

Supporting Information

Copper-Catalyzed C(sp²)-S Coupling Reactions for the Synthesis of Aryl Dithiocarbamates with Thiuram Disulfide Reagents

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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 ^1H NMR and capillary GC analysis. NMR spectra were recorded on a Bruker AM400 or Bruker AM 300 NMR instrument in 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 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), Cu_2O (42.9 mg, 0.3 mmol, 10 mol %), and Cs_2CO_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. NH_4Cl solution and subsequently extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_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.

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.49-7.45 (m, 5H), 3.56 (s, 3H), 3.50 (s, 3H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (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.

^1H NMR (400 MHz, CDCl_3): δ (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, CDCl_3): δ (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.

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.41-7.36 (m, 4H), 3.53 (s, 3H), 3.47 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (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.

^1H NMR (300 MHz, CDCl_3): δ (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, CDCl_3): δ (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.

¹H NMR (300 MHz, CDCl₃): 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); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ (ppm) 196.5, 138.4, 132.3, 130.7, 124.9, 45.7, 42.0; HRMS (ESI): calcd for C₉H₁₀BrNS₂, 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.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.29-8.24 (m, 2H), 7.67-7.63 (m, 2H), 3.56 (s, 3H), 3.53 (s, 3H); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ (ppm) 194.5, 148.5, 139.5, 137.6, 123.8, 45.6, 42.2; HRMS (ESI): calcd for C₉H₁₀N₂O₂S₂, 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.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.00-7.97 (m, 1H), 7.67-7.60 (m, 3H), 3.53 (s, 6H); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ (ppm) 193.9, 139.6, 132.6, 131.0, 126.5, 124.9, 45.6, 42.4; HRMS (ESI): calcd for C₉H₁₀N₂O₂S₂, 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.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.72-7.69 (m, 2H), 7.60-7.57 (m, 2H), 3.55 (s, 3H), 3.51 (s, 3H); ¹³C{¹H} NMR (75 MHz, CDCl₃): 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, $CDCl_3$): δ (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, $CDCl_3$): δ (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, $CDCl_3$): δ (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, $CDCl_3$): δ (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, $CDCl_3$): δ (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, $CDCl_3$): δ (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.

¹H NMR (300 MHz, CDCl₃): 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); ¹³C{¹H} NMR (75 MHz, CDCl₃): 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 C₁₀H₁₃NOS₂, 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.

¹H NMR (400 MHz, CDCl₃): 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); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ (ppm) 198.7, 161.1, 138.4, 122.6, 114.7, 55.3, 45.8, 41.9; HRMS (ESI): calcd for C₁₀H₁₃NOS₂, 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.

¹H NMR (300 MHz, CDCl₃): 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); ¹³C{¹H} NMR (75 MHz, CDCl₃): 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 C₁₀H₁₂N₂O₃S₂, 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.

¹H NMR (400 MHz, CDCl₃): 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, CDCl_3): δ (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.

^1H NMR (300 MHz, CDCl_3): δ (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, CDCl_3): δ (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.

^1H NMR (400 MHz, CDCl_3): δ (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, CDCl_3): δ (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.

^1H NMR (400 MHz, CDCl_3): δ (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, CDCl_3): δ (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.

¹H NMR (400 MHz, CDCl₃): 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); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 197.1, 133.5, 133.4, 126.9, 125.9, 45.7, 41.9; HRMS (ESI): calcd for C₇H₉NS₃, 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.

¹H NMR (400 MHz, CDCl₃): 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); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 197.3, 138.7, 133.4, 129.1, 127.8, 46.0, 41.7; HRMS (ESI): calcd for C₇H₉NS₃, 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.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.65 (s, 1H), 7.65-7.62 (m, 2H), 7.32 (s, 1H), 3.47 (s, 3H), 3.44 (s, 3H); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ (ppm) 195.0, 153.8, 150.5, 137.2, 133.4, 127.6, 124.2, 45.2, 42.4; HRMS (ESI): calcd for C₈H₁₀N₂S₂, 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.

¹H NMR (300 MHz, CDCl₃): 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, CDCl_3): δ (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.

^1H NMR (300 MHz, CDCl_3): δ (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, CDCl_3): δ (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%).

^1H NMR (400 MHz, CDCl_3): δ (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, CDCl_3): δ (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.

^1H NMR (400 MHz, CDCl_3): δ (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, CDCl_3): δ (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.

¹H NMR (400 MHz, CDCl₃): δ (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); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (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 C₁₂H₁₇NOS₂, 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%).

¹H NMR (400 MHz, CDCl₃): δ (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, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (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 C₁₅H₂₃NS₂, 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%).

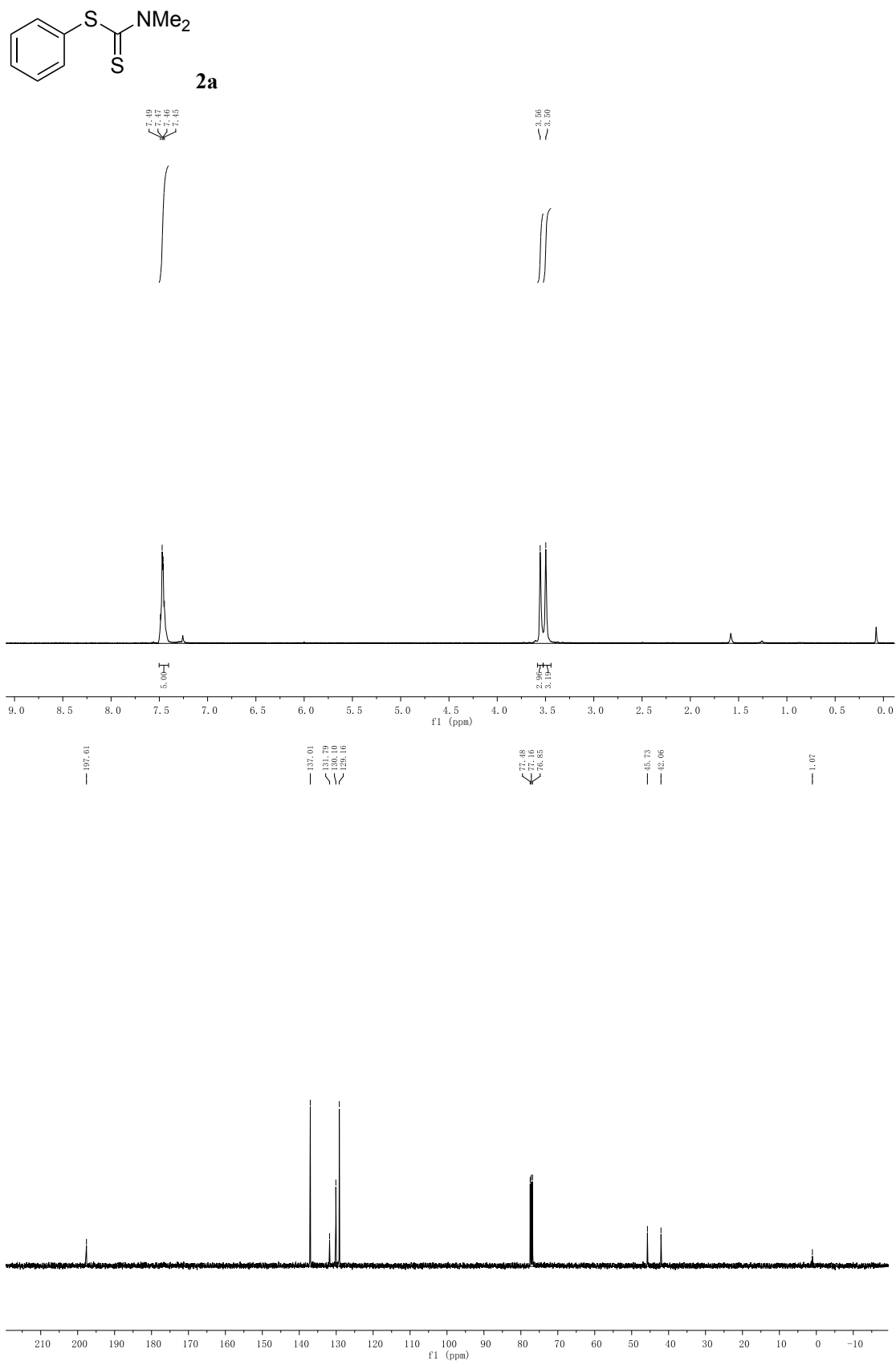
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.31 (d, *J* = 4.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.89 (t, *J* = 8.0 Hz, 2H), 3.71 (t, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 1.76-1.68 (m, 4H), 1.41-1.27 (m, 4H), 0.96 (t, *J* = 8.0 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 196.8, 140.1, 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 C₁₆H₂₅NS₂, 295.1428; found: 295.1433.

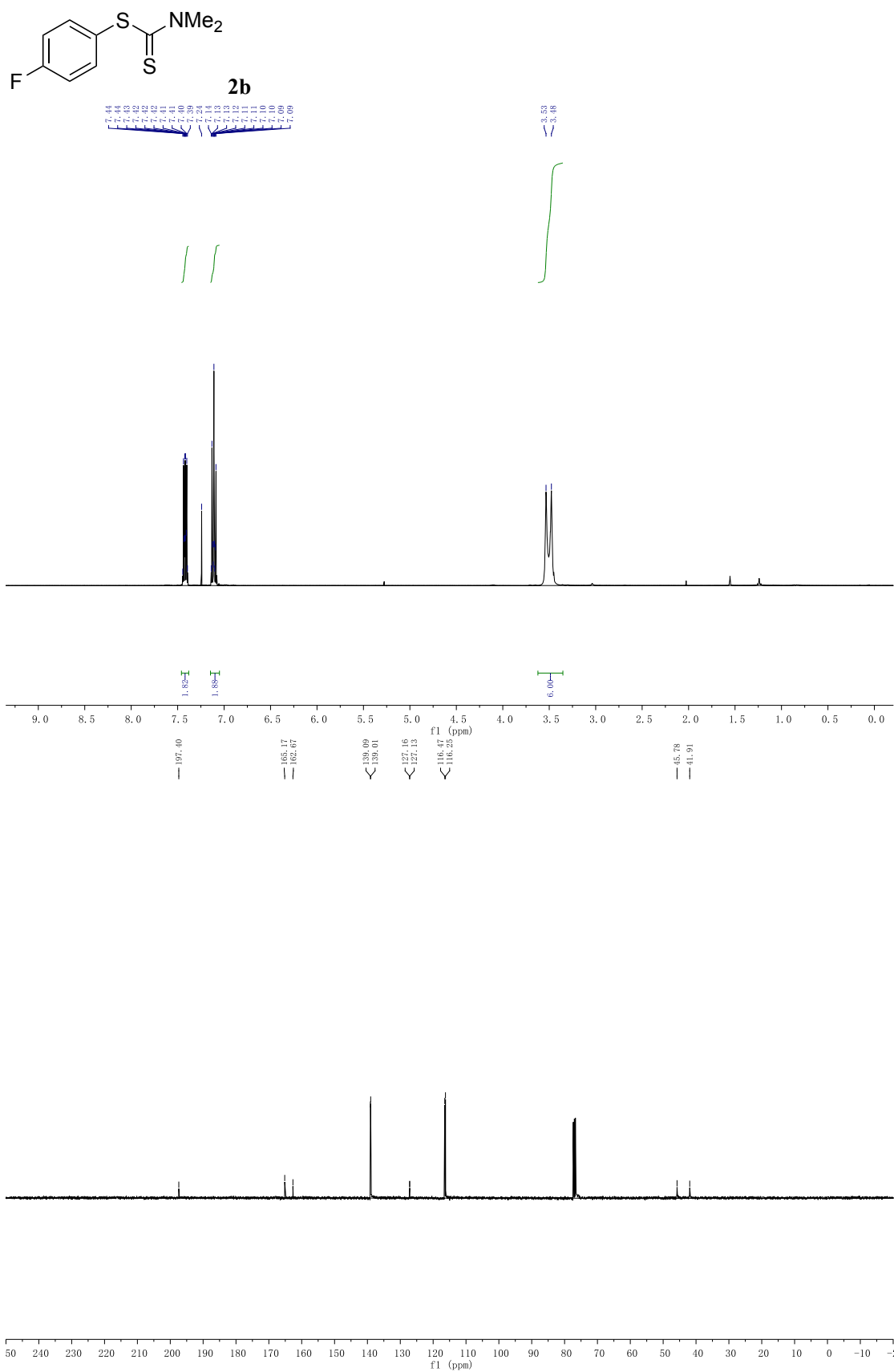
Dibutyl-dithiocarbamic acid 4-methoxy-phenyl ester (2zc)

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

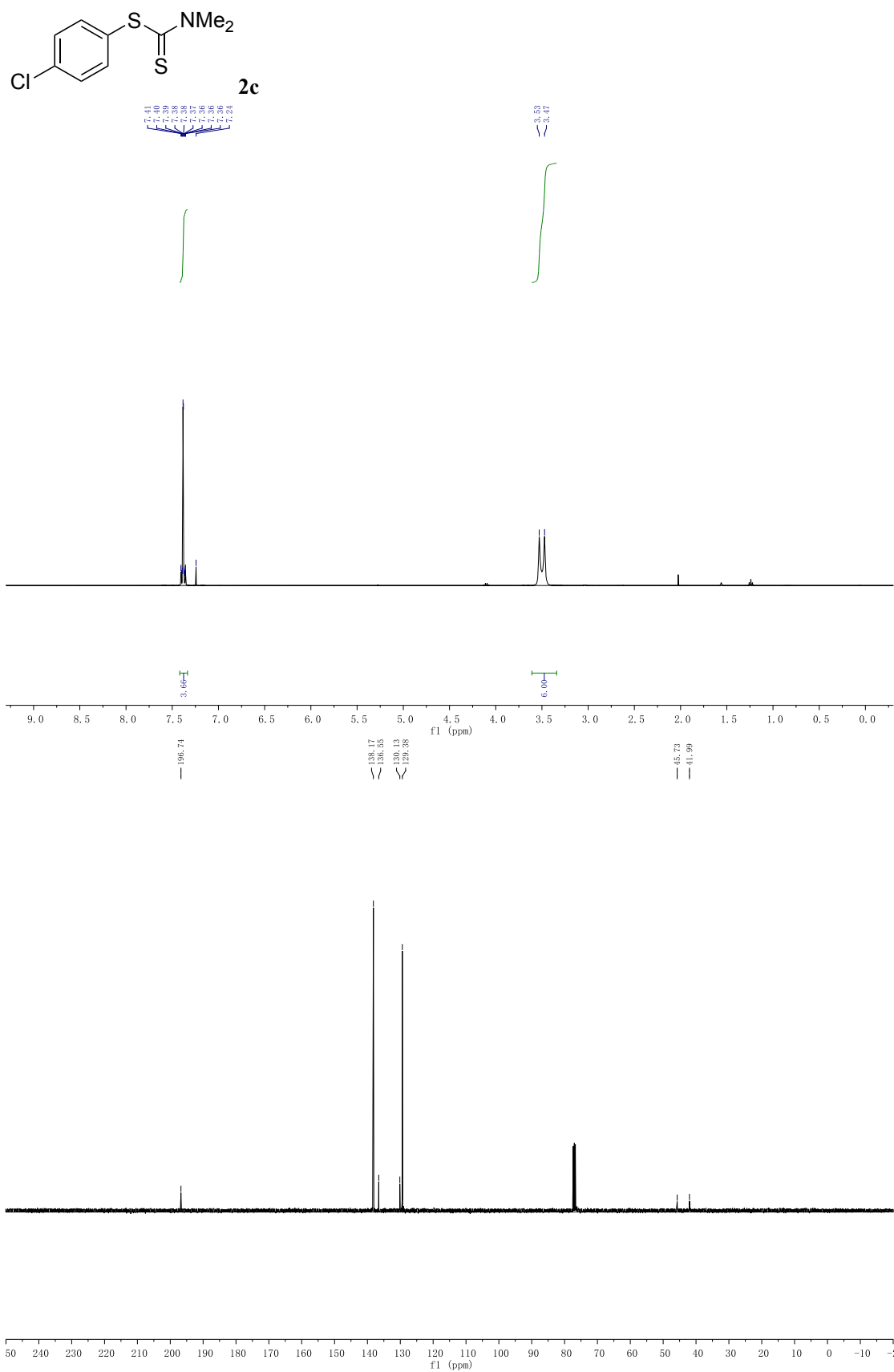
(eluent: petroleum ether/ethyl acetate = 20:1) to give **2zc** as a yellow oil (812.1 mg, 87%).

