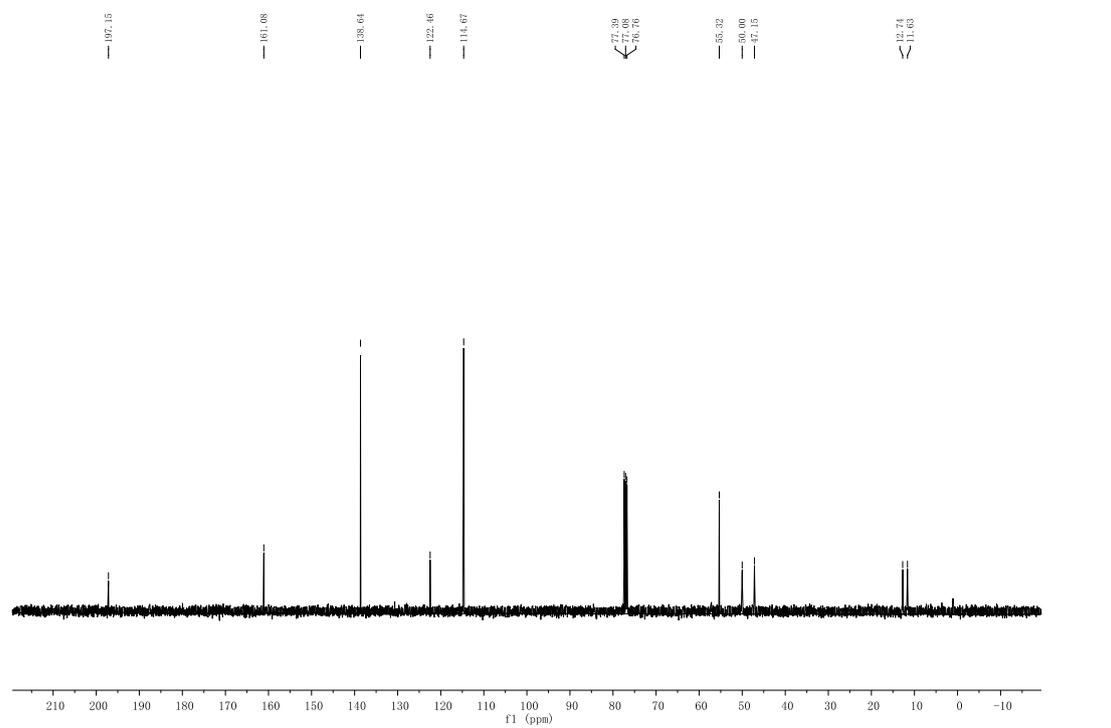
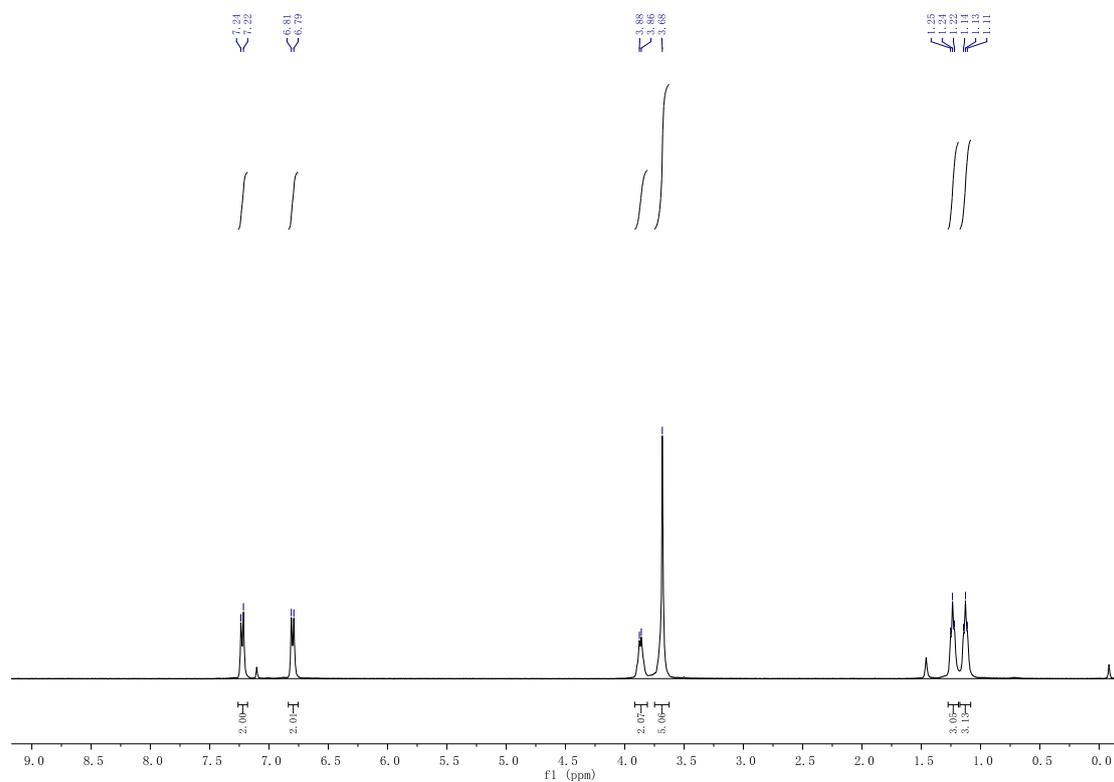
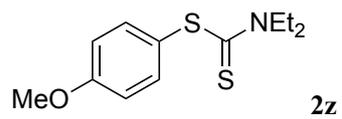


