

## Supporting Information

for

# Rapid transformation of sulfinates into sulfonates promoted by a hypervalent iodine(III) reagent

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## General procedures, synthesis of the products, spectroscopic data, and copies of $^1\text{H}$ , $^{13}\text{C}$ , NMR spectra

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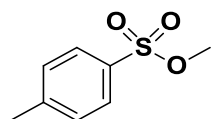
## I. General information and materials:

Unless otherwise indicated,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 300 and 75 MHz, respectively, in  $\text{CDCl}_3$  solutions. Chemical shifts are reported in ppm on the  $\delta$  scale. Multiplicities are described as s (singlet), d (doublet), dd, ddd, etc. (doublet of doublets, doublet of doublets of doublets, etc.), t (triplet), q (quartet), quin (quintuplet), sext (sextuplet), sept (septuplet), m (multiplet), and further qualified as app (apparent), br (broad). Coupling constants,  $J$ , are reported in Hz.

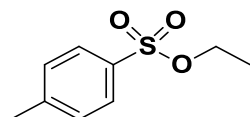
## II. Experimental procedures:

### a) General procedure for the formation of sulfonate 4:

Iodobenzene diacetate (DIB, 0.24 mmol, 1.2 equiv) was added at room temperature to a vigorously stirred solution of dichloromethane (0.5 mL), alcohol (0.5 mL), sulfinate (0.2 mmol, 1 equiv) and acetic acid (0.01 to 0.05 mL) or TBAC (55.5 mg, 0.2 mmol, 2 equiv) to solve the sulfonate salt. The mixture was then stirred for 15 min (followed by TLC with a mixture of acetic acid/ethyl acetate/hexane) and then filtered on silica with ethyl acetate. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to give sulfonate product **4**, **6** and **8**.



**Methyl 4-methylbenzenesulfonate (4a)**<sup>1</sup>: was prepared without dichloromethane and acetic acid, and was obtained by silica gel chromatography with a mixture of EtOAc/hexane (5/95) as a colorless oil: 0.20 mmol, 33 mg, 99% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J$  = 8.3 Hz, 2H), 7.35 (d,  $J$  = 8.0 Hz, 2H), 3.73 (s, 3H), 2.44 (s, 3H),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.1, 132.3, 130.0, 128.2, 56.3, 21.7; LRMS (ESI) calcd for  $\text{C}_8\text{H}_{11}\text{O}_3\text{S}$  ( $M + \text{H}$ )<sup>+</sup>: 187, found 187.

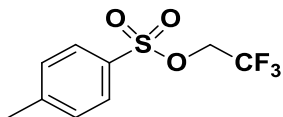


**Ethyl 4-methylbenzenesulfonate (4b)**<sup>2</sup>: was prepared without dichloromethane and acetic acid, and was obtained by silica gel chromatography with a mixture of EtOAc/hexane (5:95) as an yellow oil: 0.15 mmol, 30.5 mg, 75% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J$  = 8.4 Hz, 2H), 7.33 (d,  $J$  = 8.1 Hz, 2H), 4.09 (q,  $J$  = 7.1 Hz, 2H),

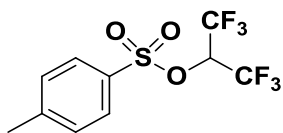
<sup>1</sup> Chandra, J.; Chaudhuri, R.; Rao Manne, S.; Mondal, S.; Mandal, B. *ChemistrySelect* **2017**, *2*, 8471

<sup>2</sup> Moussa, I. A.; Baniset, S. D.; Beinat, C.; Giboureau, N.; Reynolds, A. J.; Kassiou, M. *J. Med. Chem.* **2010**, *53*, 6228-6239

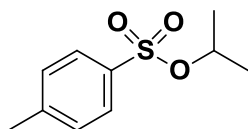
2.43 (s, 3H), 1.28 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.79, 133.38, 129.93, 127.94, 77.58, 77.16, 76.74, 66.92, 21.71, 14.80; LRMS (ESI) calcd for  $\text{C}_9\text{H}_{13}\text{O}_3\text{S}$  ( $\text{M}+\text{H}$ ) $^+$ : 201; found: 201.



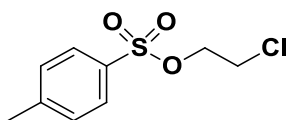
**2,2,2-Trifluoroethyl 4-methylbenzenesulfonate (4c)**<sup>3</sup>: was prepared without dichloromethane and was obtained by silica gel chromatography with a mixture of EtOAc/hexane (1:99) as a white foam: 0.190 mmol, 48.5 mg, 95% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.3$  Hz, 2H), 7.39 (d,  $J = 8.3$  Hz, 2H), 4.35 (q,  $J = 7.9$  Hz, 2H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 132.0, 130.3, 128.2, 122.0 (q,  $J = 277.7$  Hz), 64.7 (q,  $J = 38.1$  Hz), 21.8; LRMS calcd for  $\text{C}_9\text{H}_9\text{F}_3\text{O}_3\text{NaS}$  ( $\text{M}+\text{Na}$ ) $^+$ : 277; found: 277.



**1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methylbenzenesulfonate (4d)**<sup>3</sup>: was prepared without dichloromethane and was obtained by silica gel chromatography with a mixture of EtOAc/hexane (1:99) as a white foam: 0.097 mmol, 31.2 mg, 48% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 8.4$  Hz, 2H), 7.40 (d,  $J = 8.1$  Hz, 2H), 5.26 (sept,  $J = 5.7$  Hz, 1H), 2.48 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 132.1, 130.3, 128.3, 120.1 (q,  $J = 281$  Hz), 72.0 (septet,  $J = 35.5$  Hz), 22.0; LRMS calcd for  $\text{C}_{10}\text{H}_8\text{F}_6\text{NaO}_3\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 345; found: 345.



**Isopropyl 4-methylbenzenesulfonate (4e)**<sup>4</sup>: was prepared without dichloromethane and was obtained by silica gel chromatography with a mixture of EtOAc/hexane (5:95) as a yellow oil: 0.147 mmol, 31.5 mg, 74% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 8.3$  Hz, 2H), 7.32 (d,  $J = 8.0$  Hz, 2H), 4.72 (sept,  $J = 6.3$  Hz, 1H), 2.43 (s, 3H), 1.26 (d,  $J = 6.3$  Hz, 6H),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.5, 134.7, 129.9, 127.8, 77.2, 22.9, 21.7; LRMS calcd for  $\text{C}_{10}\text{H}_{15}\text{O}_3\text{S}$  ( $\text{M}+\text{H}$ ) $^+$ : 215; found: 215.



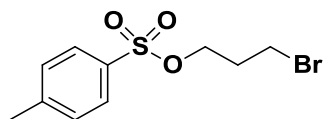
**2-Chloroethyl 4-methylbenzenesulfonate (4f)**<sup>5</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (5:95) as a yellow oil: 0.102 mmol, 24.0 mg, 51% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.3$  Hz, 2H), 7.36 (d,  $J = 8.1$  Hz,

<sup>3</sup> Miller, S. C. *J. Org. Chem.* **2010**, *75*(13), 4632-4635

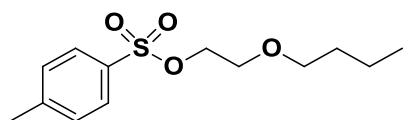
<sup>4</sup> Comagic, S.; Schirrmacher, R. *Synthesis* **2004**, *6*, 885-888

<sup>5</sup> Ameri David, R. L.; Kornfield, J. A. *Macromolecules* **2008**, *41*, 1151-1161

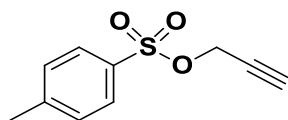
2H), 4.23 (t,  $J = 6.0$  Hz, 2H), 3.65 (t,  $J = 6.0$  Hz, 2H), 2.45 (s, 3H),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 133.7, 130.1, 128.1, 69.0, 40.9, 21.8; LRMS calcd for  $\text{C}_9\text{H}_{11}\text{ClNaO}_3\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 257; found: 257.



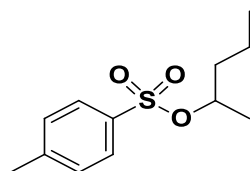
**3-Bromopropyl 4-methylbenzenesulfonate (4g)**<sup>6</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (8:92) as a colorless oil: 0.102 mmol, 30.0 mg, 51% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.3$  Hz, 2H), 7.35 (d,  $J = 8.0$  Hz, 2H), 4.17 (t,  $J = 5.8$  Hz, 2H), 3.41 (t,  $J = 6.3$  Hz, 2H), 2.45 (s, 3H), 2.23 – 2.11 (quin,  $J = 6.3$  Hz, 2H),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.1, 132.8, 130.1, 128.1, 67.9, 31.9, 28.6, 21.8; LRMS calcd for  $\text{C}_{10}\text{H}_{13}\text{BrNaO}_3\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 315; found: 315.



**2-Butoxyethyl 4-methylbenzenesulfonate (4h)**<sup>7</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (15:85) as a colorless oil: 0.114 mmol, 31.0 mg, 57% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.3$  Hz, 2H), 7.33 (d,  $J = 8.0$  Hz, 2H), 4.15 (dd,  $J = 5.4, 4.3$  Hz, 2H), 3.59 (dd,  $J = 5.4, 4.3$  Hz, 2H), 3.37 (t,  $J = 6.5$  Hz, 2H), 2.44 (s, 3H), 1.53– 1.37 (m, 2H), 1.37 – 1.20 (m, 2H), 0.88 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 133.2, 129.9, 128.1, 71.4, 69.5, 68.2, 31.7, 21.8, 19.3, 14.0; LRMS calcd for  $\text{C}_{13}\text{H}_{21}\text{O}_4\text{S}$  ( $\text{M}+\text{H}$ ) $^+$ : 273; found: 273.



**Prop-2-yn-1-yl 4-methylbenzenesulfonate (4i)**<sup>8</sup>: was prepared without dichloromethane and was obtained by silica gel chromatography with a mixture of EtOAc/hexane (15:85) as a colorless oil: 0.162 mmol, 34.0 mg, 81% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.3$  Hz, 2H), 7.37 (d,  $J = 8.0$  Hz, 2H), 4.72 (d,  $J = 2.5$  Hz, 2H), 2.50 (t,  $J = 2.5$  Hz, 1H), 2.48 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 133.0, 130.0, 128.3, 77.4, 75.5, 57.5, 21.8; LRMS calcd for  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{S}$  ( $\text{M}+\text{H}$ ) $^+$ : 211; found: 211.