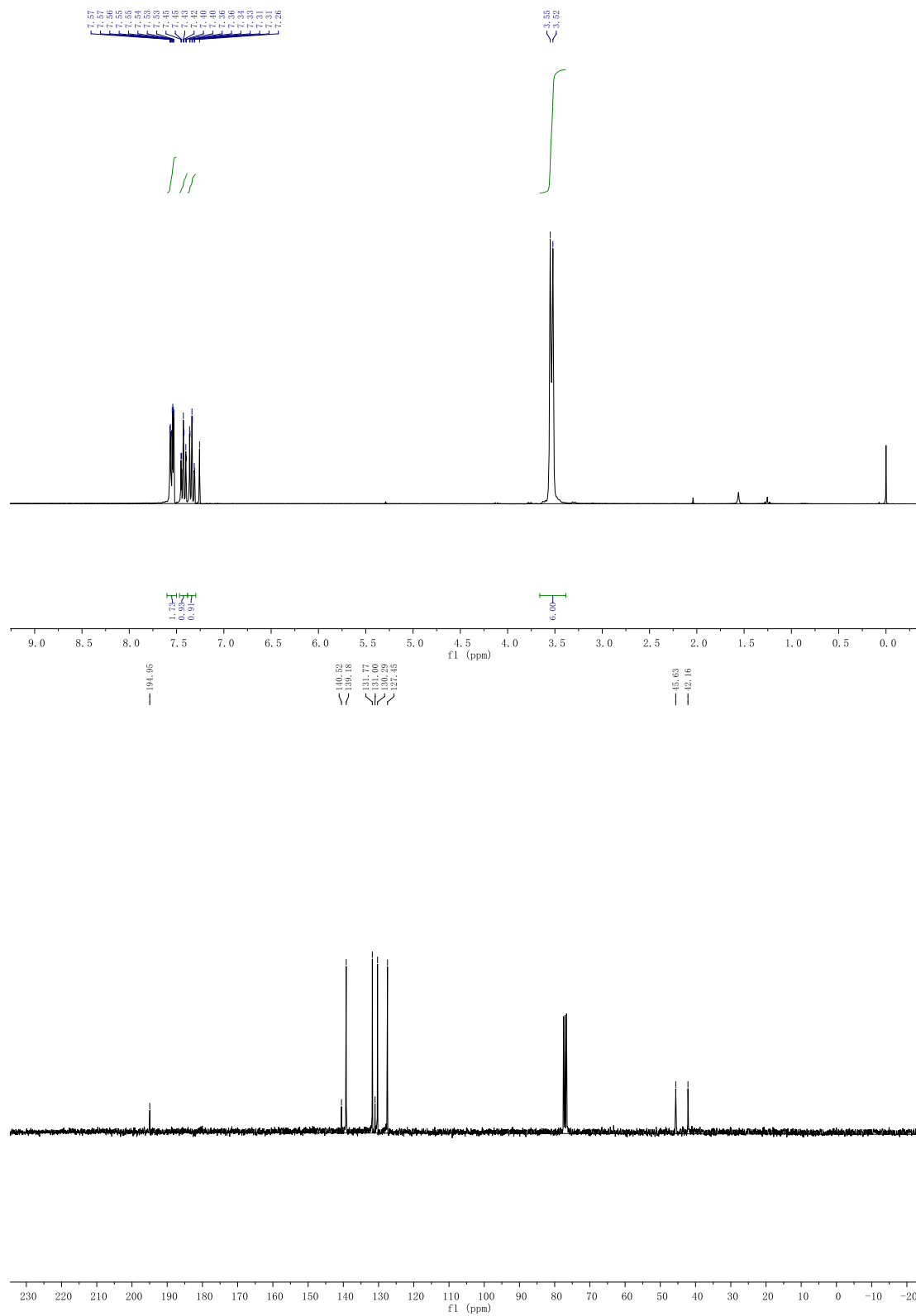
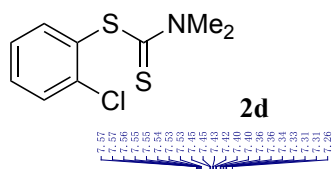
^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.29 (d, $J = 8.0$ Hz, 2H), 6.87 (d, $J = 12.0$ Hz, 2H), 3.86 (s, 2H), 3.75 (s, 3 H), 3.69 (t, $J = 8.0$ Hz, 2H), 1.76-1.72 (m, 4H), 1.38-1.23 (m, 4H), 0.93 (t, $J = 8.0$ Hz, 3), 0.86 (t, $J = 8.0$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 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.

^1H NMR and ^{13}C NMR spectra of the products

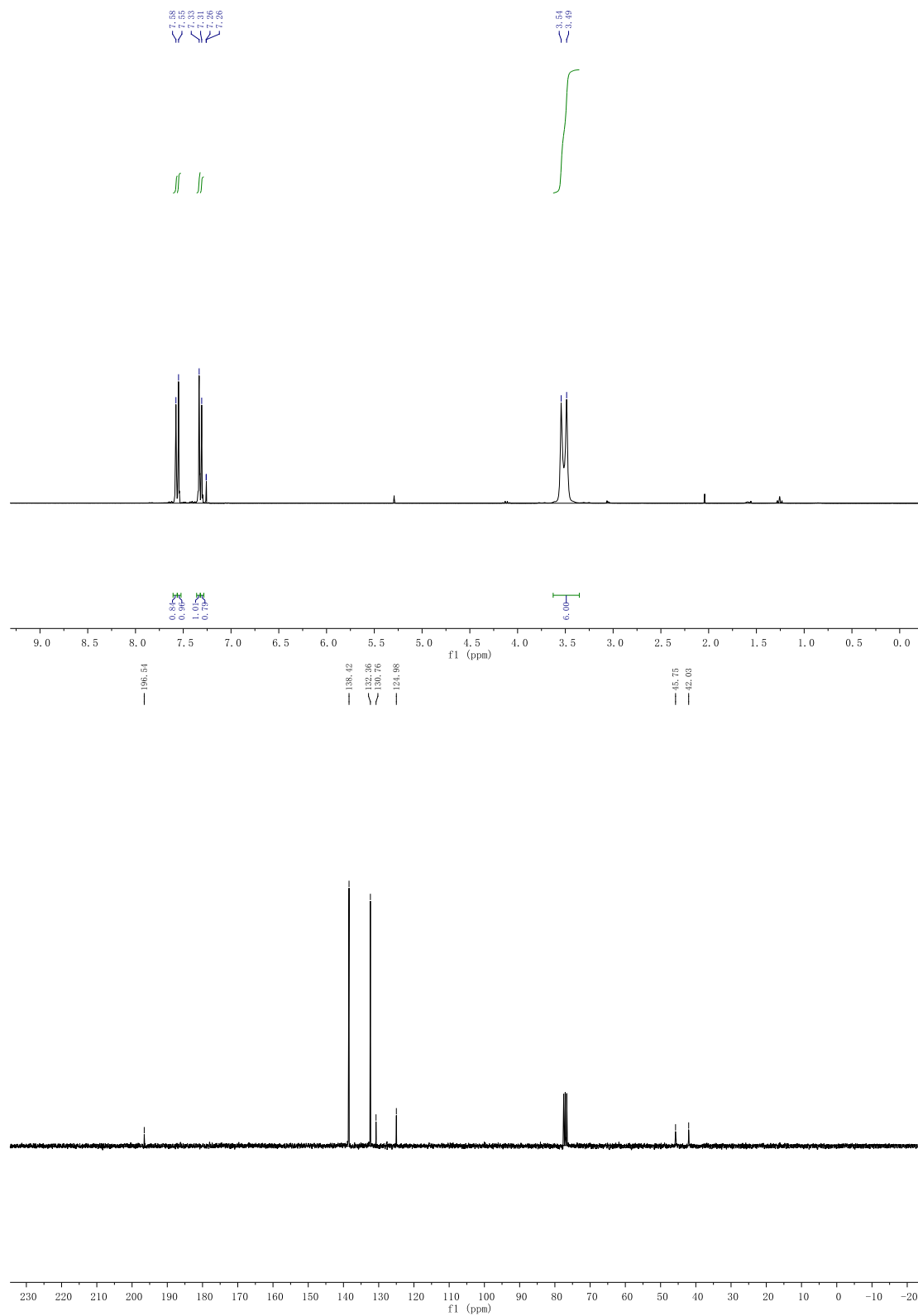
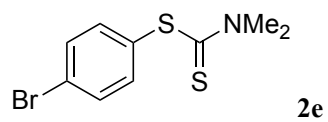


S14

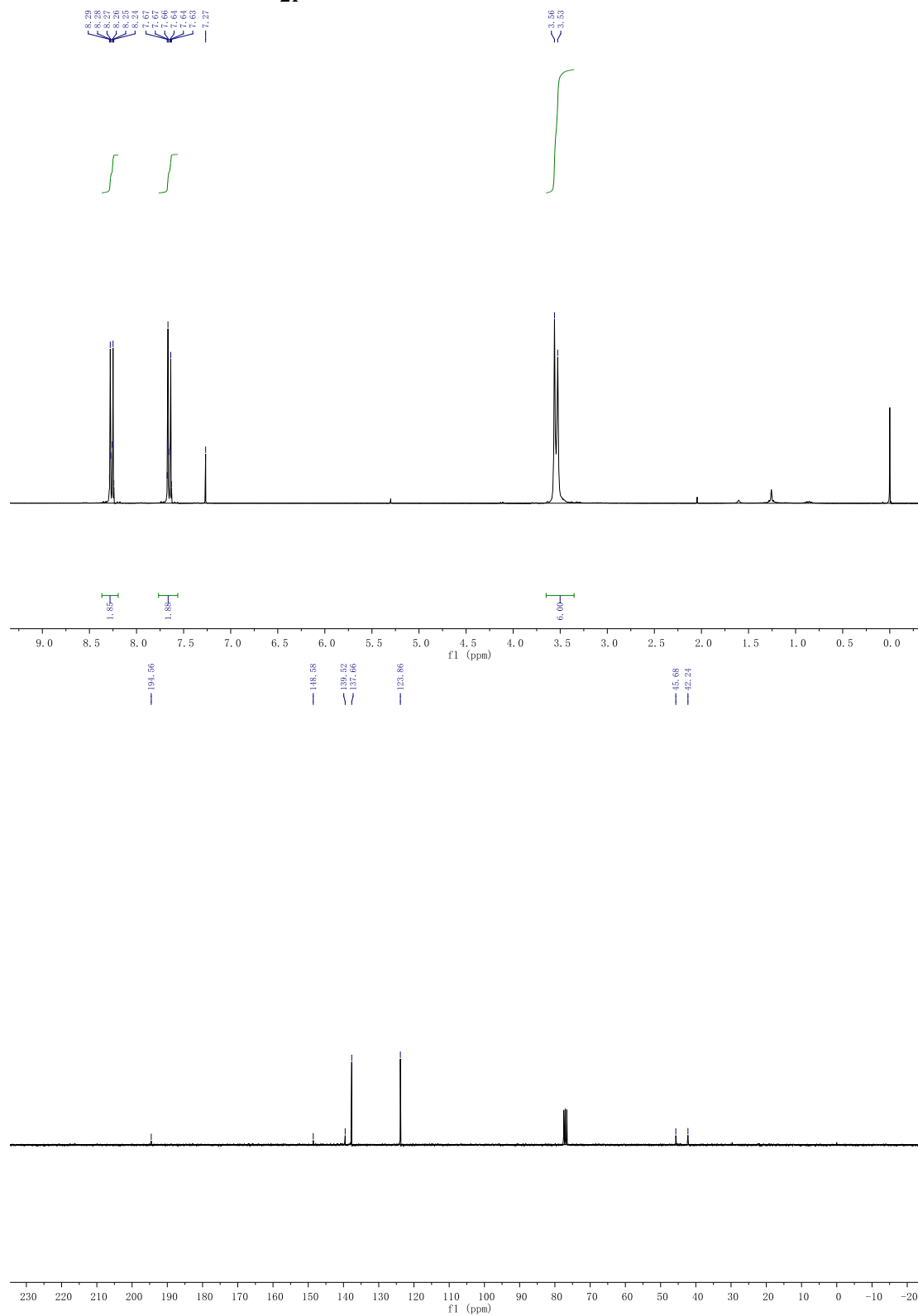
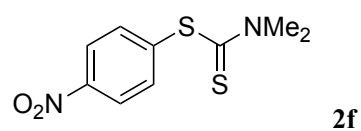




