

**SUPPORTING INFORMATION****Vicinal Diamination of Arenes with Domino Aryne  
Precursors**

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**S1.** General

**S2.** Preparation of sulfamides

**S3.** General procedure for 1,2-diamination with sulfamides

**S4.** Reaction of TPBT **1a** with furan

**S5.** LAH reduction of **3a**

**S6.** Preparation of TPBT **1b**

**S7.** General procedure for the bromination of benzene-1,3-diol

**S8.** General procedure for the preparation of TPBT **1c-1i**

**S9.** Reaction of TPBT **1b-1i** with sulfamide **2a**

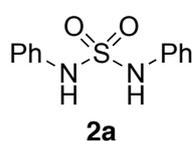
**S10.** Regioselective study with TPBTs **1h** and **1i**

**S11.** <sup>1</sup>H and <sup>13</sup>C NMR spectra

**General:** All reagents were obtained from Adamas, Aladin, Accela, or Acros and used without further purification unless otherwise noted. The products were purified by column chromatography with Huanghai Silica Gel 50-75  $\mu\text{m}$ , ultrapure silica gel.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded using a Bruker 500, a Varian 400, or a Varian 600 spectrometer. IR spectra were measured on a Nicolet iS50 FT-IR spectrometer using KBr plates. The high-resolution mass spectra (HRMS) were recorded on Waters SYNAPT G3 spectrometer (ESI).

### Preparation of sulfamides:

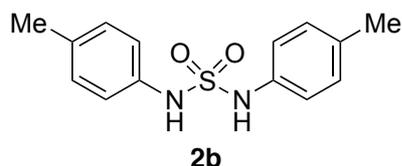
**Preparation of *N,N'*-diphenylsulfamide (2a):** *N,N'*-diphenylsulfamide (**2a**) was prepared



according to literature procedure.<sup>1</sup> To a solution of aniline (20.0 g, 214 mmol, 6.0 equiv) in anhydrous DCM (60 mL) at 0 °C was added slowly sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) (4.8 g, 36 mmol). The resulting mixture was stirred

overnight at room temperature. DCM (100 mL) was added to the solution, and the organic layer was washed by 5% aqueous HCl (50 mL x 3) and brine (30 mL). The resulting organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 4.8 g (54%) of **2a** as a white solid. Mp: 108.5-110 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (t,  $J = 7.5$  Hz, 4H), 7.13 (t,  $J = 7.5$  Hz, 2H), 7.07 (d,  $J = 7.5$  Hz, 4H), 6.83 (bs, 1H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.5, 129.6, 125.6, 121.4 ppm; IR (thin film) 3278, 1601, 1498, 1421, 1345, 1160, 949, 754, 700, 570 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{12}\text{H}_{12}\text{NaN}_2\text{O}_2\text{S}]^+$ , 271.0512; found, 271.0516.

**Preparation of sulfamide 2b:** To a solution of 4-methylaniline (2.0 g, 18.6 mmol, 3.0 equiv)

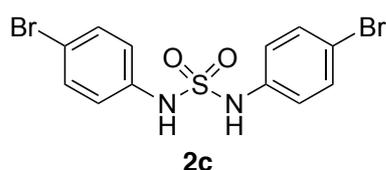


and pyridine (3.0 ml) in anhydrous DCM (30 mL) at -40 °C was added slowly sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) (0.5 ml, 6.2 mmol). The resulting mixture was stirred overnight at room

temperature. The organic layer was washed by 10% aqueous HCl (50 mL x 2) and brine (20 mL). The resulting organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 685 mg (40%) of **2b** as a white solid. Mp: 87-88 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (d,  $J = 8.0$  Hz, 4H), 6.97 (d,

$J = 8.0$  Hz, 4H), 6.49 (bs, 2H), 2.32 (s, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  135.5, 133.8, 130.1, 122.0, 21.0 ppm; IR (thin film) 3273, 3092, 2921, 2663, 1883, 1614, 1510, 1324, 1217, 1159, 958 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{SNa}]^+$ , 299.0825; found, 299.0829.

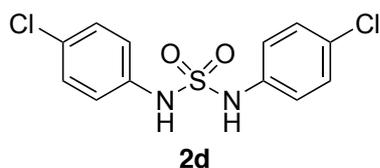
**Preparation of sulfamide 2c:** To a solution of 4-bromoaniline (3.0 g, 17.4 mmol, 6.0 equiv)



and pyridine (3.0 ml) in anhydrous DCM (30 mL) at  $-40$  °C was added slowly sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) (0.48 ml, 5.8 mmol). The resulting mixture was stirred overnight at room temperature. The organic layer was washed by 10% aqueous

HCl (50 mL x 2) and brine (20 mL). The resulting organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 1.9 g (80%) of **2c** as a white solid. Mp:  $120$ - $122$  °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J = 9.0$  Hz, 4H), 6.95 (d,  $J = 9.0$  Hz, 4H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  135.2, 132.8, 123.0, 119.0 ppm; IR (thin film) 3551, 3414, 3307, 2926, 2847, 1869, 1730, 1617, 1396, 1291, 886 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2\text{Br}_2\text{SNa}]^+$ , 426.8722; found, 426.8718.

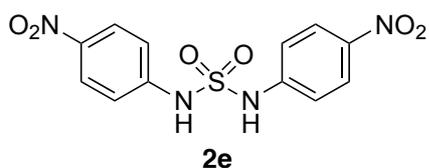
**Preparation of sulfamide 2d:** To a solution of 4-chloroaniline (1.0 g, 7.7 mmol, 3.0 equiv)



and pyridine (1.5 ml) in anhydrous DCM (20 mL) at  $-40$  °C was added slowly sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) (0.28 ml, 2.6 mmol). The resulting mixture was stirred overnight at room

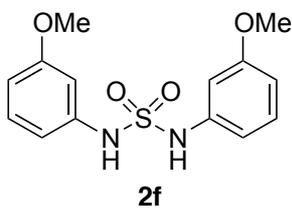
temperature. The organic layer was washed by 10% aqueous HCl (30 mL x 2) and brine (10 mL). The resulting organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 412 mg (50%) of **2d** as a white solid. Mp:  $113$ - $115$  °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (d,  $J = 8.5$  Hz, 4H), 7.01 (d,  $J = 8.5$  Hz, 4H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  134.7, 131.5, 129.9, 122.9 ppm; IR (thin film) 3551, 3414, 3233, 2960, 2926, 2855, 1617, 1334, 1186, 1016 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl}_2\text{SNa}]^+$ , 338.9732; found, 338.9735.

**Preparation of sulfamide 2e:** To a solution of 4-nitroaniline (1.0 g, 7.2 mmol, 3.0 equiv)



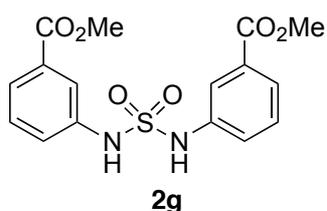
and pyridine (1.5 ml) in anhydrous DCM (20 mL) at -40 °C was added slowly sulfuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>) (0.26 ml, 2.4 mmol). The resulting mixture was stirred overnight at room temperature. The organic layer was washed by 10% aqueous HCl (30 mL x 2) and brine (10 mL). The resulting organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated to give a crude solid. Recrystallization with methanol afforded 690 mg (85%) of **2e** as a white solid. Mp: 197-199 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 11.57 (s, 2H), 8.19 (d, *J* = 9.5 Hz, 4H), 7.30 (d, *J* = 9.0 Hz, 4H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 143.8, 142.2, 125.4, 117.0 ppm; IR (thin film) 3414, 3233, 1613, 1592, 1530, 1344, 1168, 1120, 981 (cm<sup>-1</sup>); HRMS-MALDI (m/z) calcd for [C<sub>12</sub>H<sub>11</sub>N<sub>4</sub>O<sub>6</sub>S]<sup>+</sup>, 339.0394; found, 339.0387.

**Preparation of sulfamide 2f:** To a solution of 3-methoxyaniline (1.0 g, 8.0 mmol, 3.0 equiv)



and pyridine (1.5 ml) in anhydrous DCM (20 mL) at -40 °C was added slowly sulfuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>) (0.28 ml, 2.6 mmol). The resulting mixture was stirred overnight at room temperature. The organic layer was washed by 10% aqueous HCl (30 mL x 2) and brine (10 mL). The resulting organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 577 mg (72%) of **2f** as a white solid. Mp: 96-97 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.19 (t, *J* = 8.0 Hz, 2H), 6.71 (dd, *J*<sub>1</sub> = 2.0, *J*<sub>2</sub> = 8.0 Hz, 2H), 6.66 (t, *J* = 2.0 Hz, 2H), 6.63 (dd, *J*<sub>1</sub> = 2.0, *J*<sub>2</sub> = 8.0 Hz, 2H), 3.75 (s, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.7, 137.6, 130.4, 113.8, 111.4, 107.4, 55.6 ppm; IR (thin film) 3413, 3263, 2926, 1607, 1499, 1401, 1329, 1284, 1261, 1148, 863, 702 (cm<sup>-1</sup>); HRMS-MALDI (m/z) calcd for [C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>SNa]<sup>+</sup>, 331.0723; found, 331.0733.

**Preparation of sulfamide 2g:** To a solution of methyl 3-aminobenzoate (1.0 g, 6.6 mmol, 3.0 equiv) and pyridine (1.5 ml) in anhydrous DCM (20 mL) at -40 °C was added slowly sulfuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>) (0.24 ml, 2.2 mmol). The resulting mixture was stirred overnight at



room temperature. The organic layer was washed by 10% aqueous HCl (30 mL x 2) and brine (10 mL). The resulting organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated to give a crude solid. Recrystallization with DCM-pet ether afforded 656 mg (82%) of **2g** as a white solid. Mp: 187-188 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 10.63 (s, 2H), 7.70 (s, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 6H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 165.8, 138.4, 130.5, 129.5, 123.7, 122.9, 118.8, 52.2 ppm; IR (thin film) 3403, 3233, 3102, 2956, 2851, 1706, 1466, 1433, 1175, 769 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>SNa]<sup>+</sup>, 387.0621; found, 387.0624.

**Preparation of sodium phenylsulfamate:** To a solution of aniline (3.0 mL, 32.9 mmol) and triethyl amine (Et<sub>3</sub>N) (41 mL, 294.2 mmol) in anhydrous DCM (100 mL) at 0 °C was added slowly chlorosulfuric acid (ClSO<sub>3</sub>H) (2.17 mL, 32.5 mmol). The resulting mixture was stirred for 2 hours. DCM was removed under reduced pressure. The resulting crude material was dissolved in aq NaOH (1 M, 65.8 mL). Water was then removed on rotavap. The crude product was recrystallized with anhydrous ethanol to give 5.54 g (98%) sodium phenylsulfamate as a white solid. It was used directly in the next step.

**Preparation of *N*-phenyl-*N'*-arylsulfamide **2h**:** To a suspension of sodium phenylsulfamate



(1.0 g, 5.1 mmol, 1.0 equiv) in anhydrous toluene (20 mL) at room temperature was added PCl<sub>5</sub> (1.01 g, 5.1 mmol, 1.0 equiv). The resulting mixture was allowed to heat at 55 °C for 24 hours. After cooling to room temperature, the solution was filtrated to another dry round-bottom flask. A solution of 4-bromoaniline (2.3 g, 13.7 mmol, 2.5 equiv) in DCM (10 mL) was added, and the resulting solution was stirred at room temperature overnight. DCM (50 mL) was added, and the organic layer was washed by 10% aqueous HCl (30 mL x 2) and brine (10 mL). The resulting organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 860 mg (54%) of **2h** as a white solid. Mp: 132-133 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.39 (d, *J* = 9.0 Hz, 2H), 7.29 (t,

$J = 7.5$  Hz, 2H), 7.17 (t,  $J = 7.5$  Hz, 1H), 7.07 (dd,  $J_1 = 1.0$ ,  $J_2 = 8.5$  Hz, 2H), 6.95 (d,  $J = 9.0$  Hz, 2H), 6.92 (s, 1H), 6.86 (s, 1H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.2, 135.6, 132.7, 129.8, 125.9, 123.0, 121.6, 118.6 ppm; IR (thin film) 3272, 2962, 2925, 2856, 1947, 1880, 1601, 1491, 1154, 1103, 888 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_2\text{SBrNa}]^+$ , 348.9617; found, 348.9611.

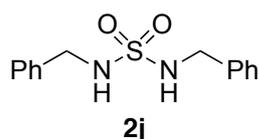
**Preparation of *N*-phenyl-*N'*-arylsulfamide **2i**:** To a suspension of sodium phenylsulfamate



(1.0 g, 5.1 mmol, 1.0 equiv) in anhydrous toluene (20 mL) at room temperature was added  $\text{PCl}_5$  (1.01 g, 5.1 mmol, 1.0 equiv). The resulting mixture was allowed to heat at 55 °C for 24 hours. After

cooling to room temperature, the solution was filtrated to another dry round-bottom flask. A solution of 4-methylaniline (1.46 g, 13.7 mmol, 2.5 equiv) in DCM (10 mL) was added, and the resulting solution was stirred at room temperature overnight. DCM (50 mL) was added, and the organic layer was washed by 10% aqueous HCl (30 mL x 2) and brine (10 mL). The resulting organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 467 mg (35%) of **2i** as a white solid. Mp: 105-106 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (t,  $J = 8.0$  Hz, 2H), 7.17 (t,  $J = 7.0$  Hz, 1H), 7.10 (dd,  $J_1 = 6.0$ ,  $J_2 = 13.5$  Hz, 4H), 6.96 (t,  $J = 9.5$  Hz, 2H), 6.47 (bs, 2H), 2.32 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.7, 135.7, 133.6, 130.1, 129.6, 125.2, 122.3, 120.9, 21.0 ppm; IR (thin film) 3416, 3283, 2963, 2920, 1603, 1512, 1398, 1158, 1082, 1034, 772 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2\text{SNa}]^+$ , 285.0668; found, 285.0678.

**Preparation of *N,N'*-dibenzylsulfamide (**2j**):** To a solution of benzylamine (20.0 g, 187

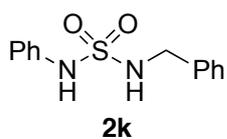


mmol, 6.0 equiv) in anhydrous DCM (60 mL) at 0 °C was added slowly sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) (4.2 g, 31 mmol). The resulting mixture was stirred overnight at room temperature. DCM (100 mL)

was added to the solution, and the organic layer was washed by 5% aqueous HCl (50 mL x 3) and brine (30 mL). The resulting organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave

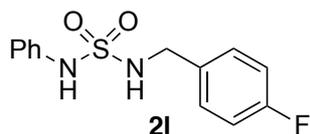
5.6 g (65%) of **2j** as a white solid. Mp: 178-180 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 7.46 (s, 2H), 7.36-7.31 (m, 8H), 7.28-7.23 (m, 2H), 4.03 (d, *J* = 3.5 Hz, 4H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 138.4, 128.2, 127.7, 127.0, 45.8 ppm; IR (thin film) 3274, 3035, 1453, 1417, 1317, 1146, 1066, 731, 699, 525 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>14</sub>H<sub>16</sub>NaN<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>, 299.0825; found, 299.0835.

**Preparation of *N*-phenyl-*N'*-benzylsulfamide (**2k**):** To a suspension of sodium phenylsulfamate (1.0 g, 5.1 mmol, 1.0 equiv) in anhydrous toluene (20 mL) at room temperature was added PCl<sub>5</sub> (1.01 g, 5.1 mmol, 1.0 equiv). The resulting mixture was allowed to heat at 55 °C for 24 hours. After



cooling to room temperature, the solution was filtrated to another dry round-bottom flask. A solution of benzylamine (1.46 g, 13.7 mmol, 2.5 equiv) in DCM (10 mL) was added, and the resulting solution was stirred at room temperature overnight. DCM (50 mL) was added, and the organic layer was washed by 10% aqueous HCl (30 mL x 2) and brine (10 mL). The resulting organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 770 mg (61%) of **2k** as a white solid. Mp: 83-85 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.27-7.23 (m, 3H), 7.17-7.10 (m, 5H), 6.93 (bs, 1H), 4.95 (t, *J* = 6.0, 1H), 4.18 (d, *J* = 6.0 Hz, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 137.1, 136.2, 129.6, 129.0, 128.3, 128.2, 124.8, 120.1, 47.6 ppm; IR (thin film) 3266, 1604, 1498, 1426, 1154, 951, 747, 738, 548 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>13</sub>H<sub>14</sub>NaN<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>, 285.0668; found, 285.0681.

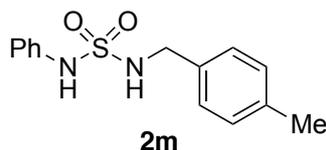
**Preparation of *N*-phenyl-*N'*-benzylsulfamide **2l**:** To a suspension of sodium phenylsulfamate (1.0 g, 5.1 mmol, 1.0 equiv) in anhydrous toluene (20 mL) at room temperature was added PCl<sub>5</sub> (1.01 g, 5.1 mmol, 1.0 equiv). The resulting mixture was allowed to heat at 55 °C for



24 hours. After cooling to room temperature, the solution was filtrated to another dry round-bottom flask. A solution of 4-fluorobenzylamine (1.7 g, 13.7 mmol, 2.5 equiv) in DCM (10 mL) was added, and the resulting solution was stirred at room temperature overnight. DCM (50 mL) was added, and the organic layer was washed by 10% aqueous HCl

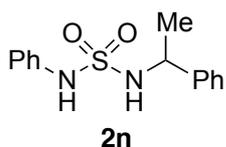
(30 mL x 2) and brine (10 mL). The resulting organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated to give a crude solid. Recrystallization with DCM-pet ether afforded 1.1 g (78%) of **2l** as a pale-green solid. Mp: 116-117 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 9.78 (s, 1H), 8.01 (t, *J* = 6.0 Hz, 1H), 7.32-7.21 (m, 4H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 9.0 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 4.01 (d, *J* = 6.0 Hz, 2H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.3 (d, *J* = 242.5 Hz), 138.8, 134.1 (d, *J* = 2.5 Hz), 129.6 (d, *J* = 7.5 Hz), 128.9, 122.4, 118.2, 114.8 (d, *J* = 21.3 Hz), 44.9 ppm; IR (thin film) 3266, 3980, 2911, 1603, 1512, 1499, 1142, 1328, 1055, 979 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>SFNa]<sup>+</sup>, 303.0574; found, 303.0579.

**Preparation of *N*-phenyl-*N'*-benzylsulfamide **2m**:** To a suspension of sodium phenylsulfamate (1.0 g, 5.1 mmol, 1.0 equiv) in anhydrous toluene (20 mL) at room temperature was added PCl<sub>5</sub> (1.01 g, 5.1 mmol, 1.0 equiv). The resulting mixture was allowed to heat at



55 °C for 24 hours. After cooling to room temperature, the solution was filtrated to another dry round-bottom flask. A solution of 4-methylbenzylamine (1.63 g, 13.7 mmol, 2.5 equiv) in DCM (10 mL) was added, and the resulting solution was stirred at room temperature overnight. DCM (50 mL) was added, and the organic layer was washed by 10% aqueous HCl (30 mL x 2) and brine (10 mL). The resulting organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 718 mg (51%) of **2m** as a white solid. Mp: 105-106 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.30 (t, *J* = 6.5 Hz, 2H), 7.13 (m, 3H), 7.06 (d, *J* = 6.5 Hz, 4H), 6.69 (s, 1H), 4.79 (s, 1H), 4.16 (d, *J* = 5.0 Hz, 2H), 2.31 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 138.5, 138.0, 137.6, 133.3, 129.6, 128.3, 124.6, 120.2, 47.4, 21.3 ppm; IR (thin film) 3414, 3339, 3289, 3133, 2934, 1601, 1518, 1402, 1159, 897 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>SNa]<sup>+</sup>, 299.0825; found, 299.0835.

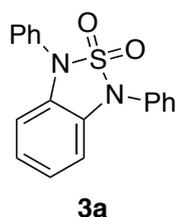
**Preparation of sulfamide **2n**:** To a suspension of sodium phenylsulfamate (1.0 g, 5.1 mmol, 1.0 equiv) in anhydrous toluene (20 mL) at room temperature was added PCl<sub>5</sub> (1.01 g, 5.1 mmol, 1.0 equiv). The resulting mixture was allowed to heat at 55 °C for 24 hours. After



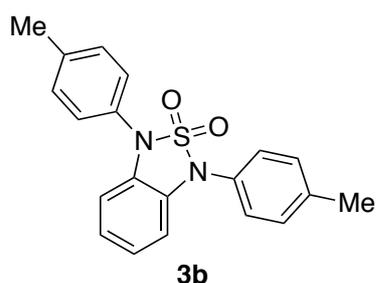
cooling to room temperature, the solution was filtrated to another dry round-bottom flask. A solution of 1-phenylethanamine (1.63 g, 13.7 mmol, 2.5 equiv) in DCM (10 mL) was added, and the resulting solution was stirred at room temperature overnight. DCM (50 mL) was added, and the organic layer was washed by 10% aqueous HCl (30 mL x 2) and brine (10 mL). The resulting organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated to give a crude solid. Flash column chromatography with pet ether/EtOAc gave 788 mg (56%) of **2n** as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.24-7.20 (m, 5H), 7.20-7.15 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 4.56 (q, *J* = 7.0 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 142.2, 137.2, 129.4, 128.9, 127.9, 126.4, 124.3, 119.5, 54.2, 23.4 ppm; IR (thin film) 3278, 2925, 1602, 1497, 1317, 1155, 973, 925, 698, 567 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>14</sub>H<sub>16</sub>NaN<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>, 299.0825; found, 299.0831.

**General procedure for 1,2-diamination with sulfamides (Procedure A):** To a mixture of sulfamide **2** (0.2 mmol), K<sub>2</sub>CO<sub>3</sub> (110.4 mg, 0.8 mmol), and 18-crown-6 (211.4 mg, 0.8 mmol) in MeCN (10 mL) at 80 °C was added a solution of TPBT **1a** (133.9 mg, 0.3 mmol, 1.5 equiv) in MeCN (10 mL) over 8 hours via a syringe pump. Acetonitrile was removed on rotary evaporator, and the resulting crude material was directly purified on flash column chromatography with pet ether/EtOAc.

The synthesis of **3a** was followed by Procedure A. 54.7 mg (85%) of pure **3a** was isolated as a white solid. Mp: 114-116 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.5 Hz, 4H), 7.57 (t, *J* = 7.5 Hz, 4H), 7.51 (t, *J* = 7.5 Hz, 2H), 6.98-6.94 (m, 2H), 6.72-6.68 (m, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 132.6, 130.4, 130.3, 129.8, 128.6, 122.3, 109.5 ppm; IR (thin film) 1592, 1484, 1330, 1301, 1173, 1155, 947, 738, 691, 568 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>18</sub>H<sub>14</sub>NaN<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>, 345.0668; found, 345.0673.



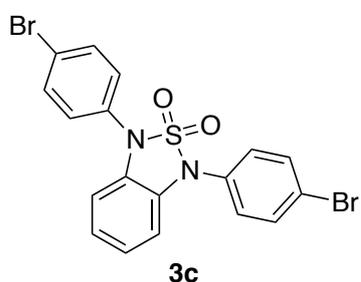
The synthesis of **3b** was followed by Procedure A. 56.7 mg (81%) of pure **3b** was isolated as a white solid. Mp: 168-170 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.5 Hz, 4H), 7.35



373.0984.

(d,  $J = 8.0$  Hz, 4H), 6.92 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H), 6.65 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H), 2.44 (s, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 131.1, 130.5, 129.7, 128.6, 122.1, 109.3, 21.5 ppm; IR (thin film) 3281, 3034, 2979, 2663, 1861, 1600, 1502, 1384, 1265, 1999, 860 ( $\text{cm}^{-1}$ ); HRMS-MALDI (m/z) calcd for  $[\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2\text{SNa}]^+$ , 373.0981; found,

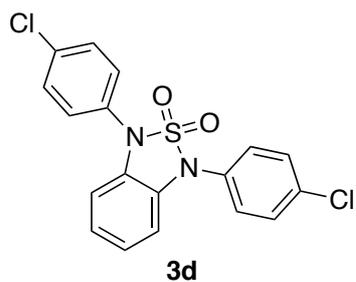
The synthesis of **3c** was followed by Procedure A. 55.7 mg (58%) of pure **3c** was isolated as



500.8878; found, 500.8881.

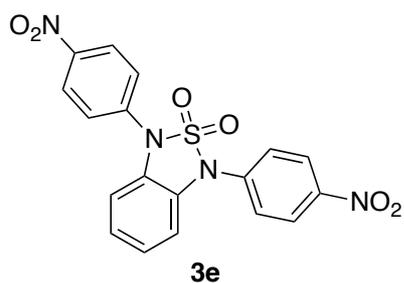
a white solid. Mp: 141-143 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 9.0$  Hz, 4H), 7.48 (d,  $J = 9.0$  Hz, 4H), 6.98 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H), 6.69 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  133.8, 131.6, 130.0, 123.0, 124.0, 122.8, 109.7 ppm; IR (thin film) 3413, 3132, 1618, 1487, 1400, 1337, 1183, 1066, 722 ( $\text{cm}^{-1}$ ); HRMS-MALDI (m/z) calcd for  $[\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2\text{Br}_2\text{SNa}]^+$ ,

The synthesis of **3d** was followed by Procedure A. 37.5 mg (48%) of pure **3d** was isolated as



412.9889.

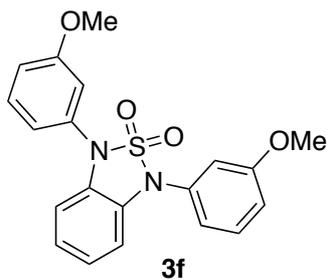
a white solid. Mp: 138.5-140 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.49 (m, 8H), 6.98 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H), 6.69 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.0, 131.0, 130.8, 130.1, 129.8, 122.8, 109.7 ppm; IR (thin film) 3414, 3300, 3131, 1892, 1639, 1620, 1399, 1152, 1091, 860 ( $\text{cm}^{-1}$ ); HRMS-MALDI (m/z) calcd for  $[\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2\text{SNa}]^+$ , 412.9889; found,



The synthesis of **3e** was followed by Procedure A. 36.3 mg (44%) of pure **3e** was isolated as a white solid. Mp: 203-205 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (d,  $J = 9.0$

Hz, 4H), 7.78 (d,  $J = 9.0$  Hz, 4H), 7.14 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H), 6.93 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.8, 138.9, 129.1, 127.2, 126.0, 124.1, 111.2 ppm; IR (thin film) 3552, 3476, 3414, 3233, 2029, 1638, 1617, 1440, 1152, 799 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{18}\text{H}_{13}\text{N}_4\text{O}_6\text{S}]^+$ , 413.0550; found, 413.0550.

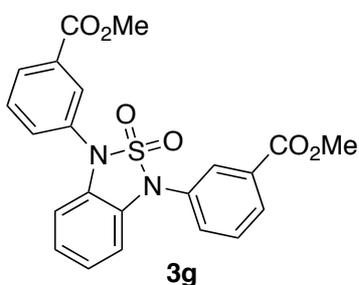
The synthesis of **3f** was followed by Procedure A. 45.8 mg (60%) of pure **3f** was isolated as a



white solid. Mp: 113-115 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (t,  $J = 8.0$  Hz, 2H), 7.21 (dd,  $J_1 = 2.0$ ,  $J_2 = 8.0$  Hz, 2H), 7.15 (t,  $J = 2.5$  Hz, 2H), 7.04 (dd,  $J_1 = 2.5$ ,  $J_2 = 8.5$  Hz, 2H), 6.96 (dd,  $J = 3.5$ ,  $J_2 = 6.0$  Hz, 2H), 6.75 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H), 3.85 (s, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.1, 133.6, 131.1,

130.1, 122.3, 120.5, 115.9, 113.6, 109.7, 55.8 ppm; IR (thin film) 3414, 3133, 3007, 2962, 2926, 2854, 1734, 1599, 1488, 1302 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_4\text{SNa}]^+$ , 405.0880; found, 405.0882.

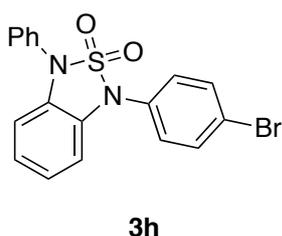
The synthesis of **3g** was followed by Procedure A. 37.7 mg (43%) of pure **3g** was isolated as a



white solid. Mp: 187-188 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 2H), 8.20 (d,  $J = 8.0$  Hz, 2H), 7.83 (d,  $J = 8.0$  Hz, 2H), 7.66 (t,  $J = 8.0$  Hz, 2H), 7.00 (t,  $J = 3.5$  Hz, 2H), 6.71 (t,  $J = 3.5$  Hz, 2H), 3.95 (s, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 133.0, 132.9, 132.8, 131.0, 130.7, 130.1, 129.6, 122.9,

109.9, 52.7 ppm; IR (thin film) 3415, 3233, 2956, 1706, 1466, 1400, 1304, 1176, 1110, 888 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_6\text{SNa}]^+$ , 461.0778; found, 461.0782.

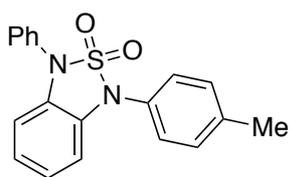
The synthesis of **3h** was followed by Procedure A. 49.7 mg (62%) of pure **3h** was isolated as a



white solid. Mp: 132-133 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 9.0$  Hz, 2H), 7.63-7.59 (m, 2H), 7.58-7.54 (m, 2H), 7.54-7.46 (m, 3H), 6.97 (dd,  $J_1 = 3.5$ ,  $J_2 = 6.0$  Hz, 2H), 6.72-6.67 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  133.8, 133.7, 132.4, 131.8, 130.5, 130.4,

130.0, 129.9, 129.9, 123.8, 122.7, 122.4, 109.7, 109.5 ppm; IR (thin film) 3414, 3127, 1592, 1489, 1400, 1337, 1299, 1179, 1013, 982 (cm<sup>-1</sup>); HRMS-MALDI (m/z) calcd for [C<sub>18</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>SBrNa]<sup>+</sup>, 422.9773; found, 422.9775.

The synthesis of **3i** was followed by Procedure A. 52.4 mg (78%) of pure **3i** was isolated as a

**3i**

white solid. Mp: 101-102 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.96 -6.91 (m, 2H), 6.68 (dd, *J*<sub>1</sub> = 9.0, *J*<sub>2</sub> = 12.5 Hz, 2H), 2.45 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 140.1, 132.7, 131.1, 130.5, 130.4, 130.2, 129.7, 129.6, 128.6, 128.5,

122.3, 122.1, 109.4, 109.4, 21.5 ppm; IR (thin film) 3414, 3125, 2968, 2858, 1644, 1508, 1484, 1328, 1301, 1167, 762 (cm<sup>-1</sup>); HRMS-MALDI (m/z) calcd for [C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>SNa]<sup>+</sup>, 359.0285; found, 359.0289.

The synthesis of **3j** was followed by Procedure A. 51.1 mg (73%) of pure **3j** was isolated as a

**3j**

white solid. Mp: 121-123 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 7.5 Hz, 4H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.33 (t, *J* = 7.5 Hz, 2H), 6.83-6.78 (m, 2H), 6.55-6.51 (m, 2H), 4.93 (s, 4H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 134.8, 129.5, 129.2, 128.4, 127.7, 121.8, 108.7, 46.9 ppm; IR (thin film) 2922, 1607, 1493, 1385, 1301, 1277, 1169, 739, 602, 529 (cm<sup>-1</sup>); HRMS-MALDI (m/z)

calcd for [C<sub>20</sub>H<sub>18</sub>NaN<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>, 373.0981; found, 373.0984.

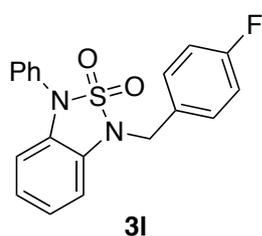
The synthesis of **3k** was followed by Procedure A. 45.7 mg (68%) of pure **3k** was isolated as

**3k**

a white solid. Mp: 92-93.5 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.58-7.48 (m, 5H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 6.90-6.86 (m, 2H), 6.67-6.55 (m, 2H), 4.97 (s, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 134.8, 132.6, 130.4, 130.3, 129.7, 129.5, 129.2, 128.4, 128.3, 127.7,

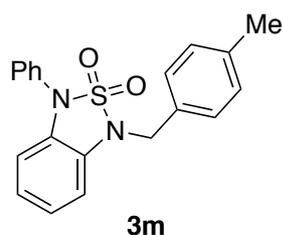
122.3, 121.9, 109.2, 109.1, 47.1 ppm; IR (thin film) 3063, 3026, 1593, 1488, 1320, 1173, 1124, 746, 693, 536 (cm<sup>-1</sup>); HRMS-MALDI (m/z) calcd for [C<sub>19</sub>H<sub>16</sub>NaN<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>, 359.0825; found, 359.0826.

The synthesis of **3l** was followed by Procedure A. 43.2 mg (61%) of pure **3l** was isolated as a

**3l**

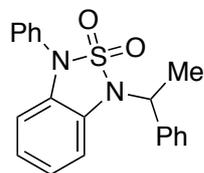
white solid. Mp: 101-103 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.61-7.54 (m, 4H), 7.53-7.48 (m, 3H), 7.09 (t, *J* = 8.5 Hz, 2H), 6.89 (dd, *J*<sub>1</sub> = 3.5, *J*<sub>2</sub> = 6.0 Hz, 2H), 6.64 (dd, *J*<sub>1</sub> = 3.5, *J*<sub>2</sub> = 6.0 Hz, 1H), 6.59 (dd, *J*<sub>1</sub> = 3.5, *J*<sub>2</sub> = 6.0 Hz, 1H), 4.94 (s, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 162.8 (d, *J* = 245 Hz), 132.5, 130.5 (d, *J* = 2.5 Hz), 130.4, 130.3, 129.8, 129.5 (d, *J* = 8.8 Hz), 129.2, 128.4, 122.3, 122.0, 116.1 (d, *J* = 22.5 Hz), 109.3, 108.9, 46.4 ppm; IR (thin film) 3415, 3131, 1606, 1509, 1489, 1449, 1400, 1302, 1178, 983 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>SFNa]<sup>+</sup>, 377.0731; found, 377.0735.

The synthesis of **3m** was followed by Procedure A. 40.6 mg (58%) of pure **3m** was isolated

**3m**

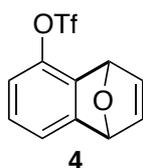
as a white solid. Mp: 105-106 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.63-7.46 (m, 5H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.87 (dd, *J*<sub>1</sub> = 3.0, *J*<sub>2</sub> = 6.0 Hz, 2H), 6.66-6.47 (m, 2H), 4.92 (s, 2H), 2.36 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 138.1, 132.6, 131.7, 130.5, 130.4, 129.8, 129.7, 129.5, 128.6, 128.4, 122.3, 121.8, 109.2, 109.1, 46.9, 21.4 ppm; IR (thin film) 3414, 3128, 2962, 2917, 2853, 1601, 1490, 1401, 1154, 979 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>SNa]<sup>+</sup>, 373.0981; found, 373.0984.

The synthesis of **3n** was followed by Procedure A. 31.5 mg (45%) of pure **3n** was isolated as

**3n**

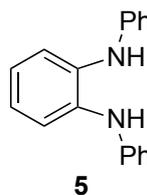
a white solid. Mp: 119-121 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.62-7.53 (m, 6H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 5.48 (q, *J* = 7.0 Hz, 1H), 2.01 (d, *J* = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.2, 132.7, 130.4, 130.3, 129.7, 129.1, 128.5, 128.2, 127.5, 127.1, 121.8, 121.3, 110.4, 109.2, 54.0, 17.4 ppm; IR (thin film) 3072, 2925, 1485, 1316, 1262, 1179, 742, 693, 550 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>20</sub>H<sub>18</sub>NaN<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>, 373.0981; found, 373.0989.

**Reaction of TPBT 1a with furan:** To a mixture of furan (40.8 mg, 0.6 mmol) and CsF (60.8 mg, 0.4 mmol) in MeCN (5 mL) at room temperature was added a solution of TPBT **1a** (89.2 mg, 0.2 mmol) in MeCN (5 mL) over 8 hours via a syringe pump. Acetonitrile was removed on rotary evaporator, and the resulting crude material was directly purified on flash column chromatography with pet ether.

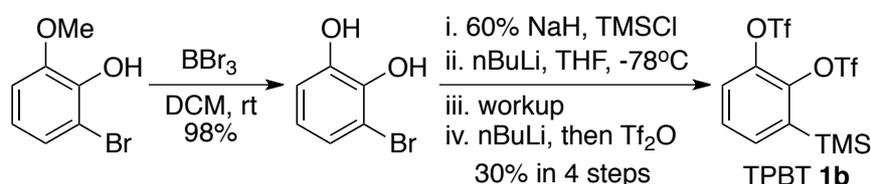


49.6 mg (85%) of adduct **4** was obtained as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 6.5$  Hz, 1H), 7.10-7.05 (m, 3H), 6.84 (d,  $J = 8.5$  Hz, 1H), 5.93 (s, 1H), 5.79 (s, 1H) ppm;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.82 (s) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.6, 143.2, 142.8, 142.6, 141.5, 128.1, 120.2, 118.9 (q,  $J = 318.8$  Hz), 118.5, 82.9, 80.7 ppm; IR (thin film) 2933, 1671, 1422, 1216, 1141, 849, 609 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{11}\text{H}_7\text{F}_3\text{NaO}_4\text{S}]^+$ , 314.9909; found, 314.9913.

**LAH reduction of 3a:** To a solution of **3a** (32.2 mg, 0.1 mmol) in anhydrous THF (5 mL) at 0 °C was added LAH (11.4 mg, 0.3 mmol, 3.0 equiv). The resulting mixture was stirred at 0 °C for 3 hours. Water was added to quench the reaction and the mixture was extracted by DCM (10 mL x 3), washed by brine (5 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. Flash column chromatography with



pet ether/EtOAc gave 25.5 mg (98%) of **5** as a white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.26 (m, 2H), 7.23 (t,  $J = 7.5$  Hz, 4H), 7.00-6.94 (m, 2H), 6.93 (d,  $J = 7.5$  Hz, 4H), 6.89 (t,  $J = 7.5$  Hz, 2H), 5.61 (bs, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.2, 135.2, 129.6, 123.2, 120.8, 120.5, 117.5 ppm.



**Preparation of TPBT 1b:** 2-bromo-6-methoxyphenol was prepared according to literature procedure.<sup>2</sup> To a solution of 2-bromo-6-methoxyphenol (11.0 g, 54.1 mmol) in anhydrous DCM (300 mL) at 0 °C was slowly added  $\text{BBr}_3$  (5.1 mL, 54.1 mmol, 1.0 equiv). The resulting solution was stirred at room temperature overnight. 10% aq  $\text{NaHCO}_3$  (100 mL) was slowly

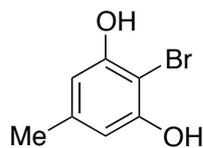
added and it was stirred for 10 min. The mixture was extracted with DCM (50 mL x 3), washed by brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. Flash column chromatography with pet ether/EtOAc on silica gel gave 10.1 g (98%) of pure 3-bromobenzen-1,2-diol as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.01 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 8.0 Hz, 1H), 5.45 (bs, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 144.9, 140.4, 123.5, 122.2, 115.1, 109.7 ppm.

To a solution of 3-bromobenzen-1,2-diol (3.0 g, 15.9 mmol) in anhydrous THF (50 mL) at 0 °C was added NaH (60 % in mineral oil, 1.5 g, 36.5 mmol, 2.3 equiv). TMSCl (4.4 mL, 34.9 mmol, 2.2 equiv) was added after 10 min. The mixture was stirred for another 10 min until the starting material was consumed completely. This mixture was cooled to -78 °C, *n*-BuLi (2.5 M in hexane, 7.6 mL, 19.1 mmol, 1.2 equiv) was added slowly. After addition, it was stirred at -78 °C for 10 min. The resulting mixture was then put in an ice-water bath and water (5 mL) was added. Ethereal workup gave crude 3-(trimethylsilyl)benzene-1,2-diol as a yellow oil. Due to the instability, this oil was used directly in the next step without further purification.

To a solution of the above crude 3-(trimethylsilyl)benzene-1,2-diol in anhydrous THF (50 mL) at -78 °C was slowly added *n*-BuLi (2.5 M in hexane, 16.5 mL, 41.1 mmol, 2.5 equiv). After 10 min, triflic anhydride (Tf<sub>2</sub>O) (5.8 mL, 34.5 mmol, 2.1 equiv) was added slowly and it was stirred for 10 min before workup. The resulting mixture was put in an ice-water bath and 10% aq. NaHCO<sub>3</sub> (50 mL) was added. After ethereal workup, flash column chromatography on silica gel with pure pet ether gave 2.1 g (30% from 3-bromobenzen-1,2-diol) TPBT **1b** as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J*<sub>1</sub> = 2.0, *J*<sub>2</sub> = 7.0 Hz, 1H), 7.49 (dd, *J*<sub>1</sub> = 2.0, *J*<sub>2</sub> = 8.0 Hz, 1H), 7.46 (t, *J* = 7.5, 1H), 0.43 (s, 9H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 143.3, 141.1, 139.1, 136.1, 129.5, 124.1, 118.8 (q, *J* = 319.0 Hz), 118.7 (q, *J* = 318.9 Hz), -0.1 ppm; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -72.56 (d, *J* = 2.3 Hz), -72.93 (d, *J* = 2.3 Hz); IR (thin film) 2926, 2852, 1436, 1214, 1140, 873, 846, 621 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>11</sub>H<sub>12</sub>F<sub>6</sub>NaO<sub>6</sub>S<sub>2</sub>Si]<sup>+</sup>, 468.9641; found, 468.9637.

**General procedure for the bromination of benzene-1,3-diol (Procedure B) :** 2-bromo-phen-1,3-diol analogs were prepared according to literature procedure.<sup>3</sup> To a solution of benzene-1,3-diol analog (10 mmol) in methanol (50 mL) at 0 °C was added NBS (8.9 g, 30 mmol, 3.0 equiv). The reaction was stirred at 0 °C for 2 h. A solution of Na<sub>2</sub>SO<sub>3</sub> (2.5 g, 20 mmol, 2.0 equiv) and NaOH (0.8 g, 20 mmol, 2.0 equiv) in water (50 mL) was added, and it was reacted for 1 h. Conc. HCl was added to tune the pH to 1.0. The crude mixture was extracted with EtOAc (15 mL x 2). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated with rotary evaporator. Flash column chromatography with pet ether/EtOAc on silica gel could afford pure 2-bromo-1,3-phenyldiol analog.

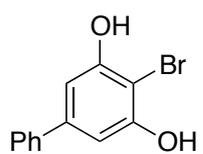
The synthesis of 2-bromo-5-methylbenzene-1,3-diol was followed by Procedure B. 1.8 g



(86 %) of pure 2-bromo-5-methylbenzene-1,3-diol was isolated as a white solid. Mp: 137-138 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 9.80 (s, 2H), 6.22 (s, 2H), 2.10 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 155.0,

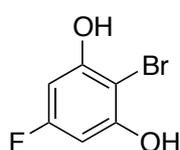
137.5, 107.6, 94.6, 20.9 ppm; IR (thin film) 3414, 3133, 1584, 1479, 1401, 1319, 1268, 1164, 1037, 834, 530 (cm<sup>-1</sup>); HRMS-MALDI (m/z) calcd for [C<sub>7</sub>H<sub>6</sub>BrO<sub>2</sub>], 200.9557; found, 200.9551.

The synthesis of 4-bromo-[1,1'-biphenyl]-3,5-diol was followed by Procedure B. 2.6 g (98 %)



of pure 4-bromo-[1,1'-biphenyl]-3,5-diol was isolated as a white solid. Mp: 167-168 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.57-7.52 (m, 2H), 7.47-7.35 (m, 3H), 6.86 (s, 2H), 5.50 (bs, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ

153.2, 142.8, 139.9, 129.0, 128.2, 127.1, 107.2, 98.5 ppm; IR (thin film) 3483, 3358, 1593, 1572, 1517, 1491, 1427, 1348, 1277, 1259, 1179, 1036, 846, 767, 703, 585 (cm<sup>-1</sup>); HRMS-MALDI (m/z) calcd for [C<sub>12</sub>H<sub>8</sub>BrO<sub>2</sub>], 262.9713; found, 262.9714.

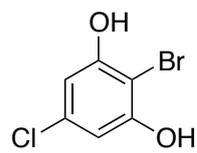


The synthesis of 2-bromo-5-fluorobenzene-1,3-diol was followed by Procedure B. 1.7 g (83%) of pure 2-bromo-5-fluorobenzene-1,3-diol was

isolated as a white solid. Mp: 107-109 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 10.46 (s, 2H), 6.22 (d, *J* = 10.5 Hz, 2H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 161.8 (d, *J*

= 238.7 Hz), 156.1 (d,  $J = 14.4$  Hz), 94.1 (d,  $J = 25.3$  Hz), 93.1 (d,  $J = 3.8$  Hz) ppm; IR (thin film) 3477, 3406, 3132, 1612, 1513, 1445, 1401, 1285, 1177, 1129, 1038, 1001, 823, 599, 521 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_6\text{H}_3\text{BrFO}_2]$ , 204.9306; found, 204.9307.

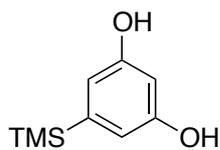
The synthesis of 2-bromo-5-chlorobenzene-1,3-diol was followed by Procedure B. 1.8 g



(82%) of pure 2-bromo-5-chlorobenzene-1,3-diol was isolated as a white solid. Mp: 131-133 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  10.51 (s, 2H), 6.44 (s, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  156.2, 132.0, 106.8,

96.8 ppm; IR (thin film) 3431, 3323, 1597, 1582, 1488, 1437, 1340, 1238, 1165, 1102, 1030, 897, 830, 817, 699, 582, 505 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_6\text{H}_3\text{BrClO}_2]$ , 220.9010; found, 220.9011.

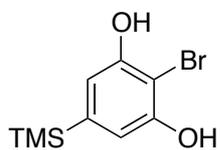
**Preparation of 5-(trimethylsilyl)benzene-1,3-diol:** The mixture of (3,5-dimethoxyphenyl)



trimethylsilane (1.5g, 7.1mmol) in DCM(50ml) was cooled to 0 °C, add  $\text{BBr}_3$  (1.4ml, 14.6mmol, 2.05 equiv) slowly. 740 mg (57%) of pure 5-(trimethylsilyl)benzene-1,3-diol was isolated as a white solid. Mp:

138-140 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  9.1 (s, 2H), 6.33 (d,  $J = 2.0$  Hz, 2H), 6.18 (t,  $J = 2.0$  Hz, 1H), 0.17 (s, 9H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  158.0, 141.4, 110.7, 103.2, 1.1 ppm; IR (thin film) 3126, 2976, 1590, 1405, 1215, 1139, 1101, 810, 669, 603 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_9\text{H}_{13}\text{O}_2\text{Si}]$ , 181.0690; found, 181.0685.

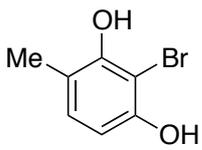
The synthesis of 2-bromo-5-(trimethylsilyl)benzene-1,3-diol was followed by Procedure B.

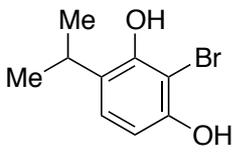


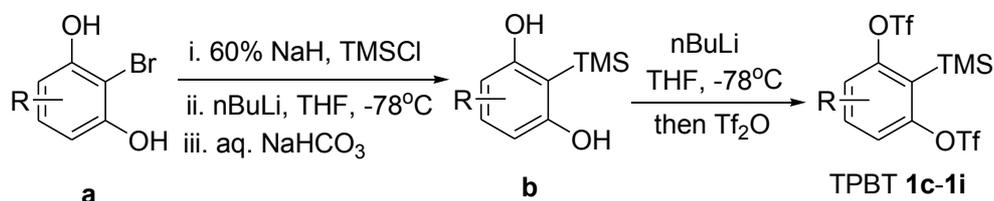
2.6 g (98%) of pure 2-bromo-5-(trimethylsilyl)benzene-1,3-diol was isolated as a white solid. Mp: 107-109 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.73 (s, 2H), 5.37 (s, 2H), 0.24 (s, 9H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

$\delta$  152.6, 142.6, 112.7, 100.2, -1.1 ppm; IR (thin film) 3361, 2954, 1589, 1396, 1250, 1031, 1019, 905, 827, 754, 469 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_9\text{H}_{12}\text{BrO}_2\text{Si}]$ , 258.9795; found, 258.9797.

The synthesis of 2-bromo-4-methylbenzene-1,3-diol was followed by Procedure B. 1.4 g


 (69%) of pure 2-bromo-4-methylbenzene-1,3-diol was isolated as a white solid. Mp: 102-104 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 9.74 (s, 1H), 8.69 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 1H), 2.10 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 153.1, 152.6, 129.0, 116.0, 106.8, 99.6, 16.3 ppm; IR (thin film) 3445, 3172, 2853, 1871, 1608, 1467, 1400, 1320, 1222, 1167, 1123, 1021, 806, 599 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>7</sub>H<sub>6</sub>BrO<sub>2</sub>]<sup>-</sup>, 200.9557; found, 200.9557.

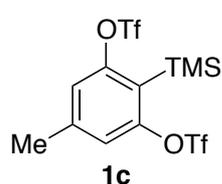
The synthesis of 2-bromo-4-methylbenzene-1,3-diol was followed by Procedure B. 1.3 g
 
 (57%) of pure 2-bromo-4-methylbenzene-1,3-diol was isolated as a white solid. Mp: 44-46 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.04 (d, *J* = 8.5 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 5.41 (s, 1H), 5.16 (s, 1H), 3.23 (heptet, *J* = 7.0 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.6, 149.9, 128.1, 126.1, 107.8, 100.0, 27.8, 22.8 ppm; IR (thin film) 3486, 3343, 2962, 2875, 1858, 1605, 1501, 1440, 1307, 1195, 1131, 1012, 804, 733 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>9</sub>H<sub>10</sub>BrO<sub>2</sub>]<sup>-</sup>, 228.9870; found, 228.9868.



**General procedure for the preparation of TPBT 1c-1i (Procedure C):** To a cooled solution of 2-bromo-1,3-phenyldiol analog **a** (5.0 mmol, 1.0 equiv) in anhydrous THF (40 mL) at 0 °C was added NaH (60% in mineral oil, 500 mg, 12.5 mmol, 2.5 equiv). After stirred for 10 minutes, chlorotrimethylsilane (1.5 mL, 11.5 mmol, 2.3 equiv) was slowly added and then stirred for another 10 minutes. The resulting solution was cooled to -78 °C and *n*-BuLi (2.5 M in hexane, 3.0 mL, 7.5 mmol, 1.5 equiv) was added dropwise and stirred for 10 minutes. Water (2 mL) was added to the solution. Aqueous 10 % NaHCO<sub>3</sub> (20 mL) was added, and the mixture was extracted with Et<sub>2</sub>O (20 mL x 2). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated with rotary evaporator. Crude 2-(trimethylsilyl)benzene-1,3-diol analog **b** was obtained, and it was used in the next step without further purification.

To the above crude 2-(trimethylsilyl)benzene-1,3-diol analog **b** in anhydrous THF (40 mL) at  $-78\text{ }^{\circ}\text{C}$  was added *n*-BuLi (2.5 M in hexane, 5.0 mL, 12.5 mmol, 2.5 equiv). Trifluoromethanesulfonic anhydride (Tf<sub>2</sub>O) (2.2 mL, 12.5 mmol, 2.5 equiv) was then added slowly. After 10 minutes, 10 % aqueous NaHCO<sub>3</sub> (20 mL) was added, and the mixture was extracted with Et<sub>2</sub>O (20 mL x 2). The combined organic layer was washed with brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated with rotary evaporator. Flash column chromatography with pet ether on silica gel could afford pure TPBT **1**.

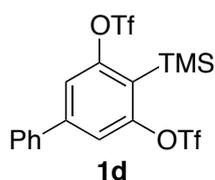
The synthesis of **1c** was followed by Procedure C. 1.0 g (44%) of pure **1c** was isolated as a



white solid. Mp: 55-57 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.19 (s, 2H), 2.44 (s, 3H), 0.45 (s, 9H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.8, 143.9, 123.3, 120.7, 118.7 (q, *J* = 318.5 Hz), 21.6, 0.9 ppm; IR (thin film) 3128, 2919, 2850, 1616, 1411, 1220, 1140, 947, 598 (cm<sup>-1</sup>);

HRMS-MALDI (*m/z*) calcd for [C<sub>12</sub>H<sub>14</sub>F<sub>6</sub>NaO<sub>6</sub>S<sub>2</sub>Si]<sup>+</sup>, 482.9798; found, 482.9801.

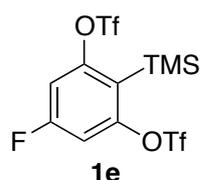
The synthesis of **1d** was followed by Procedure C. 1.5 g (56%) of pure **1d** was isolated as a



white solid. Mp: 53-54 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.60 (s, 2H), 7.57-7.46 (m, 5H), 0.52 (s, 9H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 155.2, 146.2, 137.5, 129.6, 129.6, 127.3, 124.8, 118.8 (q, *J* = 318.5 Hz), 118.5, 0.9 ppm; IR (thin film) 3084, 3067, 2957, 2908, 1612, 1532, 1417,

1208, 1134, 1095, 1048, 958, 804, 600, 509, 481, 457 (cm<sup>-1</sup>); HRMS-MALDI (*m/z*) calcd for [C<sub>17</sub>H<sub>16</sub>F<sub>6</sub>NaO<sub>6</sub>S<sub>2</sub>Si]<sup>+</sup>, 544.9954; found, 544.9959.

The synthesis of **1e** was followed by Procedure C. 1.2 g (53%) of pure **1e** was isolated as a

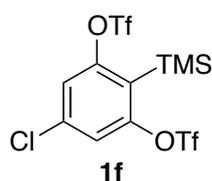


white solid. Mp: 33-35 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.19 (d, *J* = 8.5 Hz, 2H), 0.46 (s, 9H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 163.4 (d, *J* = 253.4 Hz), 155.0 (d, *J* = 12.1 Hz), 122.4 (d, *J* = 4.6 Hz), 118.6 (q, *J* = 318.8 Hz), 108.7 (d, *J* = 24.0 Hz), 0.9 ppm; IR (thin film) 3120, 2964, 2859,

1606, 1584, 1429, 1214, 1139, 1089, 1011, 978, 851, 798, 758, 613, 508 (cm<sup>-1</sup>);

HRMS-MALDI (m/z) calcd for  $[C_{11}H_{11}F_7NaO_6S_2Si]^+$ , 486.9547; found, 486.9547.

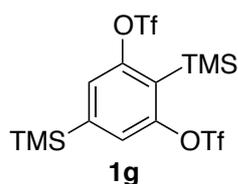
The synthesis of **1f** was followed by Procedure C. 528 mg (22%) of pure **1f** was isolated as a



white solid. Mp: 35-37 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.40 (s, 2H), 0.46 (s, 9H) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  154.7, 137.6, 125.6, 120.7, 118.6 (q,  $J = 318.5$  Hz), 0.8 ppm; IR (thin film) 3103, 2962, 1592, 1551, 1429, 1386, 1217, 1140, 1057, 967, 914, 851, 796, 758, 673, 598,

510 ( $cm^{-1}$ ); HRMS-MALDI (m/z) calcd for  $[C_{11}H_{11}ClF_6NaO_6S_2Si]^+$ , 502.9251; found, 502.9259.

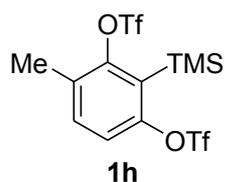
The synthesis of **1g** was followed by Procedure C. 0.9 g (35%) of pure **1g** was isolated as a



white solid. Mp: 27-28 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.44 (s, 2H), 0.47 (s, 9H), 0.31 (s, 9H) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  154.7, 148.3, 127.0, 124.2, 118.8 (q,  $J = 318.5$  Hz), 0.9, -1.5 ppm; IR (thin film) 3127, 2926, 2855, 1596, 1518, 1428, 1407, 1255, 1216, 1141, 951, 845,

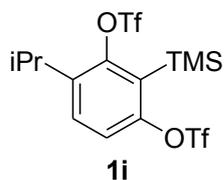
800, 760, 601 ( $cm^{-1}$ ); HRMS-MALDI (m/z) calcd for  $[C_{14}H_{20}F_6NaO_6S_2Si_2]^+$ , 541.0036; found, 541.0032.

The synthesis of **1h** was followed by Procedure C. 828 mg (36%) of pure **1h** was isolated as a



white solid. Mp: 32-34 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.39 (d,  $J = 8.5$  Hz, 1H), 7.32 (d,  $J = 8.5$  Hz, 1H), 2.39 (s, 3H), 0.47 (s, 9H) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  153.3, 149.9, 134.6, 132.5, 129.1, 120.3, 118.7 (q,  $J = 318.1$  Hz), 118.6 (q,  $J = 318.6$  Hz), 17.1, 1.0 ppm; IR (thin

film) 3105, 3001, 2962, 2909, 1596, 1398, 1202, 1014, 939, 708, 500, 448 ( $cm^{-1}$ ); HRMS-MALDI (m/z) calcd for  $[C_{12}H_{14}F_6NaO_6S_2Si]^+$ , 482.9798; found, 482.9802.



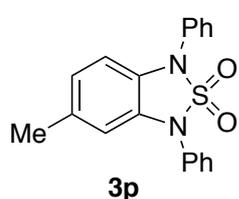
The synthesis of **1i** was followed by Procedure C. 757 mg (31%) of pure **1i** was isolated as a white solid. Mp: 29-31 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.50 (d,  $J = 9.0$  Hz, 1H), 7.39 (d,  $J = 9.0$  Hz, 1H), 3.28 (hept,  $J = 7.0$  Hz, 1H), 1.24 (d,  $J = 7.0$  Hz, 6H), 0.47 (s, 9H) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$

153.0, 147.9, 142.9, 130.5, 129.1, 120.6, 118.7 (q,  $J = 318.3$  Hz), 118.6 (q,  $J = 318.3$  Hz), 27.3, 23.6, 1.1 ppm; IR (thin film) 3126, 2976, 1405, 1215, 1596, 1171, 1139, 942, 877, 810, 669, 603 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{14}\text{H}_{18}\text{F}_6\text{NaO}_6\text{S}_2\text{Si}]^+$ , 511.0111; found, 511.0115.

### Reaction of TPBT **1b-1i** with sulfamide **2a**:

**Reaction of TPBT **1b** with sulfamide **2a**:** To a mixture of *N,N'*-diphenylsulfamide (**2a**) (0.4 mmol),  $\text{K}_2\text{CO}_3$  (110.4 mg, 0.8 mmol), and 18-crown-6 (211.4 mg, 0.4 mmol) in MeCN (10 mL) at room temperature was added a solution of TPBT **1b** (268.0 mg, 0.6 mmol, 1.5 equiv) in MeCN (10 mL) over 8 hours via a syringe pump. Acetonitrile was removed on rotary evaporator, and the resulting crude material was directly purified on flash column chromatography with pet ether/EtOAc. 48.9 mg (38%) of diaminobenzene **3a** was obtained.

