

*Supporting Information for*

**KF-Catalyzed direct thiomethylation of carboxylic acids with DMSO  
to access methyl thioesters**

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### 1. General information

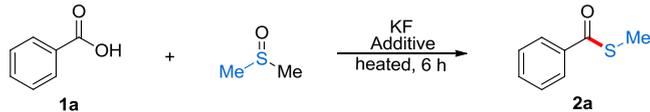
Reagents, catalysts and solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. Column Chromatography was performed with silica gel (200-300 mesh). Melting points were determined using a X-4 melting point apparatus with microscope. The IR spectra were recorded with Mattson FTIR spectrometer 5000. Absorption maxima were measured in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz) and  $^{13}\text{C}$  NMR (150 MHz) spectra were achieved in  $\text{CDCl}_3$  on a Bruker AVANCE 600 MHz spectrometer. High-resolution mass spectra were measured on a ThermoFish QE Focus facility.

### 2. General procedure for preparation of methyl thioesters (2a-2y)

To a solution of DMSO (2 mL) was added carboxylic acids **1** (0.3 mmol), KF (20 mol%, 0.06 mmol) and 4 Å MS in 5 mL sealed tube. The reaction mixture was stirred for 6 h at 180 °C. The solution was quenched with water and the organic layer was dried over  $\text{Na}_2\text{SO}_4$  and evaporated. The resulting crude compound was purified by silica gel column chromatography using hexanes/ethyl acetate mixtures to afford corresponding products.

### 3. Optimization of the reaction conditions

**Table S1** Evaluation of KF amount, additive and reaction temperature<sup>a</sup>

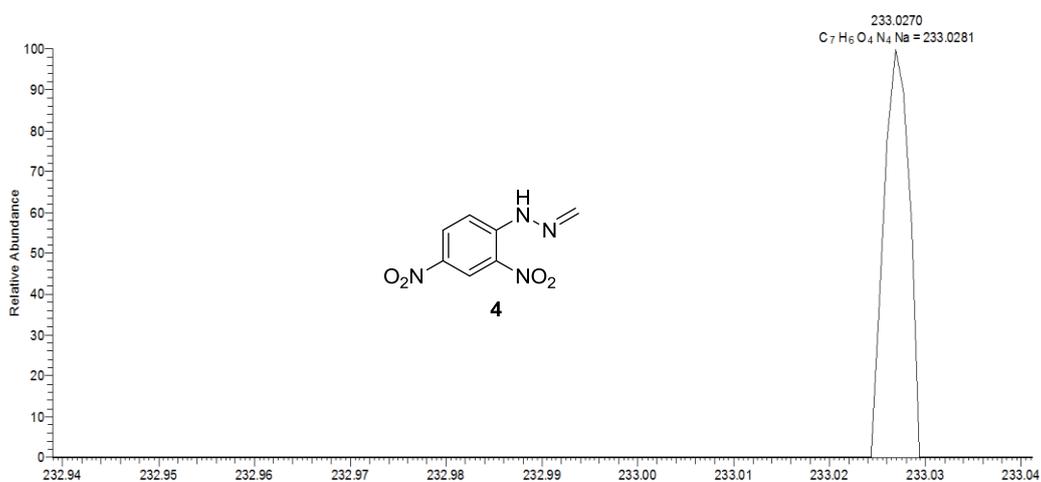
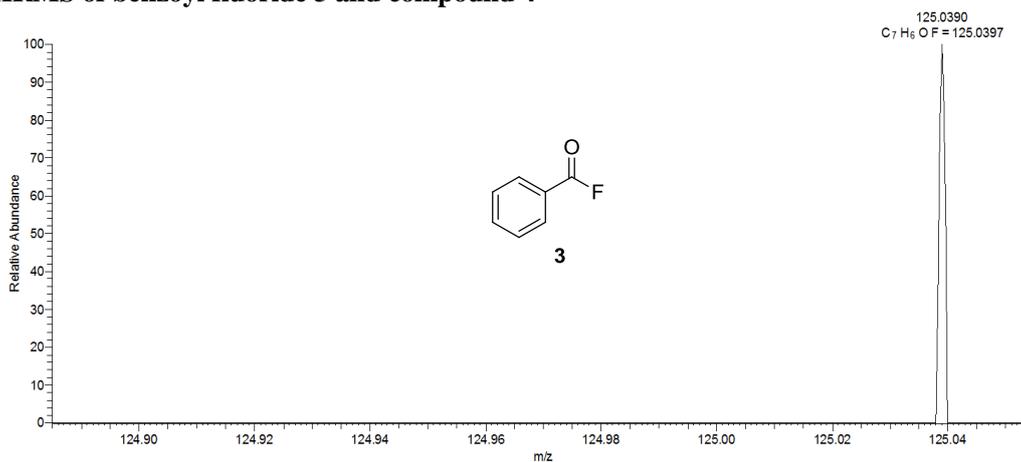


The reaction scheme shows benzoic acid (1a) reacting with dimethyl sulfide (Me-S-Me) in the presence of KF and an additive, heated for 6 hours, to produce methyl benzoate (2a).

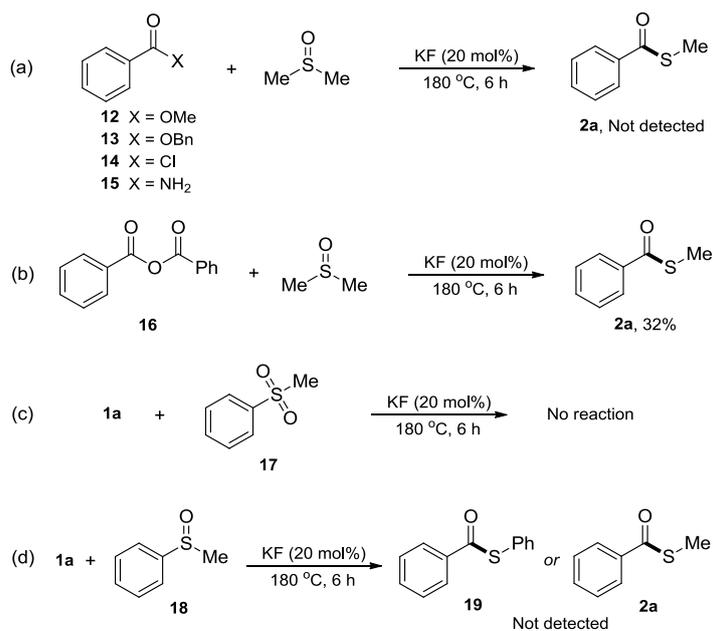
Entry	KF (mol%)	Additive	$T$ (°C)	Yield <sup>b</sup> (%)
1	10	/	180	70
2	20	/	180	75
3	30	/	180	72
4	40	/	180	76
5	20	4 Å MS	180	87
6	20	$\text{Na}_2\text{SO}_4$	180	68
7	20	$\text{MgSO}_4$	180	79
8	20	4 Å MS	170	67
9	20	4 Å MS	190	88
10	20	4 Å MS	reflux	11

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), DMSO (2 mL). <sup>b</sup> Isolated yield.

#### 4. HRMS of benzoyl fluoride 3 and compound 4



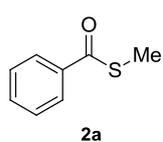
#### 5. The scope and limitation of the reaction



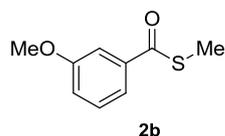
Reaction conditions: **1a/11-17** (0.3 mmol), DMSO (2 mL), DMF (2 mL), 4 Å MS.

**Scheme S1** Scope and limitation of the reaction.

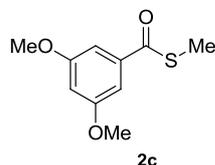
## 6. Analytical data of the products



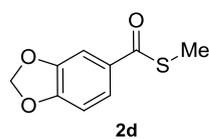
**S-methyl benzothioate (2a).** Colorless oil; Yied: 87%; IR (KBr plate): 2971, 1665, 1601, 1426, 1206, 913, 741, 691.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.98 (m, 2H), 7.61 – 7.58 (m, 1H), 7.50 – 7.46 (m, 2H), 2.51 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  192.5, 137.1, 133.3, 128.6, 127.1, 11.7. HRMS Exact mass calcd. for  $\text{C}_8\text{H}_9\text{OS}$   $[\text{M}+\text{H}]^+$ : 153.0363; found: 153.0369.



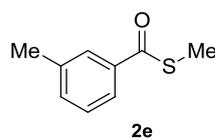
**S-methyl 3-methoxybenzothioate (2b).** Colorless oil; Yied: 80%; IR (KBr plate): 2927, 2851, 1665, 1599, 1511, 1485, 1261, 797, 698.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (dt,  $J = 7.7, 1.2$  Hz, 1H), 7.49 (dd,  $J = 2.7, 1.6$  Hz, 1H), 7.37 (t,  $J = 8.0$  Hz, 1H), 7.13 (ddd,  $J = 8.2, 2.6, 0.9$  Hz, 1H), 3.88 (s, 3H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  192.4, 159.7, 138.4, 129.6, 119.7, 119.7, 111.4, 55.5, 11.8. HRMS Exact mass calcd. for  $\text{C}_9\text{H}_{11}\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 183.0472, found, 183.0474.



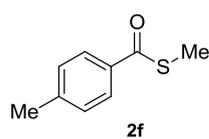
**S-methyl 3,5-dimethoxybenzothioate (2c).** White solid; Yied: 70%; MP: 55.6-59.0 $^\circ\text{C}$ ; IR (KBr plate): 2926, 2840, 1662, 1594, 1459, 1423, 1202, 918, 852, 790, 697.  $^1\text{H}$ NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 (d,  $J = 2.3$  Hz, 2H), 6.67 (t,  $J = 2.3$  Hz, 1H), 3.86 (s, 6H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  192.4, 160.8, 139.0, 105.6, 104.9, 55.6, 11.9. HRMS Exact mass calcd. for  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 235.0393, found, 235.0399.



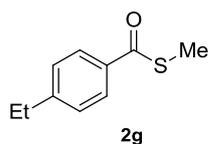
**S-methyl benzo[d][1,3]dioxole-5-carbothioate (2d).** White solid; Yied: 46%; MP: 61.0-66.1 $^\circ\text{C}$ ; IR (KBr plate): 2926, 2852, 1655, 1610, 1507, 1491, 1267, 1038, 862, 674.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (dd,  $J = 8.2, 1.8$  Hz, 1H), 7.44 (d,  $J = 1.8$  Hz, 1H), 6.87 (d,  $J = 8.2$  Hz, 1H), 6.07 (s, 2H), 2.47 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.8, 151.9, 148.0, 131.6, 123.2, 108.03, 107.2, 101.9, 11.8. HRMS Exact mass calcd. for  $\text{C}_9\text{H}_8\text{O}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 219.0095, found, 219.0086.



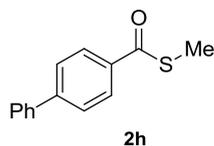
**S-methyl 3-methylbenzothioate (2e).** Yellow oil; Yied: 92%; IR (KBr plate): 2954, 2926, 1666, 1604, 1512, 1487, 1250, 942, 797, 698.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 – 7.78 (m, 2H), 7.40 (d,  $J = 7.6$  Hz, 1H), 7.35 (t,  $J = 7.8$  Hz, 1H), 2.49 (s, 3H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  192.6, 138.5, 137.1, 134.0, 128.5, 127.6, 124.36, 21.3, 11.7. HRMS Exact mass calcd. for  $\text{C}_9\text{H}_{11}\text{OS}$   $[\text{M}+\text{H}]^+$ : 167.0519, found, 167.0525.



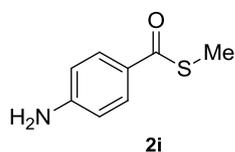
**S-methyl 4-methylbenzothioate (2f).** Colorless oil; Yied: 88%; IR (KBr plate): 3032, 2927, 1663, 1607, 1573, 1510, 1214, 912, 822, 645.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.3$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 2.49 (s, 3H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  192.1, 144.1, 134.6, 129.3, 127.2, 21.7, 11.6. HRMS Exact mass calcd. for  $\text{C}_9\text{H}_{11}\text{OS}$   $[\text{M}+\text{H}]^+$ : 167.0521, found, 167.0525.



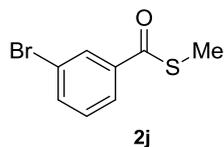
**S-methyl 4-ethylbenzothioate (2g).** Colorless oil; Yied: 79%; IR (KBr plate): 3031, 2967, 2930, 1663, 1606, 1511, 1456, 1217, 915, 842, 776, 651.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 – 7.90 (m, 2H), 7.30 – 7.28 (m, 2H), 2.72 (q,  $J = 7.6$  Hz, 2H), 2.49 (s, 3H), 1.28 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  192.1, 150.3, 134.8, 128.1, 127.3, 29.0, 15.2, 11.7. HRMS Exact mass calcd. for  $\text{C}_{10}\text{H}_{13}\text{OS}$   $[\text{M}+\text{H}]^+$ : 181.0678, found, 181.0682.



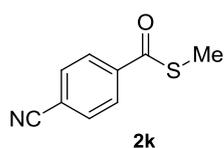
**S-methyl [1,1'-biphenyl]-4-carbothioate (2h).** White solid; Yied: 72%; MP: 92.7-99.0°C; IR (KBr plate): 2923, 1650, 1599, 1514, 1482, 1221, 915, 846, 773, 642.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 – 8.05 (m, 2H), 7.71 – 7.68 (m, 2H), 7.66 – 7.63 (m, 2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 1H), 2.53 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  192.1, 146.2, 140.0, 135.9, 129.1, 128.4, 127.8, 127.4, 11.9. HRMS Exact mass calcd. for  $\text{C}_{14}\text{H}_{12}\text{OSNa}$   $[\text{M}+\text{Na}]^+$ : 251.0495, found, 251.0501.



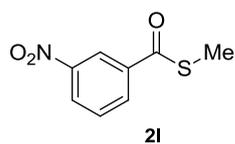
**S-methyl 4-aminobenzothioate (2i).** Yellow solid; Yied: 66%; MP: 86.2-91.3°C; IR (KBr plate): 3330, 2926, 1633, 1591, 1436, 1304, 1169, 911, 832, 649.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.82 (m, 2H), 6.67 – 6.64 (m, 2H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.6, 151.3, 129.5, 127.4, 113.8, 11.5. HRMS Exact mass calcd. for  $\text{C}_8\text{H}_9\text{ONSNa}$   $[\text{M}+\text{Na}]^+$ : 190.0294, found, 190.0297.



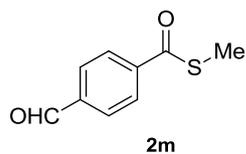
**S-methyl 3-bromobenzothioate (2j).** Colorless oil; Yied: 42%; IR (KBr plate): 2926, 1664, 1566, 1514, 1468, 1199, 928, 711, 694.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (t,  $J = 1.9$  Hz, 1H), 7.91 (d,  $J = 7.8$  Hz, 1H), 7.72 (d,  $J = 7.9$  Hz, 1H), 7.36 (t,  $J = 7.9$  Hz, 1H), 2.51 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.3, 138.9, 136.2, 130.3, 130.2, 125.9, 123.0, 12.0. HRMS Exact mass calcd. for  $\text{C}_8\text{H}_7\text{OSBrNa}$   $[\text{M}+\text{Na}]^+$ : 252.9299, found, 252.9293.



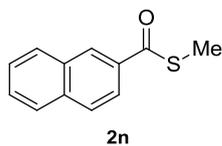
**S-methyl 4-cyanobenzothioate (2k).** Yellow solid; Yied: 75%; MP: 71.8-74.0°C; IR (KBr plate): 2927, 2226, 1659, 1551, 1513, 1460, 1209, 919, 855, 641.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 – 8.06 (m, 2H), 7.80 – 7.77 (m, 2H), 2.55 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.1, 140.1, 132.5, 127.6, 117.9, 116.6, 12.0. HRMS Exact mass calcd. for  $\text{C}_9\text{H}_8\text{ONS}$   $[\text{M}+\text{H}]^+$ : 178.0328, found, 178.0321.



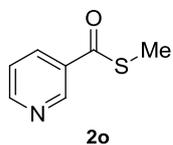
**S-methyl 3-nitrobenzothioate (2l).** Colorless oil; Yied: 52%; IR (KBr plate): 2927, 1651, 1611, 1574, 1528, 1347.22, 1204, 991, 720, 688.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (t,  $J = 2.0$  Hz, 1H), 8.45 – 8.41 (m, 1H), 8.28 (dt,  $J = 7.7, 1.4$  Hz, 1H), 7.67 (t,  $J = 8.0$  Hz, 1H), 2.55 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4, 138.3, 132.6, 129.9, 127.5, 122.2, 12.0. HRMS Exact mass calcd. for  $\text{C}_8\text{H}_8\text{O}_3\text{NS}$   $[\text{M}+\text{H}]^+$ : 198.0210, found, 198.0219.



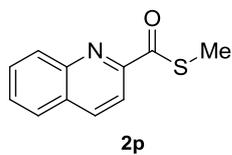
**S-methyl 4-formylbenzothioate (2m)**; White solid; Yied: 65%; MP: 51.0-57.1°C; IR (KBr plate): 2926, 1708, 1665, 1606, 1547, 1510, 1204, 918, 827. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 10.12 (s, 1H), 8.15 – 8.12 (m, 2H), 8.01 – 7.98 (m, 2H), 2.55 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 192.0, 191.6, 141.5, 139.4, 130.0, 127.9, 12.1. HRMS Exact mass calcd. for C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 181.0314, found, 181.0318.



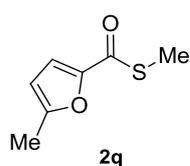
**S-methyl naphthalene-2-carbothioate (2n)**. Colorless oil; Yied: 71%; IR (KBr plate): 2921, 1660, 1464, 1428, 1169, 803, 750, 691. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.56 (s, 1H), 8.04 – 7.98 (m, 2H), 7.91 (t, *J* = 8.8 Hz, 2H), 7.62 (dd, *J* = 8.1, 6.7 Hz, 1H), 7.58 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 2.56 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 192.4, 135.7, 134.4, 132.5, 129.6, 128.5, 128.5, 128.4, 127.8, 126.9, 123.1, 11.9. HRMS Exact mass calcd. for C<sub>12</sub>H<sub>11</sub>OS [M+H]<sup>+</sup>: 203.0525, found, 203.0523.



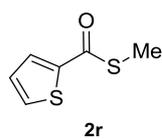
**S-methyl pyridine-3-carbothioate (2o)**. Yellow oil; Yied: 58%; IR (KBr plate): 2924, 1666, 1584, 1547, 1419, 1221, 916, 814, 705. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.20 (d, *J* = 2.0 Hz, 1H), 8.81 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.24 (ddd, *J* = 8.0, 2.3, 1.7 Hz, 1H), 7.44 (ddd, *J* = 8.0, 4.8, 0.9 Hz, 1H), 2.54 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 191.0, 153.7, 148.4, 134.5, 132.6, 123.6, 11.7. HRMS Exact mass calcd. for C<sub>7</sub>H<sub>8</sub>ONS [M+H]<sup>+</sup>: 154.0316, found, 154.0321.



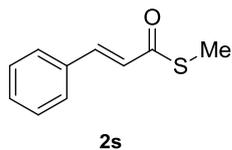
**S-methyl quinoline-2-carbothioate (2p)**. Colorless oil; Yied: 42%; IR (KBr plate): 2954, 2924, 1724, 1666, 1591, 1505, 1489, 1204, 918, 837, 760. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.33 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 2.52 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 194.7, 151.6, 147.1, 137.5, 130.5, 130.3, 130.2, 128.7, 127.7, 117.0, 11.7. HRMS Exact mass calcd. for C<sub>11</sub>H<sub>9</sub>ONSNa [M+Na]<sup>+</sup>: 226.0290, found, 226.0297.



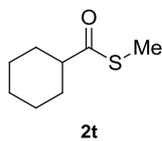
**S-methyl 5-methylfuran-2-carbothioate (2q)**. Yellow oil; Yied: 49%; IR (KBr plate): 2926, 2855, 1656, 1517, 1258, 859, 797. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.13 (d, *J* = 3.5 Hz, 1H), 6.19 – 6.16 (m, 1H), 2.46 (s, 3H), 2.41 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 180.5, 157.3, 149.6, 117.1, 108.9, 14.1, 10.7. HRMS Exact mass calcd. for C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>SNa [M+Na]<sup>+</sup>: 179.0136, found, 179.0137.



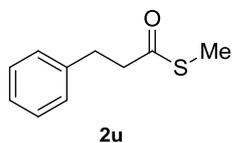
**S-methyl thiophene-2-carbothioate (2r)**. Colorless oil; Yied: 60%; IR (KBr plate): 2956, 2919, 1728, 1657, 1208, 822 720. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.82 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.63 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.14 (dd, *J* = 4.9, 3.9 Hz, 1H), 2.51 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 184.5, 142.1, 132.4, 130.9, 127.9, 11.8. HRMS Exact mass calcd. for C<sub>6</sub>H<sub>6</sub>OS<sub>2</sub>Na [M+Na]<sup>+</sup>: 180.9763, found, 180.9752.



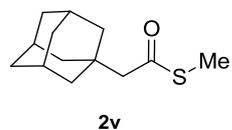
**S-methyl (*E*)-3-phenylprop-2-enethioate (2s).** Colorless oil; Yied: 68%; IR (KBr plate): 3031, 2924, 1659, 1616, 1574, 1495, 1448, 1043, 974, 754, 692.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 15.8$  Hz, 1H), 7.58 (dd,  $J = 6.7, 2.8$  Hz, 2H), 7.44 – 7.40 (m, 3H), 6.77 (d,  $J = 15.8$  Hz, 1H), 2.46 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.3, 140.3, 134.1, 130.6, 129.0, 128.4, 124.8, 11.7. HRMS Exact mass calcd. for  $\text{C}_{10}\text{H}_{11}\text{OS}$   $[\text{M}+\text{H}]^+$ : 179.0519, found, 179.0525.



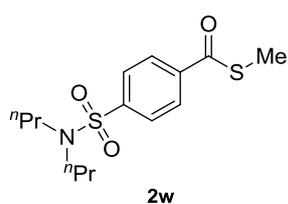
**S-methyl cyclohexanecarbothioate (2t).** Colorless oil; Yied: 61%; IR (KBr plate): 2930, 2855, 1688, 1449, 1051, 975, 773.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  2.51 (tt,  $J = 11.6, 3.5$  Hz, 1H), 2.28 (s, 3H), 1.95 – 1.90 (m, 2H), 1.80 (dt,  $J = 12.2, 3.0$  Hz, 2H), 1.70 – 1.65 (m, 1H), 1.48 (qd,  $J = 12.3, 3.2$  Hz, 2H), 1.34 – 1.18 (m, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  203.6, 52.6, 29.6, 25.6, 25.5, 11.3. HRMS Exact mass calcd. for  $\text{C}_8\text{H}_{14}\text{OSNa}$   $[\text{M}+\text{Na}]^+$ : 181.0653, found, 181.0658.



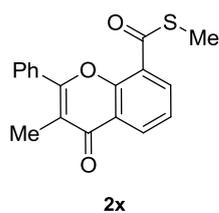
**S-methyl 3-phenylpropanethioate (2u).** Colorless oil; Yied: 40%; IR (KBr plate): 3029, 2923, 1690, 1604, 1497, 1452, 1050, 745, 701.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.32 (t,  $J = 7.5$  Hz, 2H), 7.25 – 7.21 (m, 3H), 3.03 – 3.00 (m, 2H), 2.93 – 2.89 (m, 2H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  199.1, 140.1, 128.5, 128.3, 126.4, 45.4, 31.5, 11.6. HRMS Exact mass calcd. for  $\text{C}_{10}\text{H}_{13}\text{OSNa}$   $[\text{M}+\text{Na}]^+$ : 203.0491, found, 203.0501.



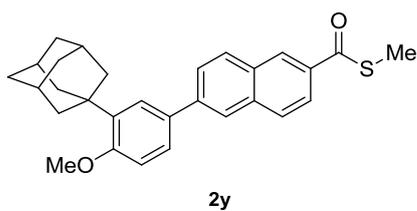
**S-methyl 2-((3*R*,5*R*,7*R*)-adamantan-1-yl)ethanethioate (2v).** Colorless oil; Yied: 58%; IR (KBr plate): 2903, 2848, 2669, 1689, 1448, 1024, 740, 615.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  2.34 (s, 2H), 2.30 (s, 3H), 1.98 (p,  $J = 3.1$  Hz, 3H), 1.71 (dt,  $J = 12.2, 3.0$  Hz, 3H), 1.65 (d,  $J = 3.1$  Hz, 9H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  197.9, 57.8, 42.5, 36.7, 33.7, 28.6, 12.0. HRMS Exact mass calcd. for  $\text{C}_{13}\text{H}_{20}\text{OSNa}$   $[\text{M}+\text{Na}]^+$ : 247.1119, found, 247.1127.



**S-methyl 4-(*N,N*-dipropylsulfamoyl)benzothioate (2w).** Colorless oil; Yied: 53%; IR (KBr plate): 2967, 2927, 1669, 1567, 1461, 1344, 1163, 921, 747, 608.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 – 8.07 (m, 2H), 7.92 – 7.90 (m, 2H), 3.14 – 3.11 (m, 4H), 2.54 (s, 3H), 1.62 – 1.53 (m, 4H), 0.90 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.4, 144.4, 139.7, 127.7, 127.3, 50.0, 22.0, 12.0, 11.2. HRMS Exact mass calcd. for  $\text{C}_{14}\text{H}_{21}\text{O}_3\text{NS}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 338.0846, found, 338.0855.

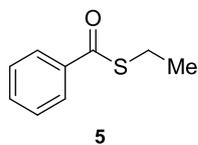


**S-methyl 3-methyl-4-oxo-2-phenyl-4H-chromene-8-carbothioate (2x).** Yellow solid; Yied: 42%; MP: 150.0-156.2°C; IR (KBr plate): 2953, 2921, 1685, 1645, 1619, 1594, 1248, 1051, 860, 754, 695.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47 (dd,  $J = 7.9, 1.7$  Hz, 1H), 8.18 (dd,  $J = 7.5, 1.7$  Hz, 1H), 7.81 – 7.78 (m, 2H), 7.59 – 7.55 (m, 3H), 7.48 (t,  $J = 7.7$  Hz, 1H), 2.51 (s, 3H), 2.25 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  189.7, 178.2, 161.2, 152.8, 133.6, 132.7, 130.5, 130.4, 129.5, 128.5, 127.7, 124.2, 123.2, 118.0, 29.7, 12.6, 11.9. HRMS Exact mass calcd. for  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 333.0546, found, 333.0556.