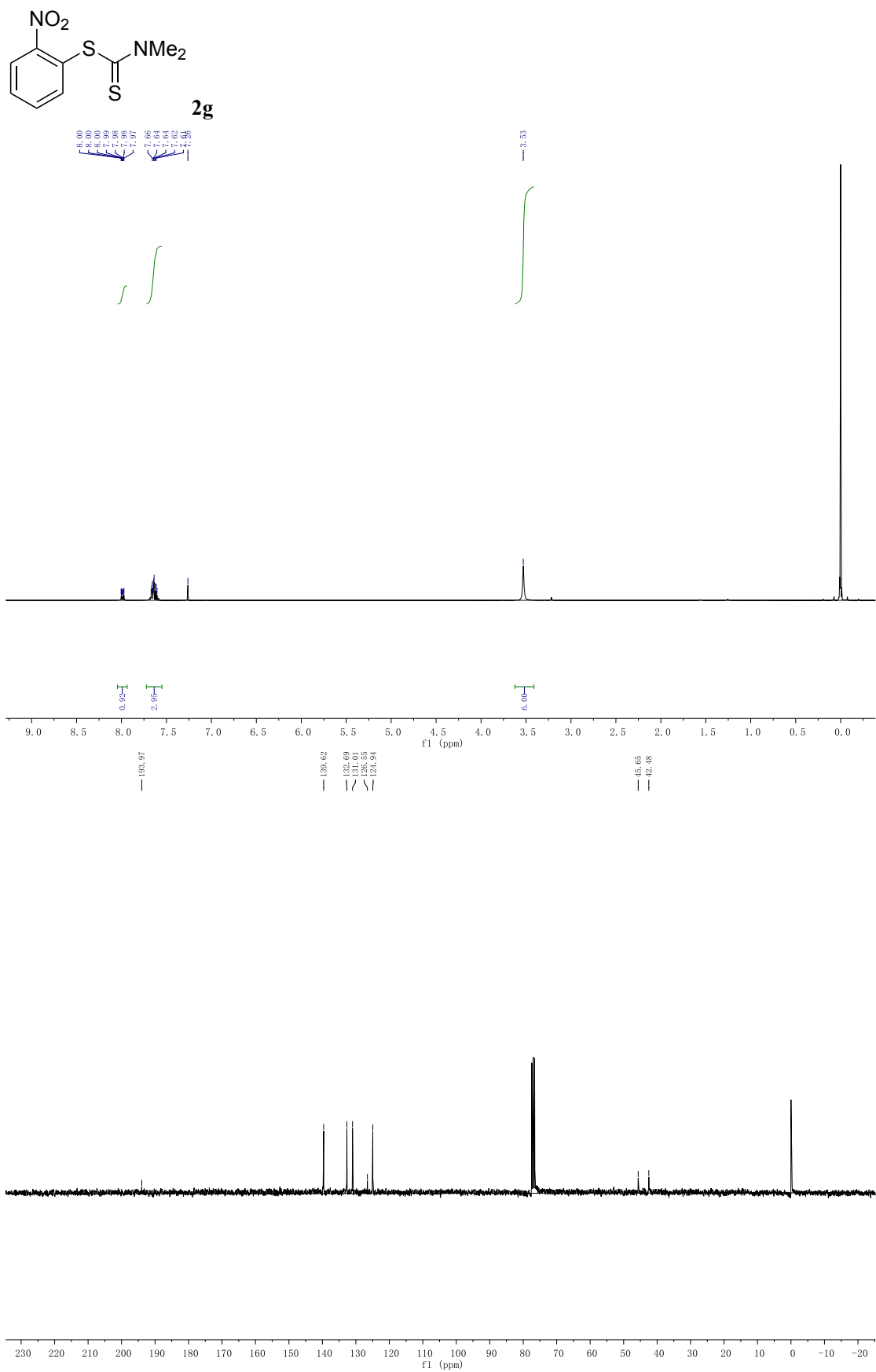
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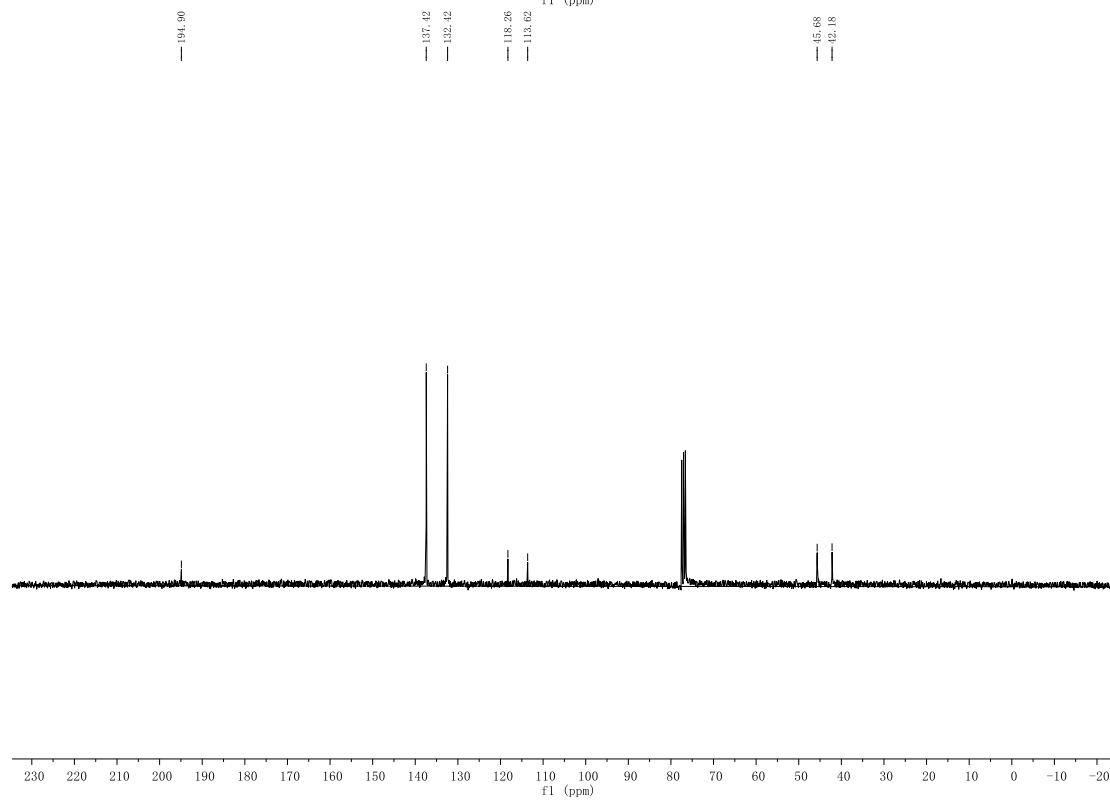
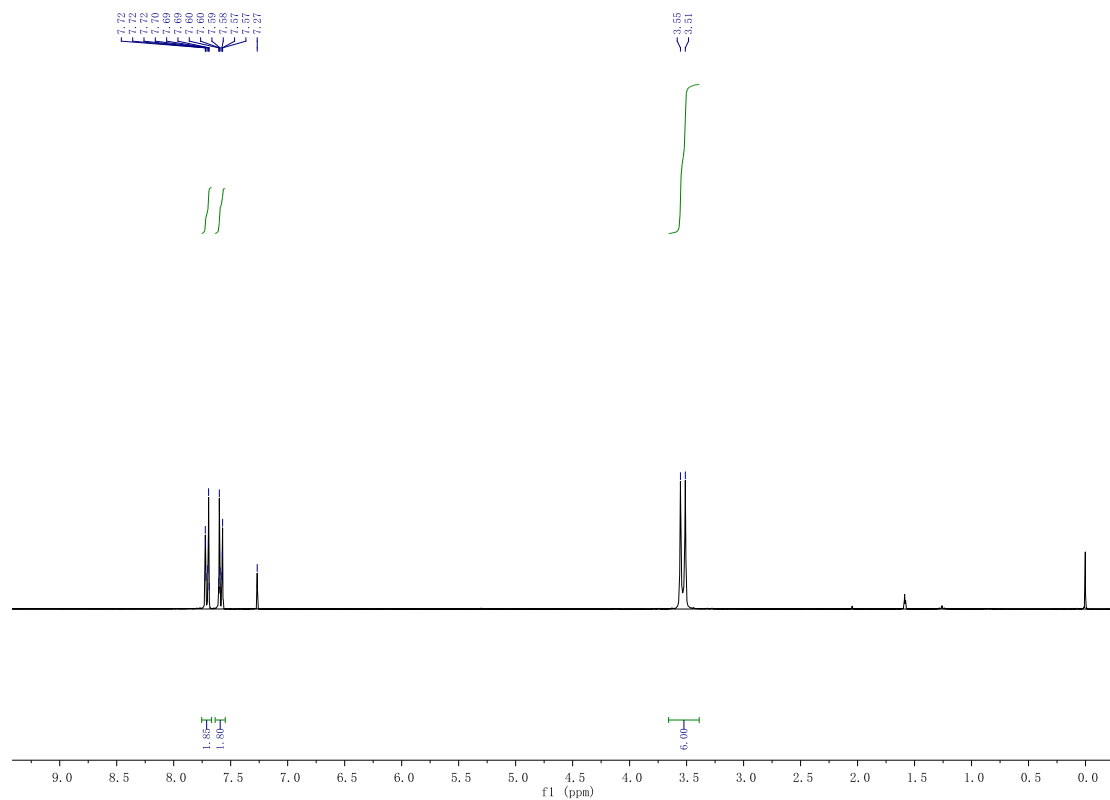
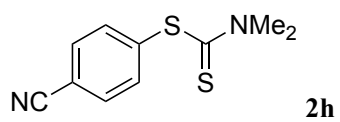
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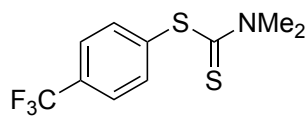
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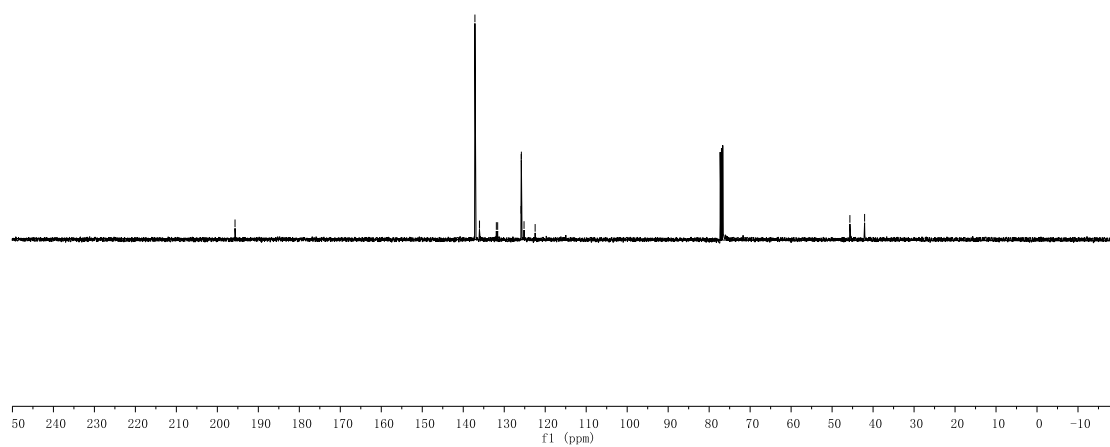
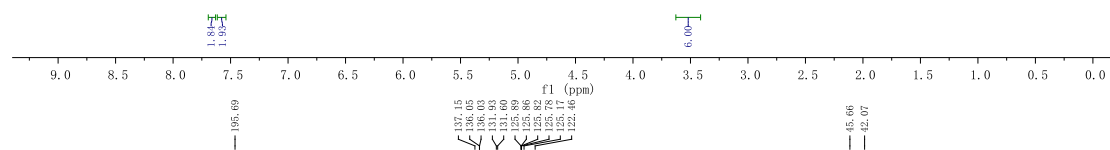
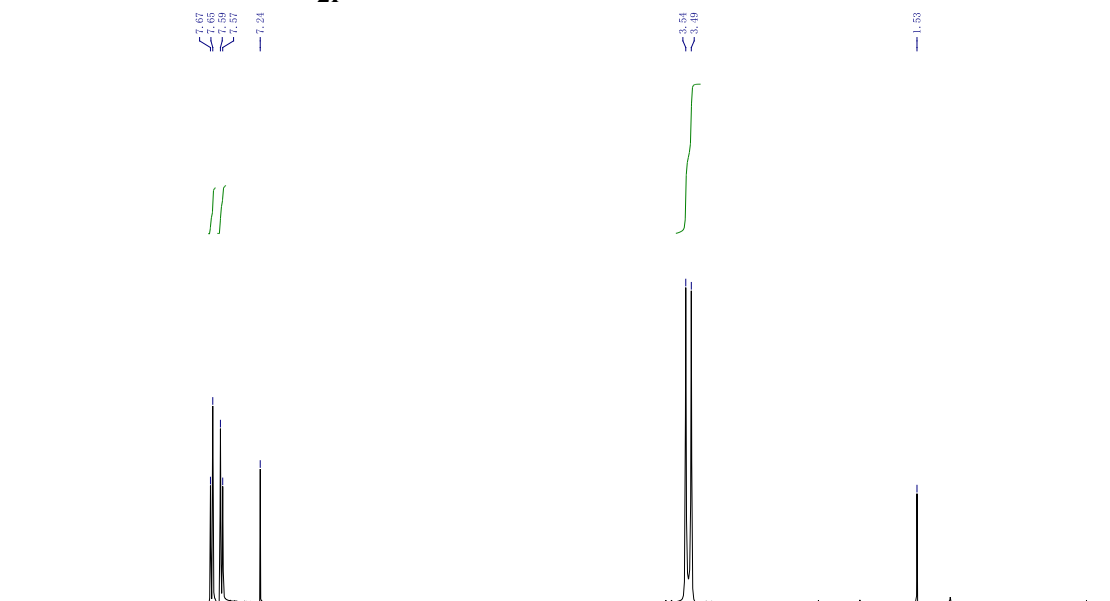
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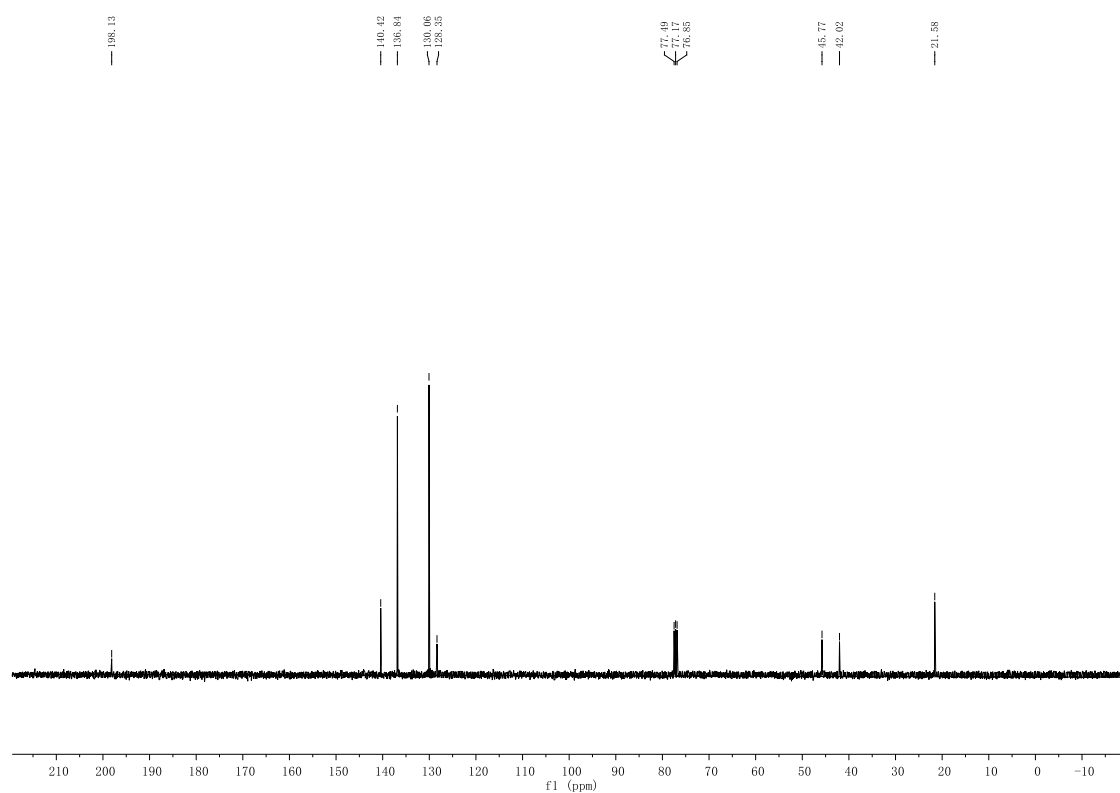
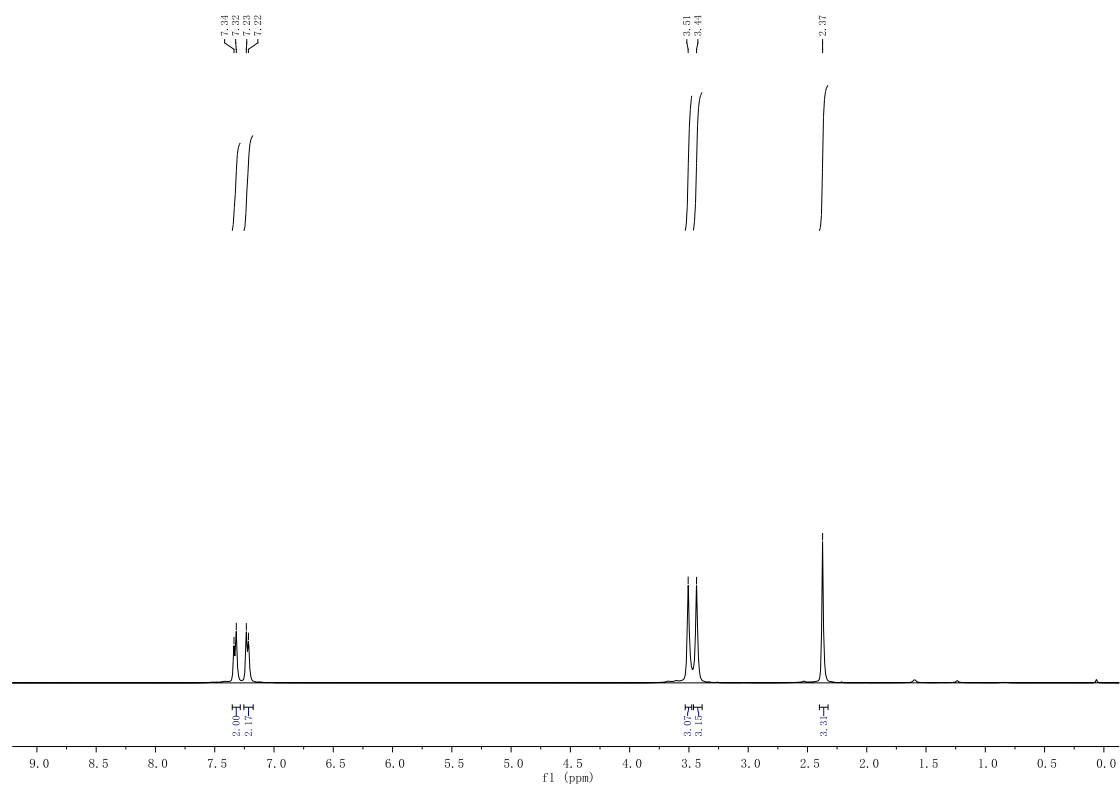
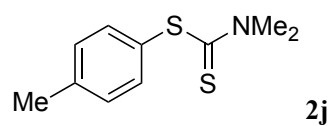
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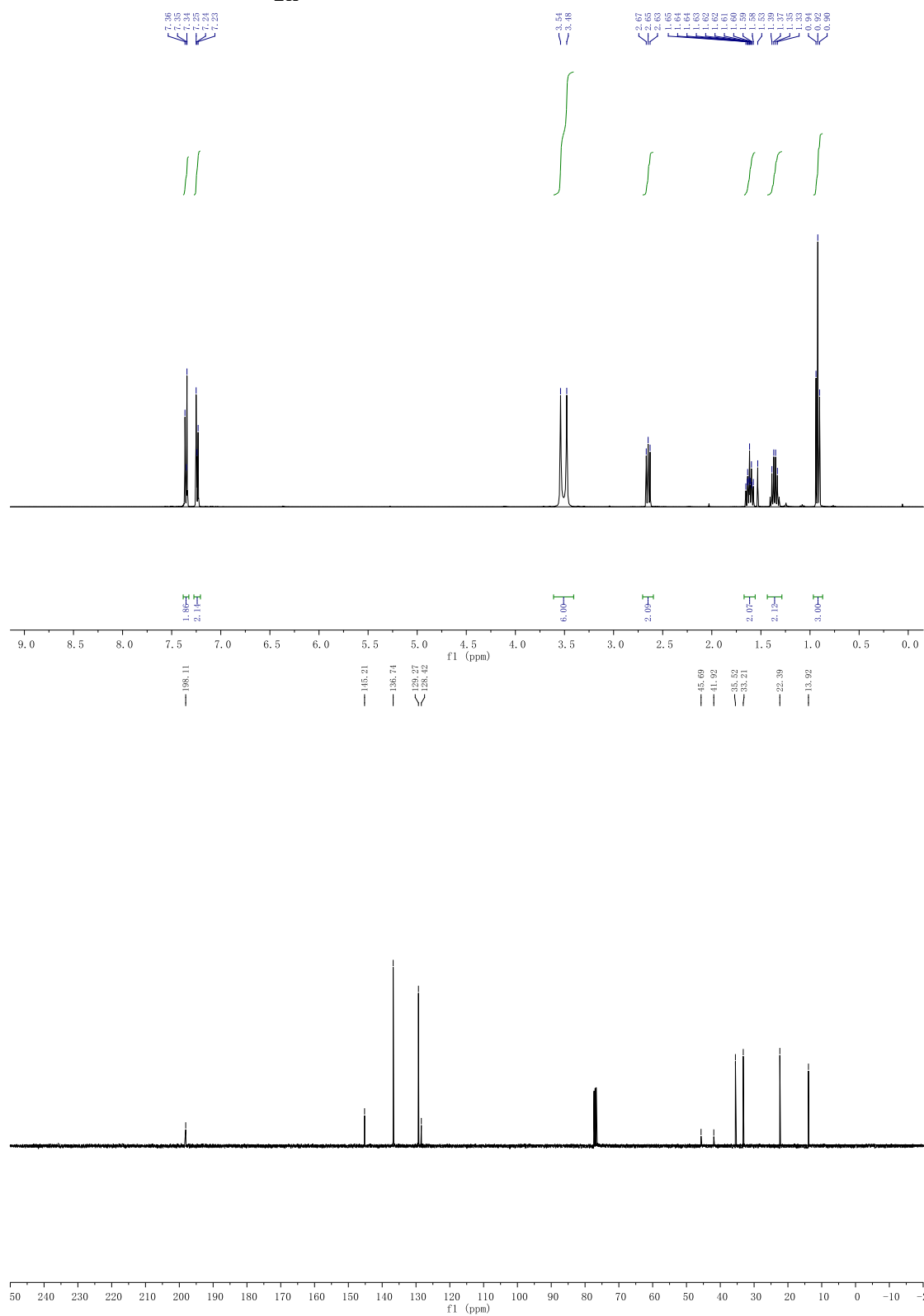
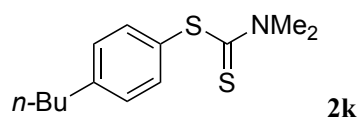