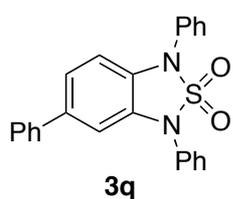
The synthesis of **3p** was followed by Procedure A. 52.4 mg (78%) of pure **3p** was isolated as



a white solid. Mp: 143-144 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70-7.42 (m, 10H), 6.75 (d,  $J = 8.0$  Hz, 1H), 6.60 (d,  $J = 8.0$  Hz, 1H), 6.51 (s, 1H), 2.27 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  133.1, 132.7, 132.4, 130.4, 130.4, 130.4, 129.7, 129.5, 128.7, 128.3, 128.1, 122.6, 110.2,

109.6, 21.5 ppm; IR (thin film) 3473, 3414, 3133, 1726, 1637, 1618, 1494, 1400, 1299, 1112 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_2\text{SNa}]^+$ , 359.0825; found, 359.0828.

The synthesis of **3q** was followed by Procedure A. 32.6 mg (41%) of pure **3q** was isolated as

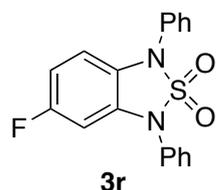


a white solid. Mp: 154-155 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (dd,  $J_1 = 3.0$ ,  $J_2 = 7.5$  Hz, 4H), 7.58 (t,  $J = 8.0$  Hz, 4H), 7.53 (t,  $J = 7.0$  Hz, 2H), 7.45 (d,  $J = 7.5$  Hz, 2H), 7.38 (t,  $J = 7.5$  Hz, 2H), 7.30 (t,  $J = 7.0$  Hz, 1H), 7.18 (dd,  $J_1 = 1.5$ ,  $J_2 = 8.0$  Hz, 1H), 6.90 (d,  $J = 1.5$  Hz, 1H), 6.78 (d,

$J = 8.2$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 136.2, 132.7, 132.5, 130.8, 130.6, 130.5, 129.9, 129.8, 129.6, 129.0, 128.7, 128.5, 127.5, 127.2, 121.2, 109.8, 108.3 ppm; IR

(thin film) 3552, 3414, 3232, 3133, 1638, 1617, 1401, 1327, 1290, 1179 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{SNa}]^+$ , 421.0981; found, 421.0984.

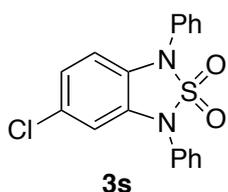
The synthesis of **3r** was followed by Procedure A. 15.0 mg (22%) of pure **3r** was isolated as



a white solid. Mp: 124-126 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72-7.43 (m, 10H), 6.72-6.57 (m, 2H), 6.46 (dd,  $J_1 = 2.5$ ,  $J_2 = 8.5$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6 (d,  $J = 238.0$  Hz), 123.6, 132.1, 130.6 (d,  $J = 10.0$  Hz), 130.2, 129.9, 128.6, 128.5, 127.3, 126.3 (d,  $J = 2.5$  Hz),

124.2, 110.3 (d,  $J = 8.8$  Hz), 108.2 (d,  $J = 23.8$  Hz), 98.2 (d,  $J = 30.0$  Hz) ppm; IR (thin film) 3125, 2962, 2926, 2855, 1616, 1592, 1490, 1366, 1333, 1176, 1025 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{18}\text{H}_{13}\text{FN}_2\text{NaO}_2\text{S}]^+$ , 363.0574; found 363.0574.

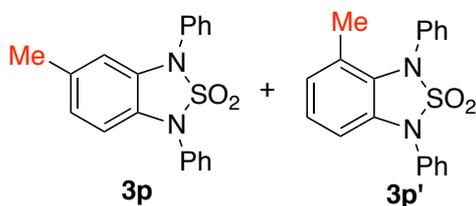
The synthesis of **3s** was followed by Procedure A. 17.8 mg (25%) of pure **3s** was isolated as a



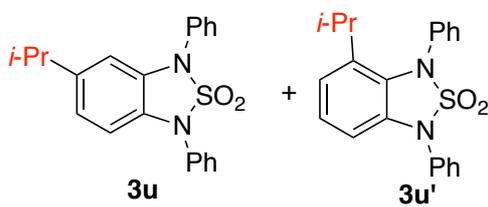
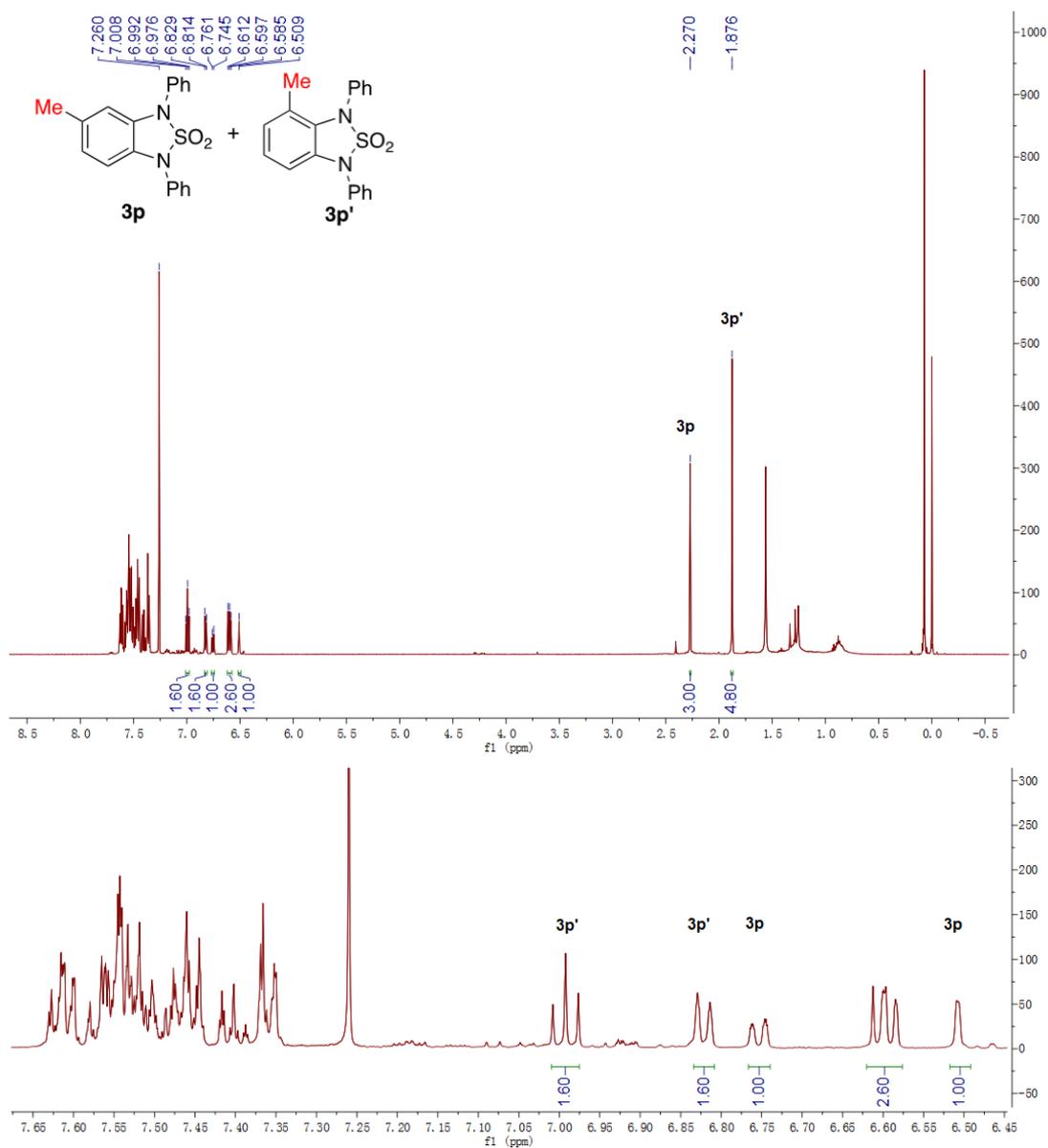
colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75-7.50 (m, 10H), 6.97-6.85 (m, 1H), 6.67 (d,  $J = 2.0$  Hz, 1H), 6.61 (d,  $J = 8.5$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  131.9, 130.7, 130.6, 130.5, 130.3, 130.1, 128.7, 128.5, 127.6, 127.4, 124.2, 122.0, 110.3, 109.7 ppm; IR (thin film)

3415, 3127, 2963, 2920, 2853, 1392, 1493, 1401, 1137, 1094, 1073 ( $\text{cm}^{-1}$ ); HRMS-MALDI ( $m/z$ ) calcd for  $[\text{C}_{18}\text{H}_{13}\text{ClN}_2\text{NaO}_2\text{S}]^+$ , 379.0279; found 379.0283.

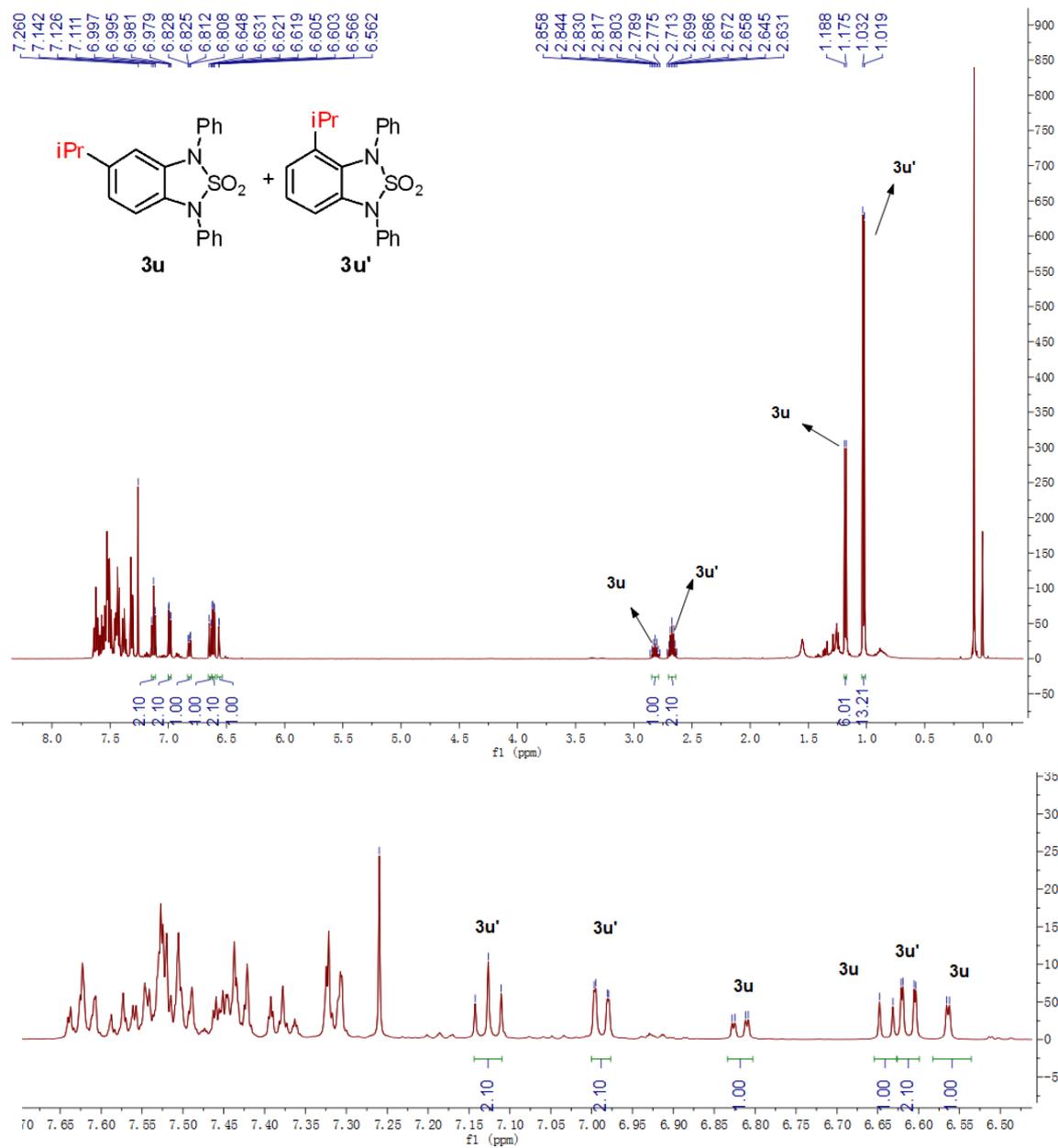
### Regioselectivity study on TPBT **1h** and **1i**:



The synthesis of **3p** and **3p'** was followed by Procedure A in 0.1 mmol scale. 15.8 mg (47 %) of a mixture of **3p** and **3p'** was obtained with a ratio of **3p**:**3p'** = 1:1.6.

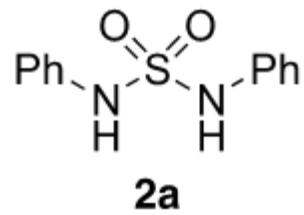


The synthesis of **3u** and **3u'** was followed by Procedure A in 0.1 mmol scale. 21.4 mg (59%) of a mixture of **3u** and **3u'** was obtained with a ratio of **3u:3u'** = 1:2.1; HRMS-MALDI (*m/z*) calcd for  $[C_{21}H_{20}N_2NaO_2S]^+$ , 387.1138; found, 387.1147.



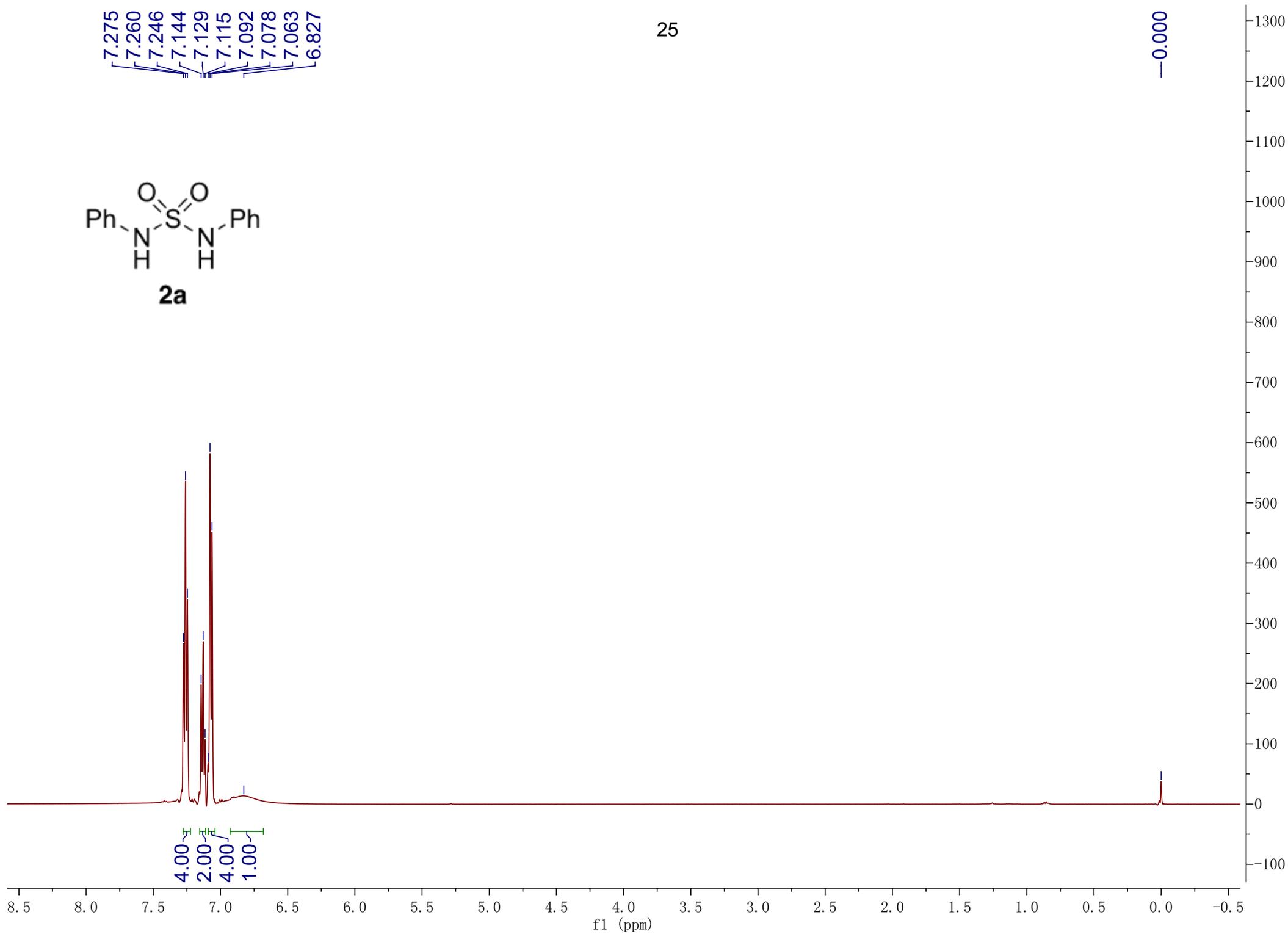
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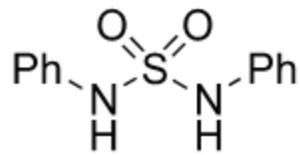
- (1) Gavernet, L.; Cabrera, M. J. D.; Bruno-Blanch, L. E.; Estiú, G. L. *Bioorg. Med. Chem.* **2007**, *15*, 1556-1567.
- (2) Bungard, C. J.; Morris, J. C. *Synthesis* **2001**, 741-744.
- (3) Staats, H.; Eggers, F.; Haß, O.; Fahrenkrug, F.; Matthey, J.; Lüning, U.; Lützen, A. *Eur. J. Org. Chem.* **2009**, 4777-4792.



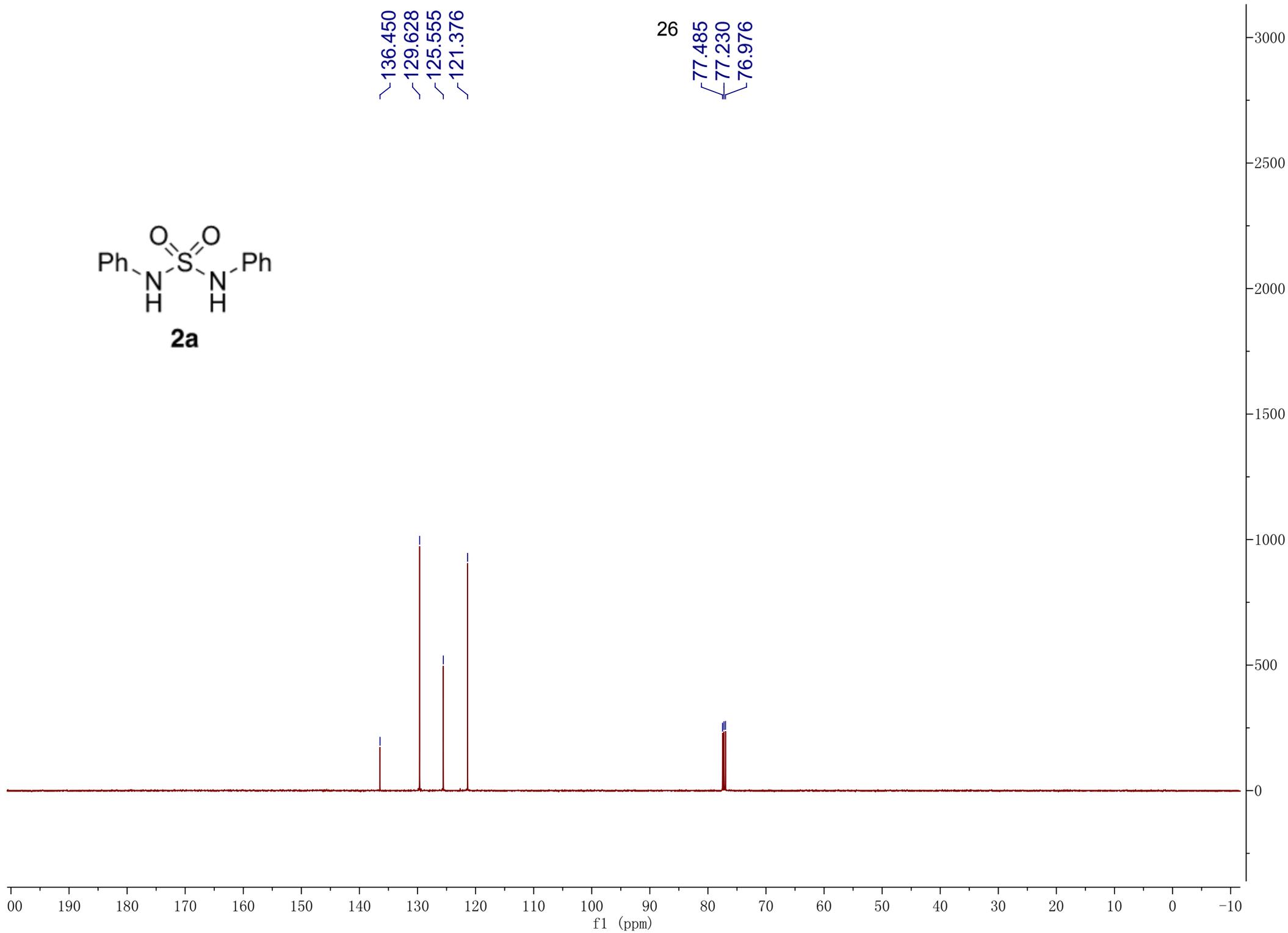
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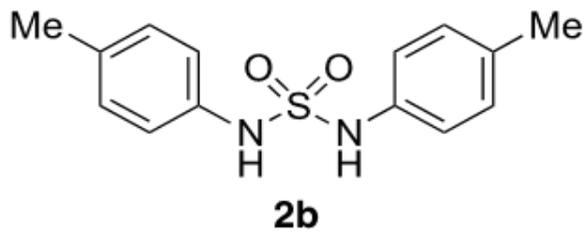
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**2a**



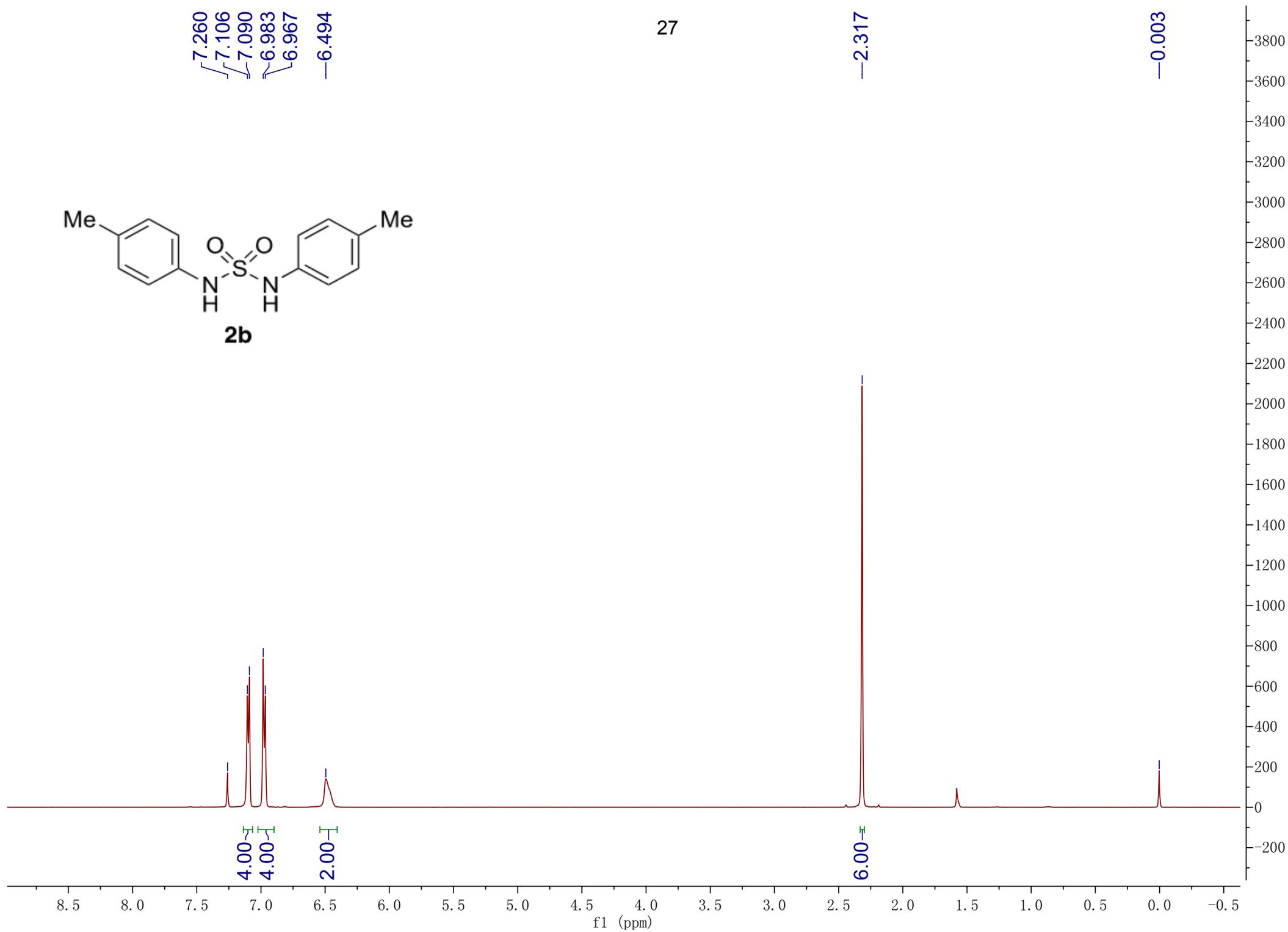


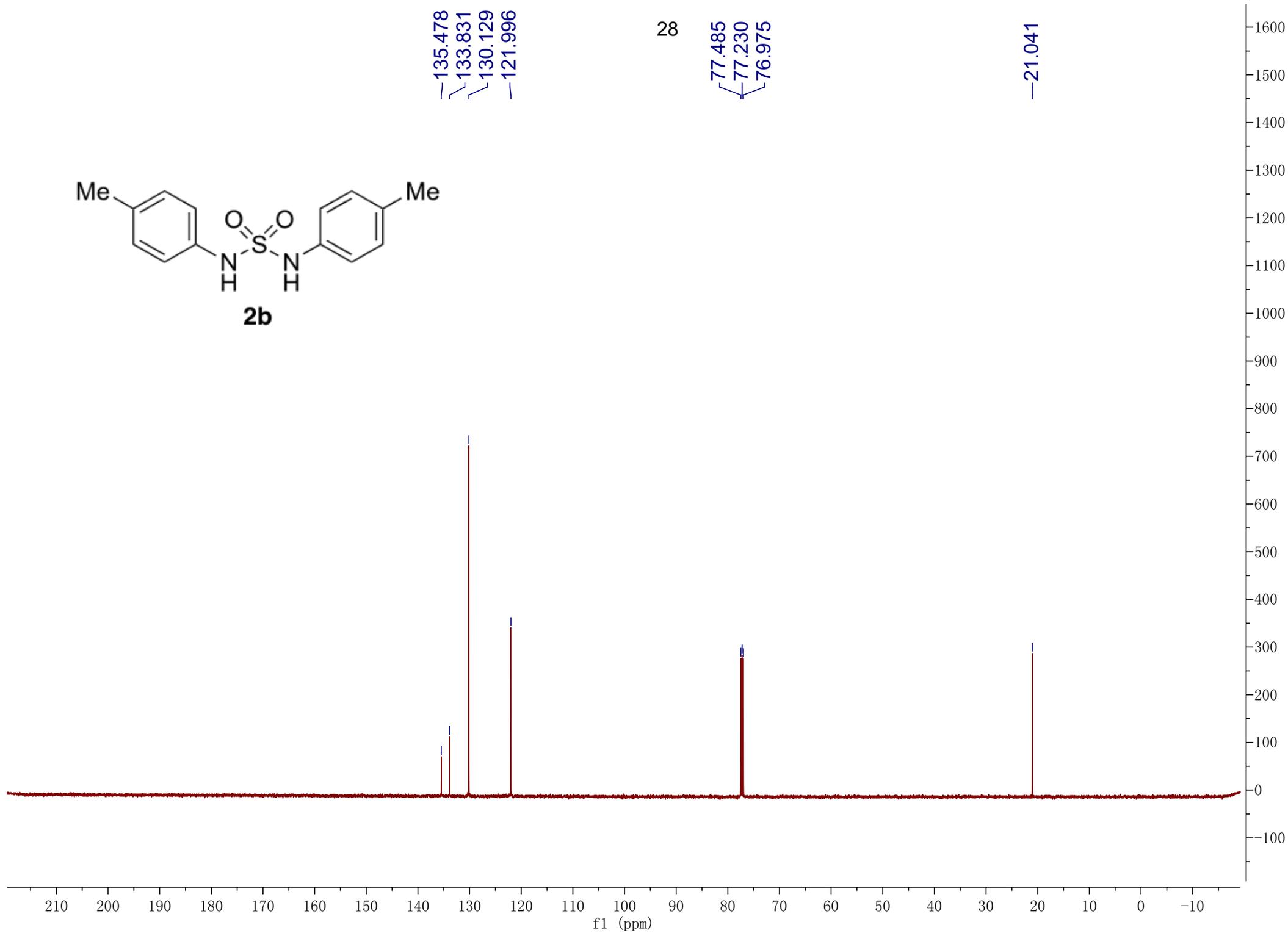
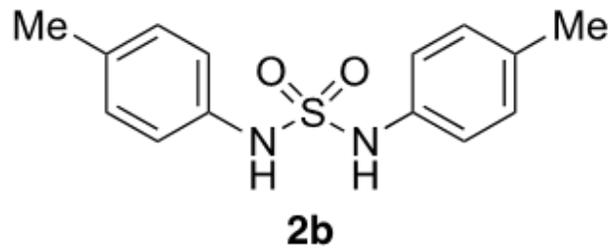
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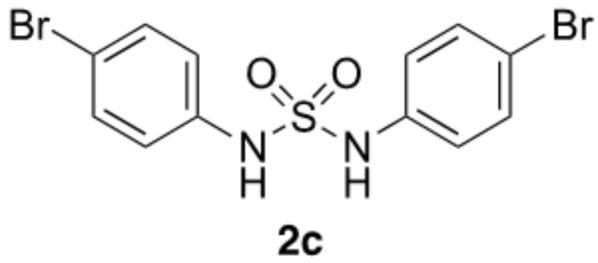
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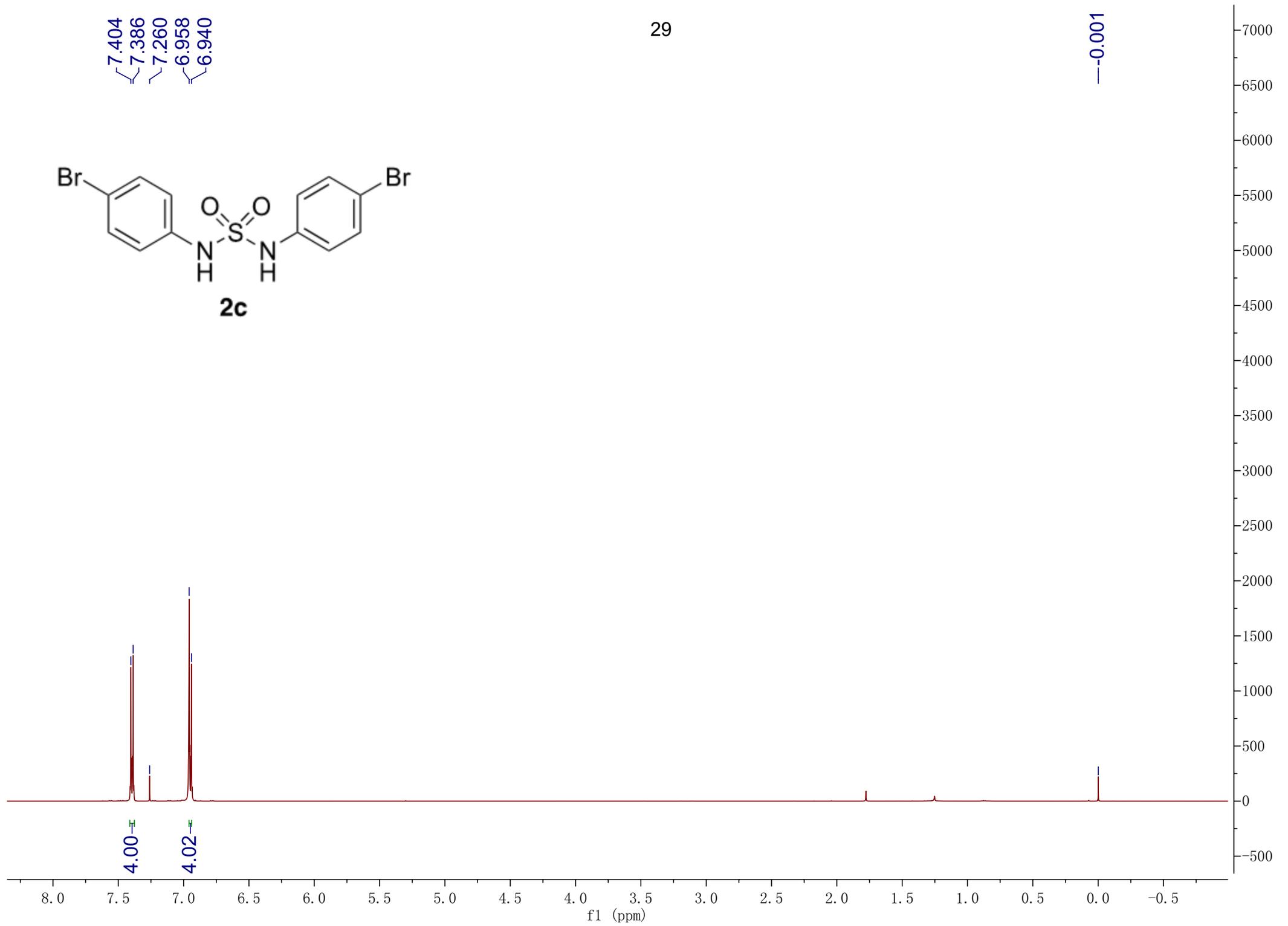
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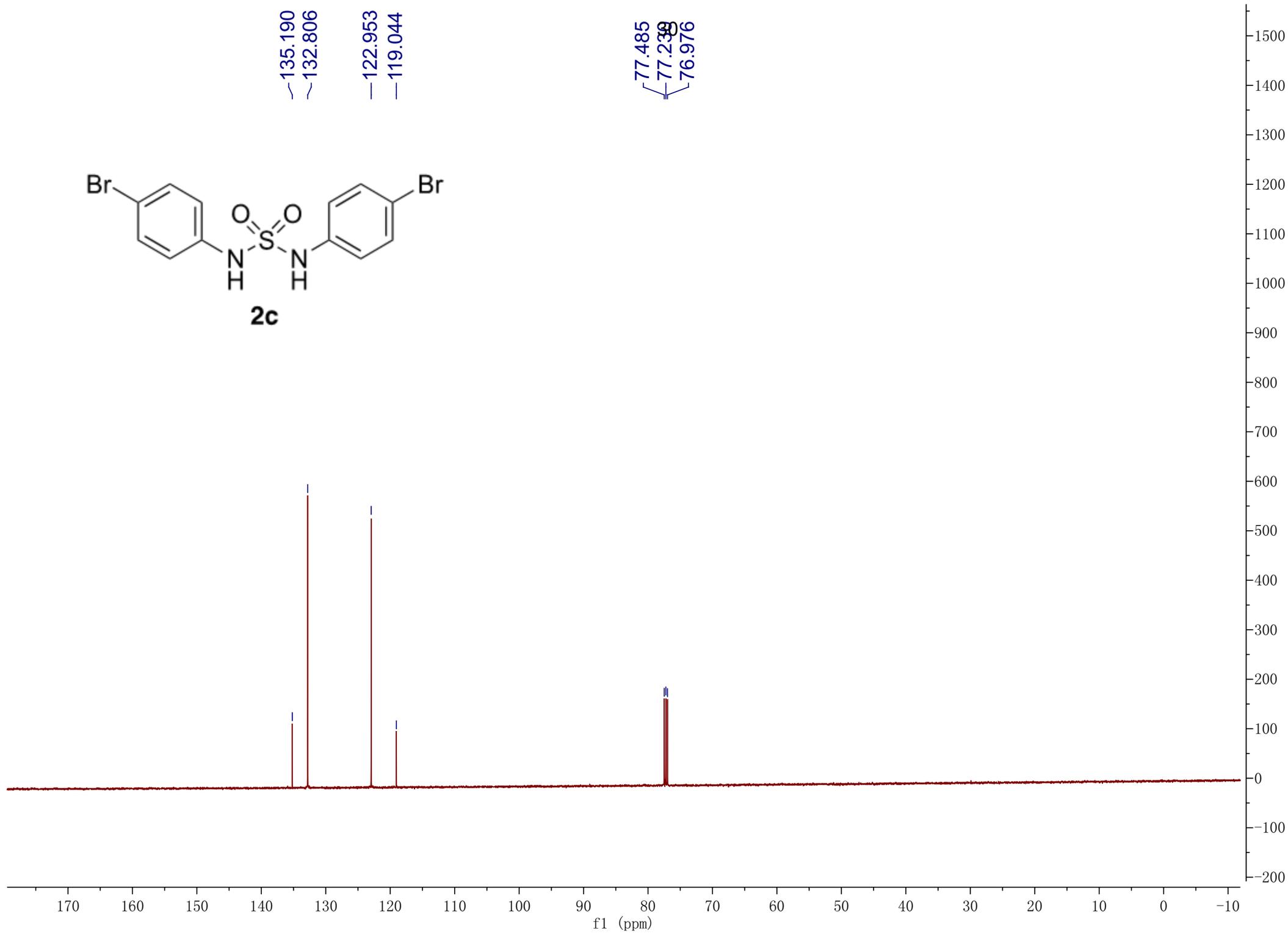
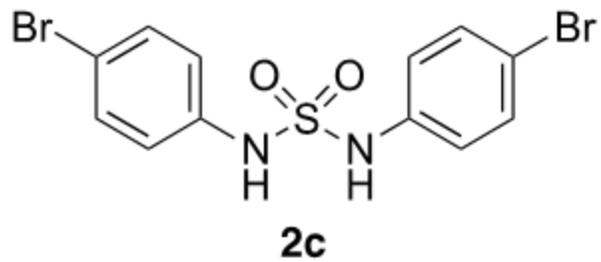


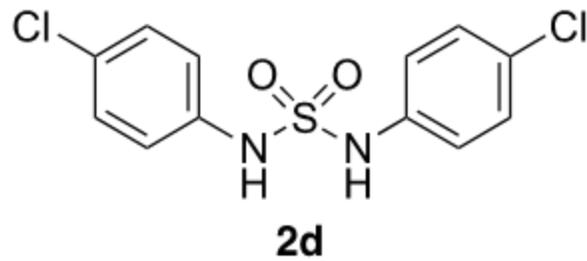




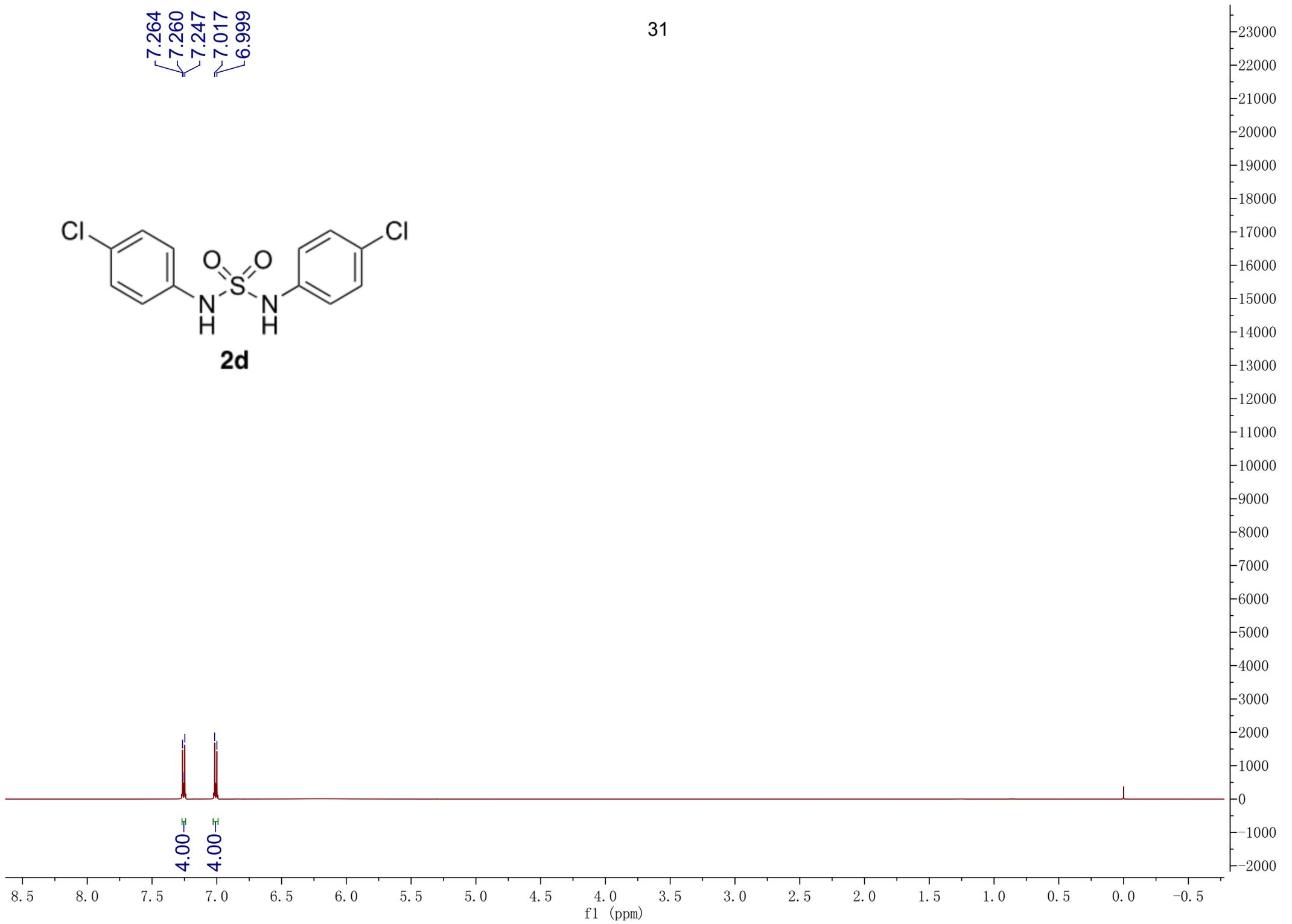
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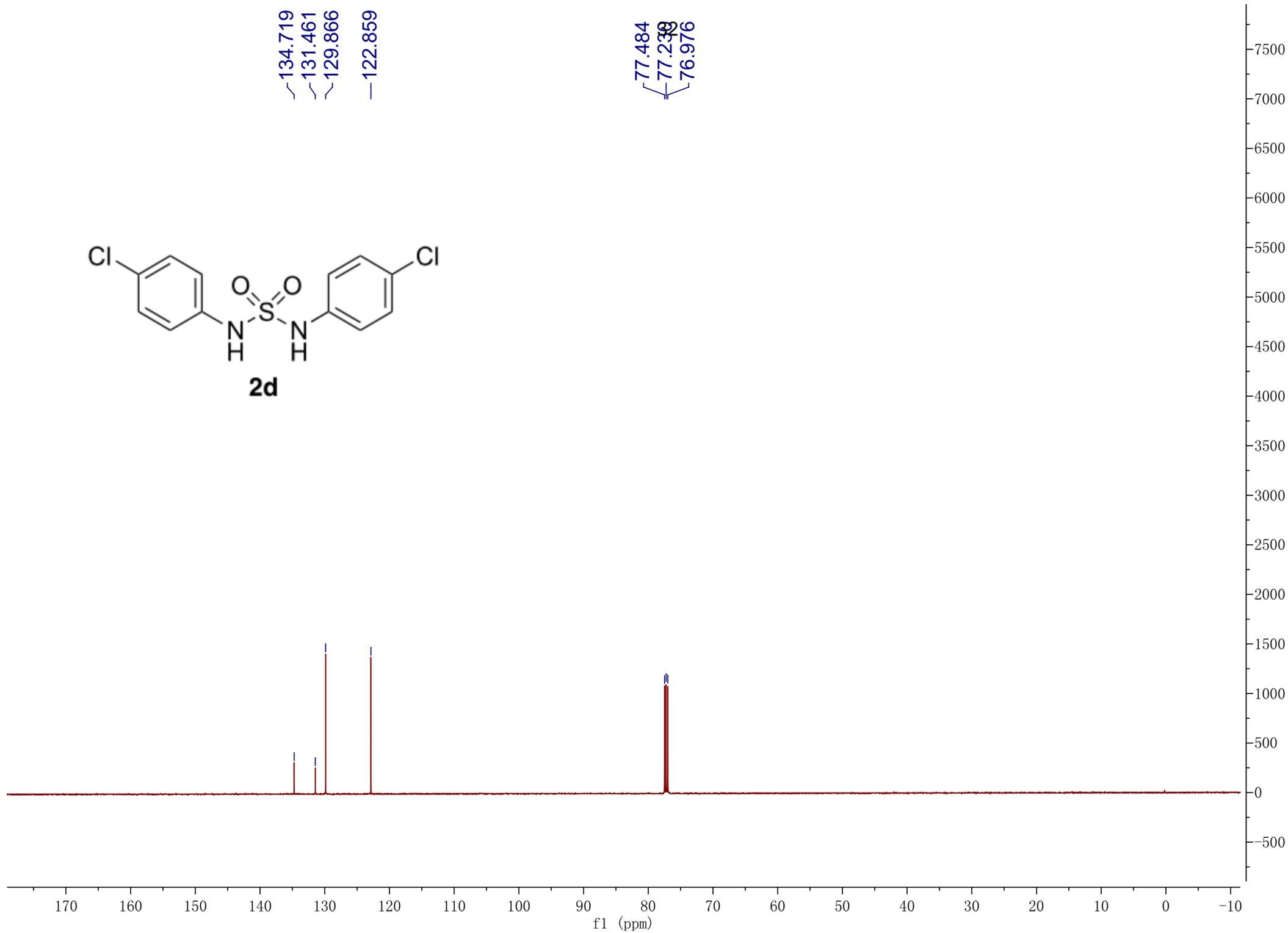
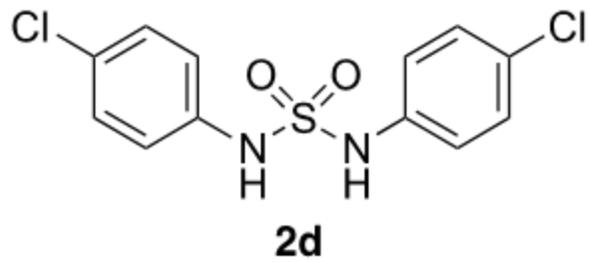


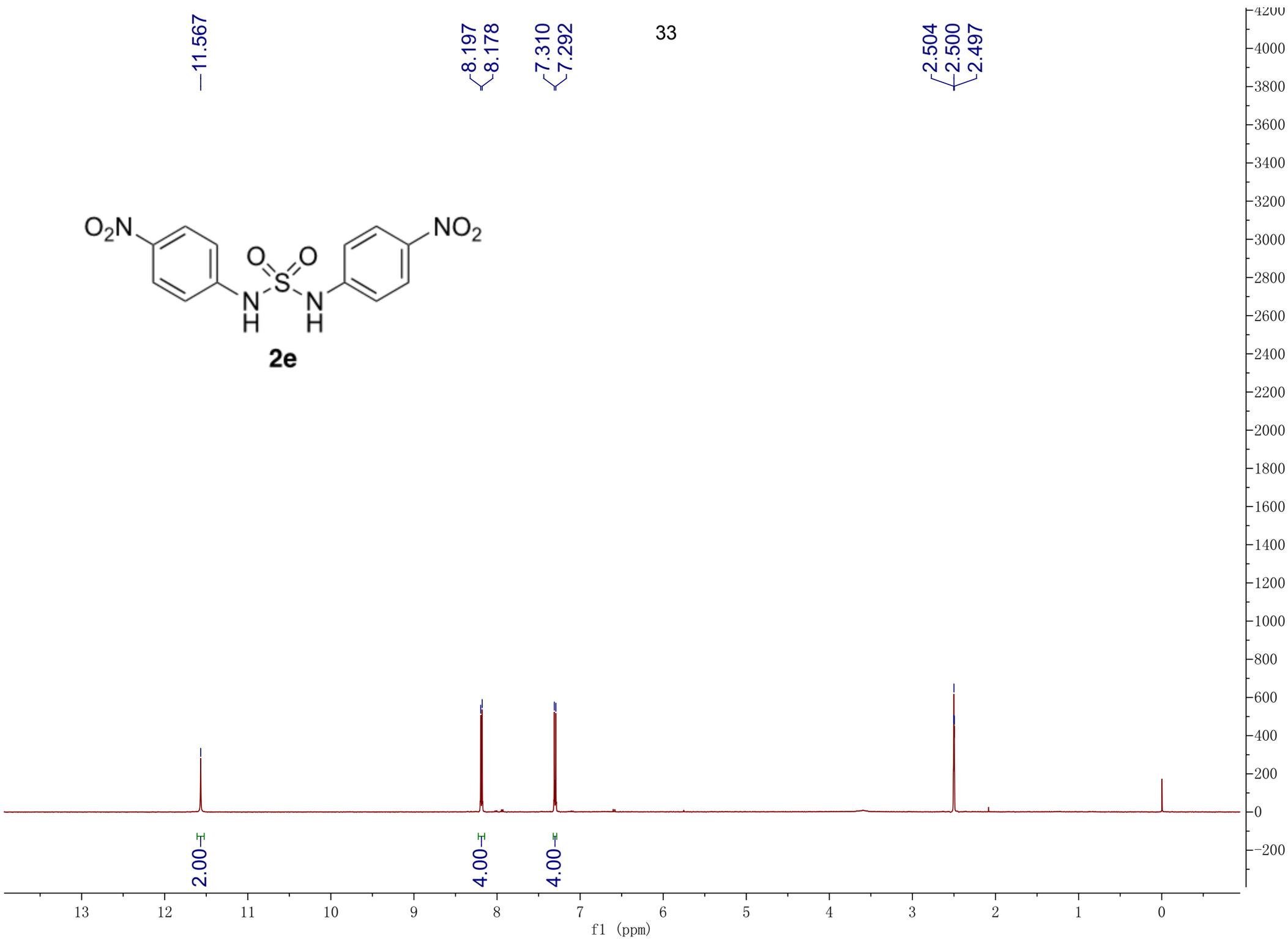
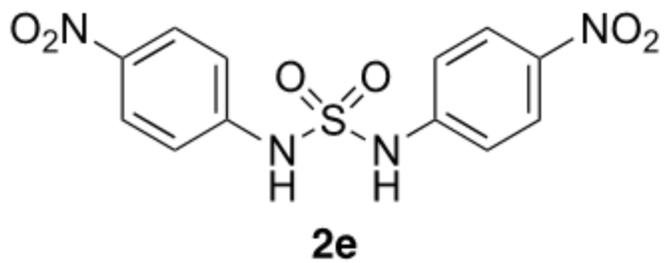


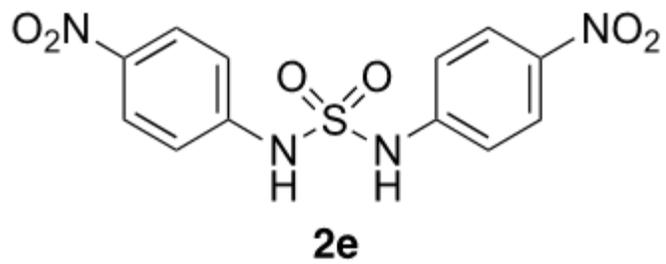


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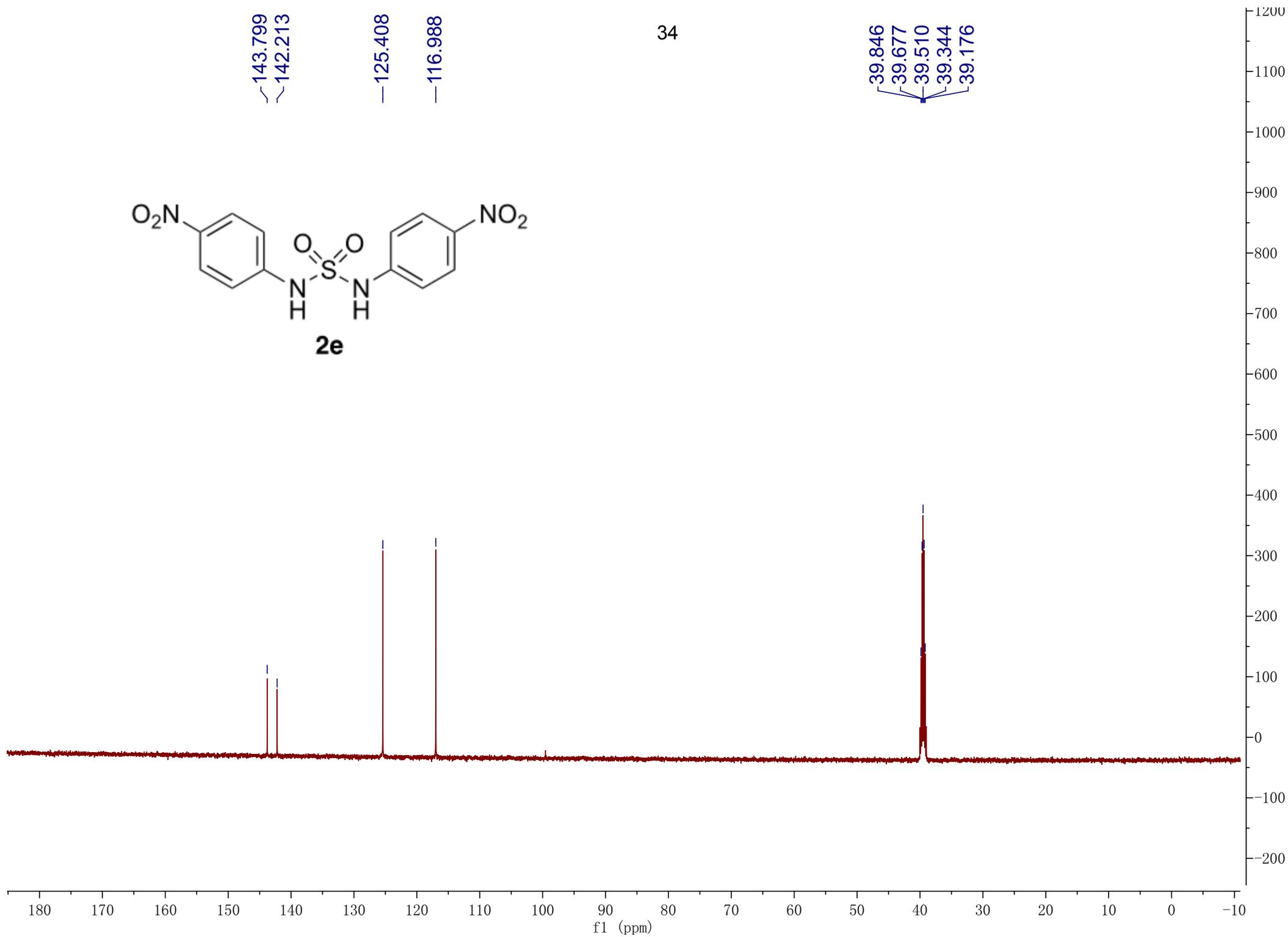


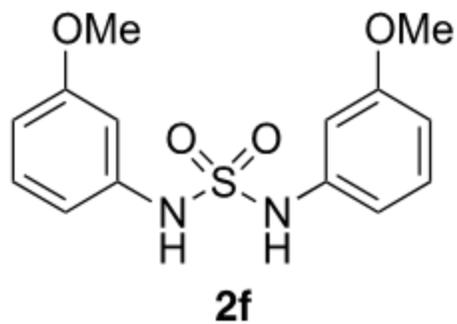
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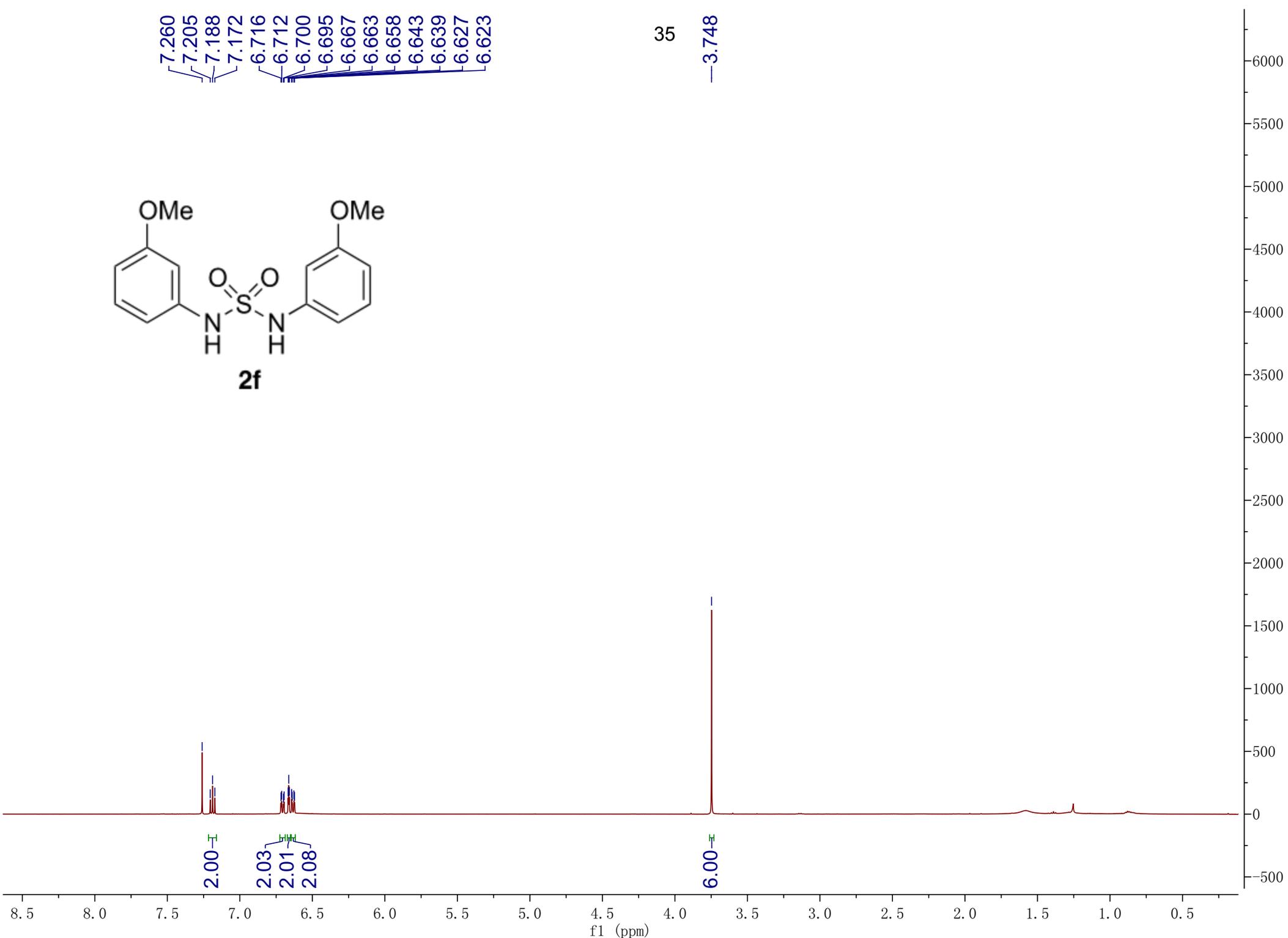