**Pentan-2-yl 4-methylbenzenesulfonate (4j)**<sup>9</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (2:98) as a colorless oil: 0.120 mmol, 29.0

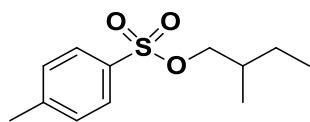
<sup>6</sup> Hromatka, O.; Stehlik, G.; Sauter, F. *Monatshefte fuer Chemie* **1960**, *91*, 107-116

<sup>7</sup> Hermet, P.; Lois-Sierra, S.; Bantignies, J.-L.; Rols, S.; Sauvajol, J.-L.; Serein-Spirau, F.; Lère-Porte, J.-P.; Moreau, J. J. E. *J. Phys. Chem. B* **2009**, *113*, 4197–4202

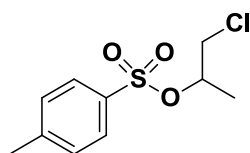
<sup>8</sup> Asano, K.; Matsubara, S. *Org. Lett.*, **2009**, *11*(8), 1757-1759

<sup>9</sup> Roque Pena, J. E., Alexanian, E. *J. Org. Lett.* **2017**, *19*(17), 4413-4415

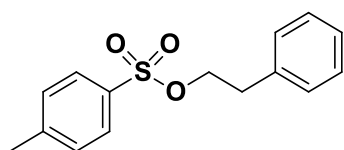
mg, 60% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.3$  Hz, 2H), 7.33 (d,  $J = 8.0$  Hz, 2H), 4.63 (sext,  $J = 6.2$  Hz, 1H), 2.44 (s, 3H), 1.70 – 1.37 (m, 2H), 1.37 – 1.15 (m, 5H), 0.82 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.5, 134.8, 129.8, 127.9, 80.6, 38.8, 21.8, 21.0, 18.3, 13.8; LRMS calcd for  $\text{C}_{12}\text{H}_{19}\text{O}_3\text{S}$  ( $\text{M}+\text{H}$ ) $^+$ : 243; found: 243.



**2-Methylbutyl 4-methylbenzenesulfonate (4k)**<sup>10</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (2:98) as a yellow oil: 0.152 mmol, 36.9 mg, 76% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 8.3$  Hz, 2H), 7.33 (d,  $J = 8.0$  Hz, 2H), 3.84 (qd,  $J = 9.4, 6.1$  Hz, 2H), 2.44 (s, 3H), 1.77 – 1.59 (m, 1H), 1.46 – 1.28 (m, 1H), 1.22 – 1.05 (m, 1H), 0.87 (d,  $J = 6.8$  Hz, 3H), 0.82 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 133.3, 129.9, 128.0, 74.9, 34.4, 25.5, 21.7, 16.1, 11.1; LRMS calcd for  $\text{C}_{12}\text{H}_{19}\text{O}_3\text{S}$  ( $\text{M}+\text{H}$ ) $^+$ : 243; found: 243.



**1-Chloropropan-2-yl 4-methylbenzenesulfonate (4l)**<sup>11</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (5:95) as a colorless oil: 0.129 mmol, 32.0 mg, 65% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.4$  Hz, 2H), 7.35 (d,  $J = 8.0$  Hz, 2H), 4.73 (sext,  $J = 6.0$  Hz, 1H), 3.53 (qd,  $J = 11.7, 5.4$  Hz, 2H), 2.45 (s, 3H), 1.37 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.1, 133.8, 130.0, 128.0, 77.7, 46.5, 21.8, 18.7; LRMS calcd for  $\text{C}_{10}\text{H}_{13}\text{ClNaO}_3\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$ : 271; found: 271.

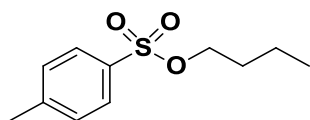


**Phenylethyl 4-methylbenzenesulfonate (4m)**<sup>12</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (10/90) as a colorless oil: 0.10 mmol, 27 mg, 50% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 8.3$  Hz, 2H), 7.31 (d,  $J = 8.0$  Hz, 2H), 7.28 - 7.24 (m, 3H), 7.14 (dd,  $J = 7.5, 1.8$  Hz, 2H), 4.24 (t,  $J = 7.1$  Hz, 2H), 2.98 (t,  $J = 7.1$  Hz, 2H), 2.45 (d,  $J = 4.9$  Hz, 3H),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.8, 136.3, 133.1, 129.9, 129.0, 128.7, 127.9, 127.0, 70.7, 35.4, 21.7. LRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{17}\text{O}_3\text{S}$  ( $\text{M} + \text{H}$ ) $^+$ : 277, found 277.

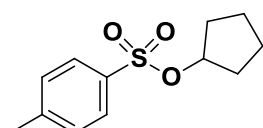
<sup>10</sup> Yang, Z.; Jin, X.; Guaciaro, M.; Molino, B. F. *J. Org. Chem.* **2012**, *77*, 3191–3196

<sup>11</sup> Sletzinger, M.; Chamberlin, E. M.; Tishl, M. *J. Am. Chem. Soc.*, **1952**, *74*, 5619–5620

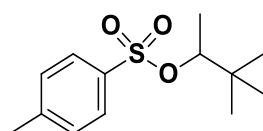
<sup>12</sup> Gao, J.; Pan, X.; Liu, J.; Lai, J.; Chang, L.; Yuan, G. *RSC Adv.*, **2015**, *5*, 27439



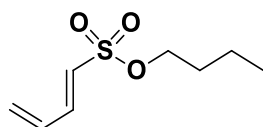
**Butyl 4-methylbenzenesulfonate (4o)**<sup>1</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (10/90) as a colorless oil: 0.14 mmol, 32 mg, 70% yield; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 2.45 (s, 3H), 1.68 – 1.56 (m, 2H), 1.34 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 144.8, 133.3, 129.9, 128.0, 70.5, 30.9, 21.7, 18.7, 13.5. LRMS (ESI) calcd for C<sub>11</sub>H<sub>17</sub>O<sub>3</sub>S (M + H)<sup>+</sup>: 229, found 229.



**Cyclopentyl 4-methylbenzenesulfonate (4p)**<sup>9</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (2:98) as a colorless foam: 0.125 mmol, 30.0 mg, 63% yield; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.01 – 4.90 (m, 1H), 2.45 (s, 3H), 1.89 – 1.64 (m, 6H), 1.60 – 1.44 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 144.5, 134.7, 129.9, 127.8, 85.6, 33.2, 23.2, 21.7; LRMS calcd for C<sub>12</sub>H<sub>17</sub>O<sub>3</sub>S (M+H)<sup>+</sup>: 241; found: 241.

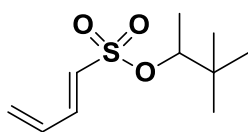


**3,3-Dimethylbutan-2-yl 4-methylbenzenesulfonate (6)**<sup>13</sup>: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (98:2) as a yellow foam: 0.090 mmol, 23.0 mg, 45% yield; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.40 (q, *J* = 6.4 Hz, 1H), 2.45 (s, 3H), 1.22 (d, *J* = 6.4 Hz, 3H), 0.85 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 144.4, 134.9, 129.8, 127.9, 87.8, 35.0, 25.7, 21.6, 16.1; LRMS Calc. for C<sub>13</sub>H<sub>20</sub>NaO<sub>3</sub>S (M+Na)<sup>+</sup>: 279; found: 279.

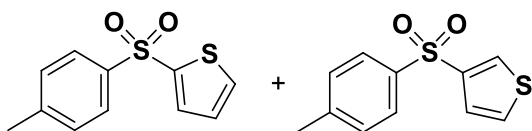


**(E)-Butyl buta-1,3-diene-1-sulfonate (8a)**: was obtained by silica gel chromatography with a mixture of EtOAc/hexane (90/10) as a colorless oil: 0.14 mmol, 27 mg, 72% yield; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.27 (m, 1H), 6.71 (t, *J* = 11.2 Hz, 1H), 6.09 (dd, *J* = 11.0, 0.7 Hz, 1H), 5.68 (s, 1H), 5.66 – 5.62 (m, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 1.77 – 1.64 (m, 2H), 1.42 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 143.2, 130.4, 129.1, 122.6, 70.5, 31.1, 18.8, 13.6; LRMS (ESI) calcd for C<sub>8</sub>H<sub>15</sub>O<sub>3</sub>S (M + H)<sup>+</sup> 191, found 191.

<sup>13</sup>Yoshida, Y.; Sakakura, Y.; Aso, N.; Okada, S.; Tanabe, Yo. *Tetrahedron* **1999**, *55* (8), 2183-2192



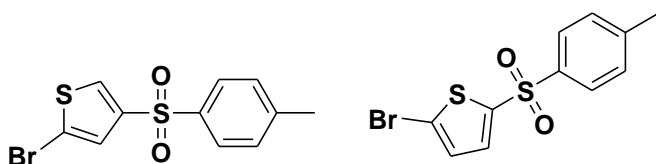
**(E) 3,3-Dimethylbutan-2-yl buta-1,3-diene-1-sulfonate (8b):** was obtained by silica gel chromatography with a mixture of EtOAc/hexane (10/90) as a colorless oil: 0.74 mmol, 16 mg, 37% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.30 (m, 1H), 6.64 (t,  $J$  = 11.2 Hz, 1H), 6.12 (dd,  $J$  = 11.1, 0.8 Hz, 1H), 5.66 (d,  $J$  = 0.6 Hz, 1H), 5.61 (dd,  $J$  = 3.2, 2.4 Hz, 1H), 4.43 (q,  $J$  = 6.4 Hz, 1H), 1.36 (d,  $J$  = 6.4 Hz, 3H), 0.95 (s, 9H),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 130.5, 128.6, 124.2, 88.0, 35.1, 25.8, 16.3; LRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{18}\text{O}_3\text{SNa}$  ( $\text{M} + \text{Na}$ ) $^+$  241, found 241.



**2-Tosylthiophene and 3-tosylthiophene (9a and 9b):** Iodobenzene diacetate (DIB, 0.24 mmol, 1.2 equiv) in solution of thiophene (1.0 mL) was added at room temperature to a vigorously stirred solution of thiophene (1.0 mL) with sulfinate (0.2 mmol, 1 equiv) and acetic acid (0.05 mL) to dissolve the sulfonate salt. The mixture was then stirred for 25 min (followed by TLC with a mixture of acetic acid/ethyl acetate/hexane) and then concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of (50/50) dichloromethane/hexane.

**9a<sup>14</sup>** was obtained as a white foam: 0.031 mmol, 7.4 mg, 15% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J$  = 8.1 Hz, 2H), 7.67 (dd,  $J$  = 3.9, 1.3 Hz, 1H), 7.62 (dd,  $J$  = 5.0, 1.5 Hz, 1H), 7.31 (d,  $J$  = 8.1 Hz, 2H), 7.06 (dd,  $J$  = 5.1, 3.9 Hz, 1H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.47, 143.68, 139.29, 133.68, 133.18, 130.09, 127.89, 127.54, 77.58, 77.16, 76.74, 21.75; LRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{S}_2$  ( $\text{M} + \text{H}$ ) $^+$ : 239; found: 239.

**9b<sup>15</sup>** was obtained as a white foam: 0.016 mmol, 3.8 mg, 8% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (dd,  $J$  = 3.0, 1.5 Hz, 1H), 7.84 (d,  $J$  = 8.1 Hz, 2H), 7.38-7.35 (m, 1H), 7.34 – 7.28 (m, 2H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.41, 142.60, 138.84, 131.32, 130.07, 128.37, 127.68, 125.96, 77.58, 77.16, 76.74, 21.73; LRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{S}_2$  ( $\text{M} + \text{H}$ ) $^+$ : 239; found: 239.