2i

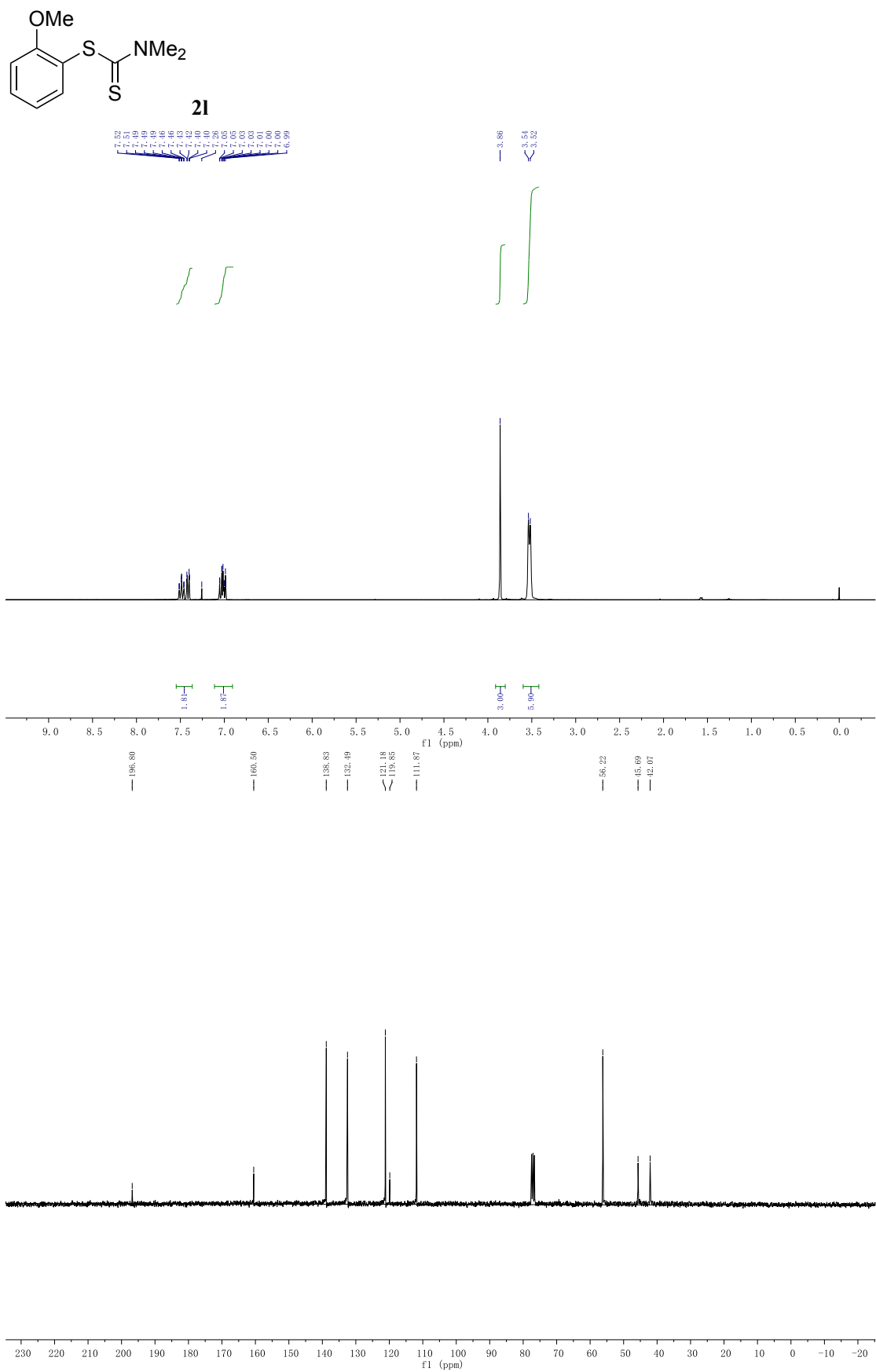


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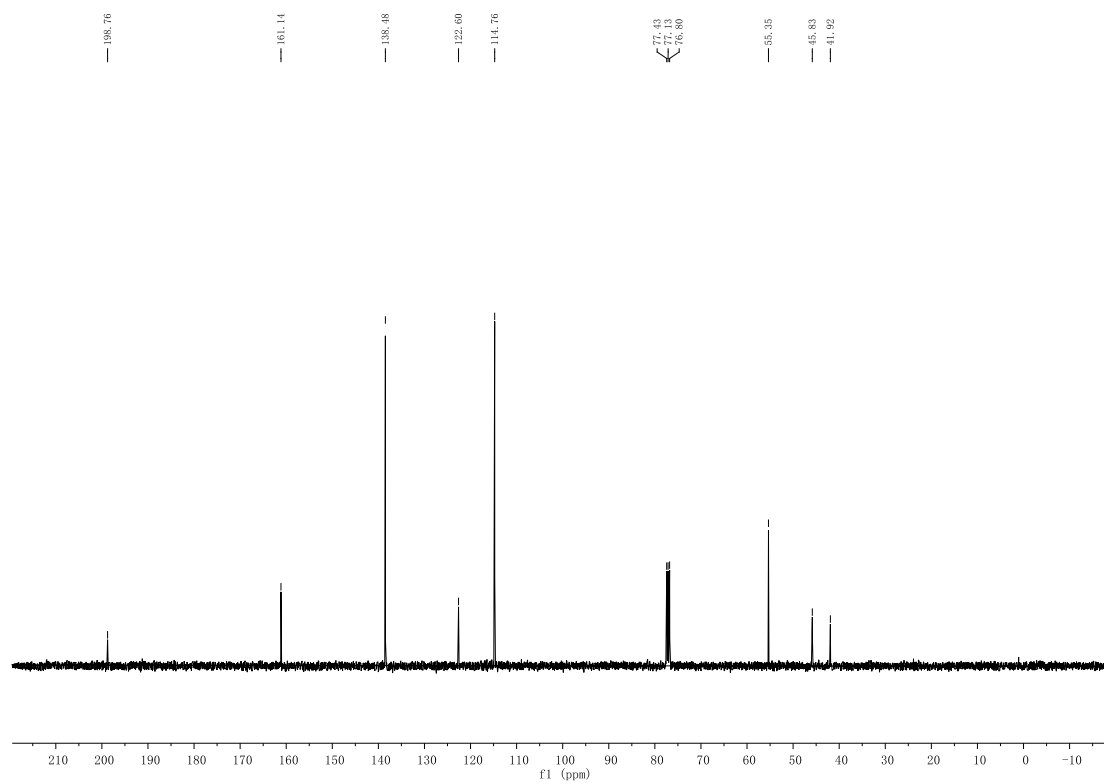
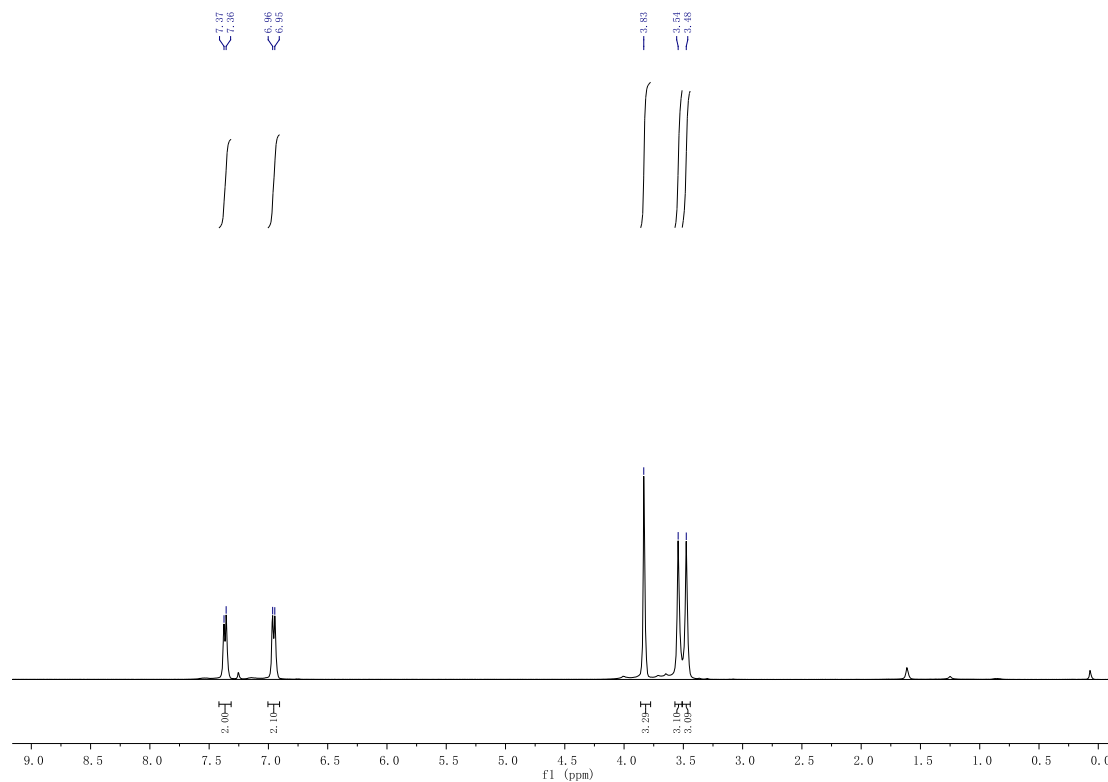
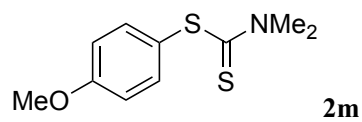