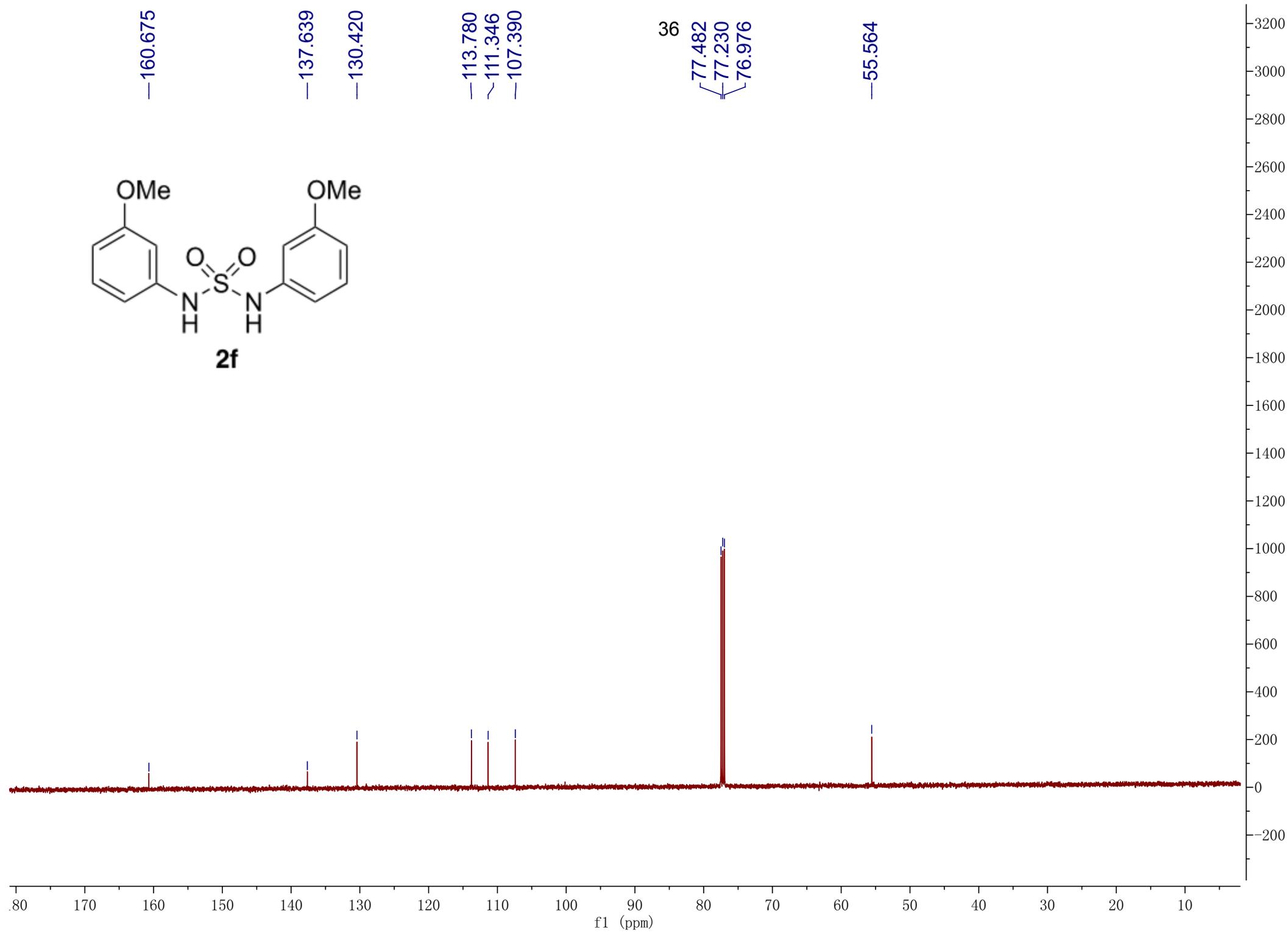
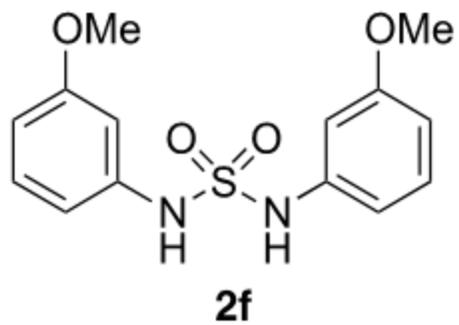


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35

3.748





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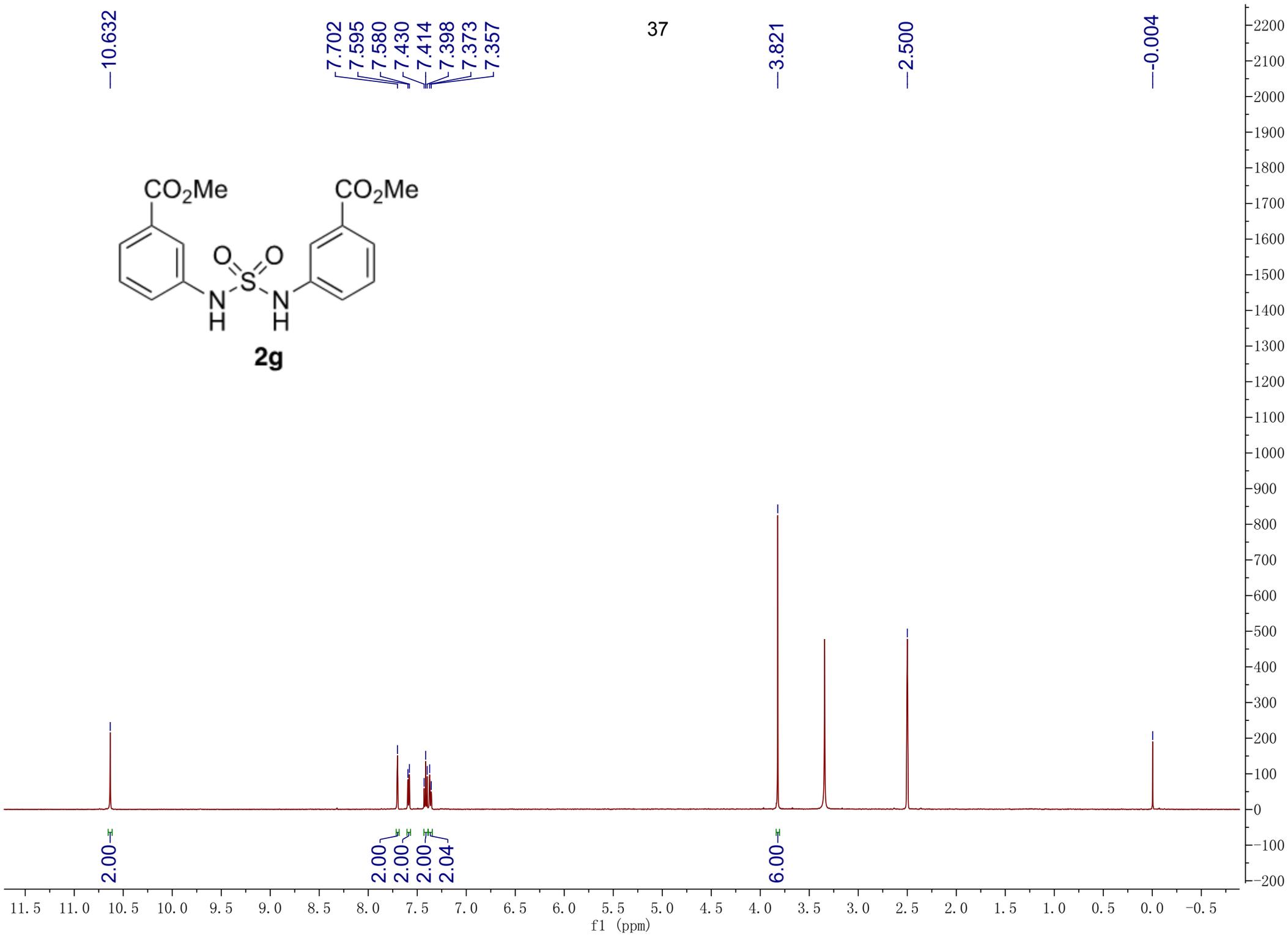
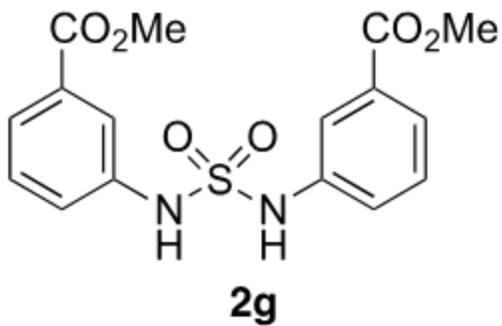
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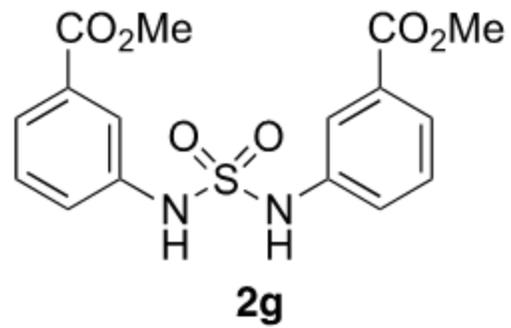
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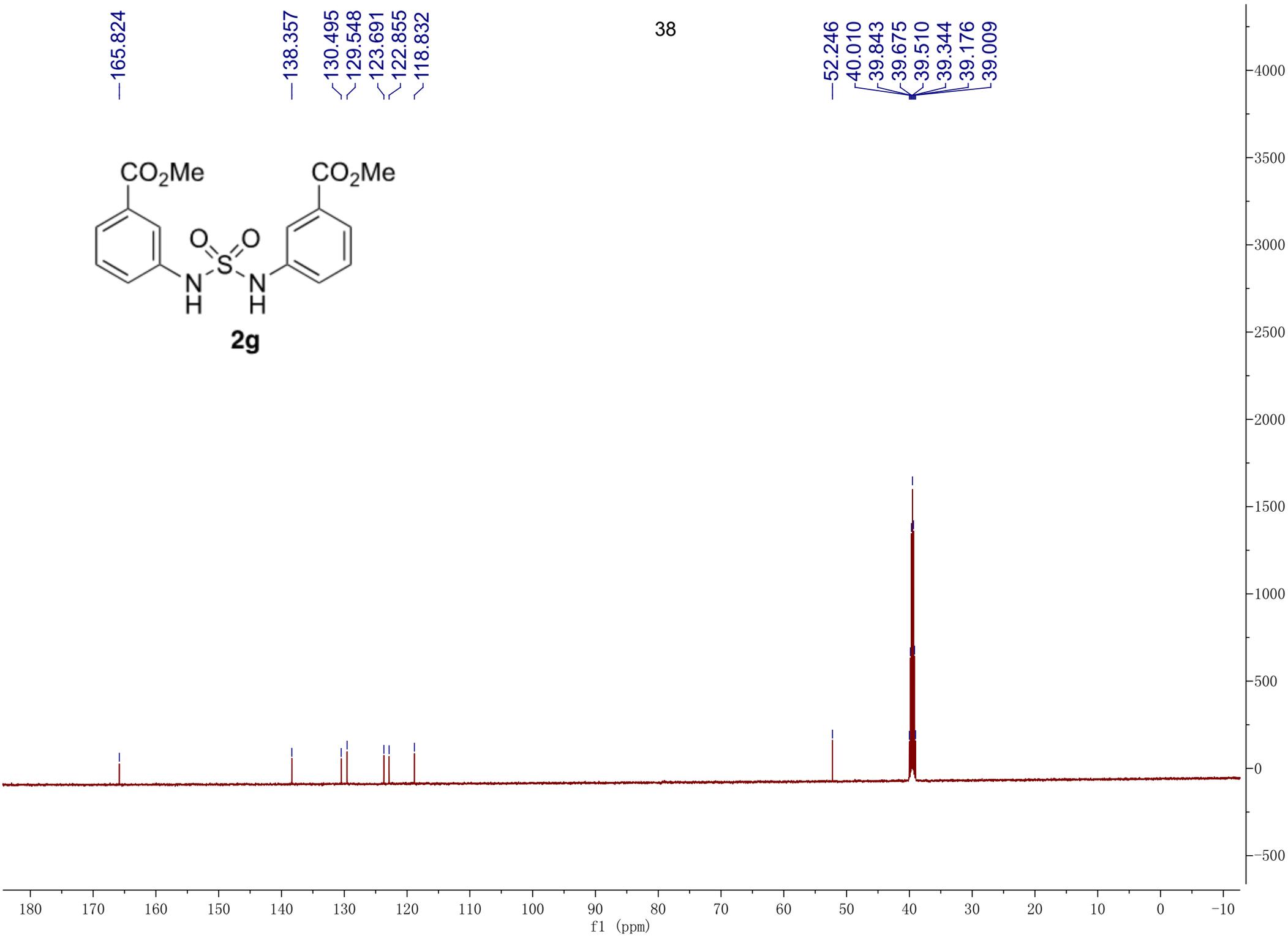
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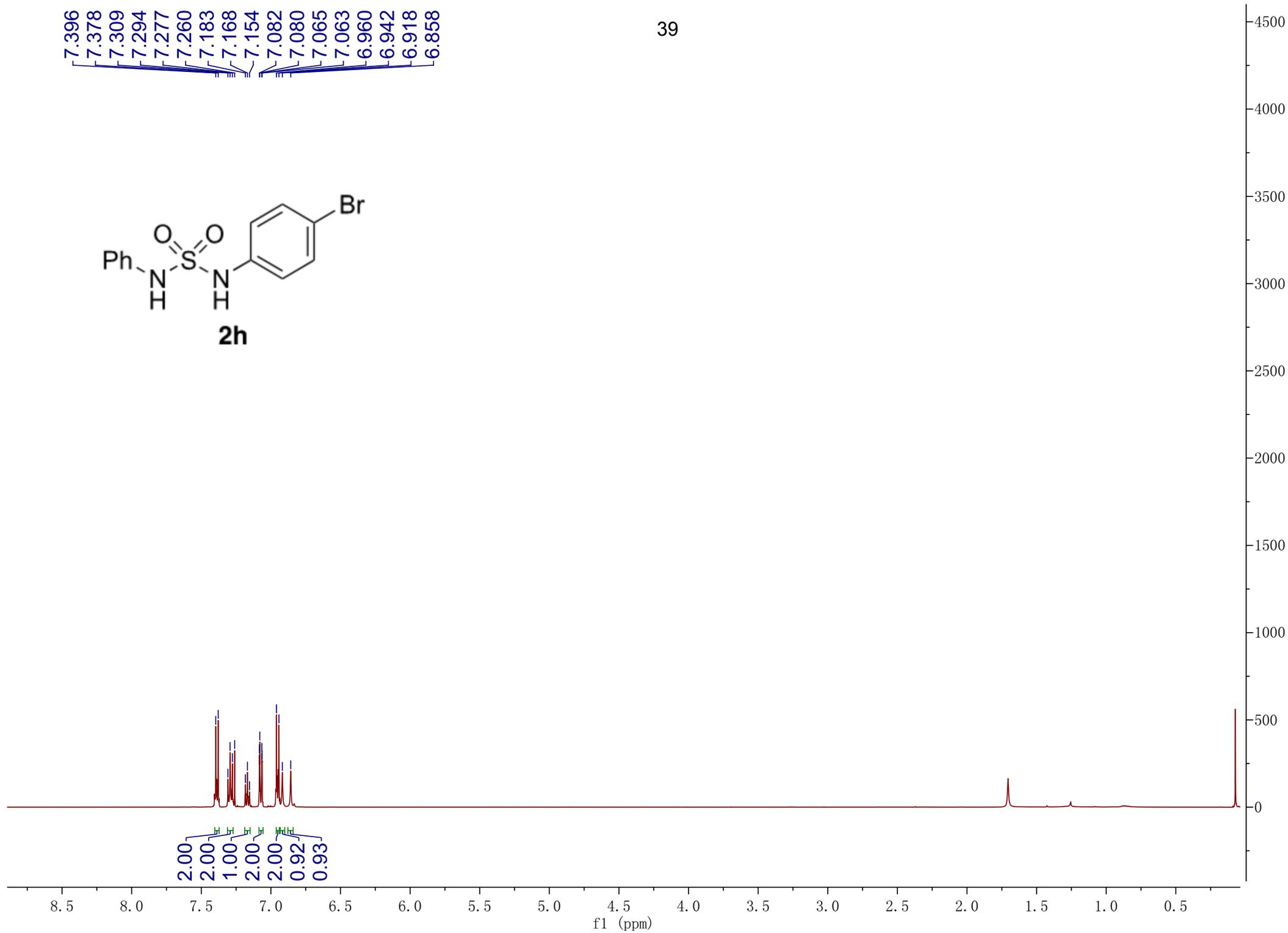
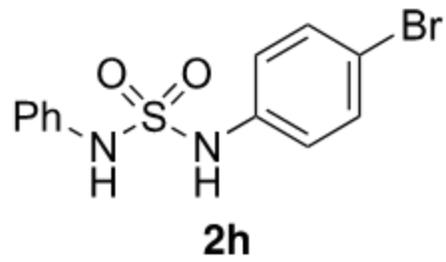
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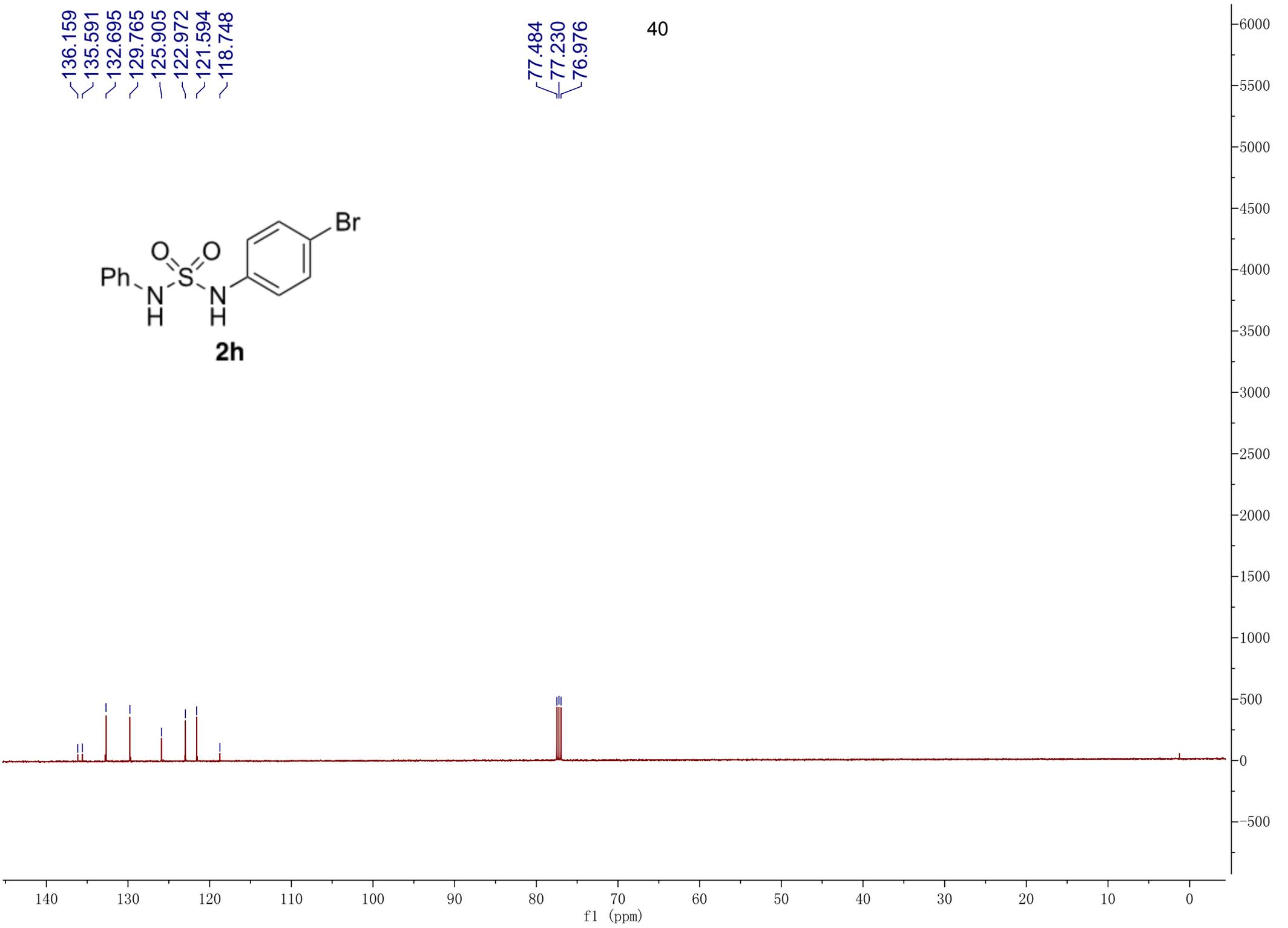
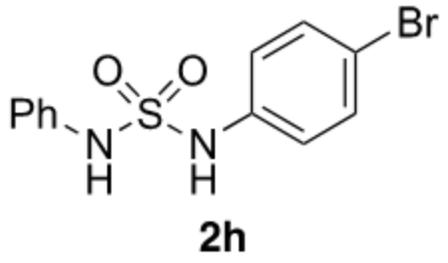




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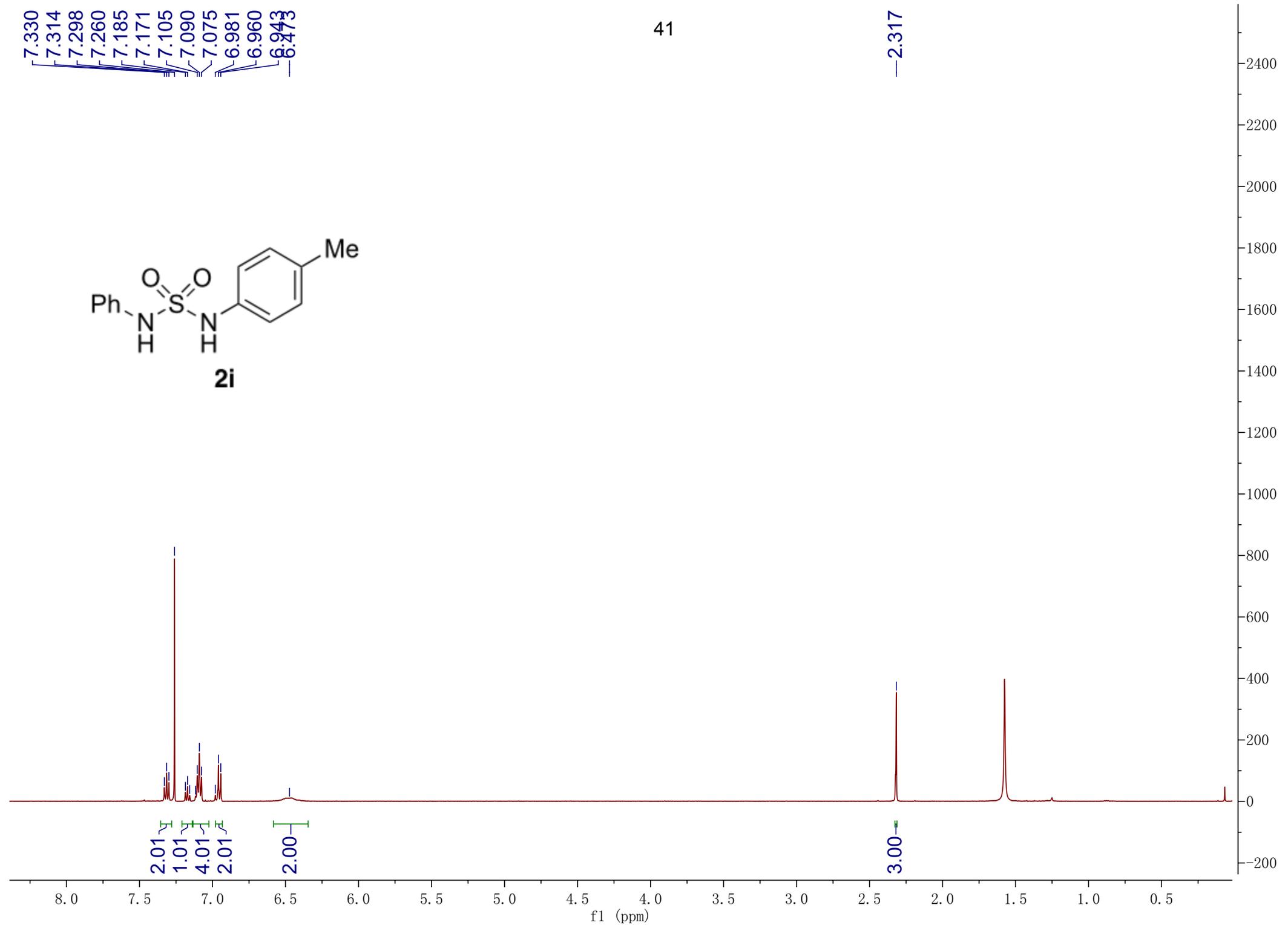
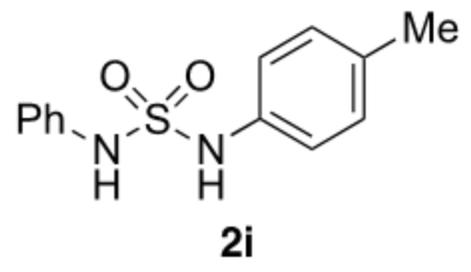
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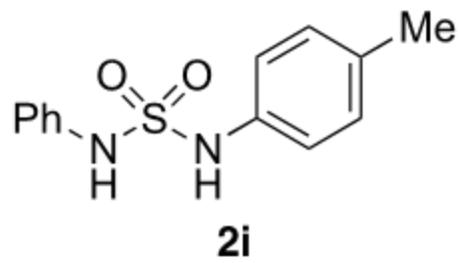


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41

2.317

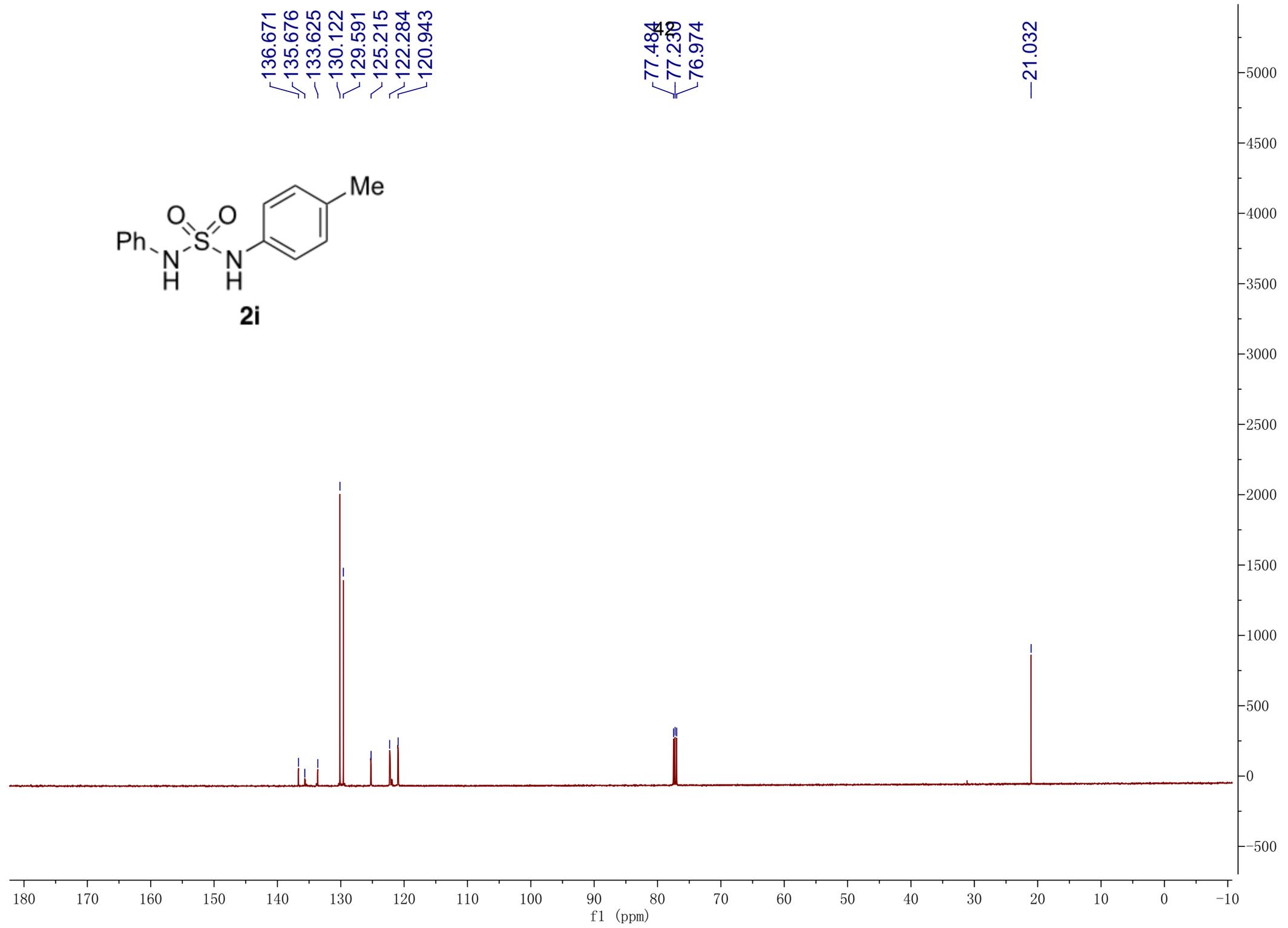




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125.215  
122.284  
120.943

77.484  
77.239  
76.974

21.032

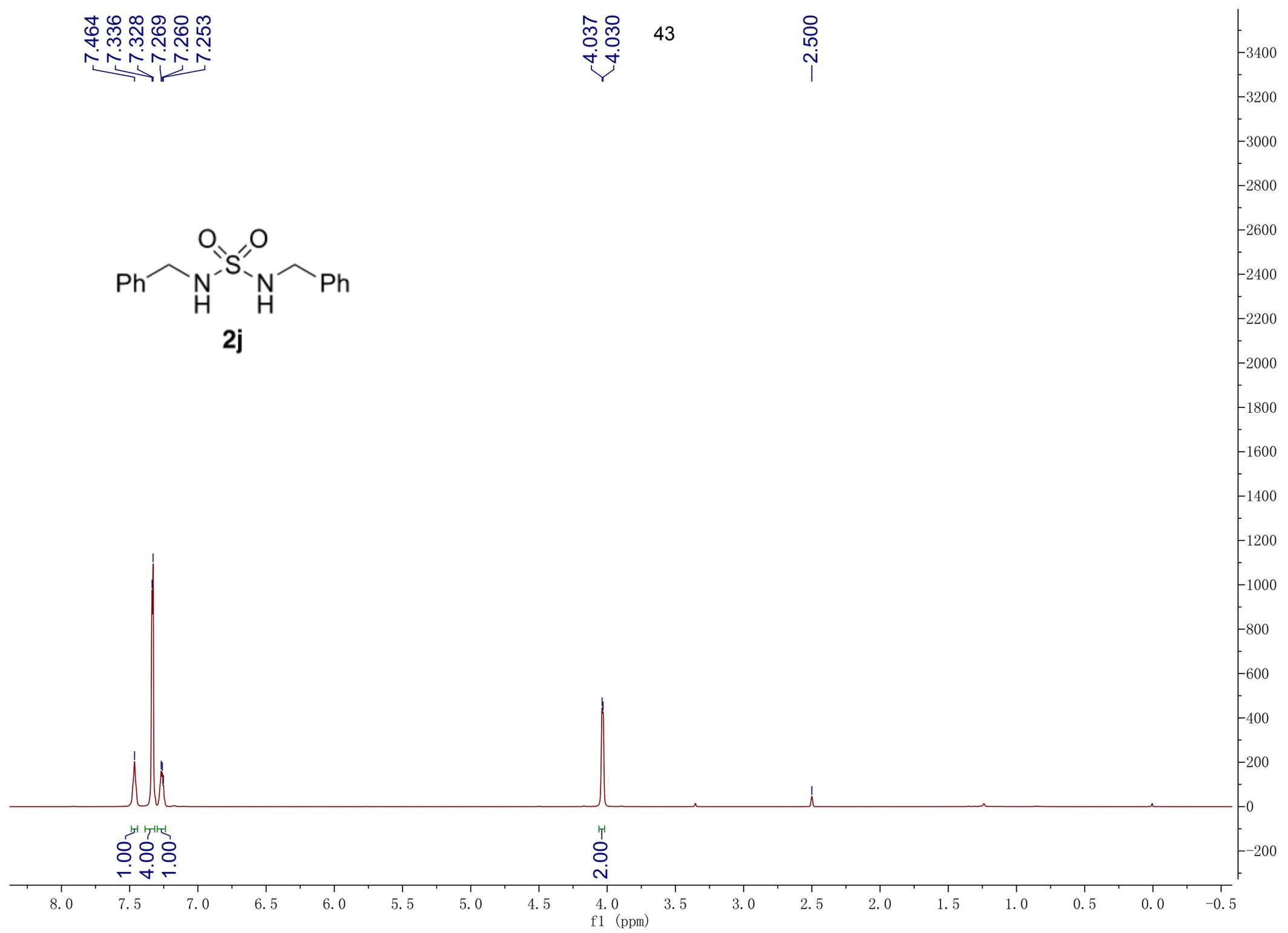
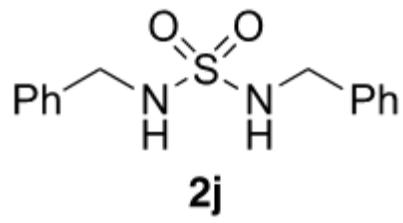


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7.260  
7.253

4.037  
4.030

43

2.500

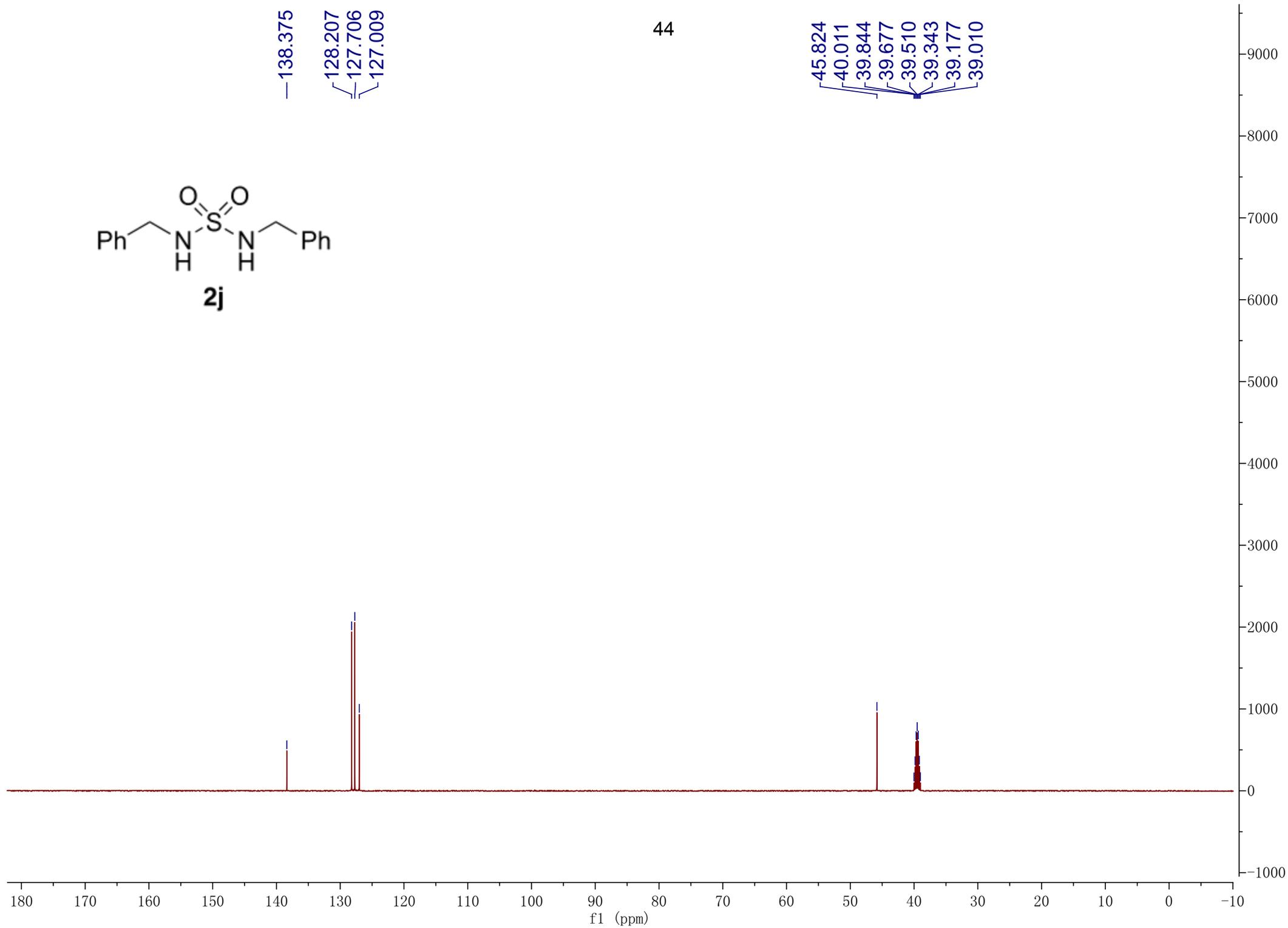
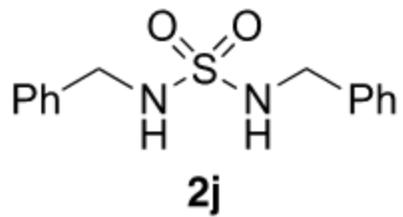


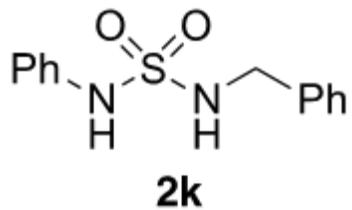
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4.00  
1.00

2.00

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f1 (ppm)





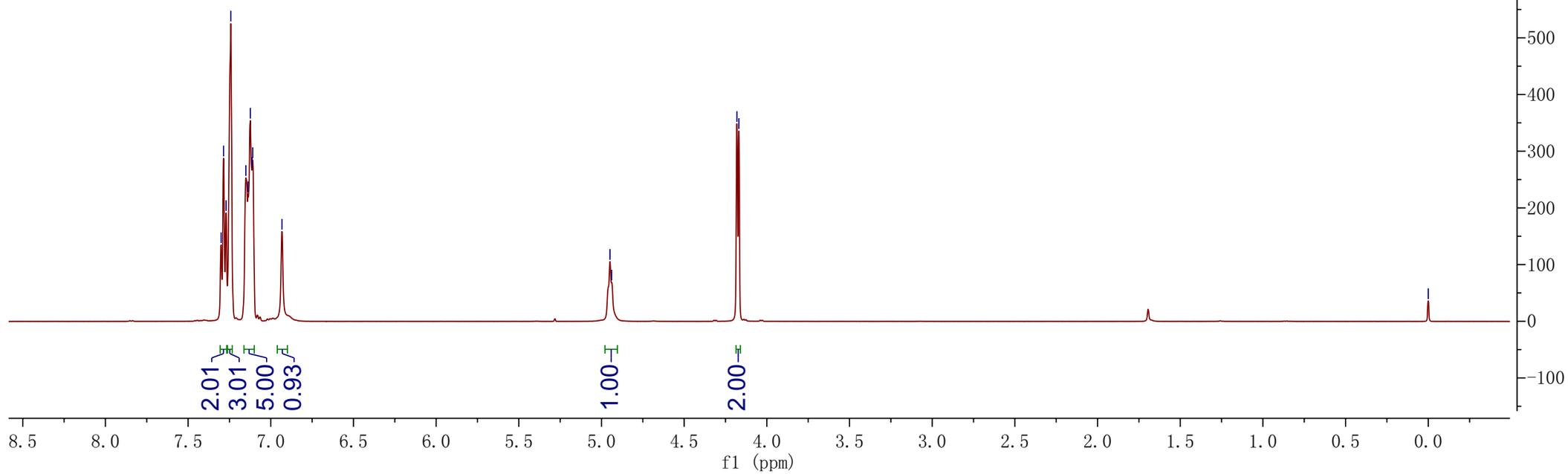
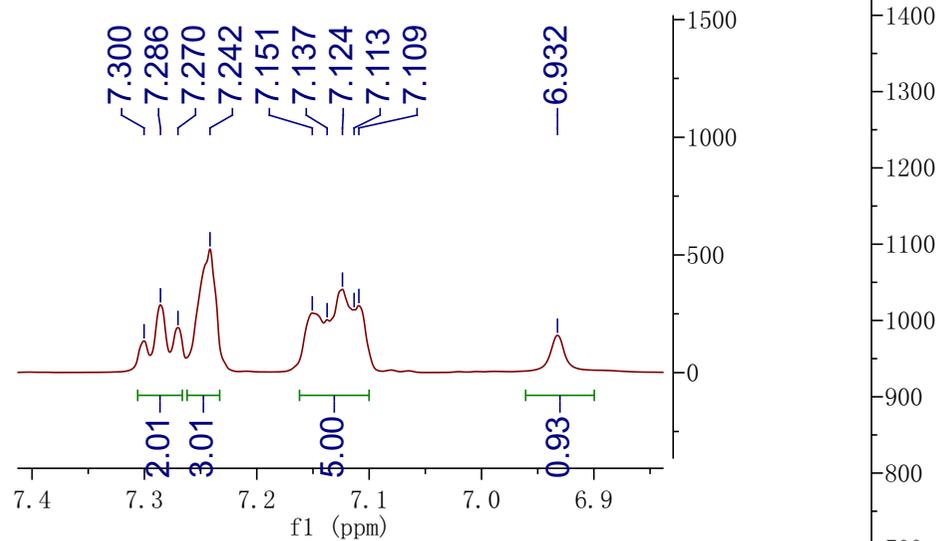
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7.151  
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7.124  
7.113  
7.109  
6.932

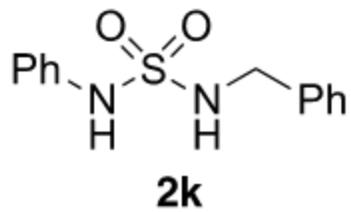
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4.181  
4.169

45

0.000

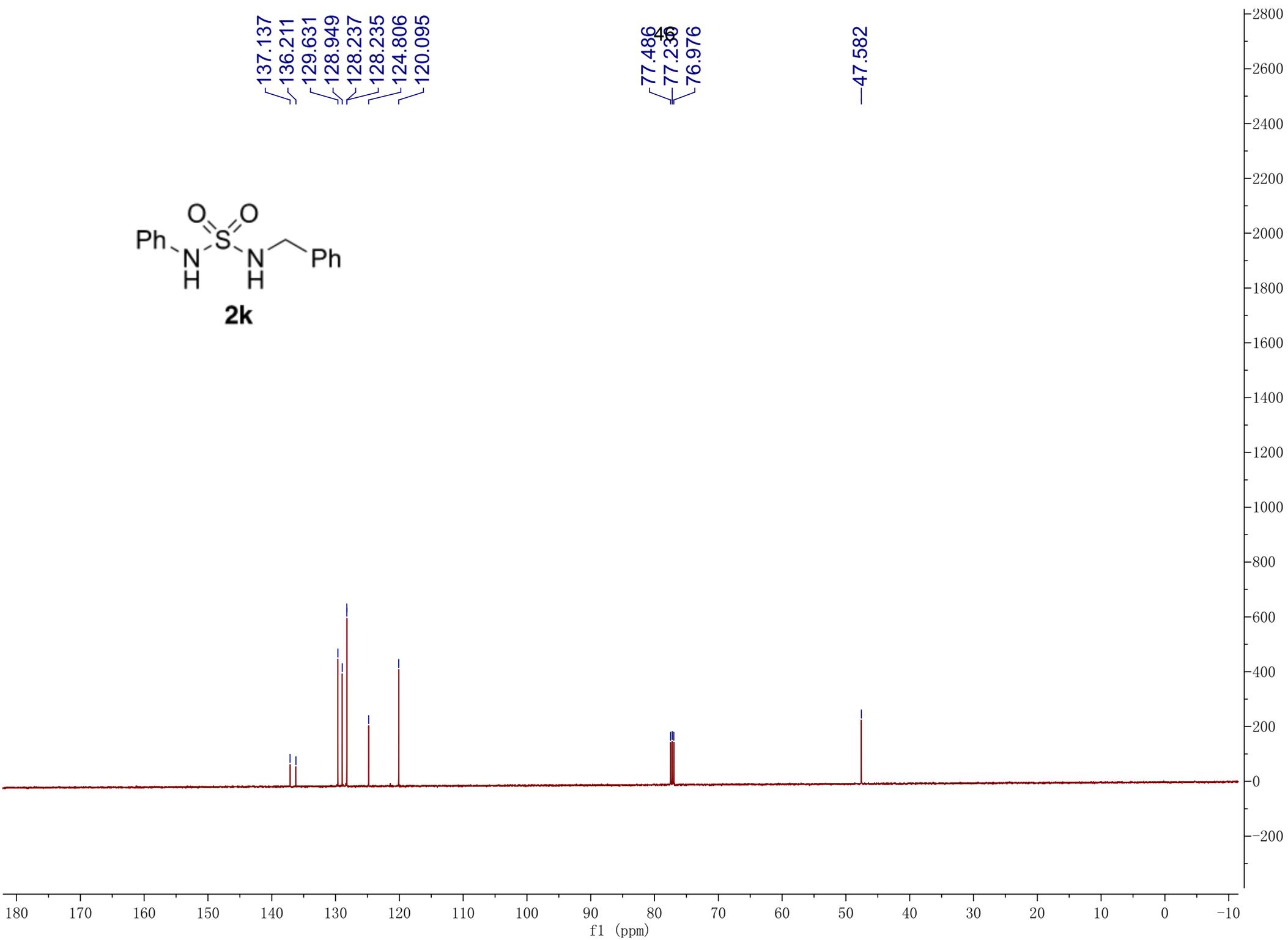


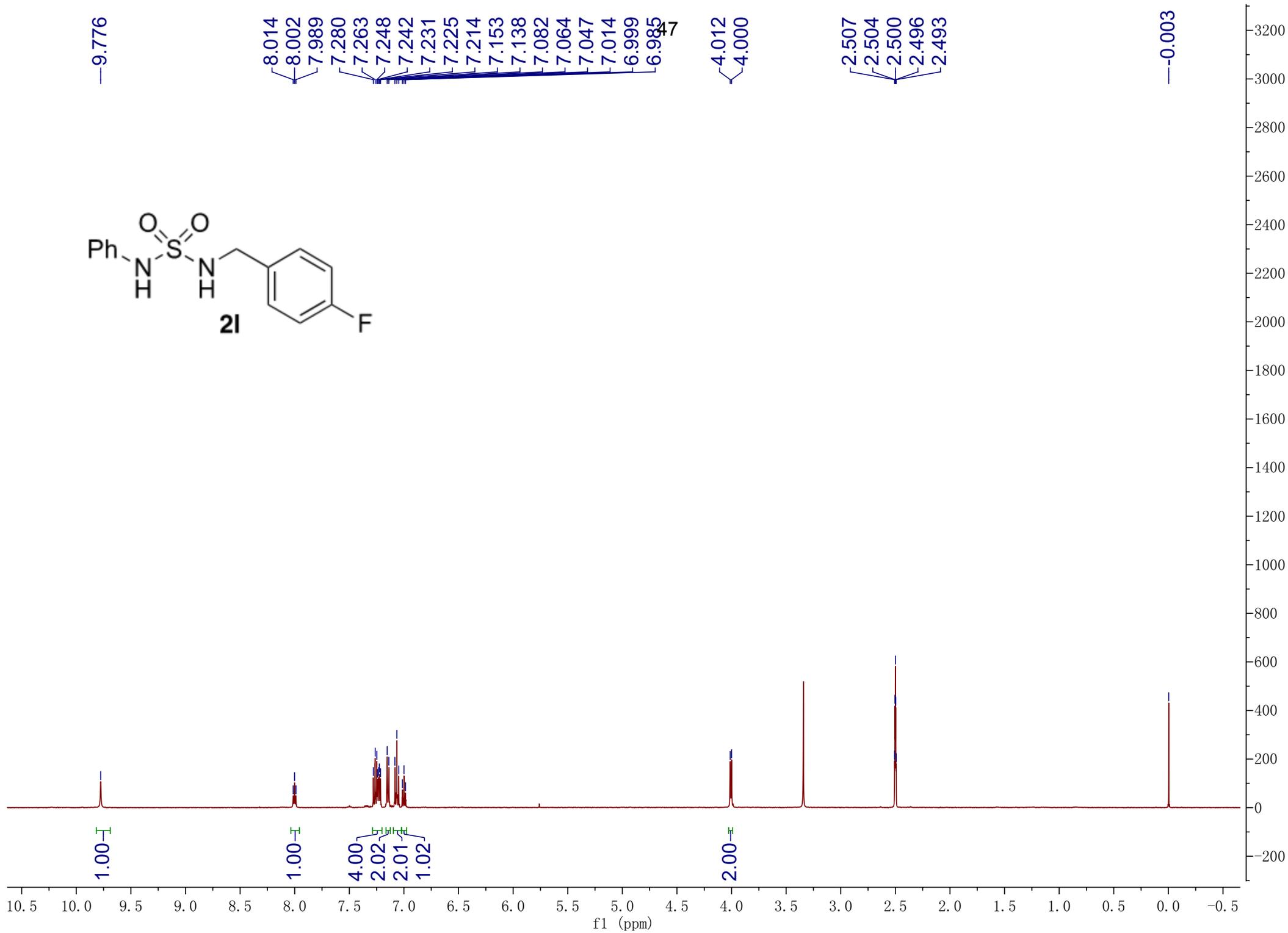
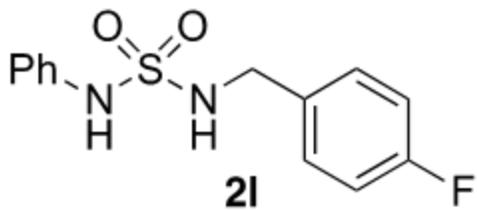


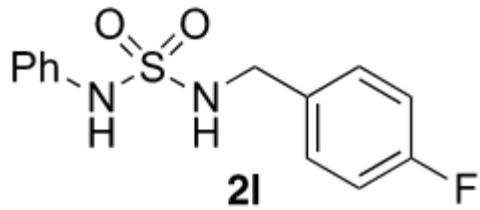
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129.631  
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128.237  
128.235  
124.806  
120.095

77.486  
77.236  
76.976

47.582





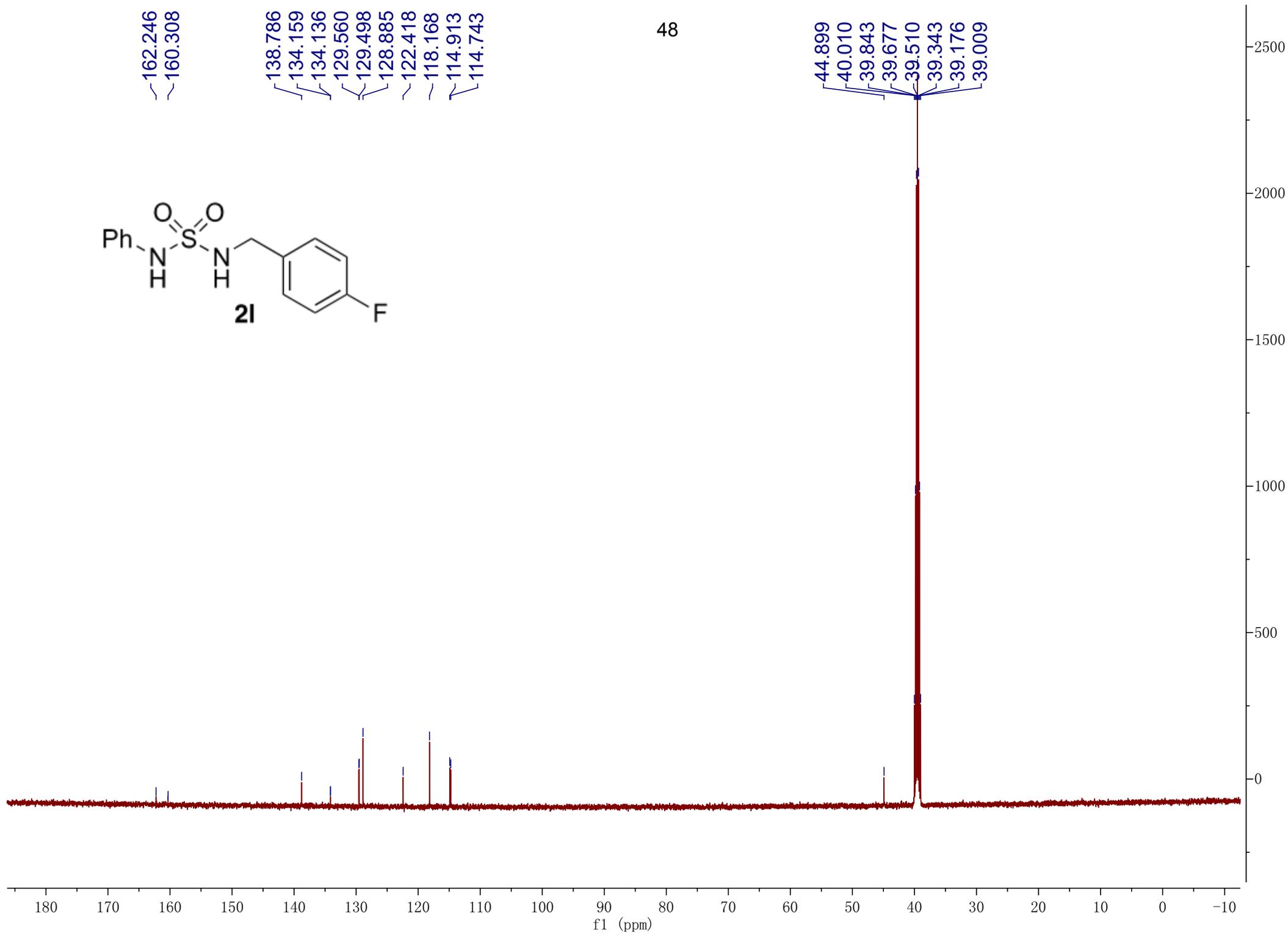


162.246  
160.308

138.786  
134.159  
134.136  
129.560  
129.498  
128.885  
122.418  
118.168  
114.913  
114.743

48

44.899  
40.010  
39.843  
39.677  
39.510  
39.343  
39.176  
39.009



7.311  
7.298  
7.284  
7.141  
7.116  
7.102  
7.060  
6.684

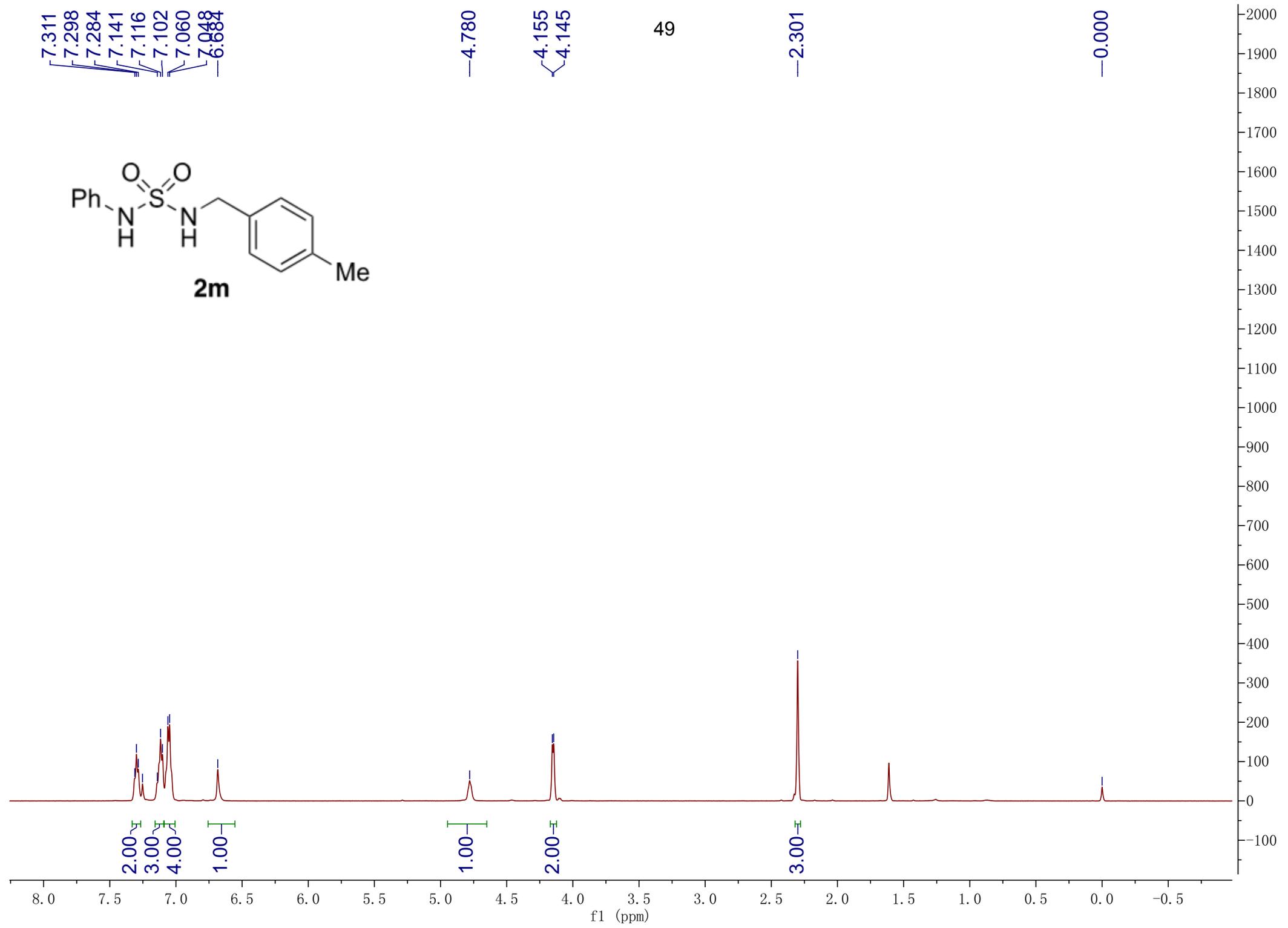
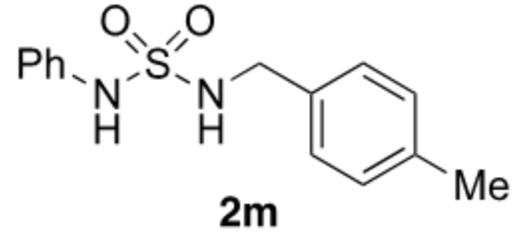
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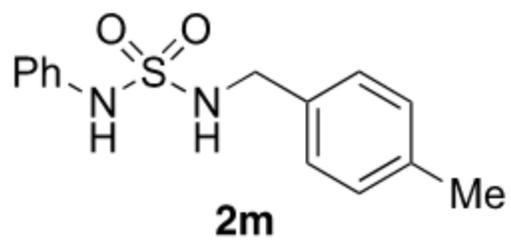
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4.145