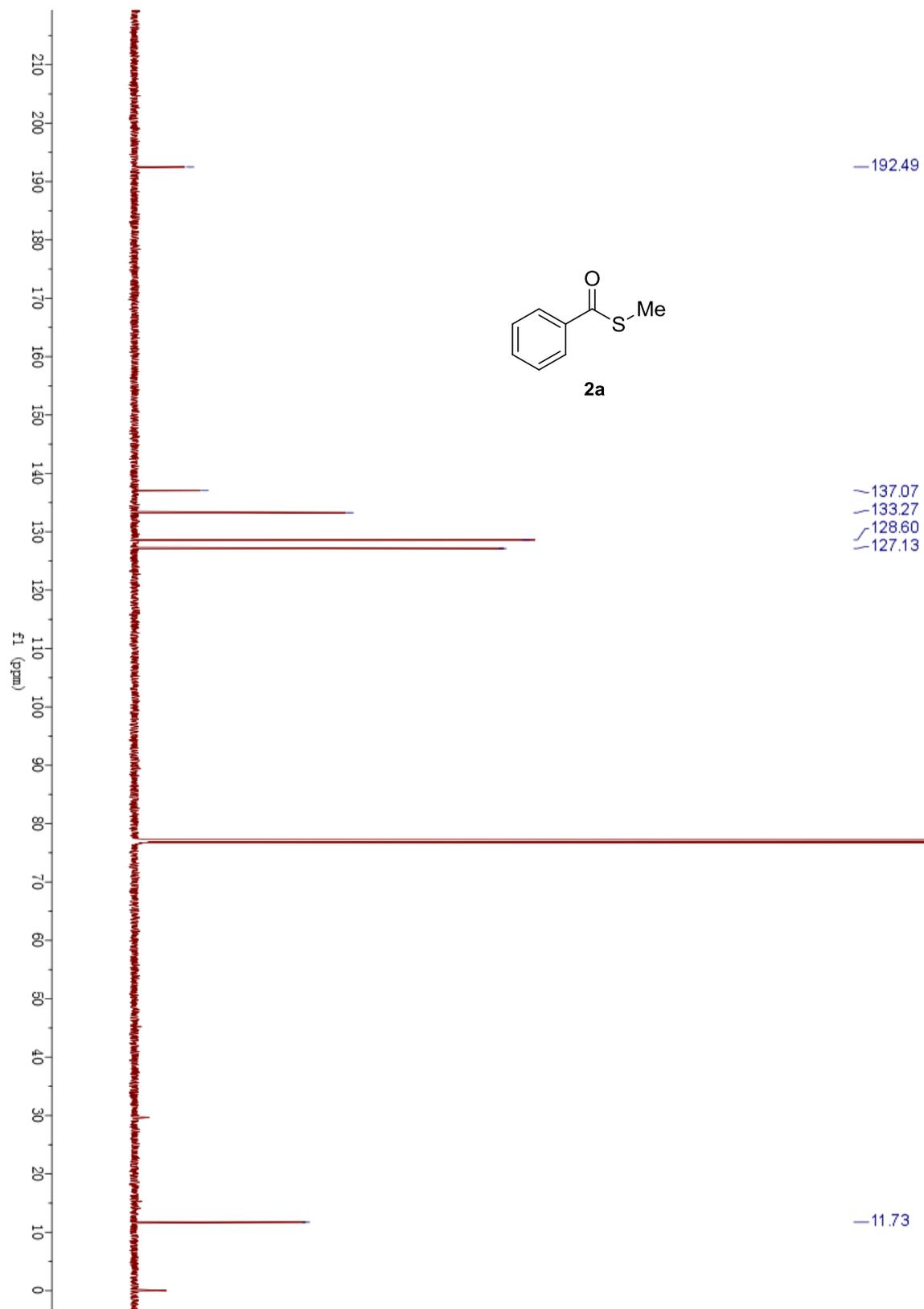
**S-methyl 6-(3-((3R,5R,7R)-adamantan-1-yl)-4-methoxyphenyl)naphthalene-2-carbothioate (2y).** White solid; Yied: 46%; MP: 210-215°C; IR (KBr plate): 2904, 2848, 1650, 1624, 1600, 1468, 1237, 1027, 892, 807, 704. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.56 (d, *J* = 1.7 Hz, 1H), 8.04 (td, *J* = 5.6, 2.6 Hz, 3H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.84 (dd,

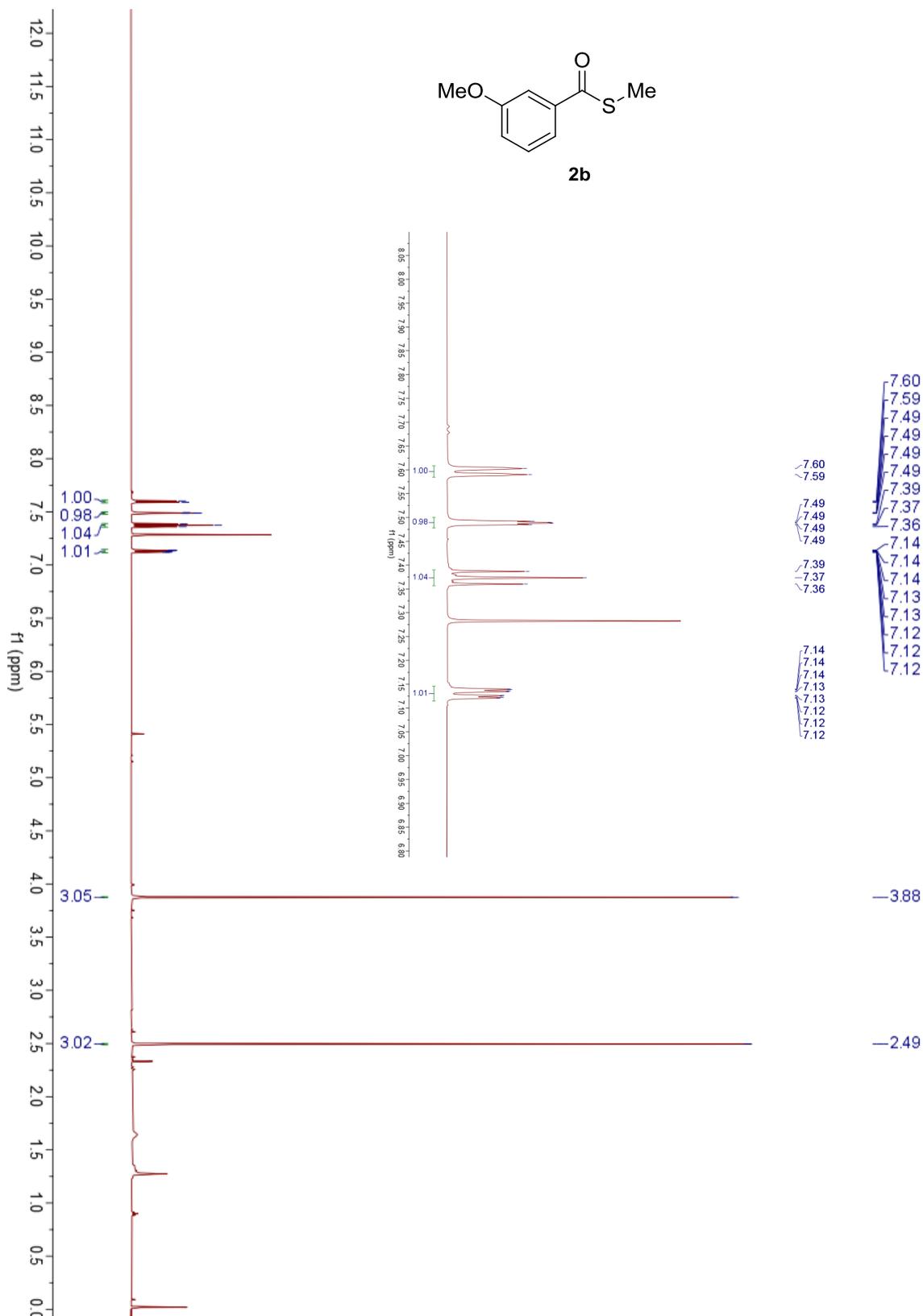
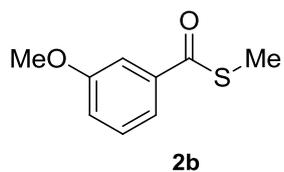
*J* = 8.6, 1.8 Hz, 1H), 7.63 (d, *J* = 2.4 Hz, 1H), 7.57 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 2.57 (s, 3H), 2.22 (d, *J* = 3.0 Hz, 6H), 2.17 – 2.11 (m, 3H), 1.83 (d, *J* = 3.2 Hz, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 192.3, 159.0, 141.6, 139.0, 136.2, 133.9, 132.4, 131.2, 129.9, 128.5, 128.3, 126.7, 126.0, 125.8, 124.7, 123.5, 112.1, 55.2, 40.6, 37.2, 37.1, 29.1, 11.9. HRMS Exact mass calcd. for C<sub>29</sub>H<sub>31</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 443.2030, found, 443.2039.

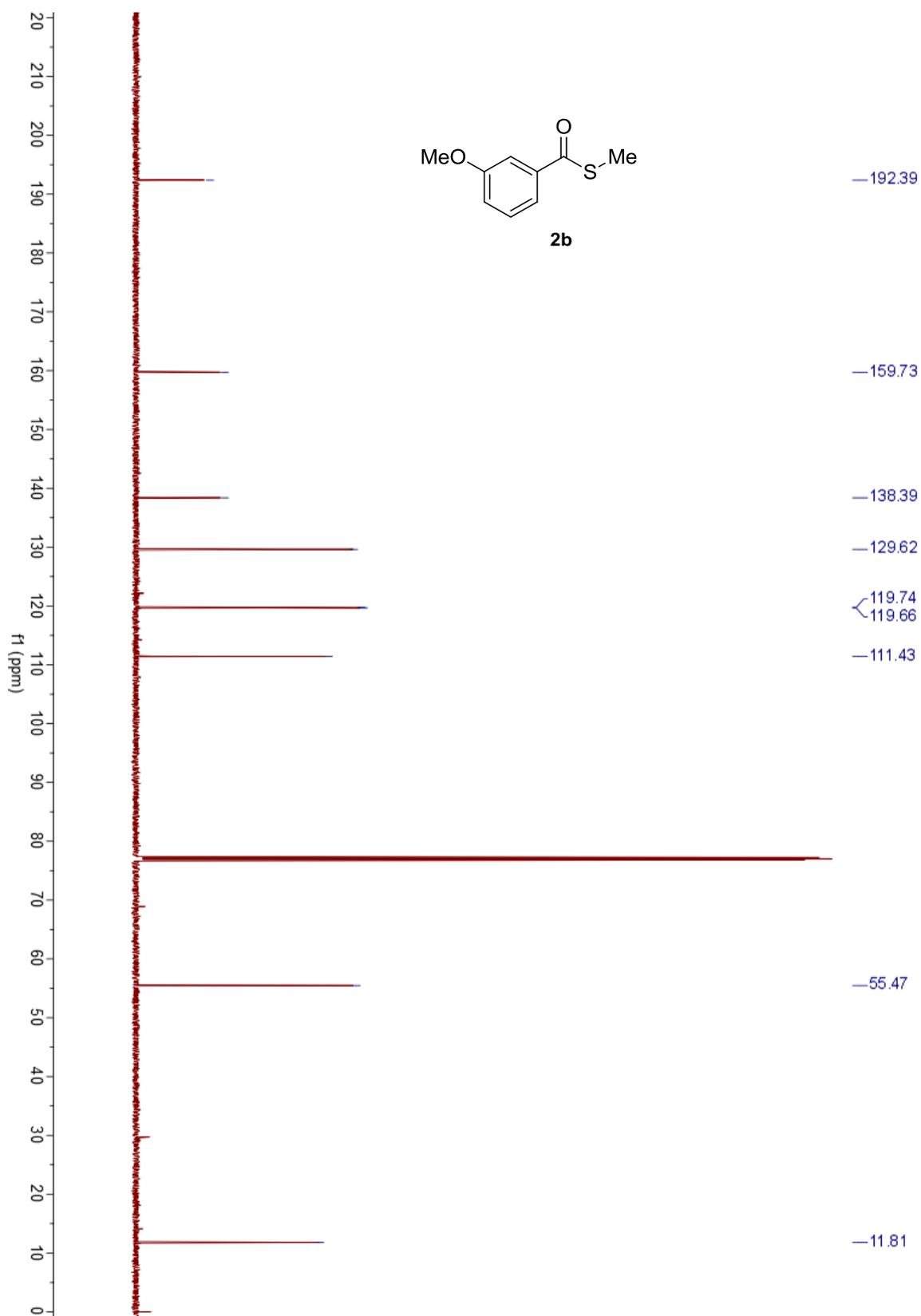


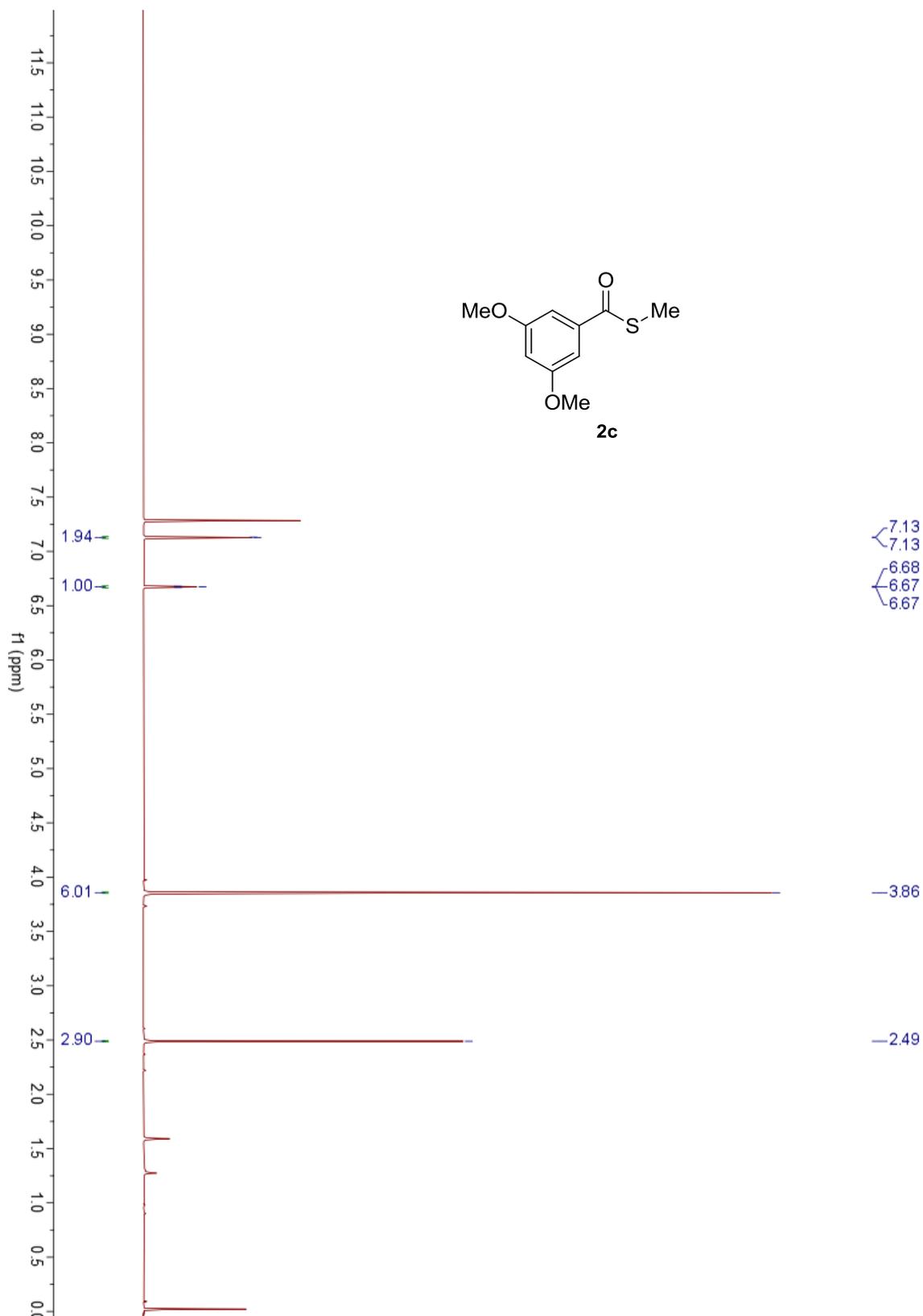
**S-ethyl benzothioate (5).** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.98 – 7.95 (m, 2H), 7.59 – 7.54 (m, 1H), 7.47 – 7.43 (m, 2H), 3.08 (q, *J* = 7.4 Hz, 2H), 1.36 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 192.3, 137.4, 133.4, 128.7, 127.3, 23.6, 14.9.