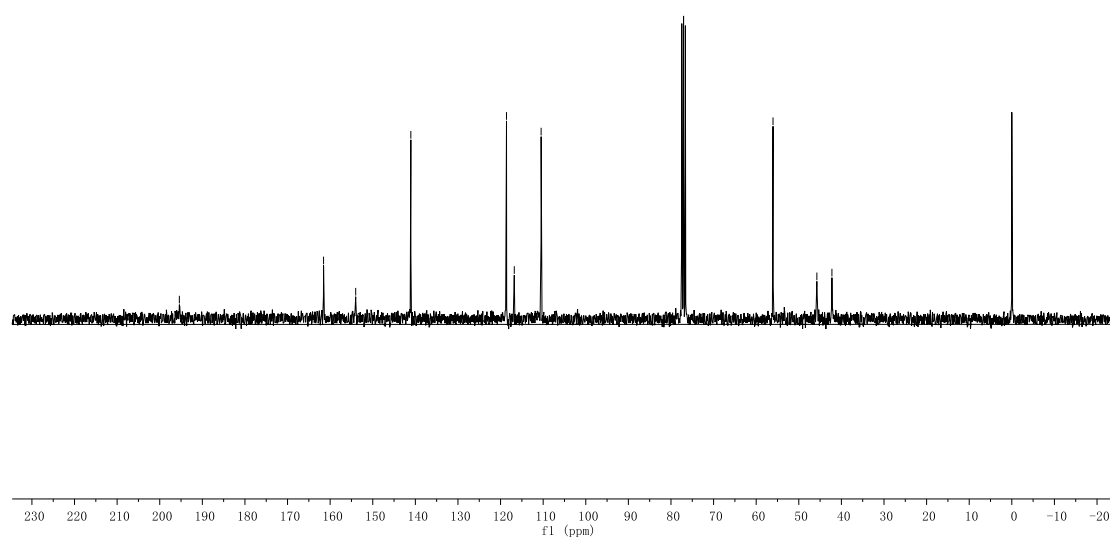
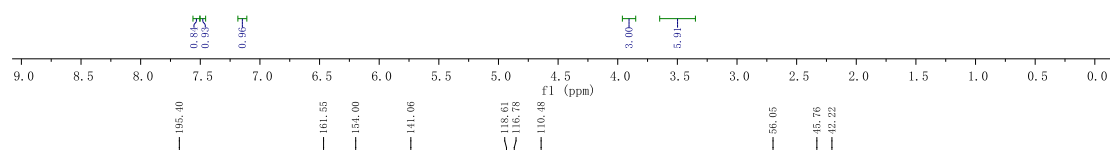
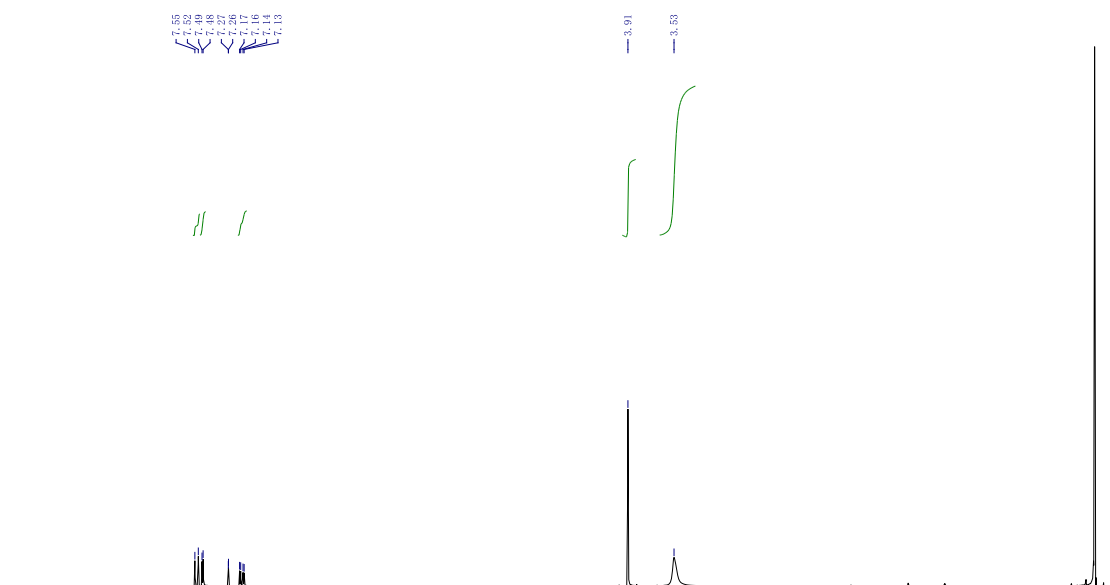
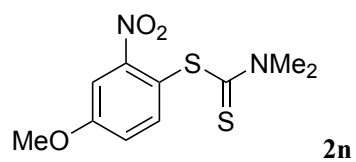
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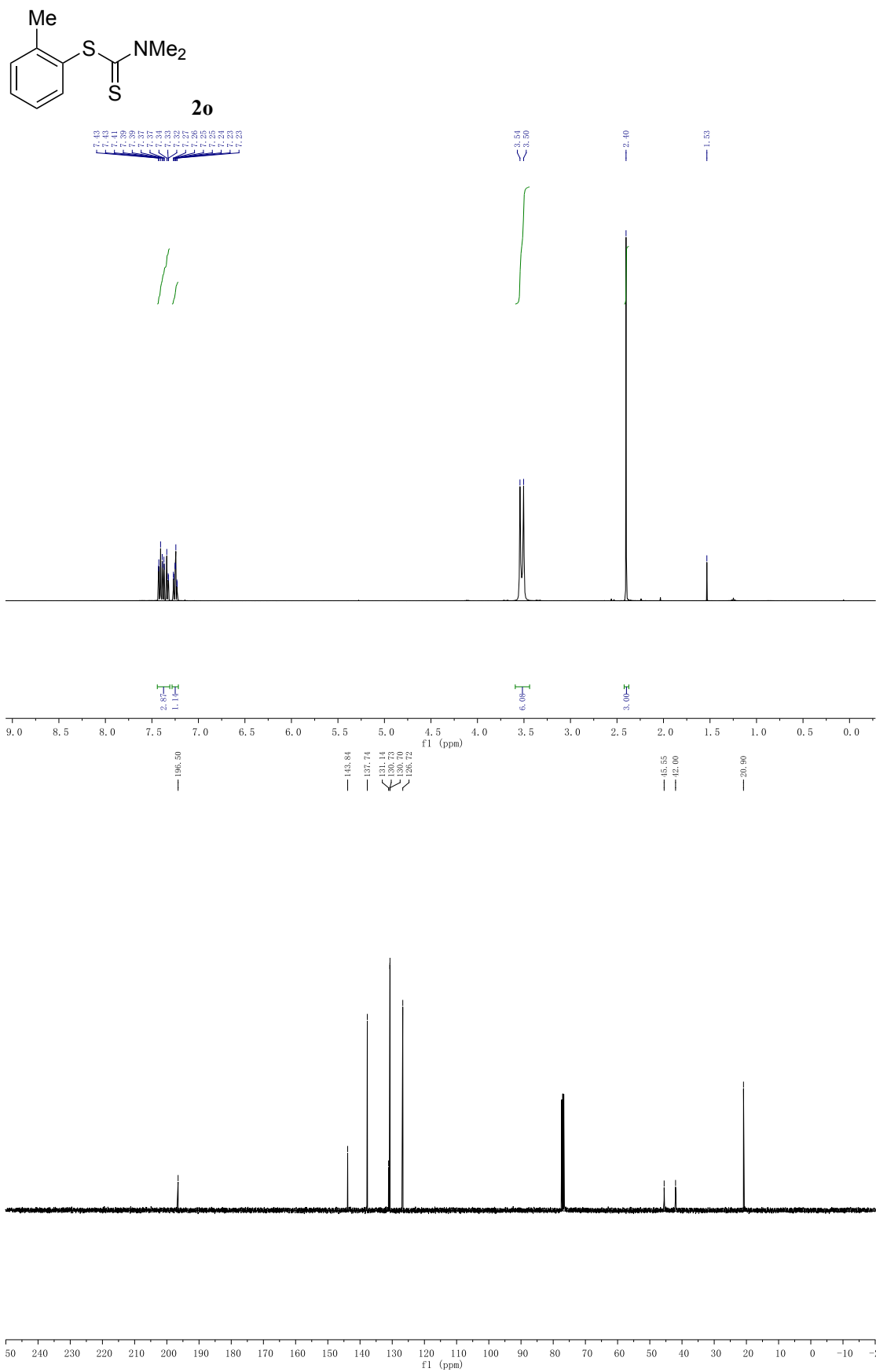
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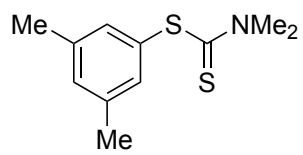
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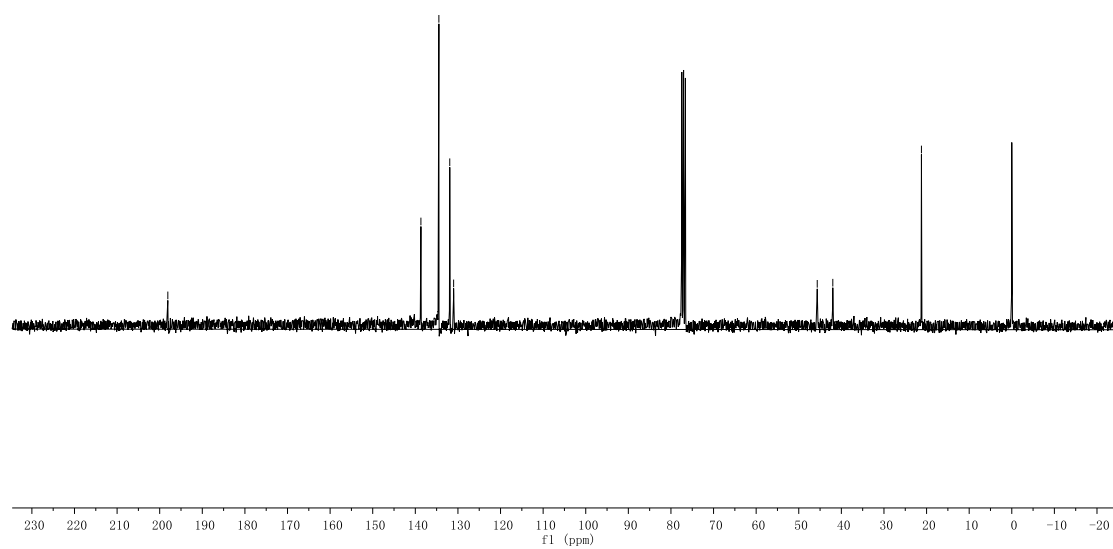
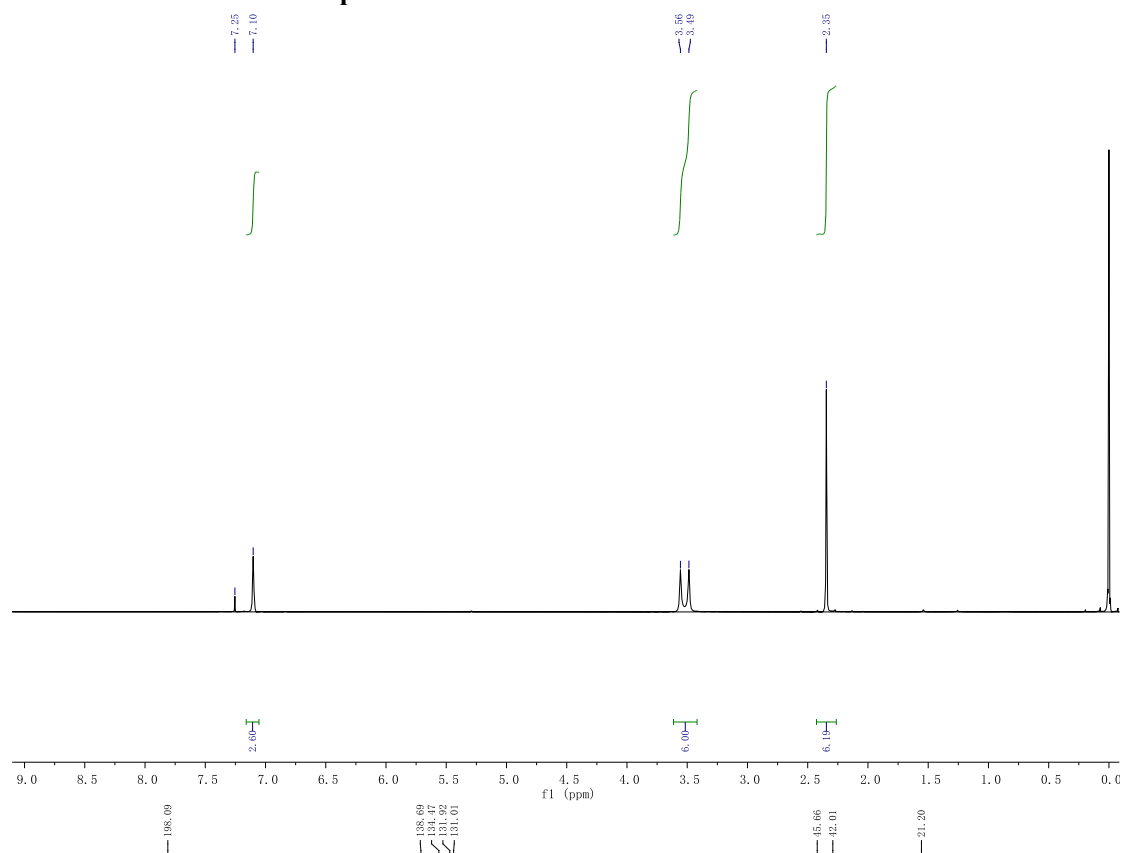
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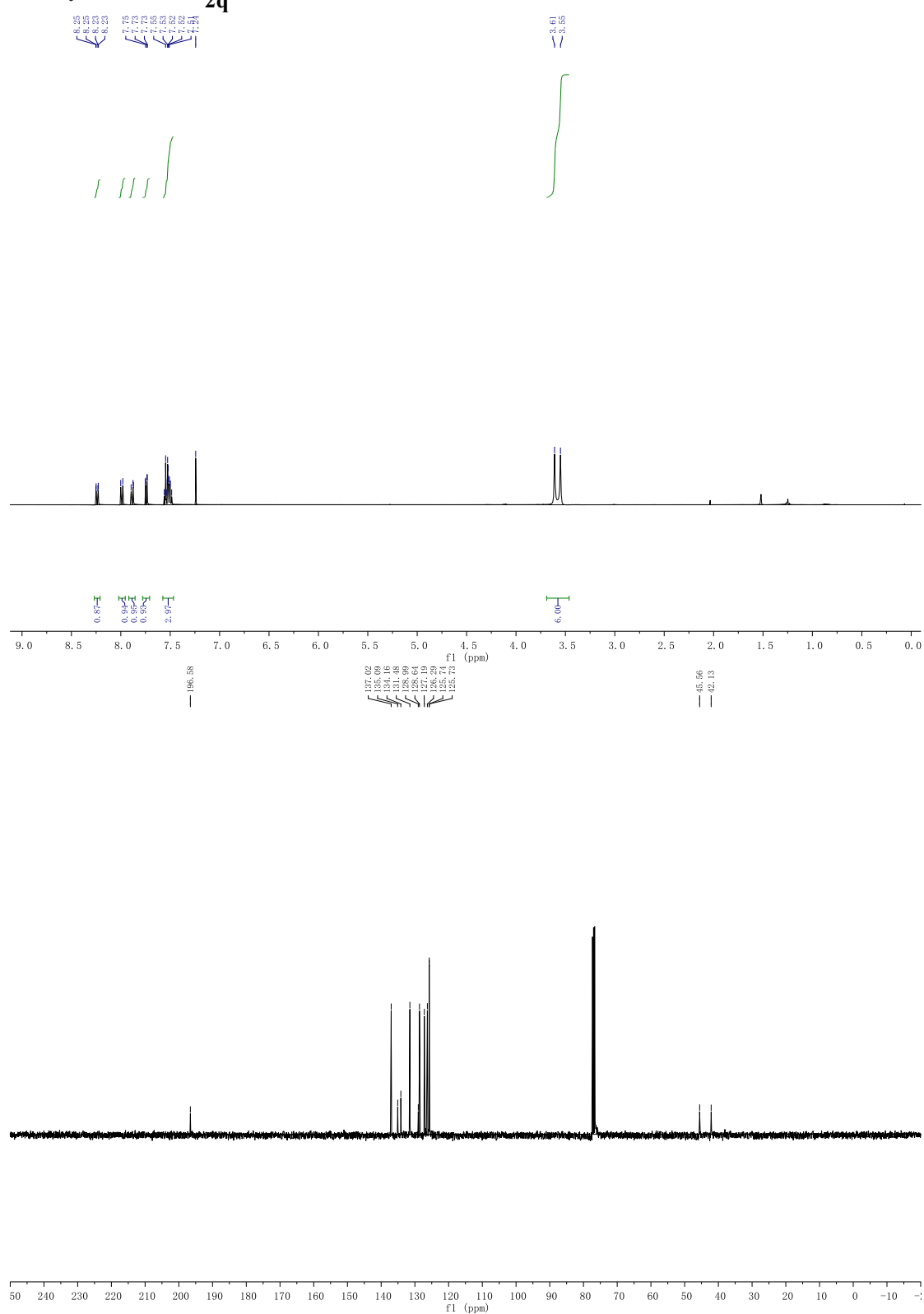
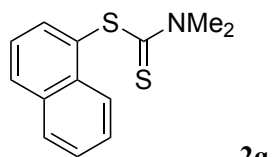
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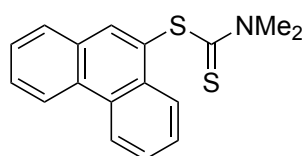
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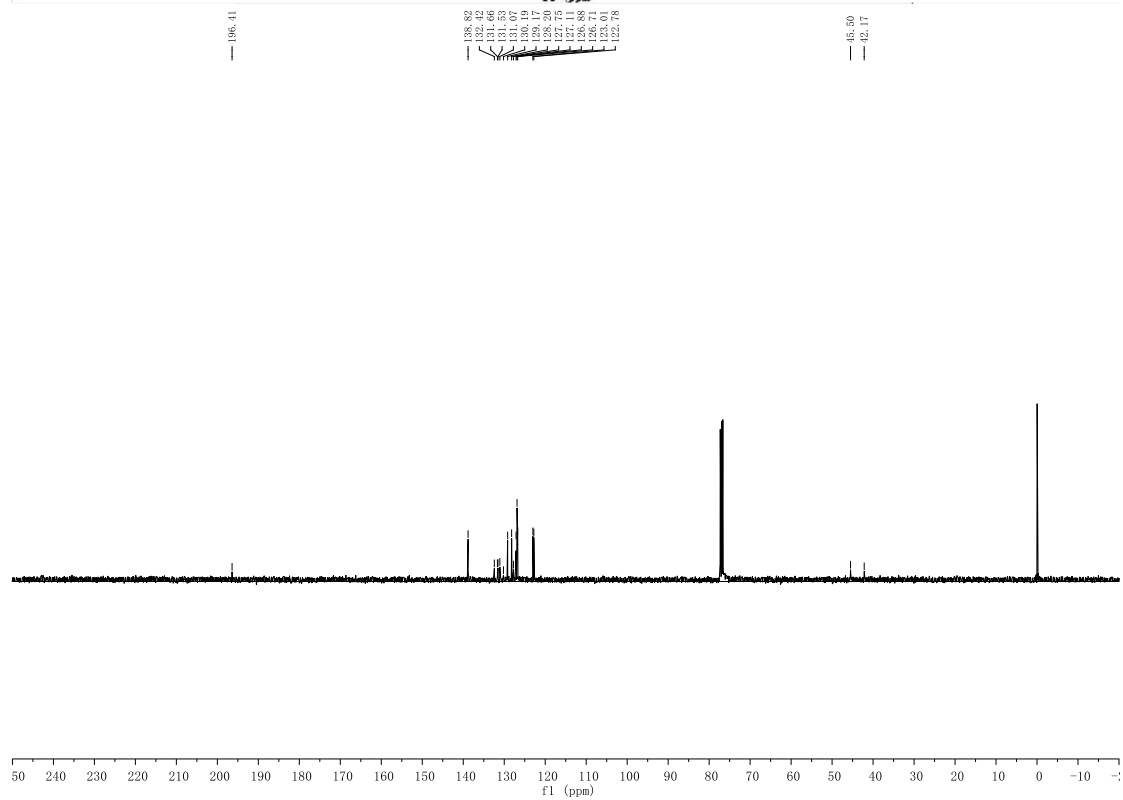
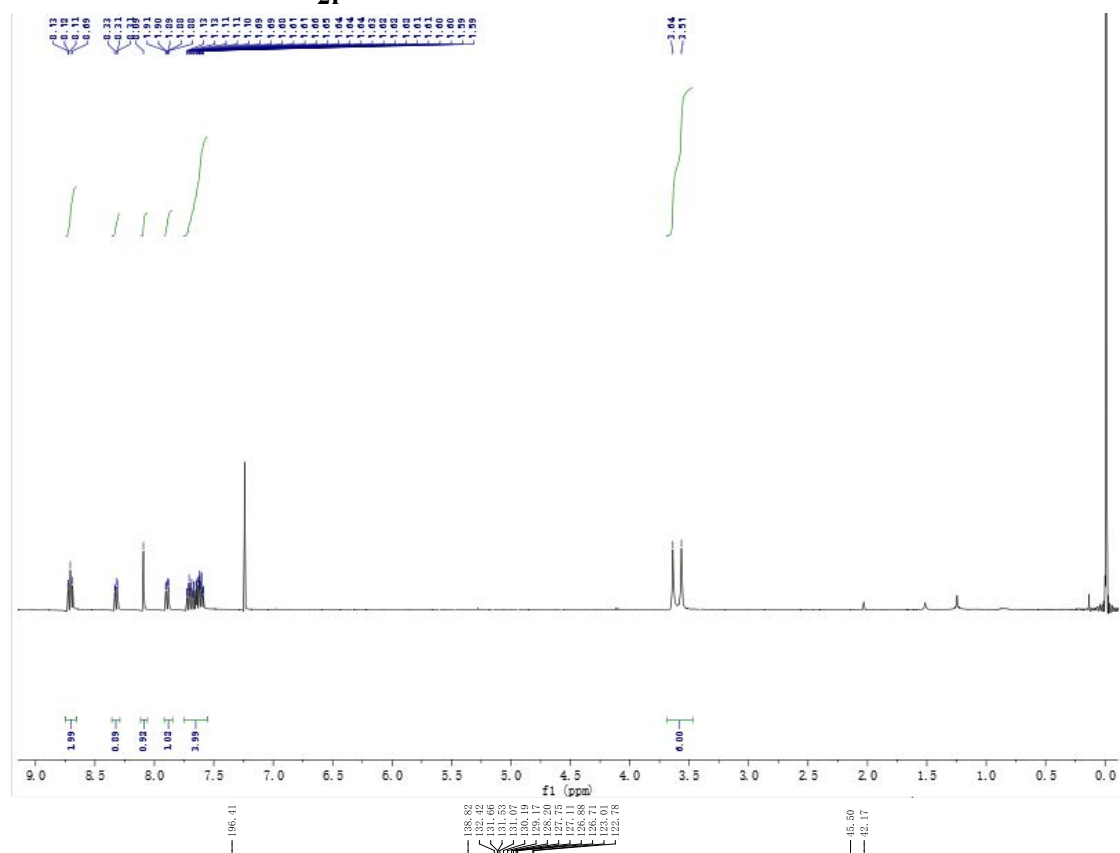
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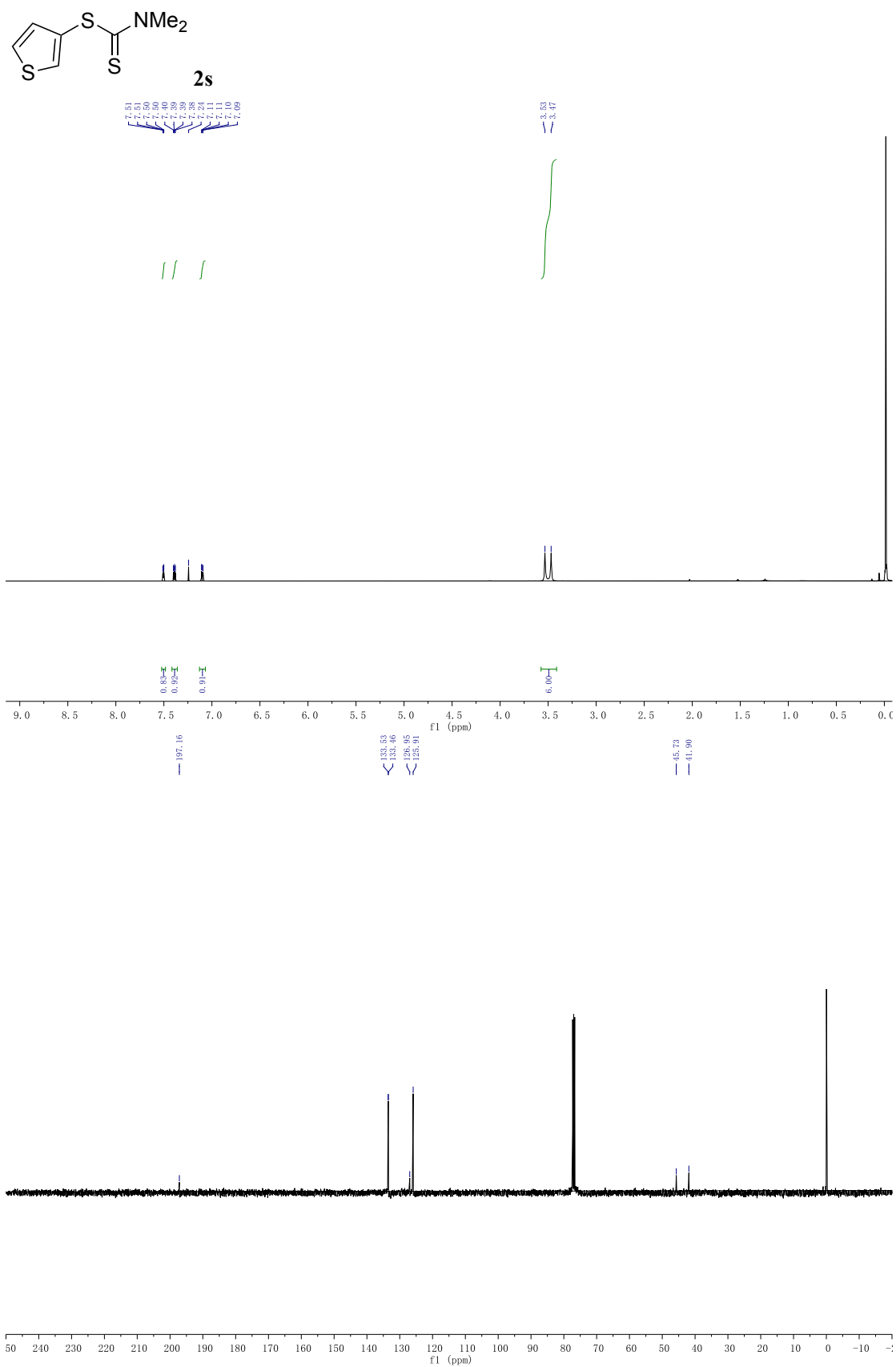
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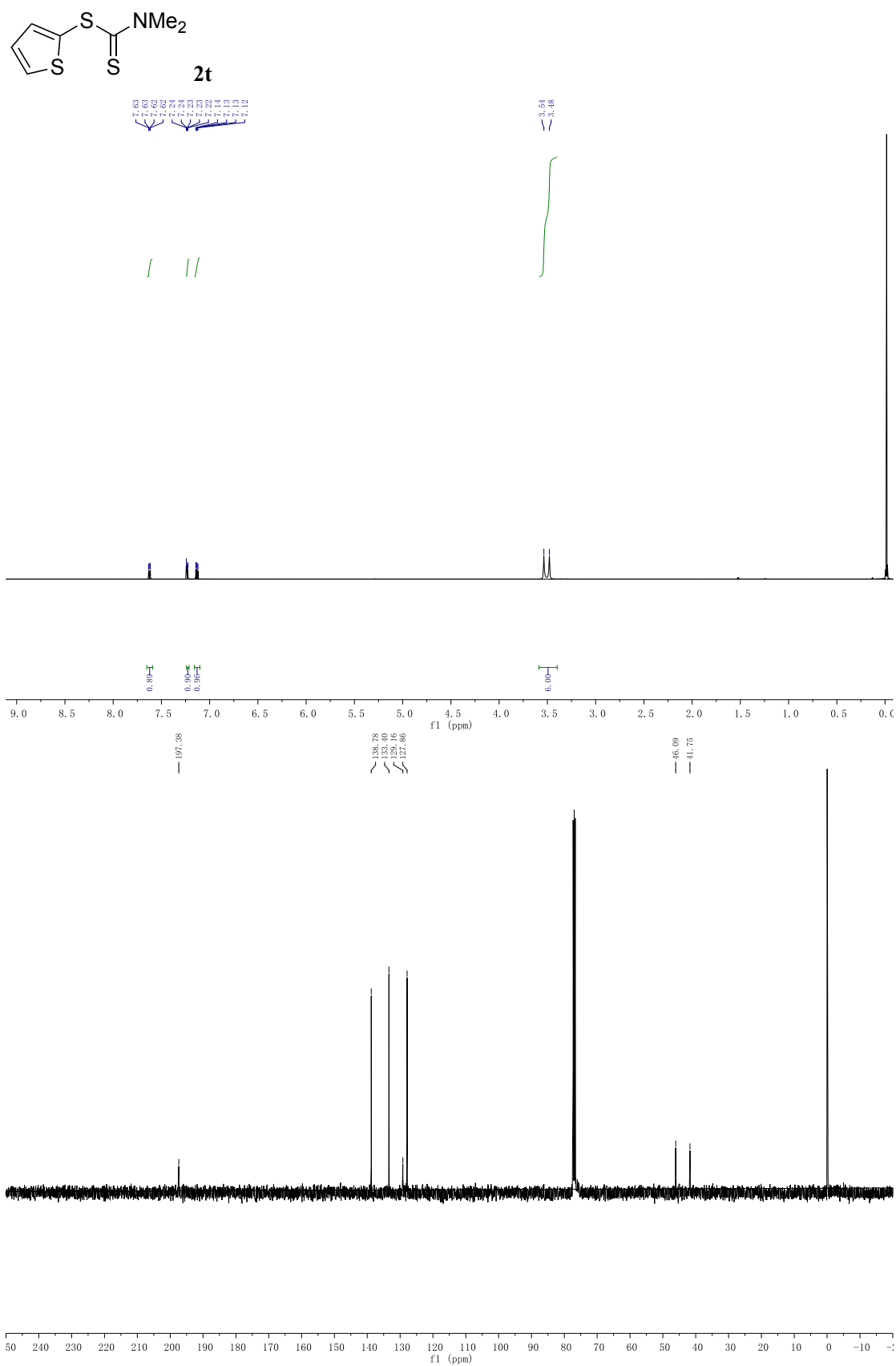
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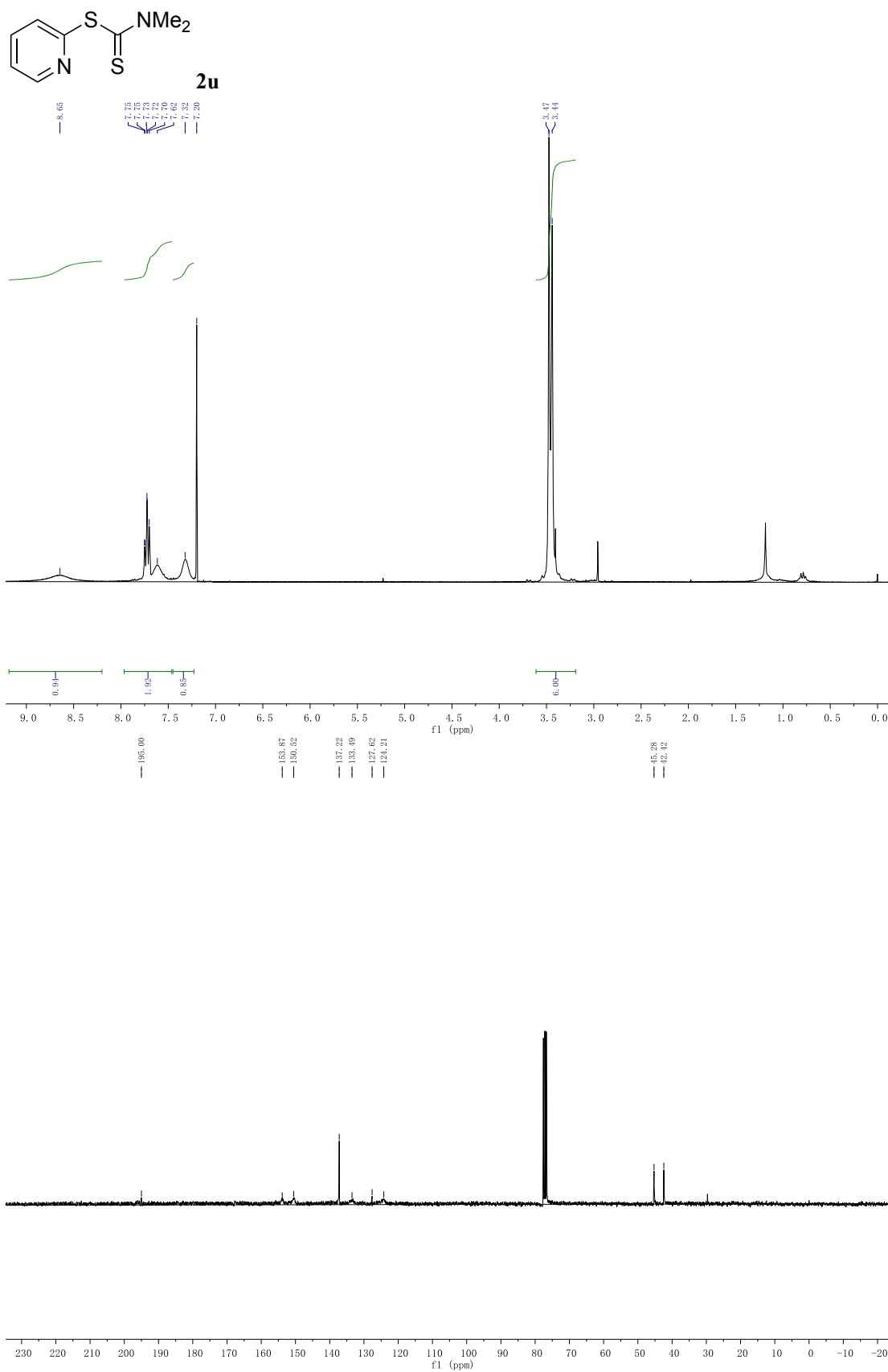