49

2.301

0.000



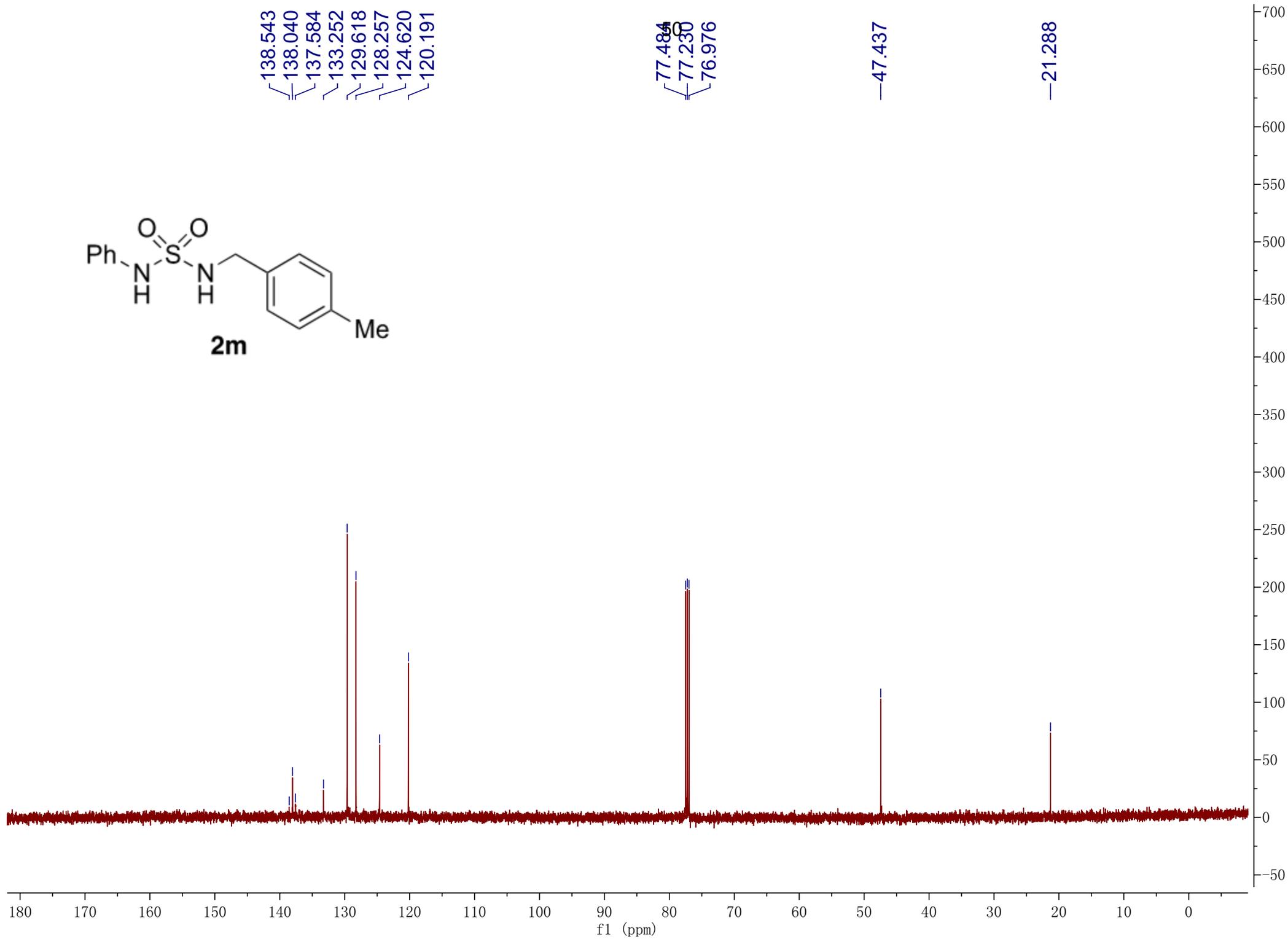


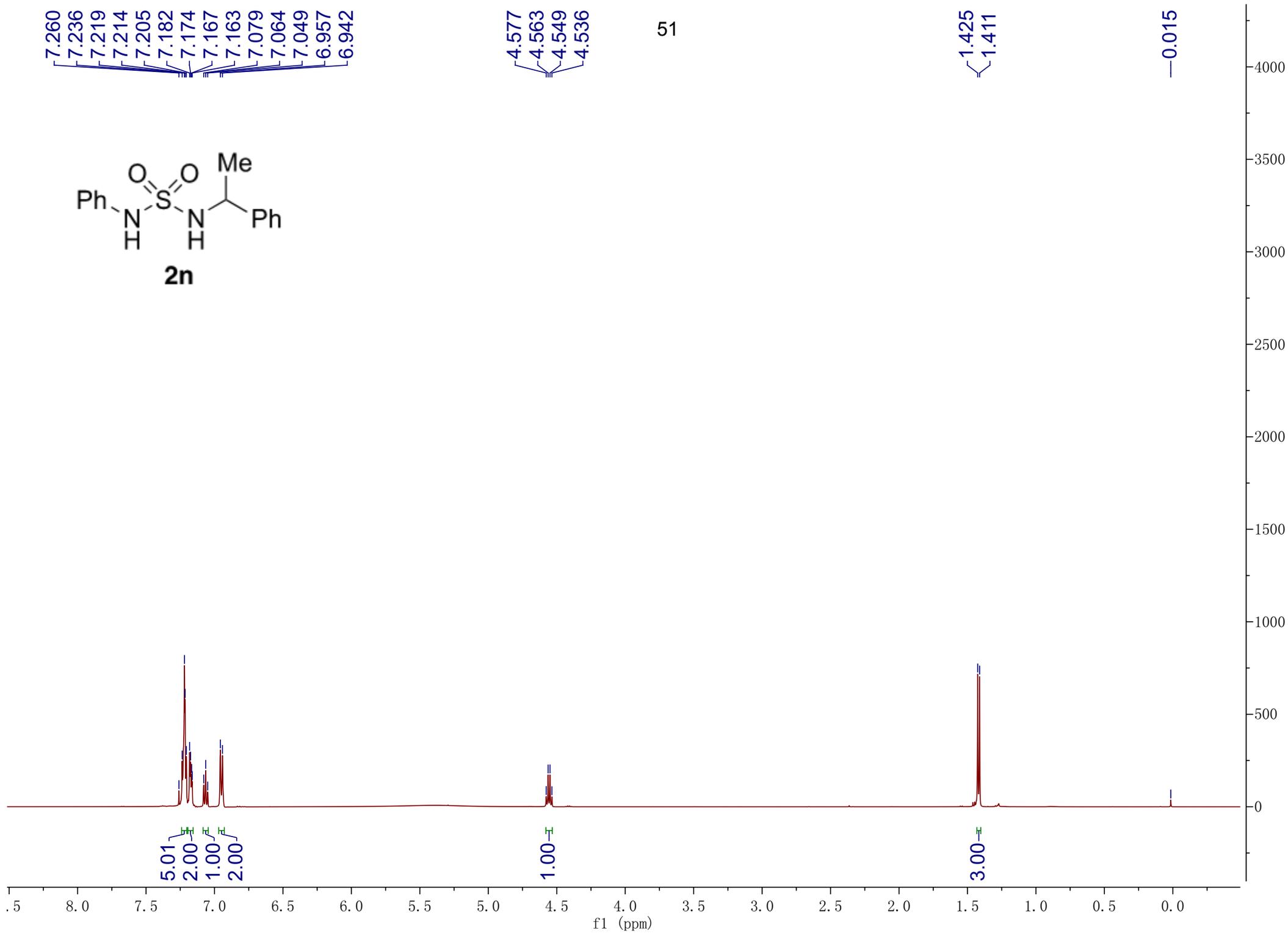
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124.620  
120.191

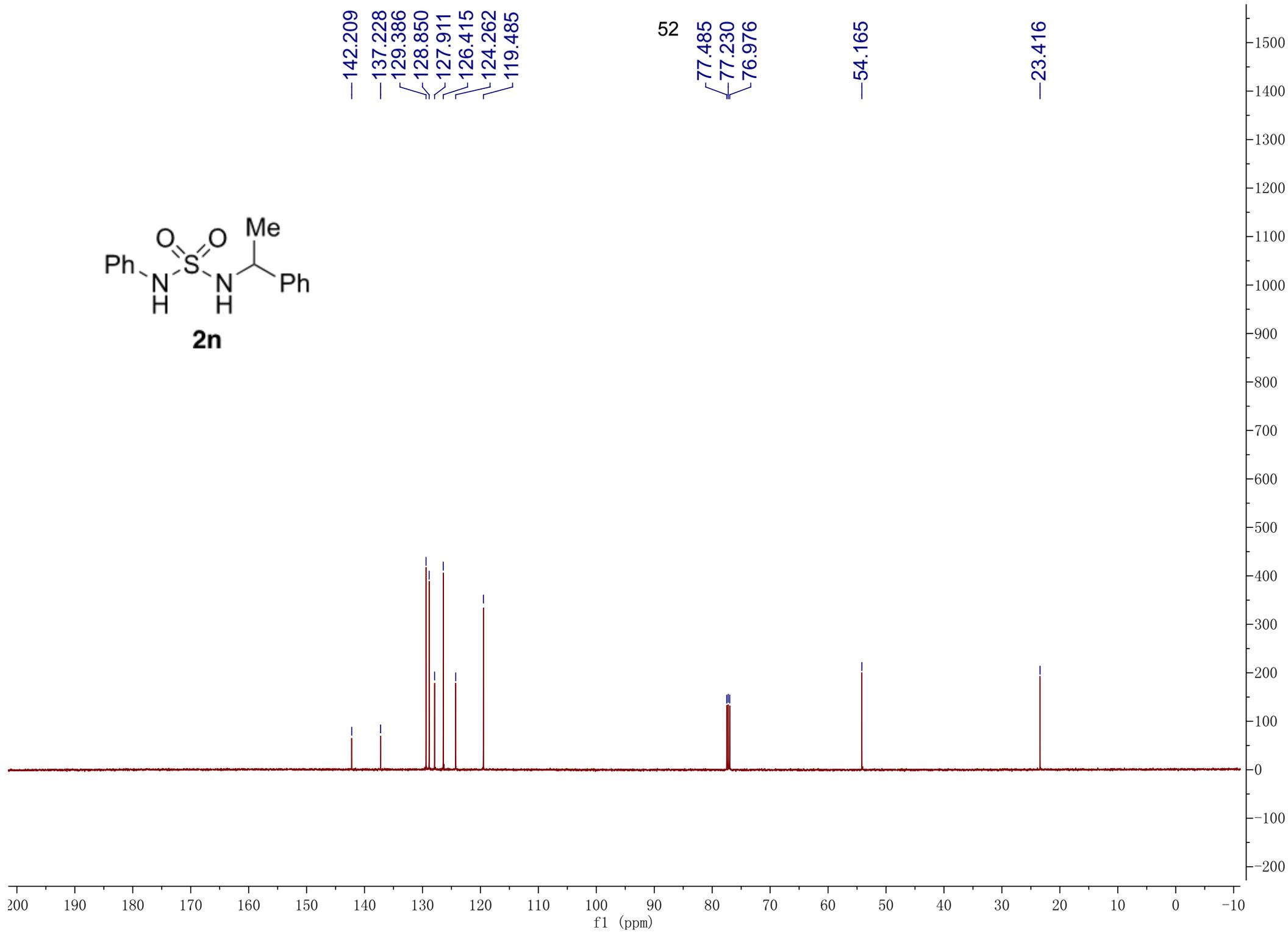
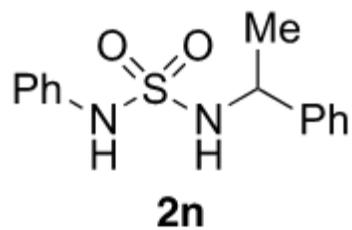
77.484  
77.230  
76.976

—47.437

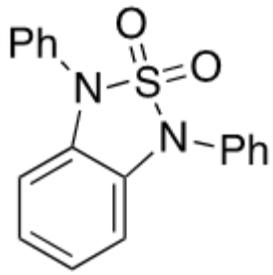
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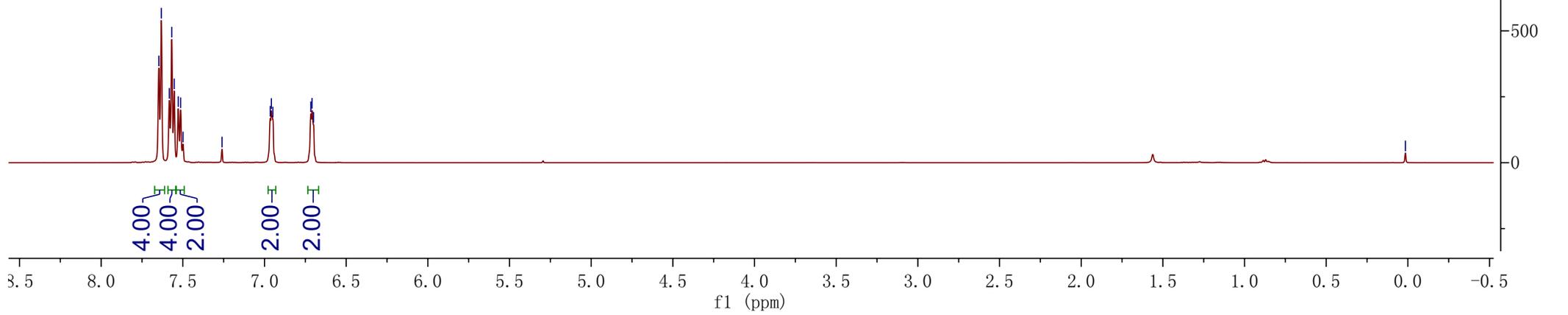
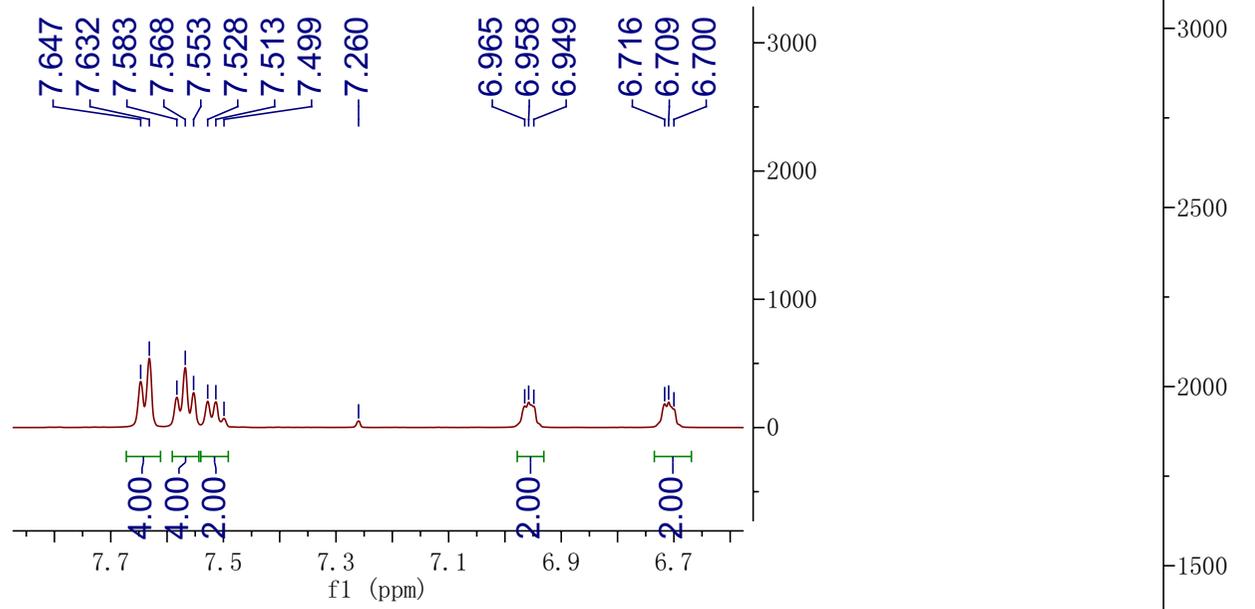
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7.528  
7.513  
7.499  
7.260  
6.965  
6.958  
6.949  
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6.709  
6.700

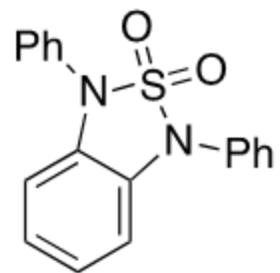


**3a**

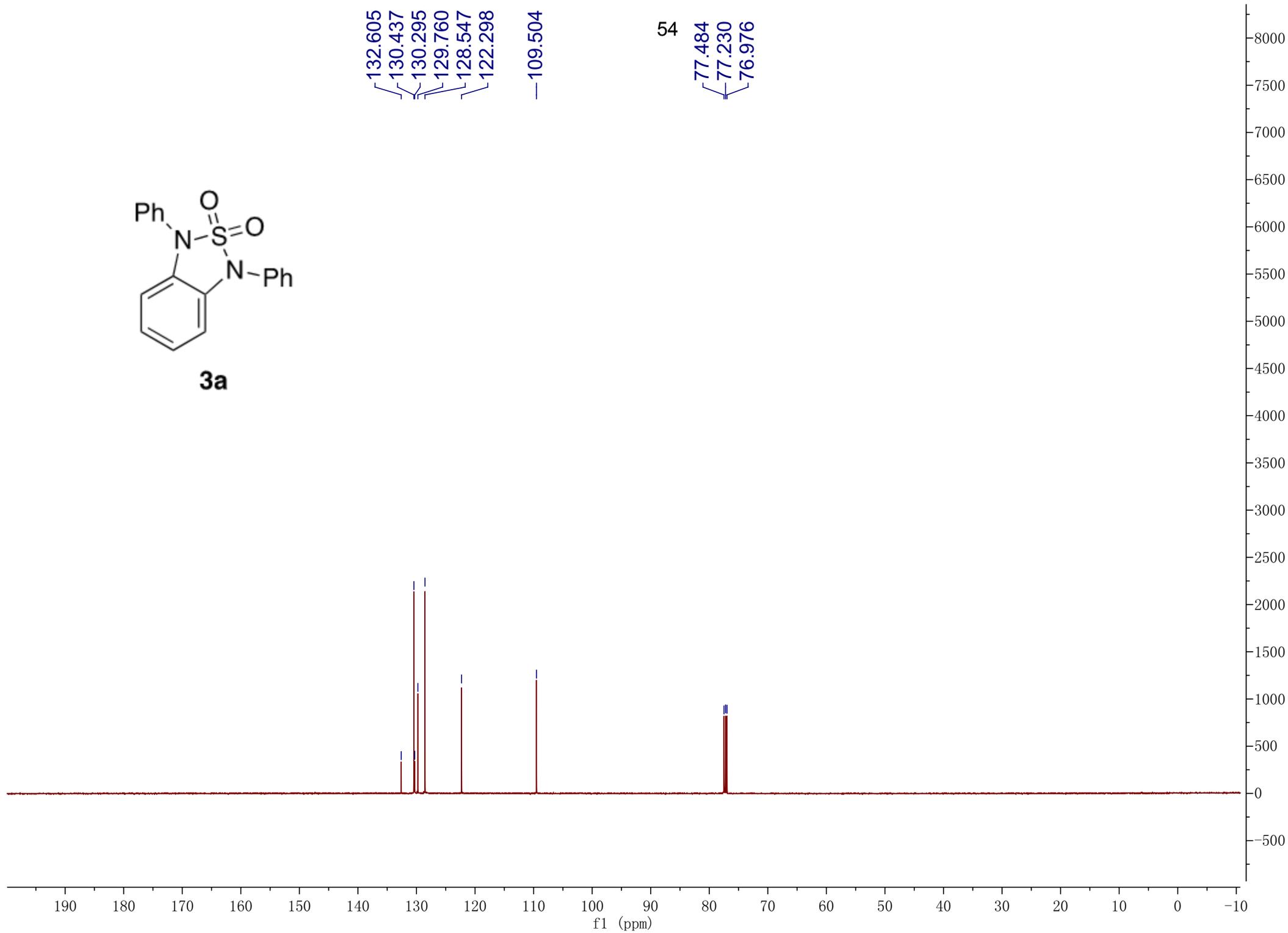
53

—0.015





**3a**

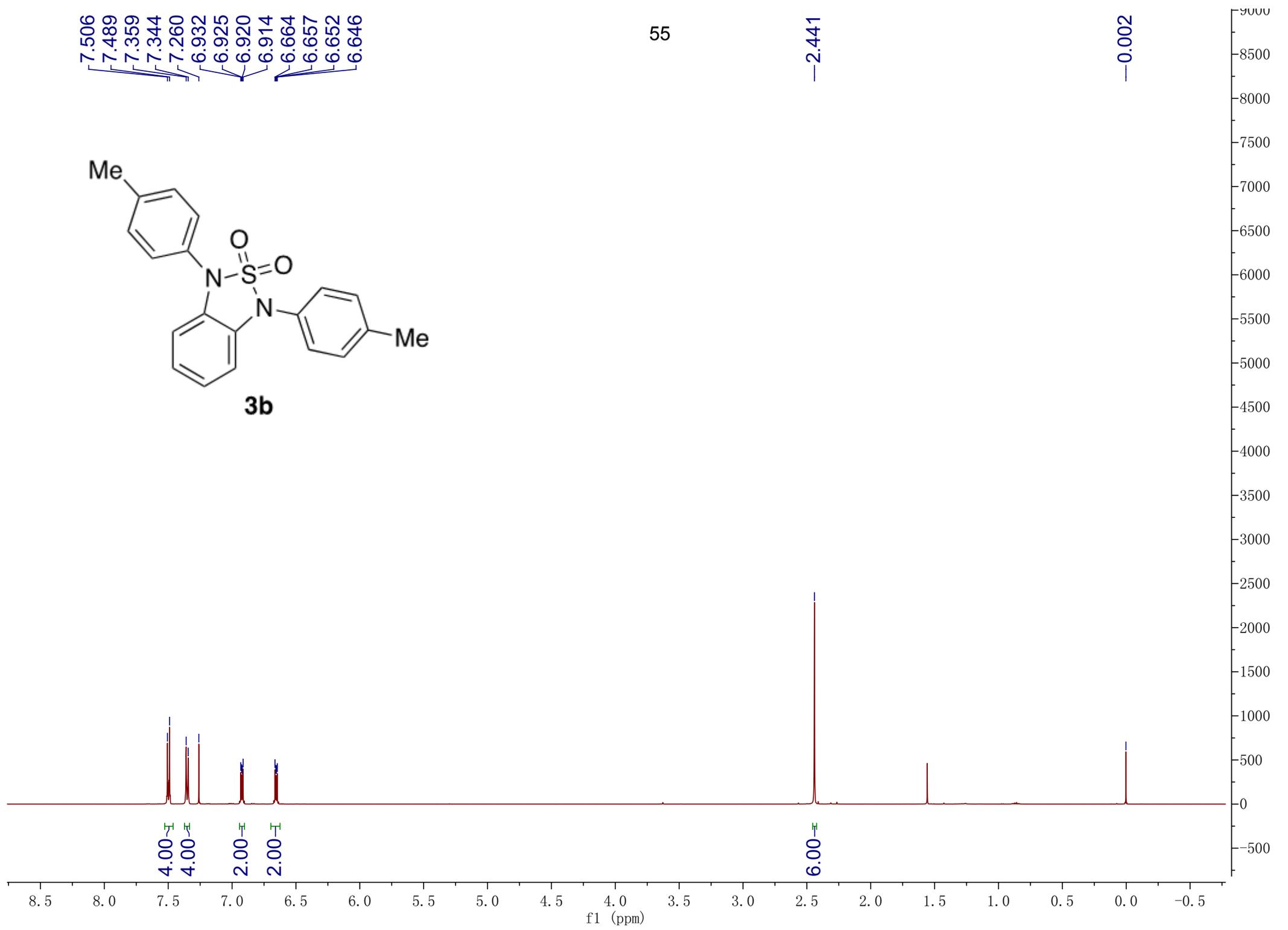
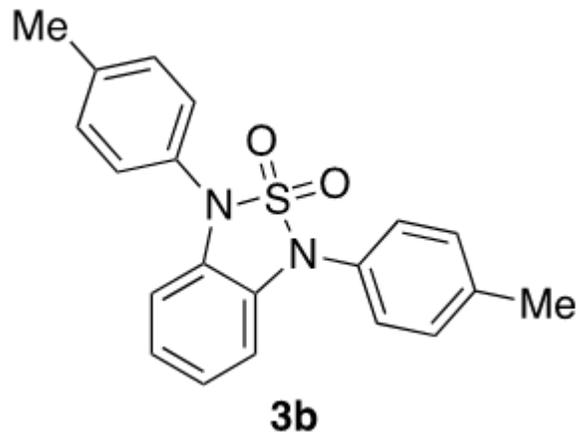


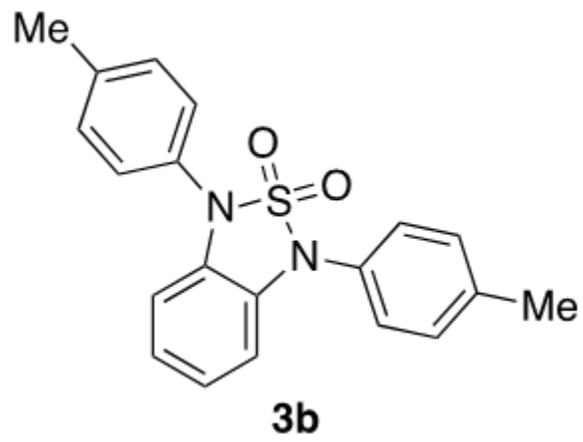
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7.359  
7.344  
7.260  
6.932  
6.925  
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6.914  
6.664  
6.657  
6.652  
6.646

55

-2.441

-0.002

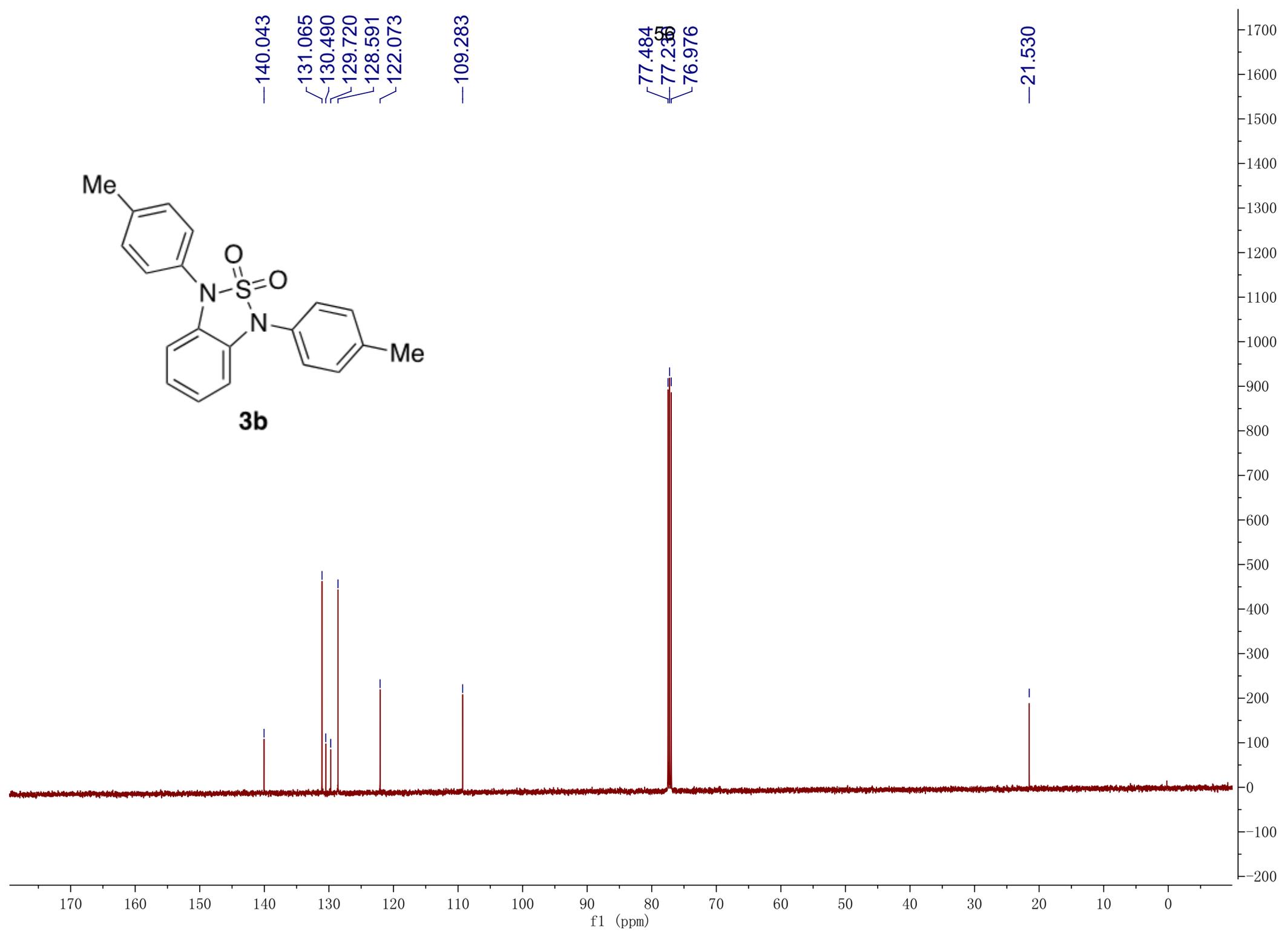




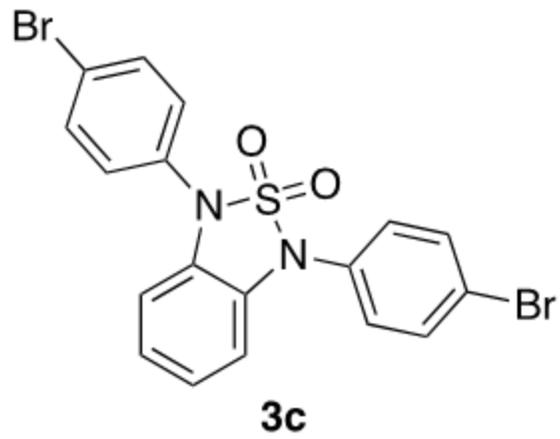
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129.720  
128.591  
122.073  
—109.283

77.484  
77.235  
76.976

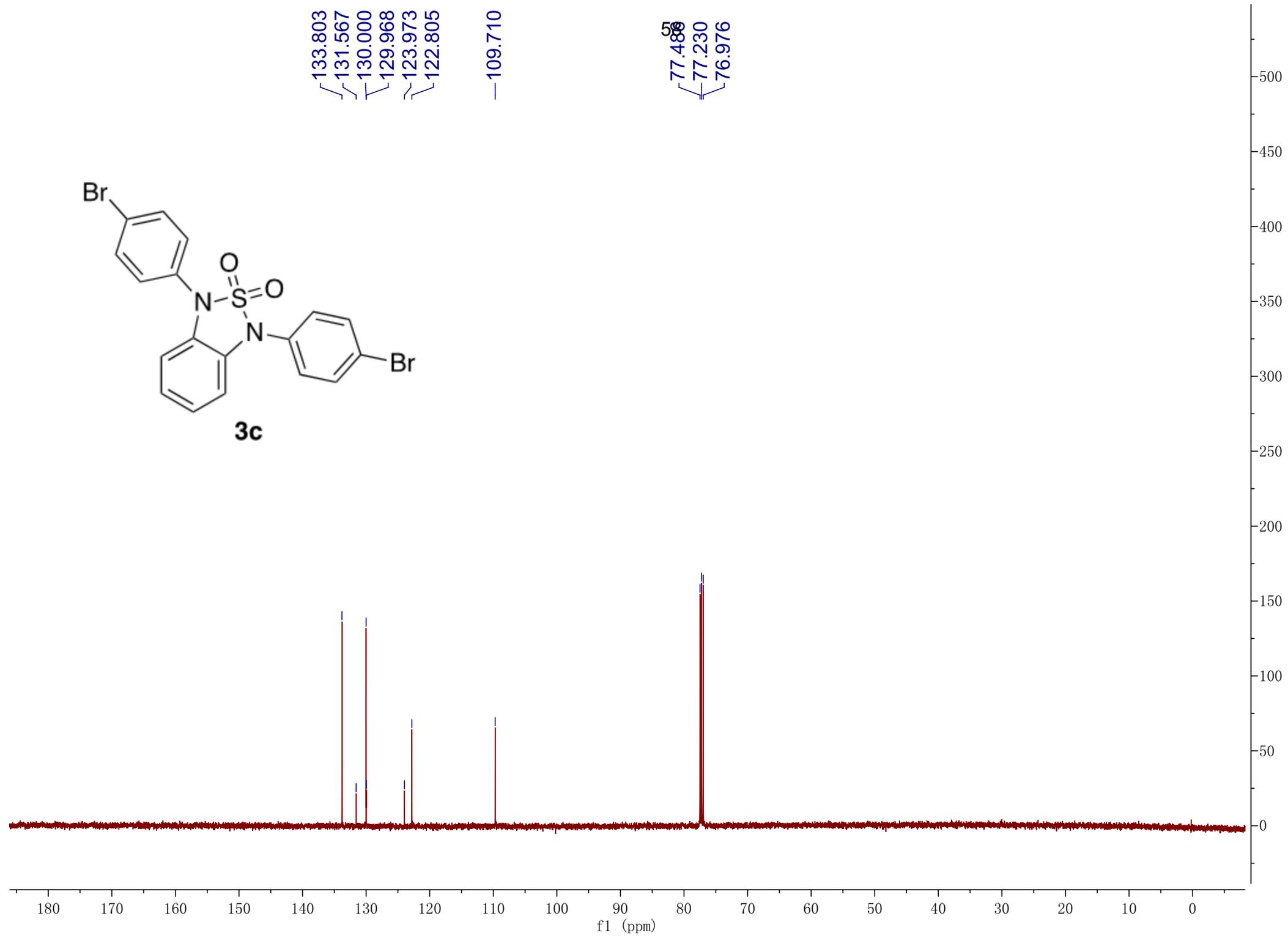
—21.530





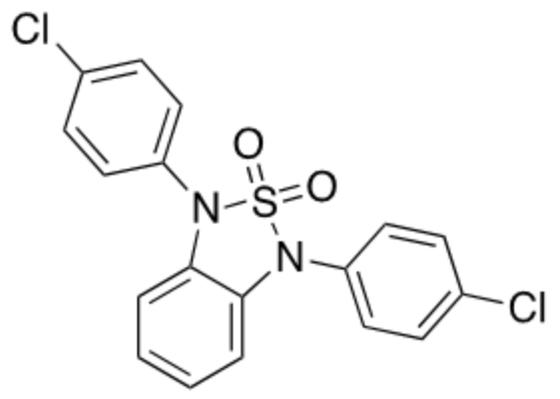


133.803  
131.567  
130.000  
129.968  
123.973  
122.805  
— 109.710  
56  
77.486  
77.230  
76.976

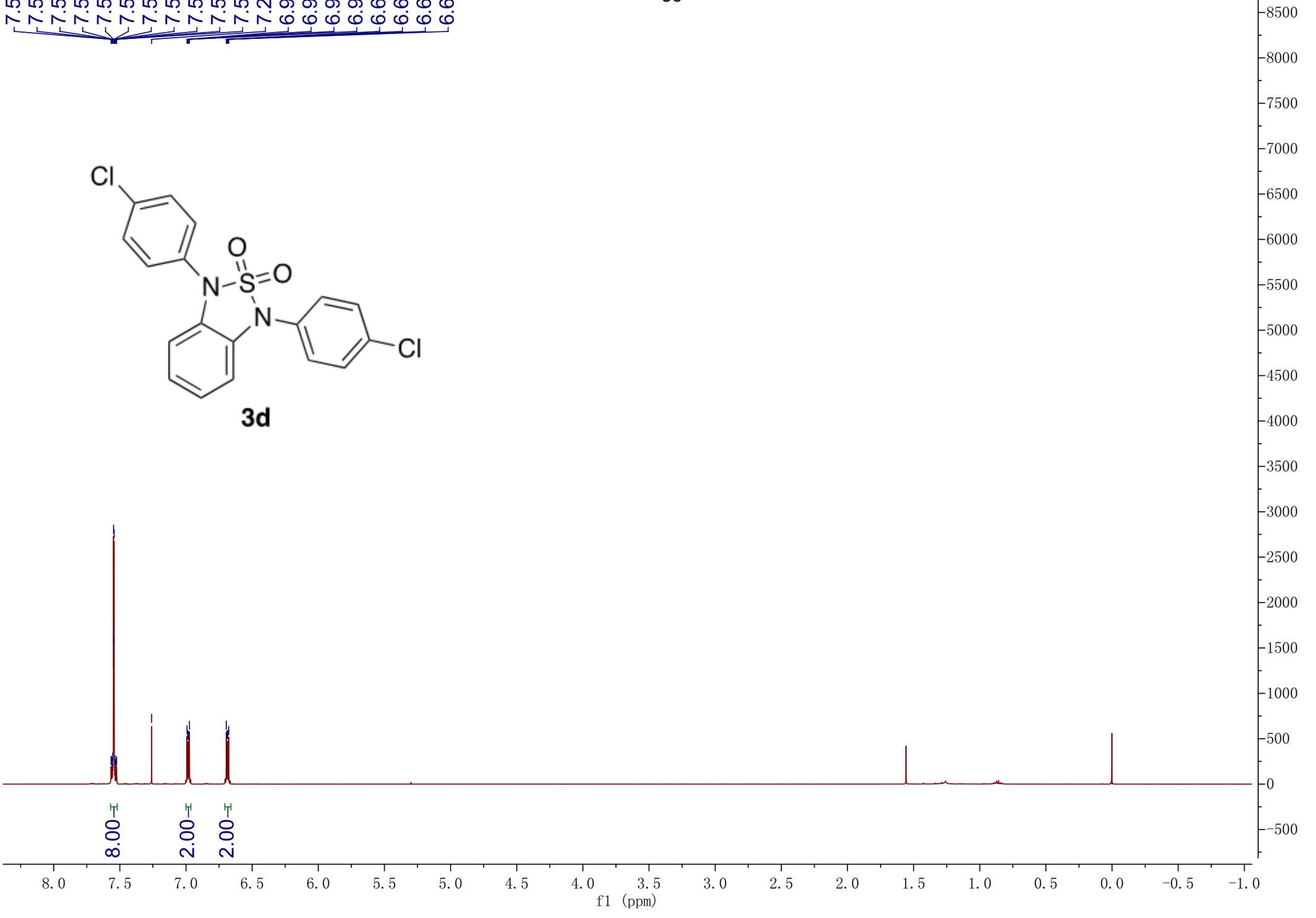


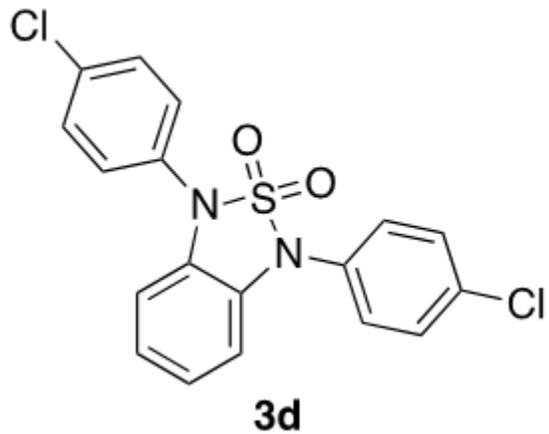
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7.545  
7.543  
7.537  
7.531  
7.526  
7.525  
7.260  
6.992  
6.986  
6.980  
6.974  
6.695  
6.689  
6.684  
6.677

59



3d

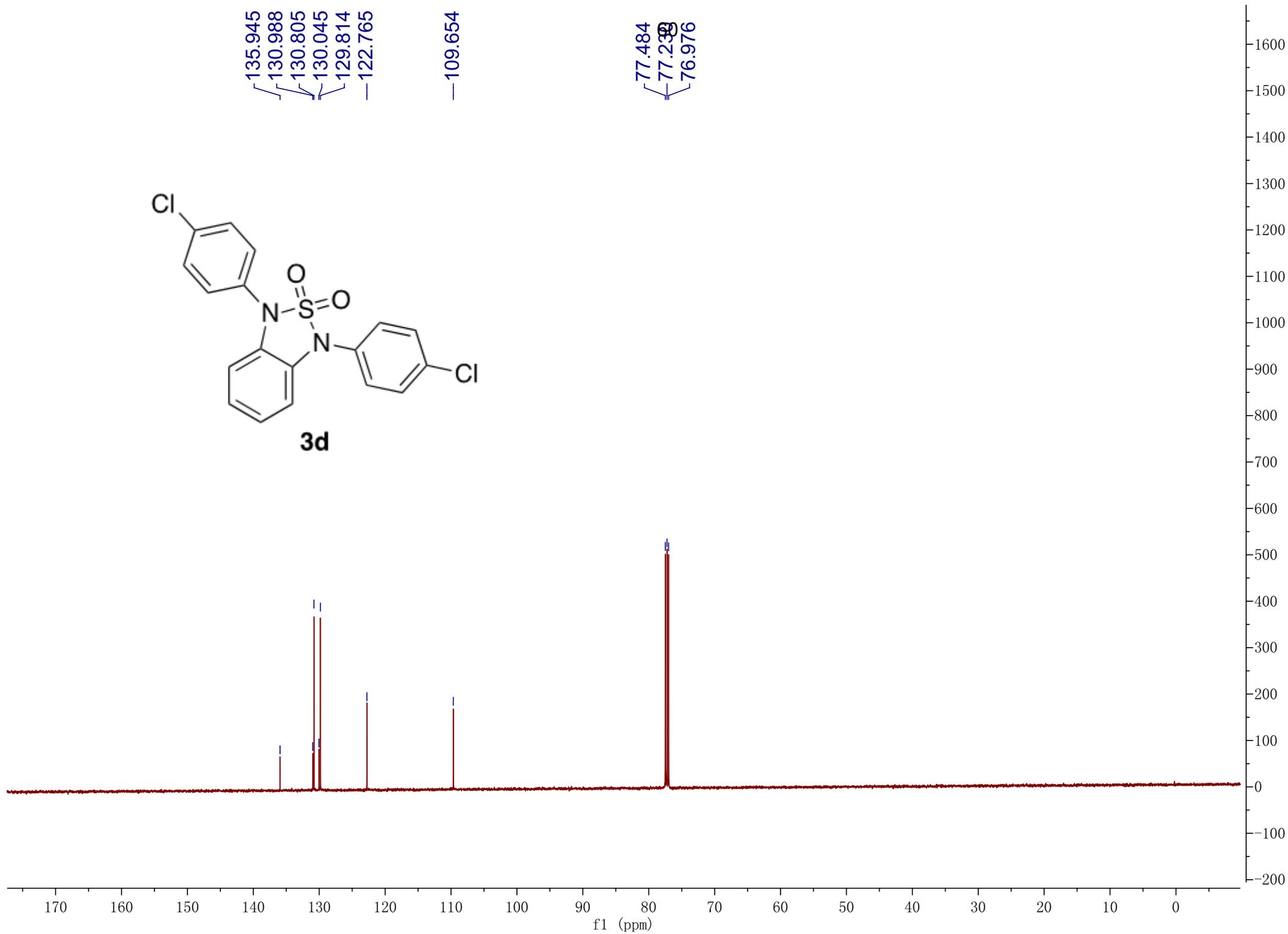




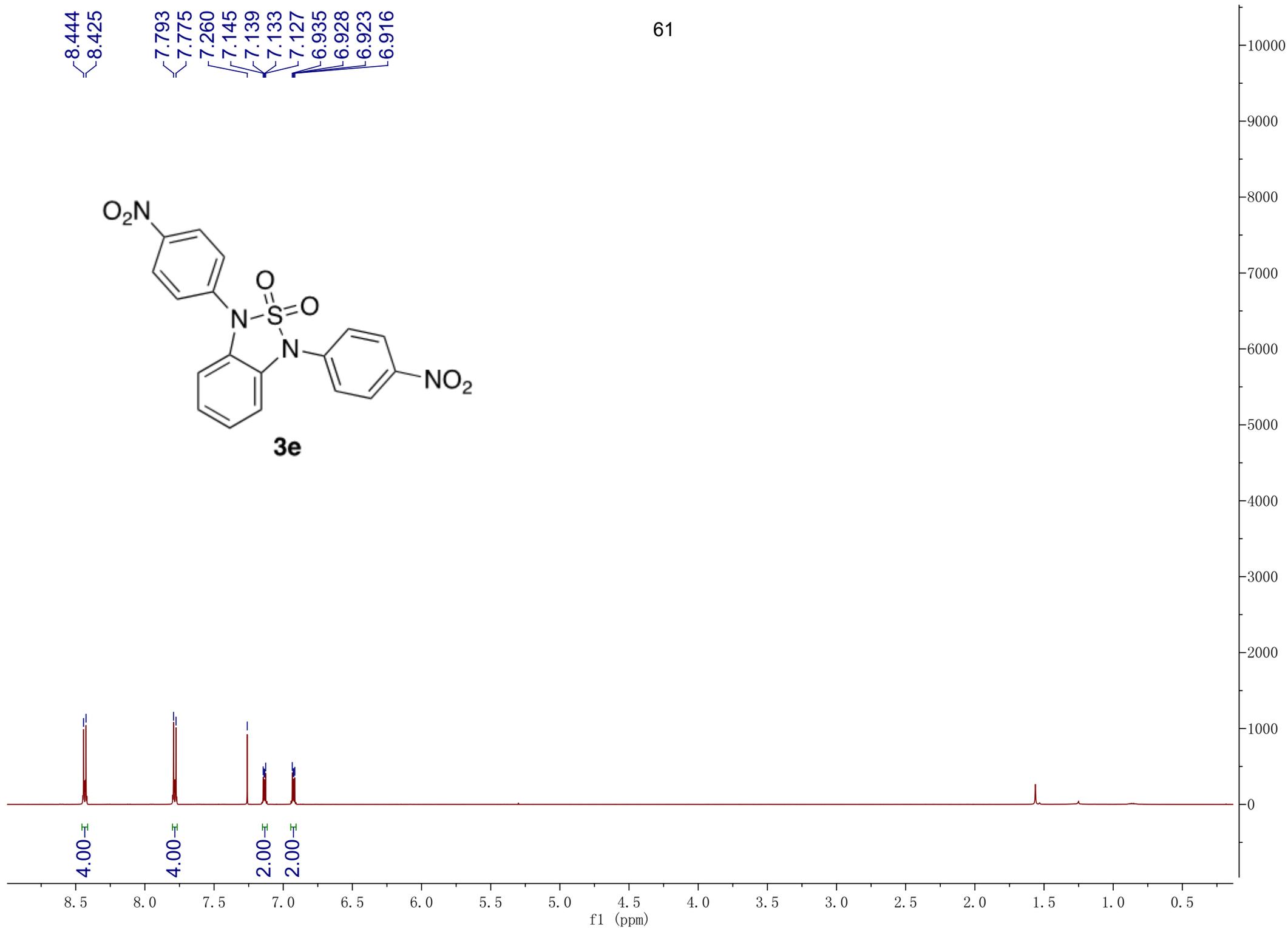
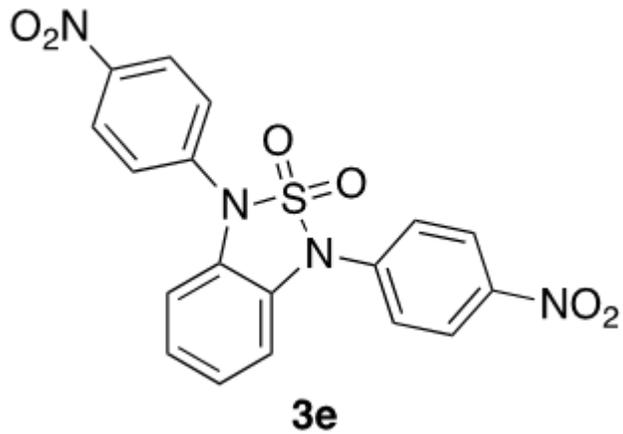
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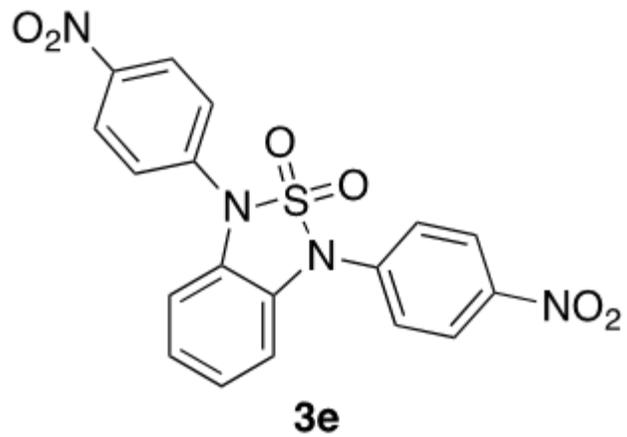
109.654

77.484  
77.238  
76.976



8.444  
8.425  
7.793  
7.775  
7.260  
7.145  
7.139  
7.133  
7.127  
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6.928  
6.923  
6.916





147.747

138.877

129.074

127.147

126.003

124.124

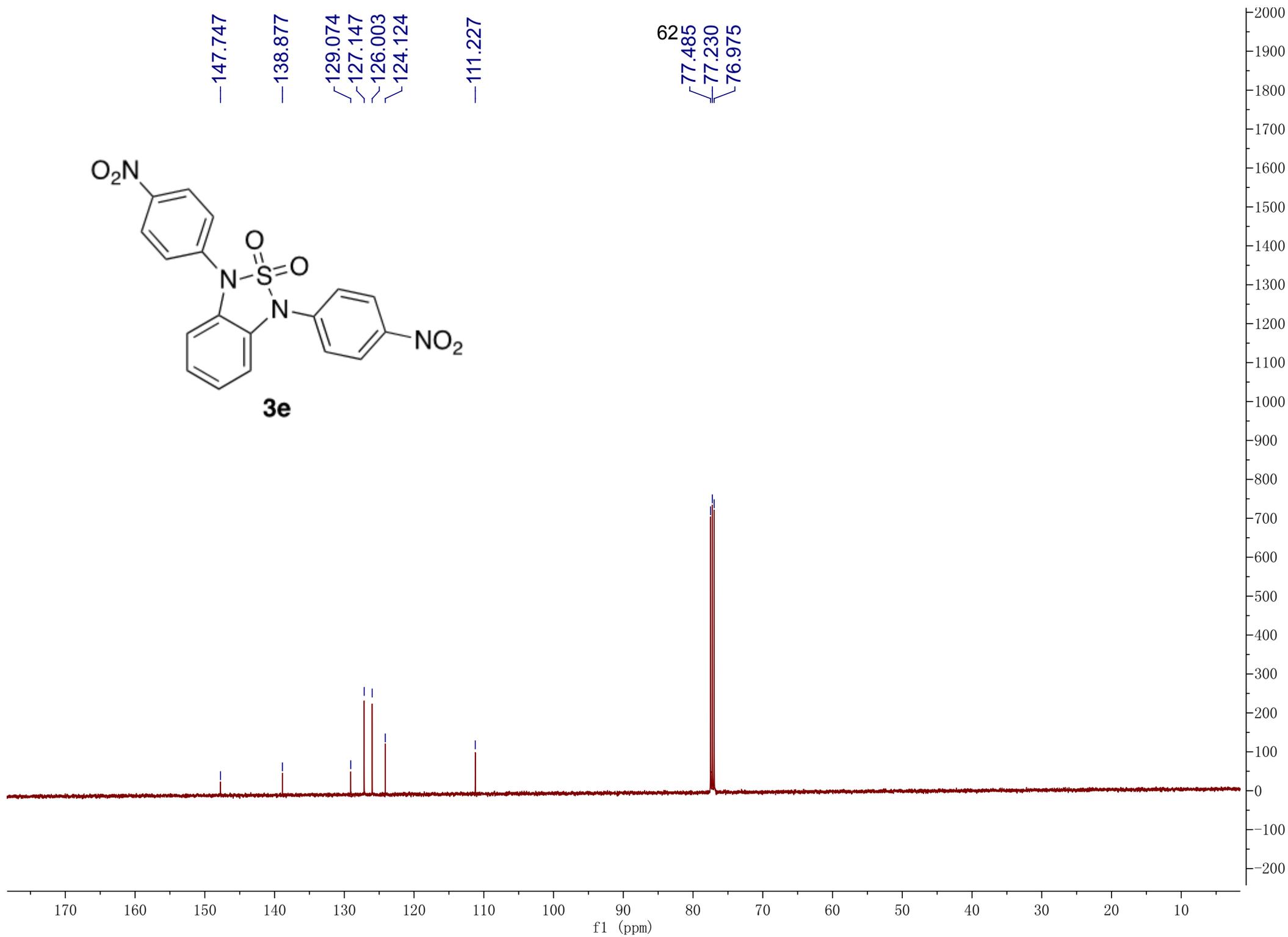
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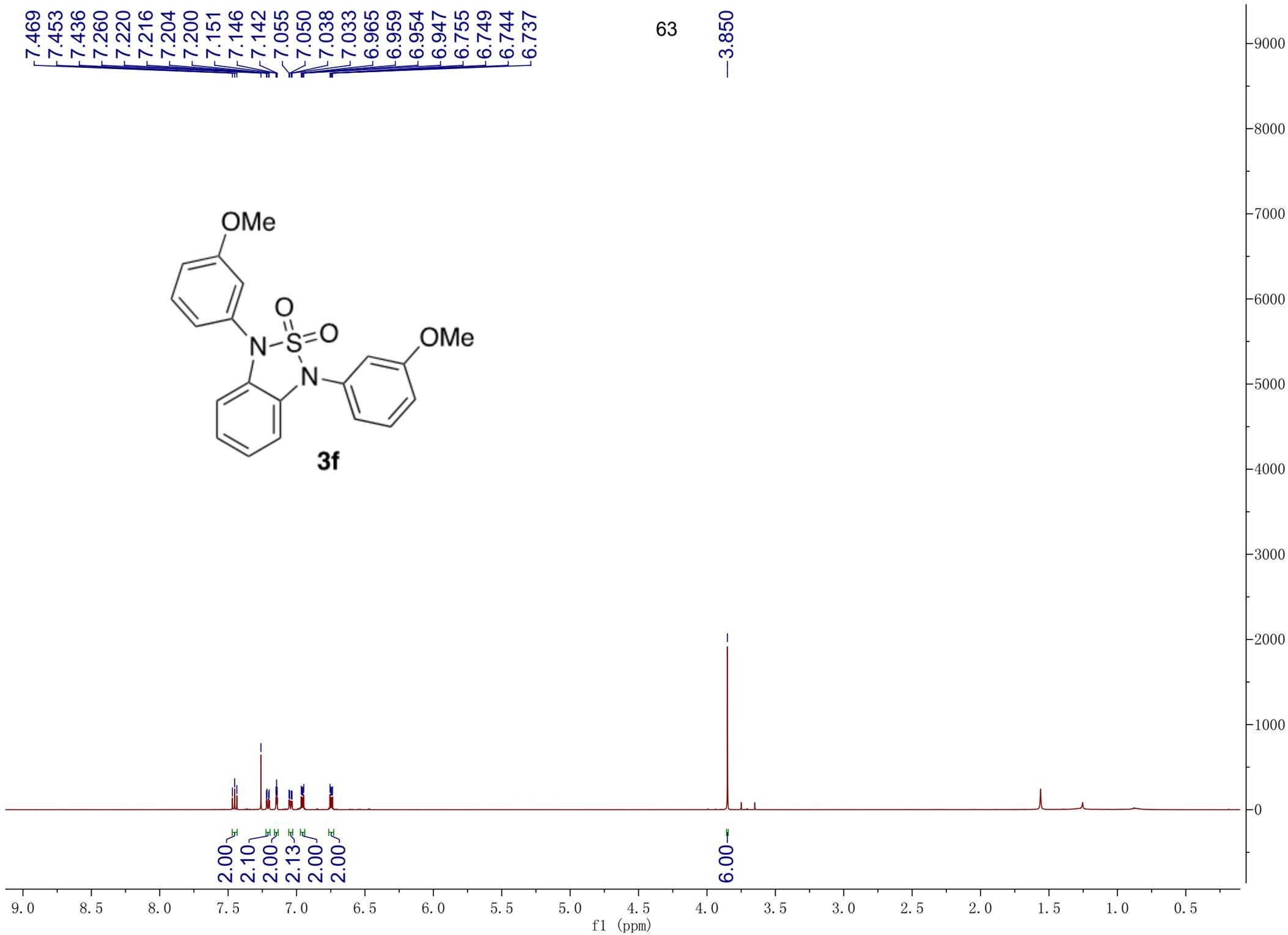
62