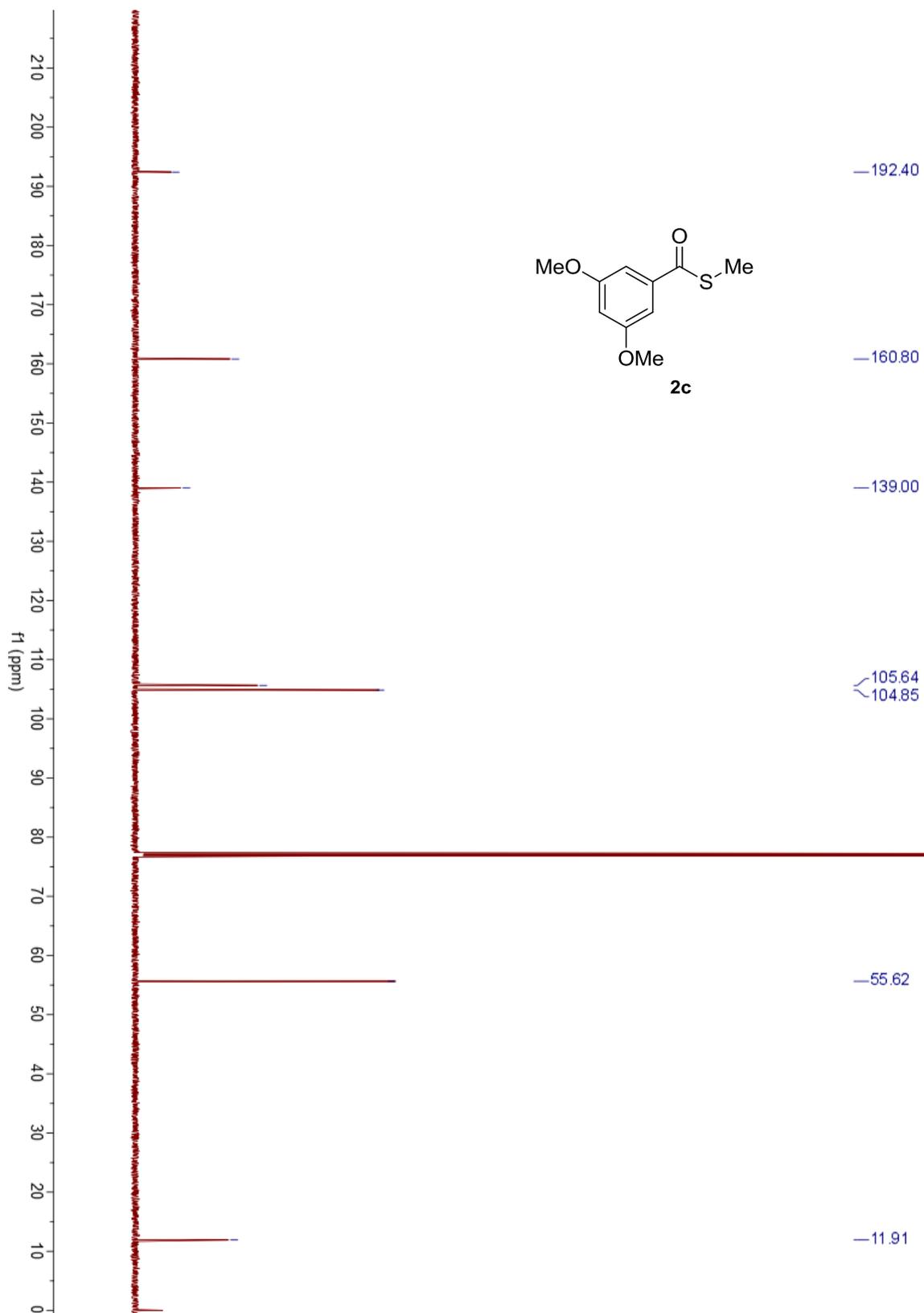


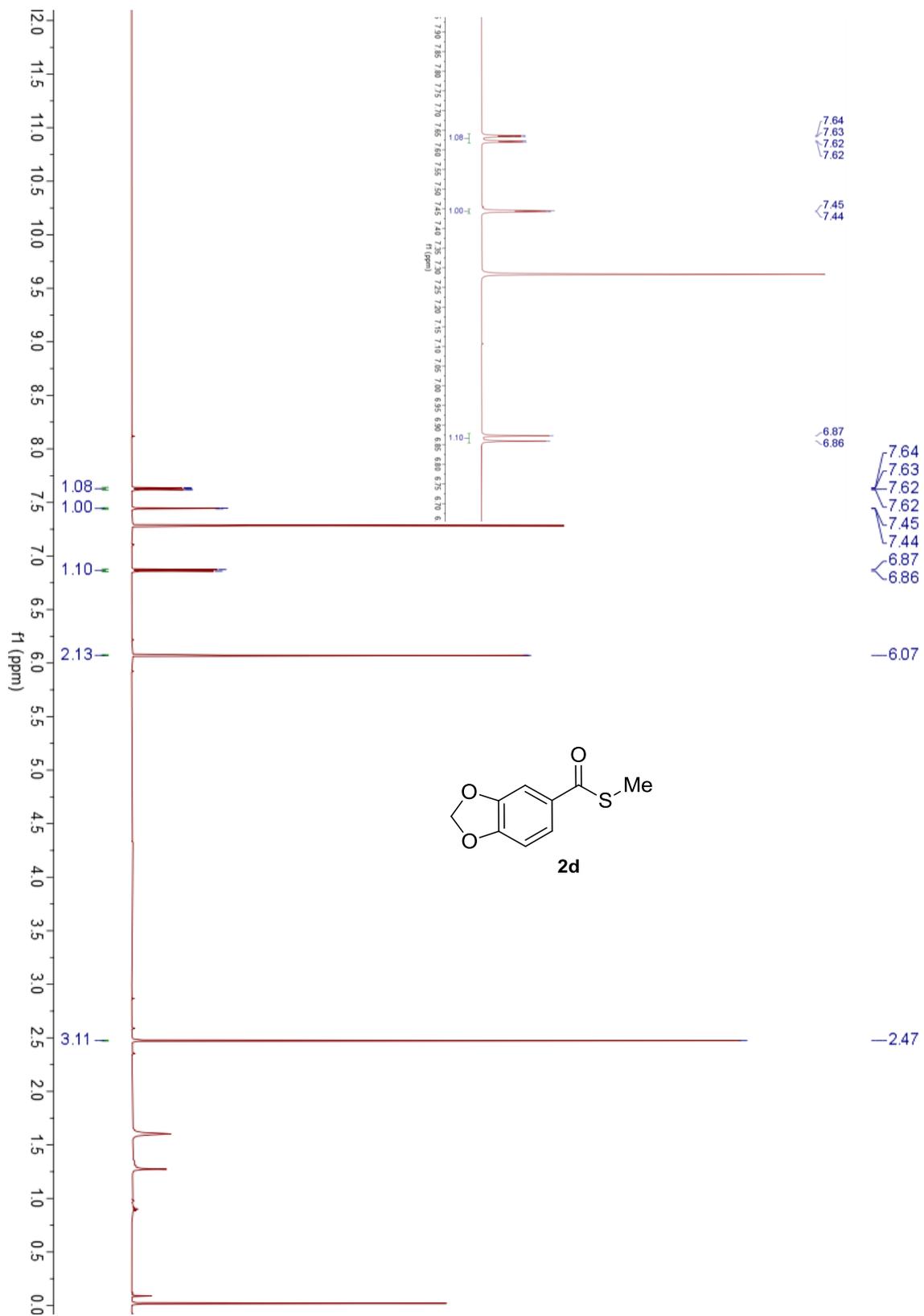


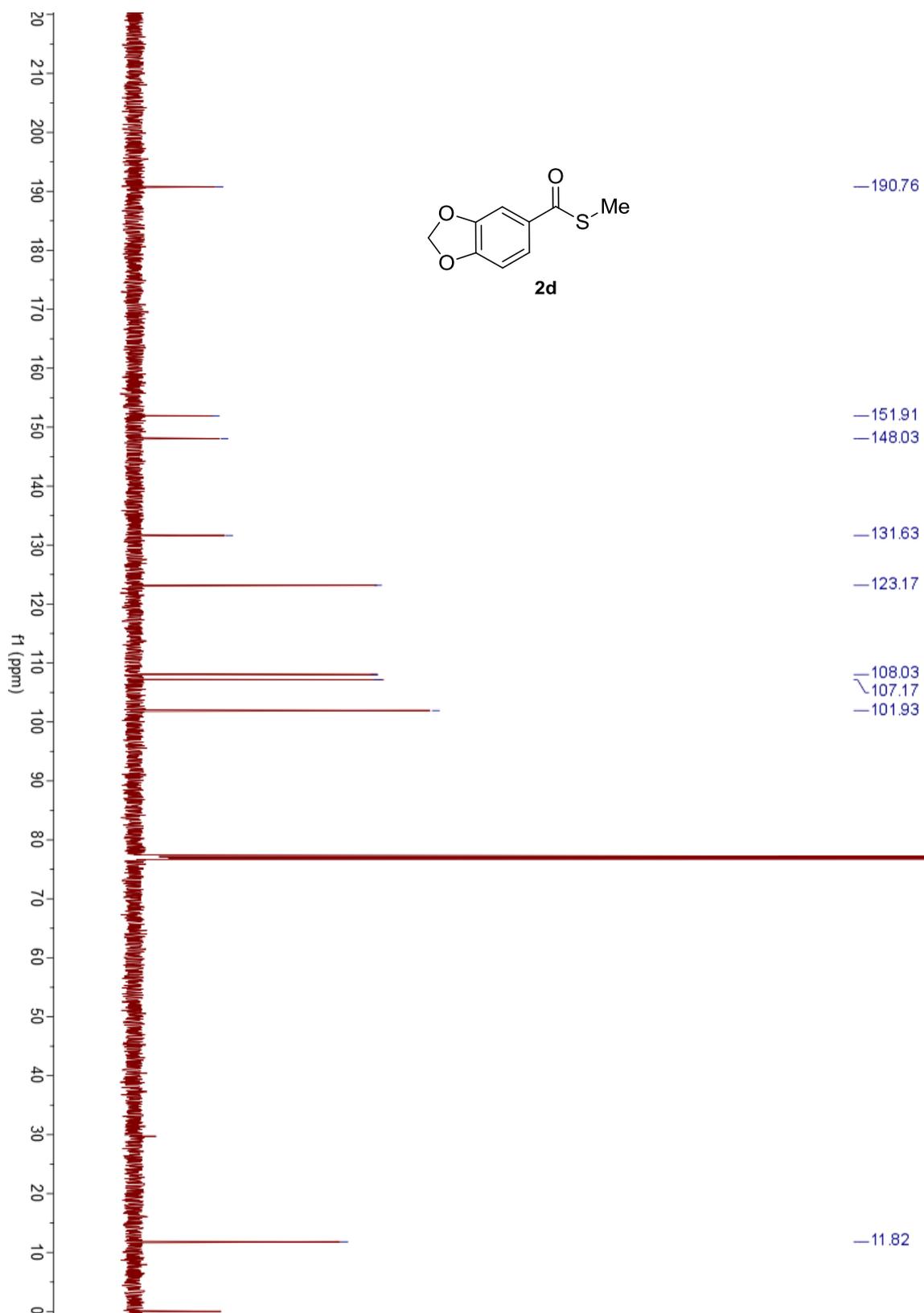


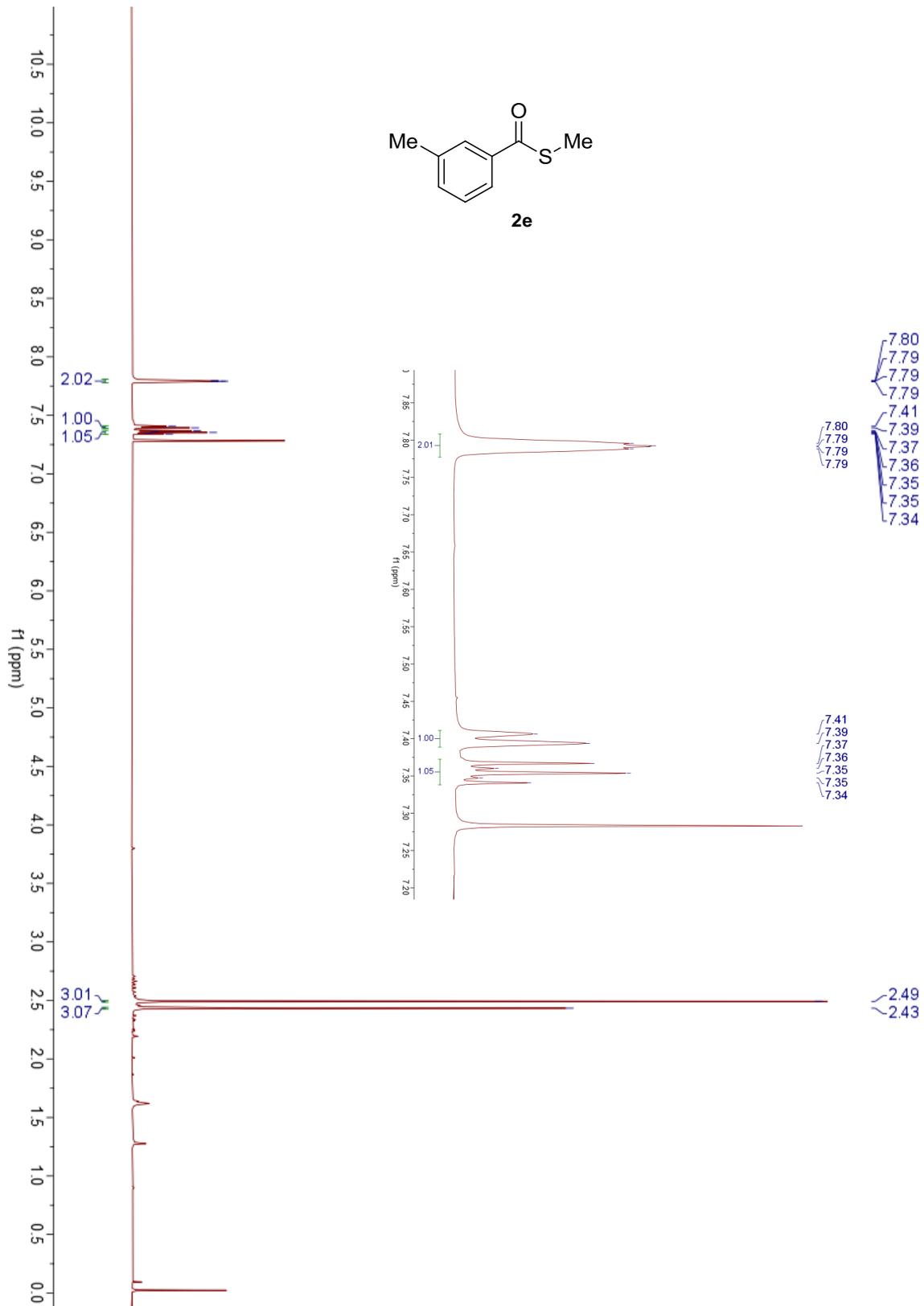


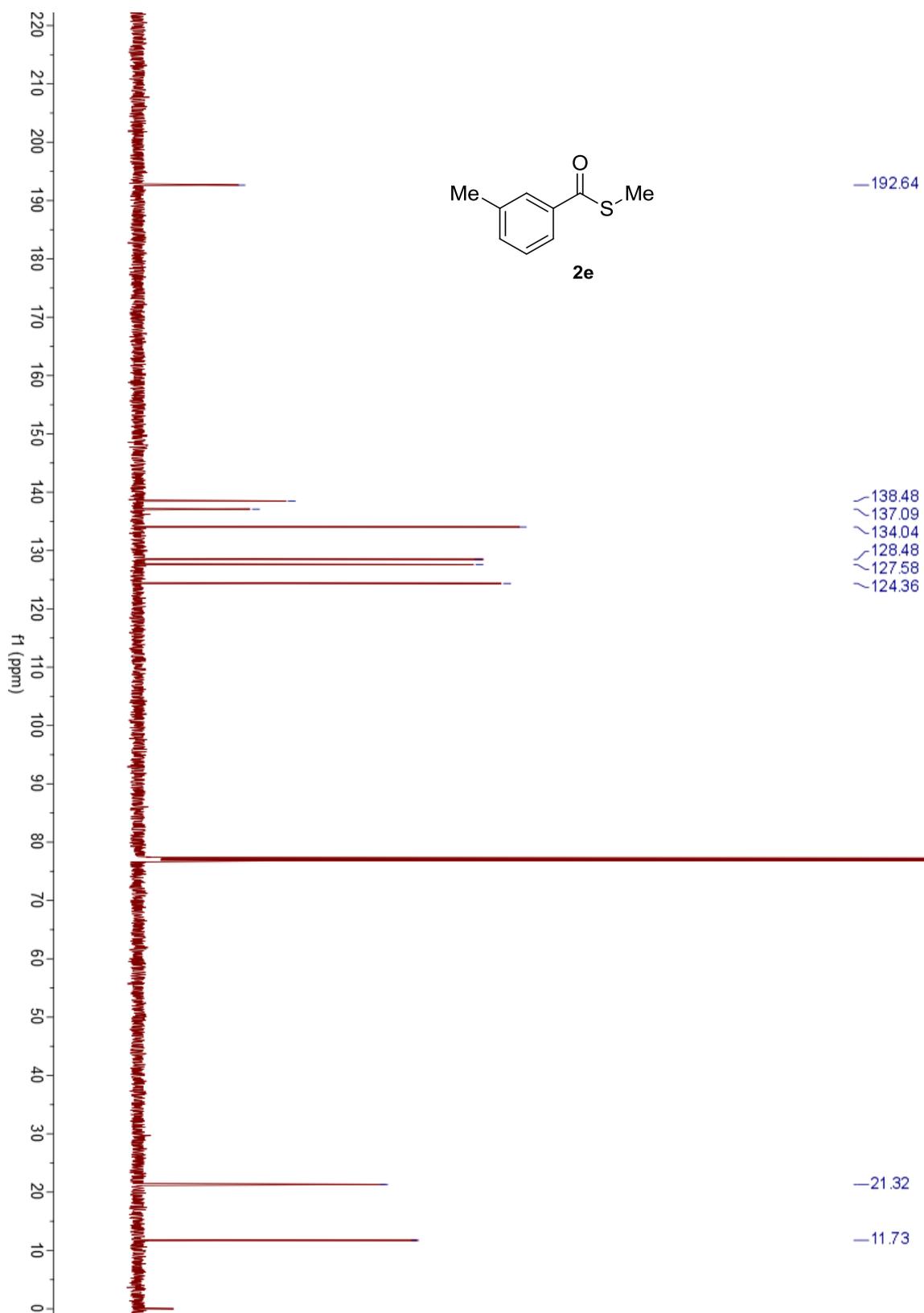