**2-Bromo-4-tosylthiophene and 2-bromo-5-tosylthiophene (10a and 10b):** Iodobenzene diacetate (DIB, 0.40 mmol, 2 equiv) in DCM

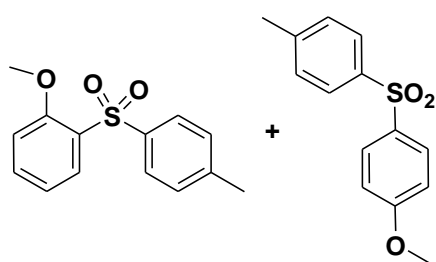
<sup>14</sup> Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Parisi, L. M. *Org. Lett.* **2002**, *4*, 4719-4721

<sup>15</sup> Olah, G. A.; Kobayashi, S.; Nishimura, J. *J. Am. Chem. Soc.* **1973**, *95*, 564-569

(0.5 mL) was added to a vigorously stirred solution of sulfinate **1** (0.2 mmol, 1 equiv) in (0.5 mL) 2-bromothiophene and (0.5 mL) dichloromethane and trifluoroacetic acid (0.05 mL) was introduced to dissolve the sulfinate, at room temperature. The mixture was then stirred for 25 min (followed by TLC with a mixture of acetic acid/ethyl acetate/hexane) and then concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of 5/95 ethyl acetate/hexane. **10a** was obtained as a brown solid, 13 mg, 20% yield and **10b** 6mg 10% yield.

**(10a):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J$  = 8.3 Hz, 2H), 7.42 (d,  $J$  = 4.0 Hz, 1H), 7.32 (d,  $J$  = 8.1 Hz, 2H), 7.03 (d,  $J$  = 4.0 Hz, 1H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.85, 144.46, 138.77, 133.20, 130.88, 130.23, 127.57, 121.90, 21.77. LRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{10}\text{BrO}_2\text{S}_2$  ( $\text{M} + \text{H}$ ) $^+$ : 316, found: 316.

**(10b):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J$  = 8.3 Hz, 2H), 7.44 (d,  $J$  = 5.8 Hz, 1H), 7.33 (d,  $J$  = 8.0 Hz, 2H), 7.29 (d,  $J$  = 5.8 Hz, 1H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  144.8, 140.4, 138.0, 129.9, 128.8, 128.1, 126.9, 117.7, 21.8; LRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{10}\text{BrO}_2\text{S}_2$  ( $\text{M} + \text{H}$ ) $^+$ : 316, found: 316.



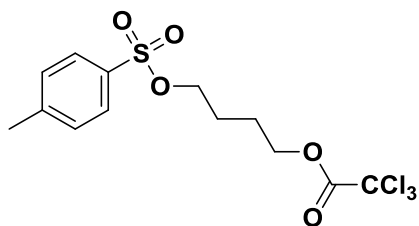
**ortho-Tosylanisole and para-tosylanisole (11a and 11b):**

Iodobenzene diacetate (DIB, 0.24 mmol, 1.2 equiv) in solution in (1.0 mL) of anisole was added to a vigorously stirred solution of sulfinate (0.2 mmol, 1 equiv) in anisole (1.0 mL) and acetic acid (0.05 mL) was introduced at room temperature. The mixture was then stirred for 25 min (followed by TLC with a mixture of acetic acid/ethyl acetate/hexane) and then concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of 5:95 ethyl acetate/hexane (for compound **11**). It was obtained as a white foam: 0.027mmol, (3.6 mg each) 7.2 mg, 14% total yield.

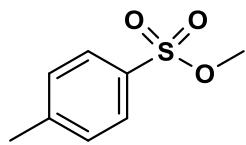
**(11a)**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (dd,  $J$  = 6.3, 1.5 Hz, 1H), 7.85 (d,  $J$  = 8.4 Hz, 2H), 7.50 (dt,  $J$  = 5.7, 1.8 Hz, 1H), 7.28 (d,  $J$  = 8.4 Hz, 2H), 7.09 (dt,  $J$  = 7.5, 0.9 Hz, 1H), 6.89 (d,  $J$  = 8.7 Hz, 1H), 3.77 (s, 3H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  157.19, 143.89, 138.73, 135.45, 129.95, 129.49, 129.26, 128.63, 120.64, 112.57, 77.58, 77.16, 76.74, 56.00, 21.74.

**(11b)**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J$  = 8.7 Hz, 2H), 7.79 (d,  $J$  = 8.4 Hz, 2H), 7.28 (d,  $J$  = 8.7 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 143.9, 139.6, 133.7, 130.0, 129.9, 127.5, 114.6, 77.6, 77.2, 76.7, 55.8, 21.7. LRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{15}\text{O}_3\text{S}$  ( $\text{M} + \text{H}$ ) $^+$ : 263, found : 263.





**4-(Tosyloxy)butyl 2,2,2 trichloroacetate (12):** Iodobenzene diacetate (DIB, 0.24 mmol, 1.2 equiv) in solution of tetrahydrofuran (1.0 mL) was added at room temperature to a vigorously stirred solution of tetrahydrofuran (1.0 mL) with sulfinate (0.2 mmol, 1 equiv) and trichloroacetic acid (0.05 mL) to dissolve the sulfonate salt. The mixture was then stirred for 25 min (followed by TLC with a mixture of acetic acid/ethyl acetate/hexane) and then concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of 5/95 ethyl acetate/hexane. **12** was obtained as a white foam: 0.80mmol, 31.4 mg, 40% yield;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.4$  Hz, 2H), 7.35 (d,  $J = 8.1$  Hz, 2H), 4.33 (t,  $J = 6.0$  Hz, 2H), 4.09 (t,  $J = 5.8$  Hz, 2H), 2.45 (s, 3H), 1.95 – 1.66 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.02, 145.09, 133.07, 130.06, 128.03, 89.87, 77.58, 77.16, 76.74, 69.59, 68.52, 25.48, 24.65, 21.79.