77.485

77.230

76.975





—161.132

—133.611

—131.048

—130.122

—122.323

—120.459

—115.881

—113.600

—109.682

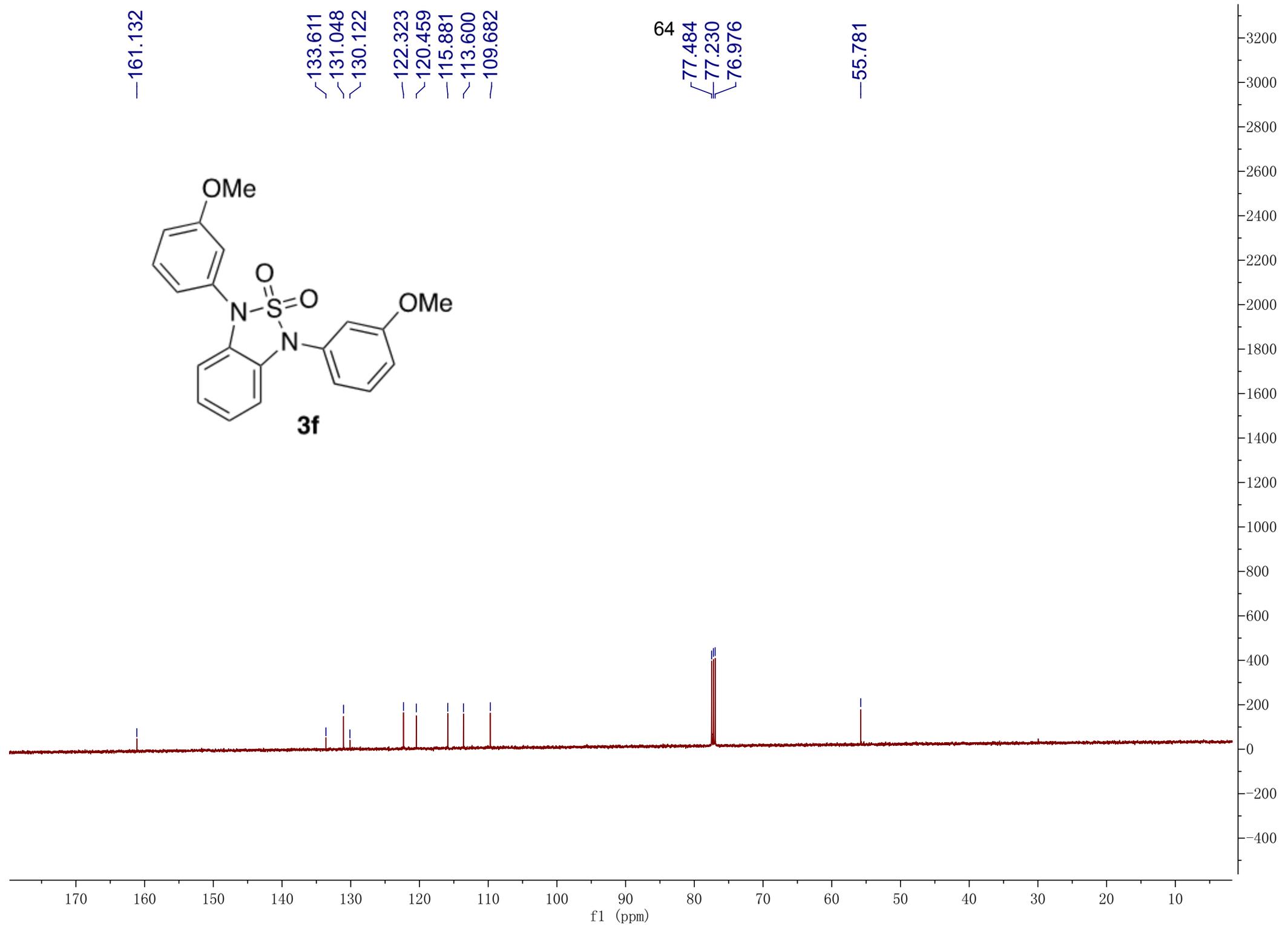
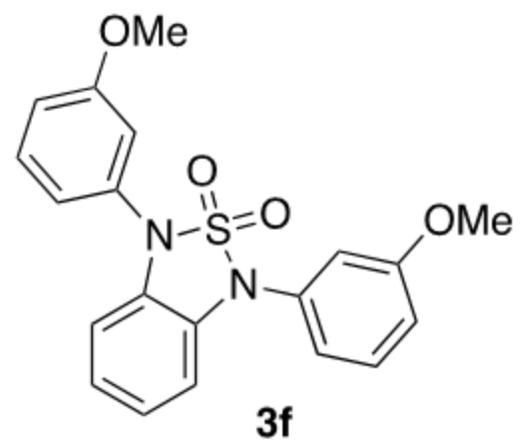
64

—77.484

—77.230

—76.976

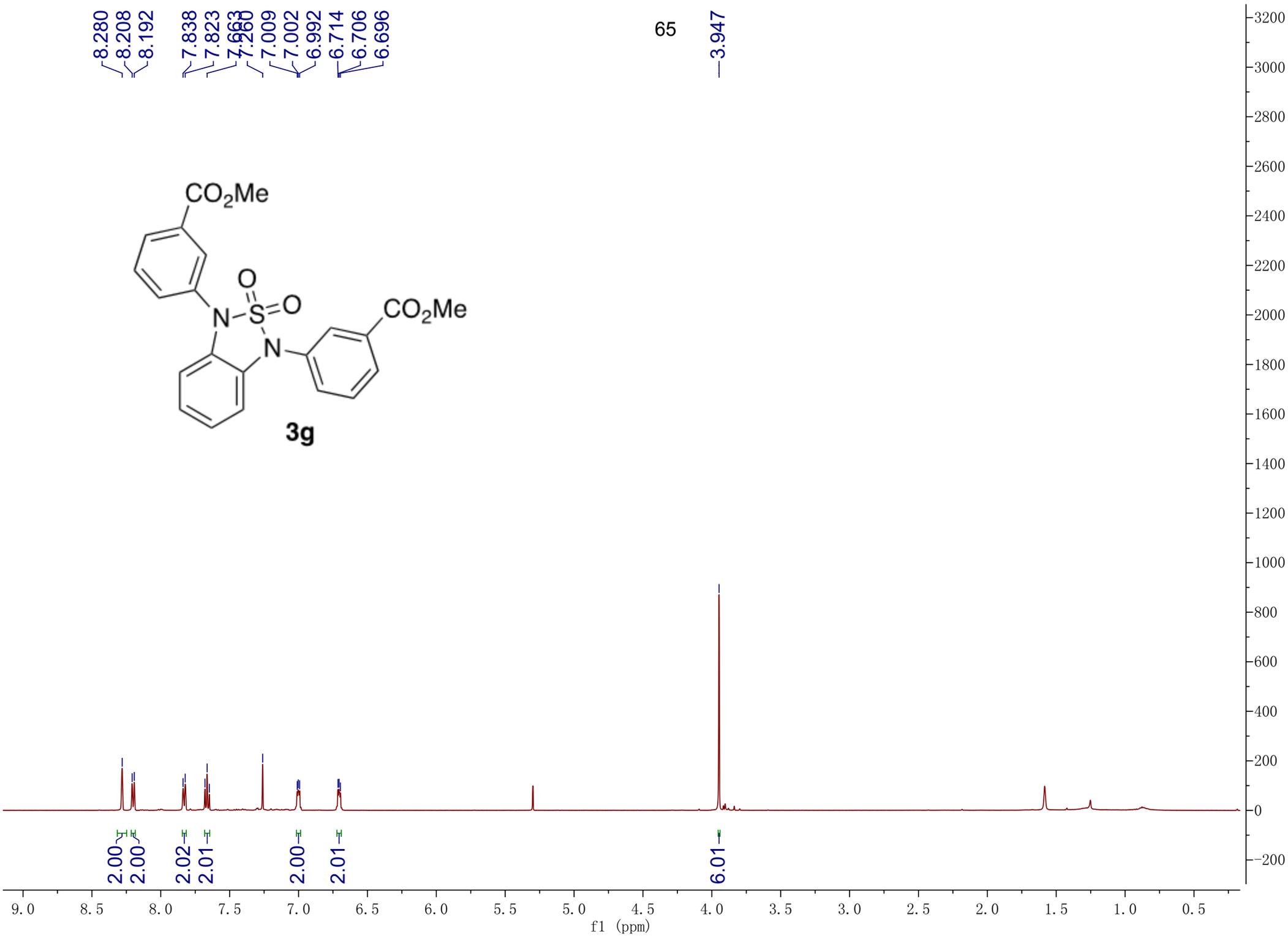
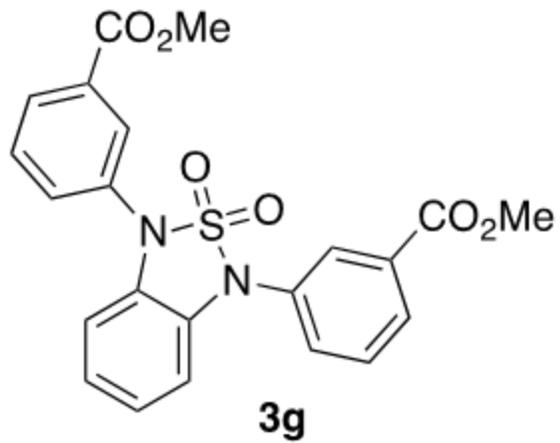
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8.208  
8.192  
7.838  
7.823  
7.663  
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7.002  
6.992  
6.714  
6.706  
6.696

65

3.947

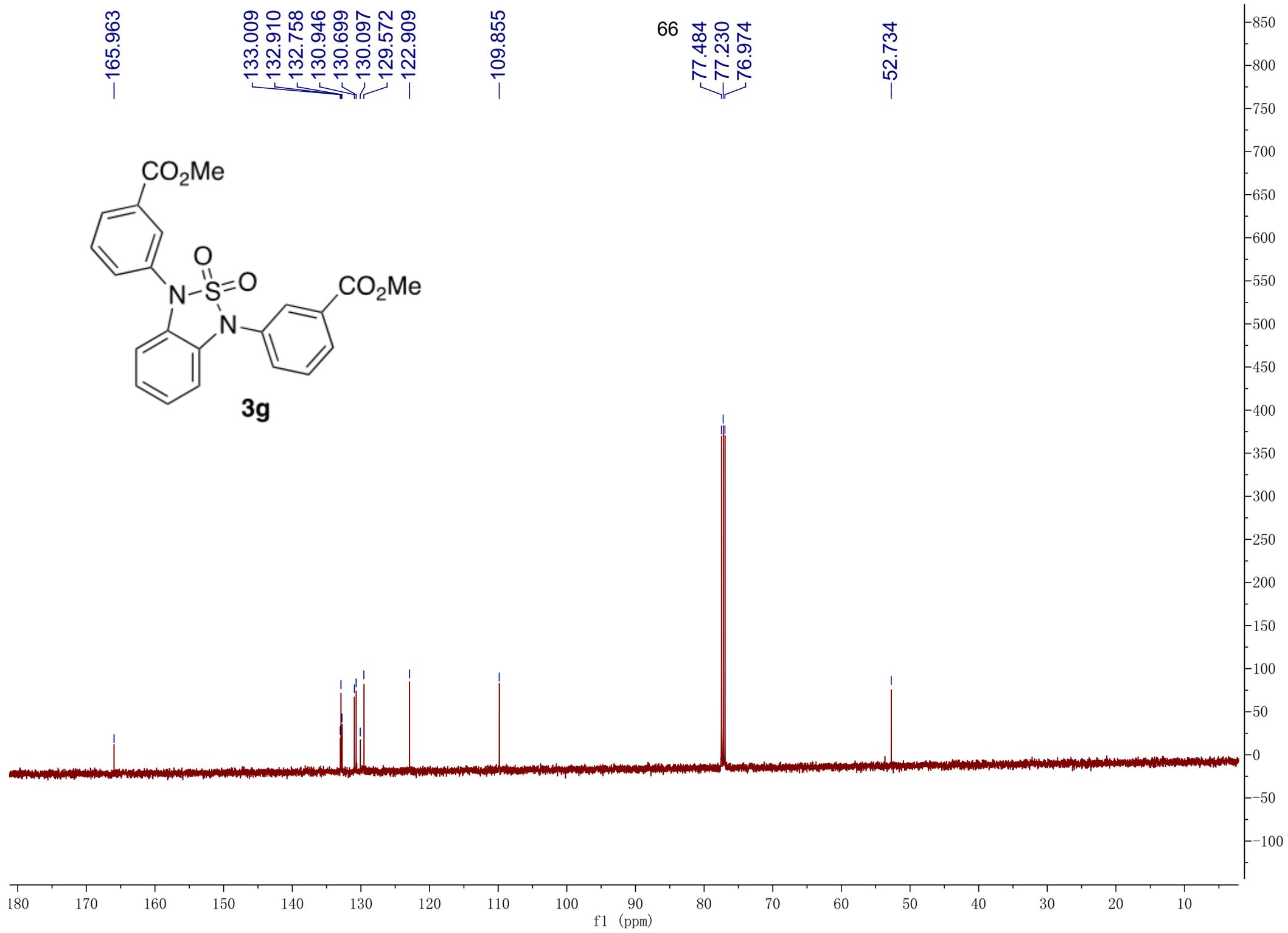
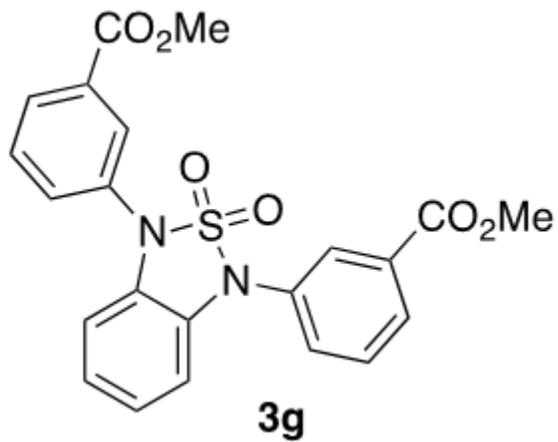


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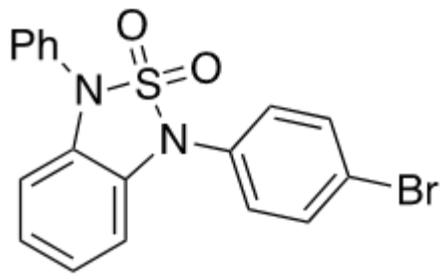
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76.974

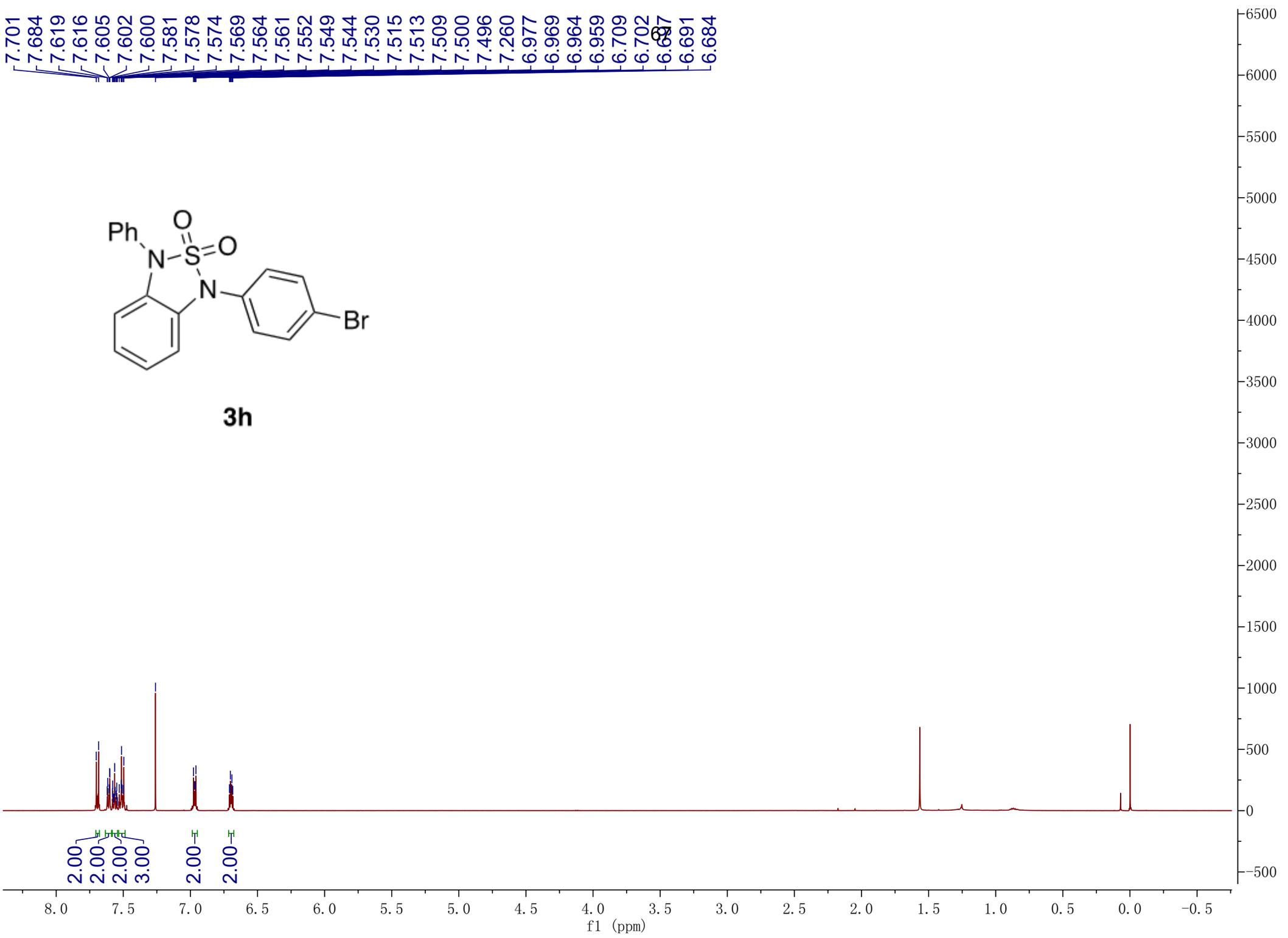
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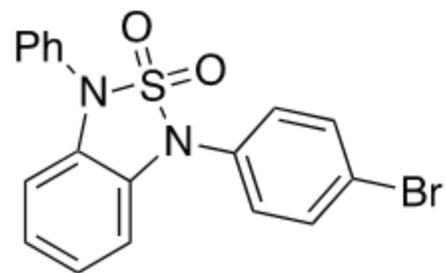


7.701  
7.684  
7.619  
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7.605  
7.602  
7.600  
7.581  
7.578  
7.574  
7.569  
7.564  
7.561  
7.552  
7.549  
7.544  
7.530  
7.515  
7.513  
7.509  
7.500  
7.496  
7.260  
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6.959  
6.709  
6.702  
6.697  
6.691  
6.684



**3h**

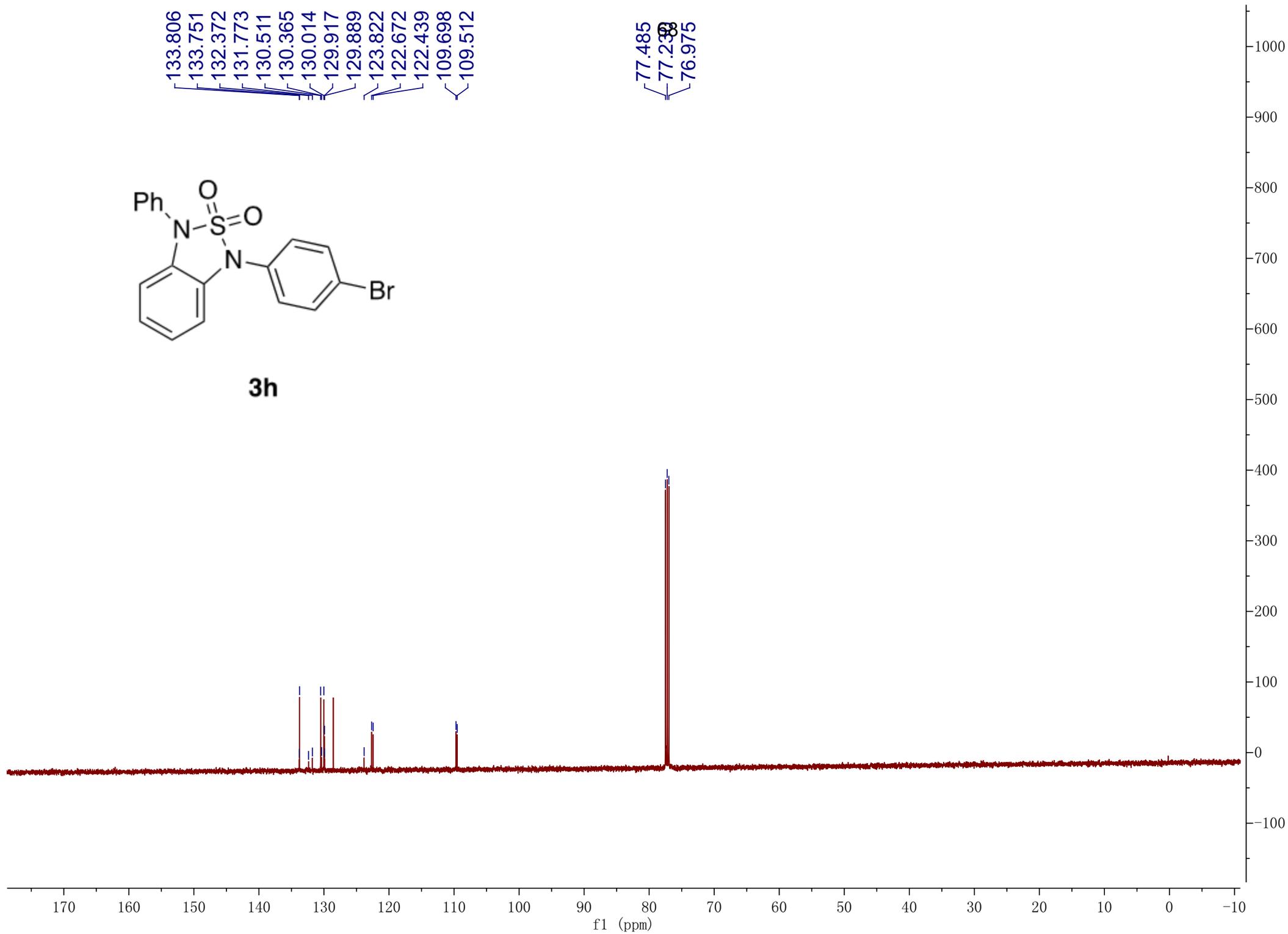




**3h**

133.806  
133.751  
132.372  
131.773  
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129.889  
123.822  
122.672  
122.439  
109.698  
109.512

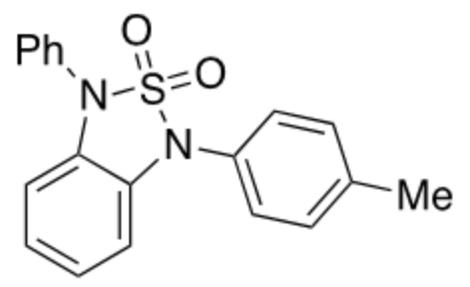
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77.238  
76.975



7.637  
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7.514  
7.498  
7.369  
7.353  
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6.660

69

-2.447



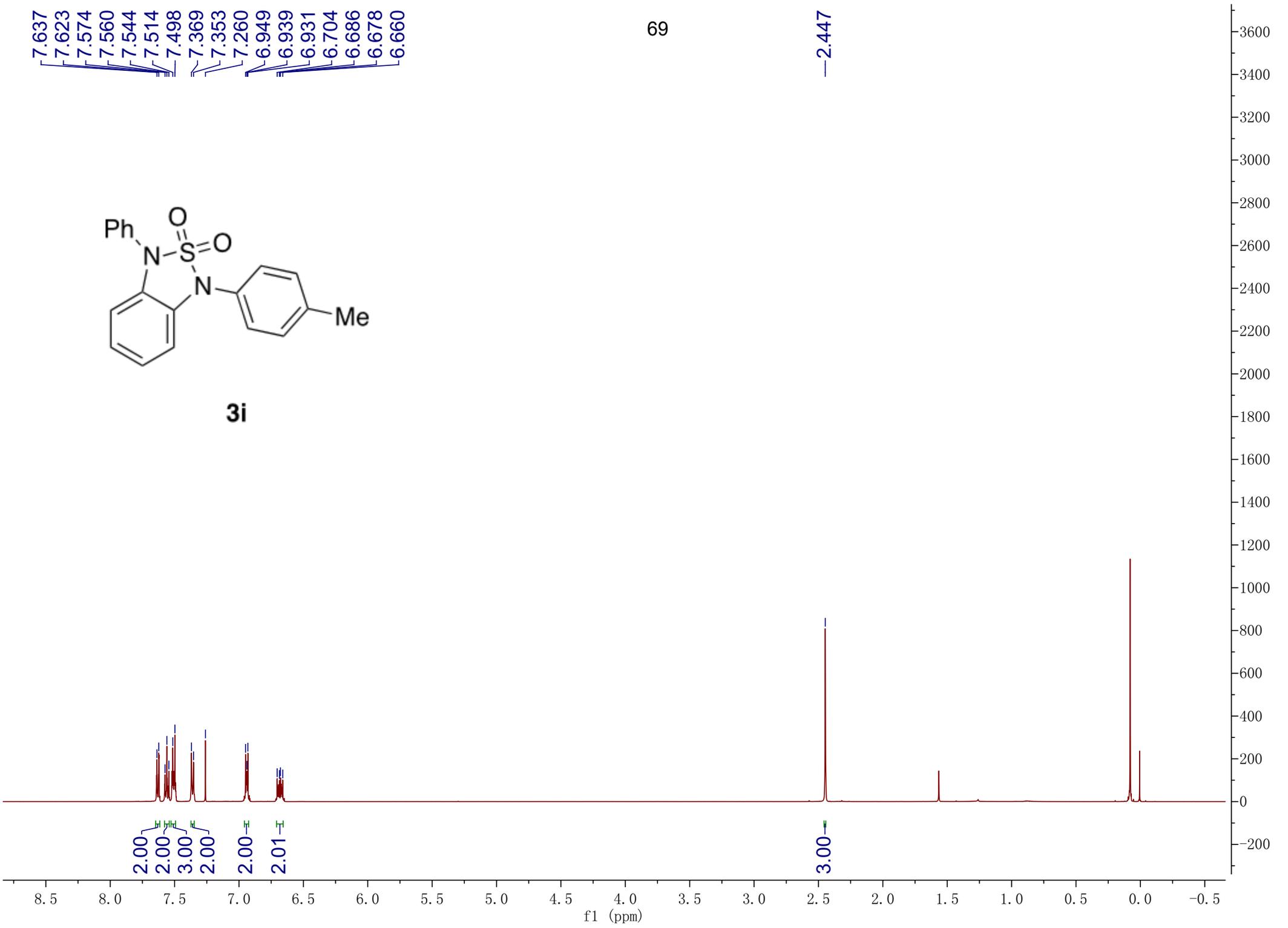
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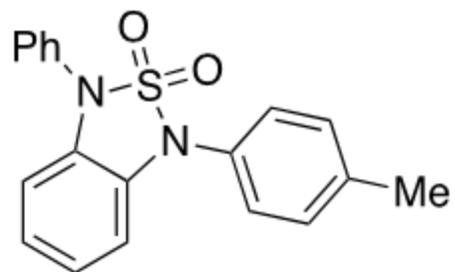
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3.00  
2.00

2.00

2.01

3.00



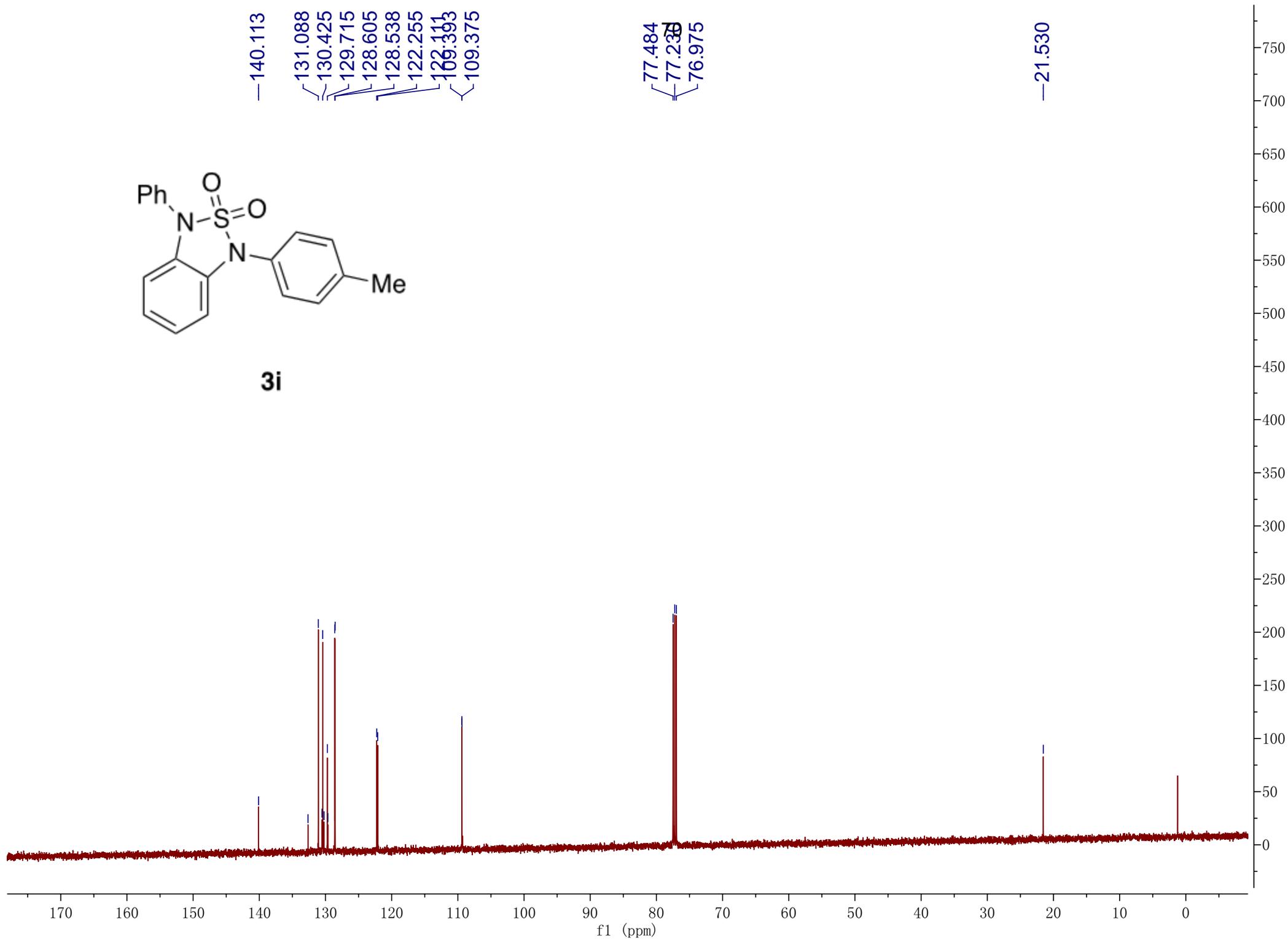


**3i**

140.113  
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129.715  
128.605  
128.538  
122.255  
122.111  
109.393  
109.375

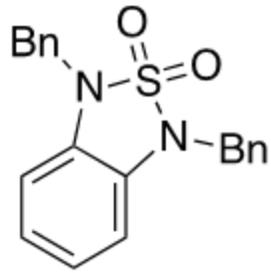
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77.239  
76.975

21.530



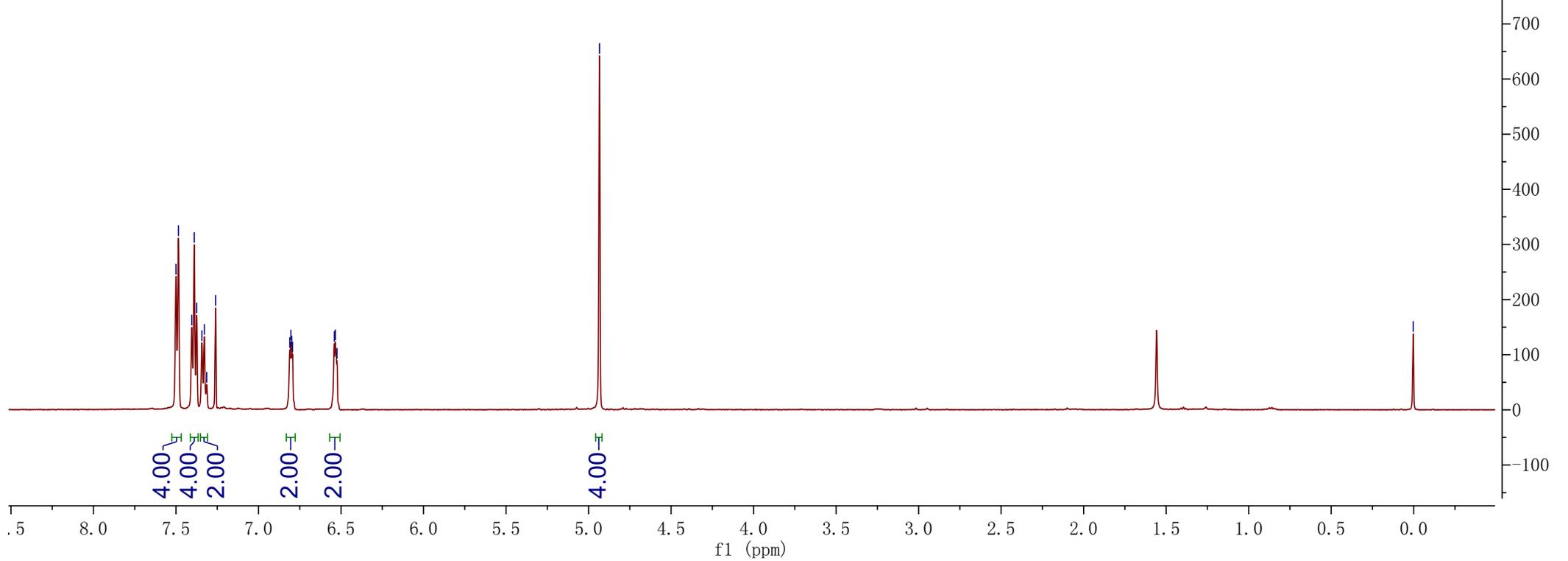
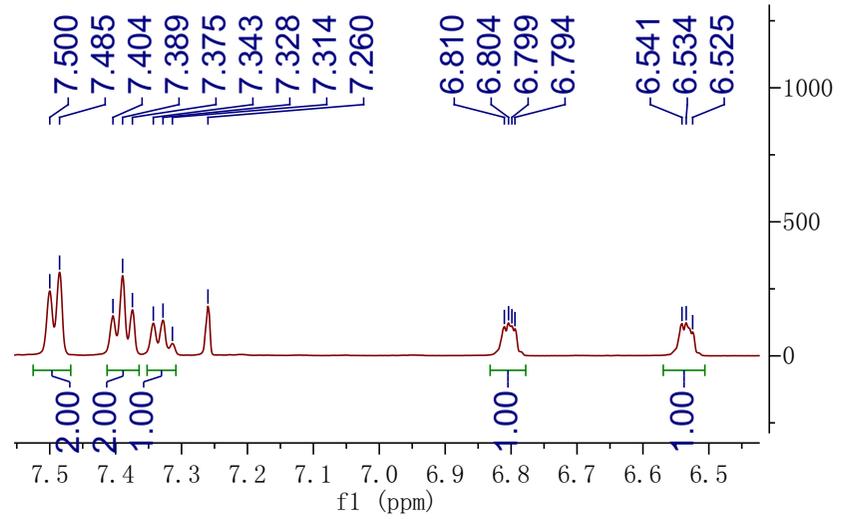
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6.804  
6.799  
6.794  
6.541  
6.534  
6.525

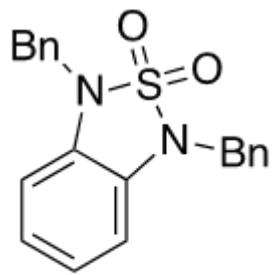
4.934



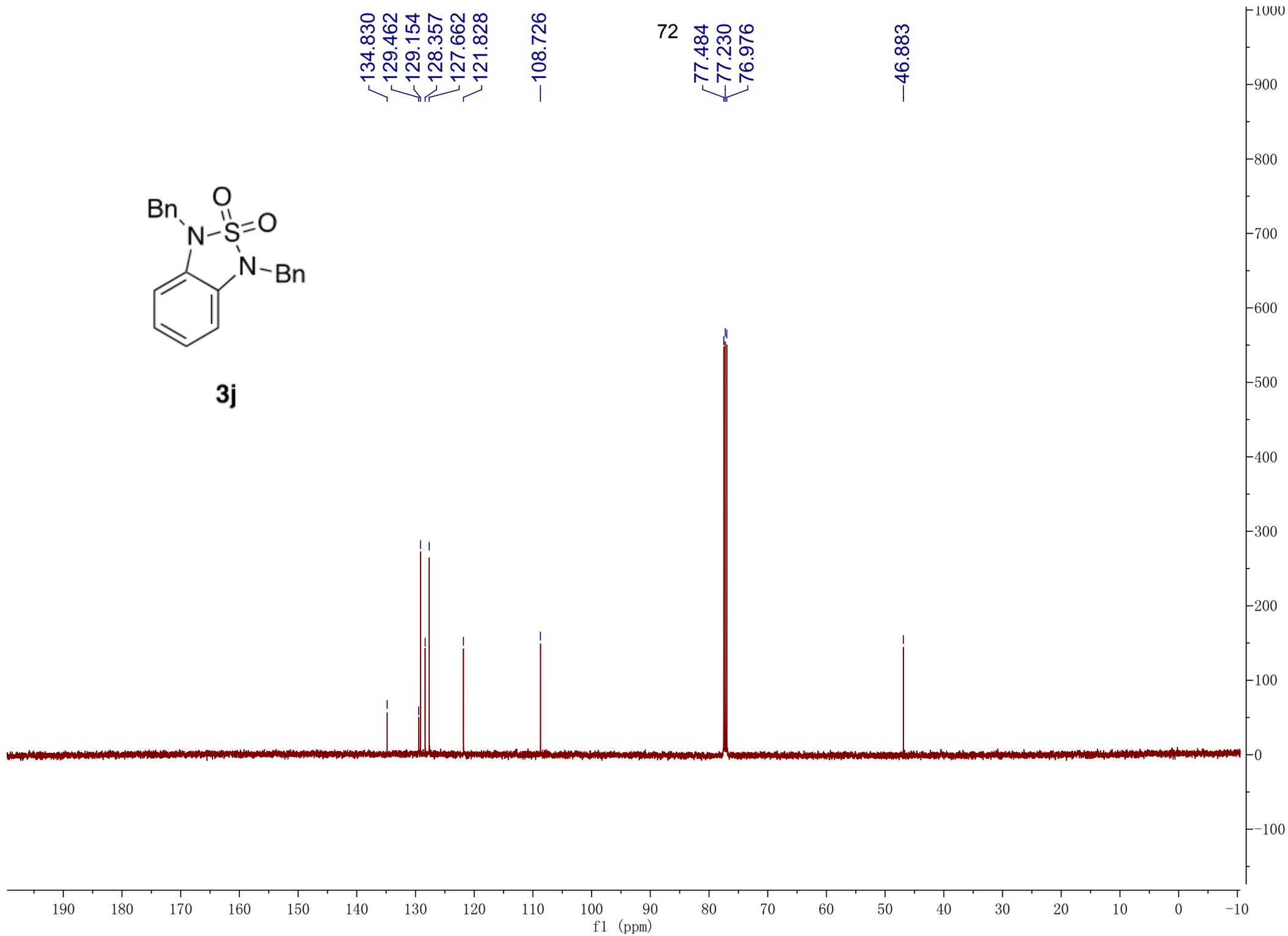
3j

71



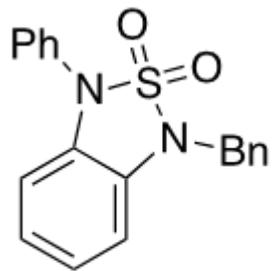


**3j**



7.610  
7.595  
7.556  
7.532  
7.517  
7.402  
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6.878  
6.872  
6.649  
6.642  
6.634  
6.611  
6.602  
6.596

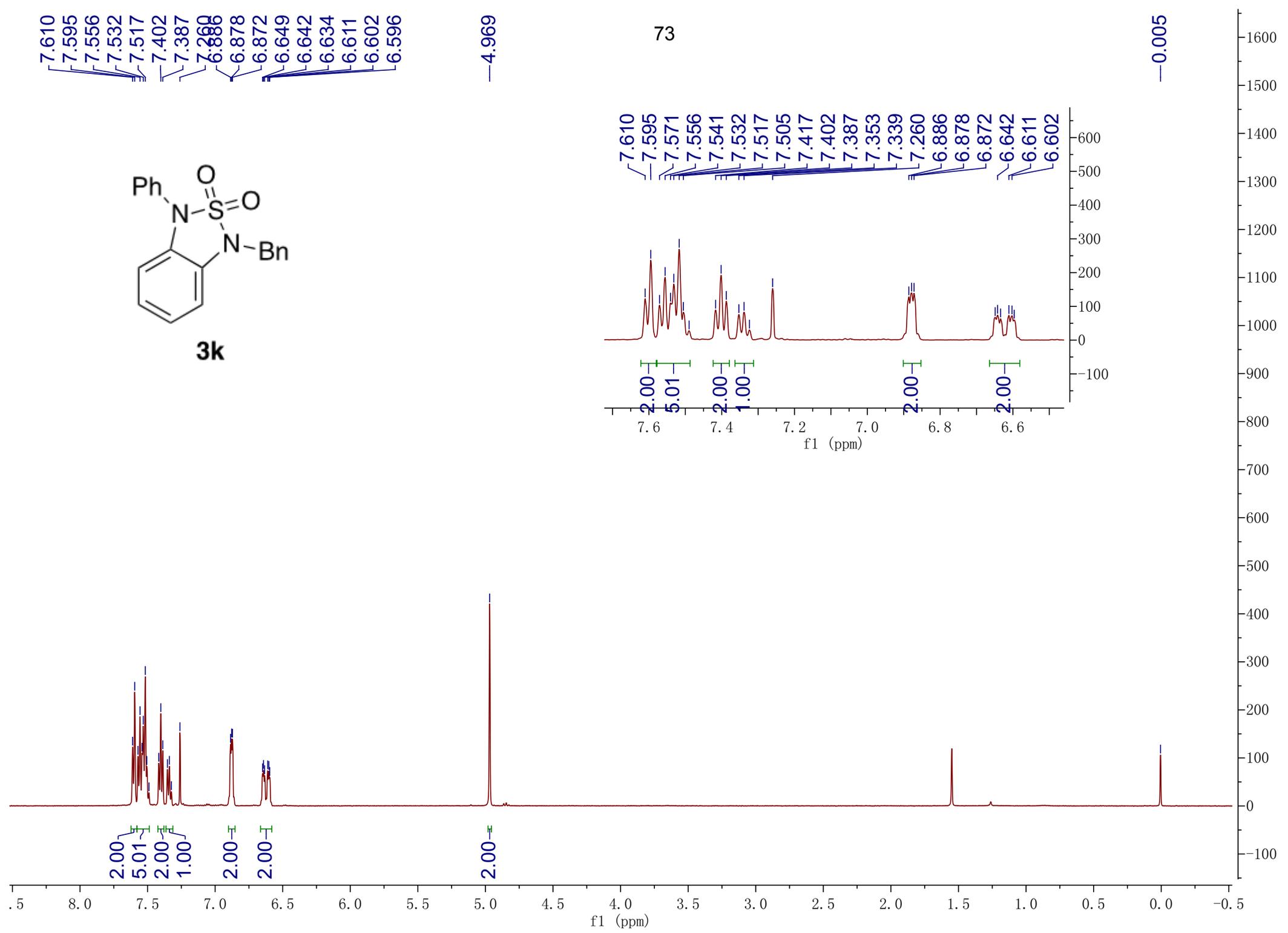
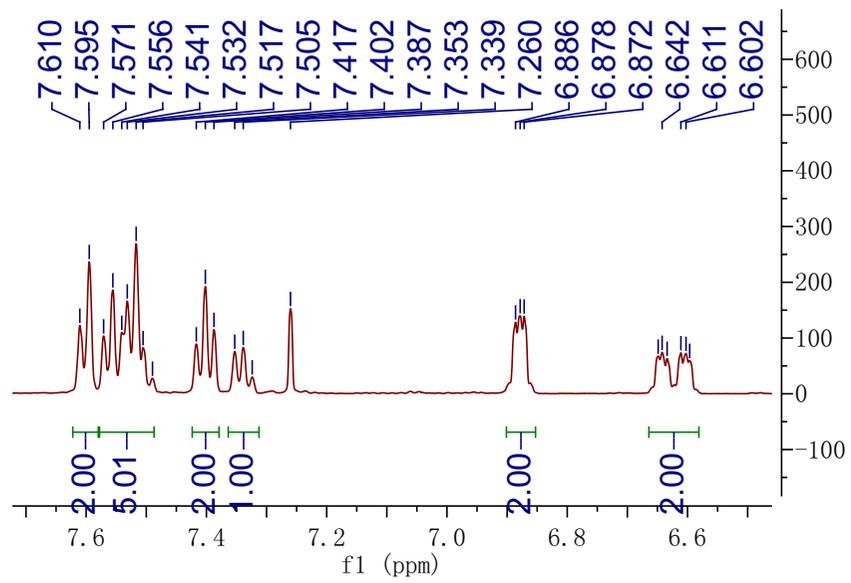
4.969

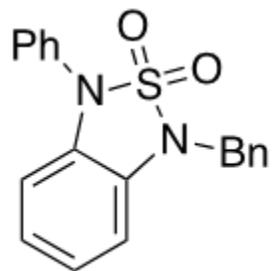


3k

73

0.005





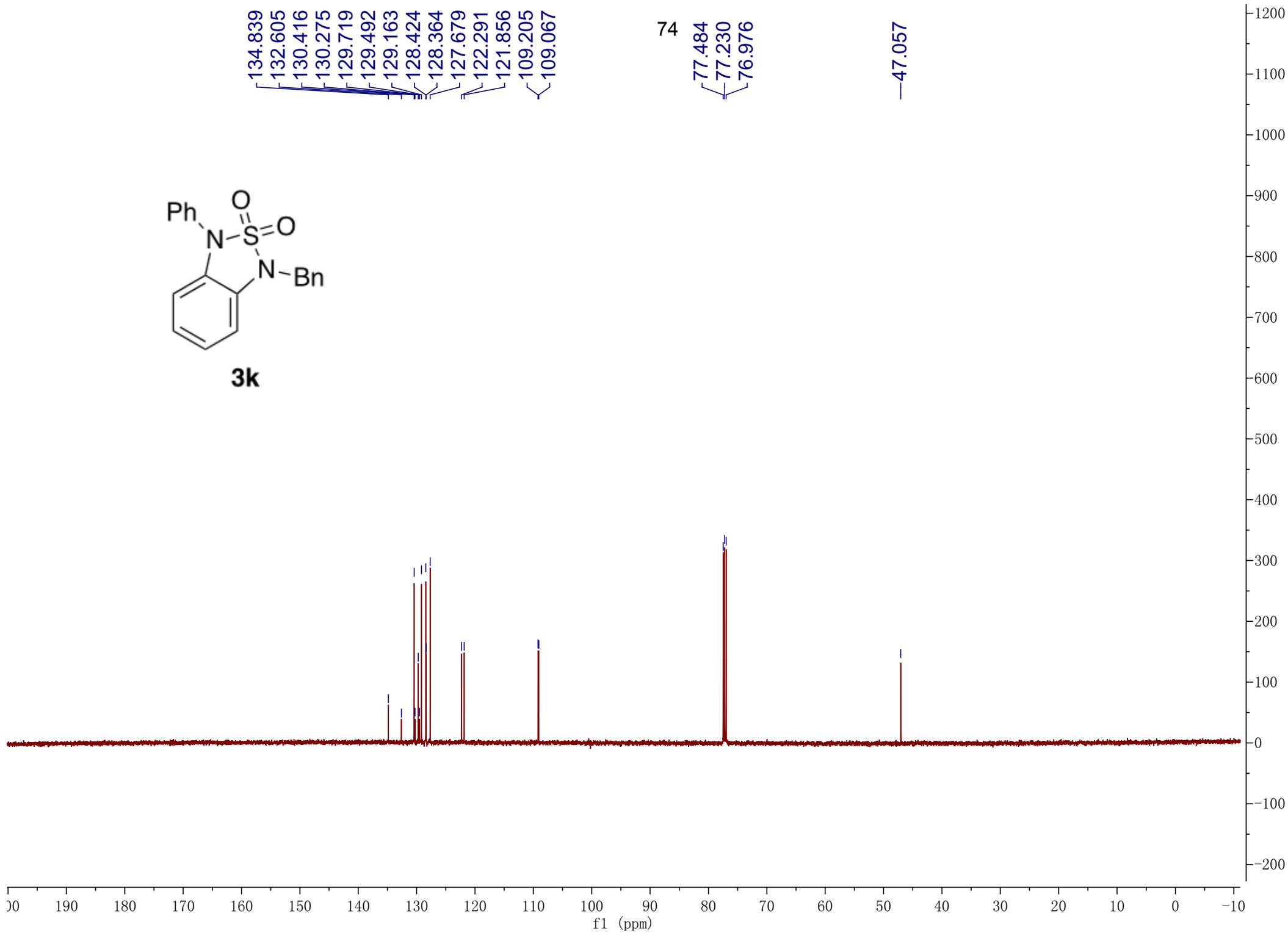
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109.067

74

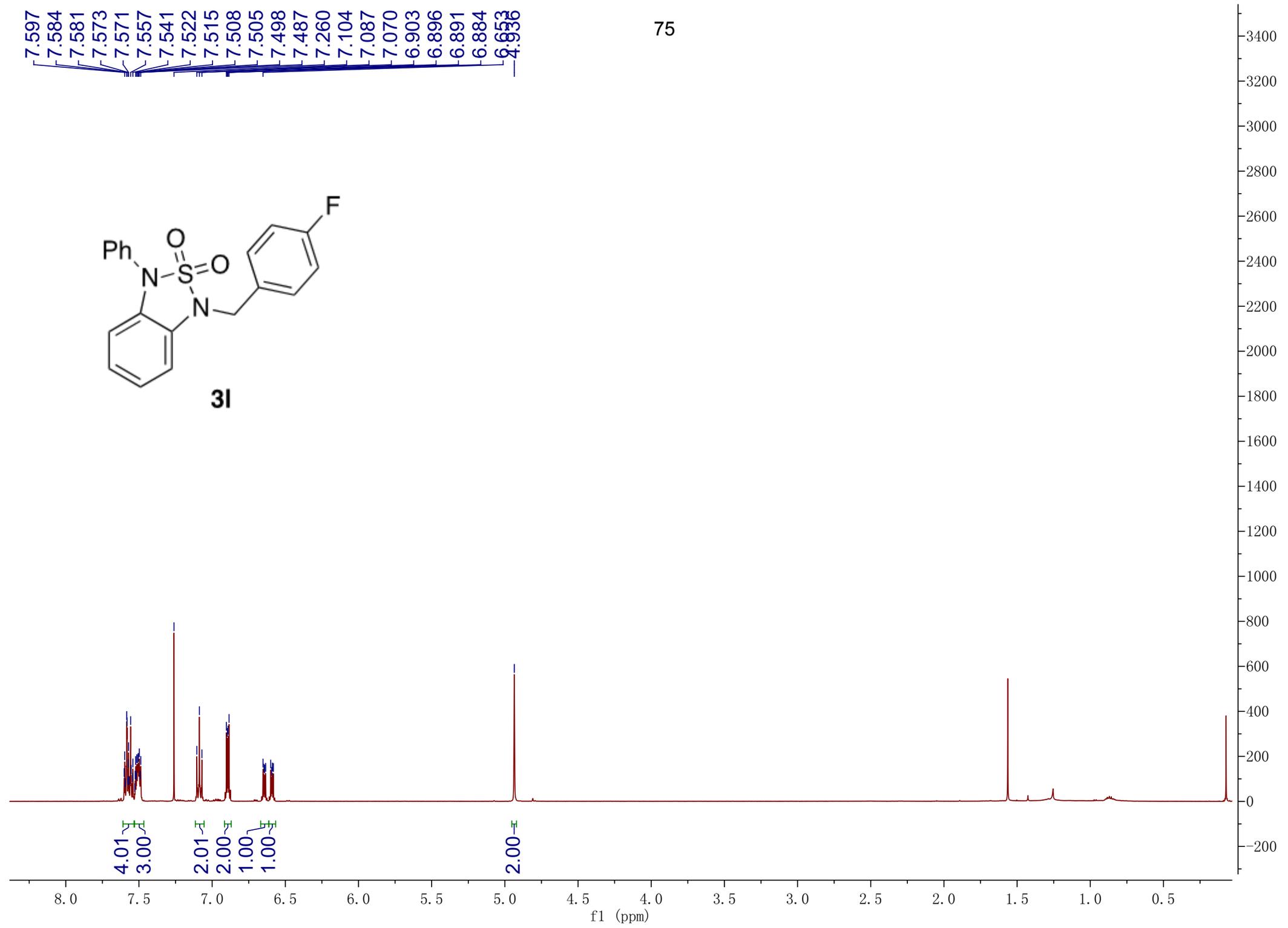
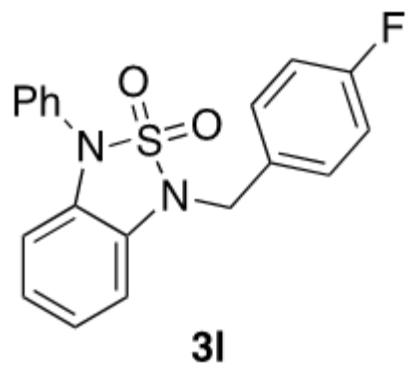
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76.976

47.057



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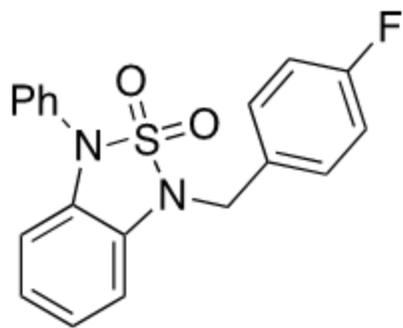
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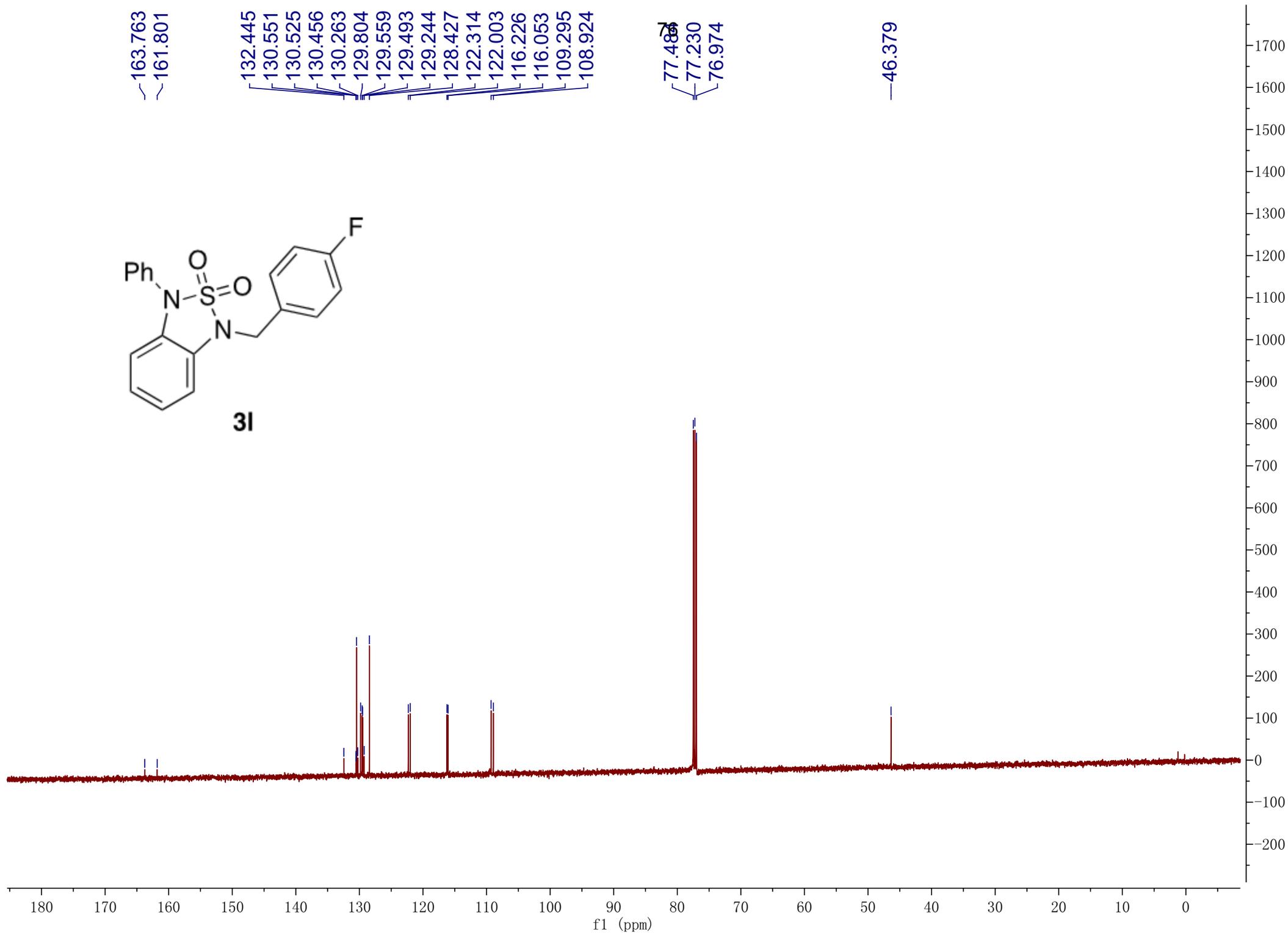
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77.486  
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46.379