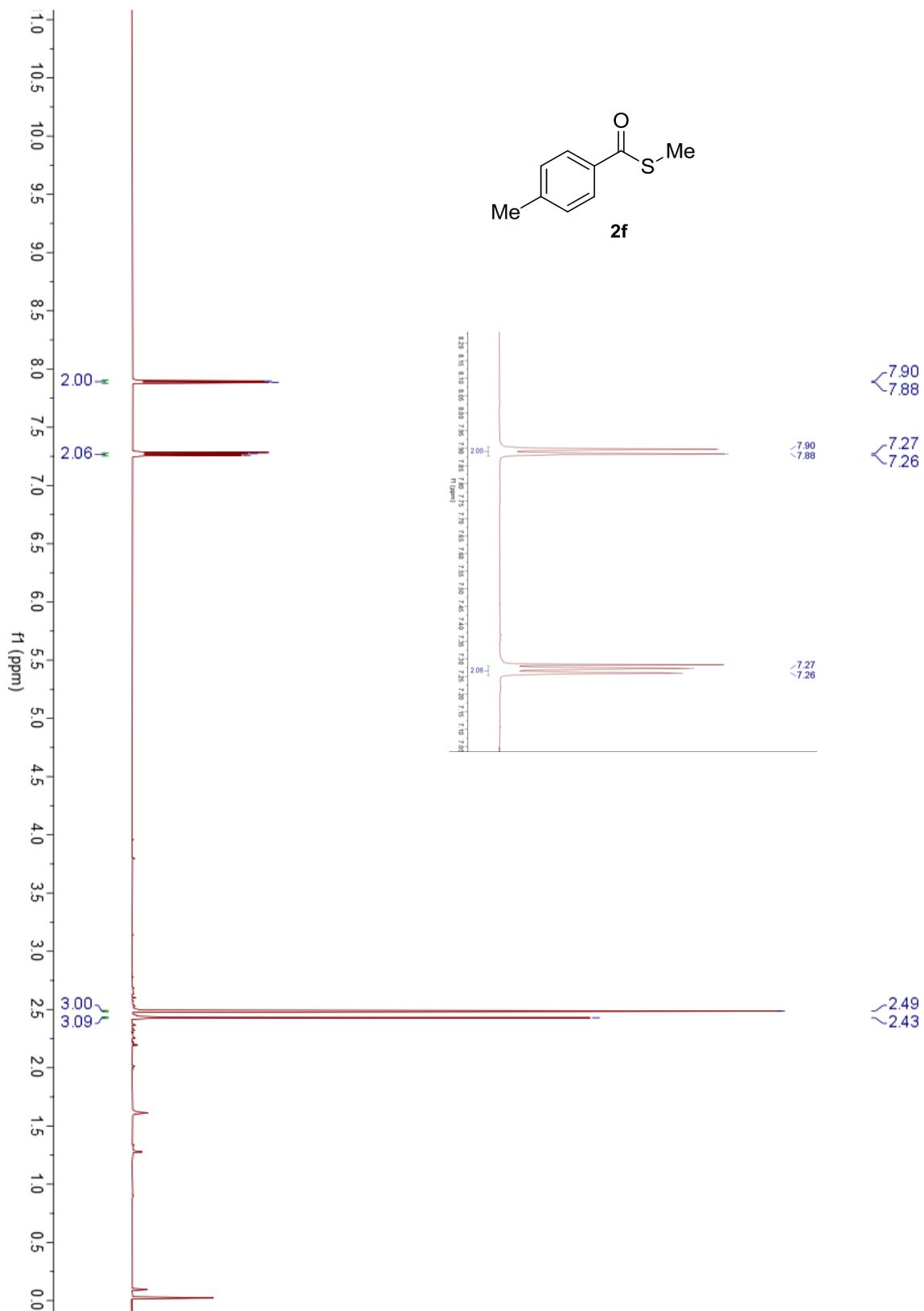


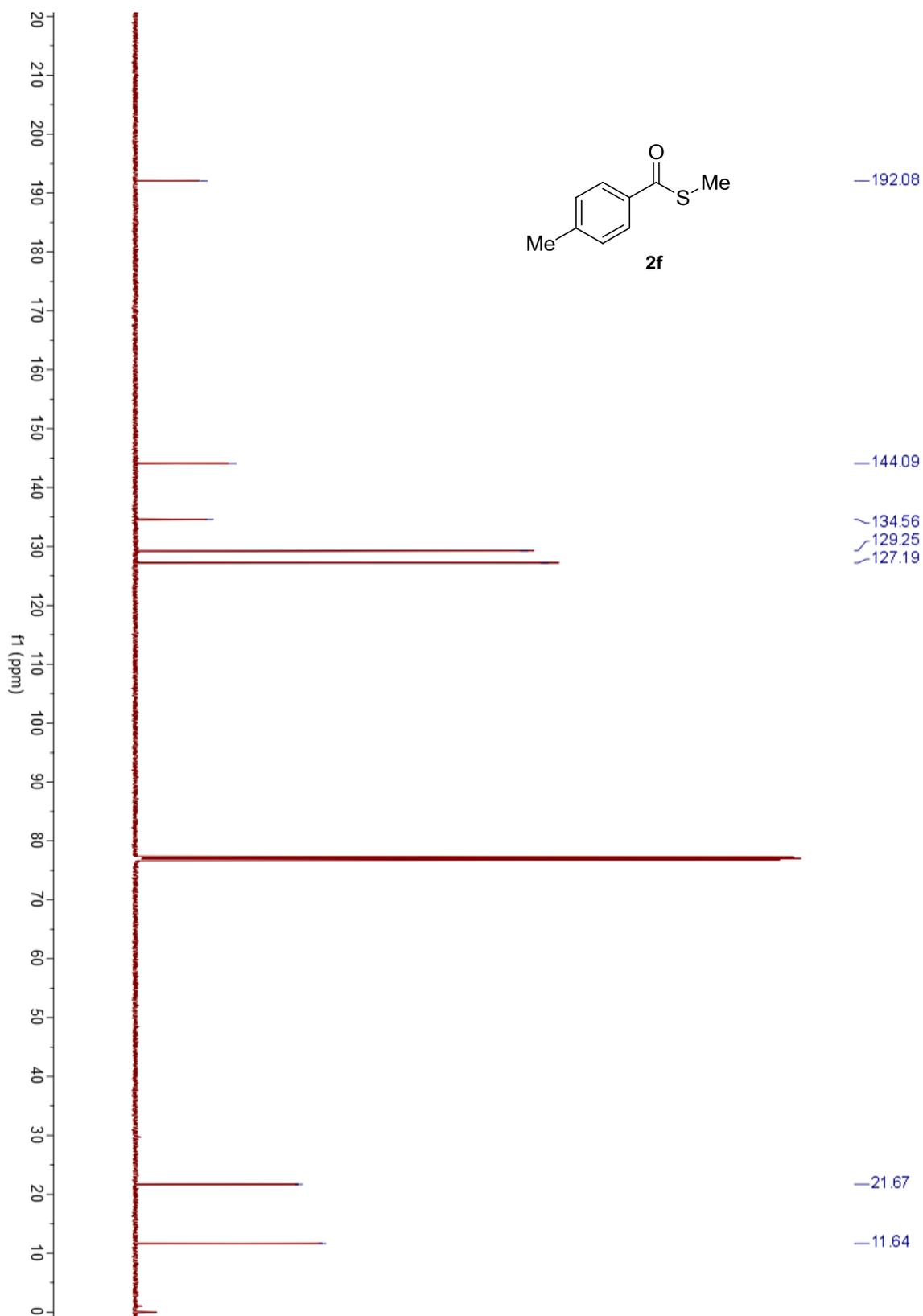


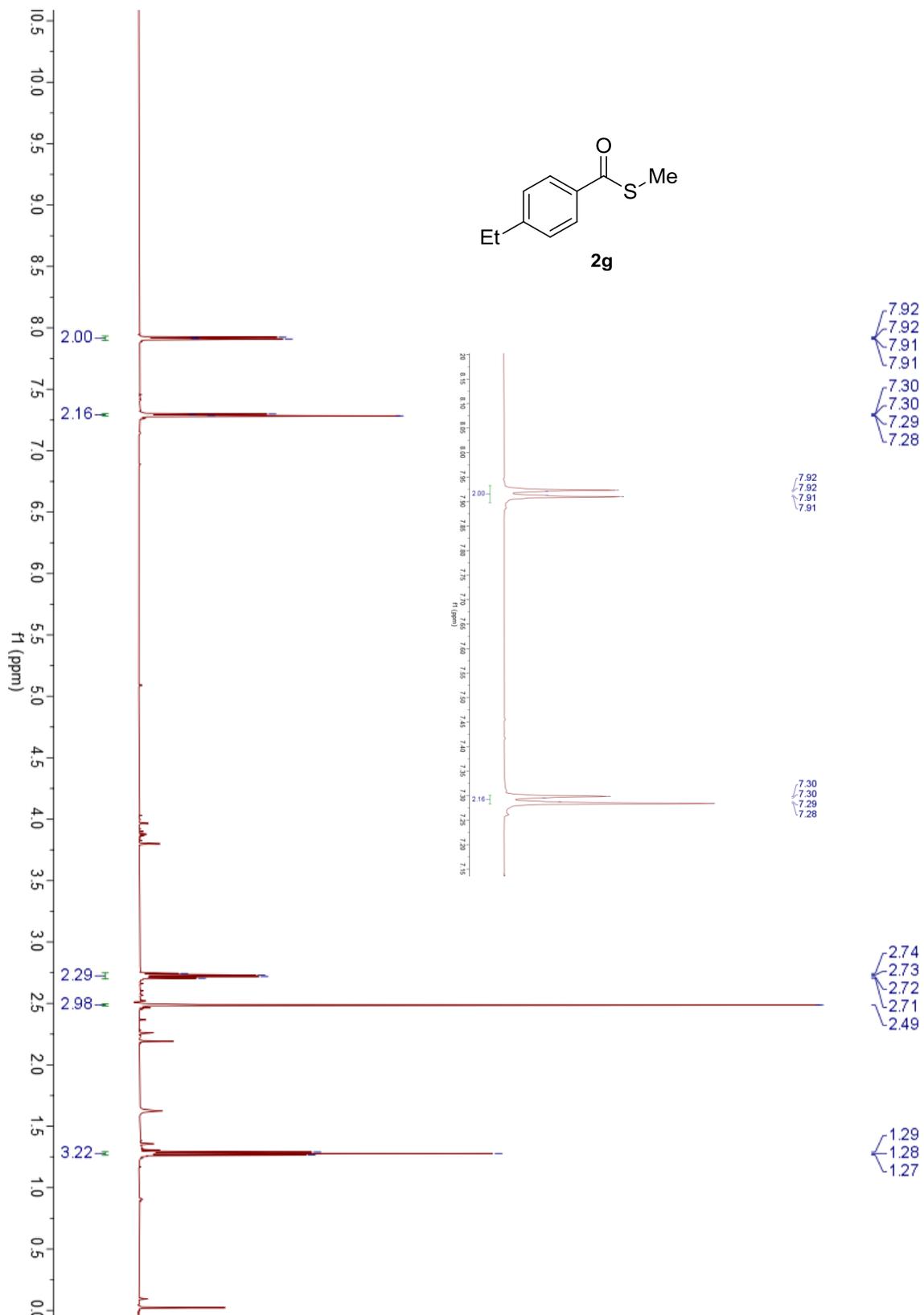


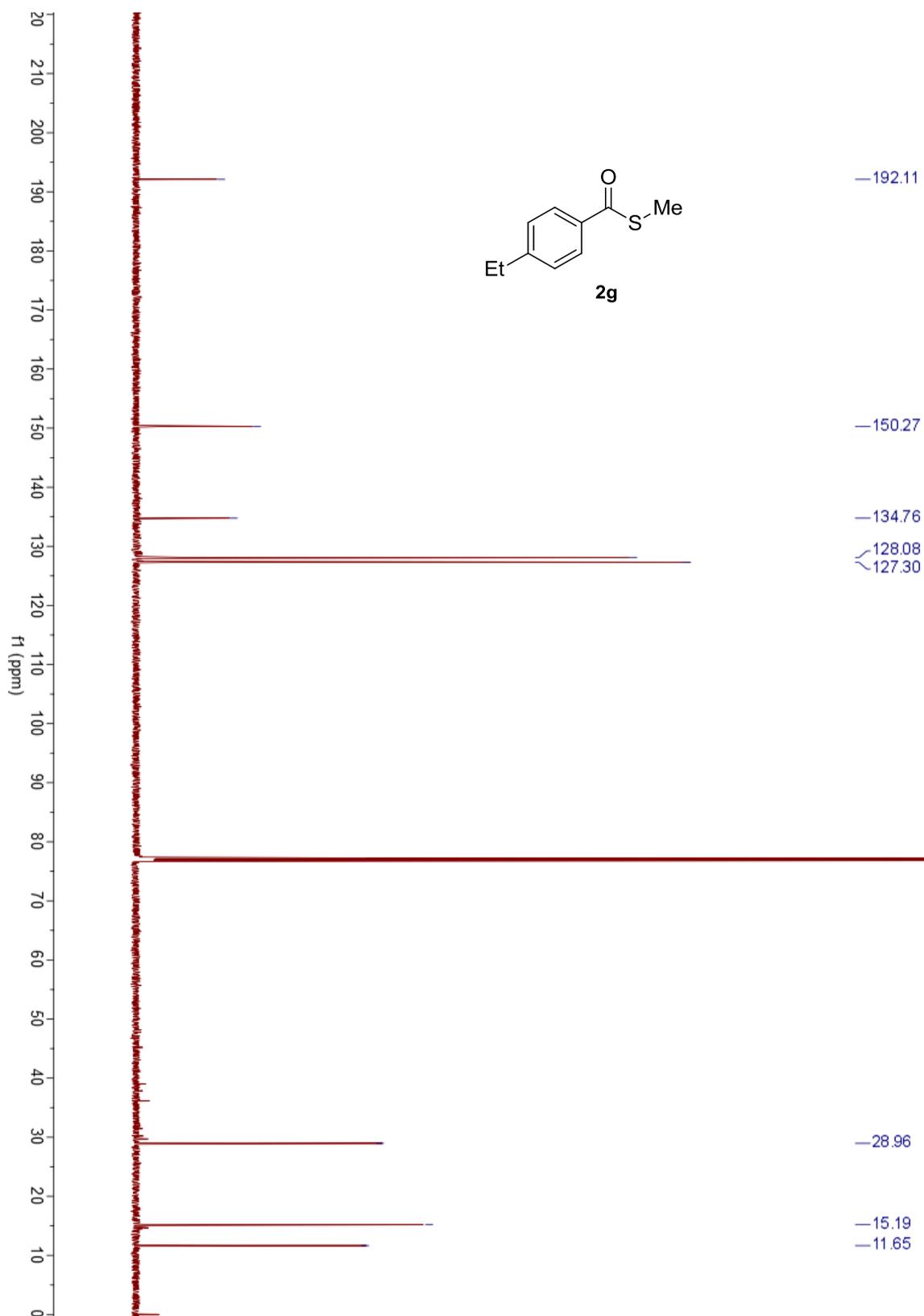


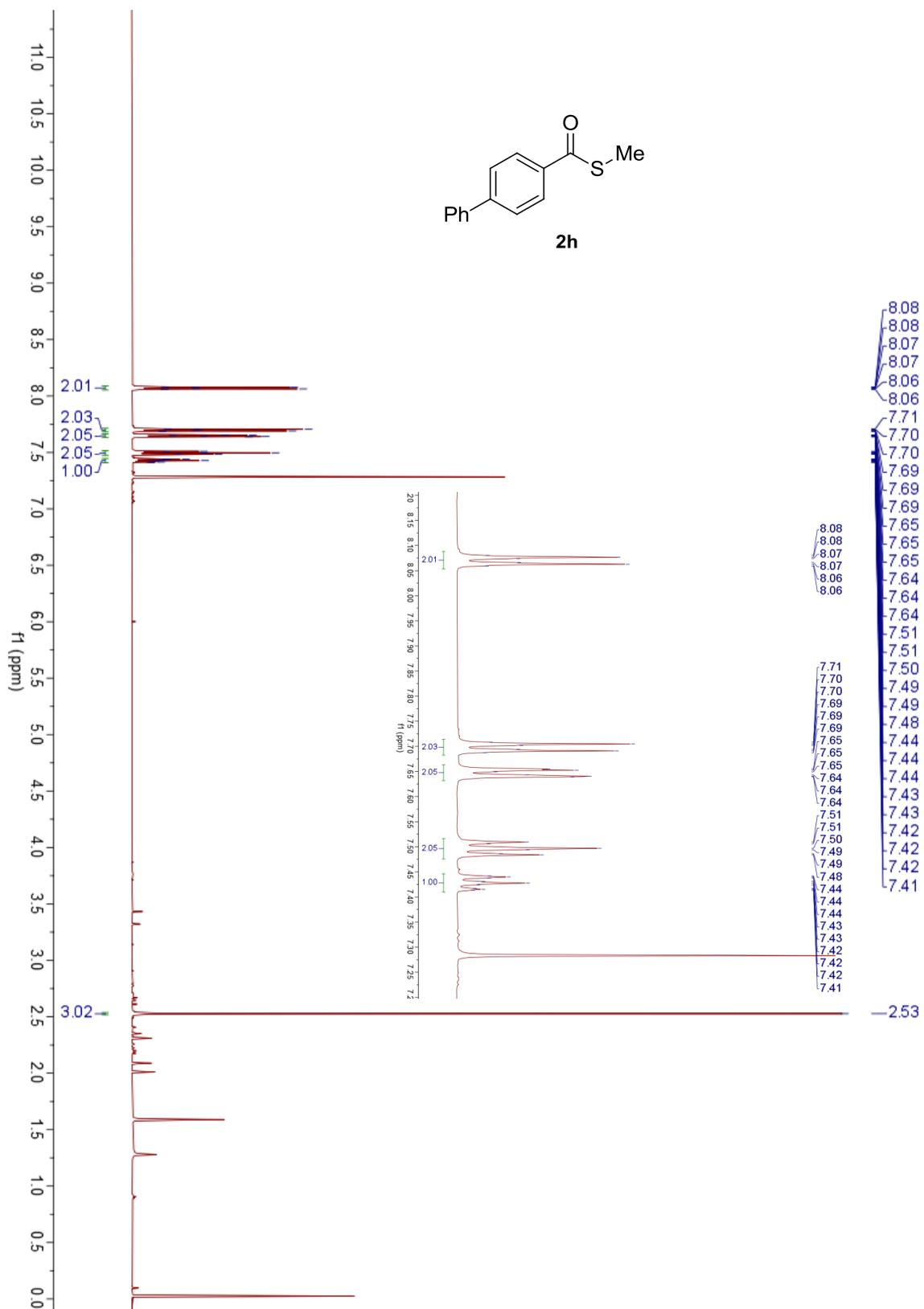
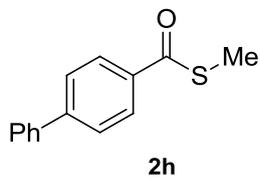