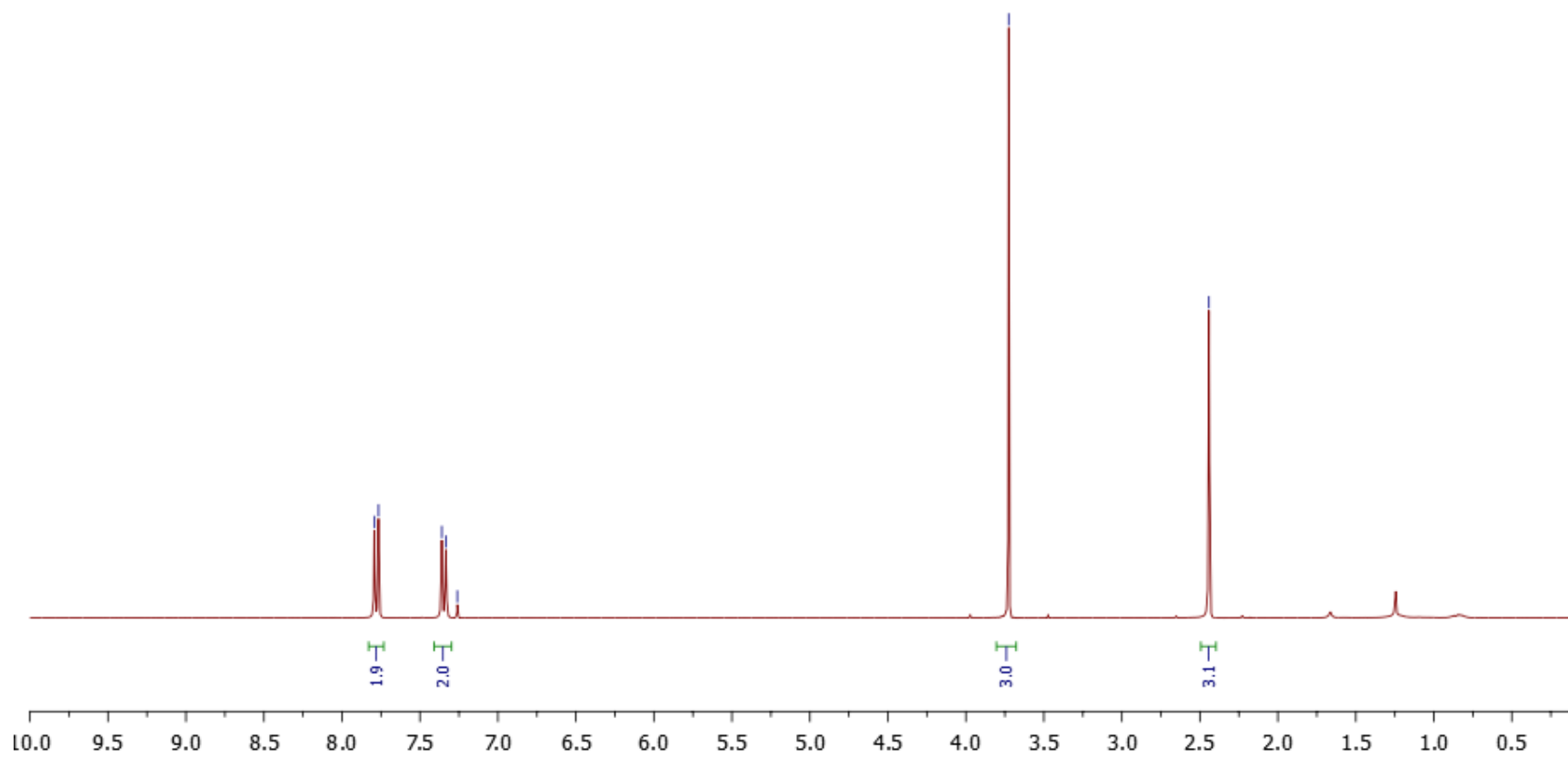
4a

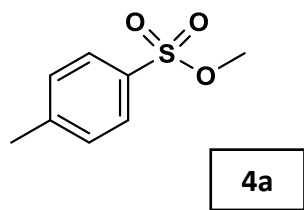
7.793  
7.765  
7.360  
7.333  
7.260

CDCl<sub>3</sub>, 300 MHz

3.726

2.442





— 145.047

— 132.271

— 129.981

— 128.149

CDCl<sub>3</sub>, 75 MHz

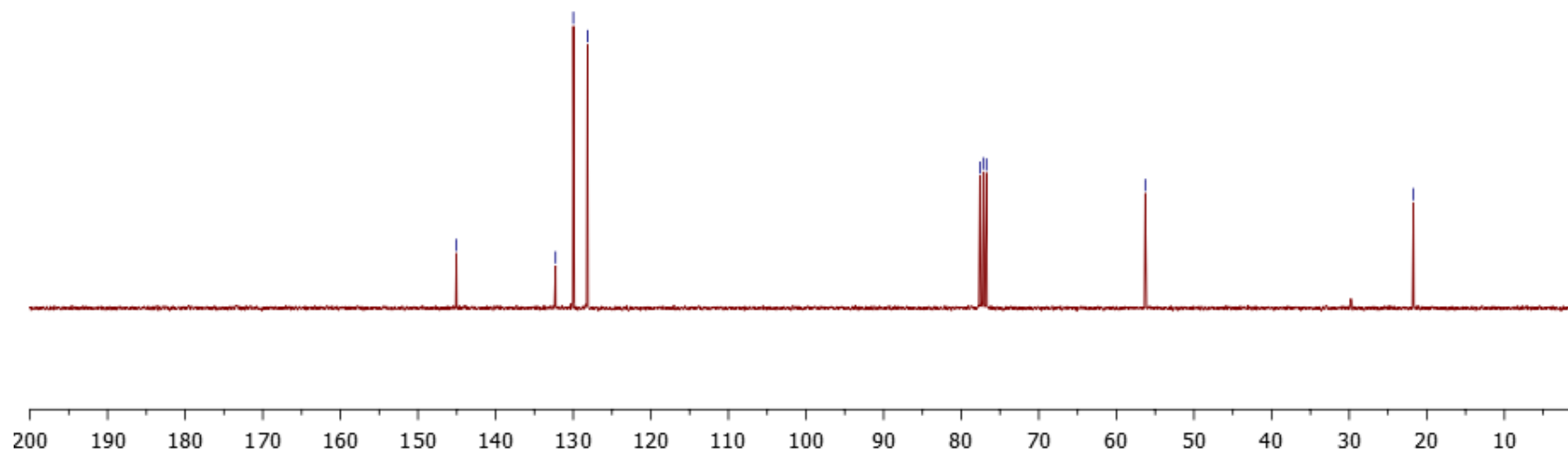
— 77.584

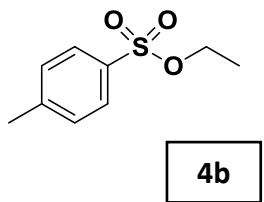
— 77.160

— 76.736

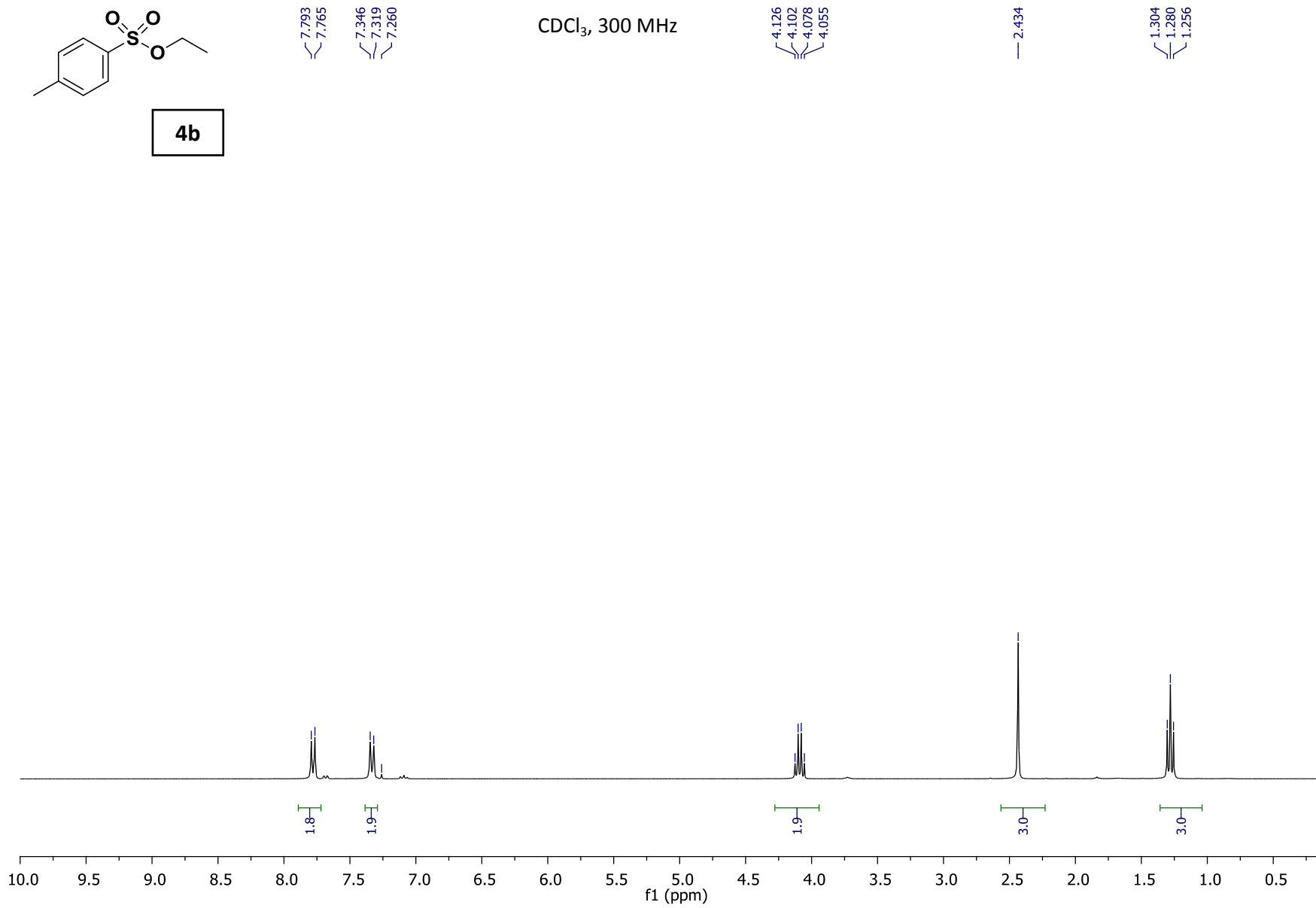
— 56.279

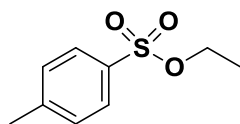
— 21.717





CDCl<sub>3</sub>, 300 MHz





4b

CDCl<sub>3</sub>, 75 MHz