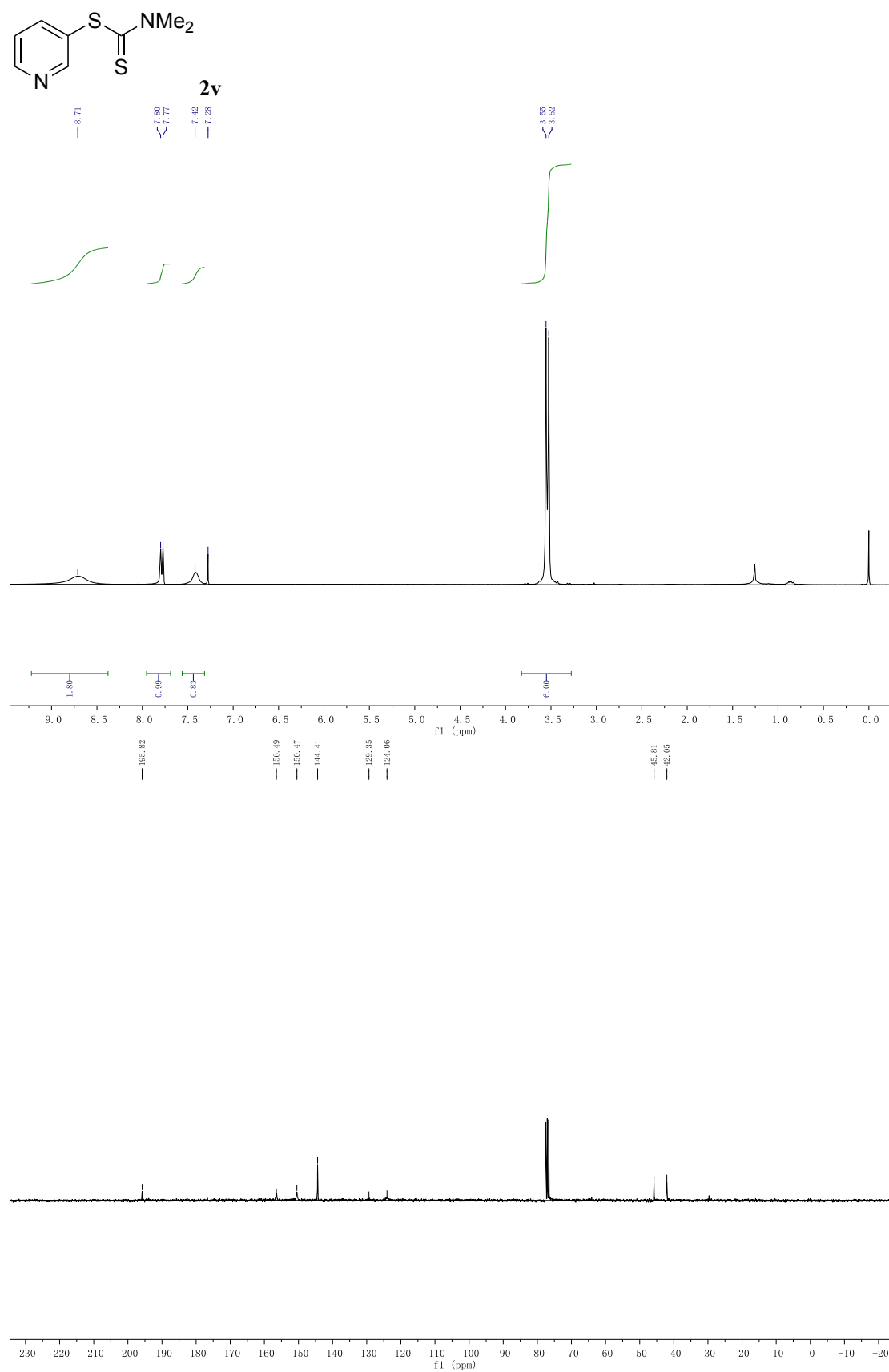
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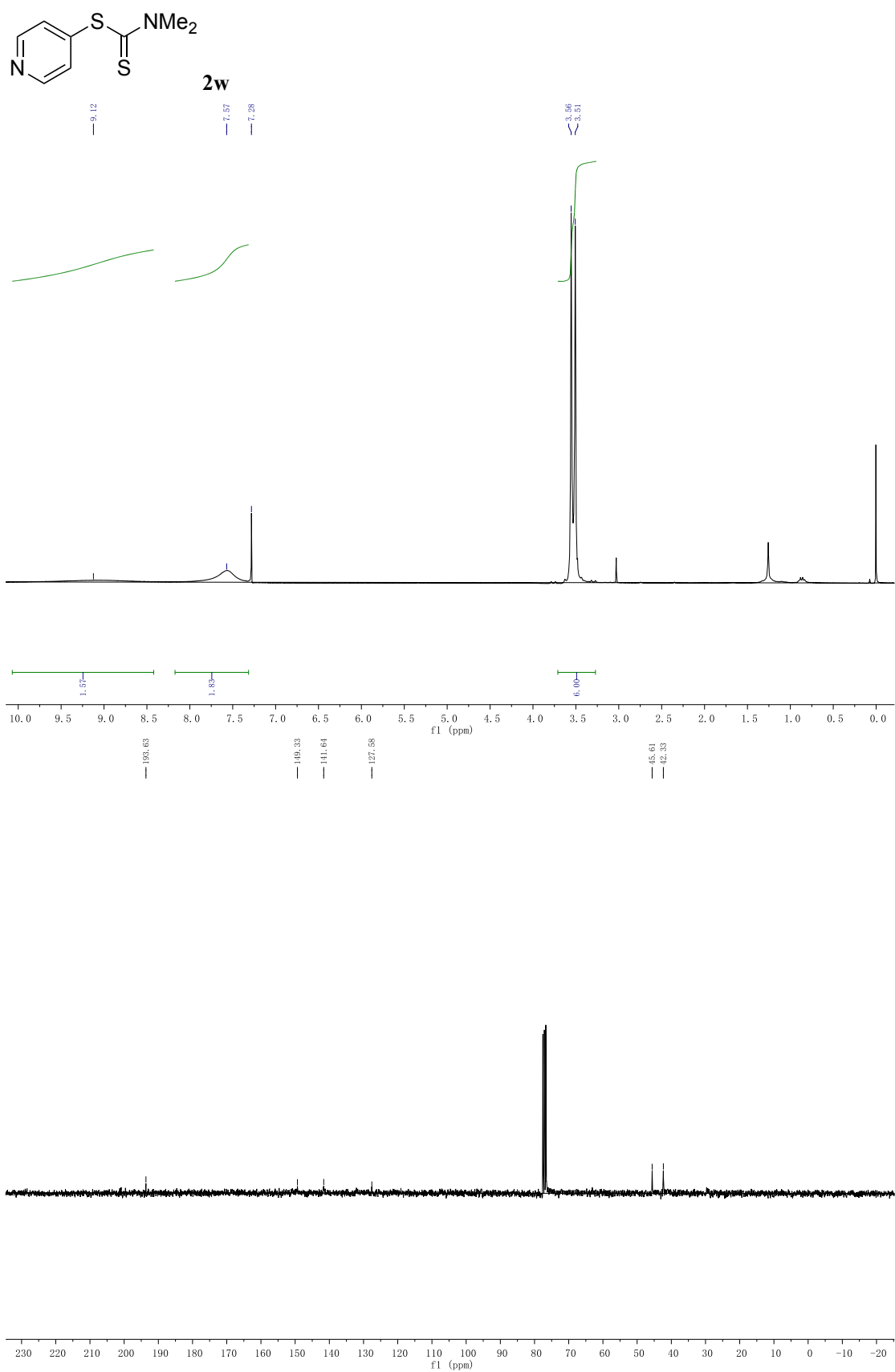
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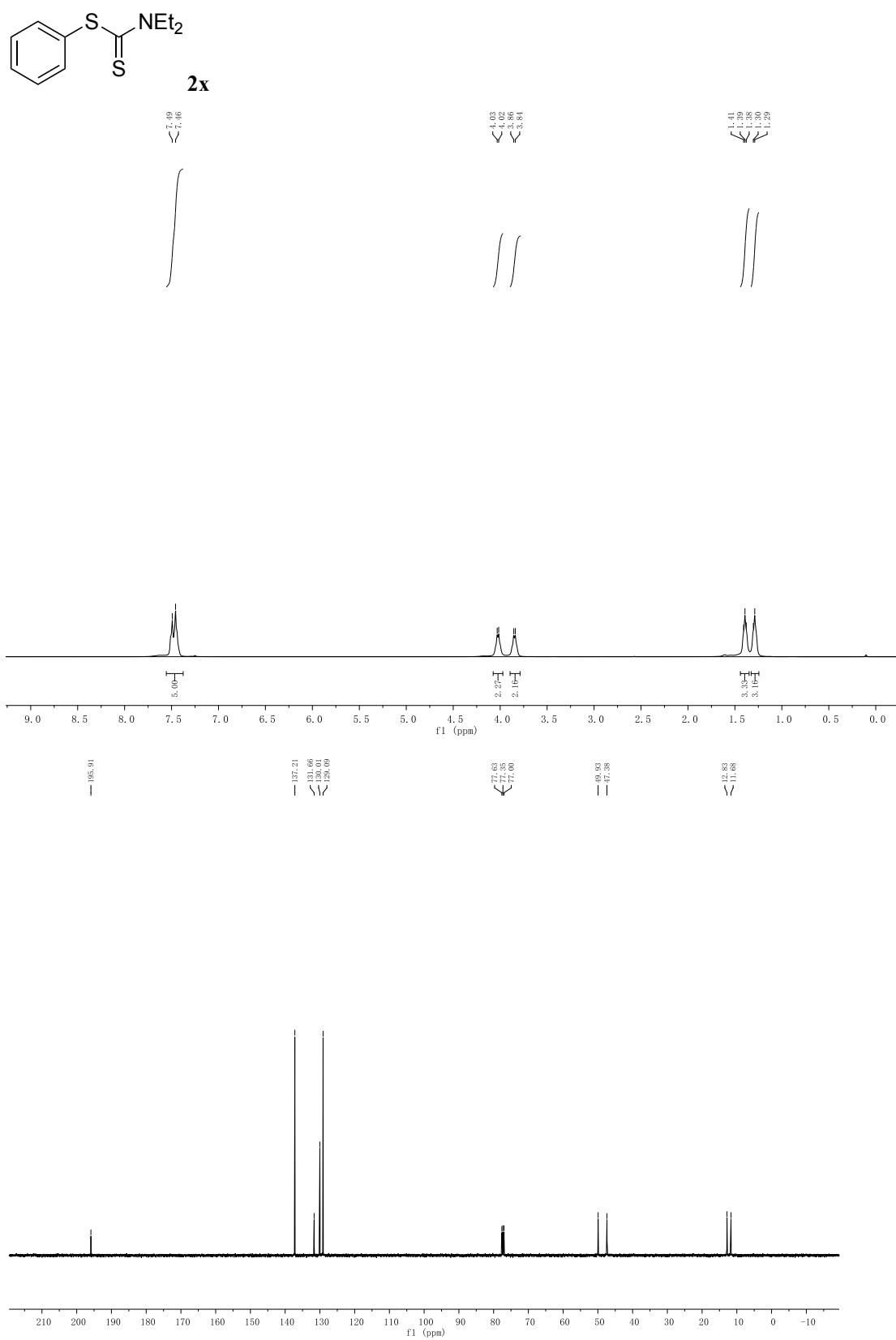