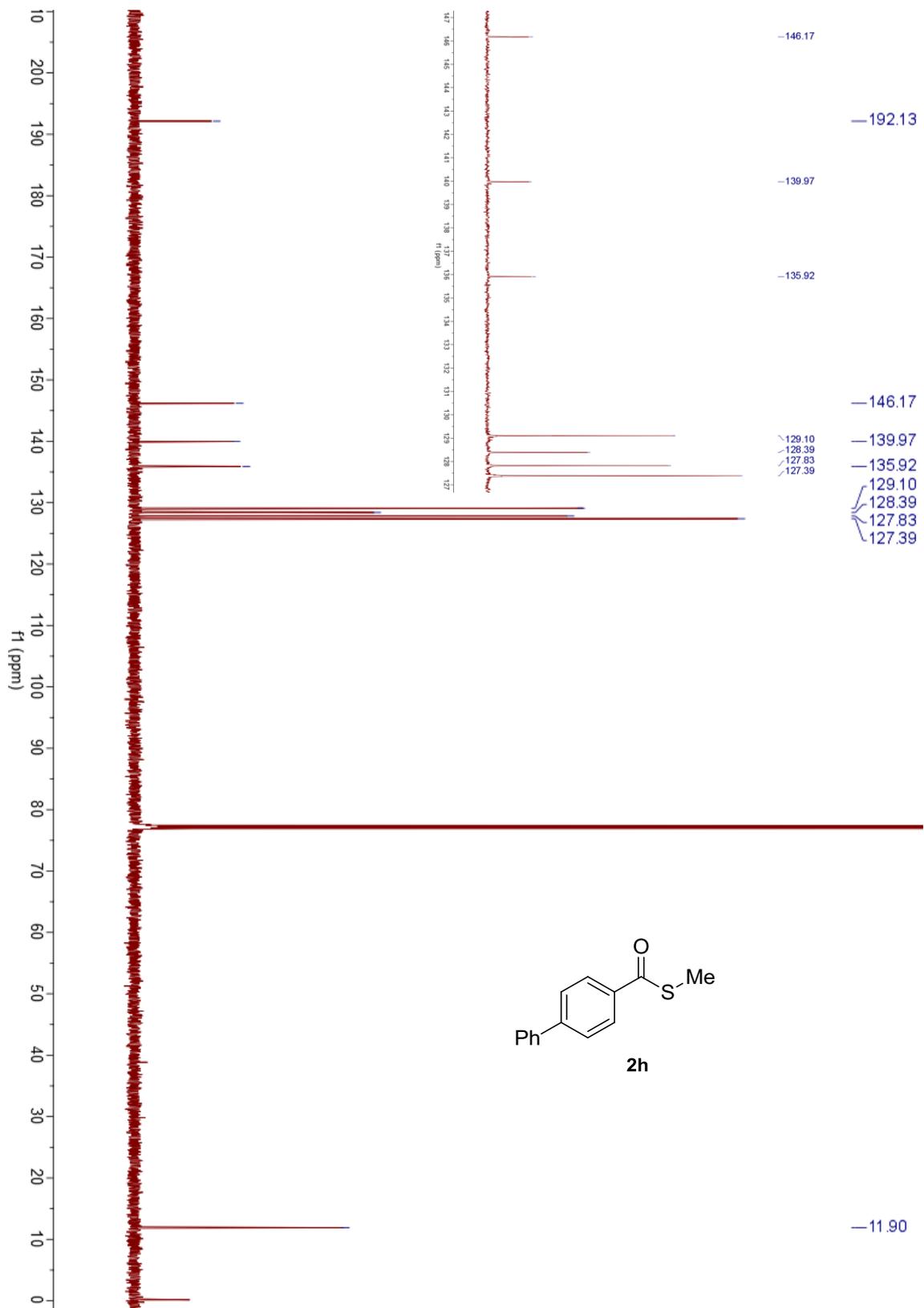


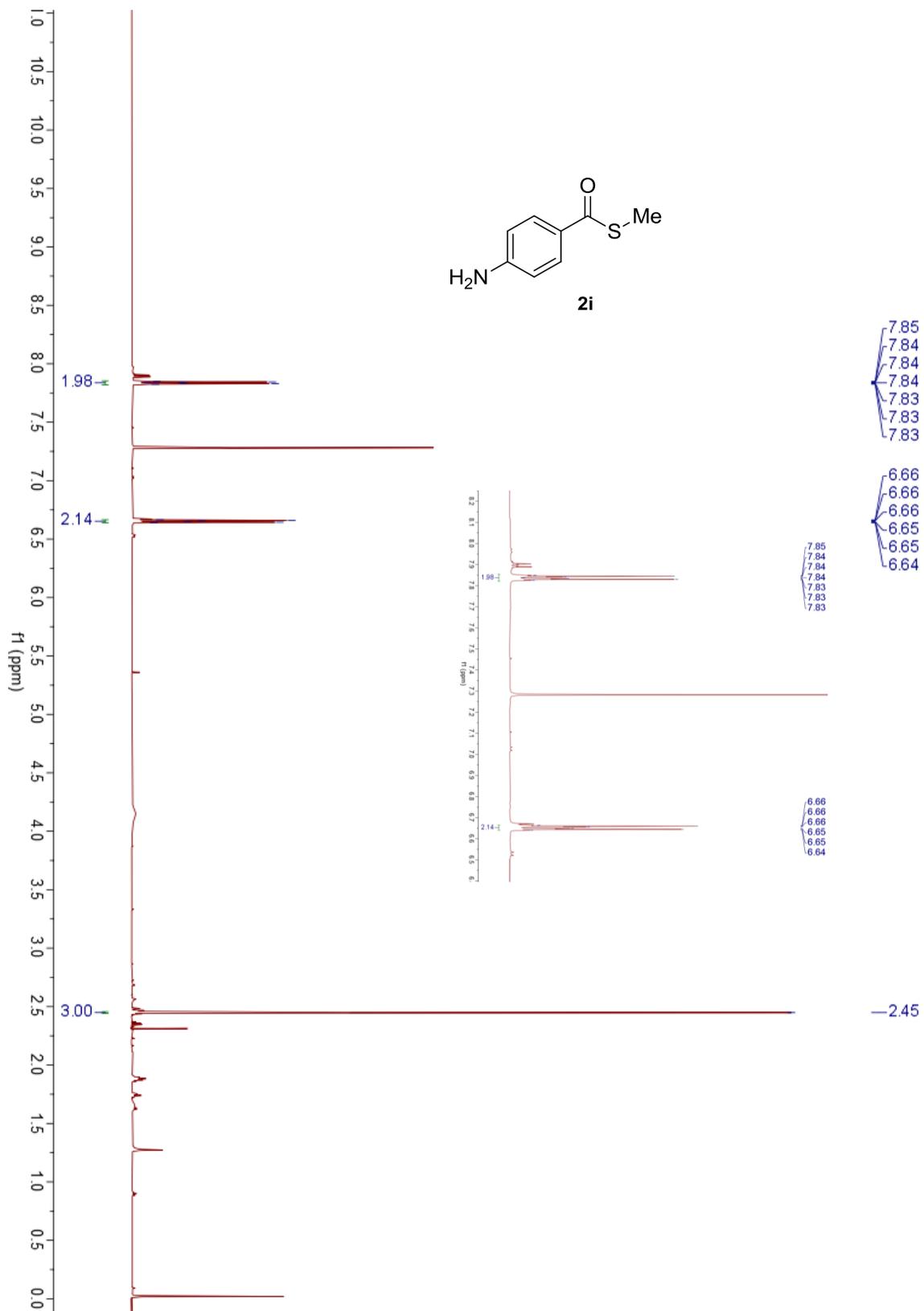


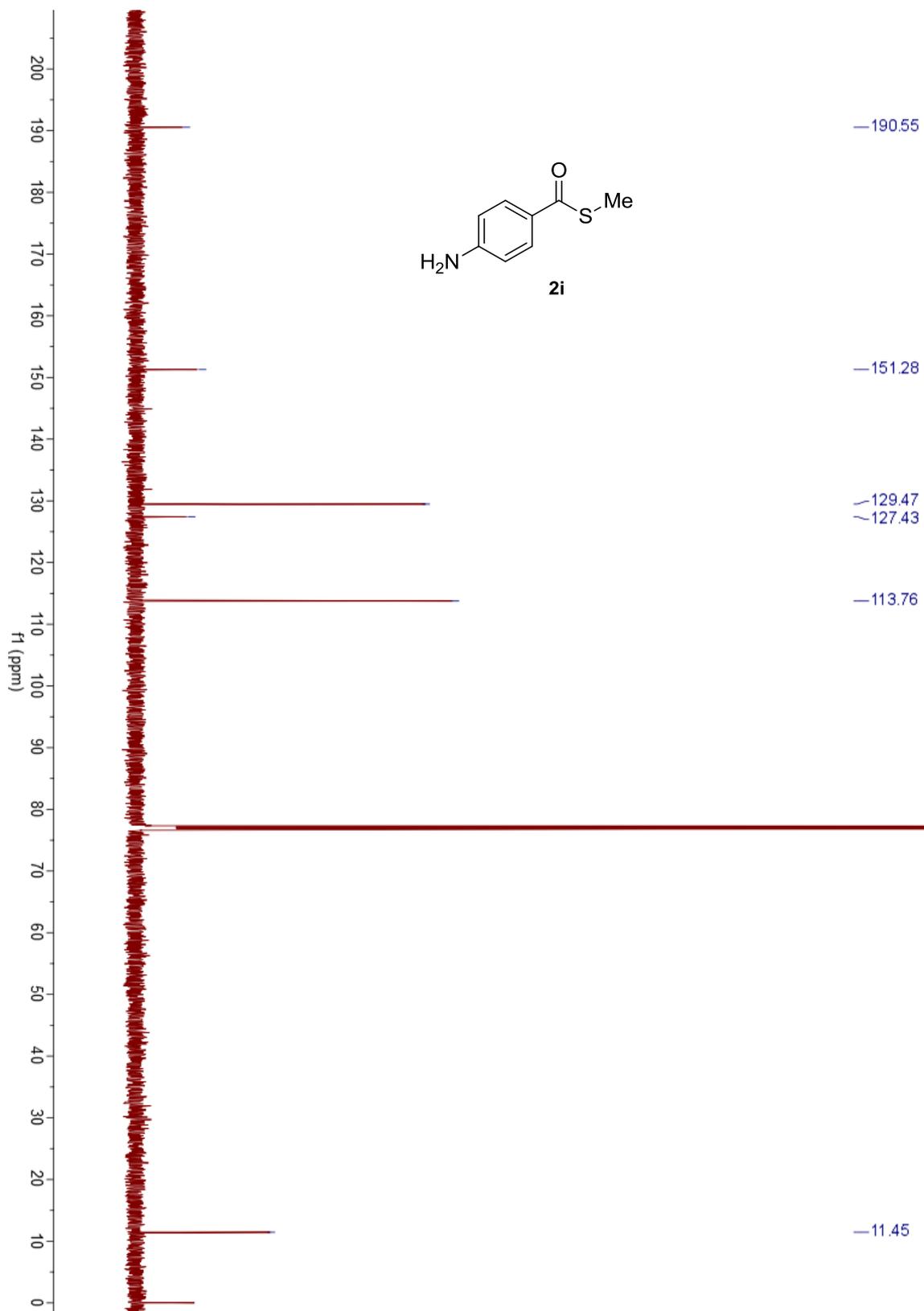


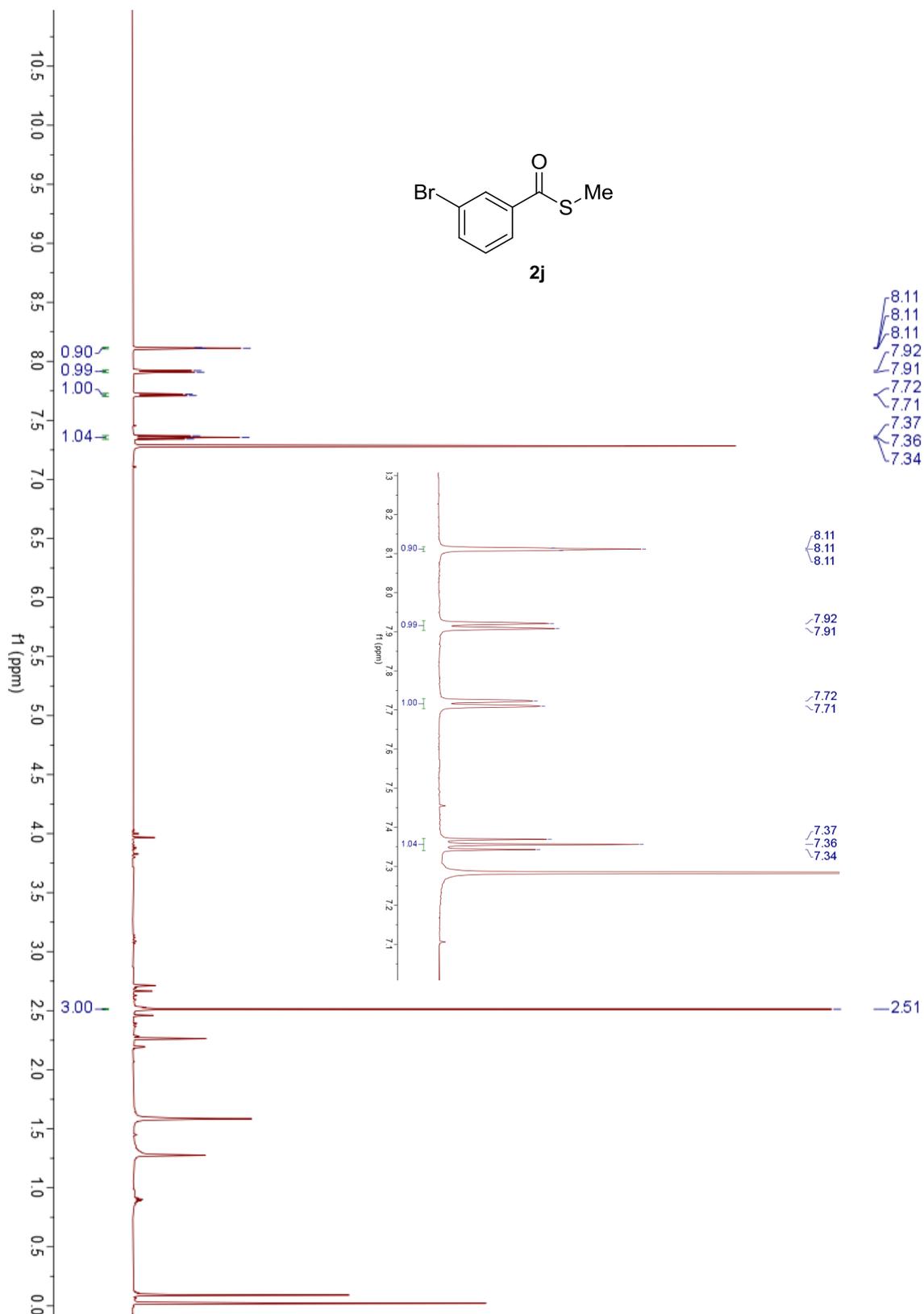


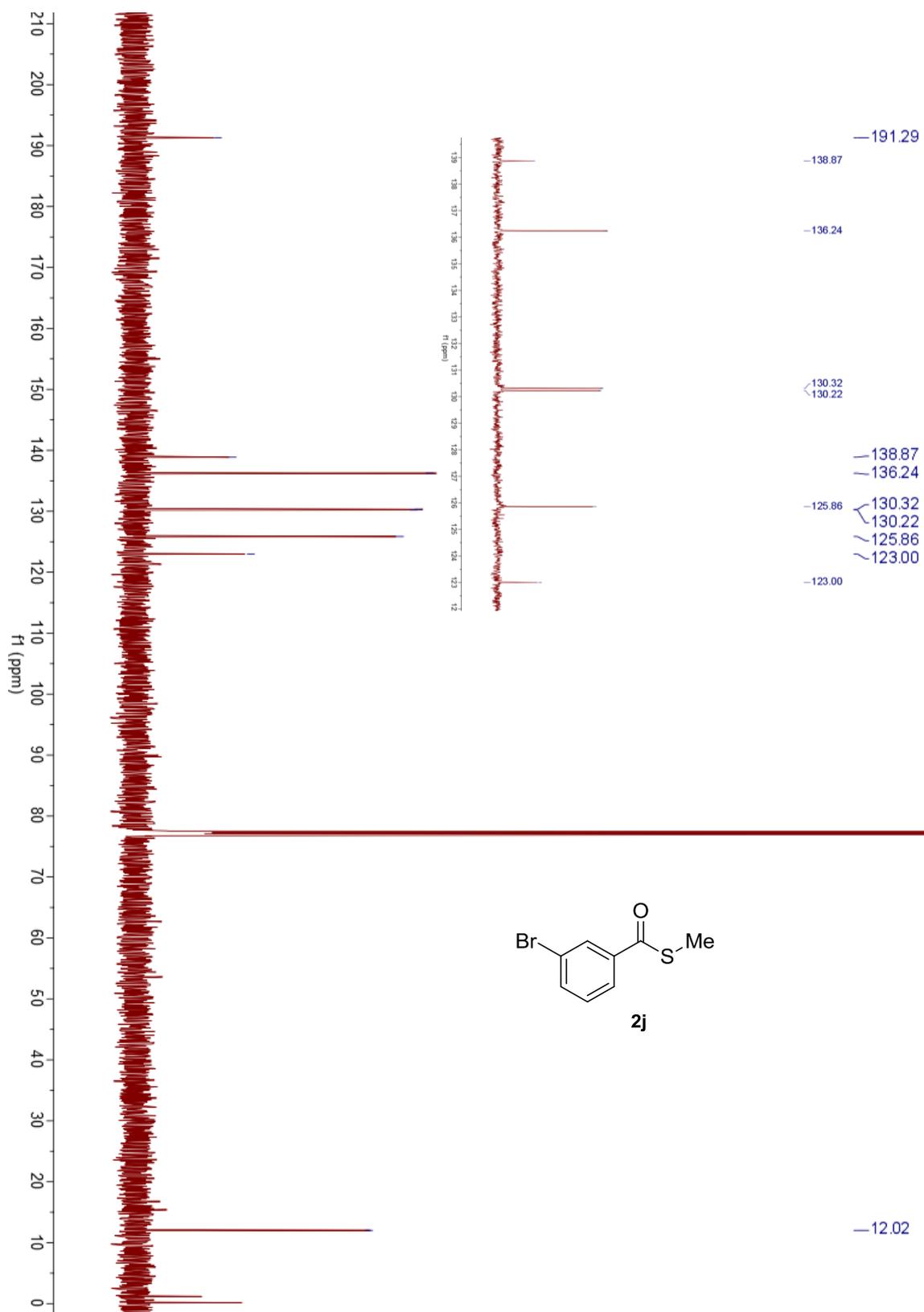


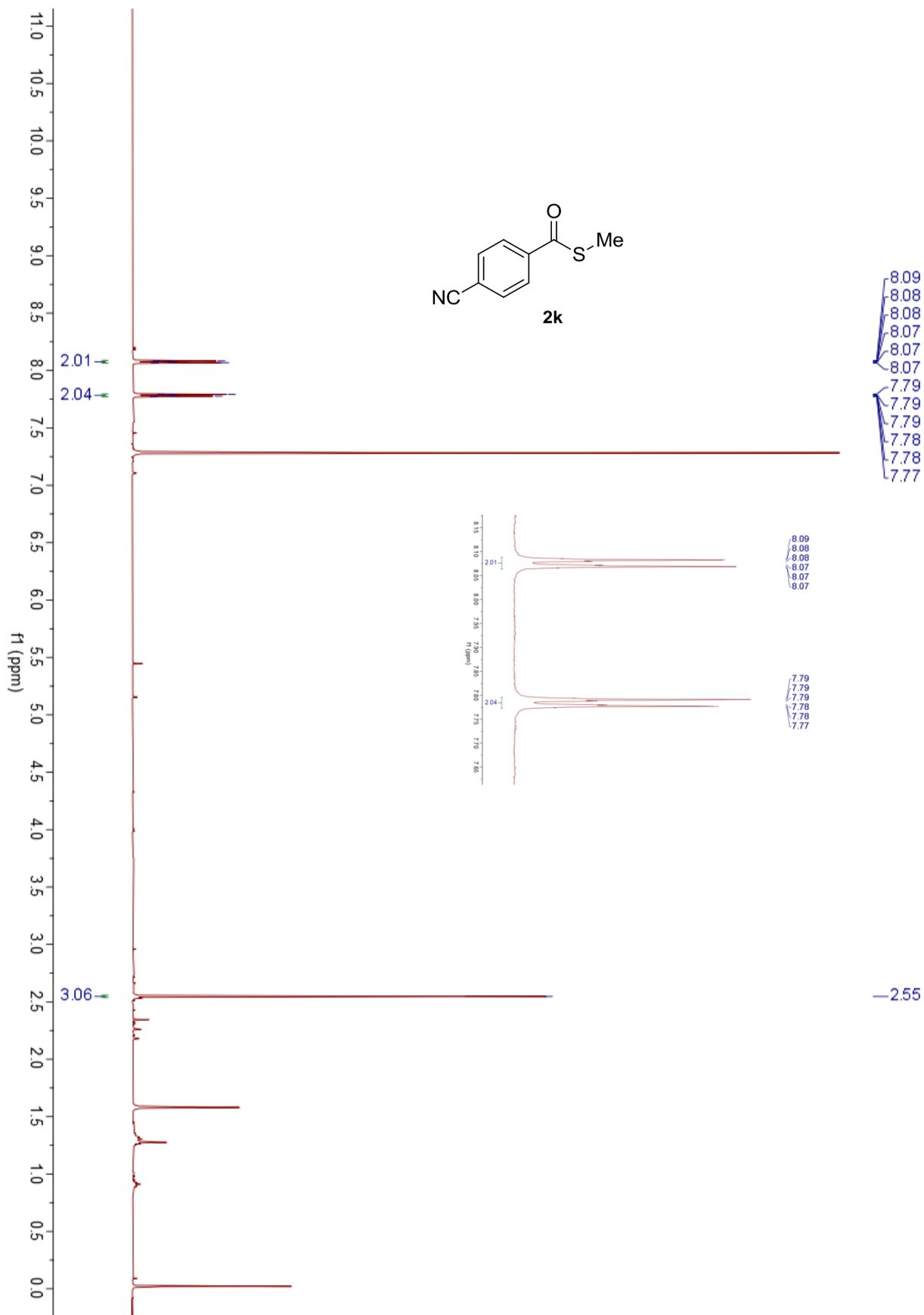


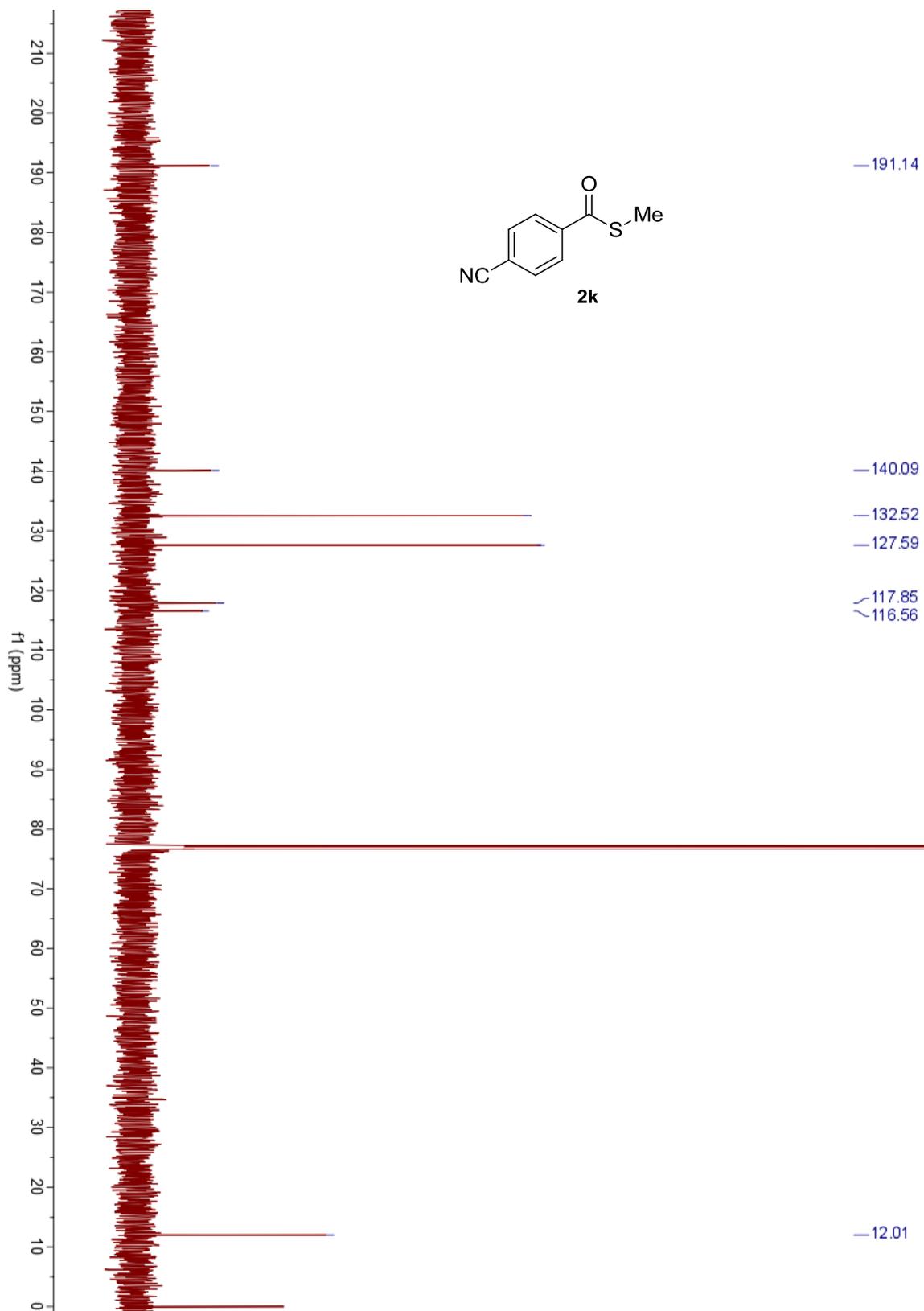


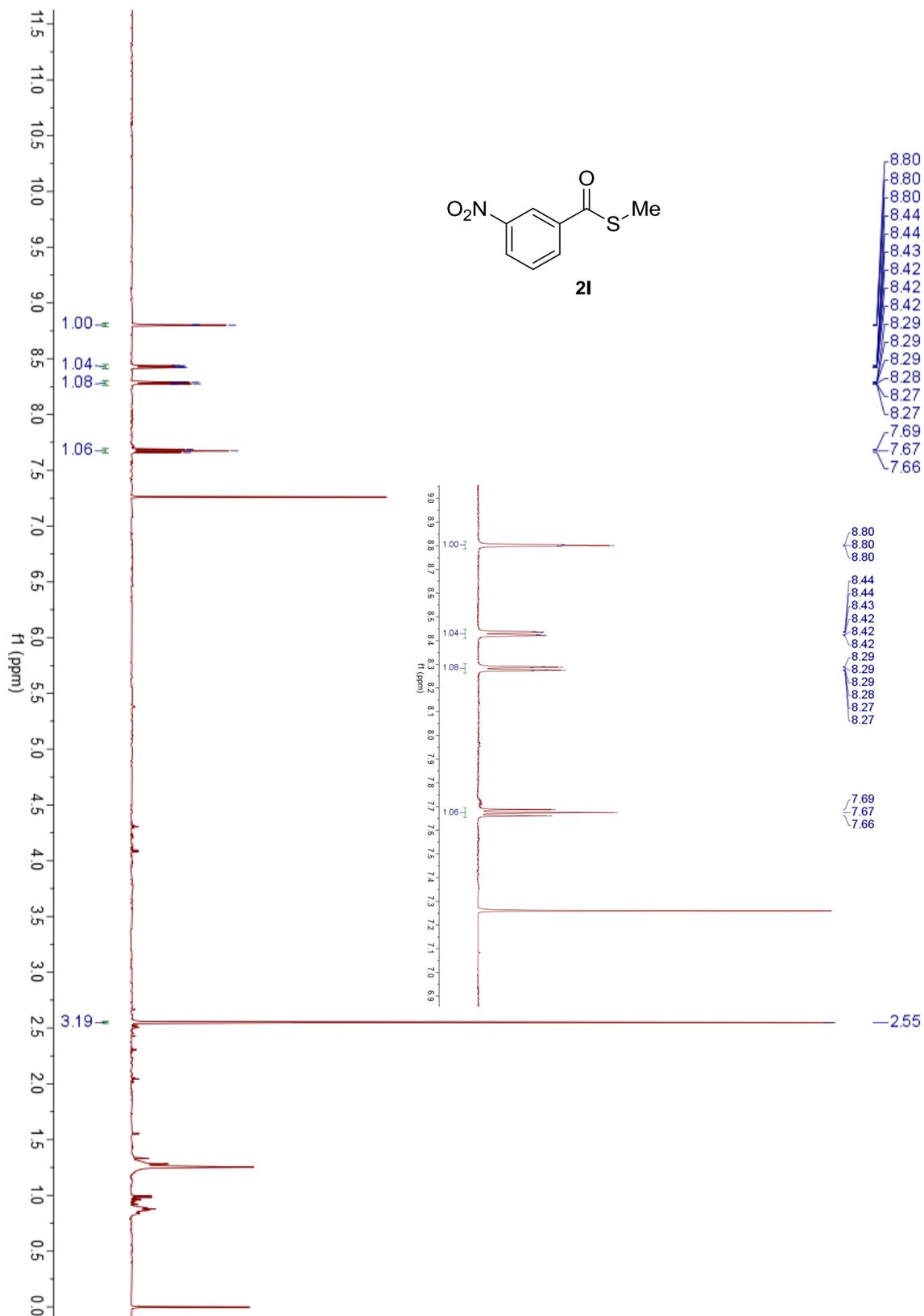