144.791

133.383

129.928

127.937

77.584

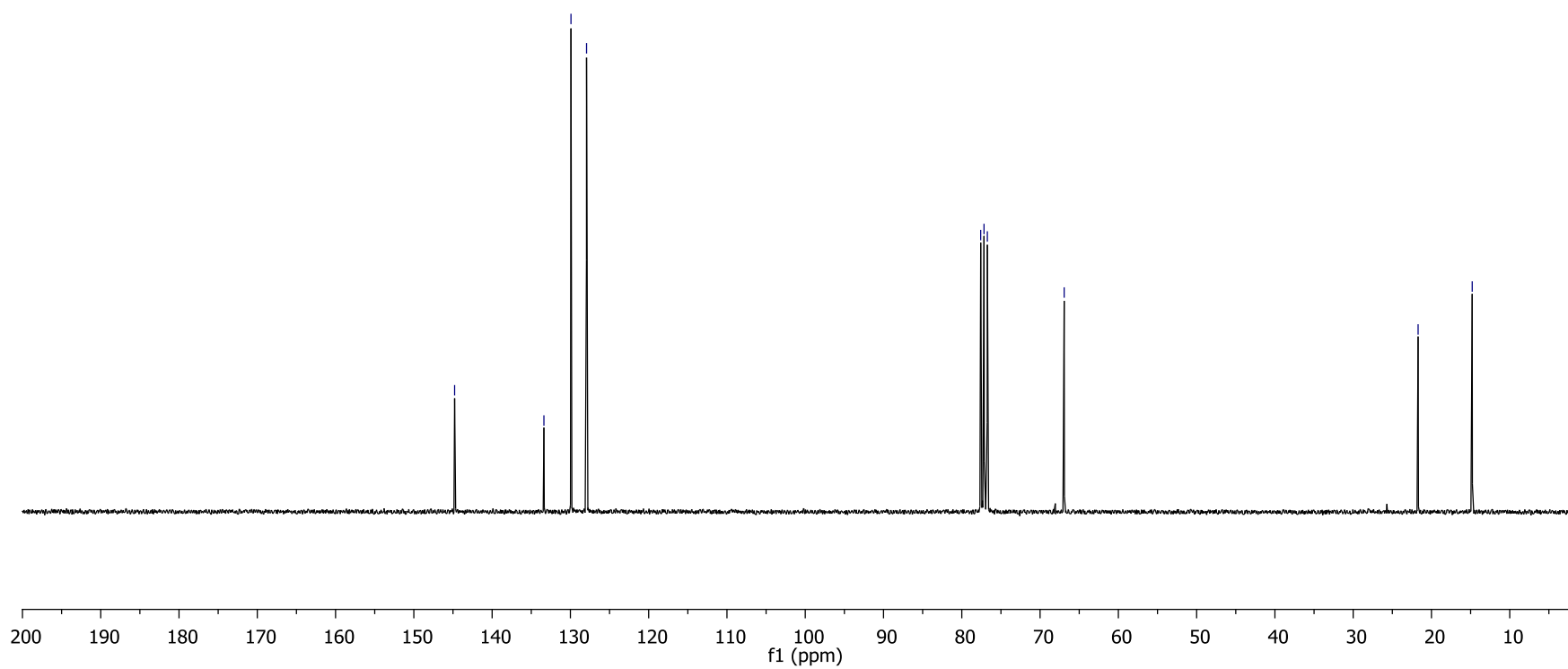
77.160

76.736

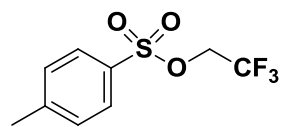
66.921

21.707

14.796



S13



4c

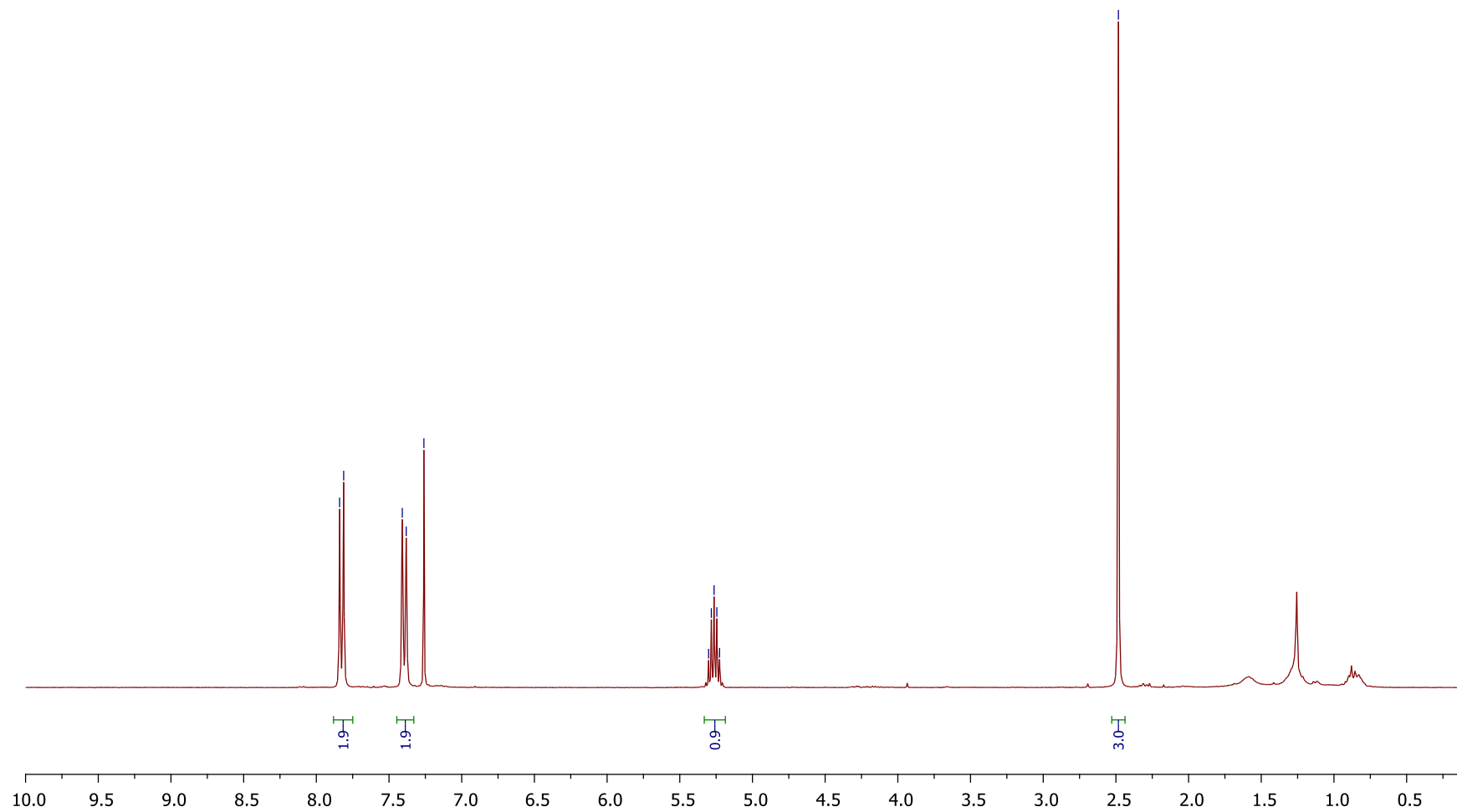
7.840  
7.812

7.409  
7.382  
7.260

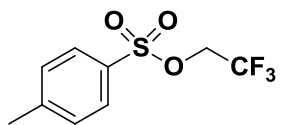
CDCl<sub>3</sub>, 300 MHz

5.302  
5.283  
5.264  
5.245  
5.226

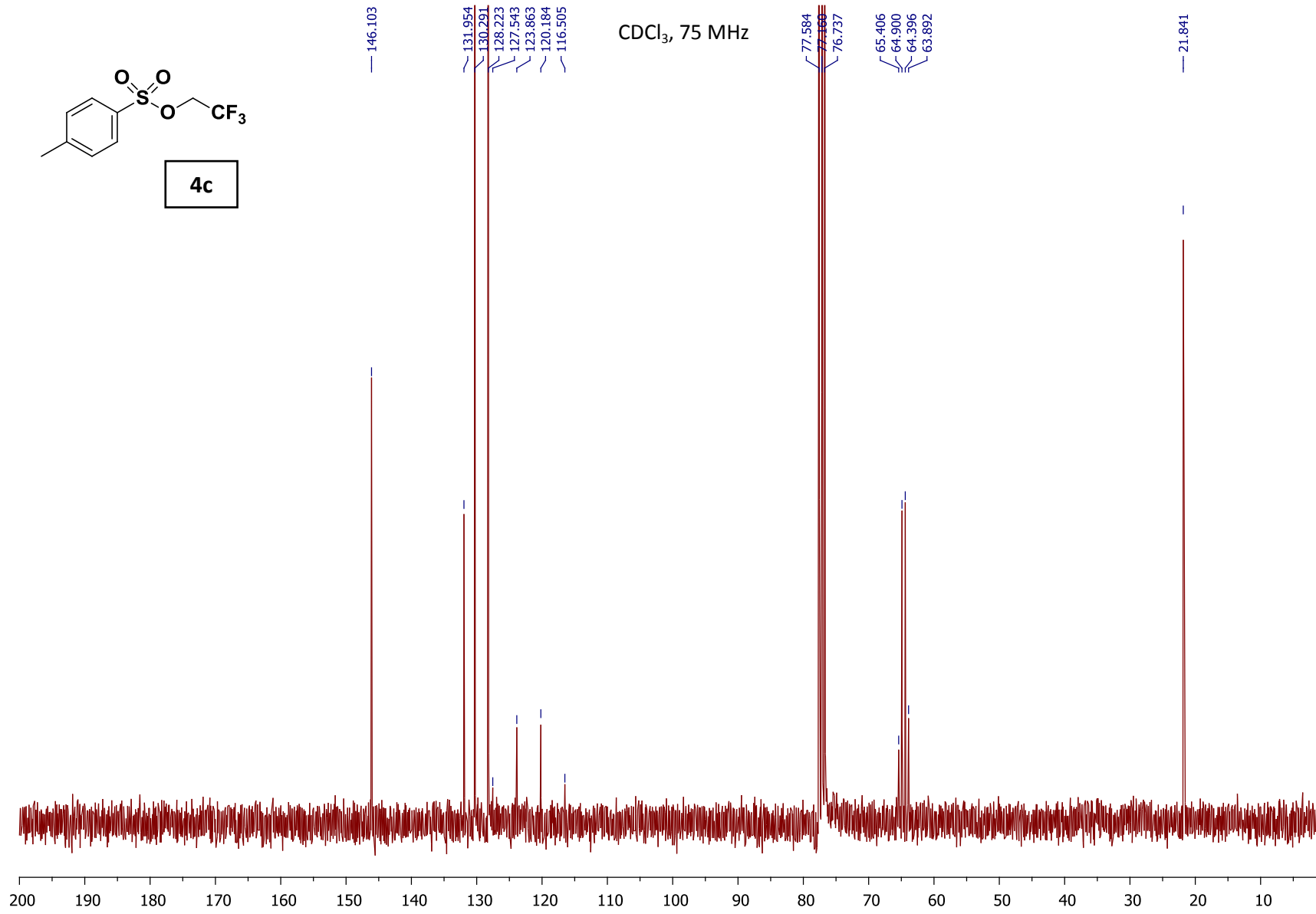
2.483

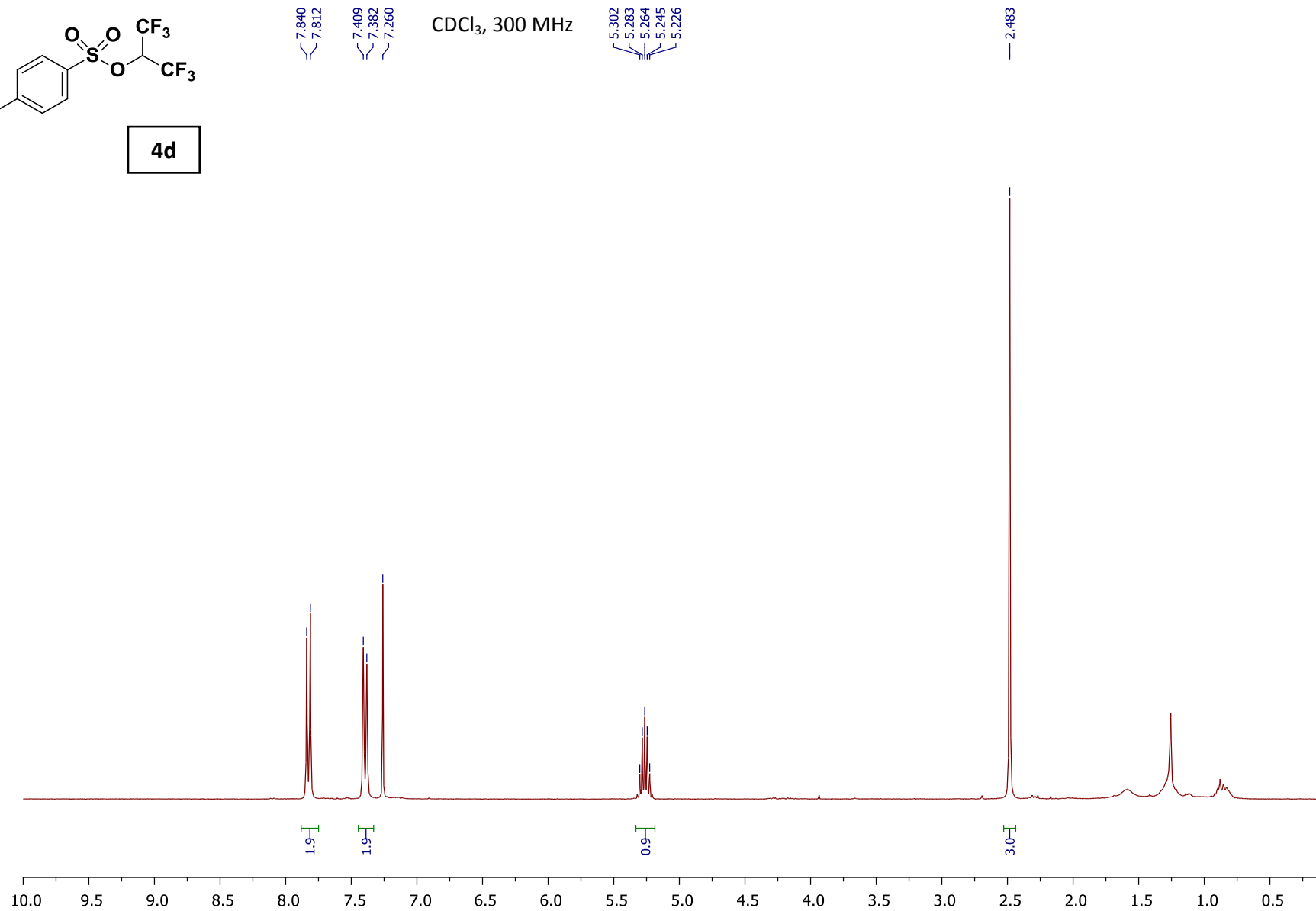
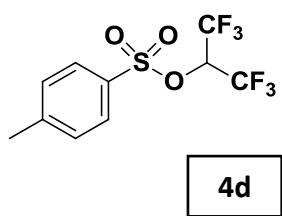