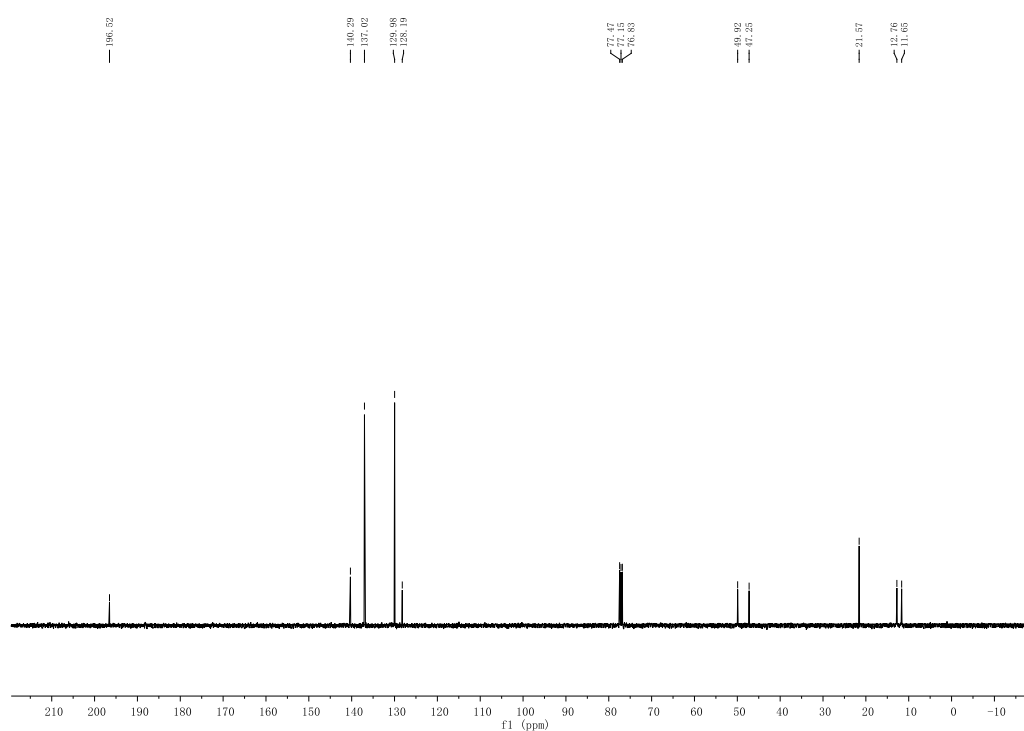
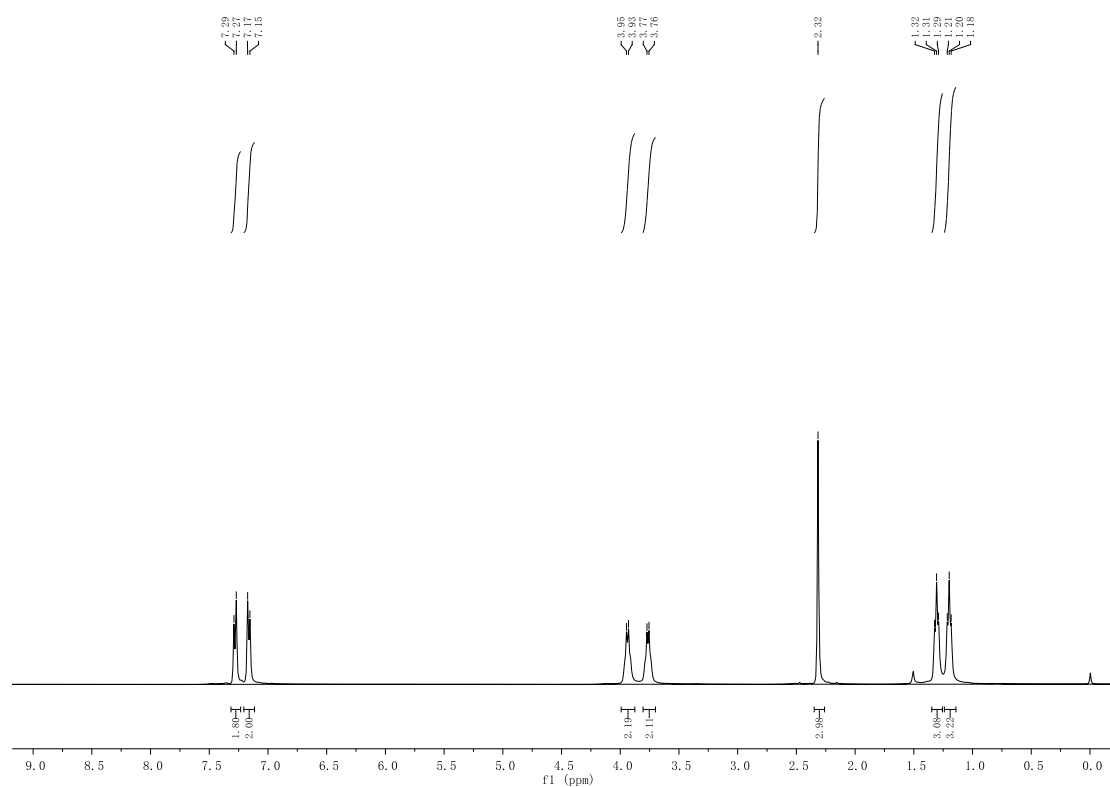
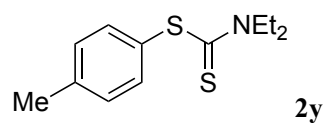