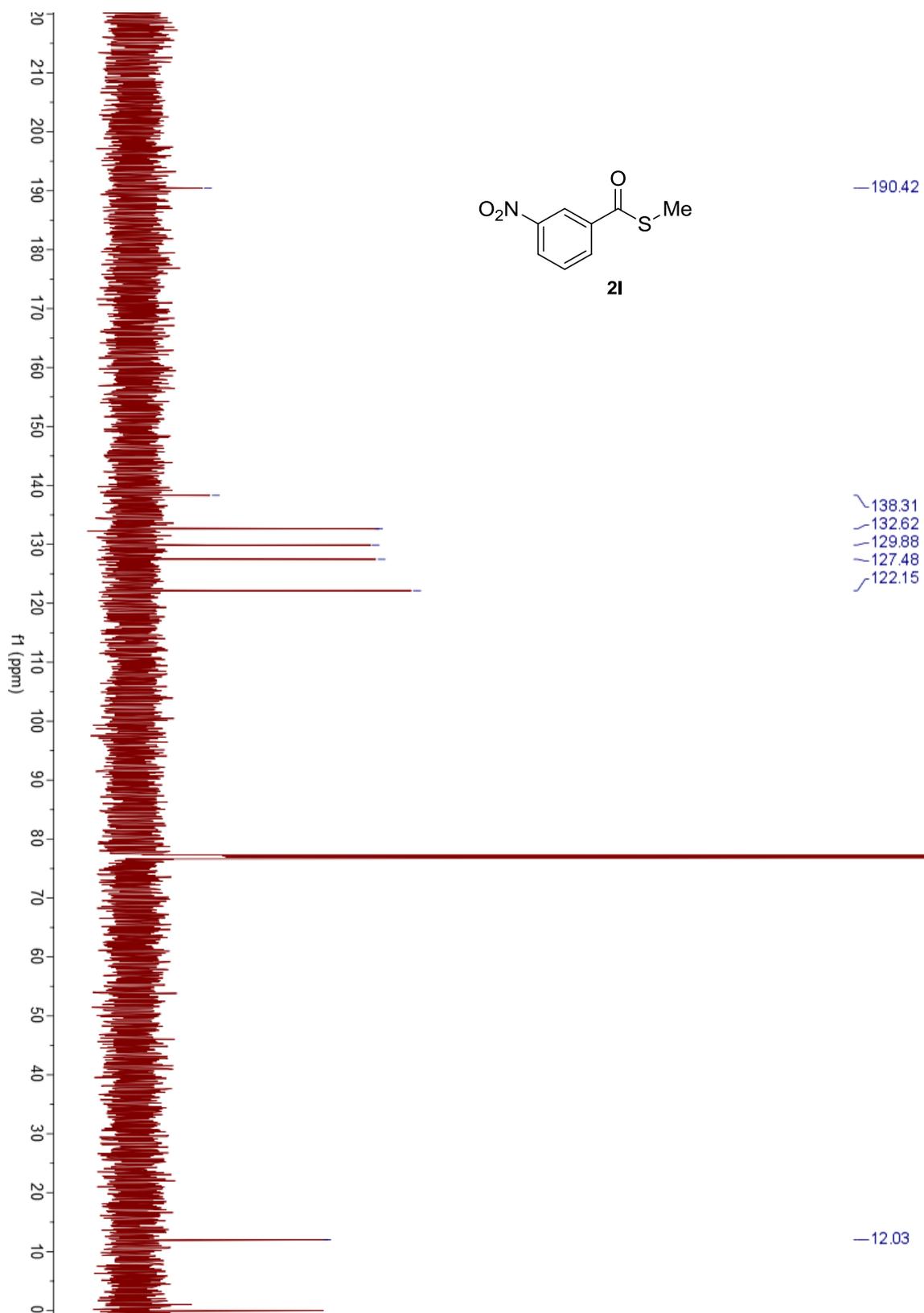


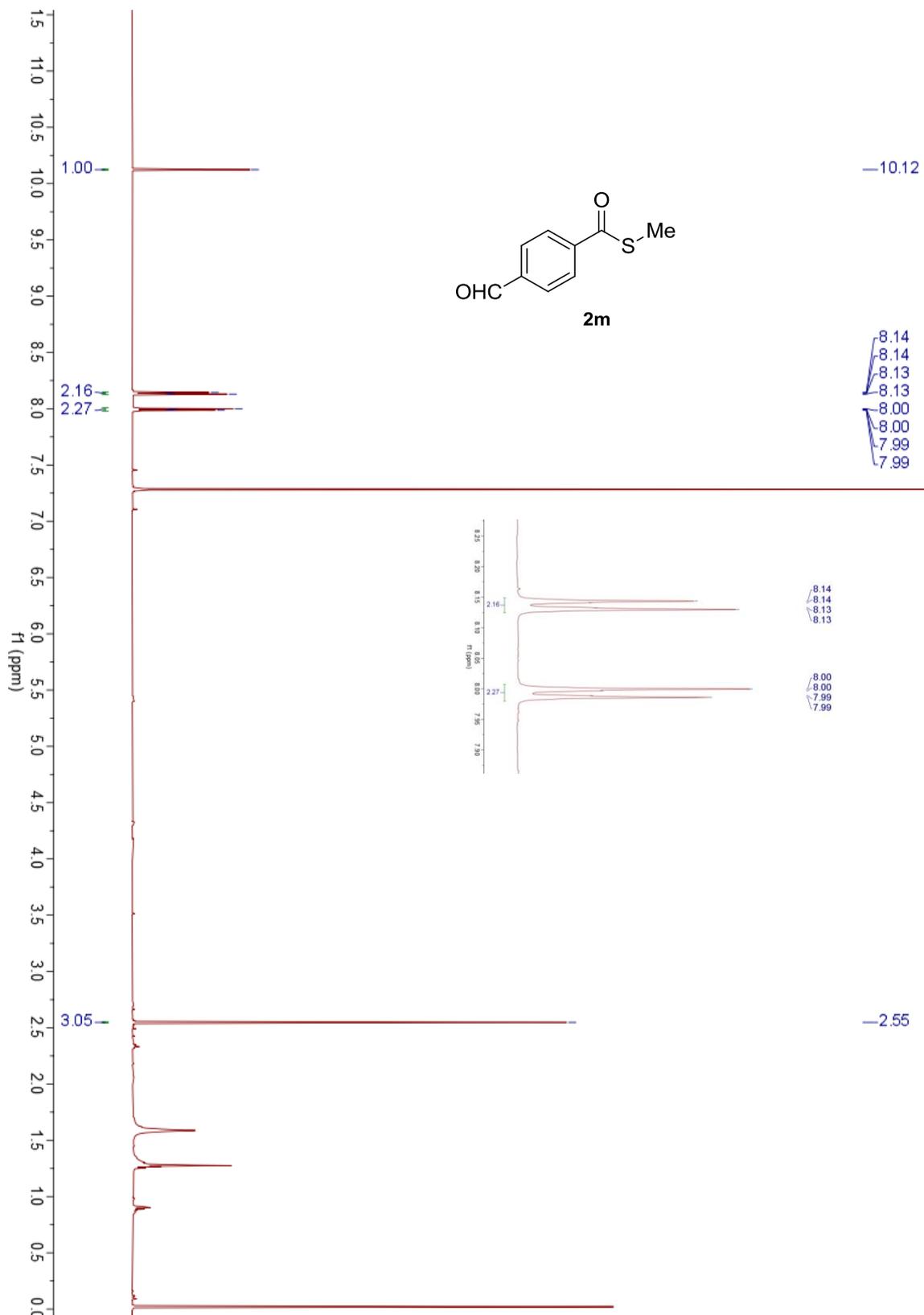


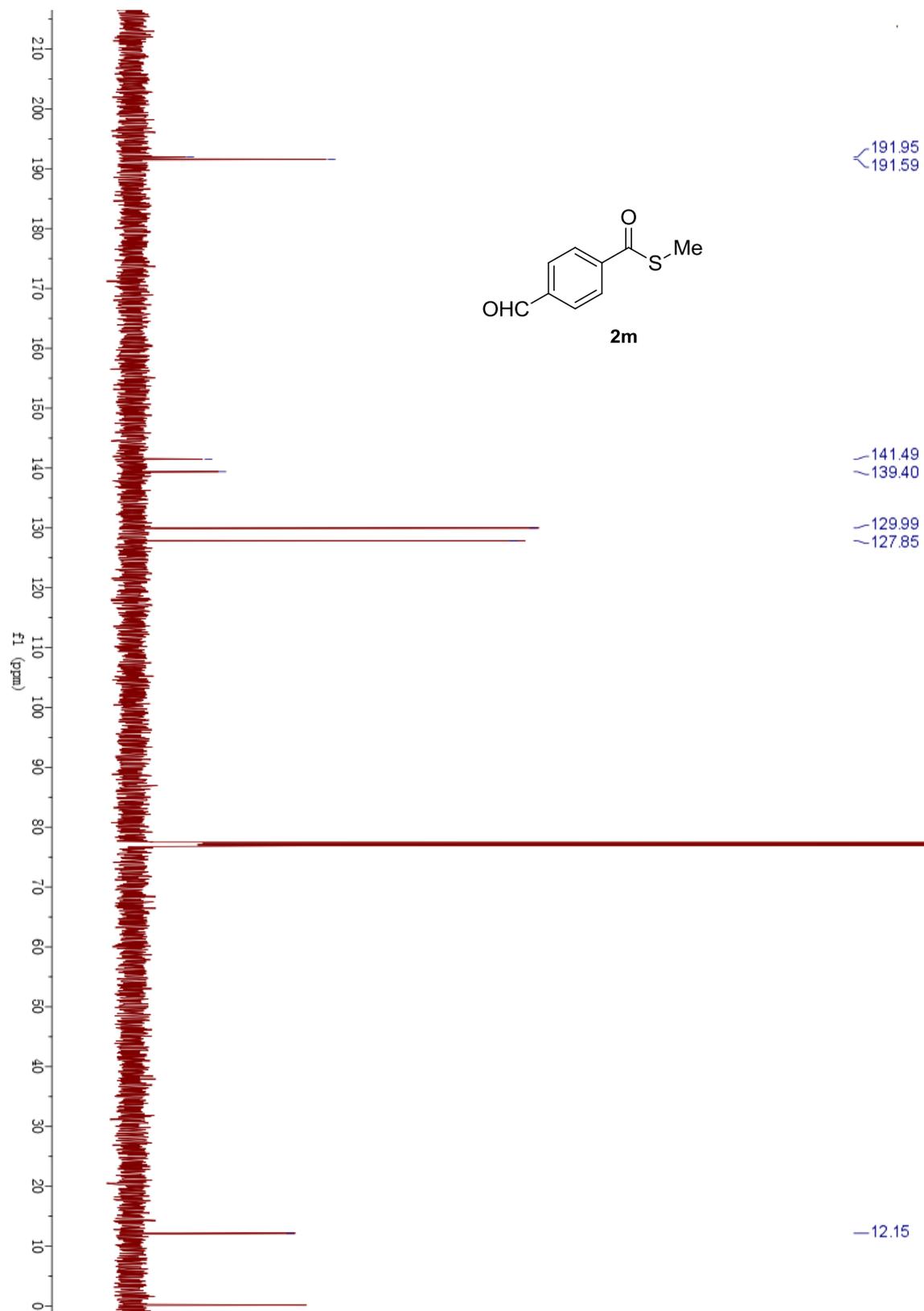


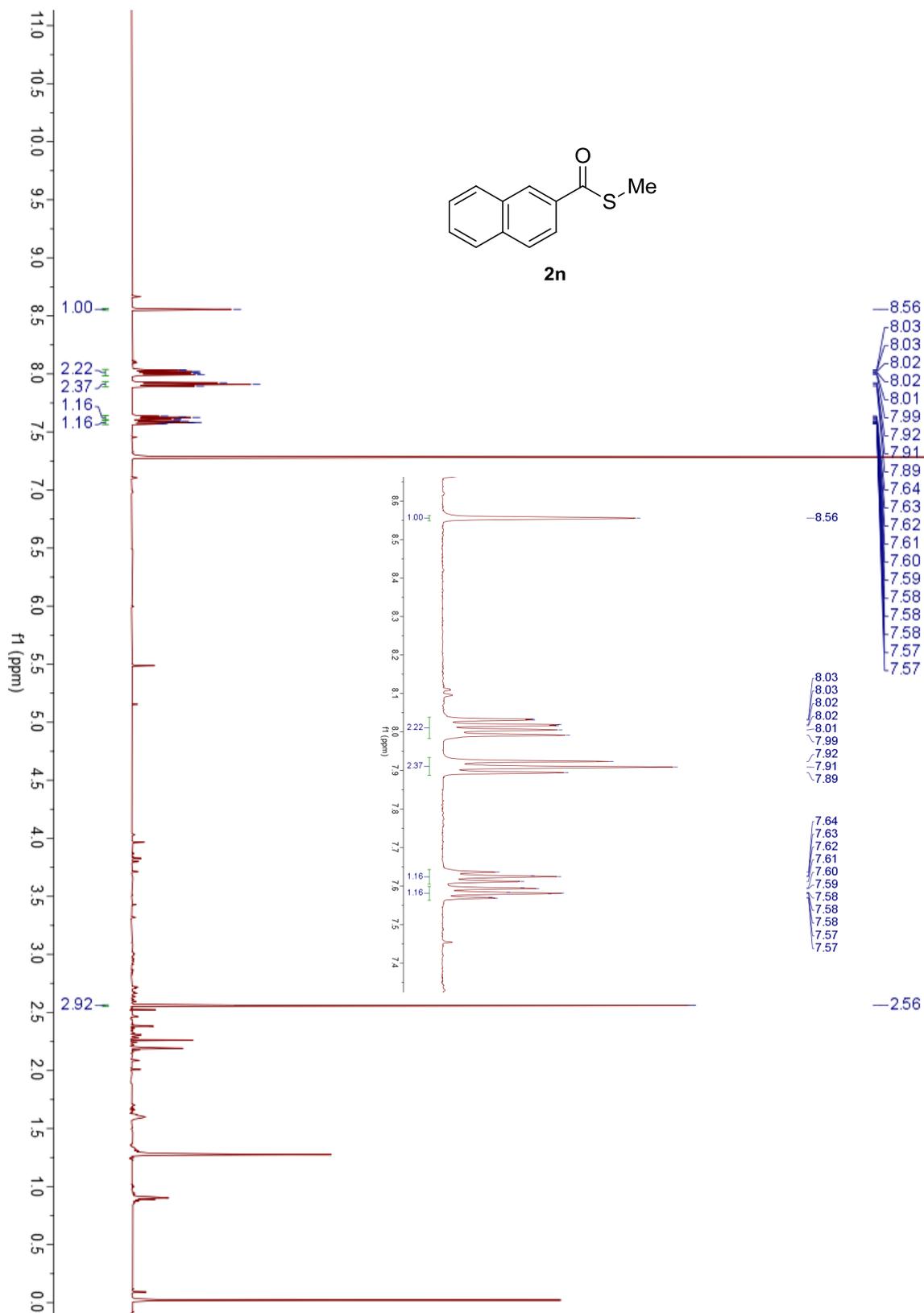


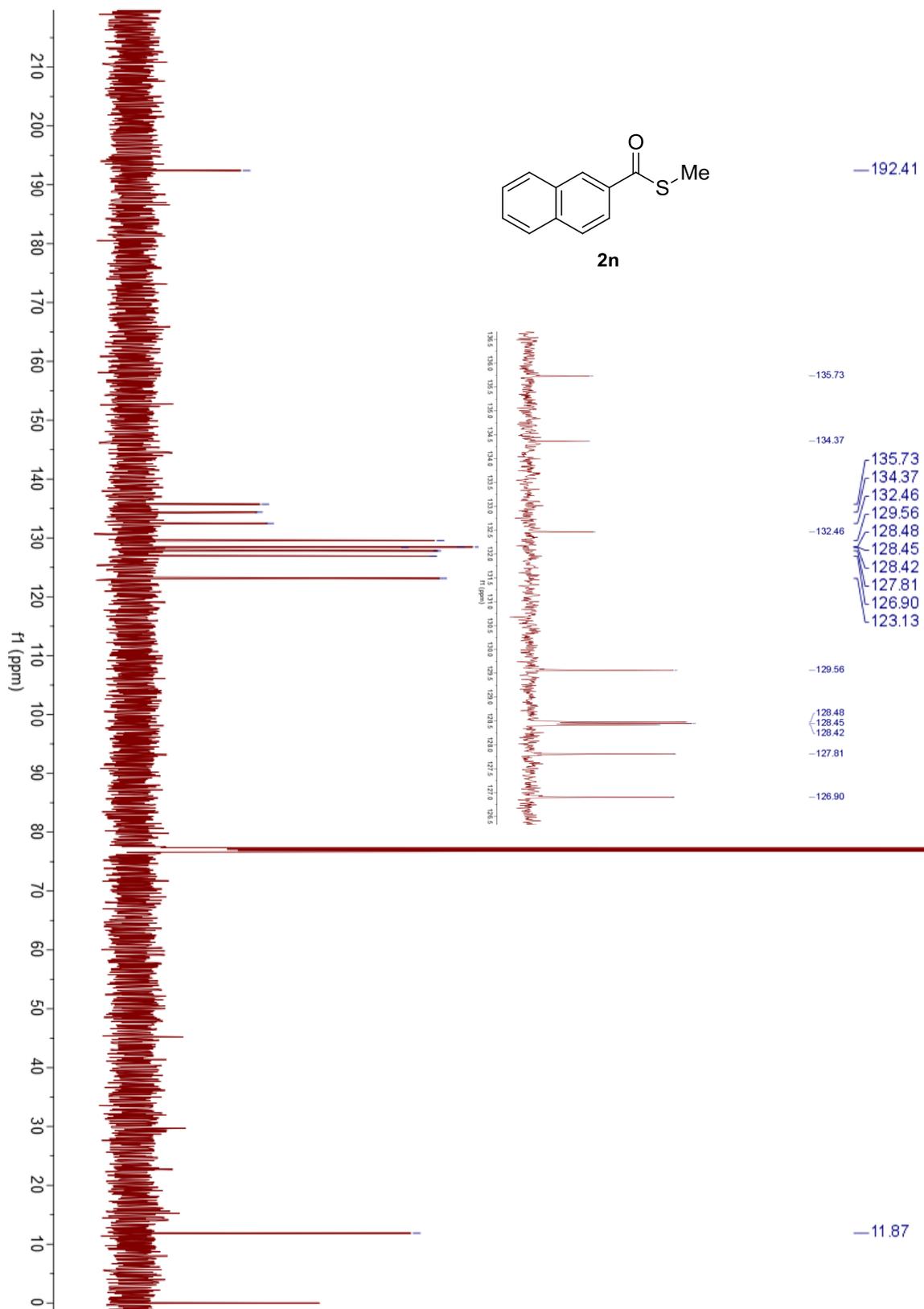


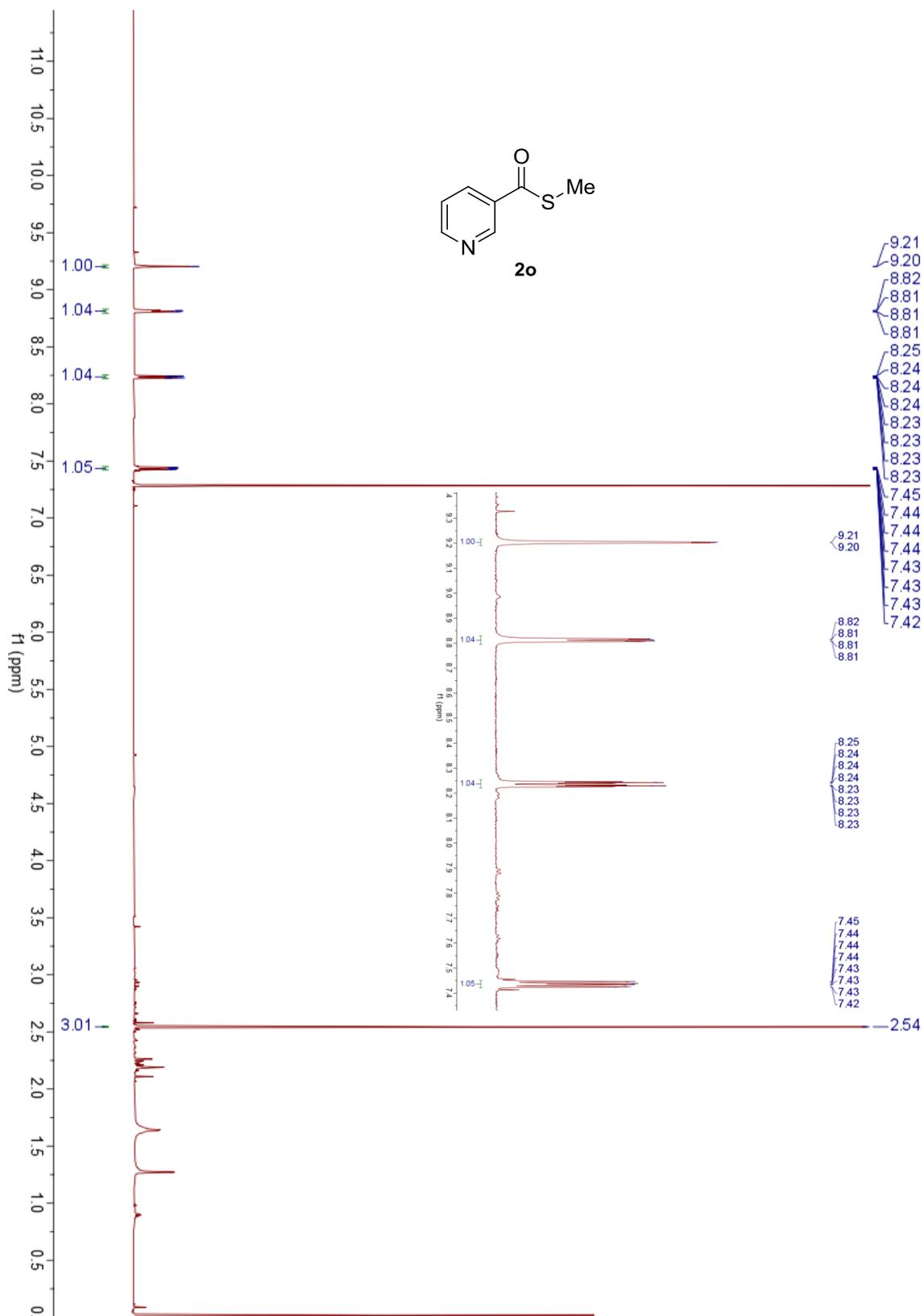


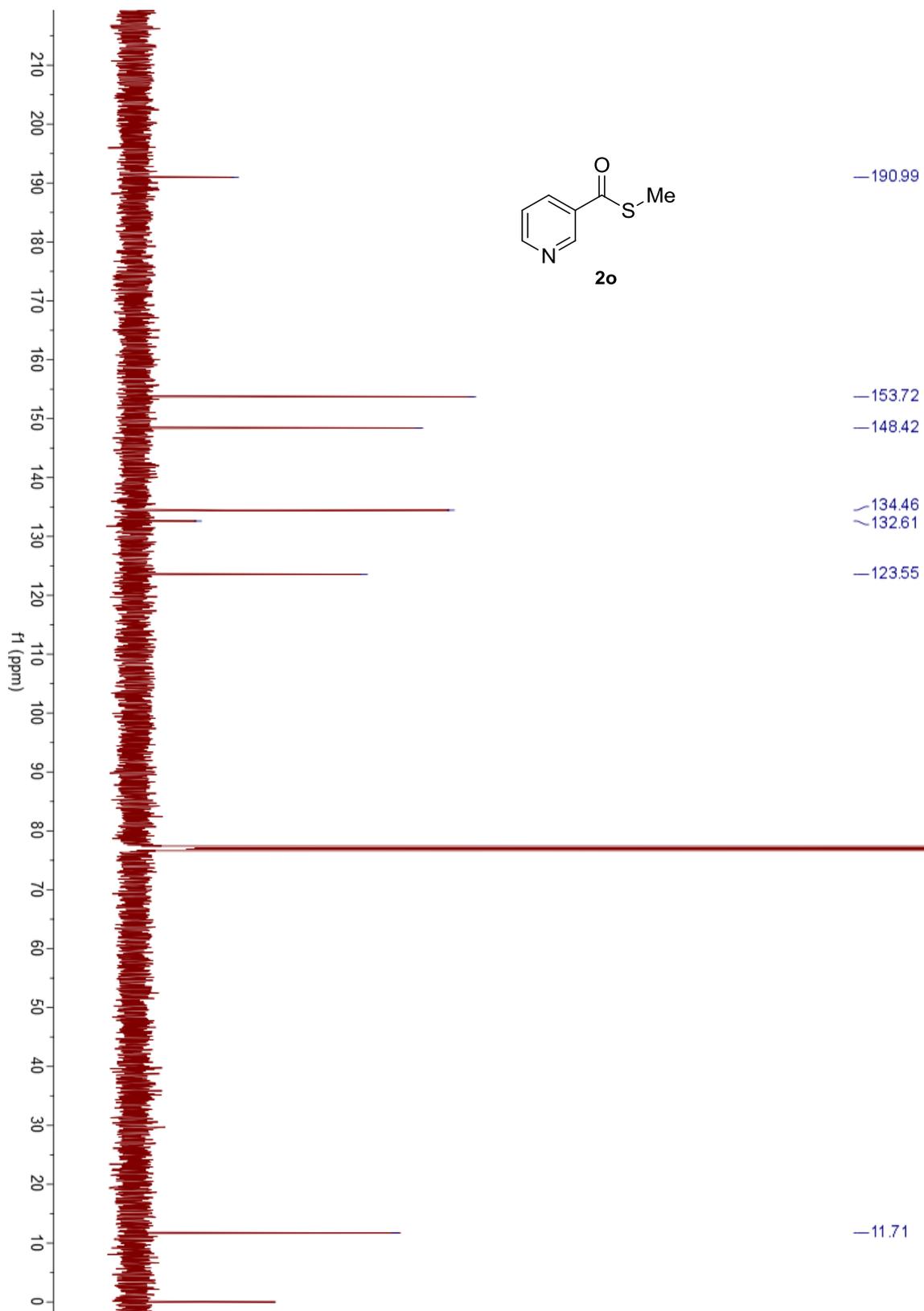


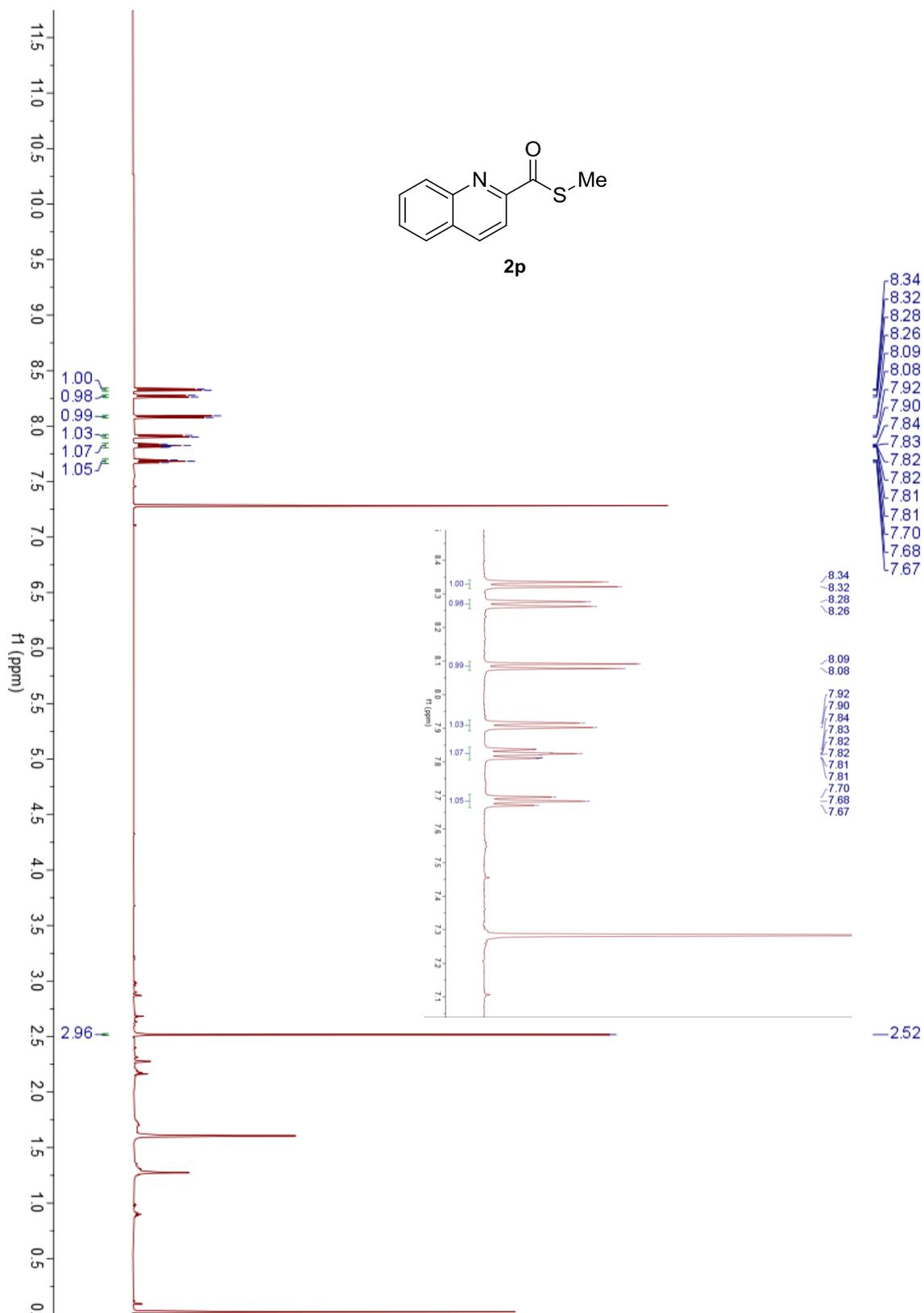
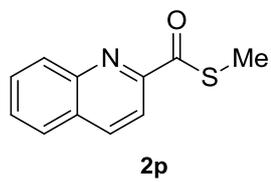