S14

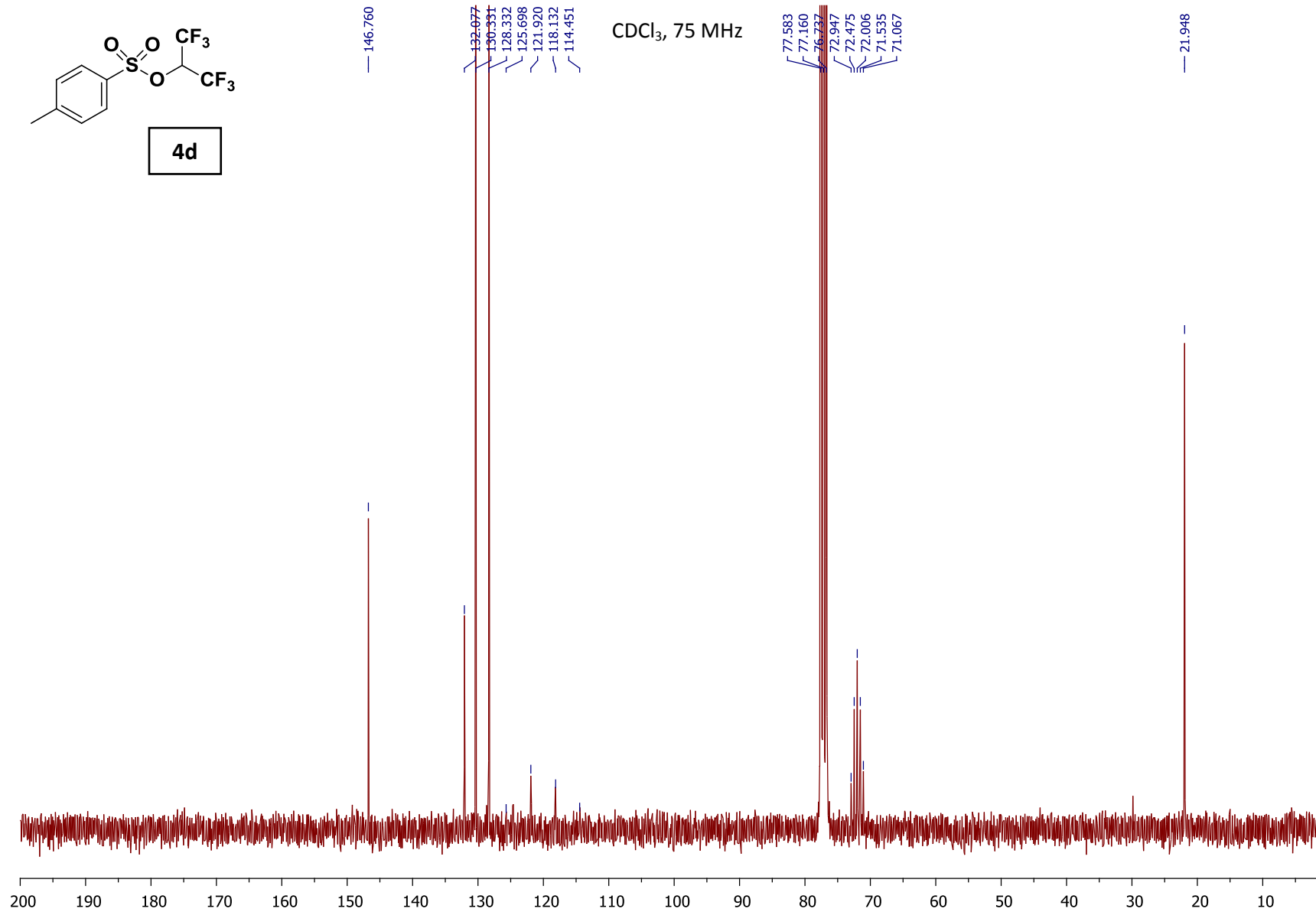
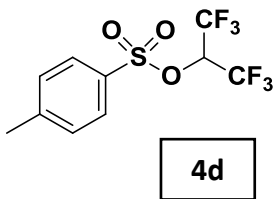