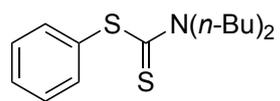
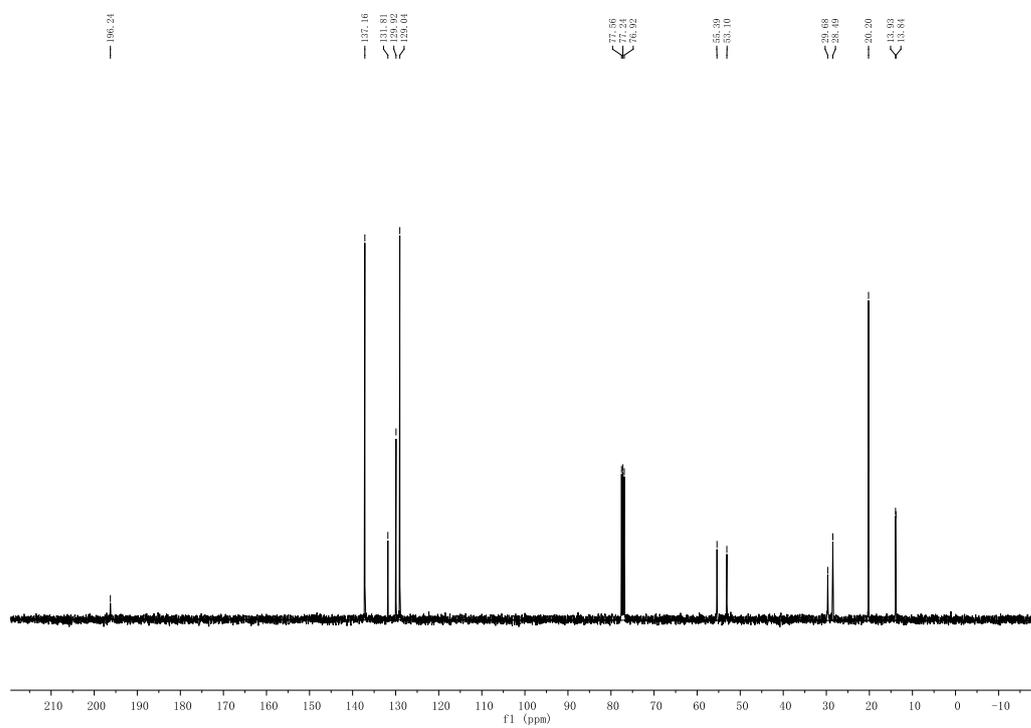
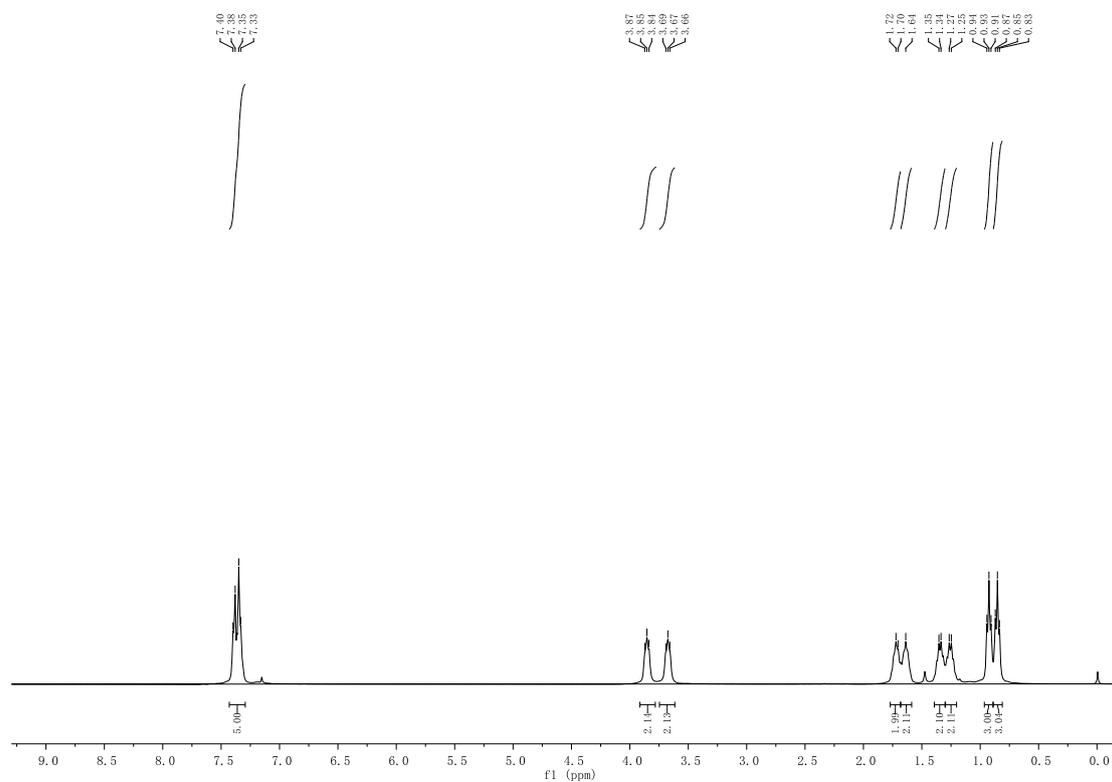


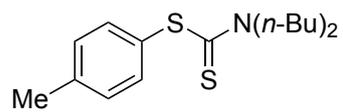








**2za**



2b