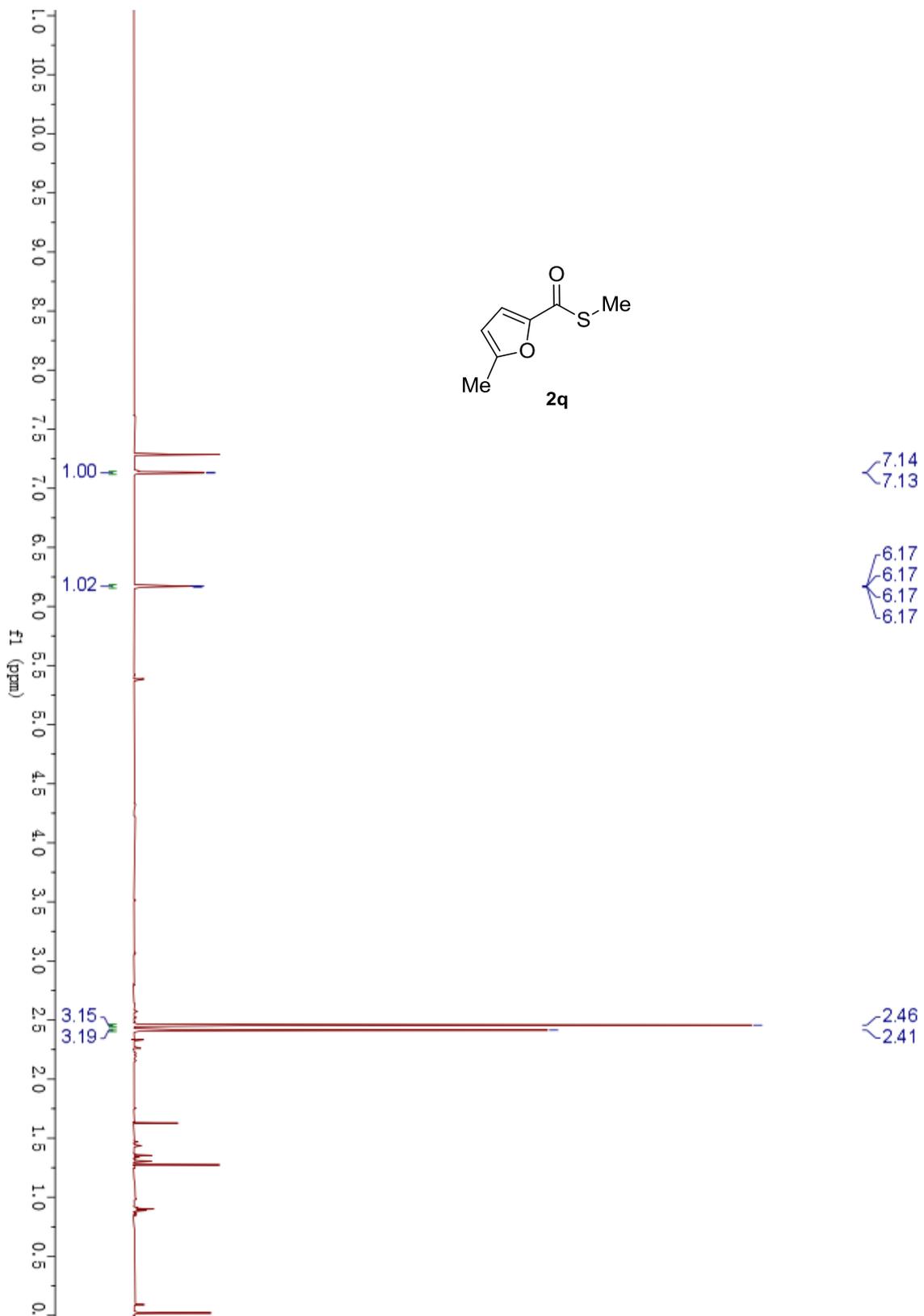


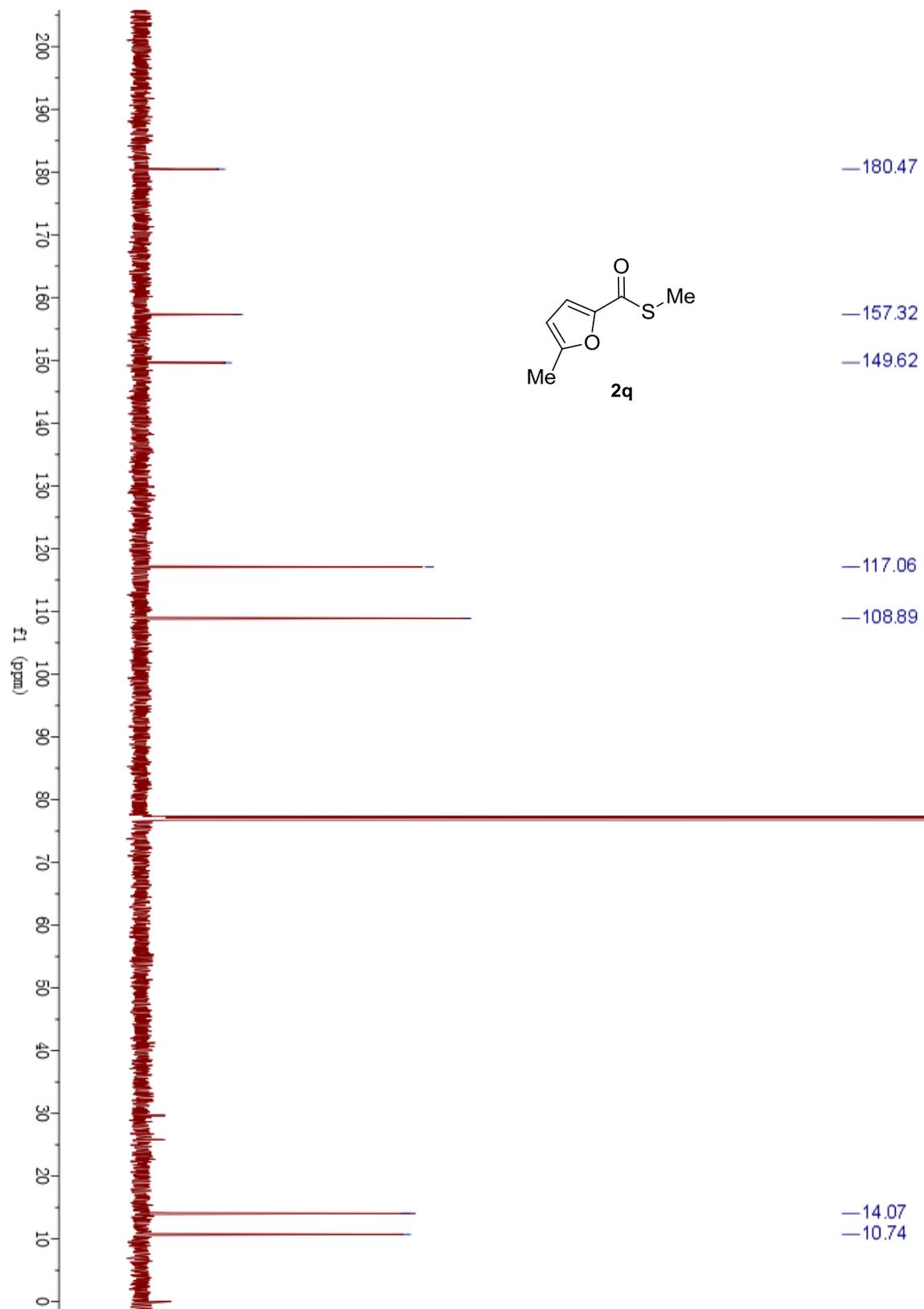


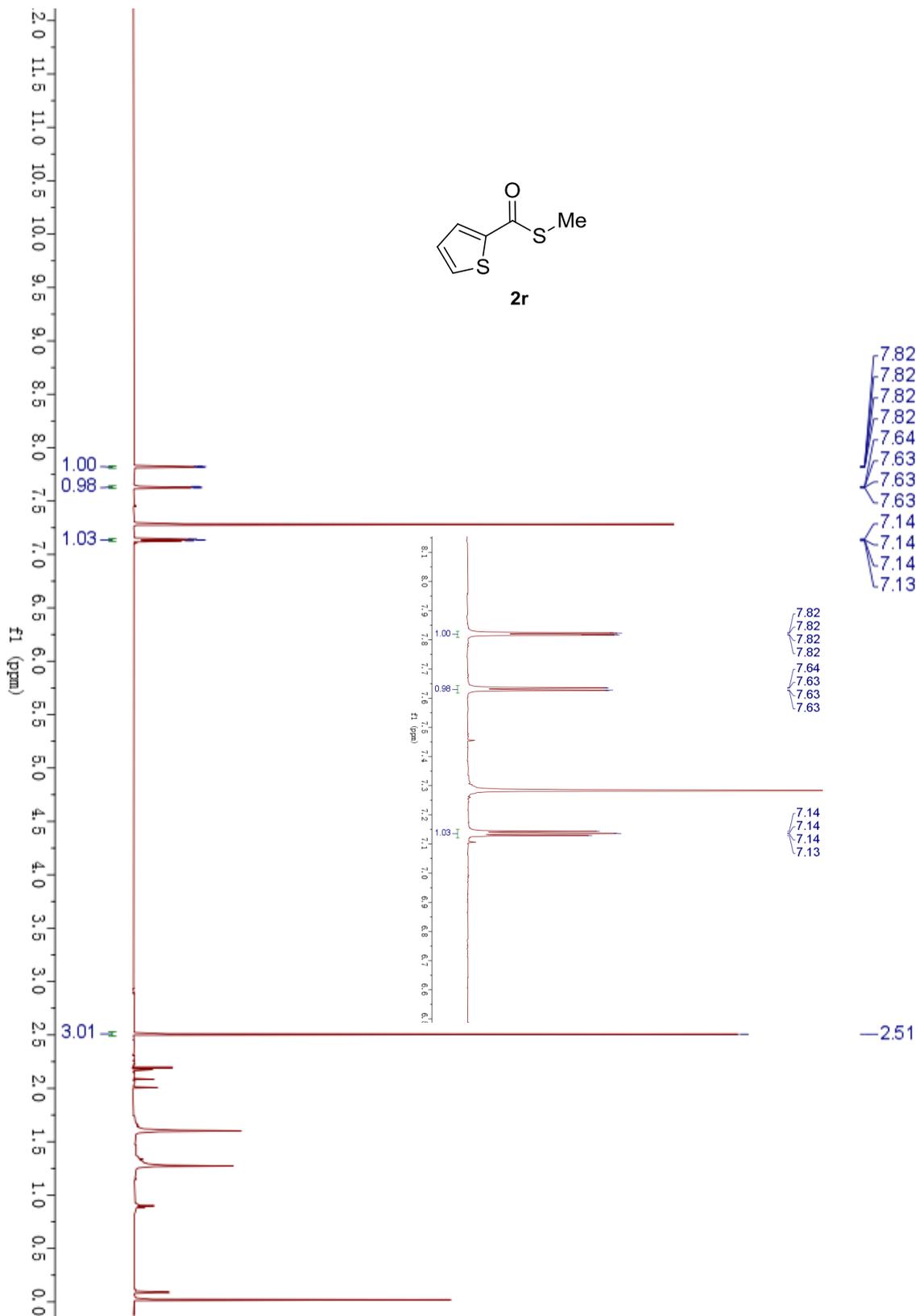


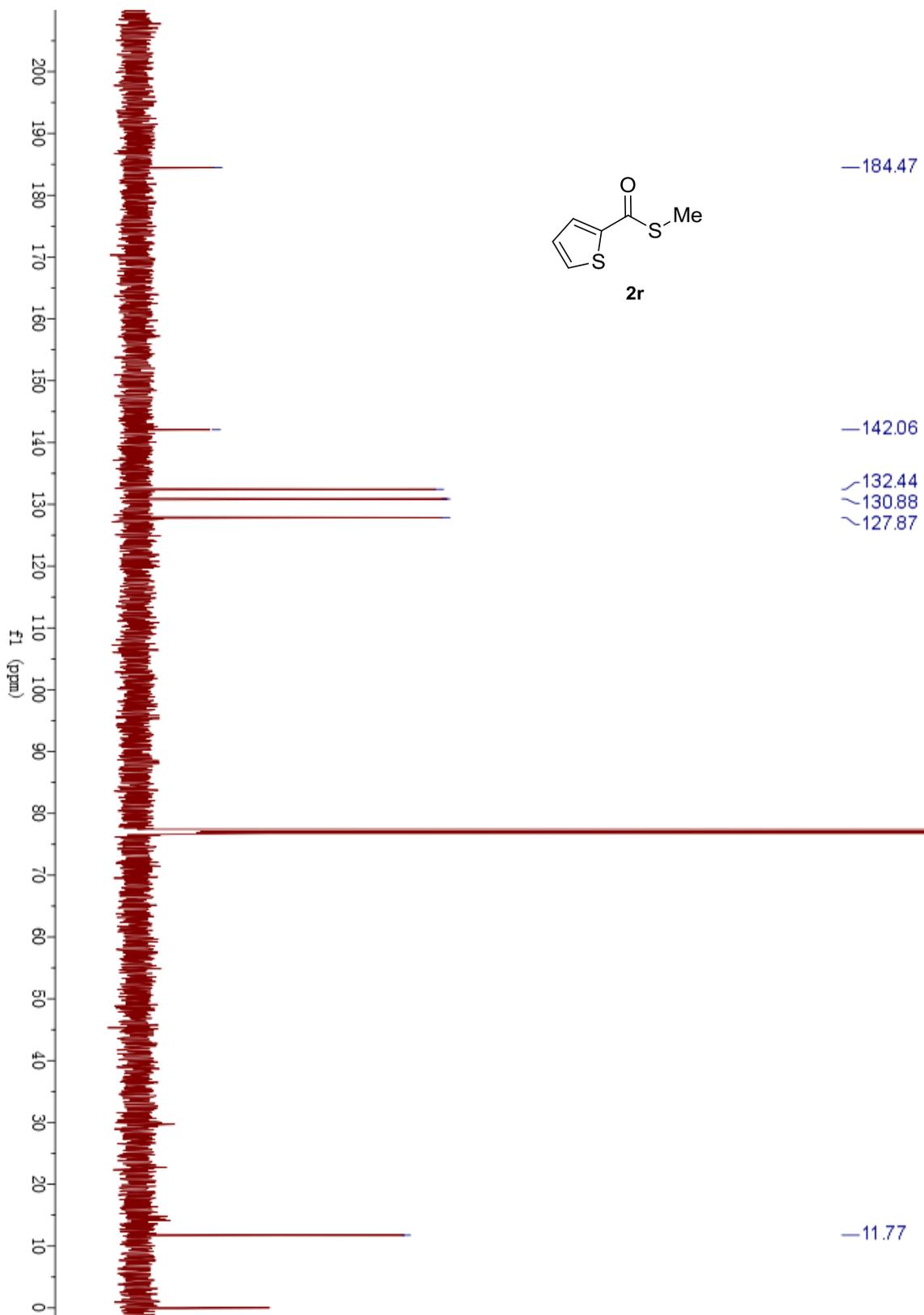


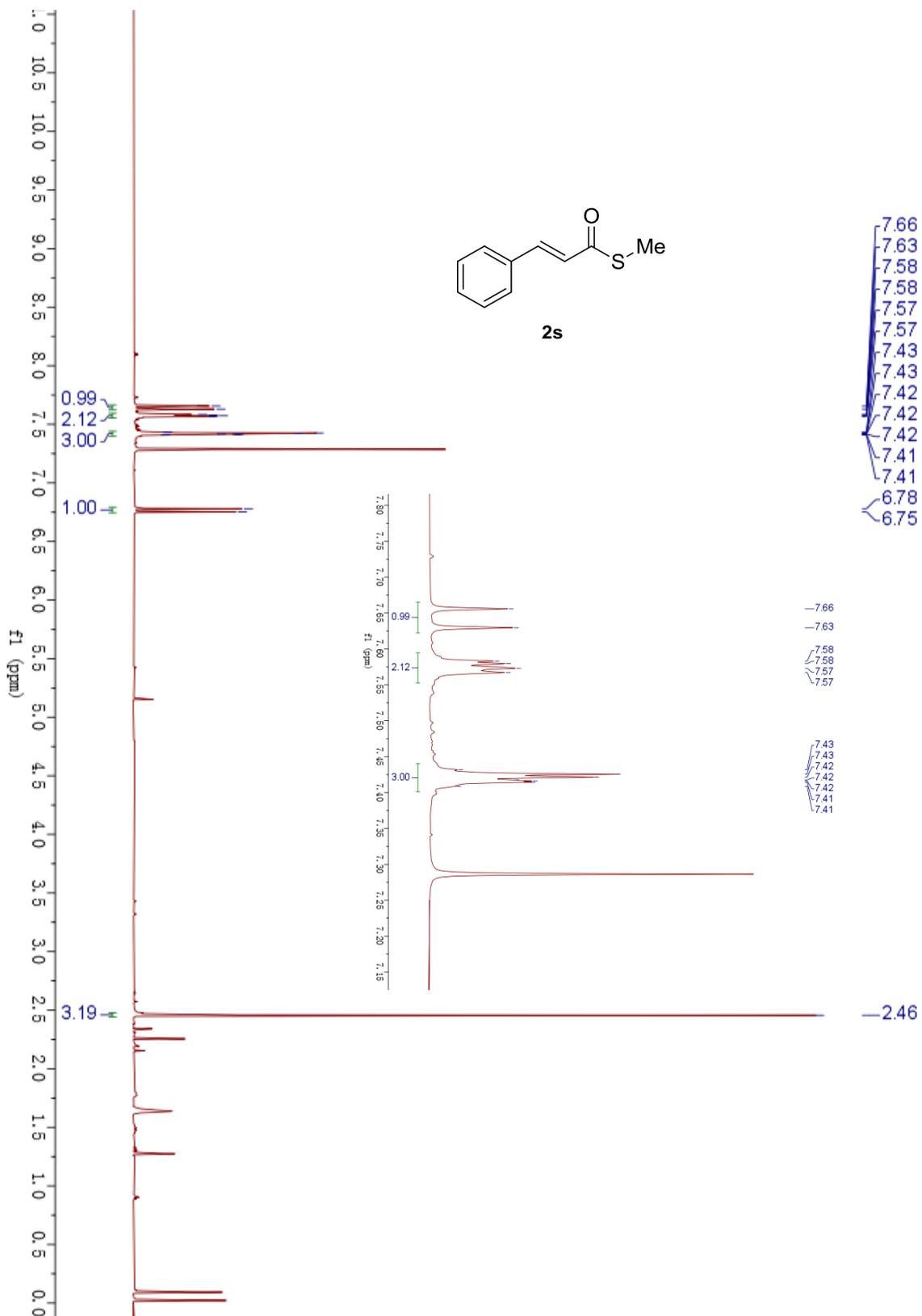


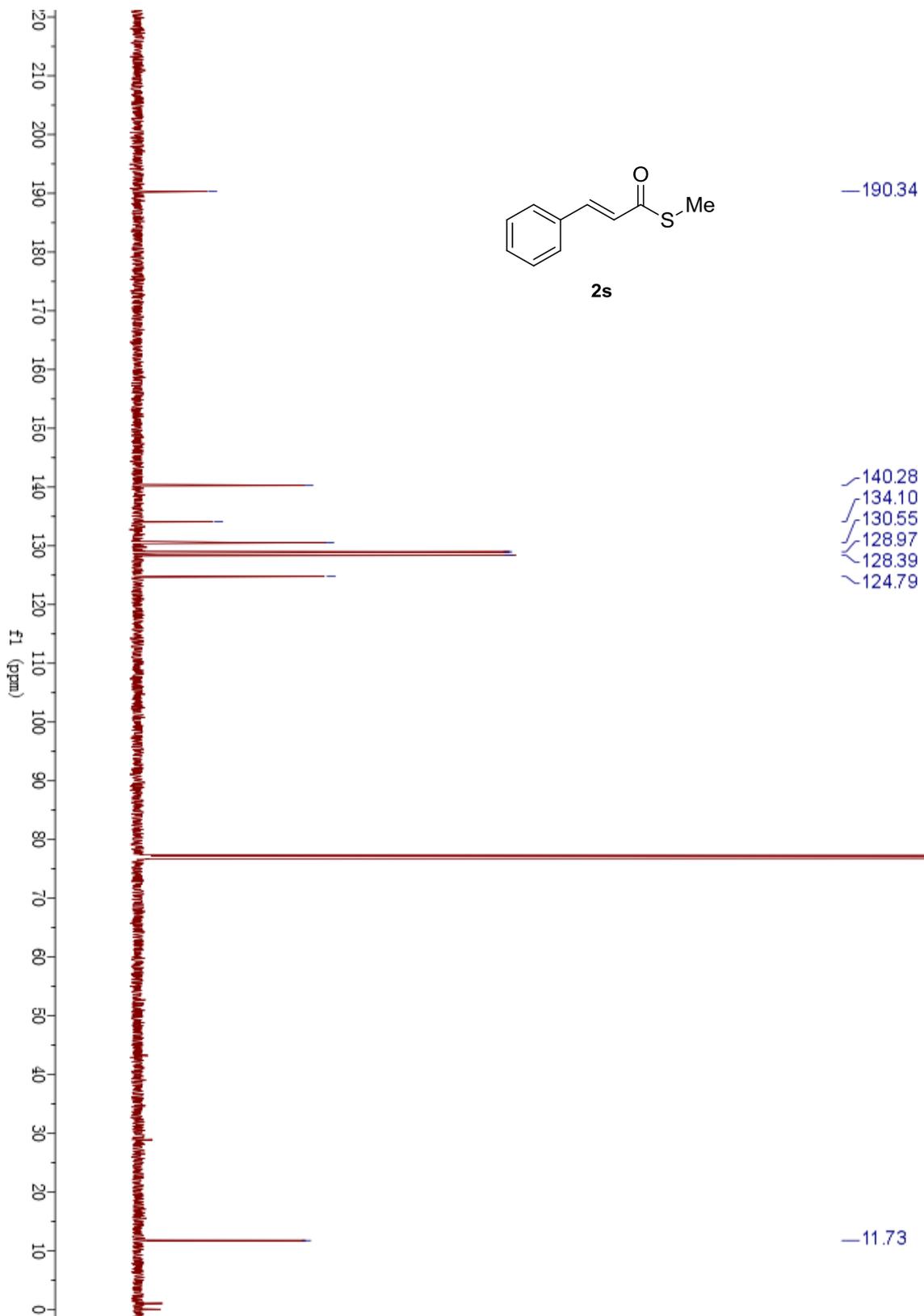


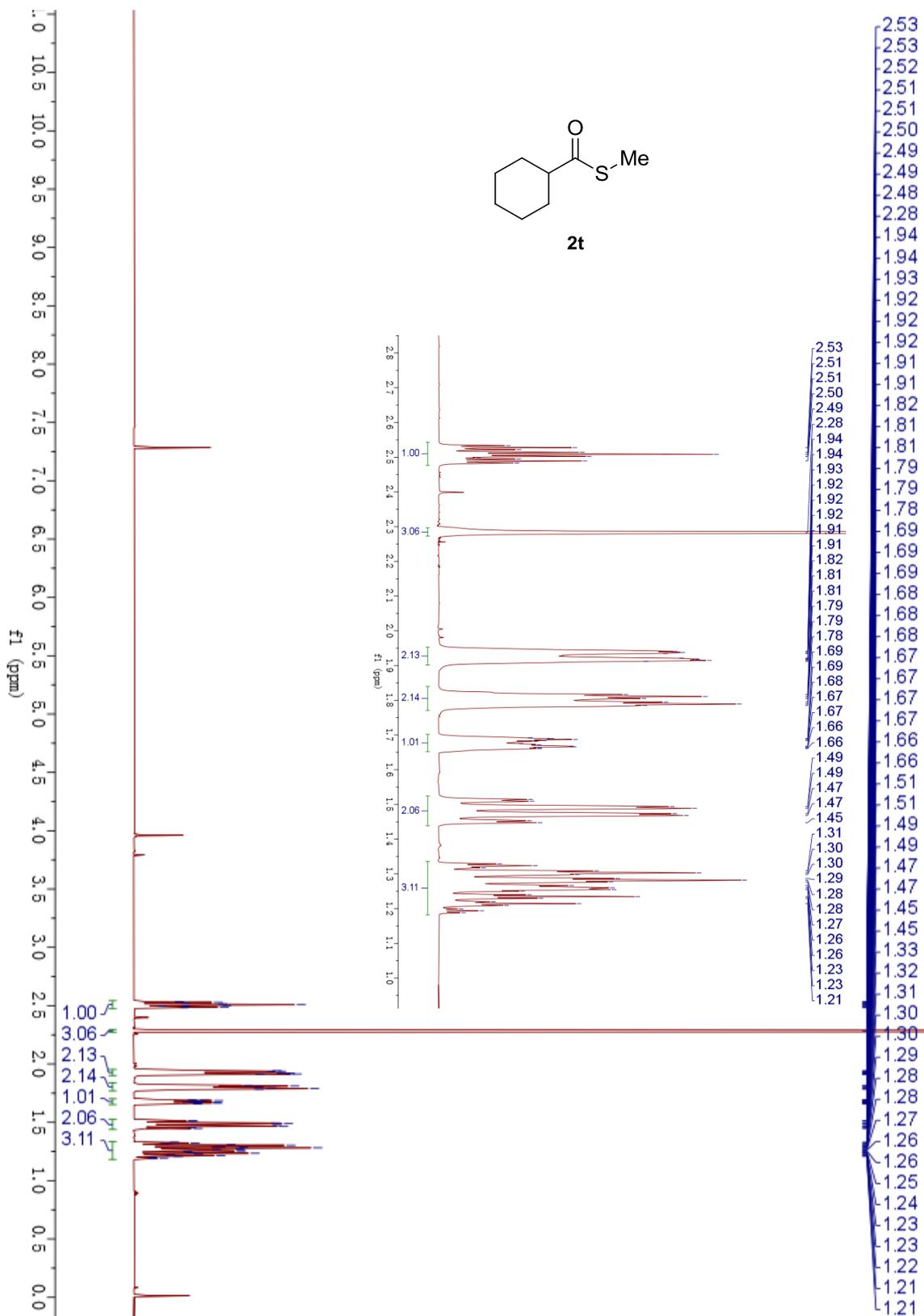


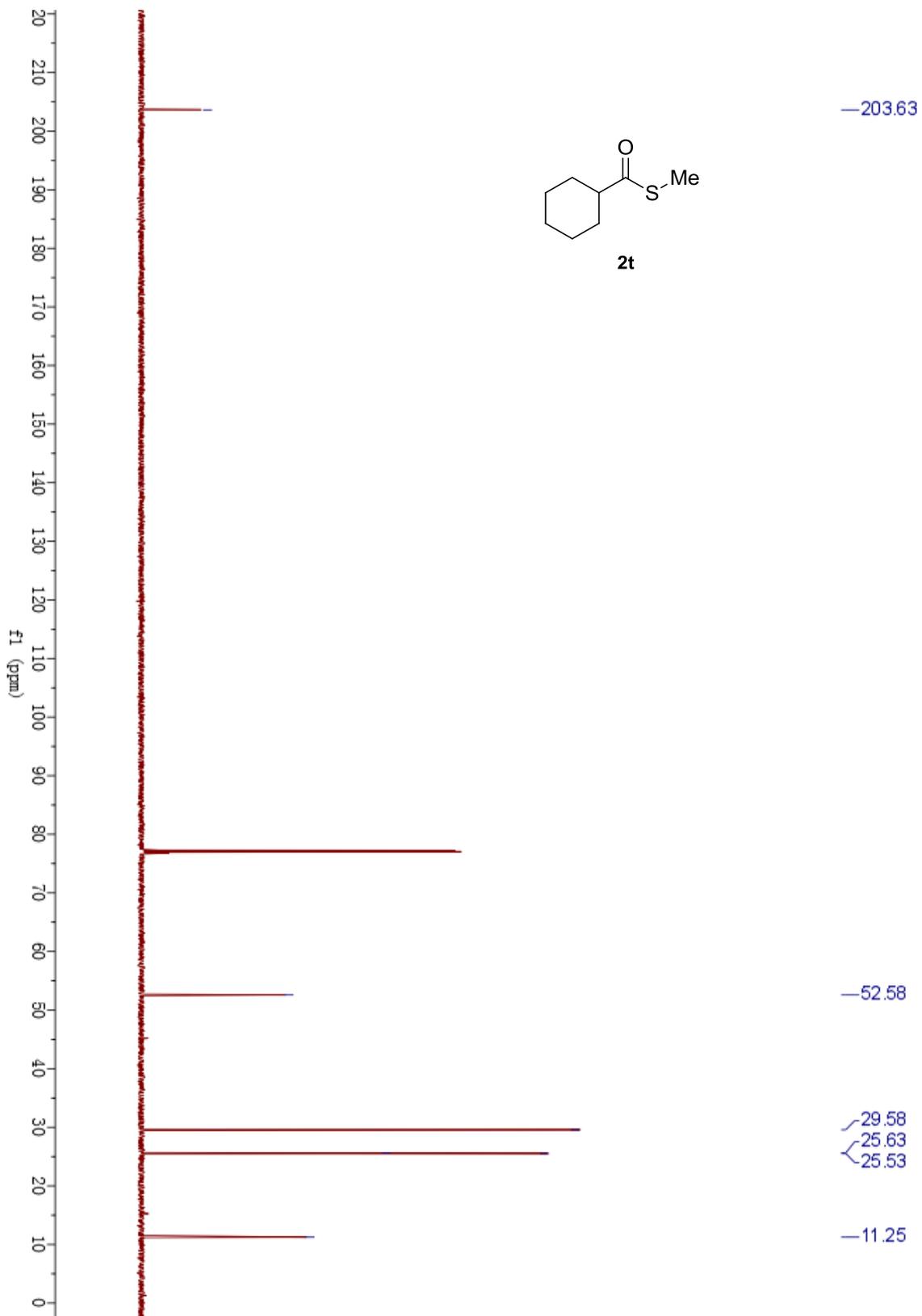


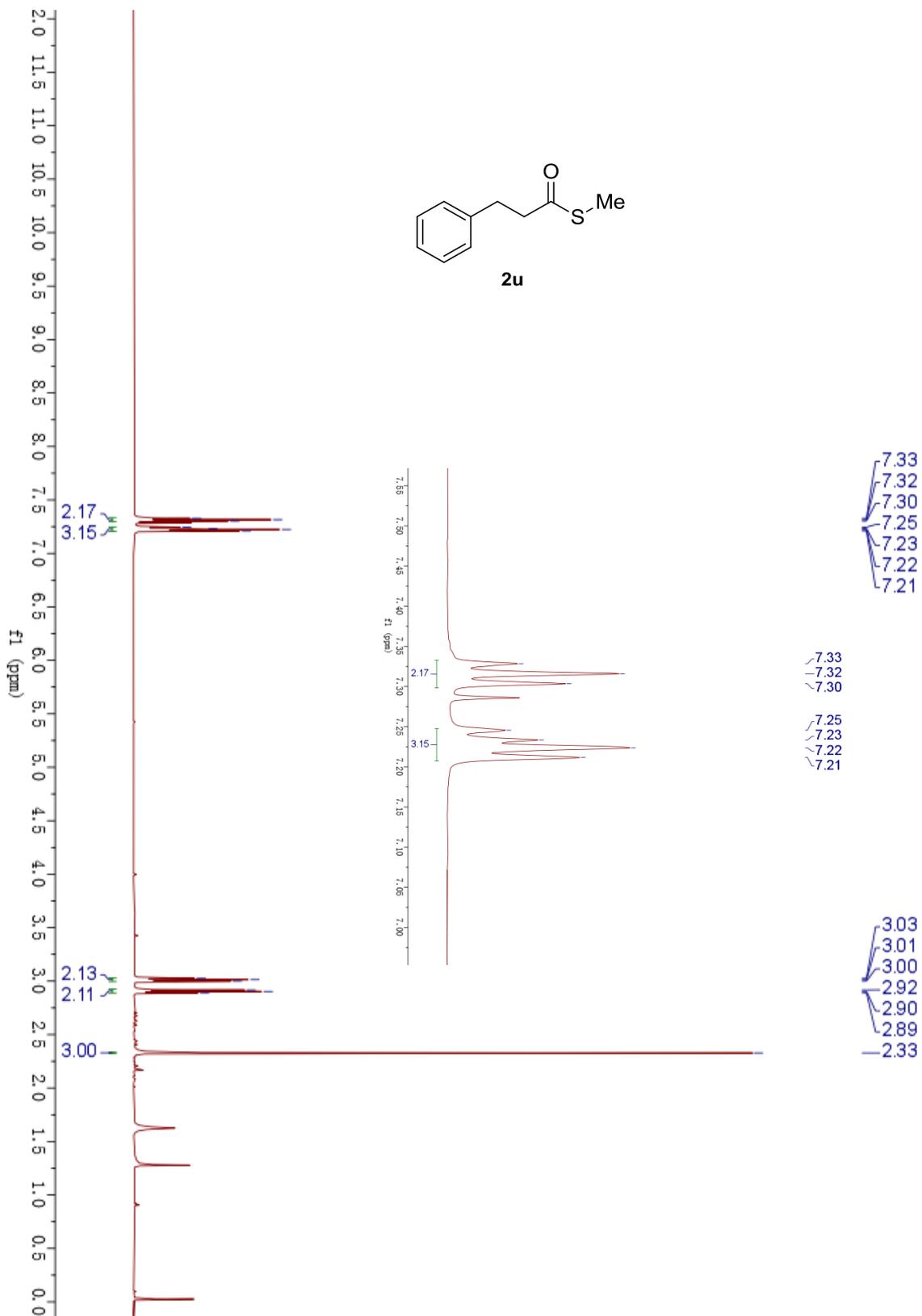
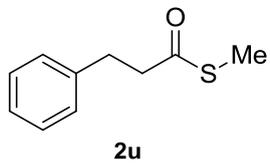