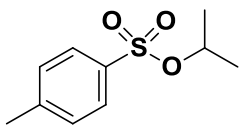
4c











4e

7.796  
7.769

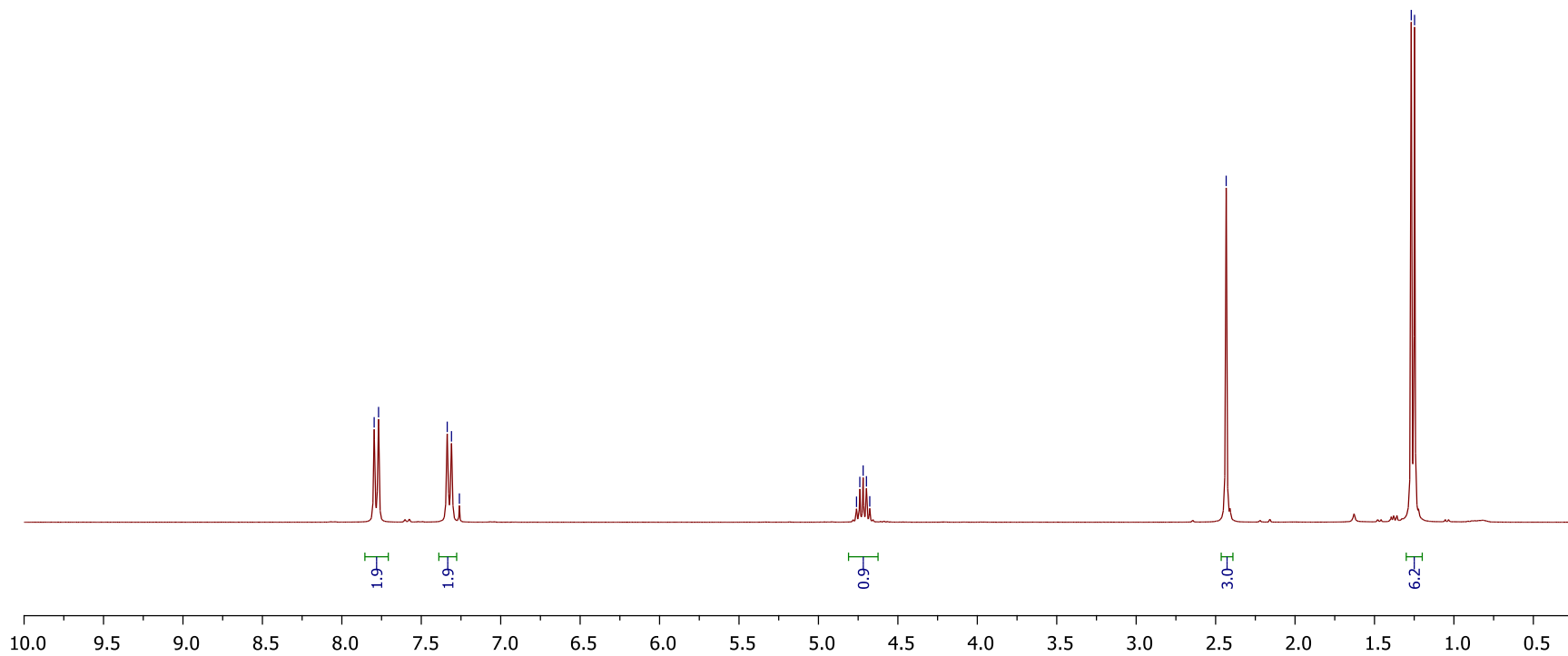
7.337  
7.310  
7.260

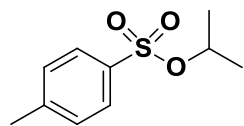
CDCl<sub>3</sub>, 300 MHz

4.760  
4.739  
4.719  
4.698  
4.677

2.433

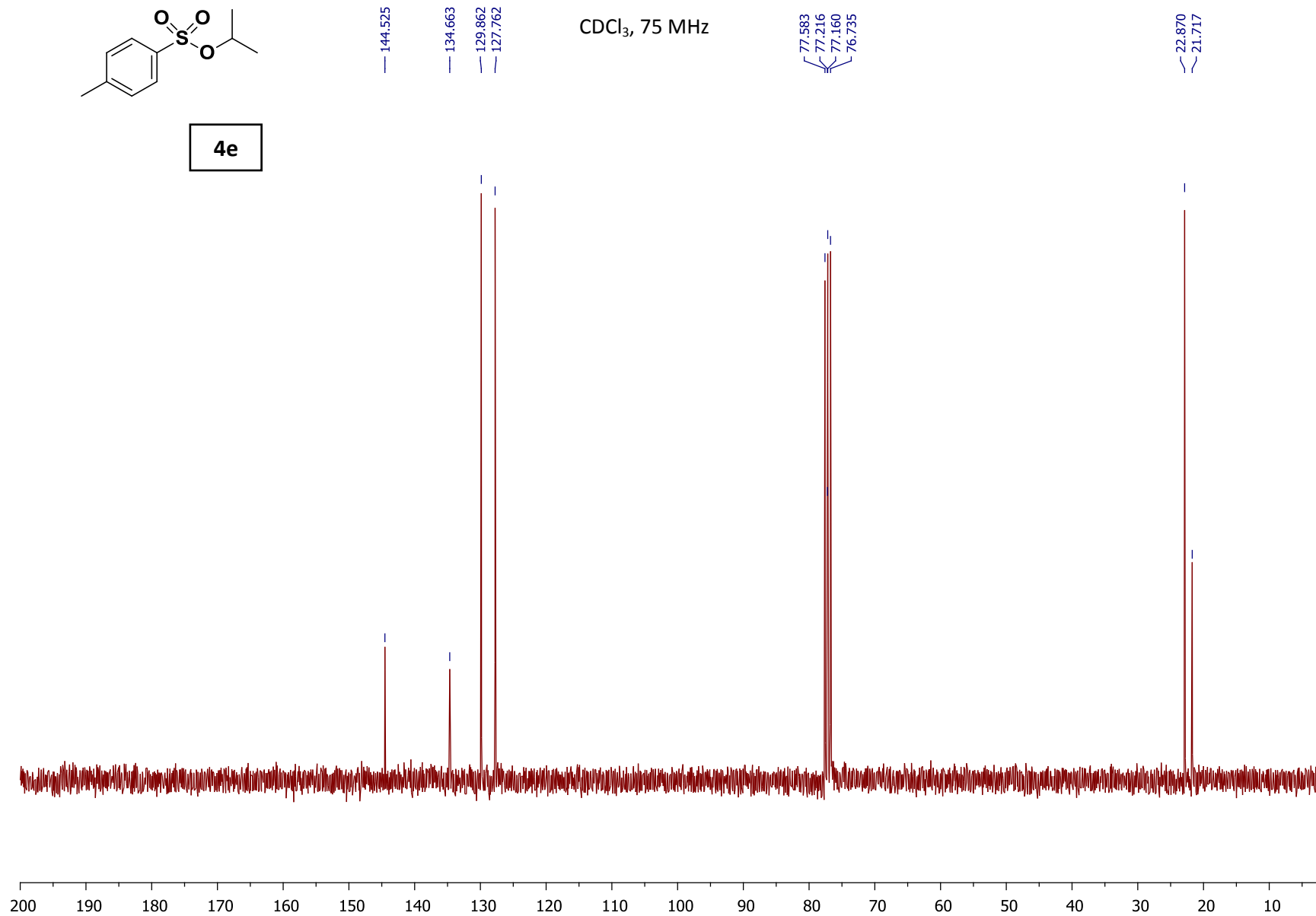
1.269  
1.248

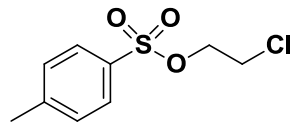




4e

CDCl<sub>3</sub>, 75 MHz





4f

CDCl<sub>3</sub>, 300 MHz

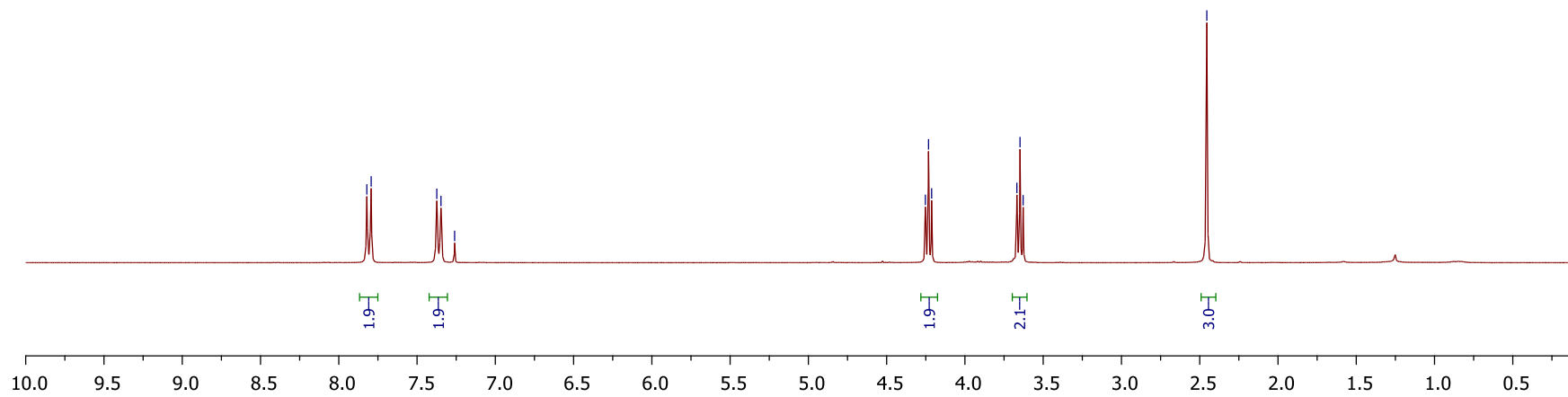
7.821  
7.793

7.374  
7.347  
7.260

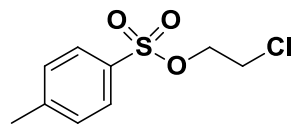
4.252  
4.233  
4.213

3.668  
3.648  
3.628

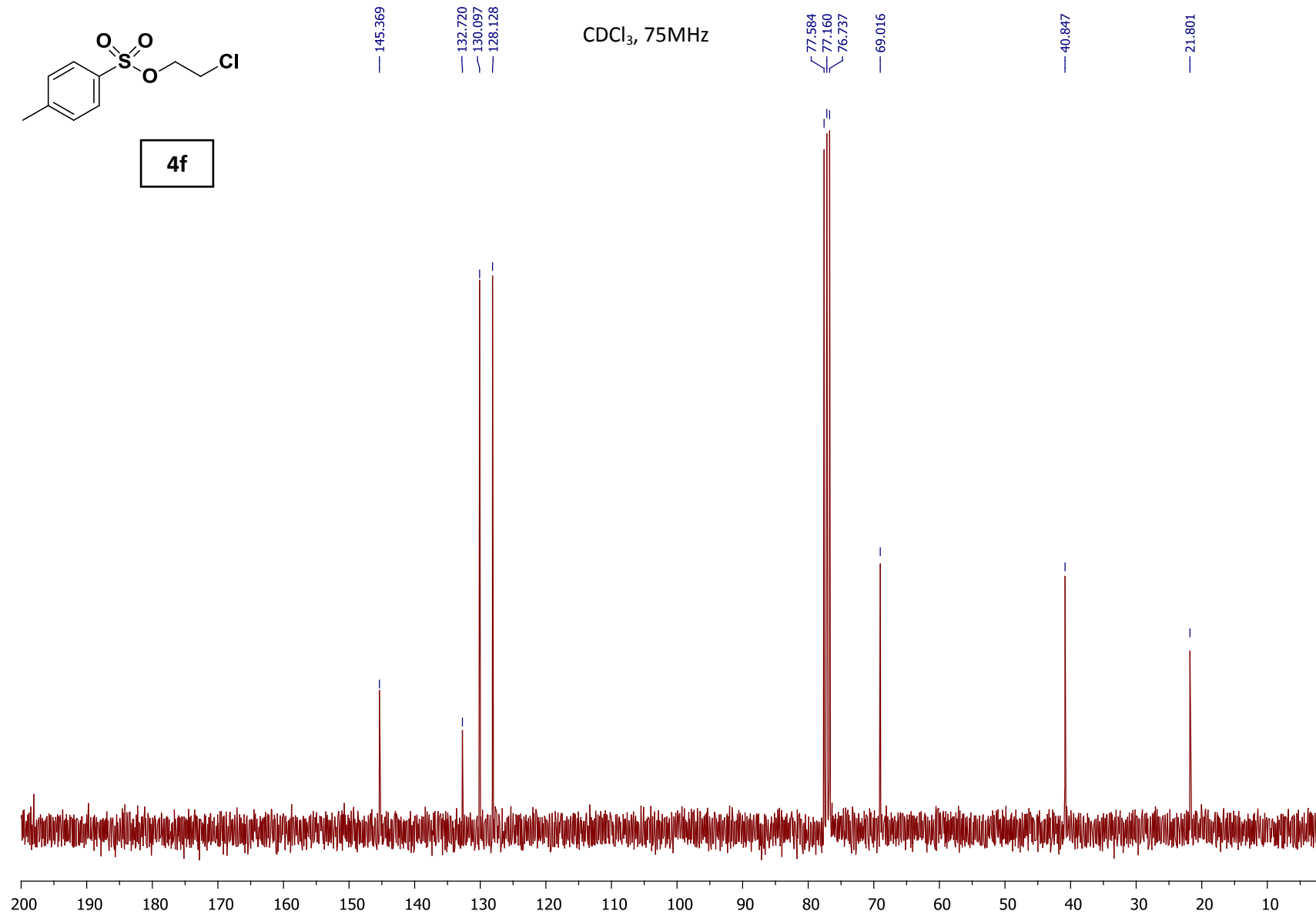
2.455

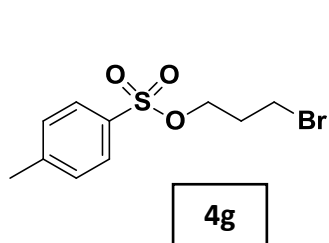


S20