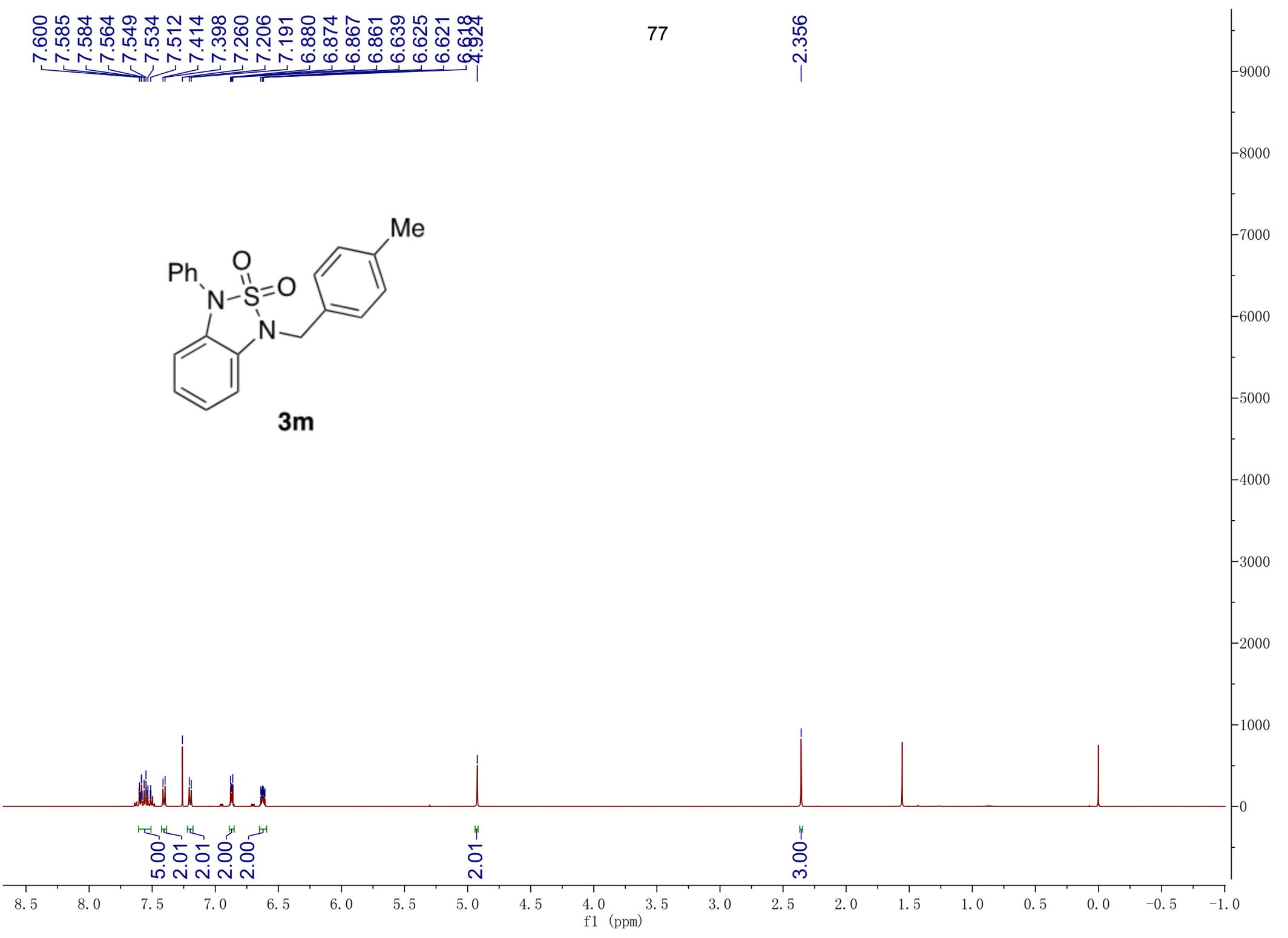
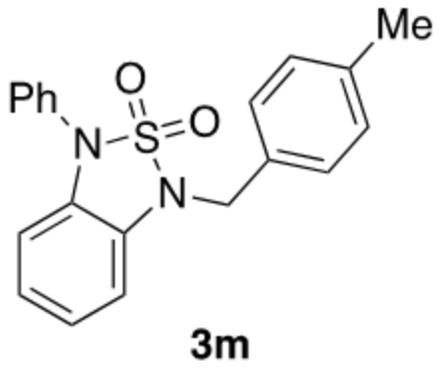
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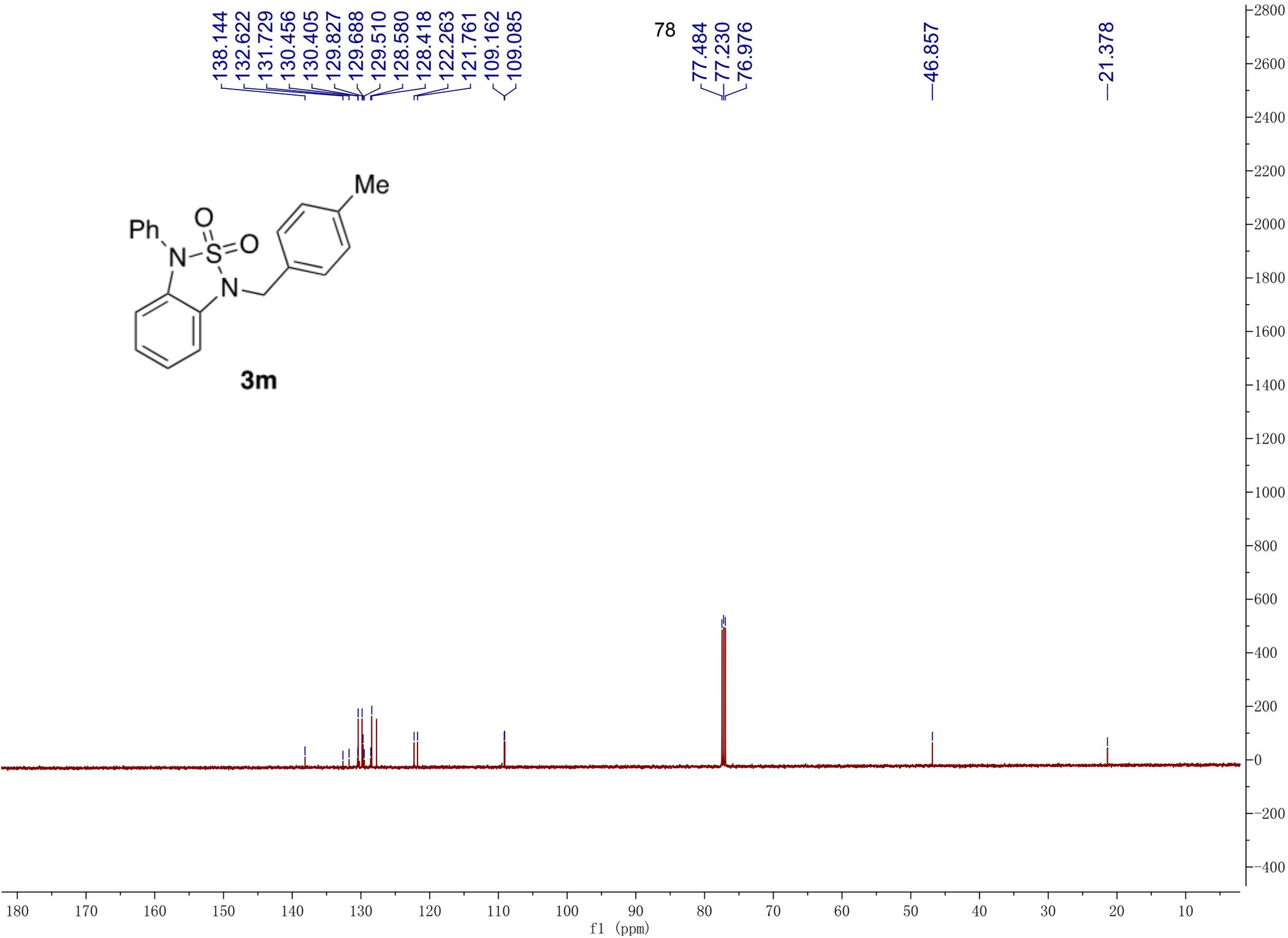
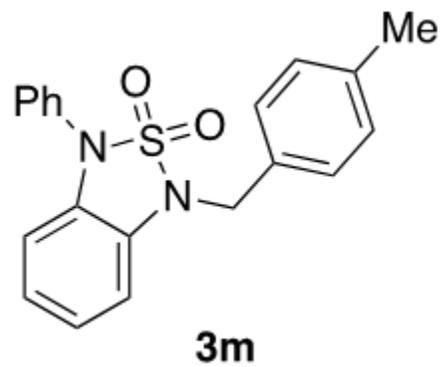


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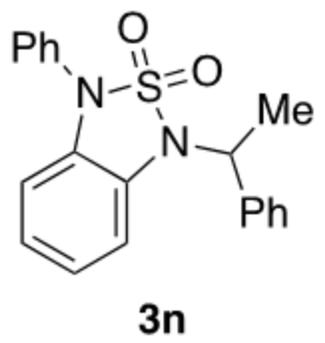
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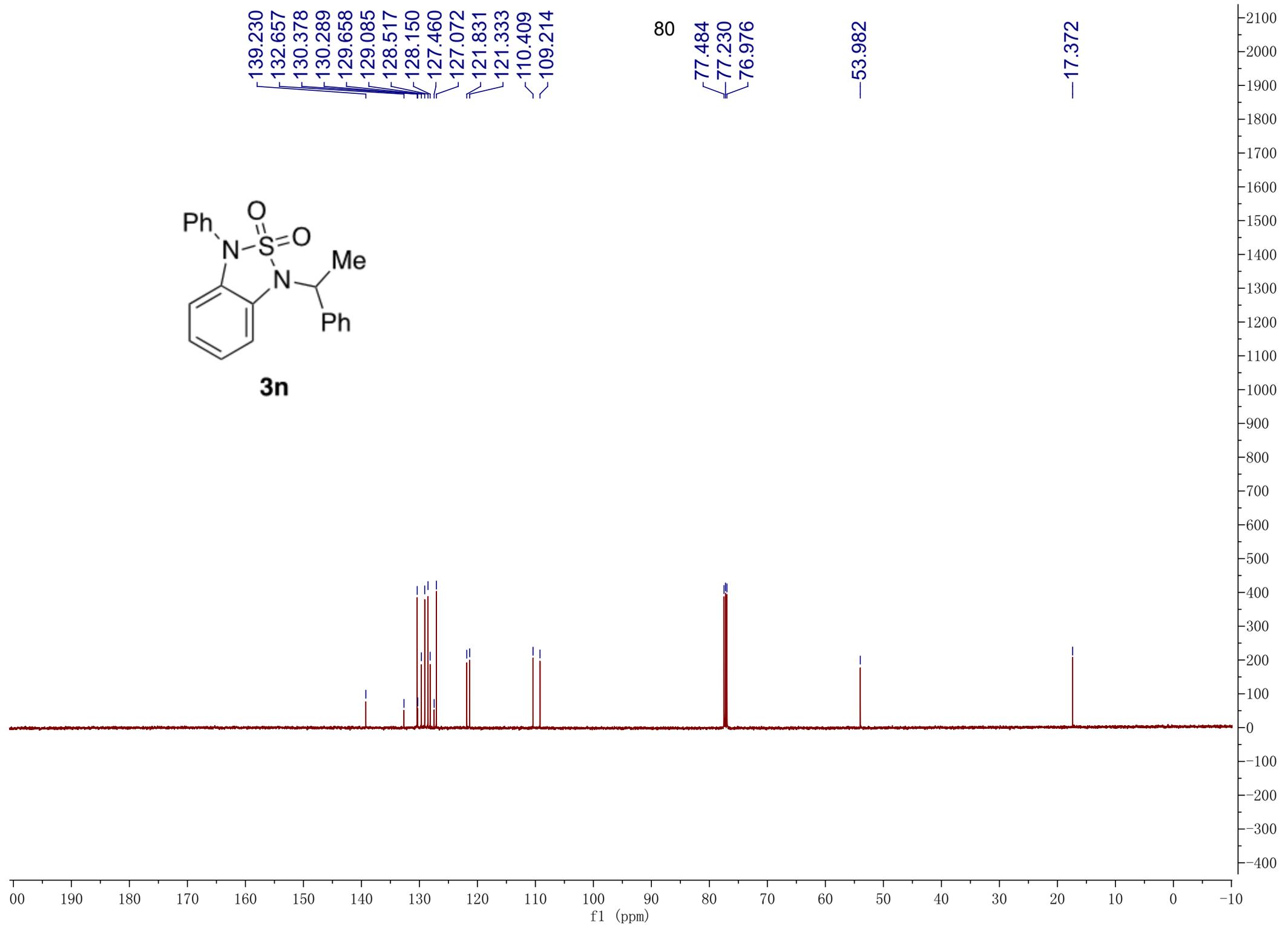
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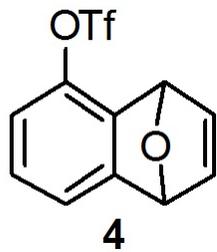
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17.372



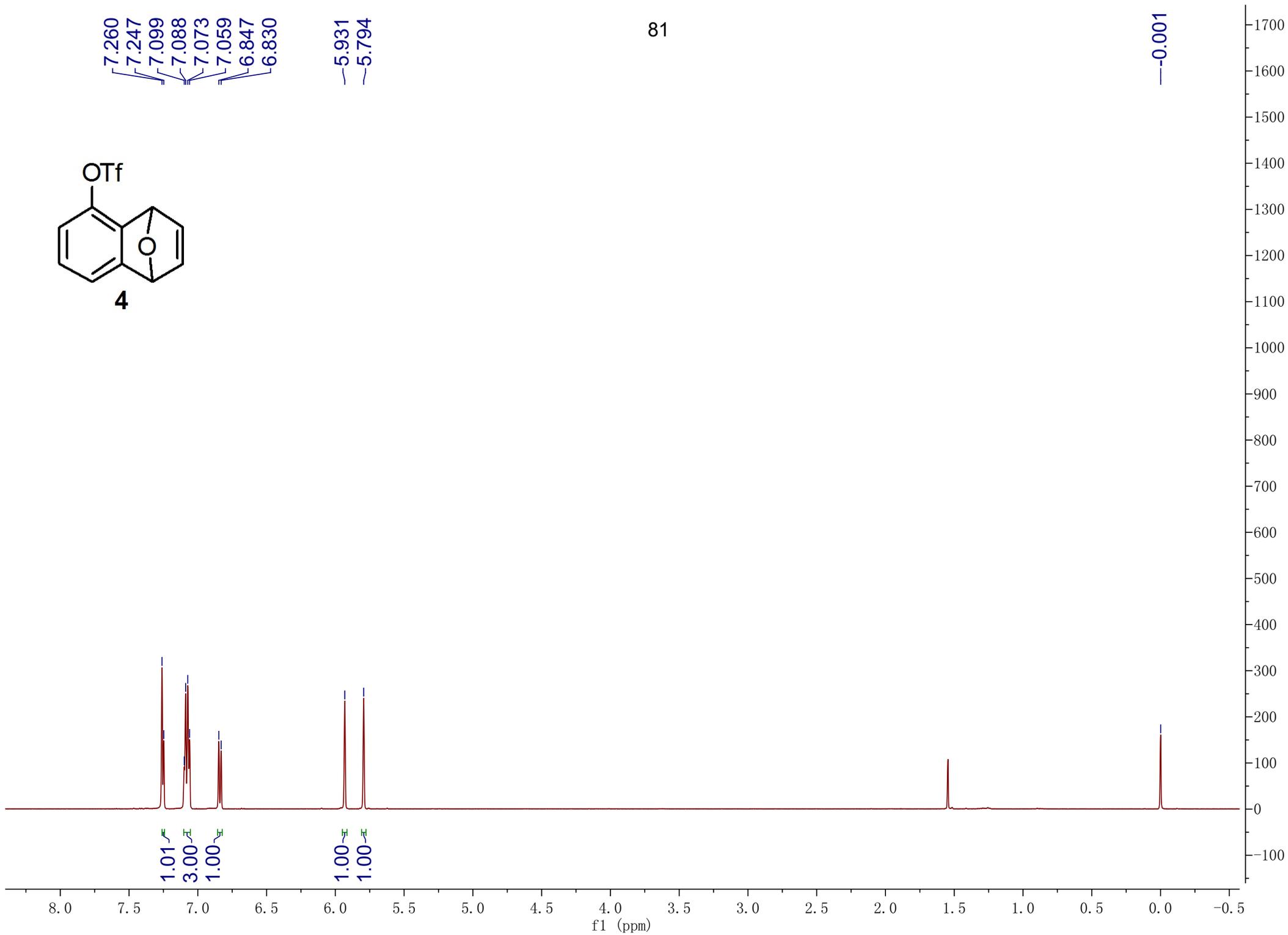


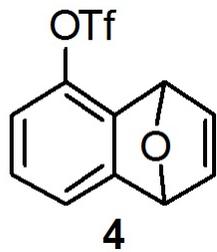
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5.794

81

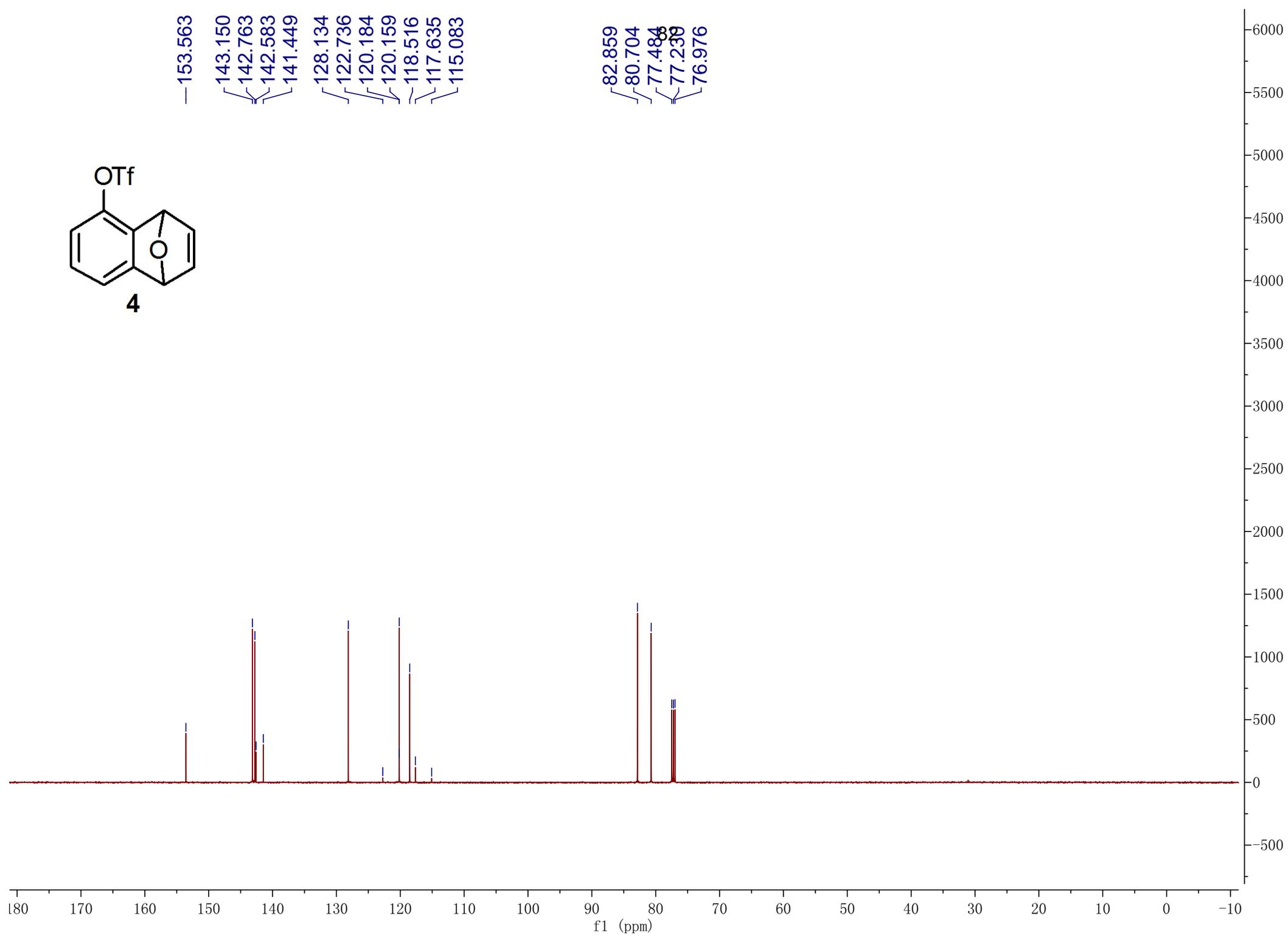
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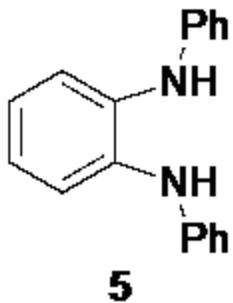




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76.976



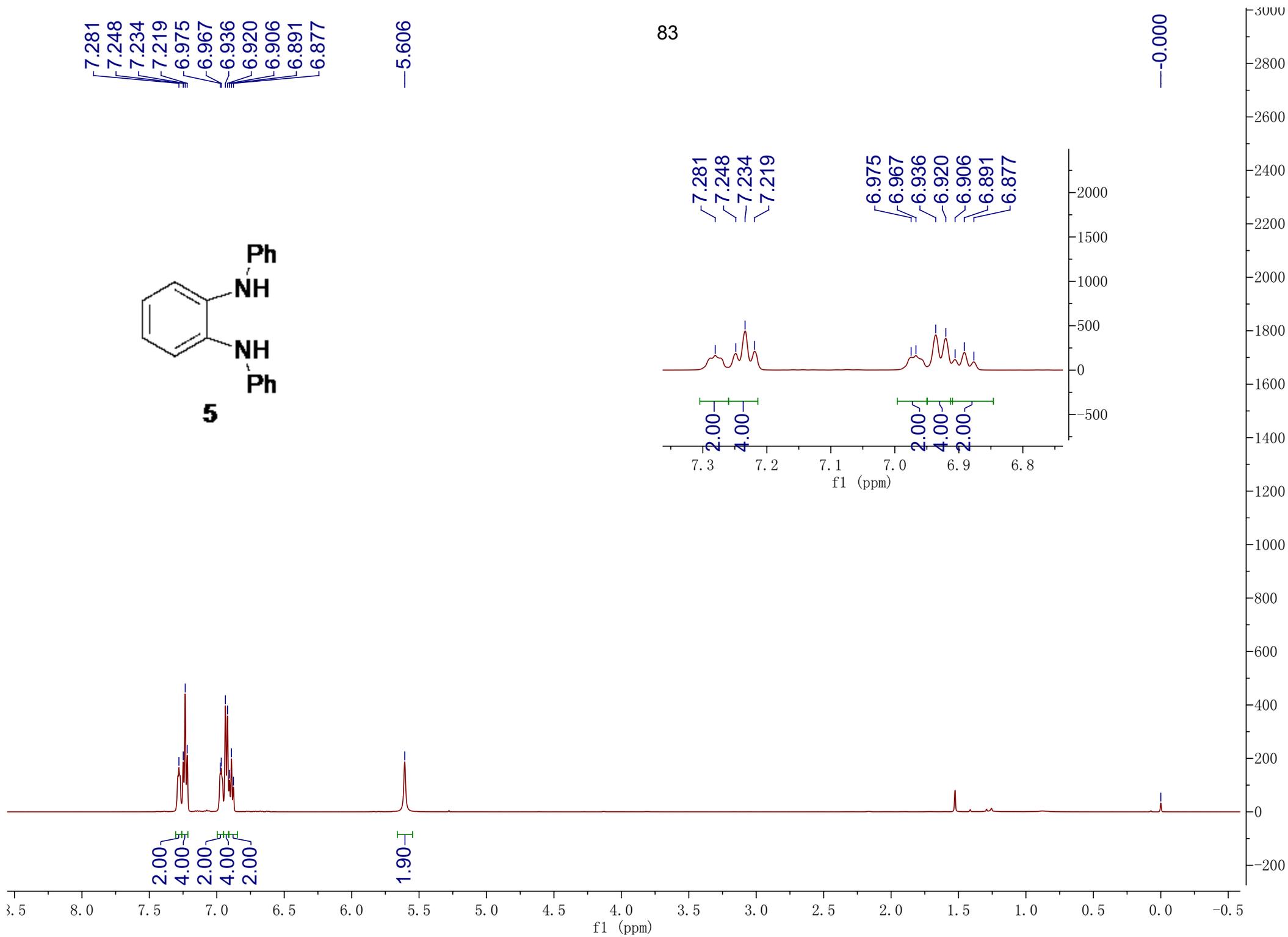


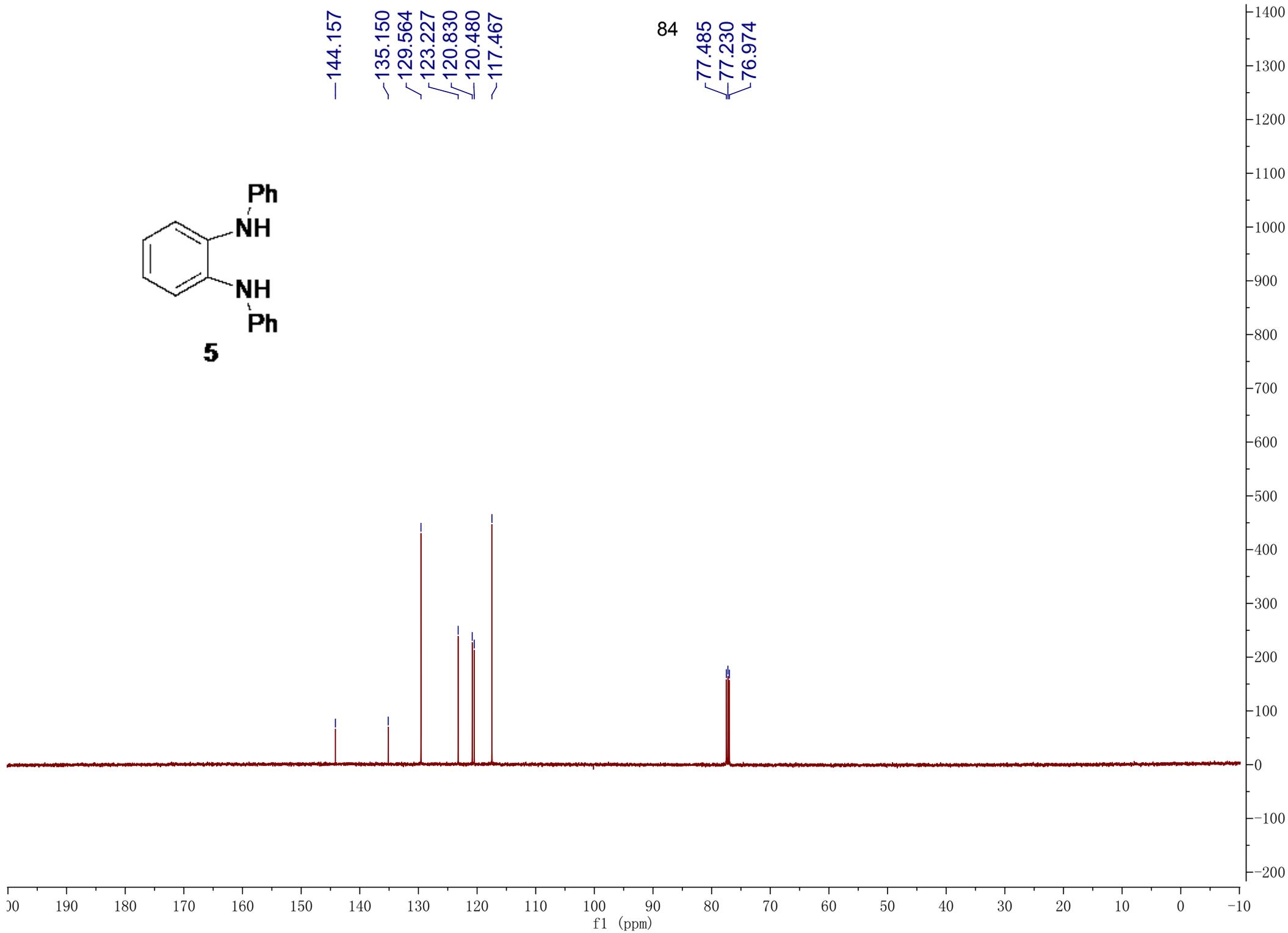
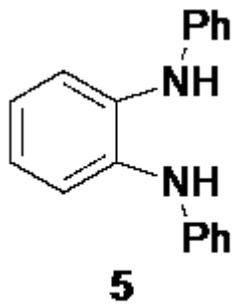
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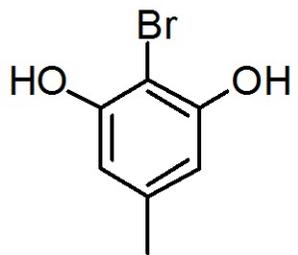
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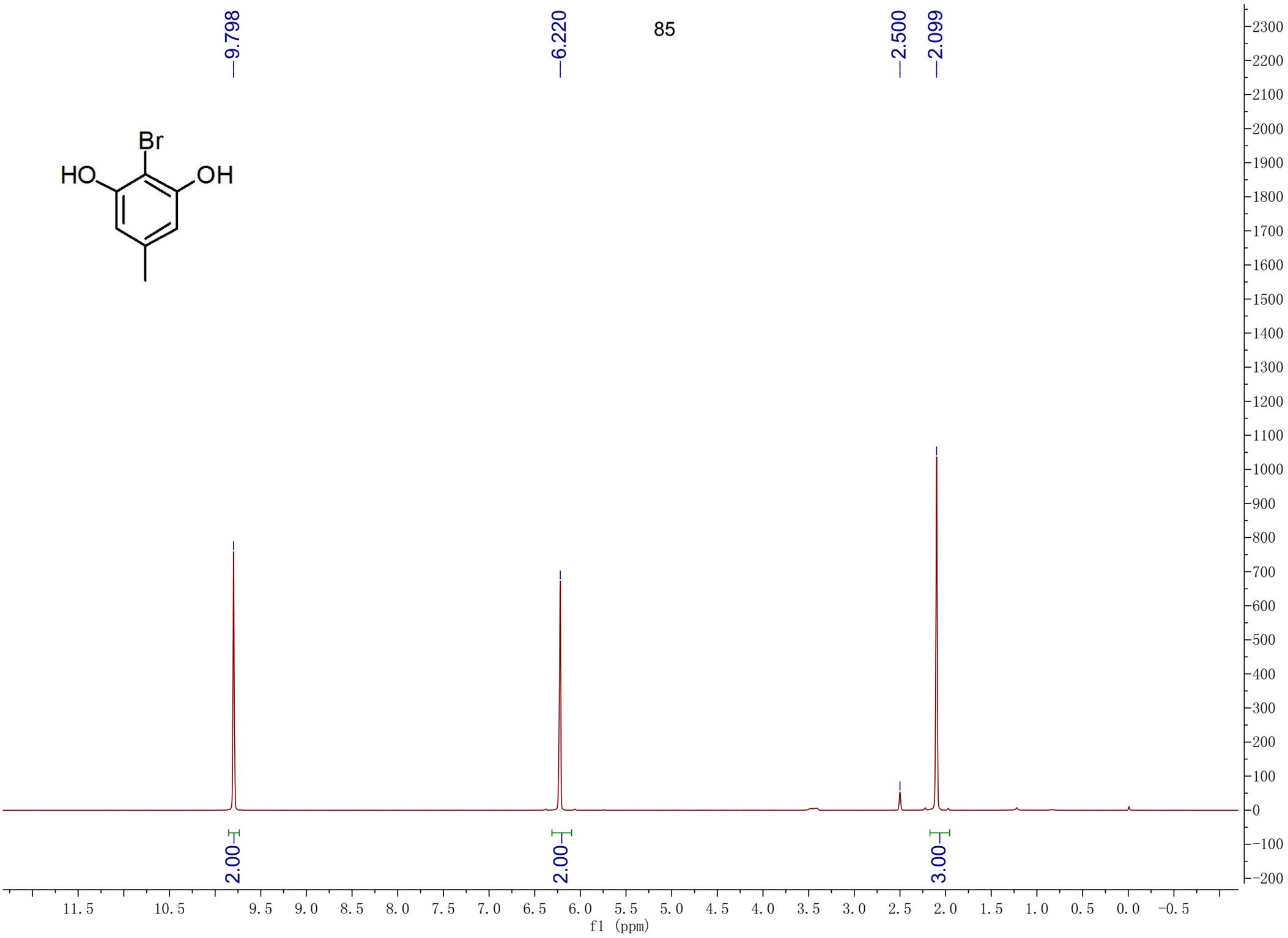
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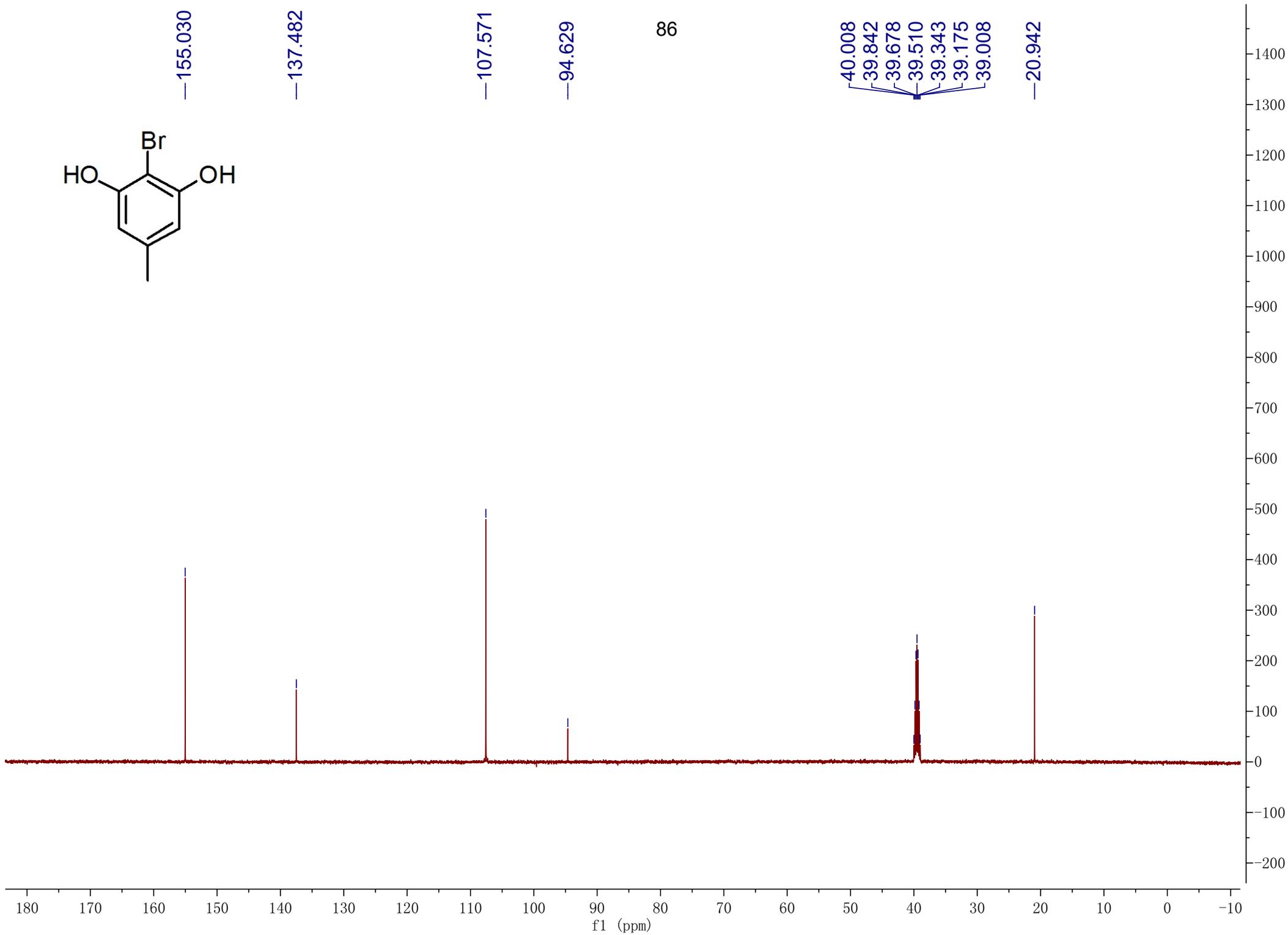
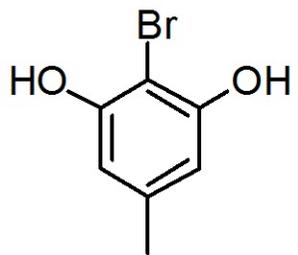
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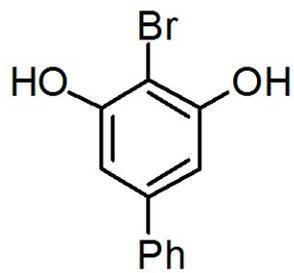
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2.099





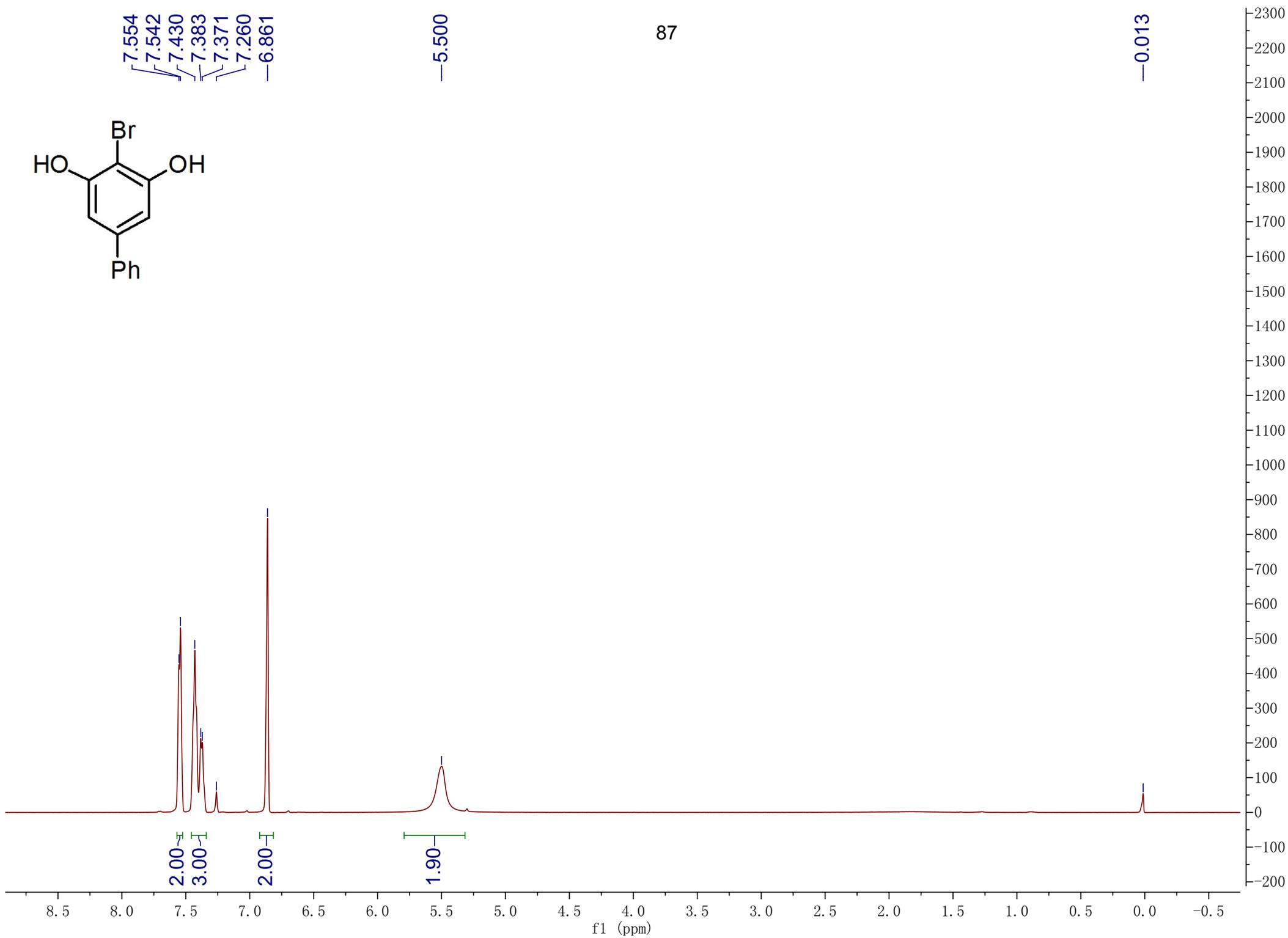


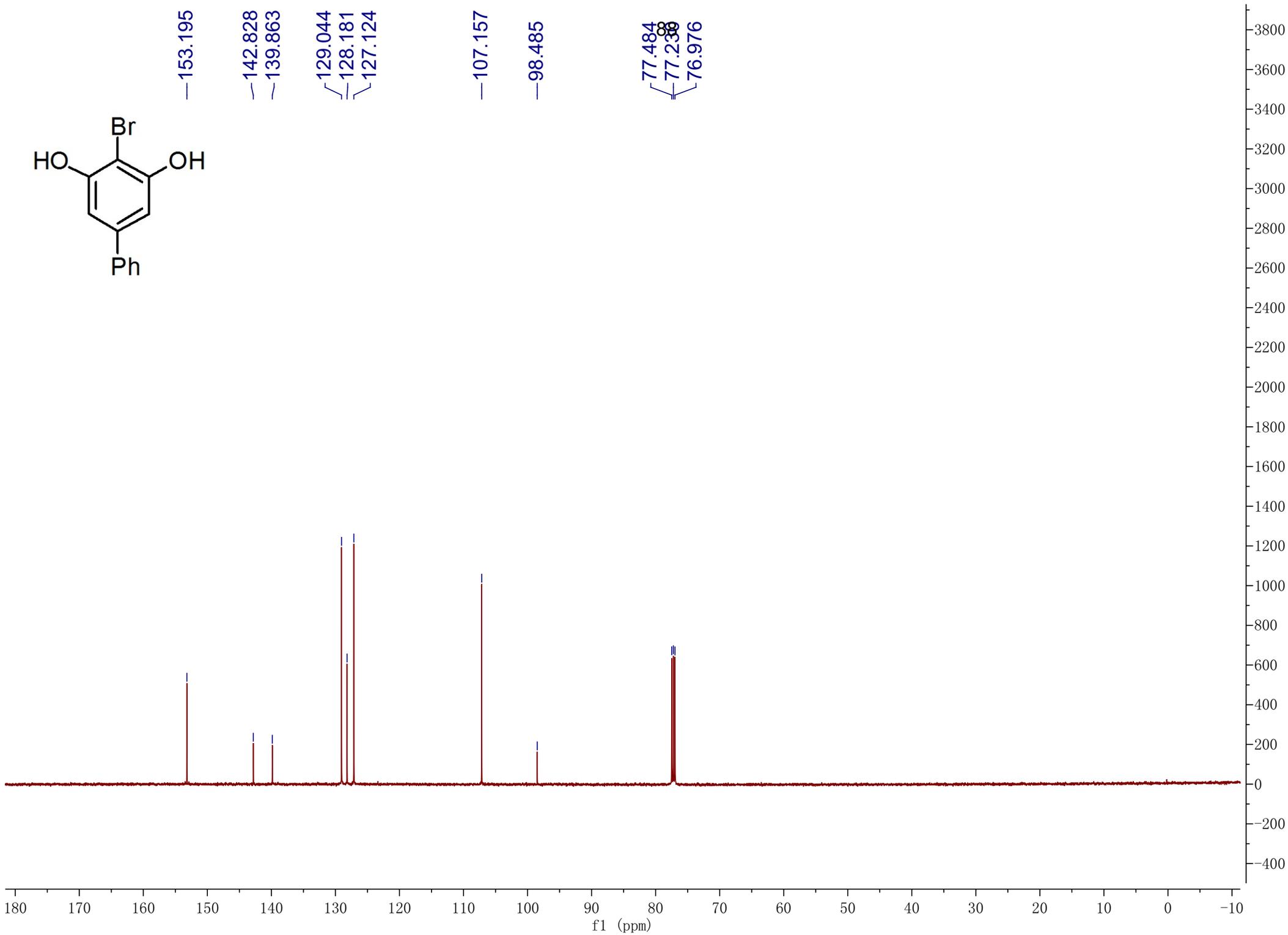
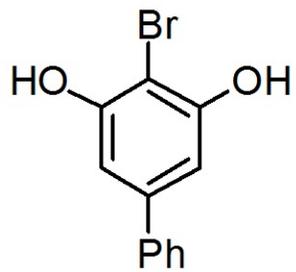
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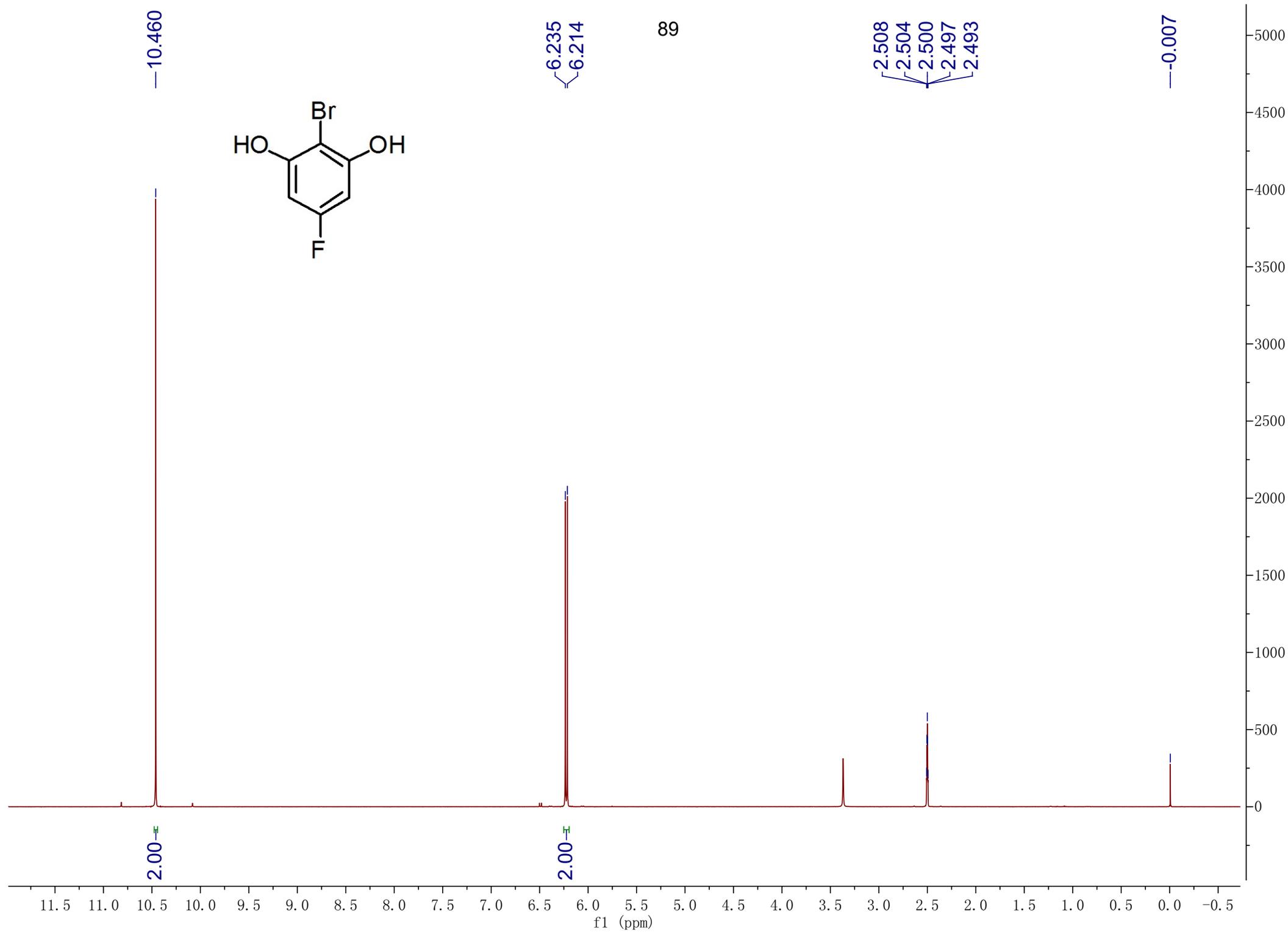
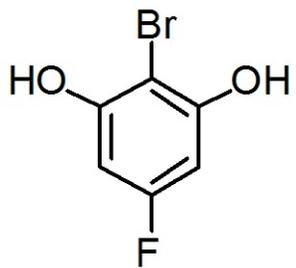
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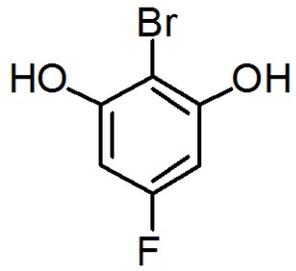
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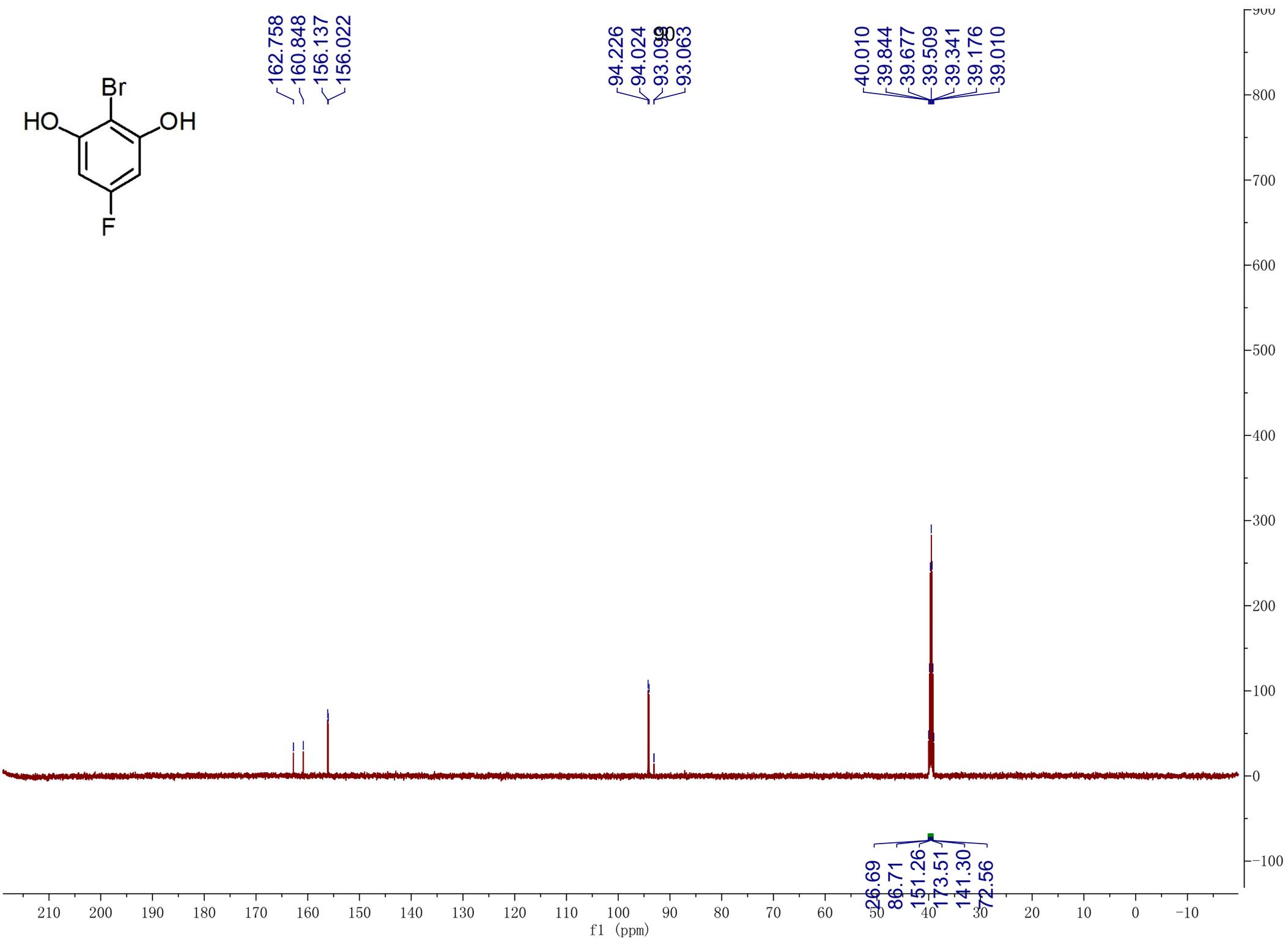


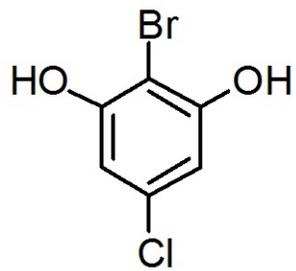


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94.226  
94.024  
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40.010  
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39.010