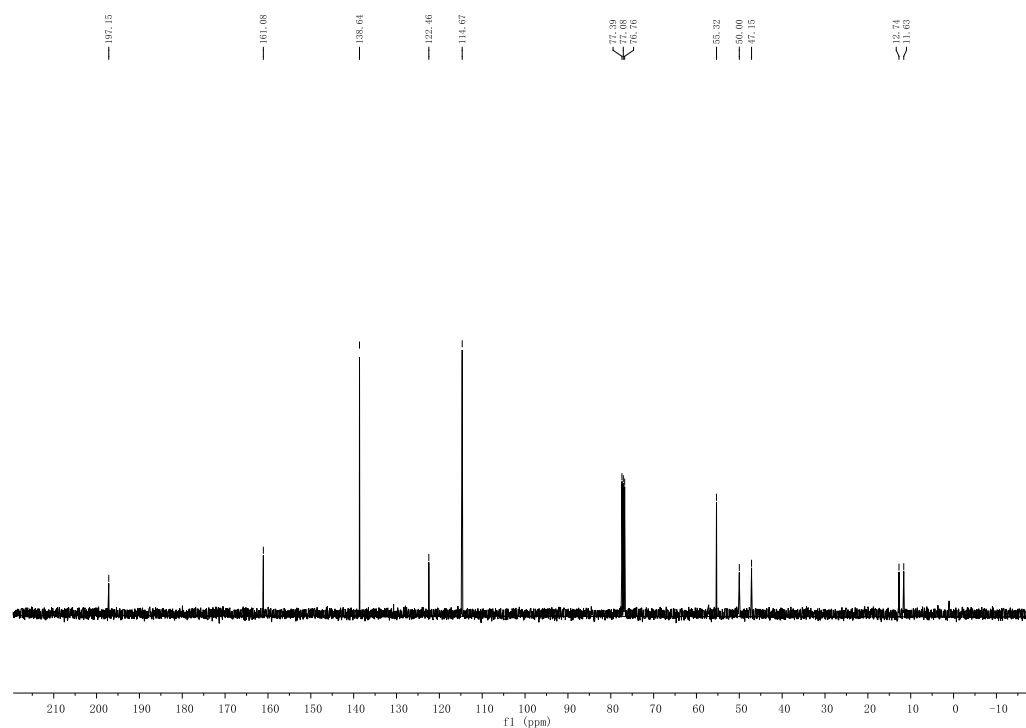
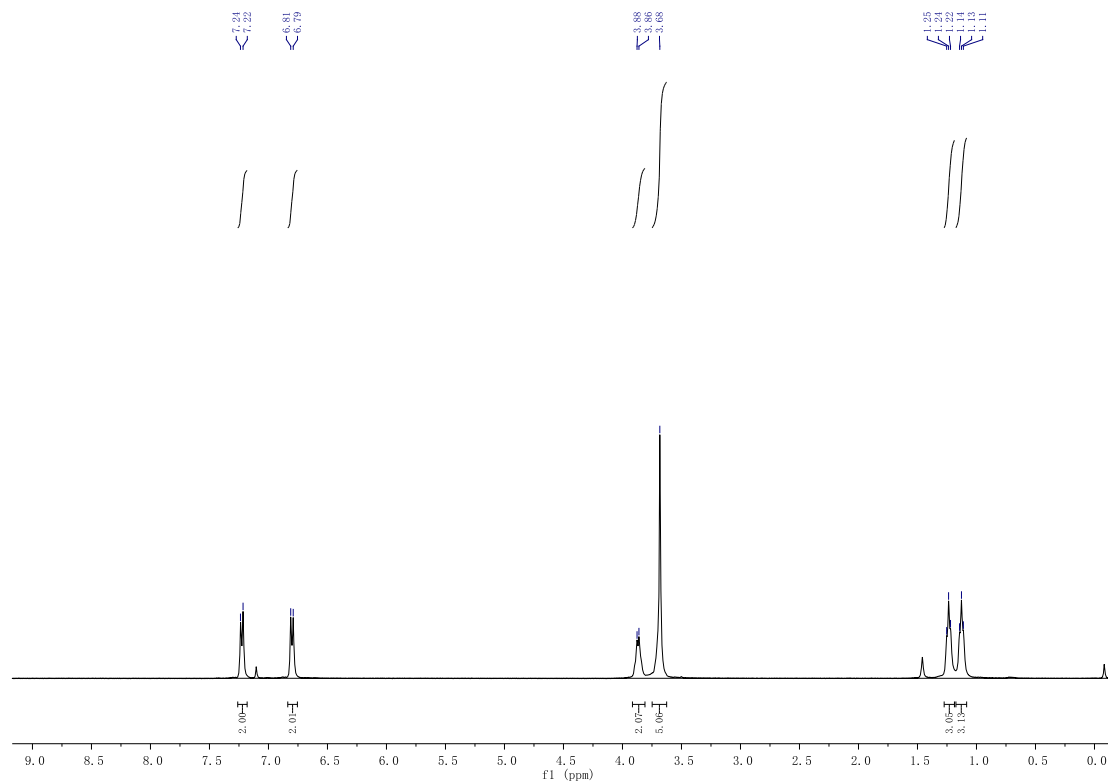
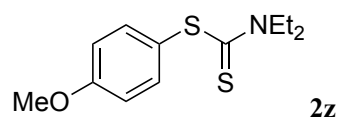
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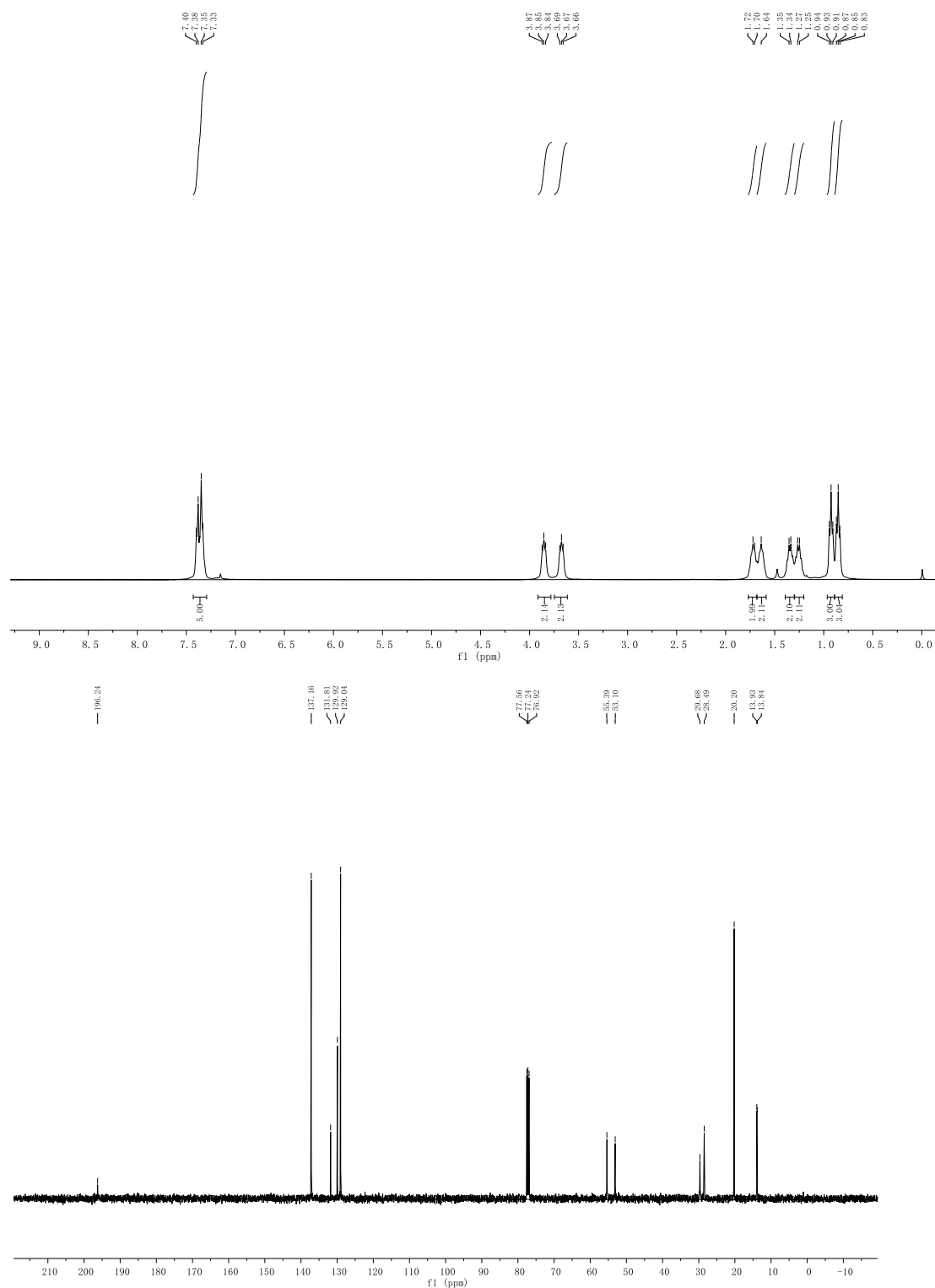
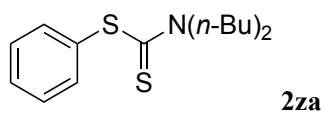


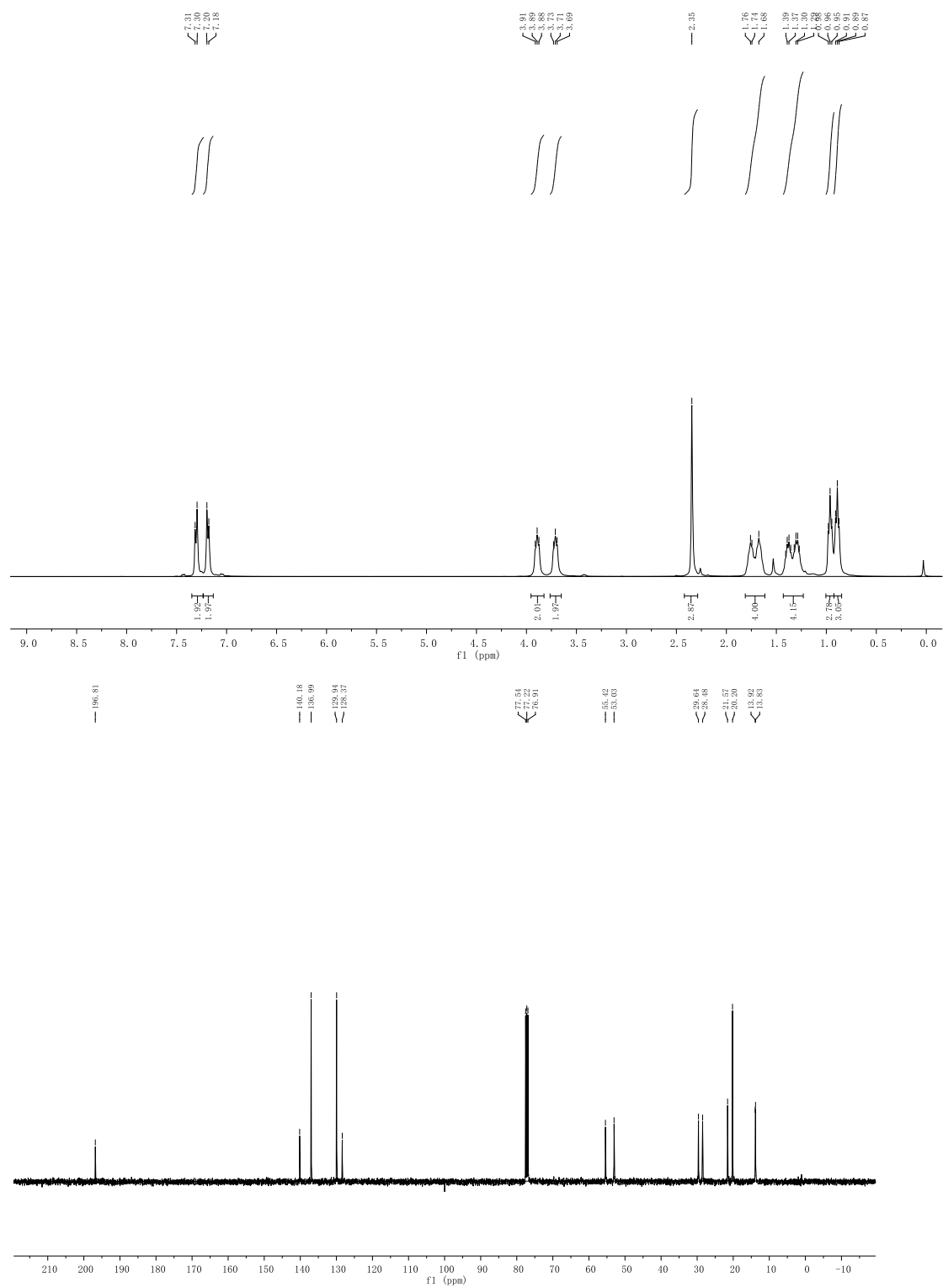
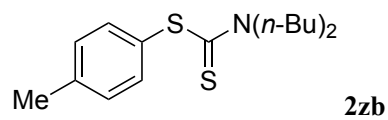




S37







S40