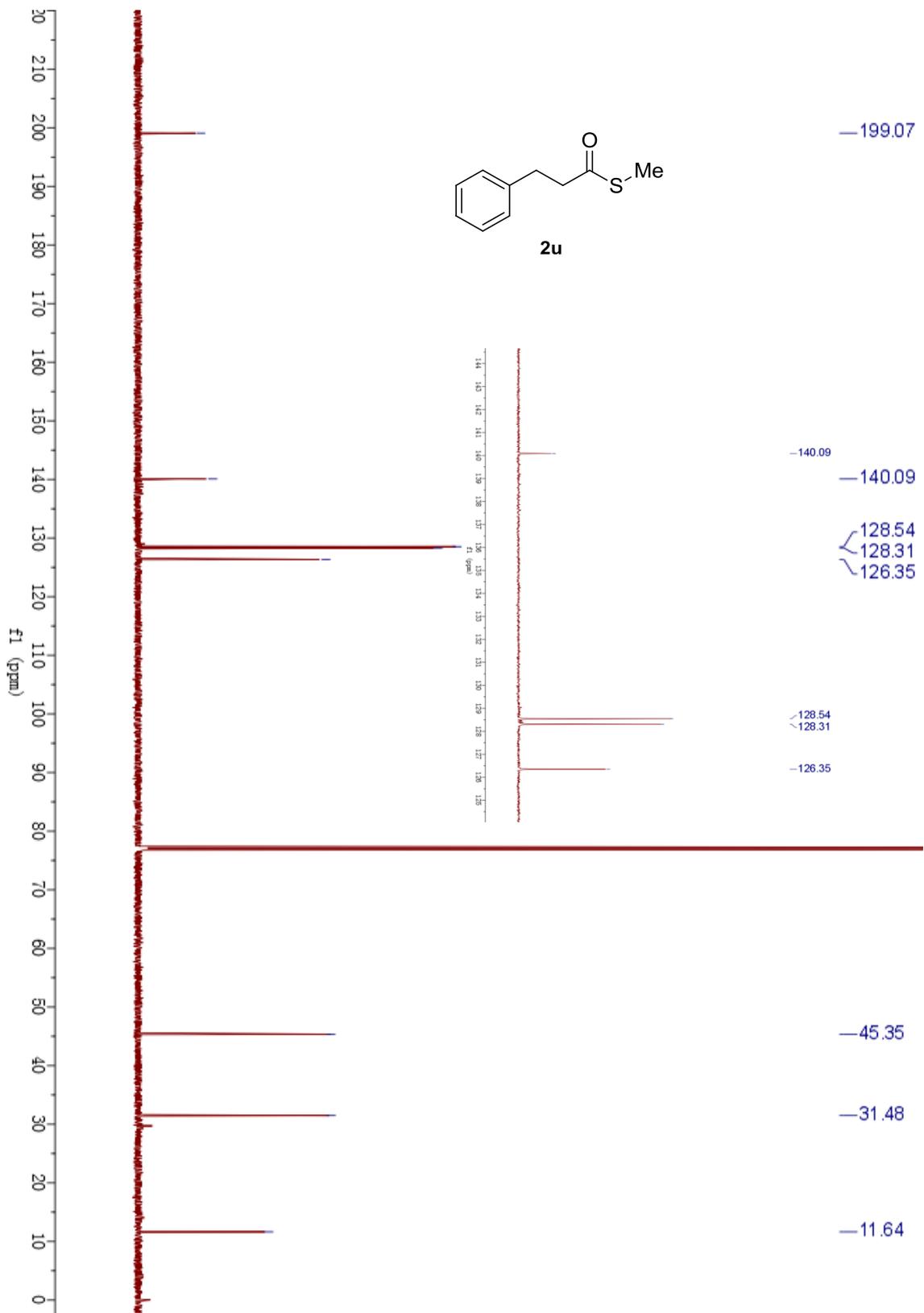


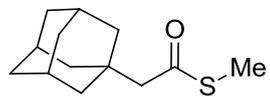




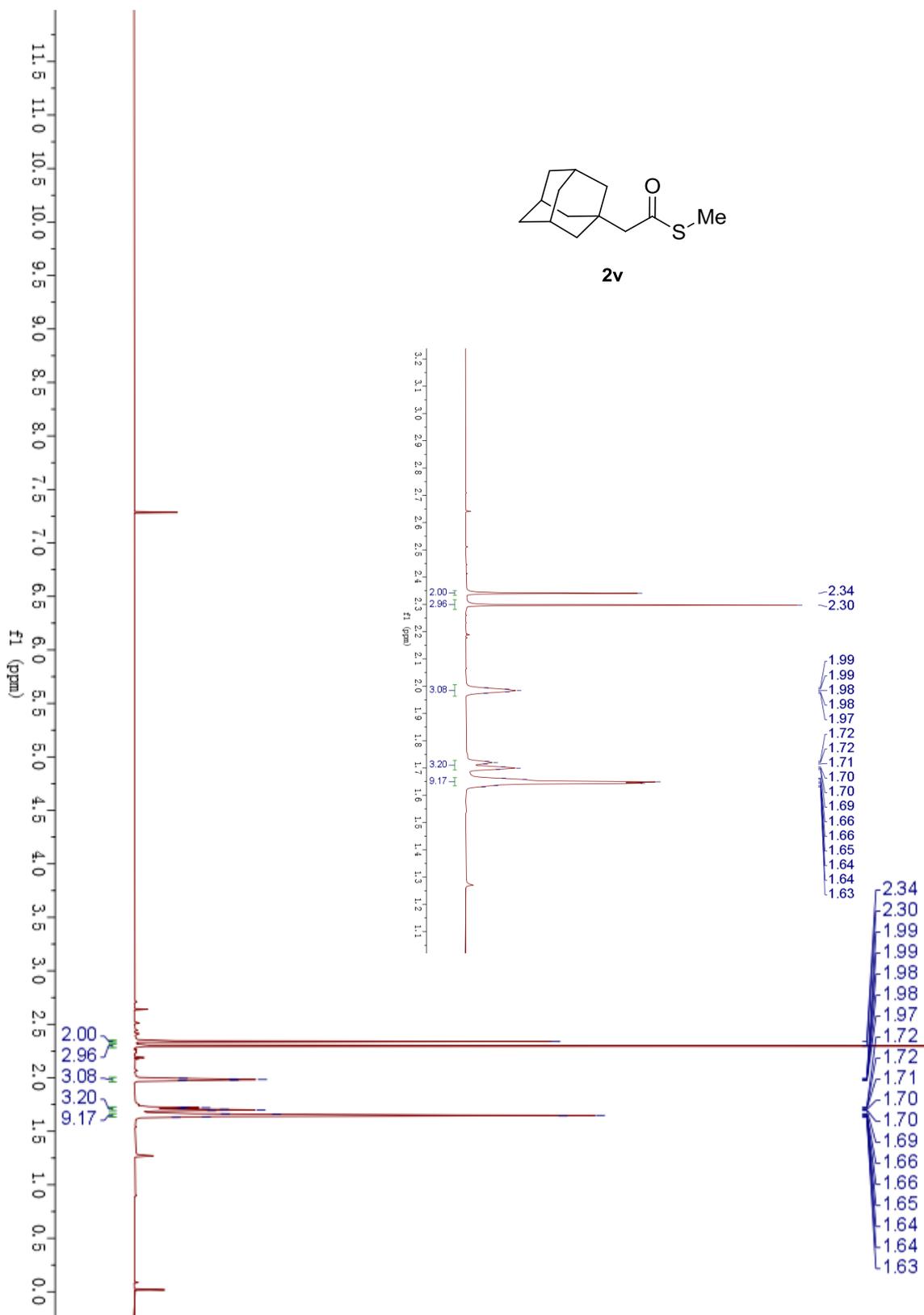


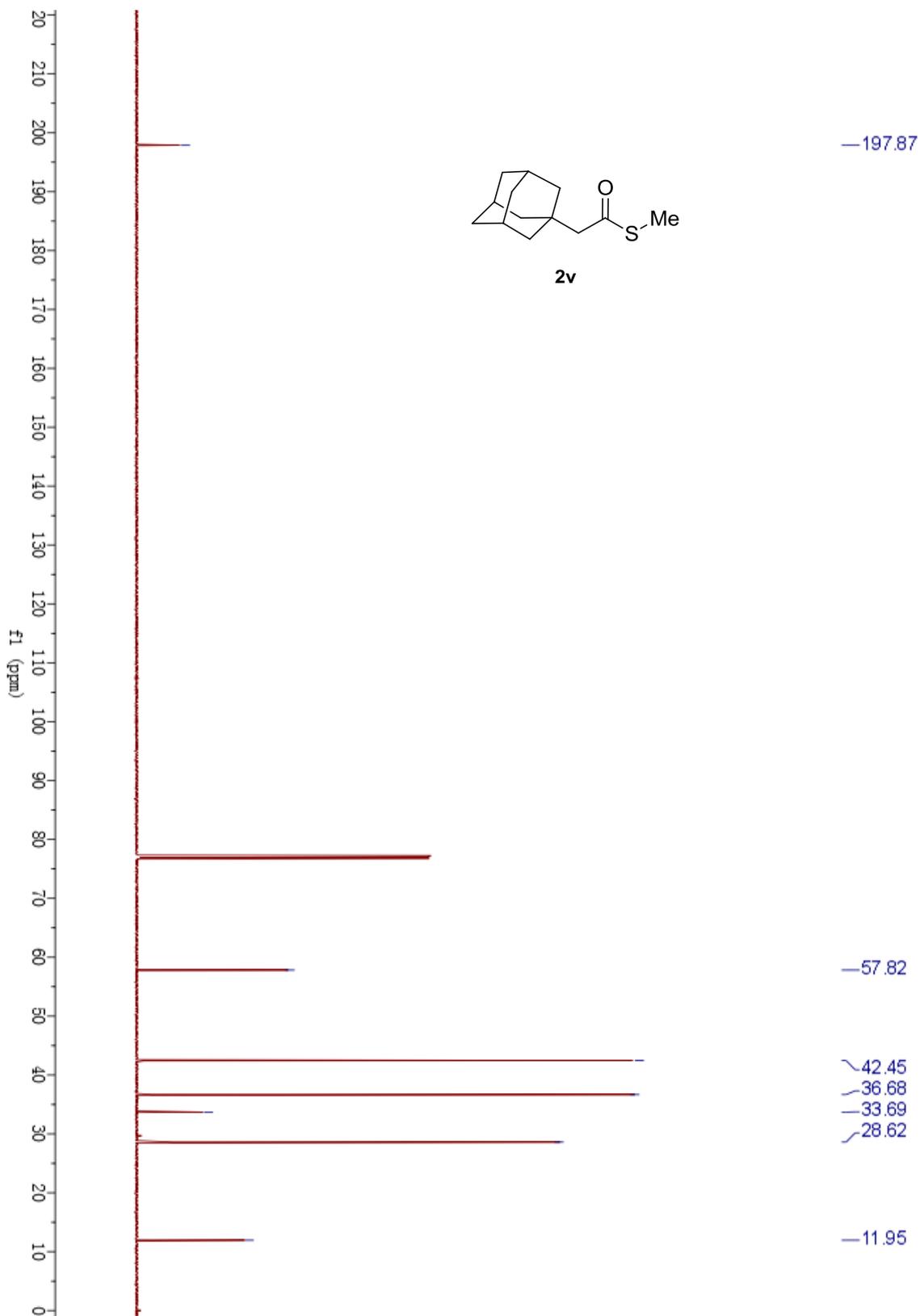


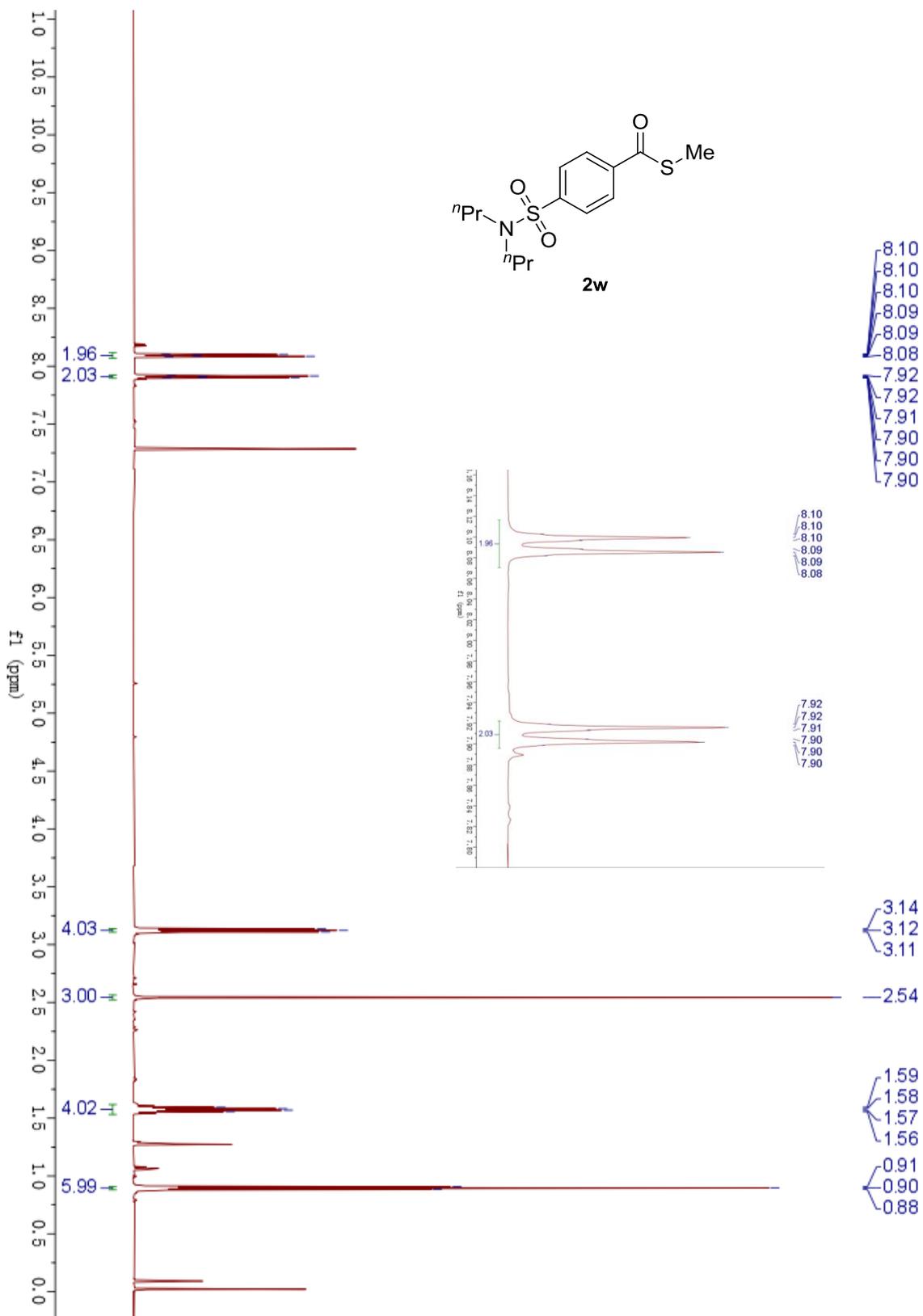


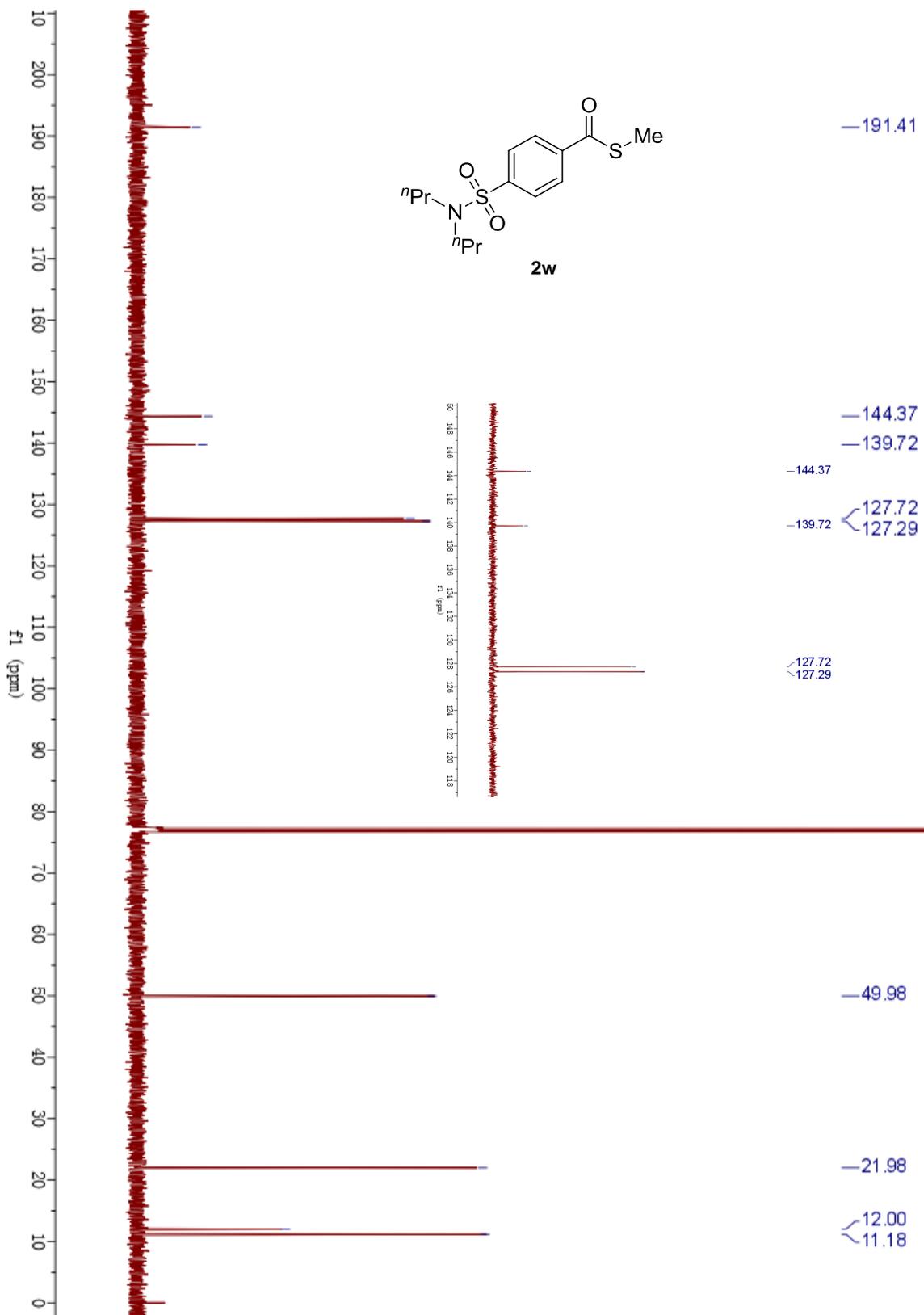


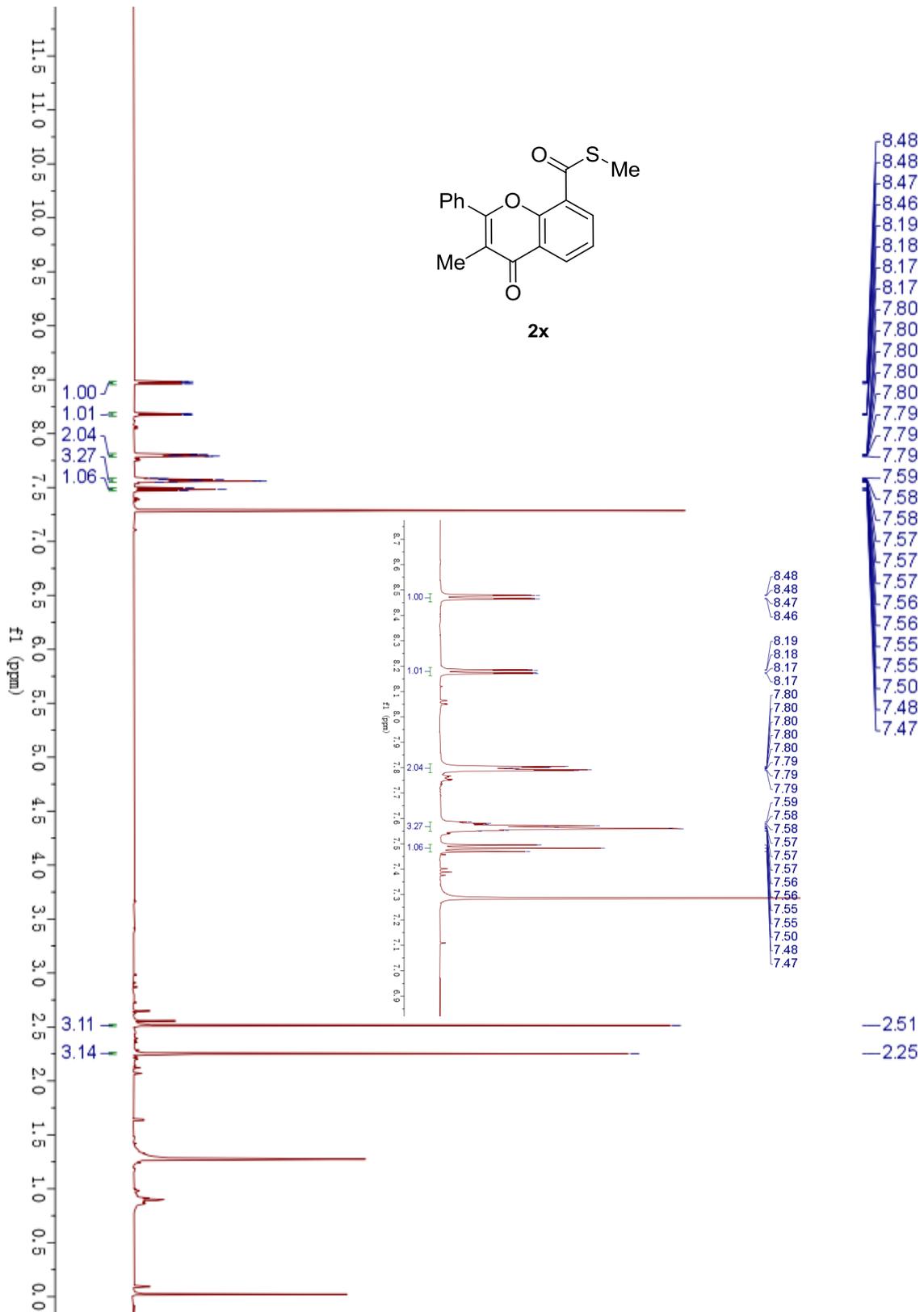
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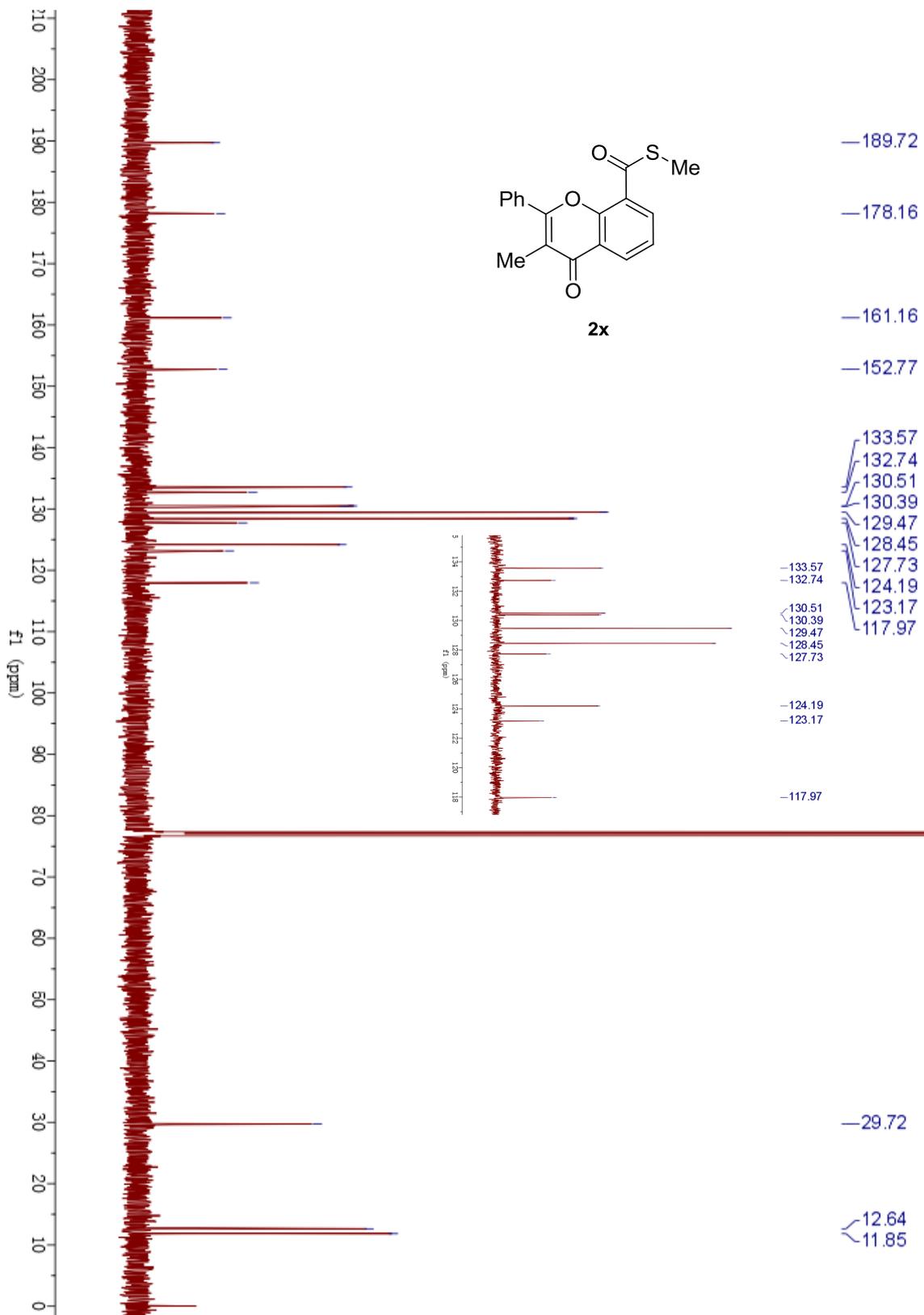


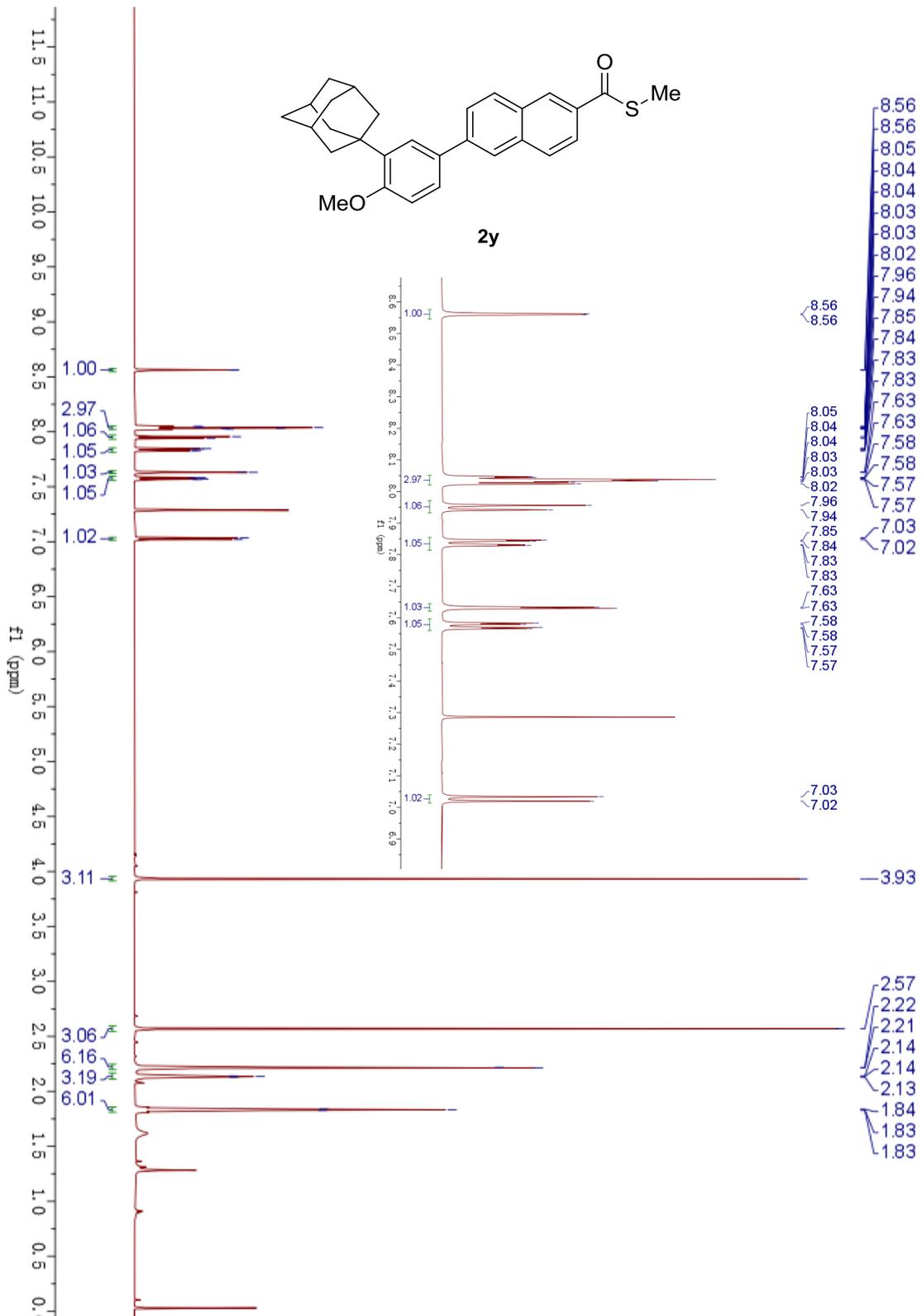


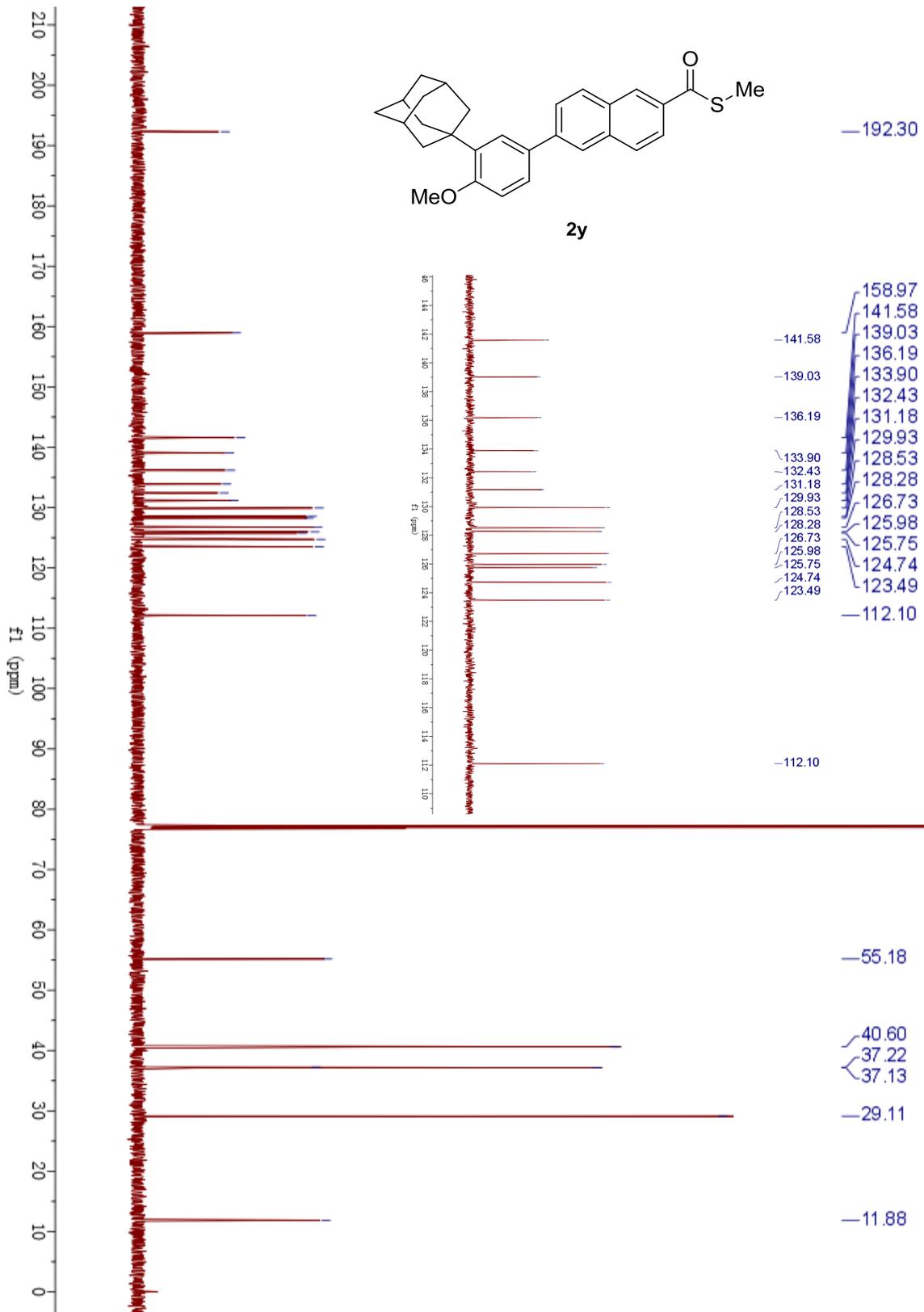


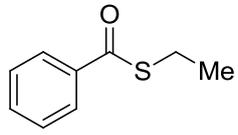












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