10.511

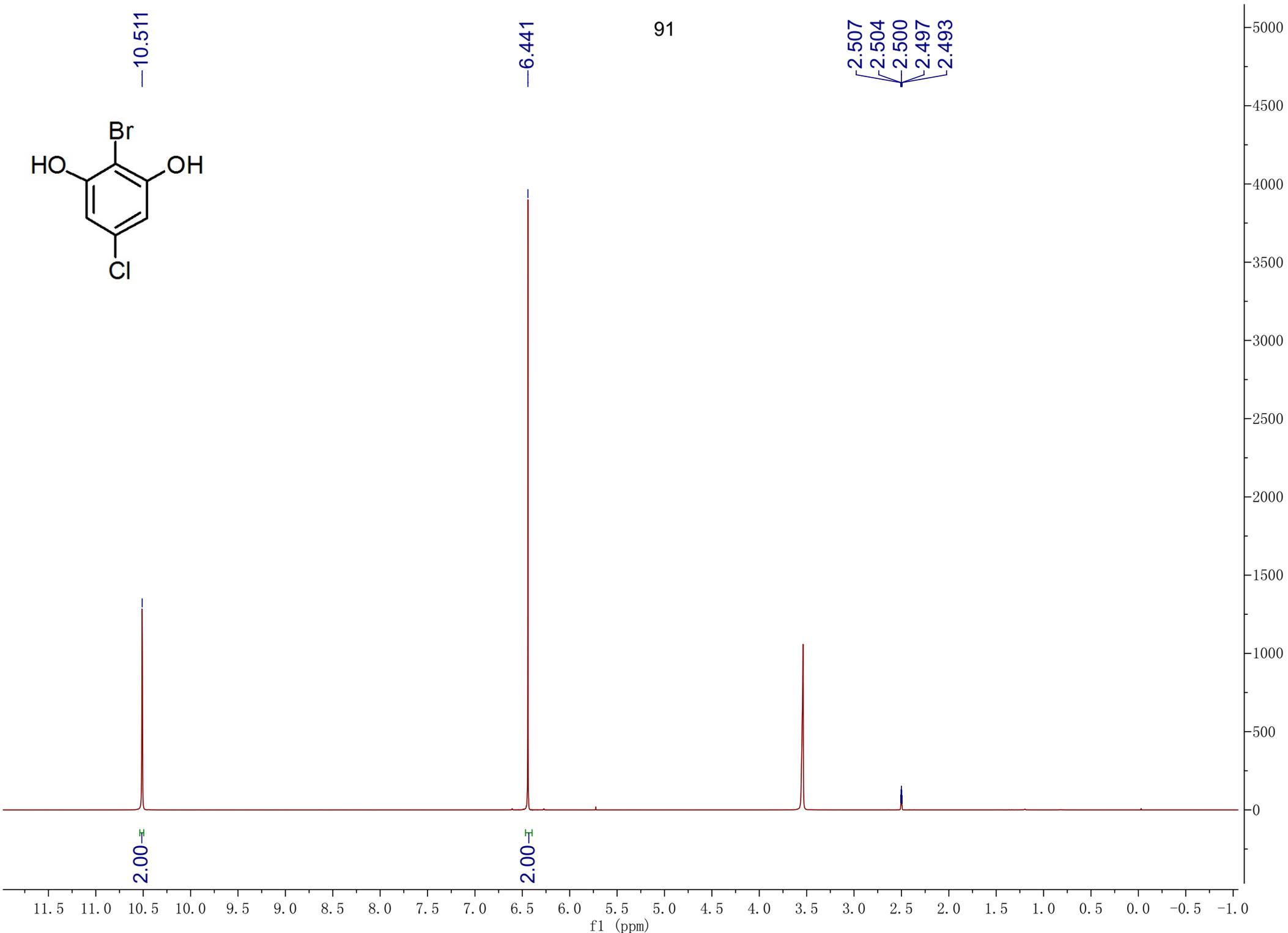
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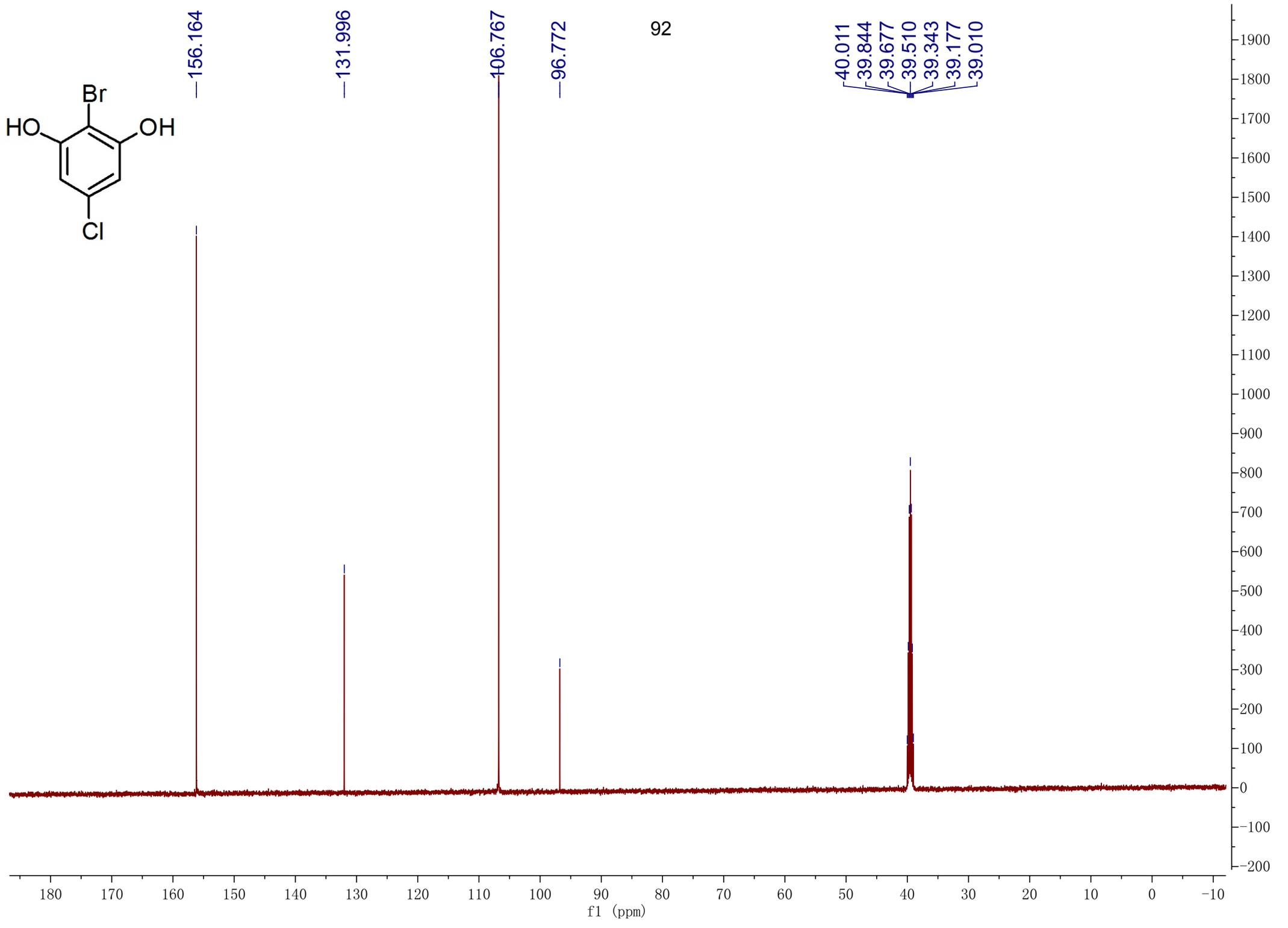
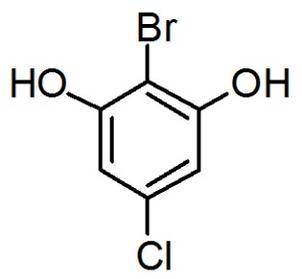
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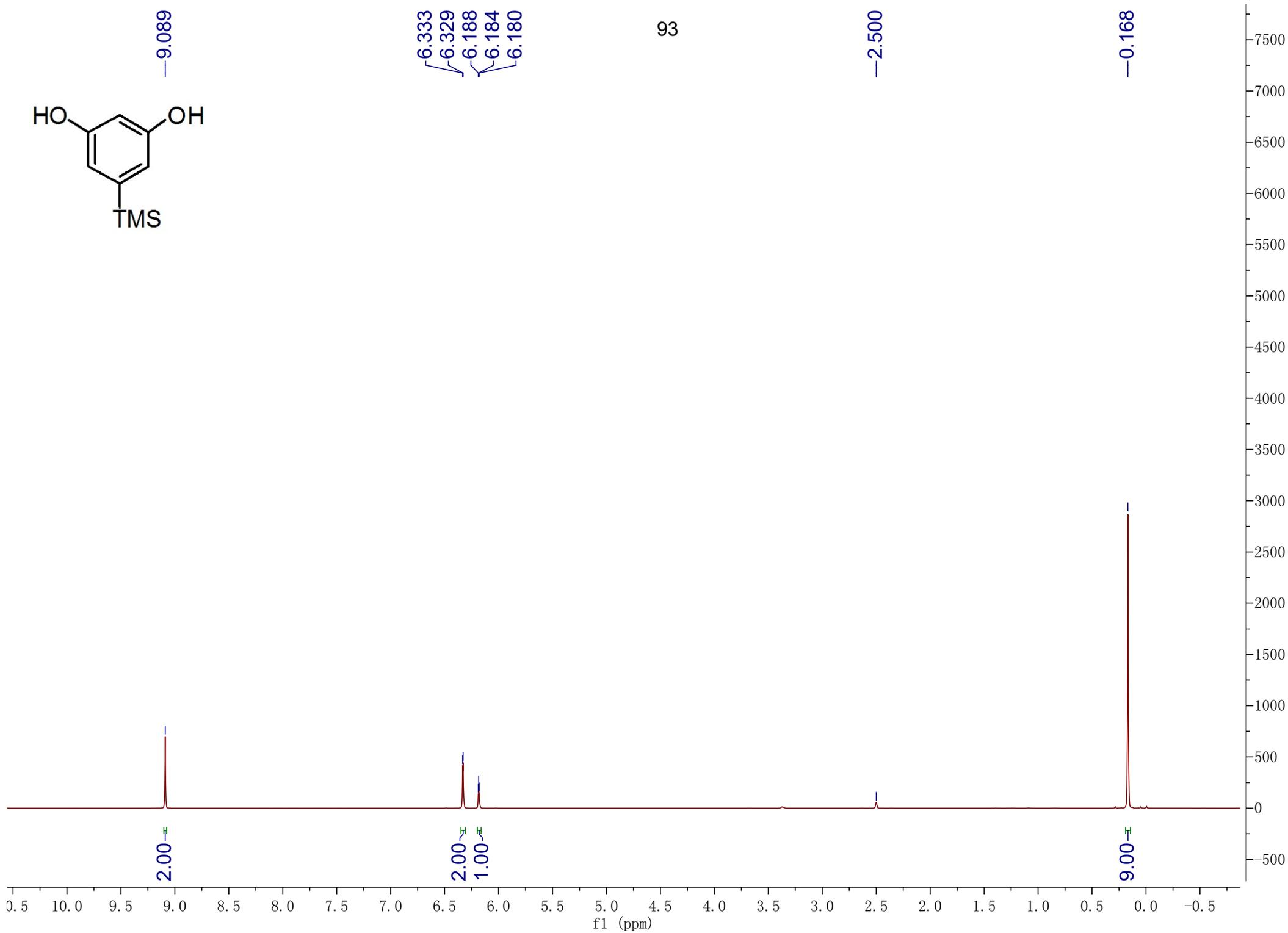
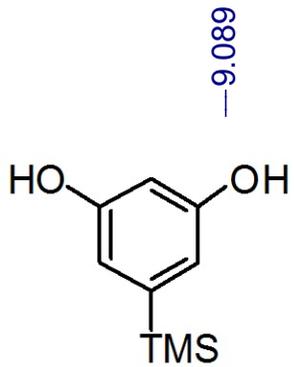
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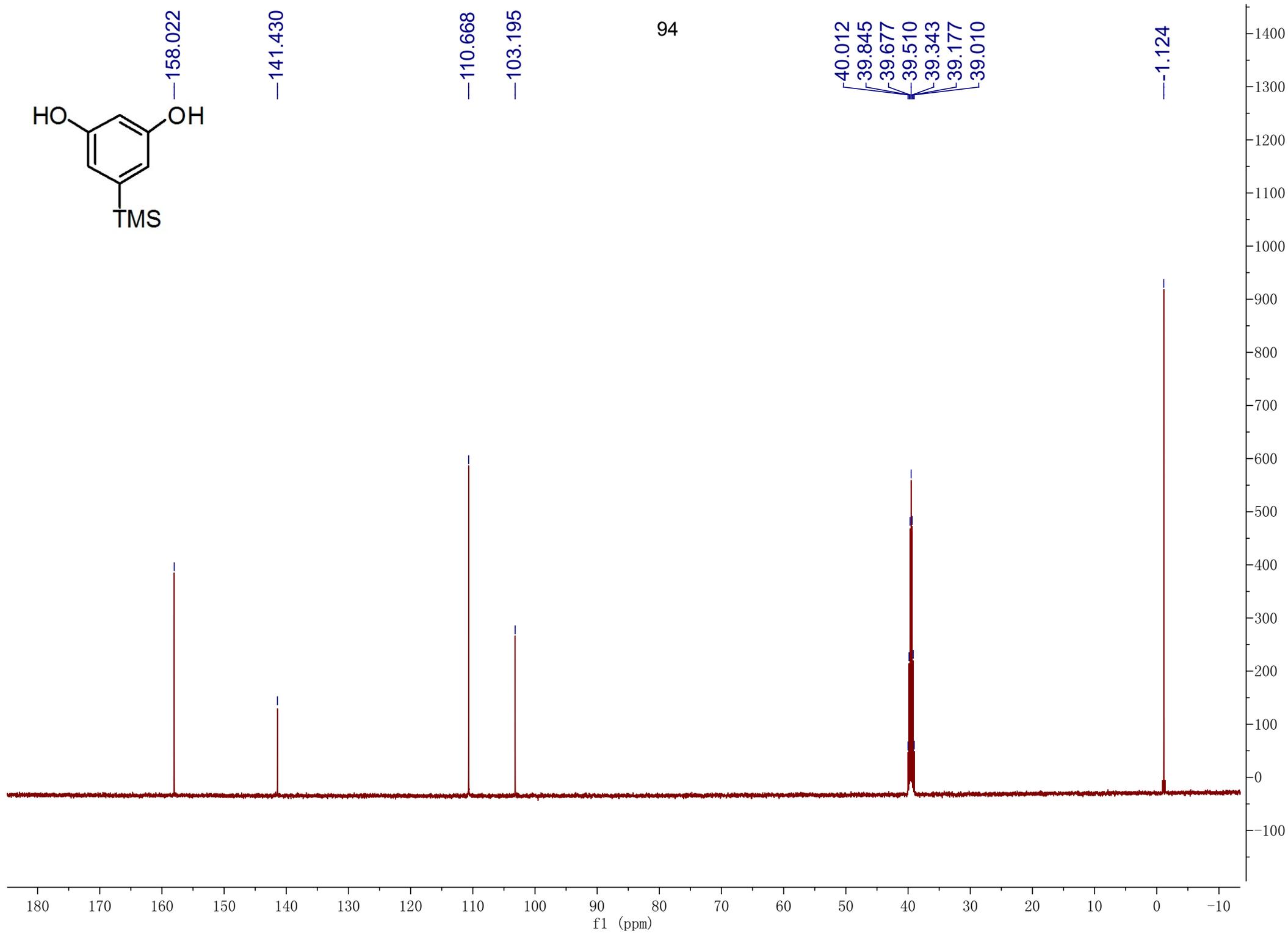
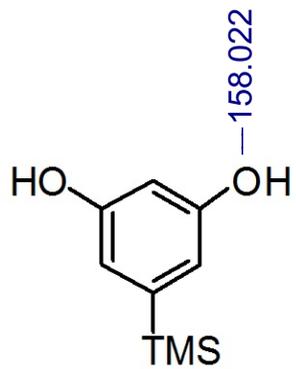
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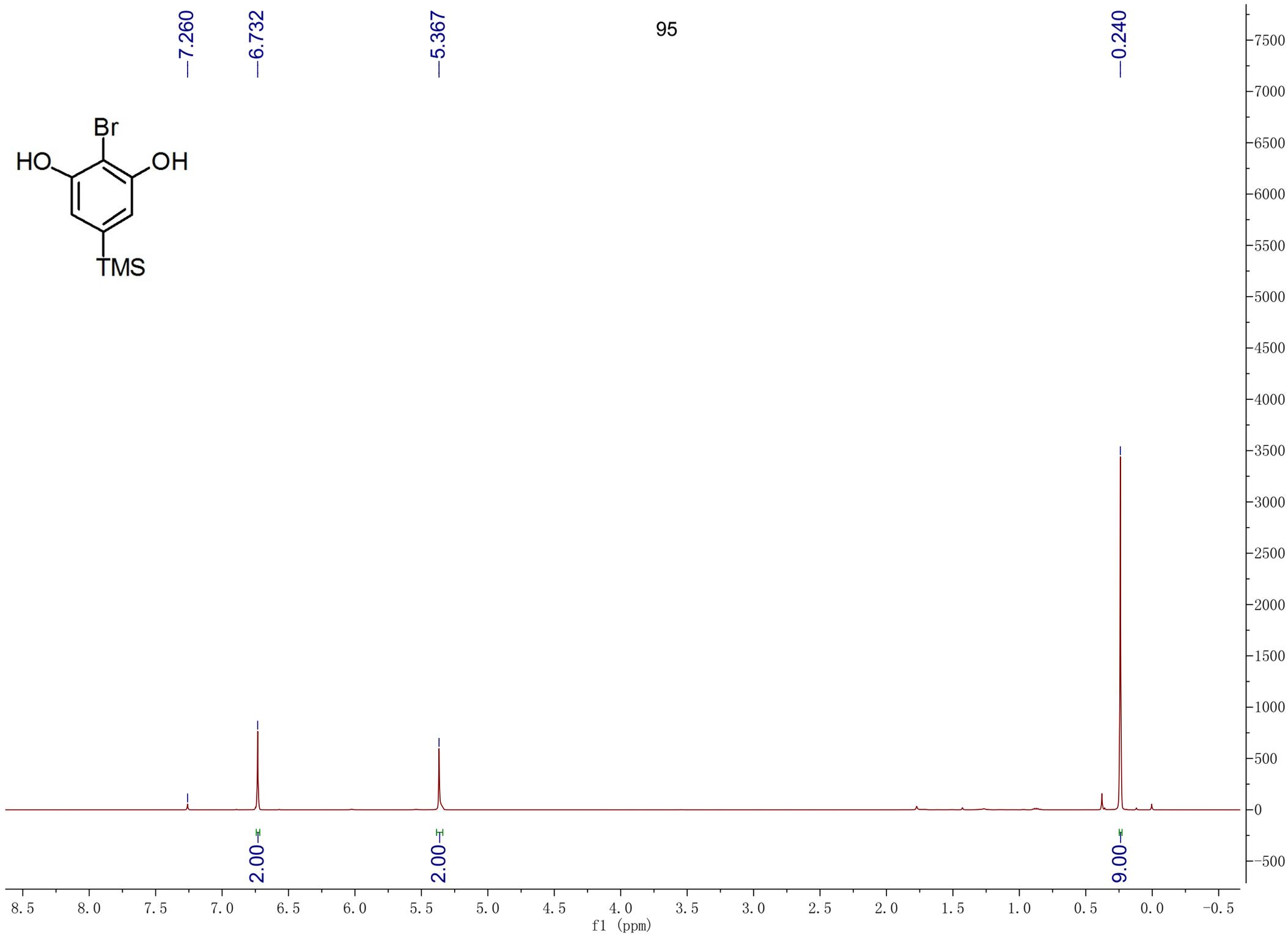
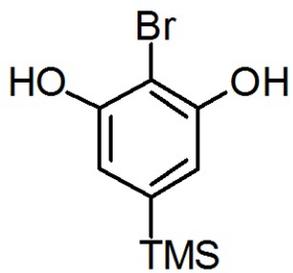
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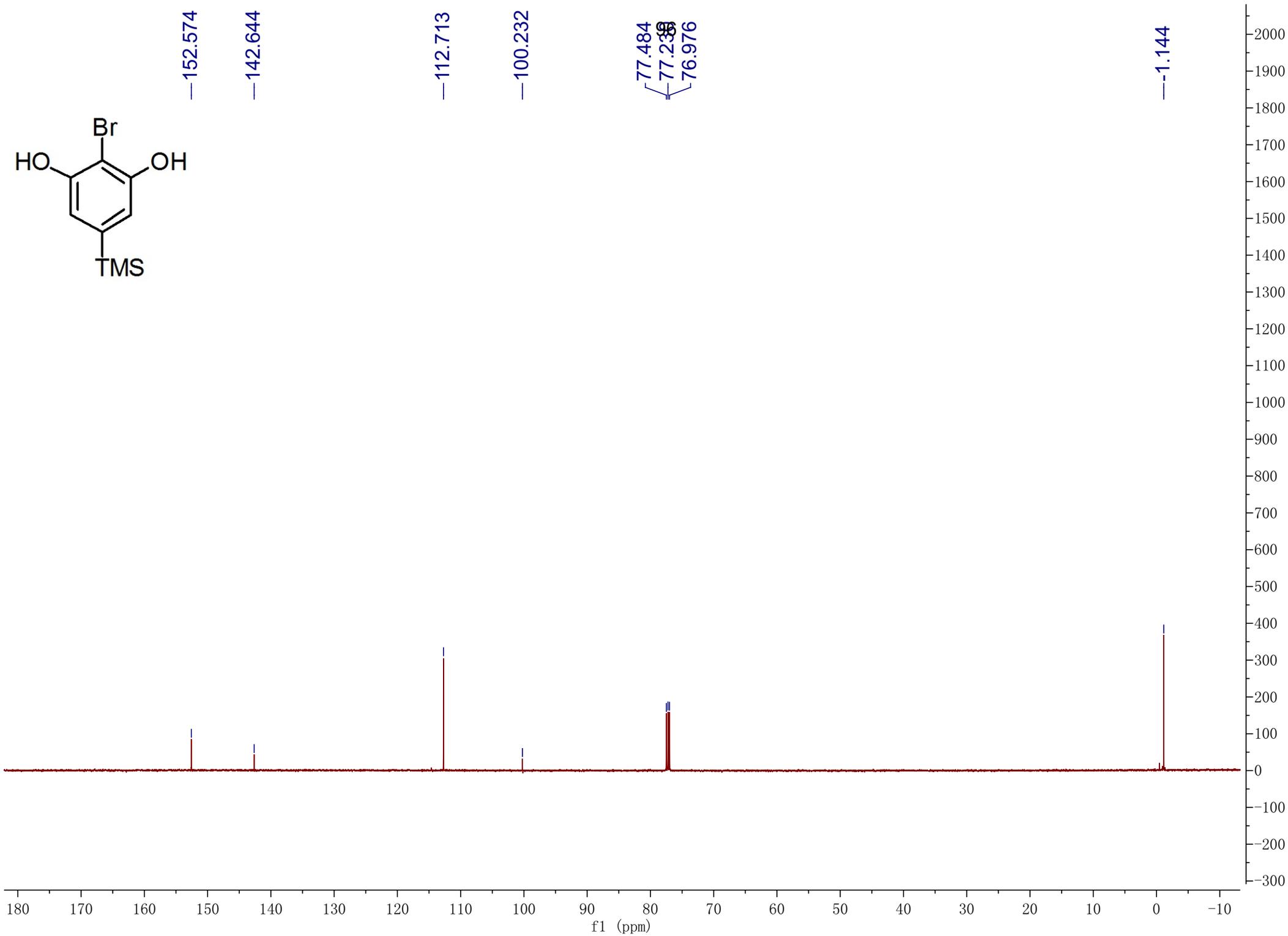
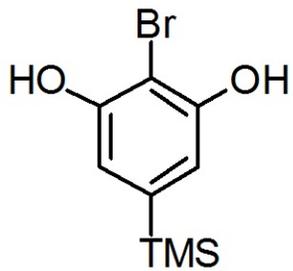


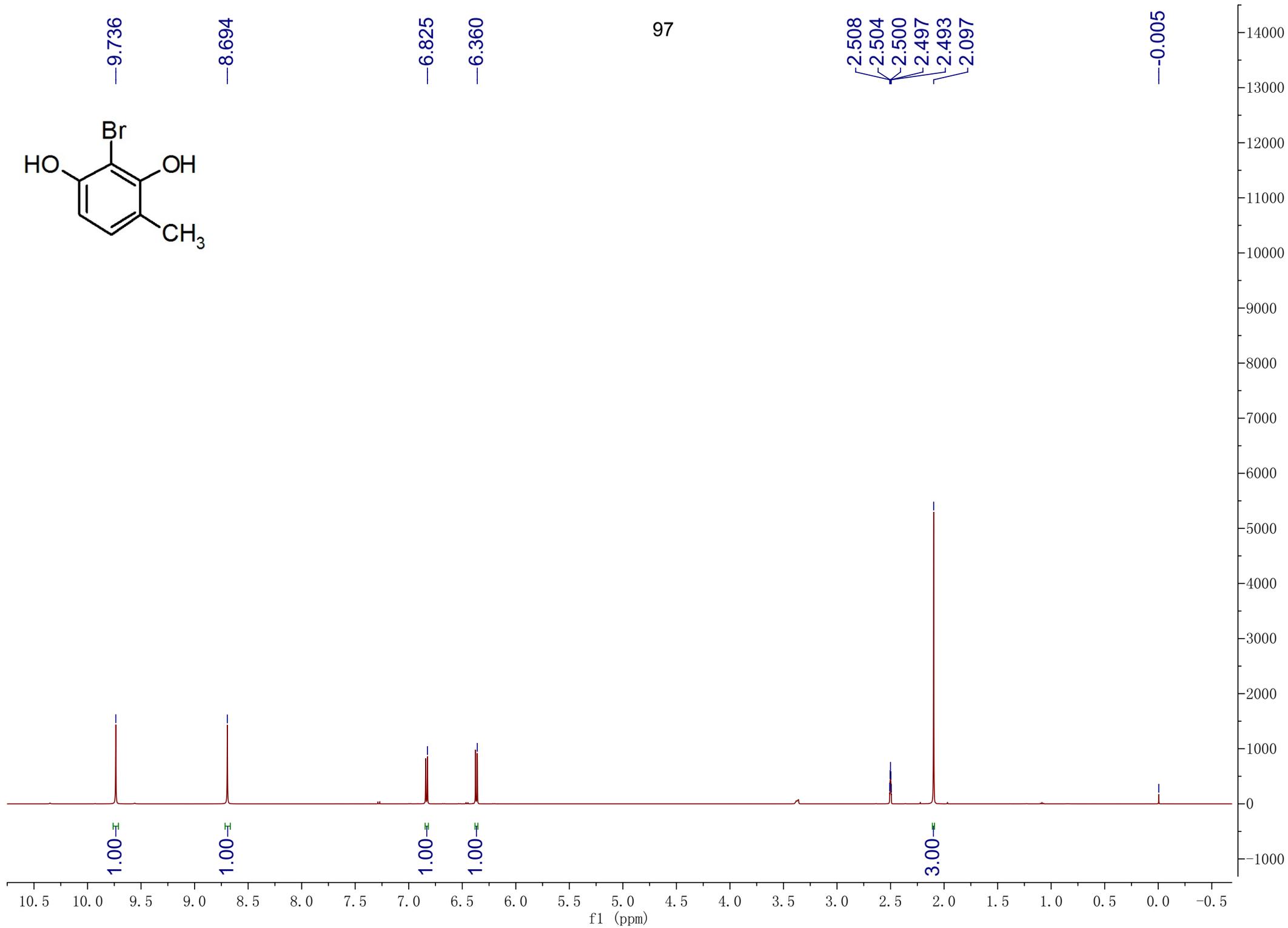
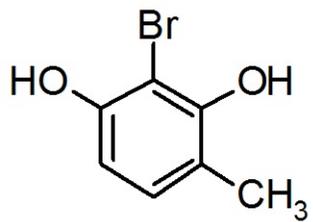


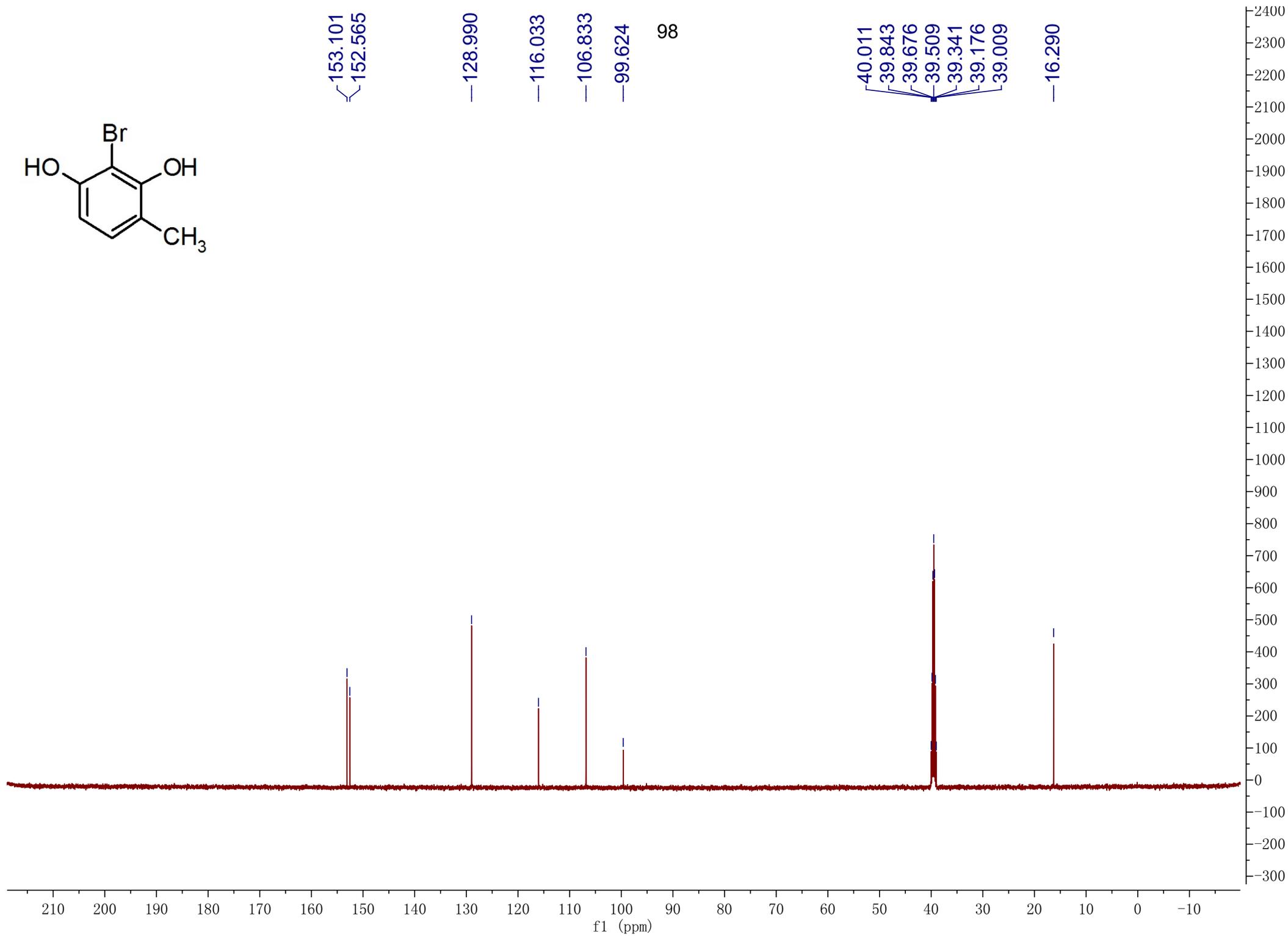
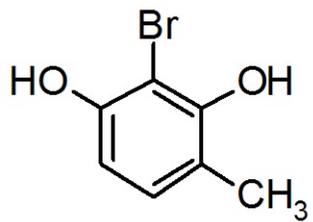


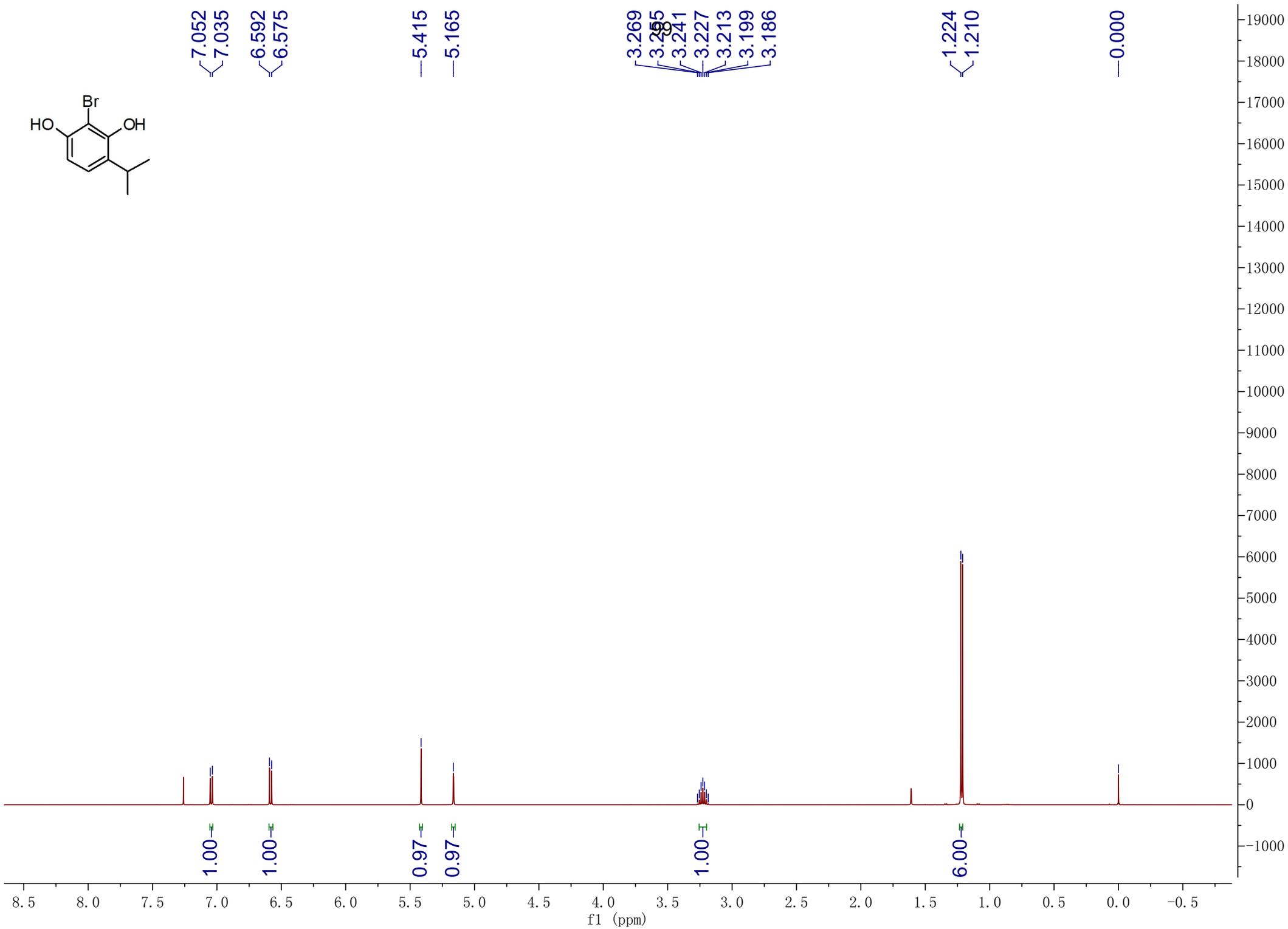
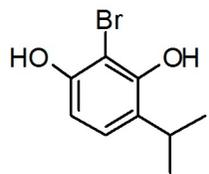


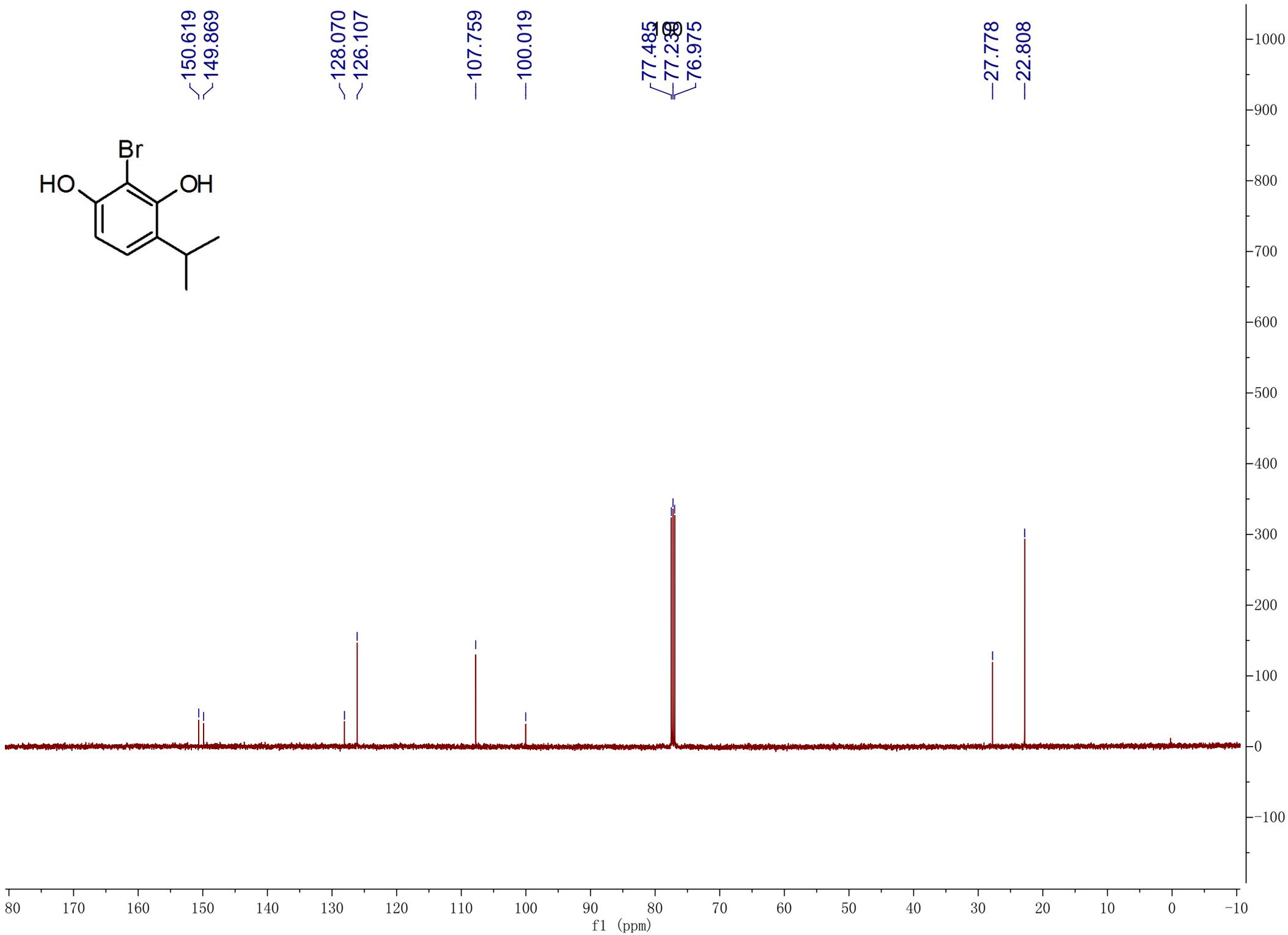
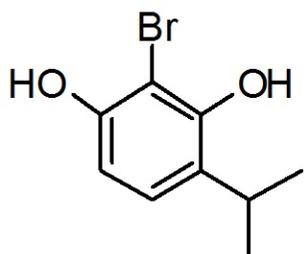


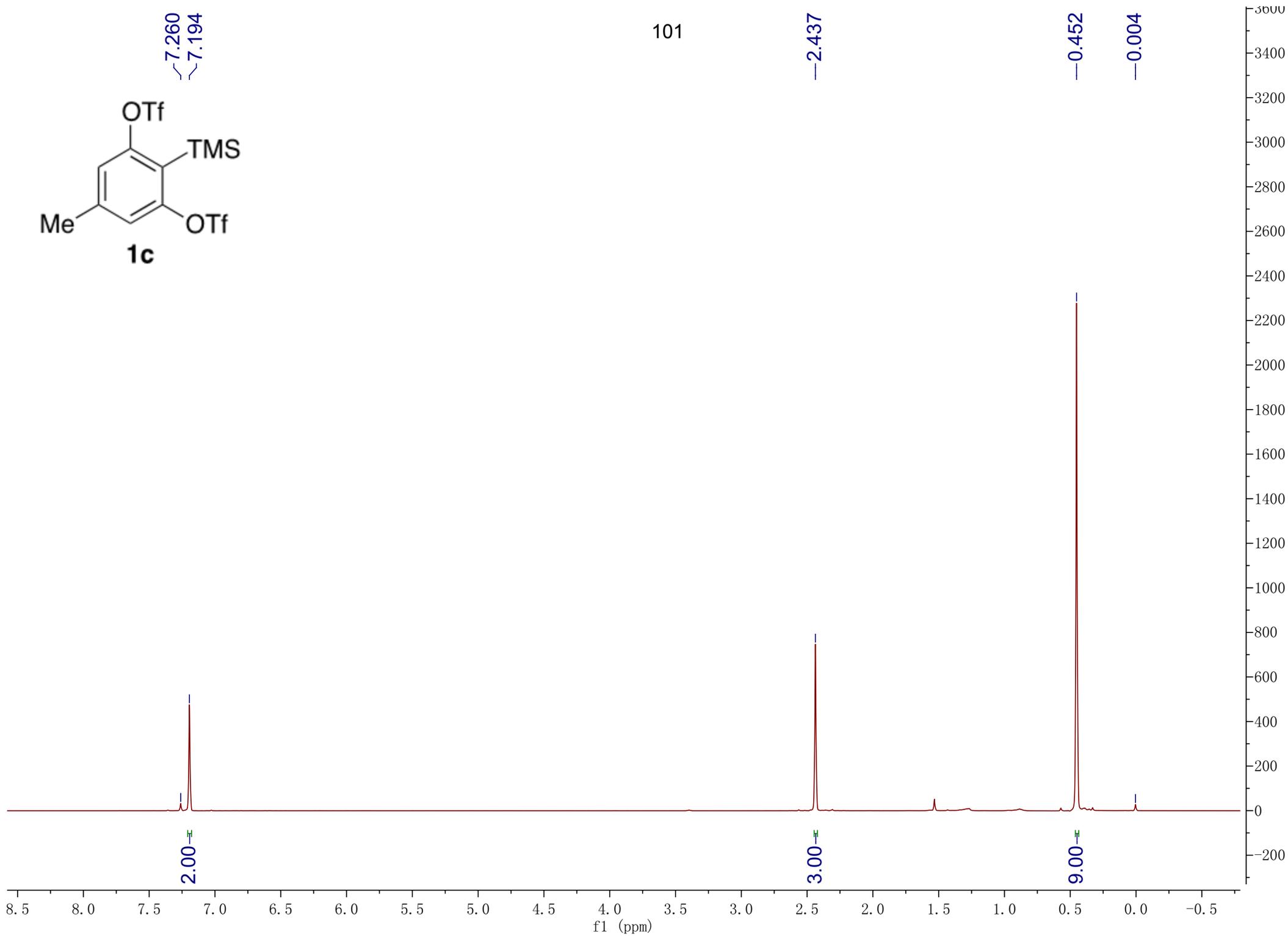
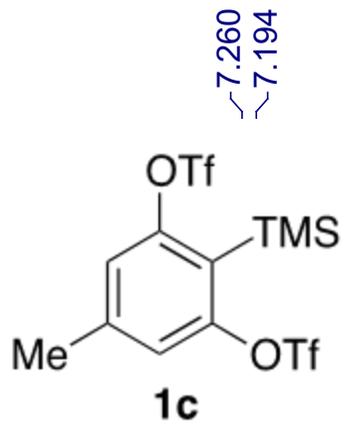


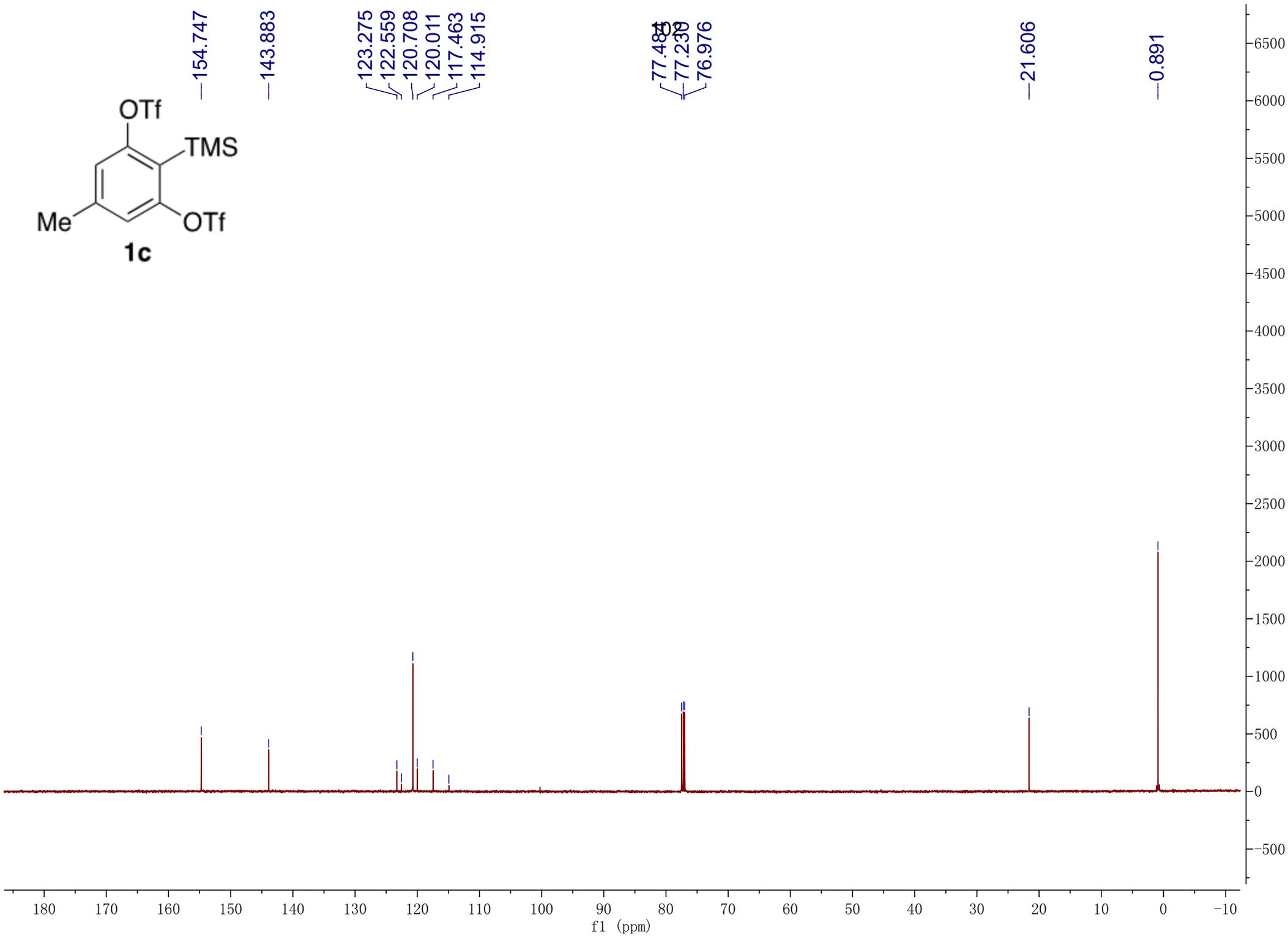
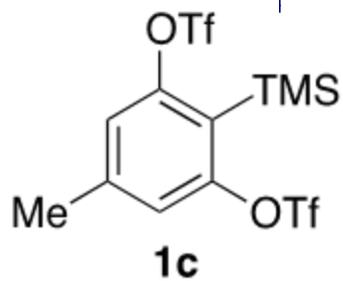




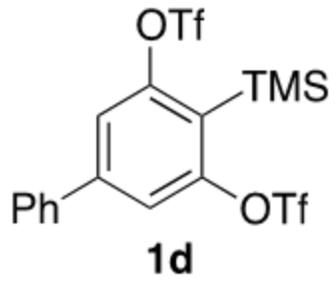






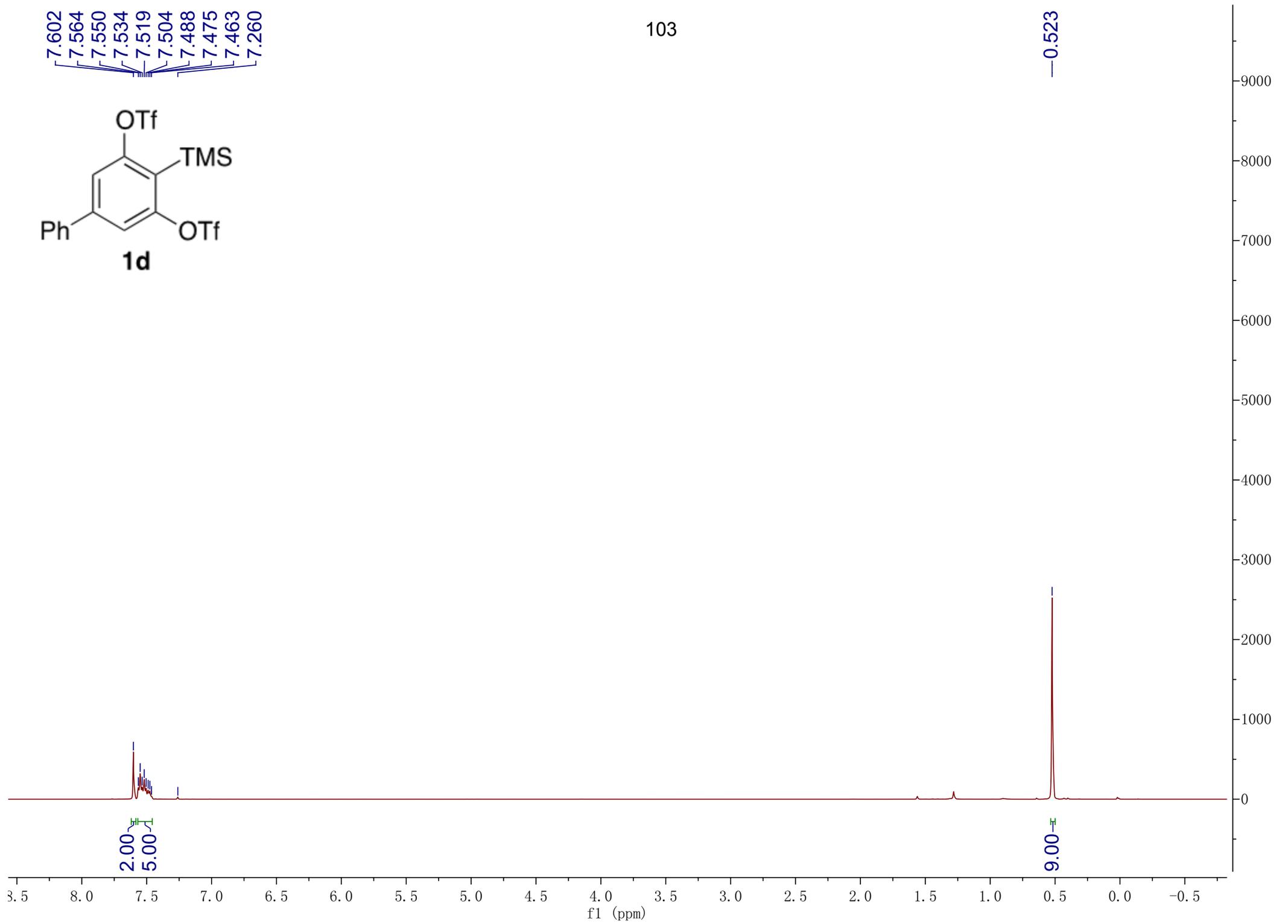


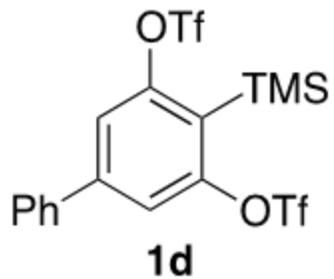
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103

-0.523





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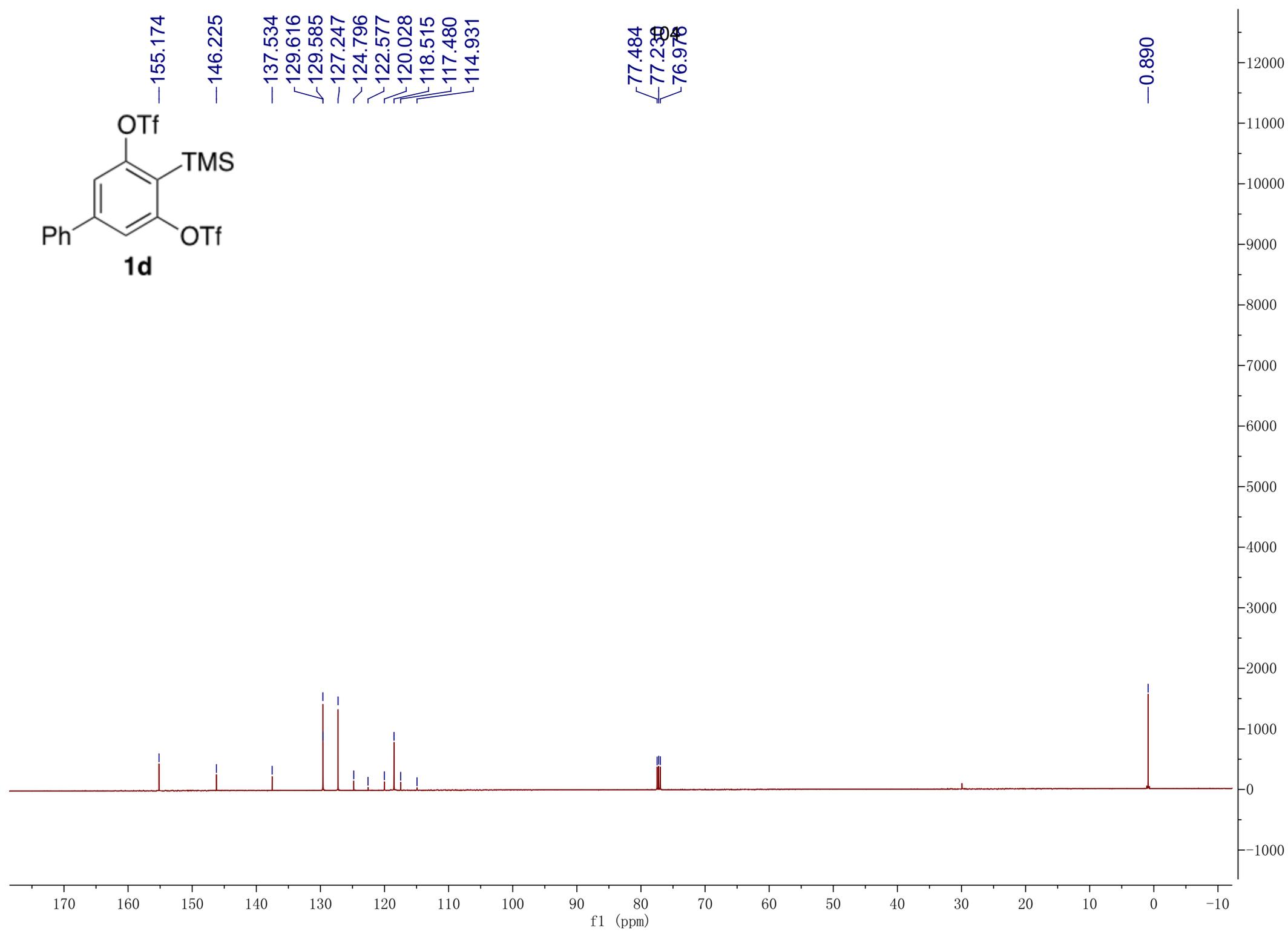
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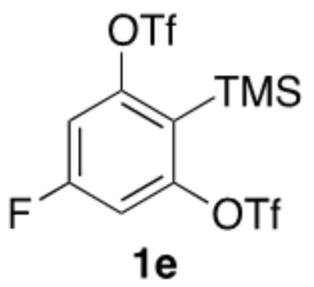
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f1 (ppm)

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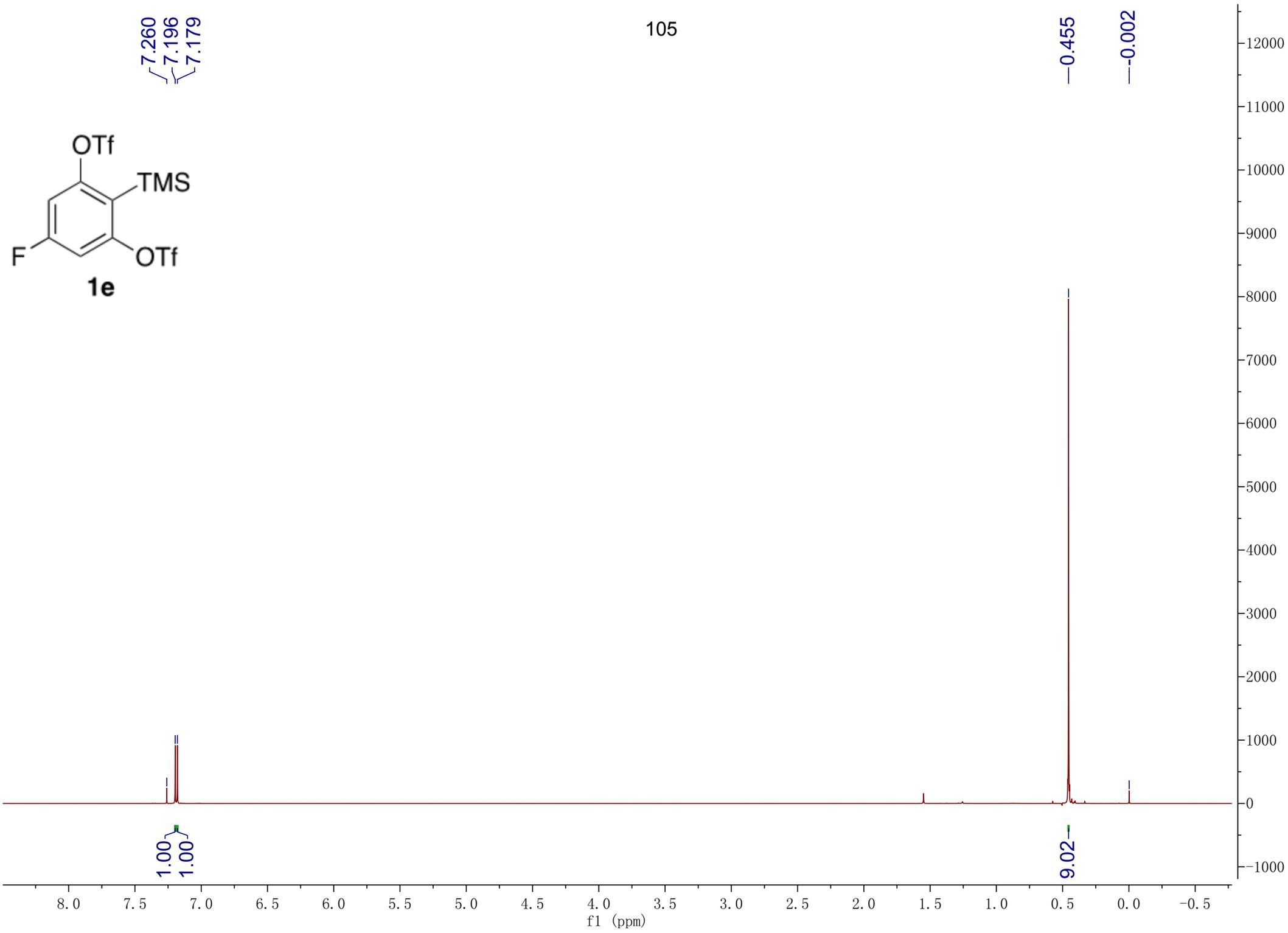
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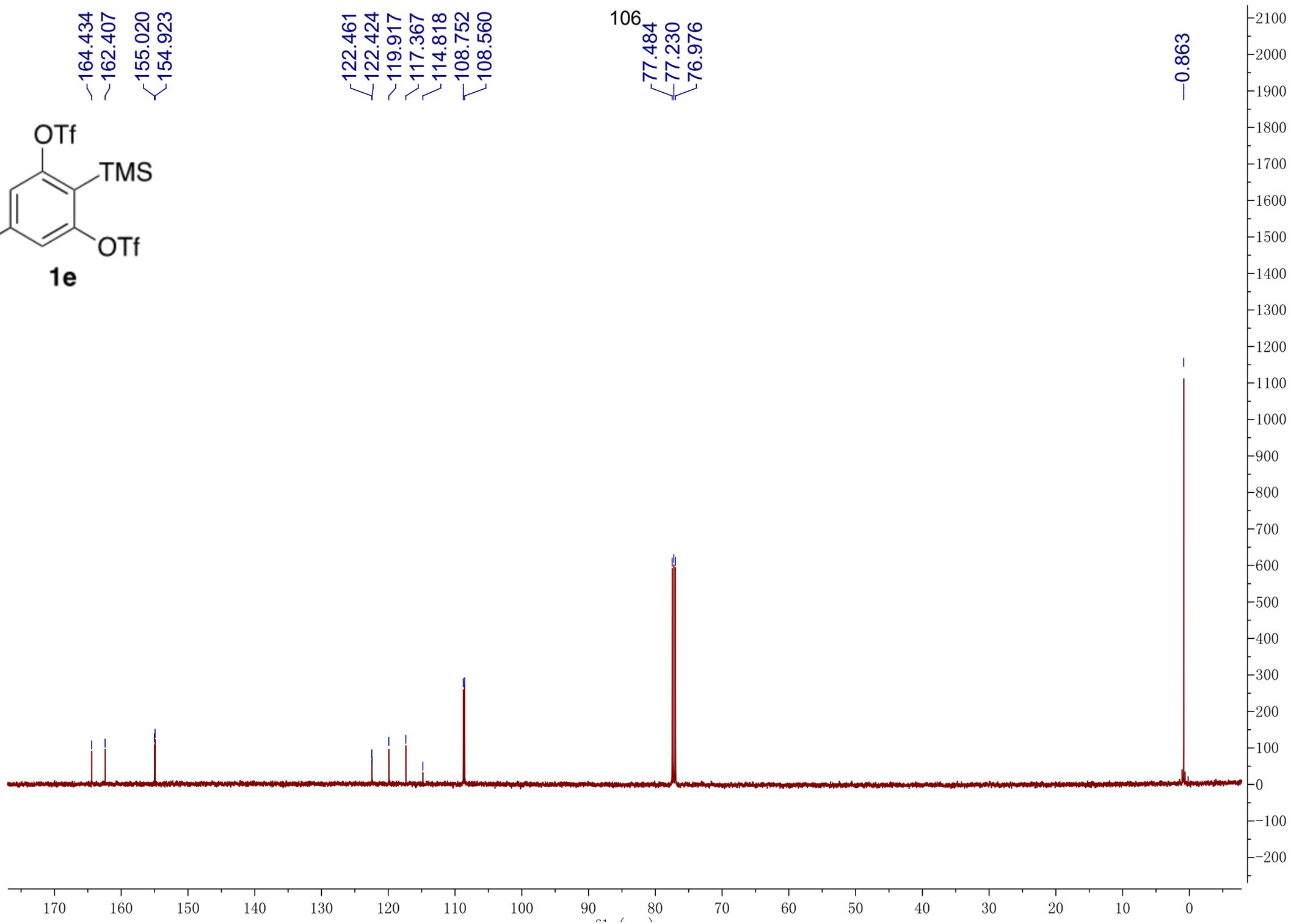
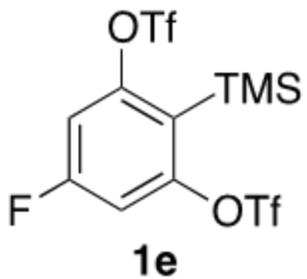
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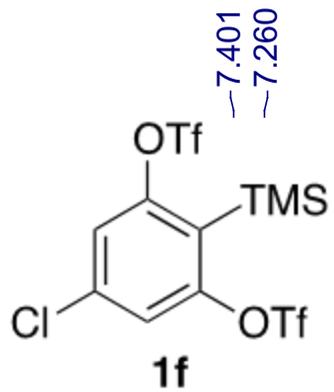
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1.00

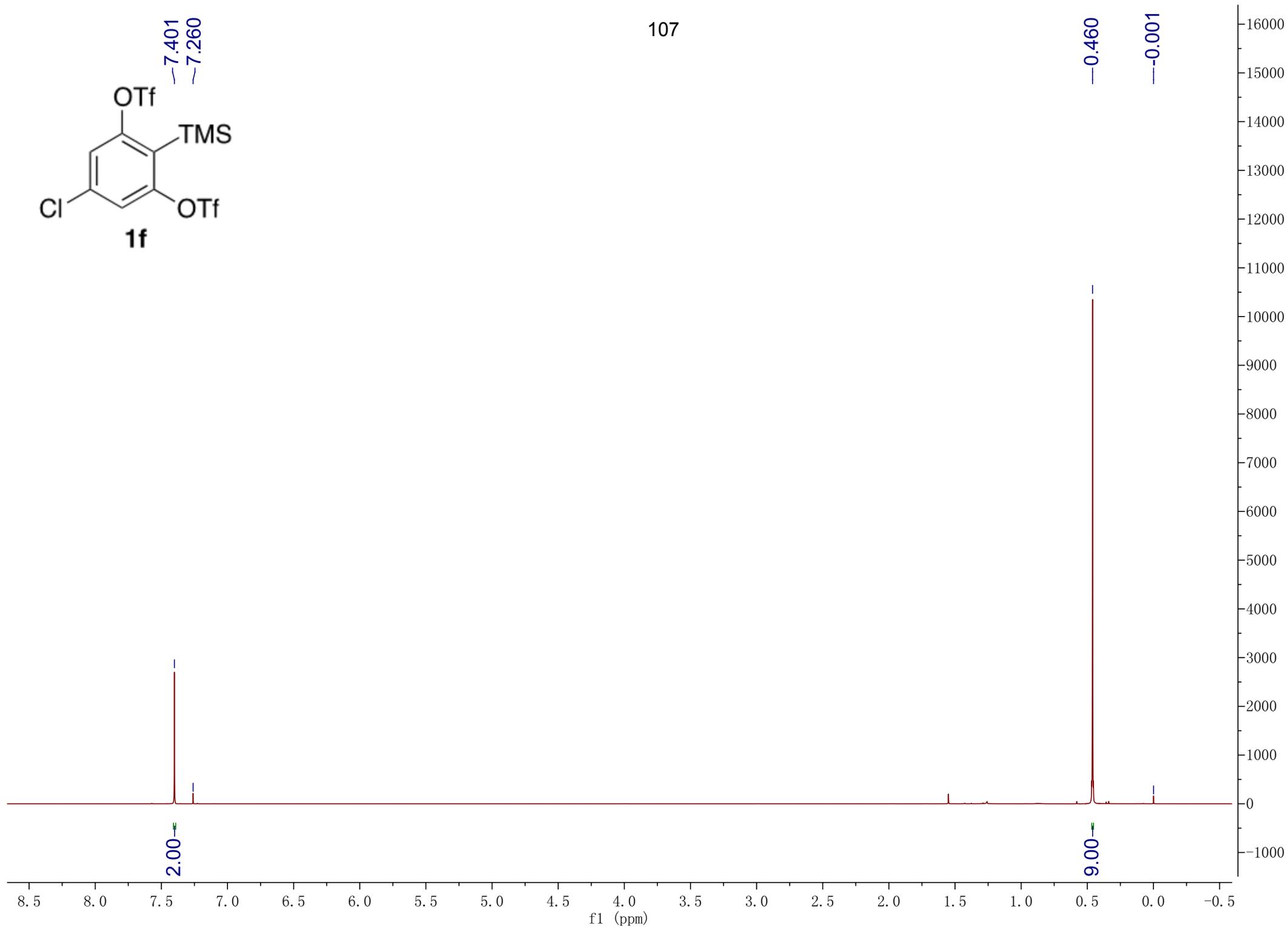
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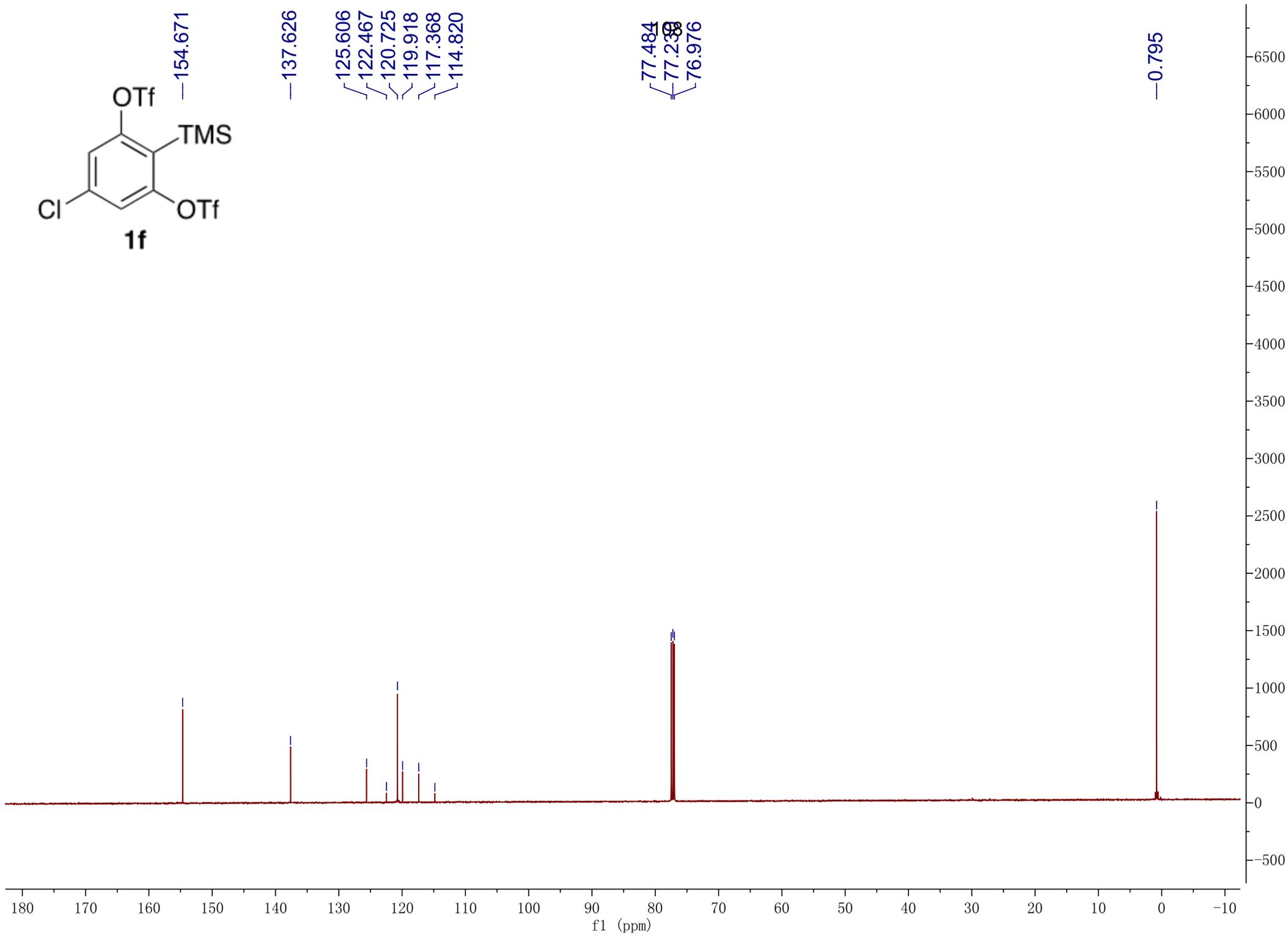
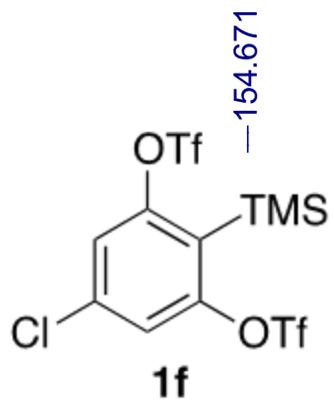


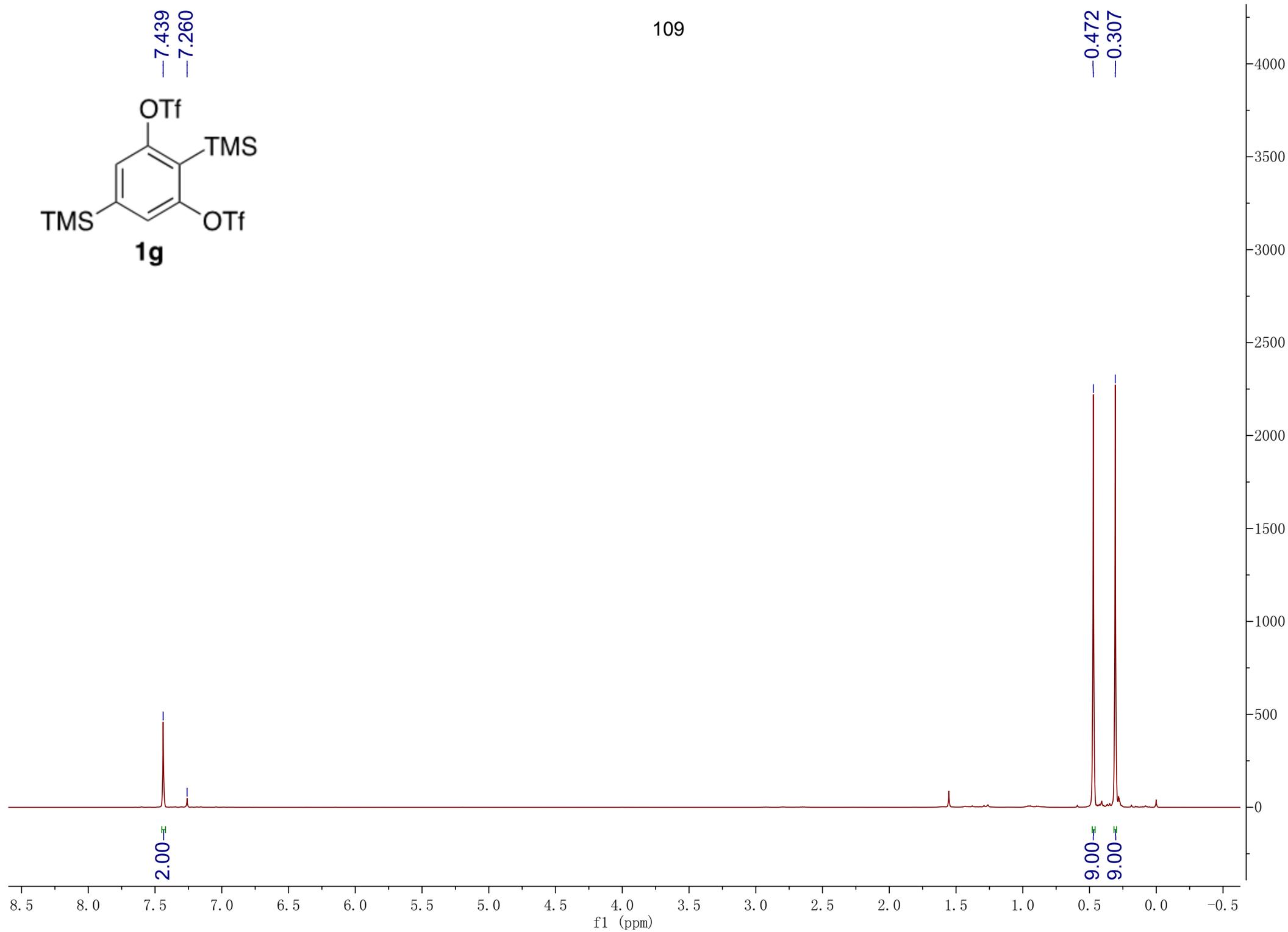
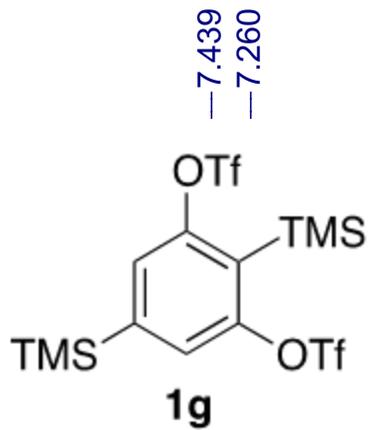


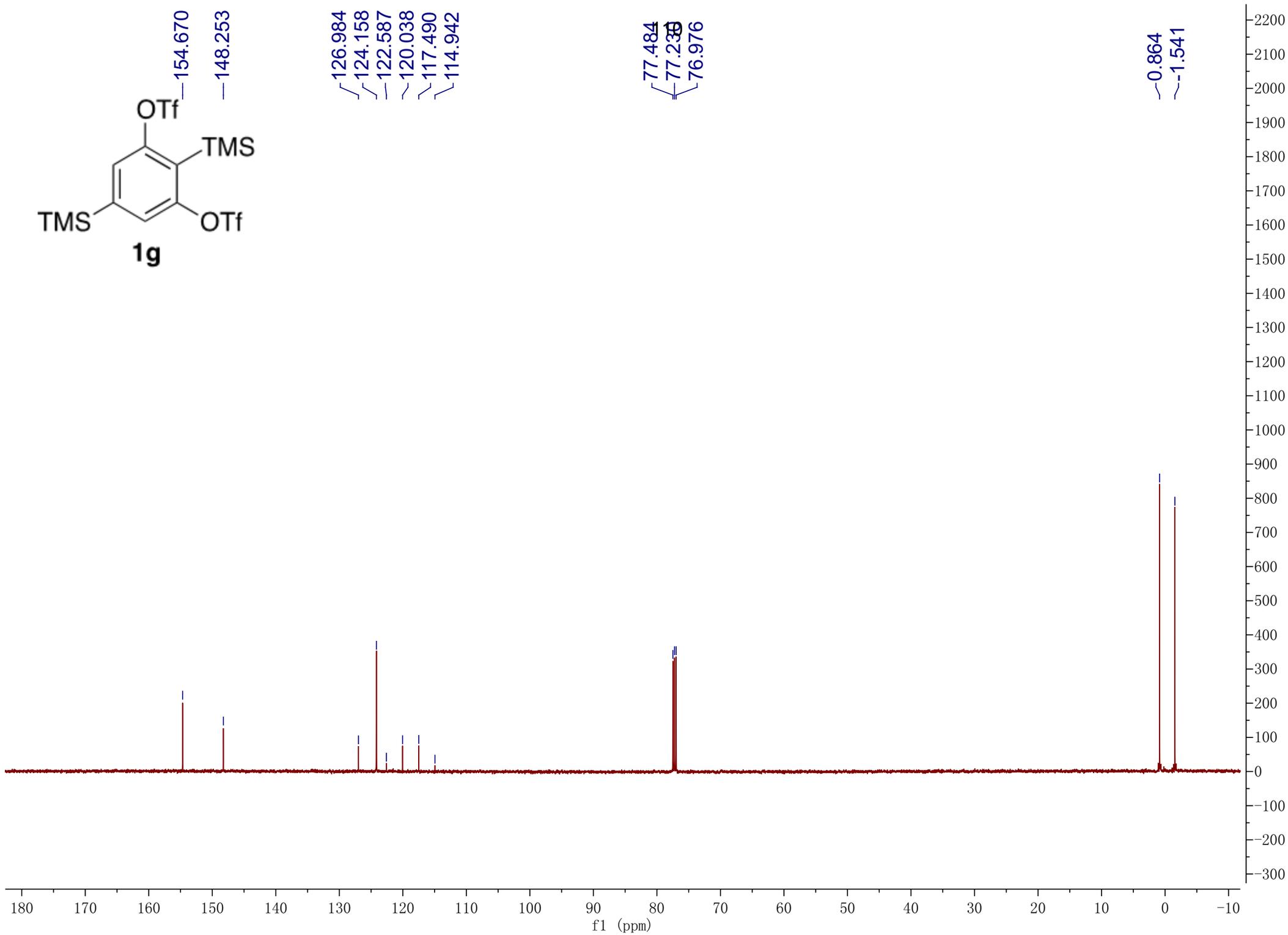
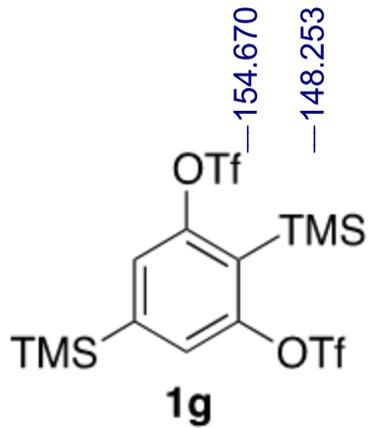


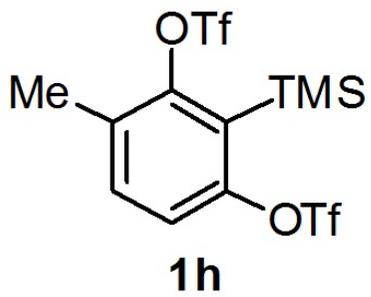
107











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7.260

111

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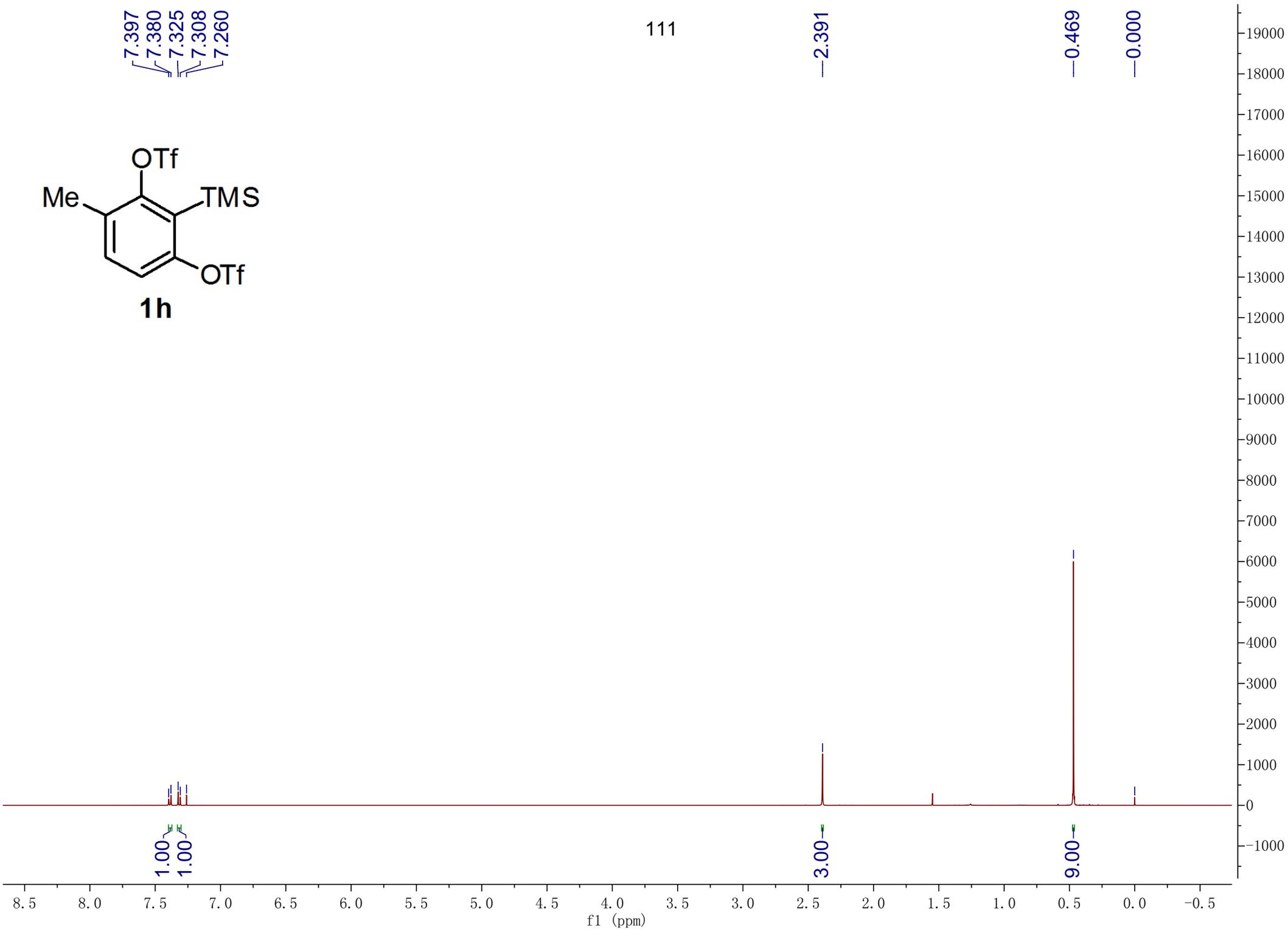
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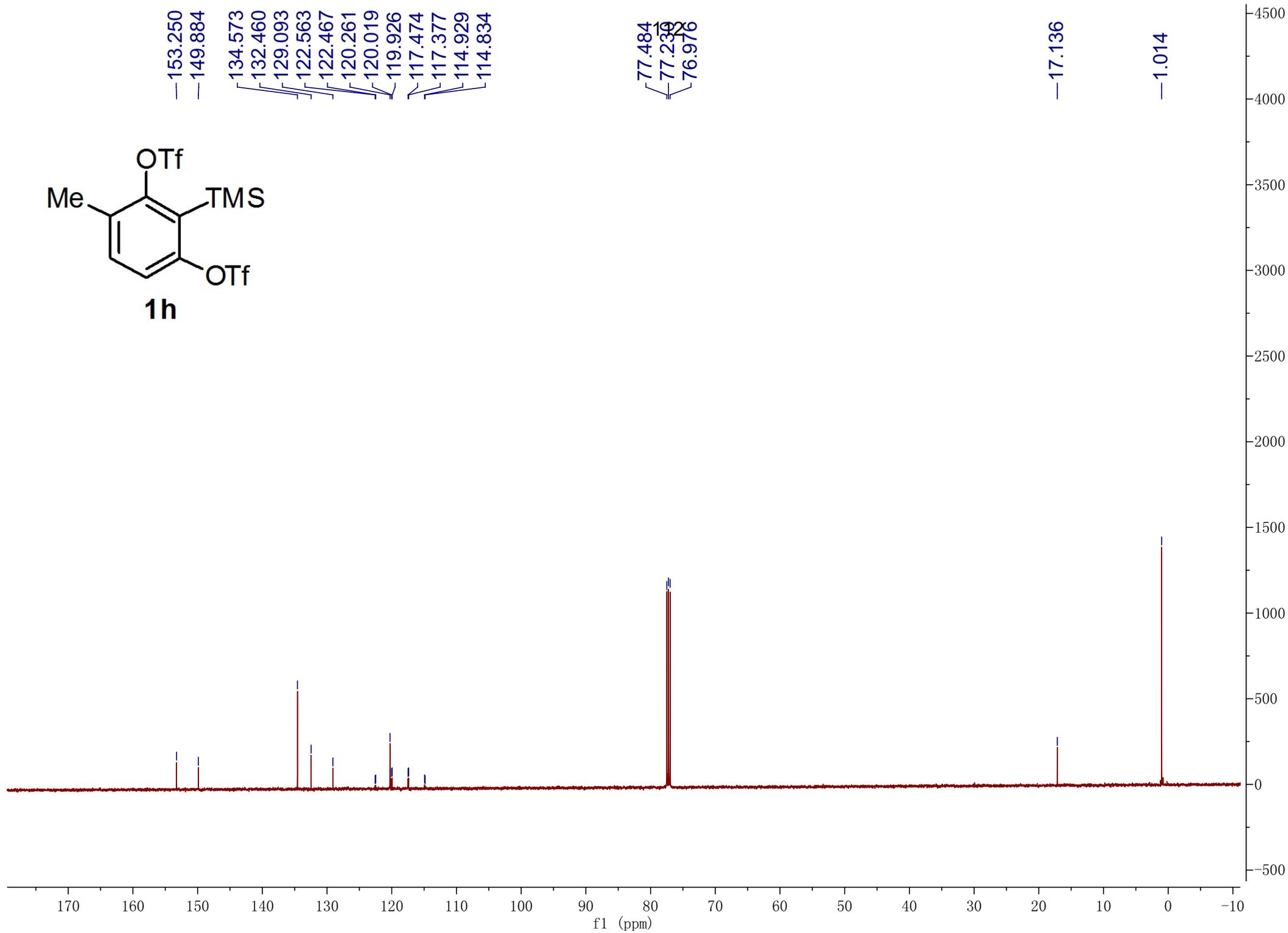
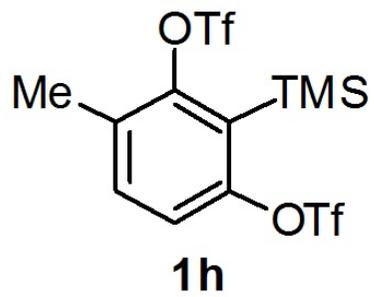
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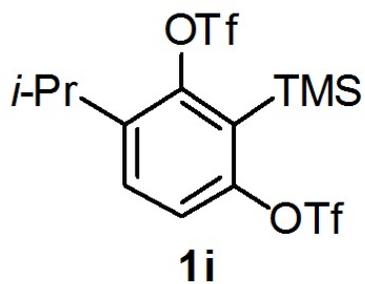
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3.00

9.00







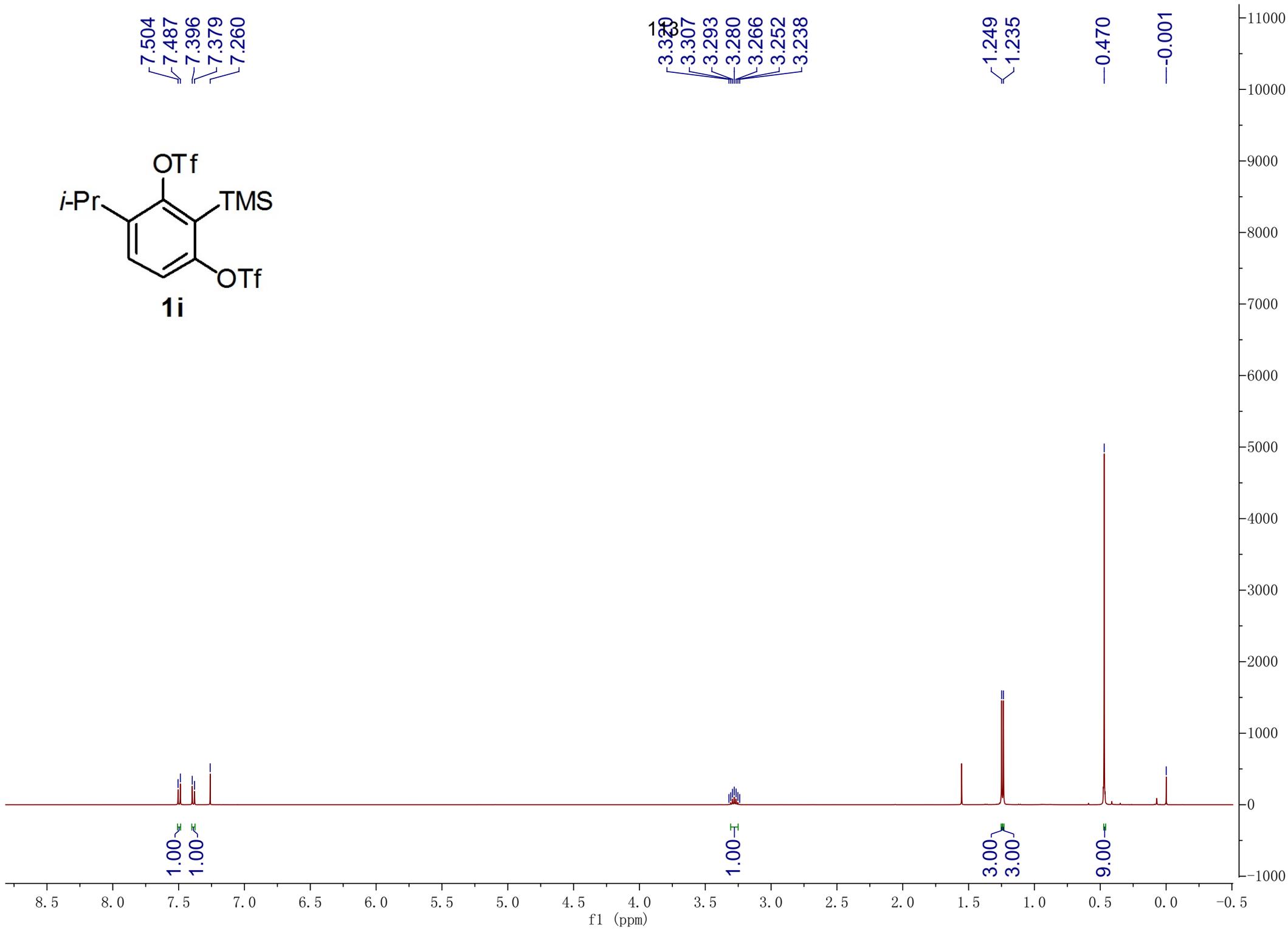
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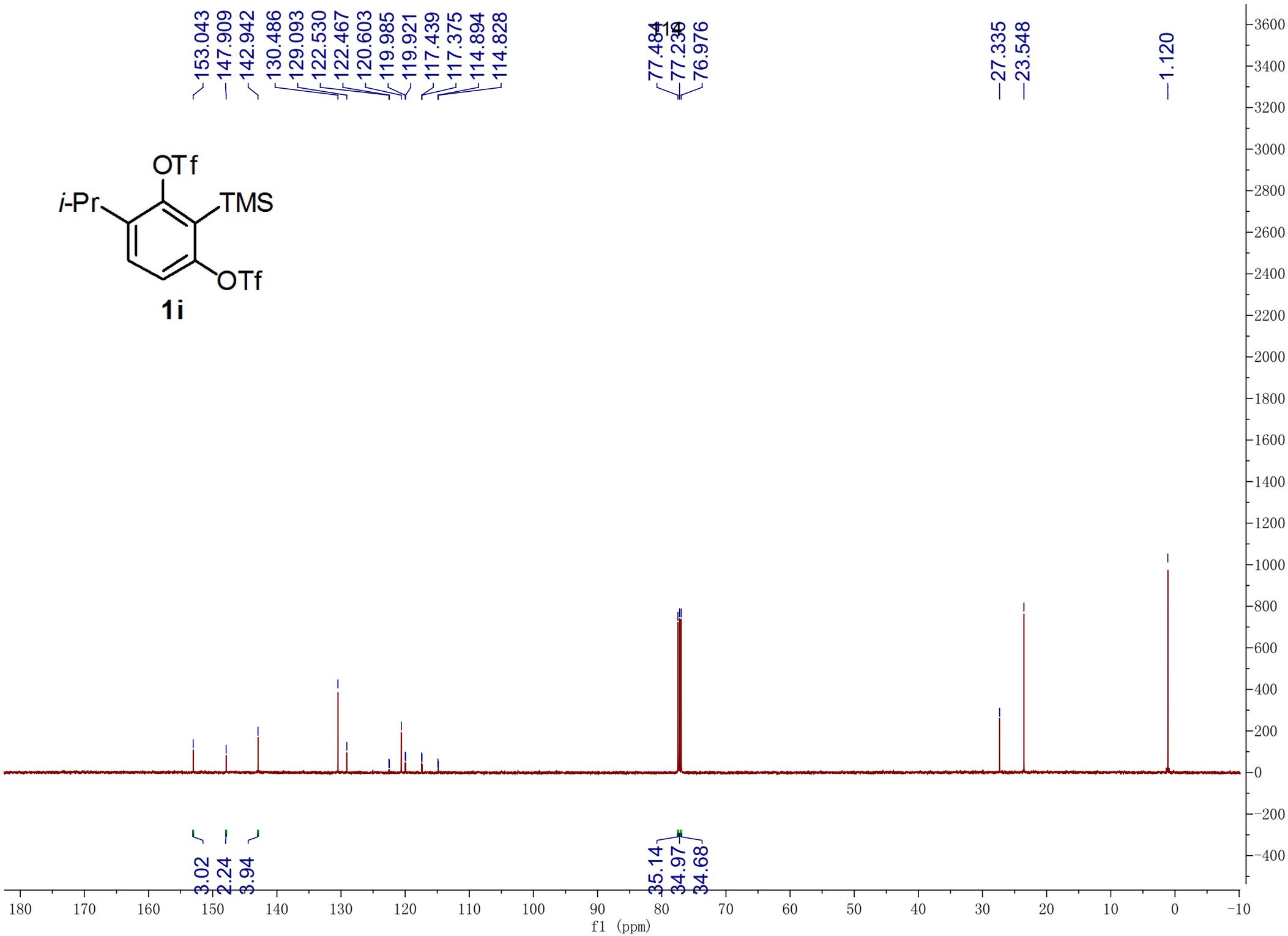
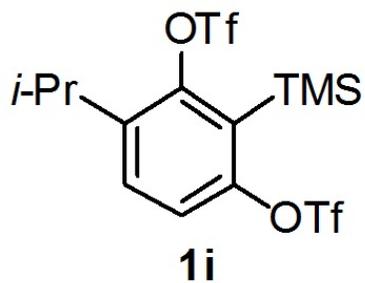
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-0.001

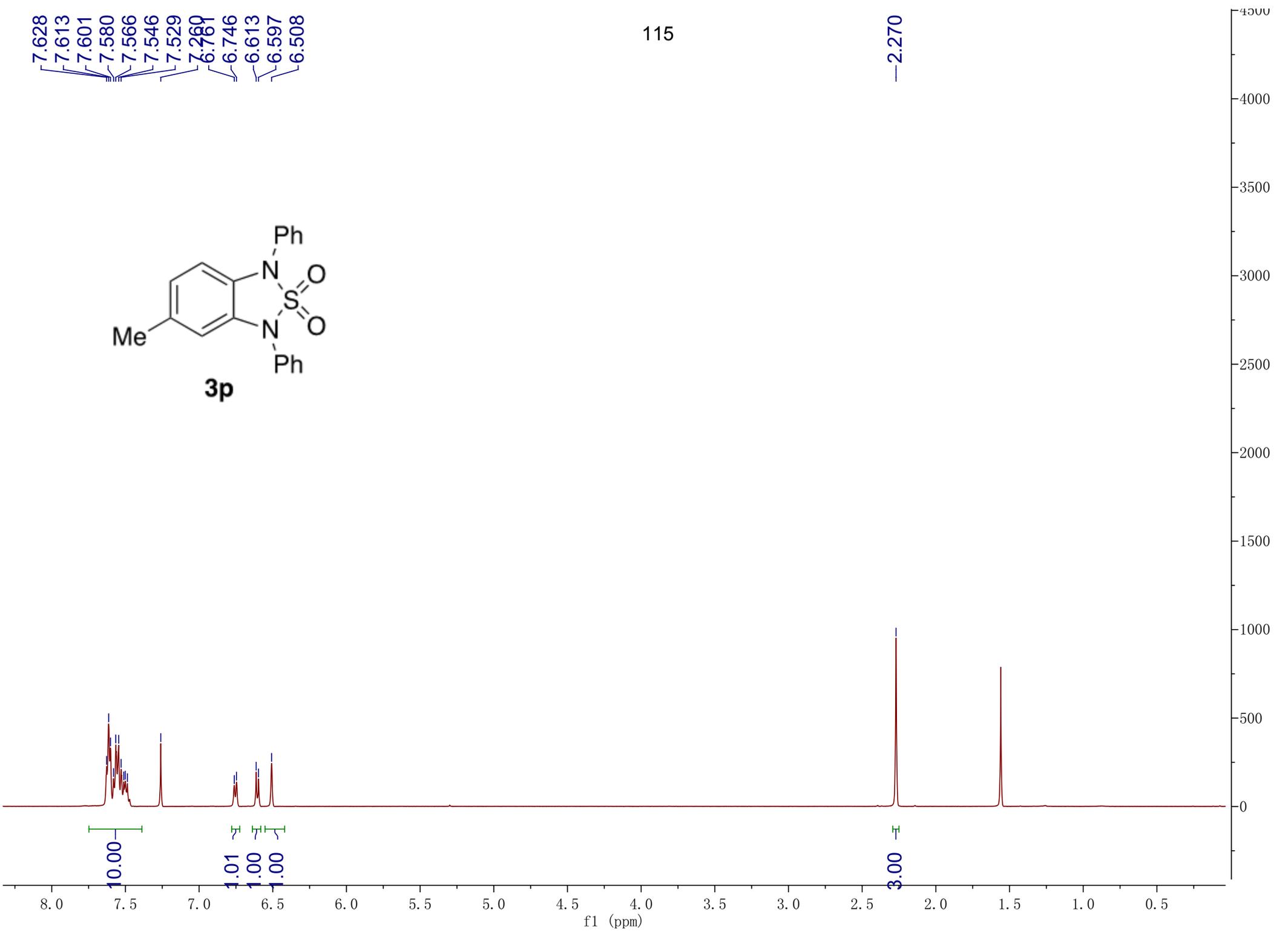
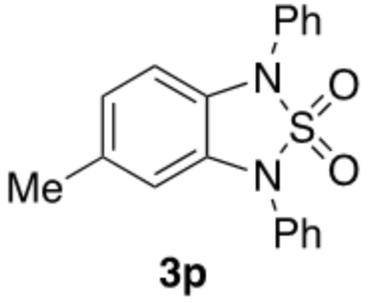


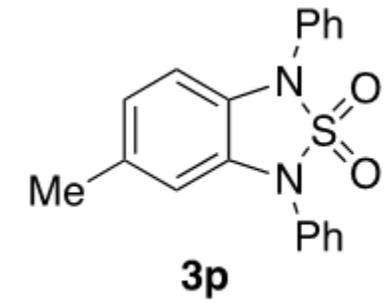


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6.508

115

-2.270

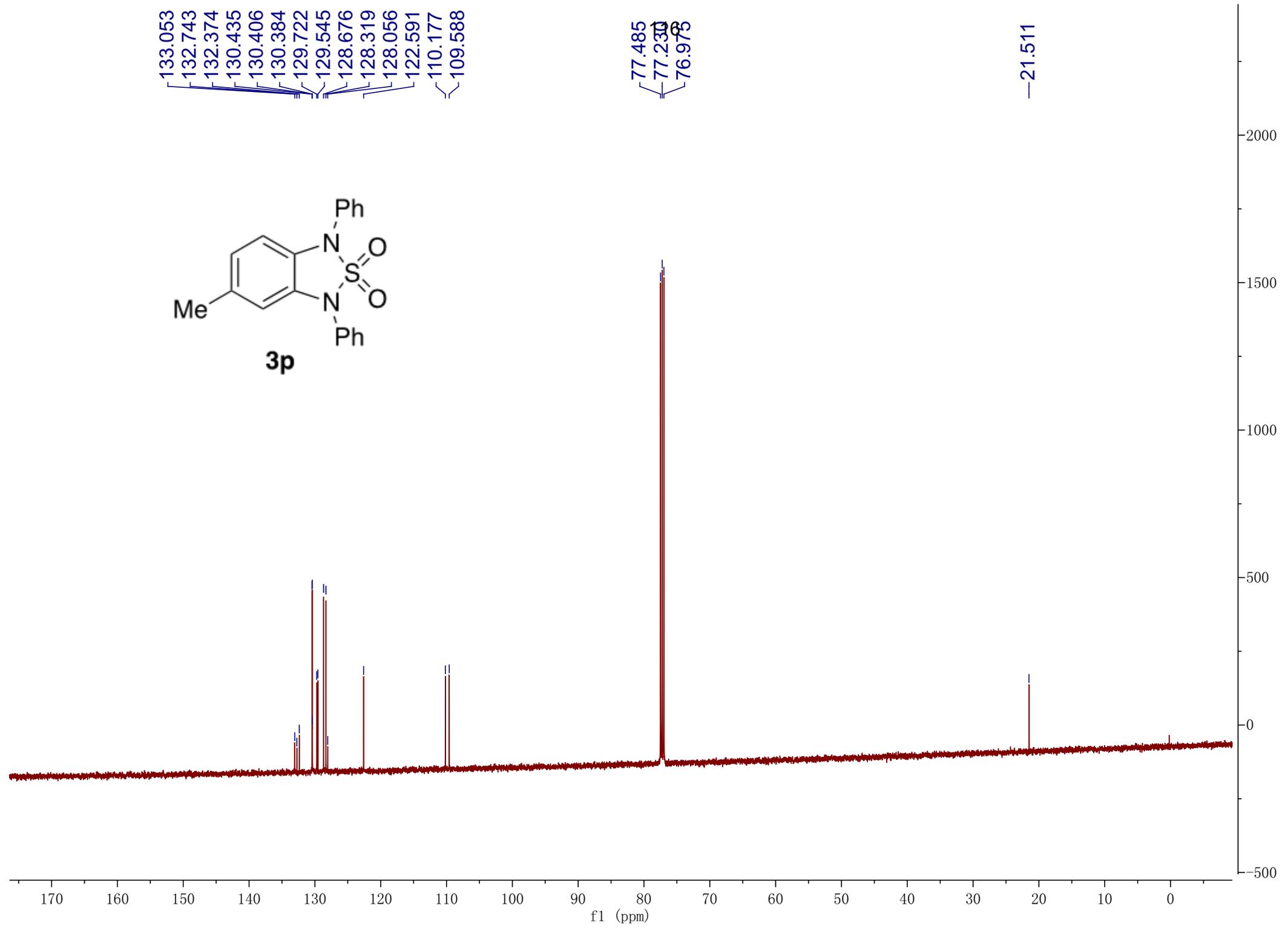




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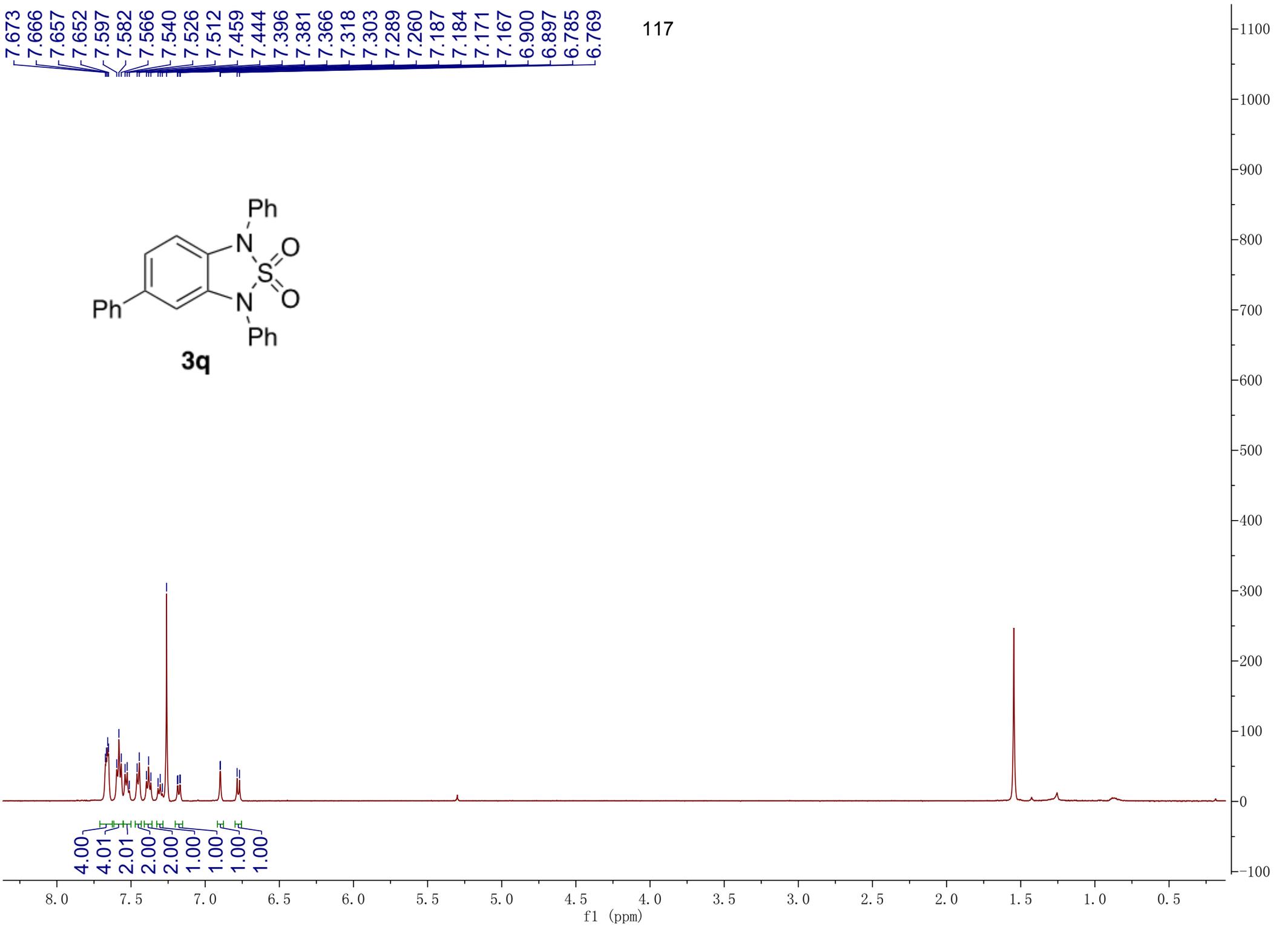
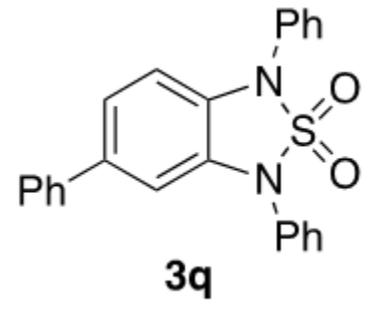
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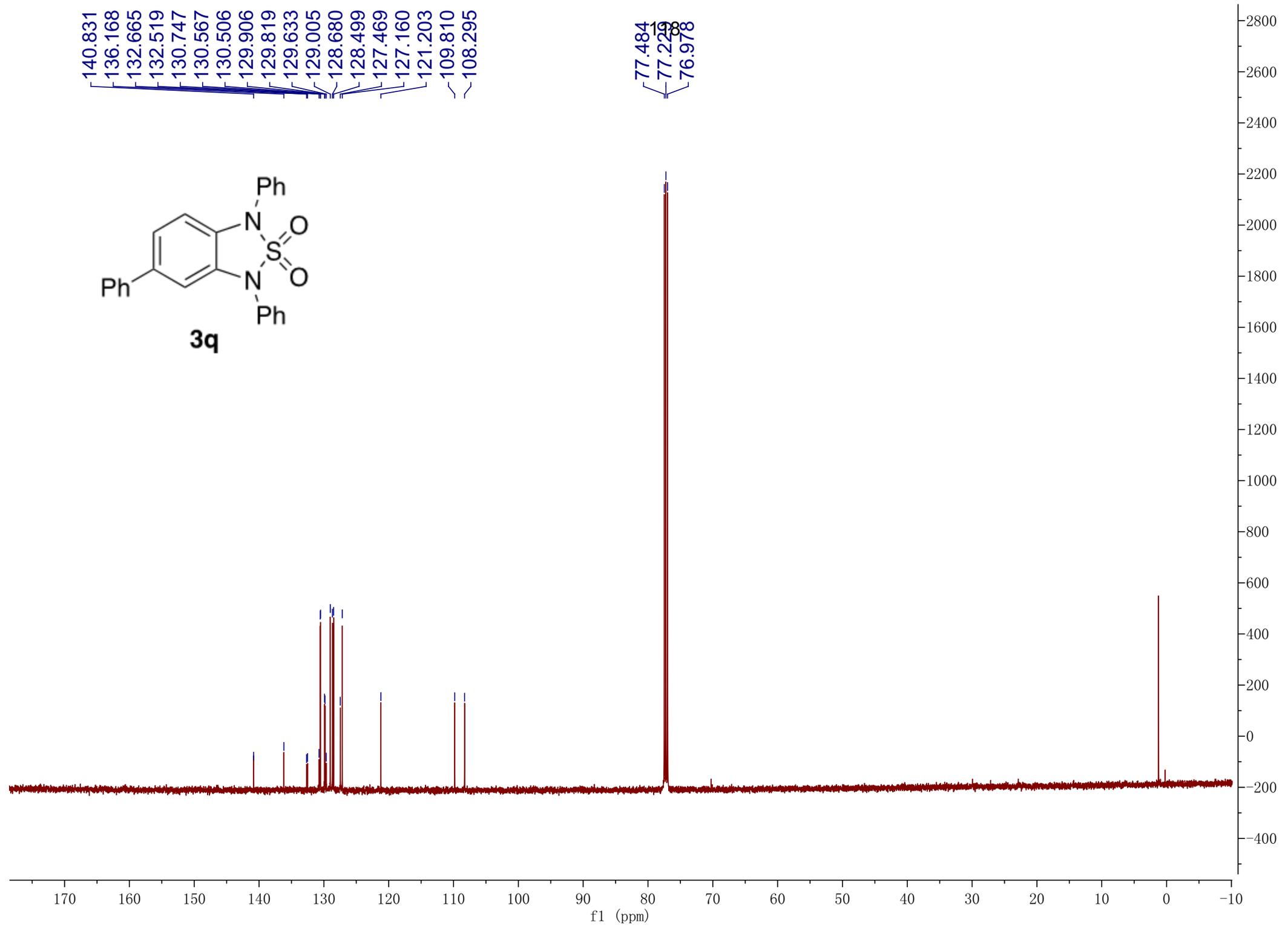
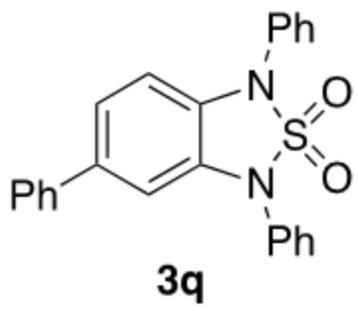
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6.769

117



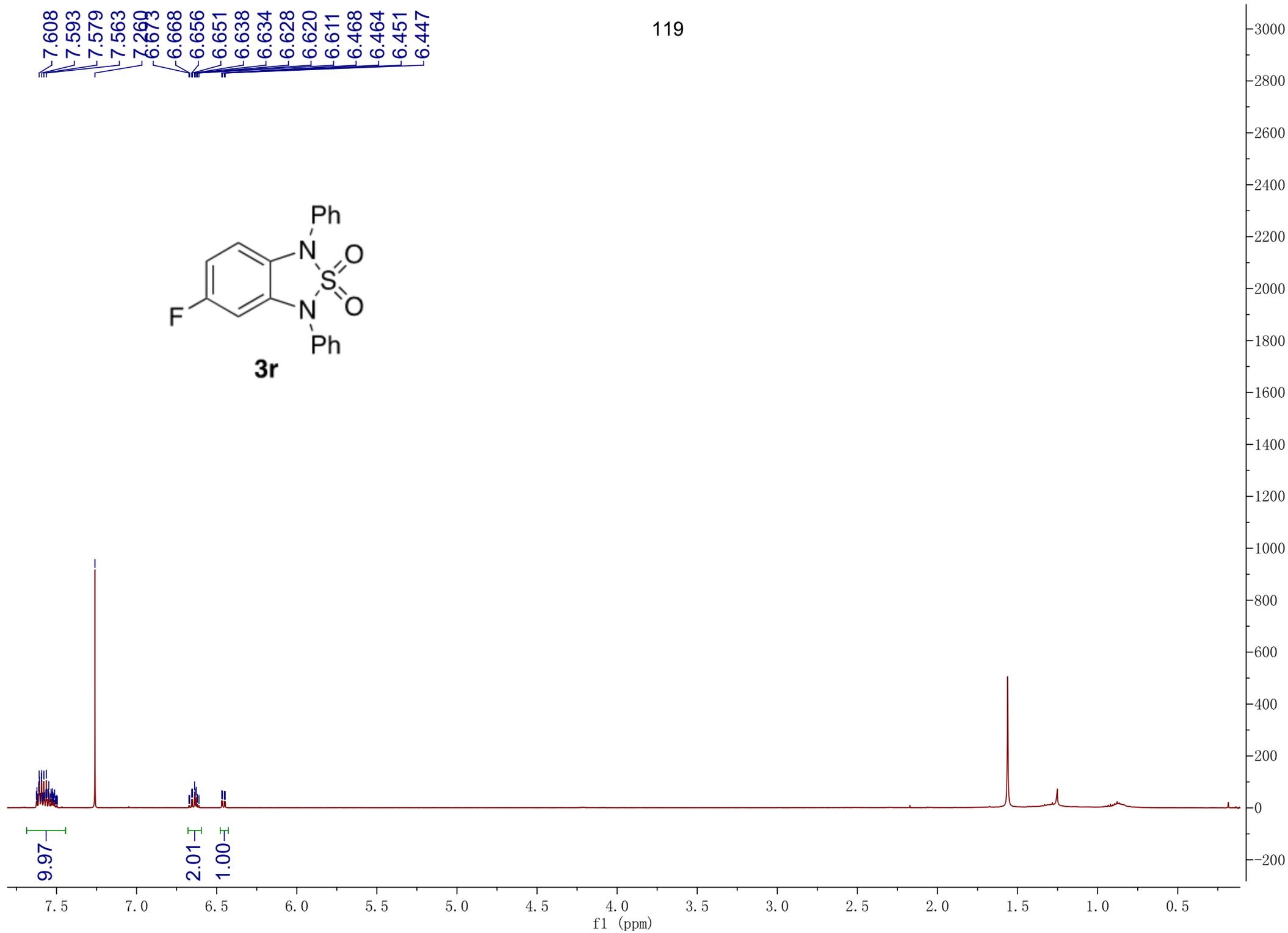
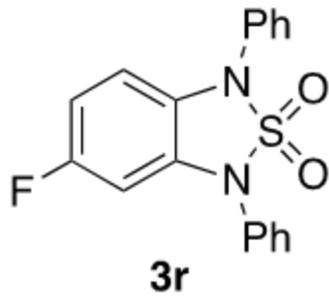
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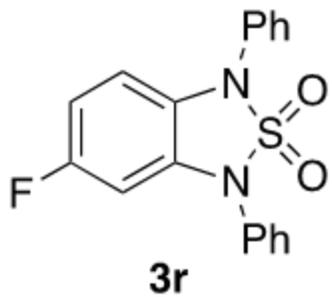
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77.229  
76.978



119

7.608  
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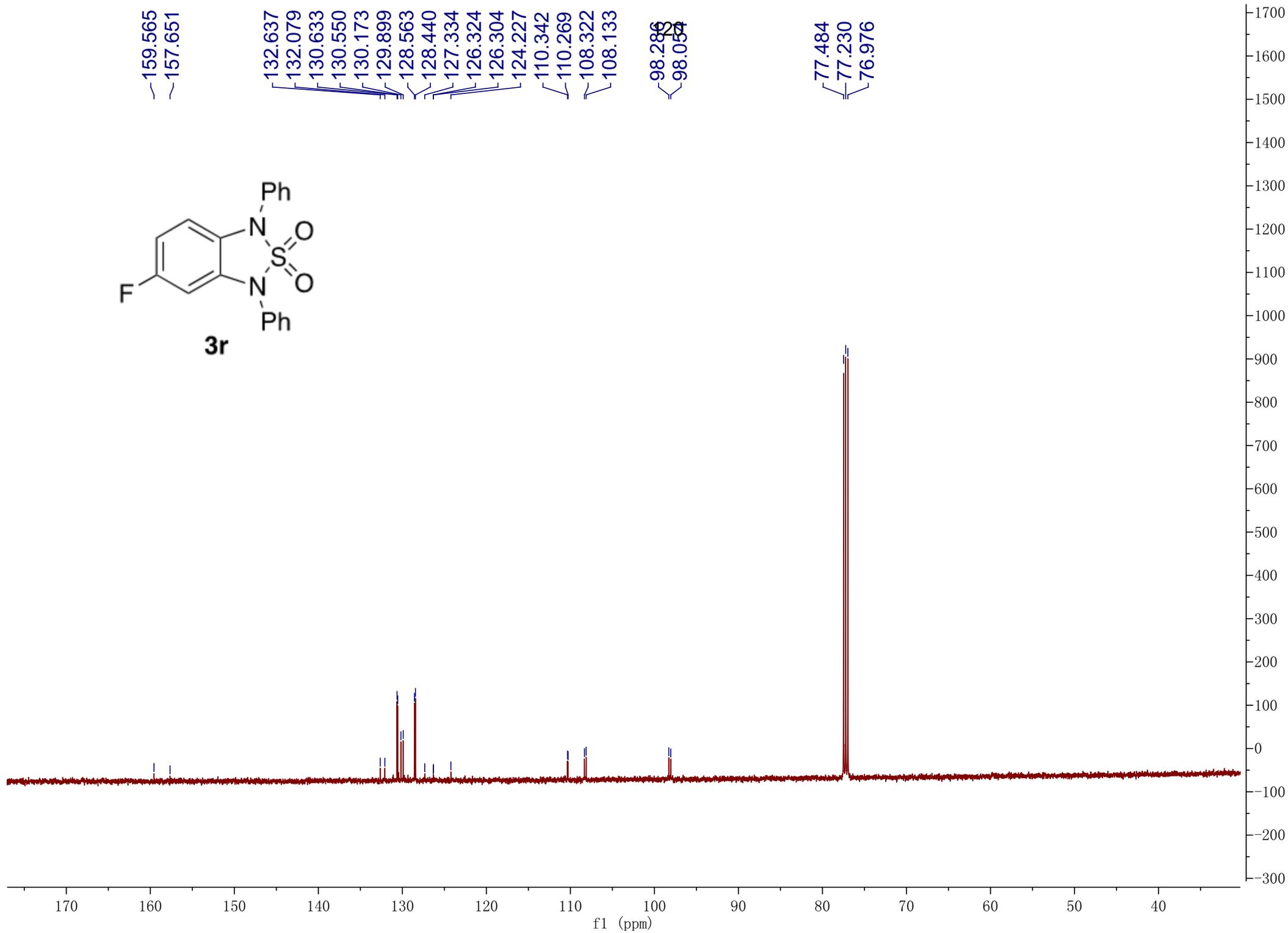


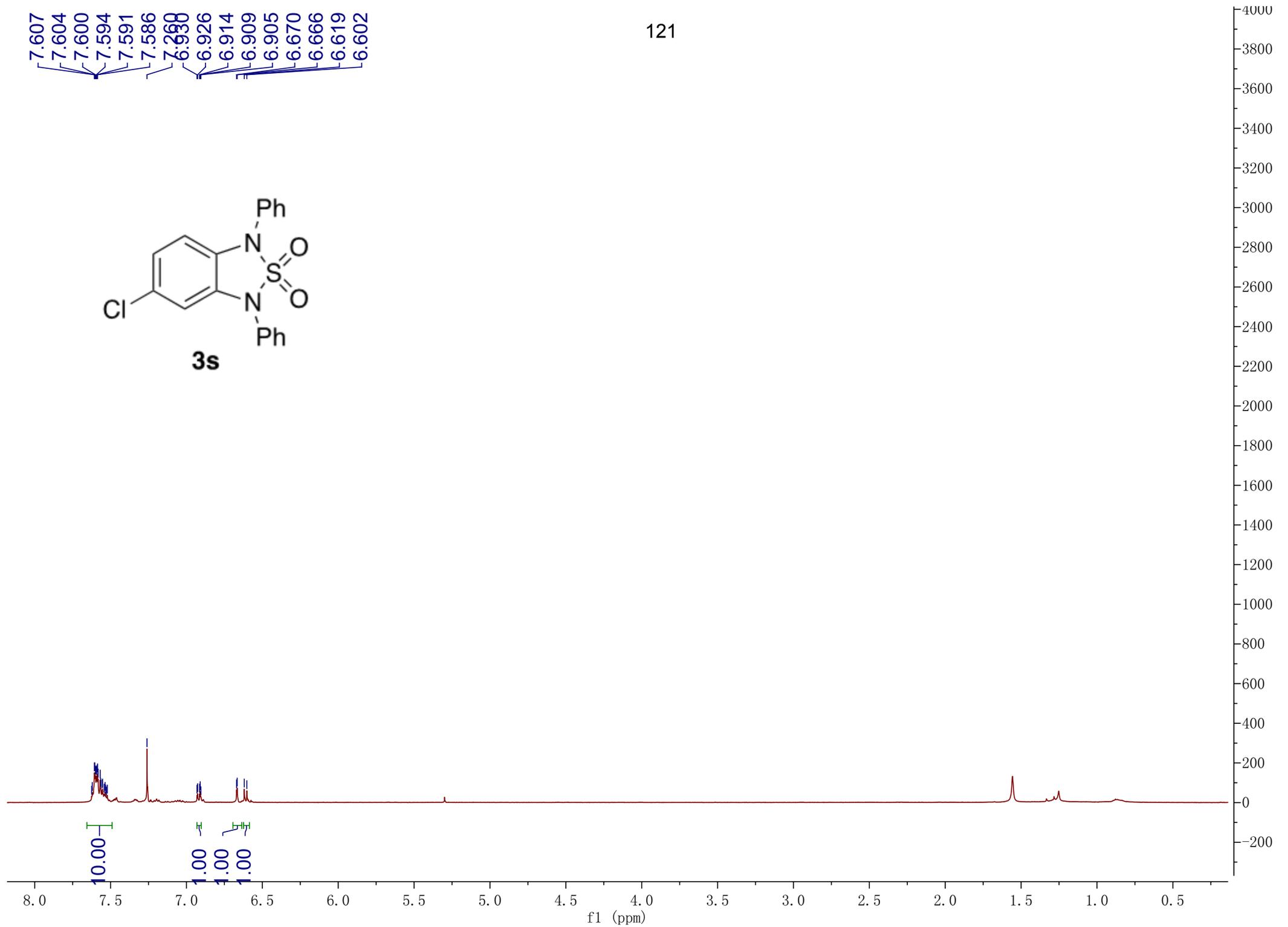
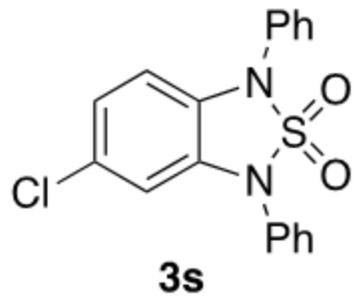
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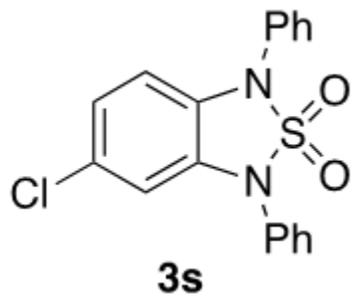
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77.484  
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