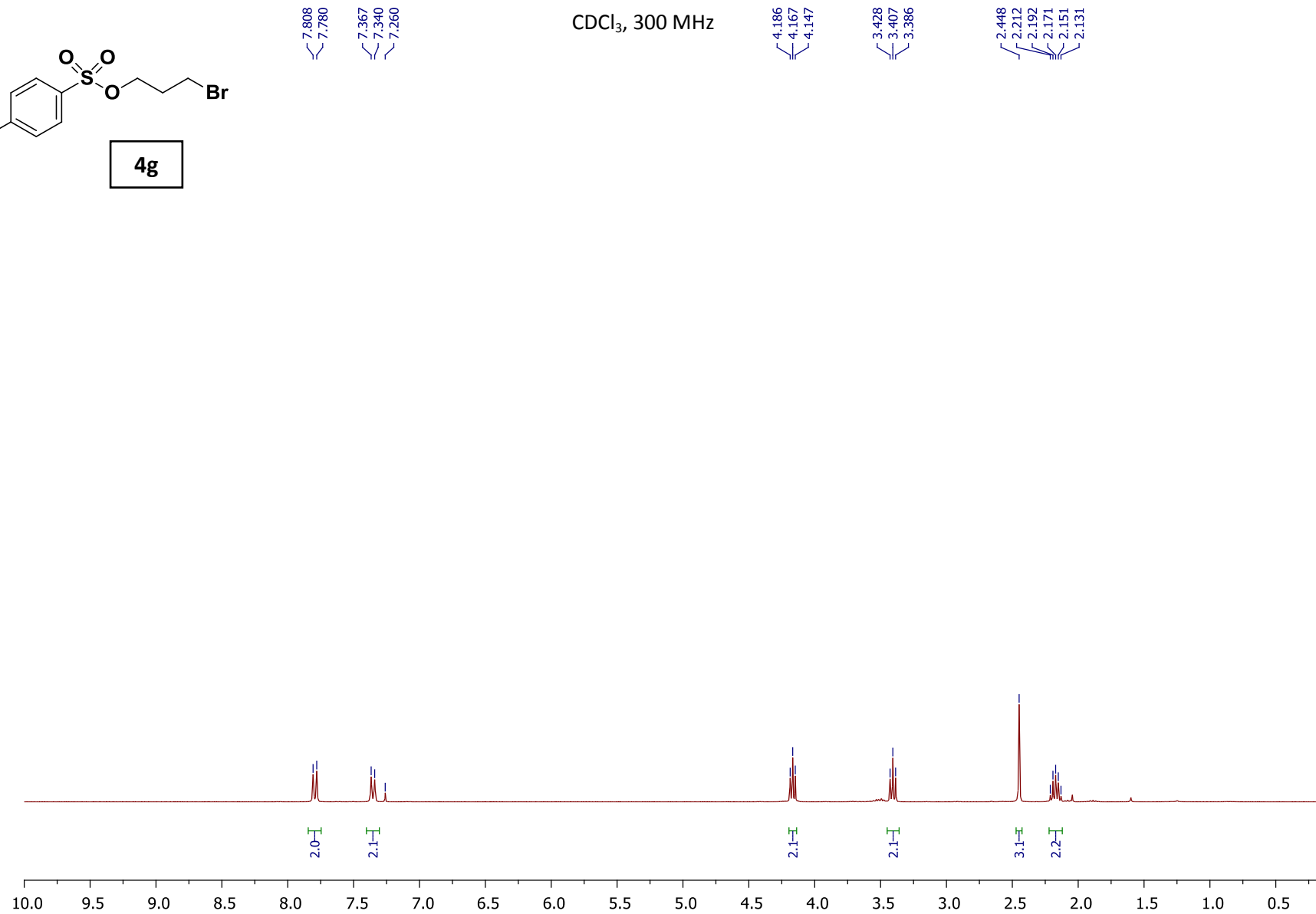


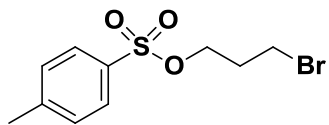
4f





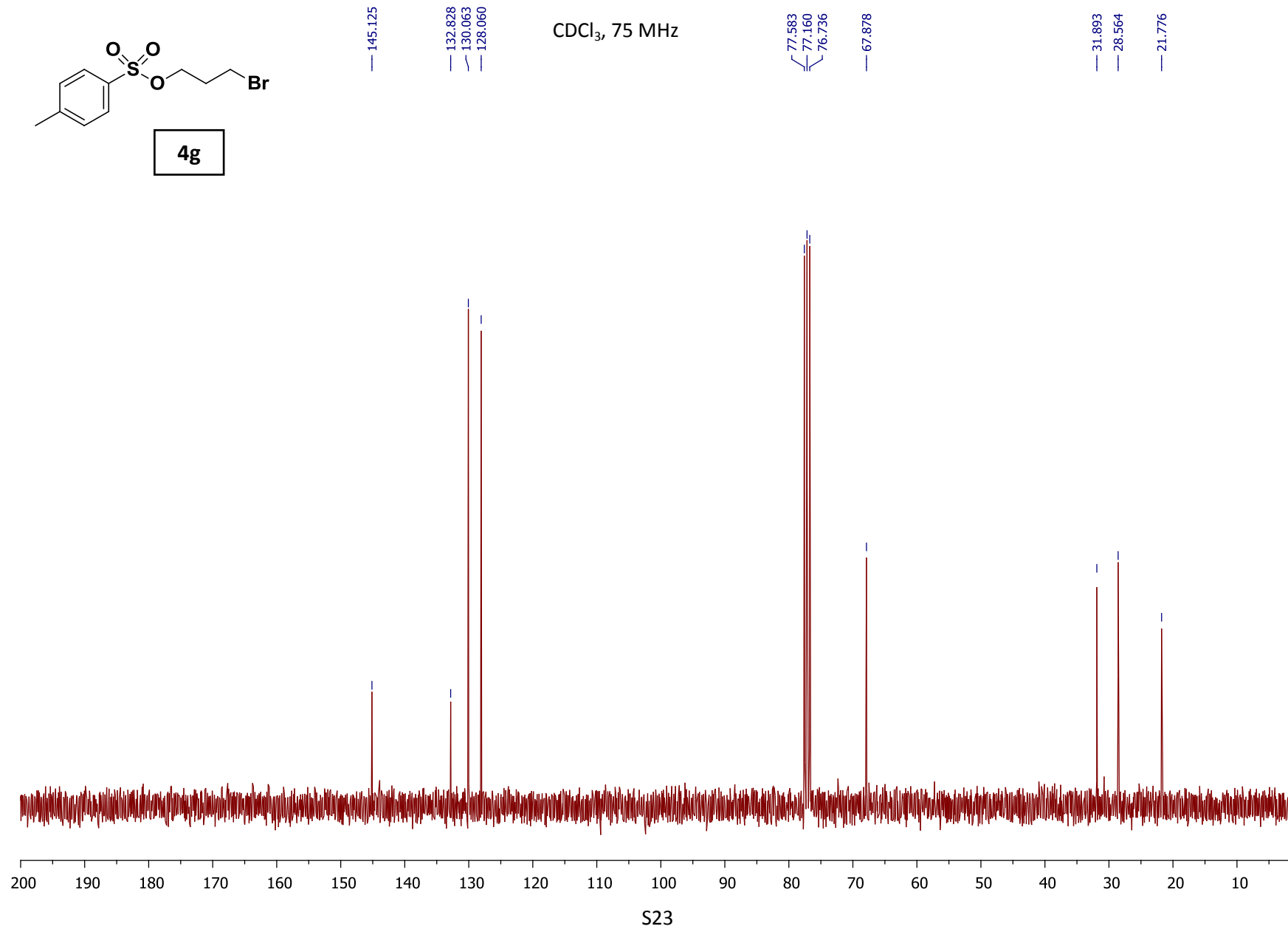
CDCl<sub>3</sub>, 300 MHz

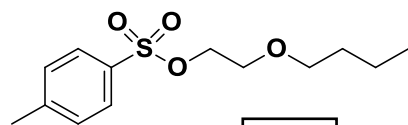




4g

CDCl<sub>3</sub>, 75 MHz





4h

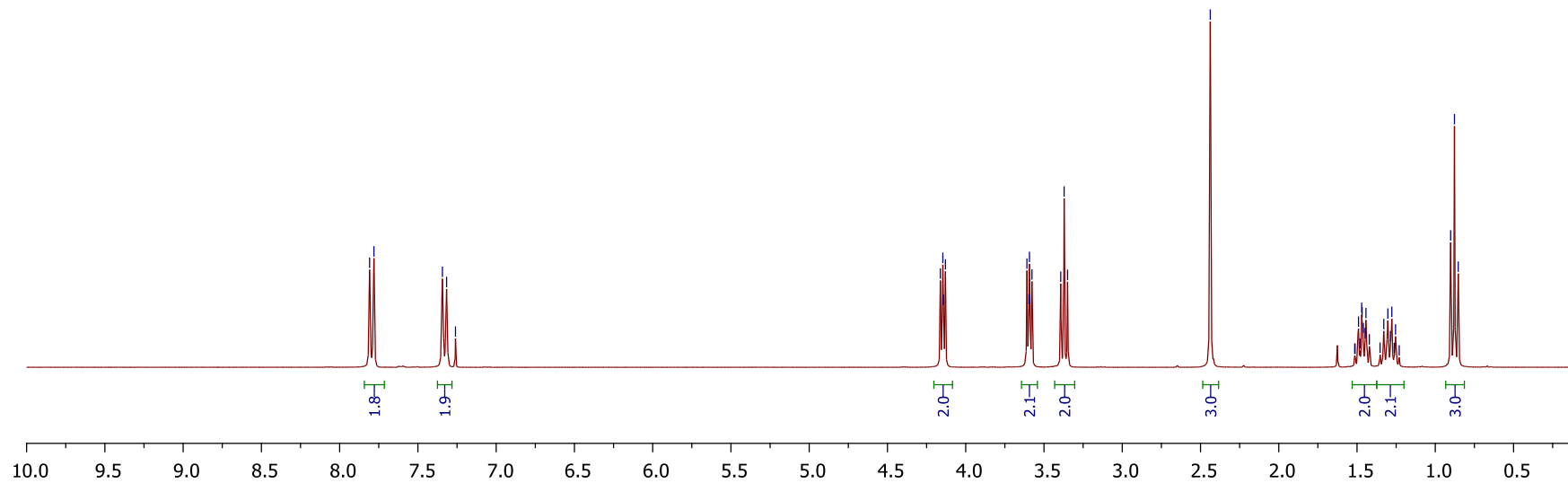
7.809  
7.781

7.343  
7.317  
7.260

CDCl<sub>3</sub>, 300 MHz

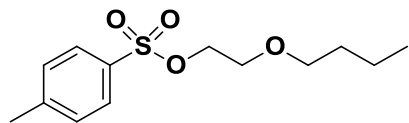
4.162  
4.146  
4.143  
4.130  
3.609  
3.596  
3.593  
3.577  
3.393  
3.371  
3.349

2.438  
1.491  
1.470  
1.467  
1.460  
1.448  
1.443  
1.329  
1.303  
1.286  
1.278  
0.954  
0.878  
0.853



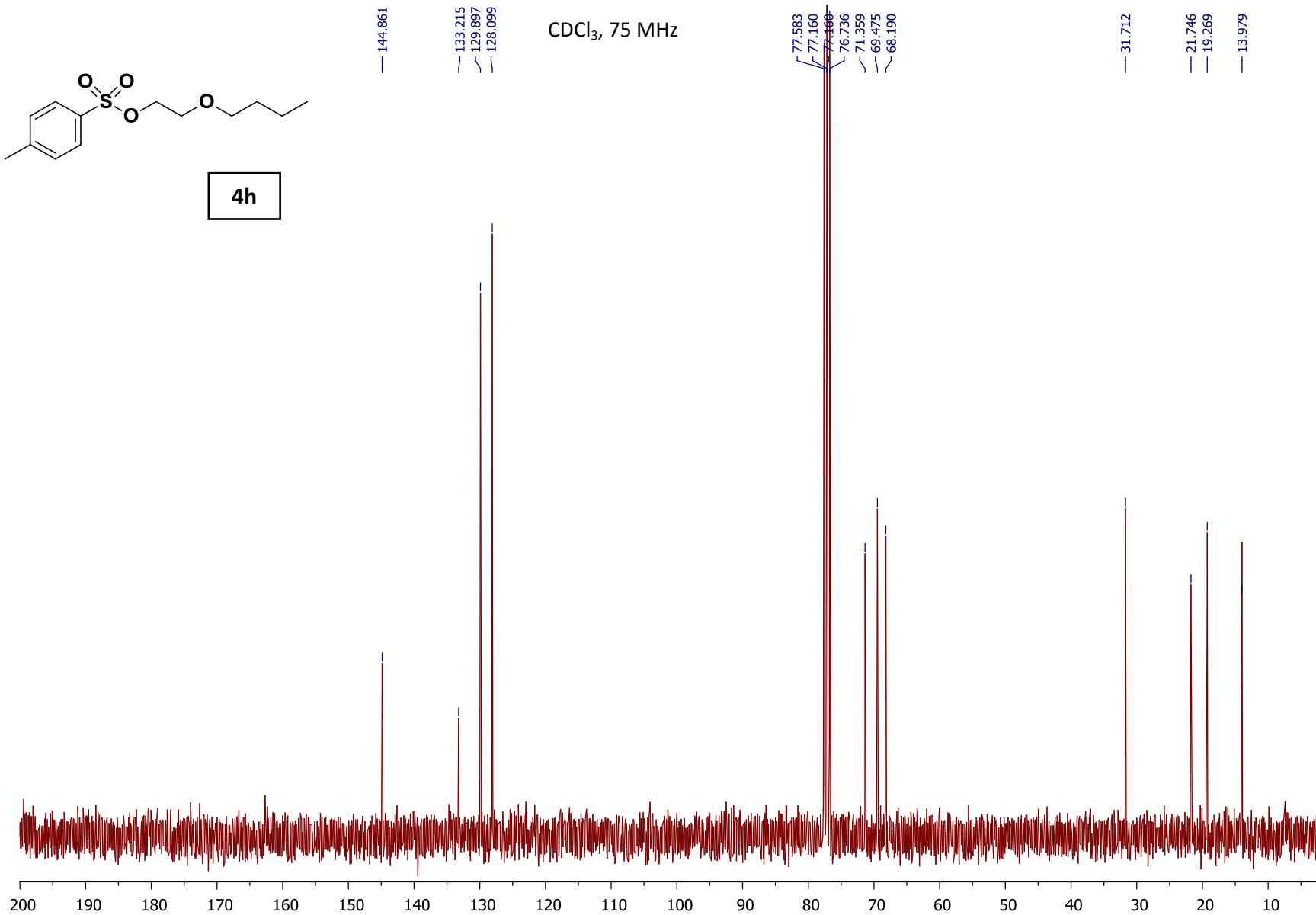
S24

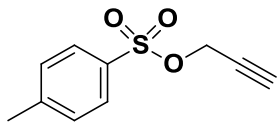




4h

CDCl<sub>3</sub>, 75 MHz





4i

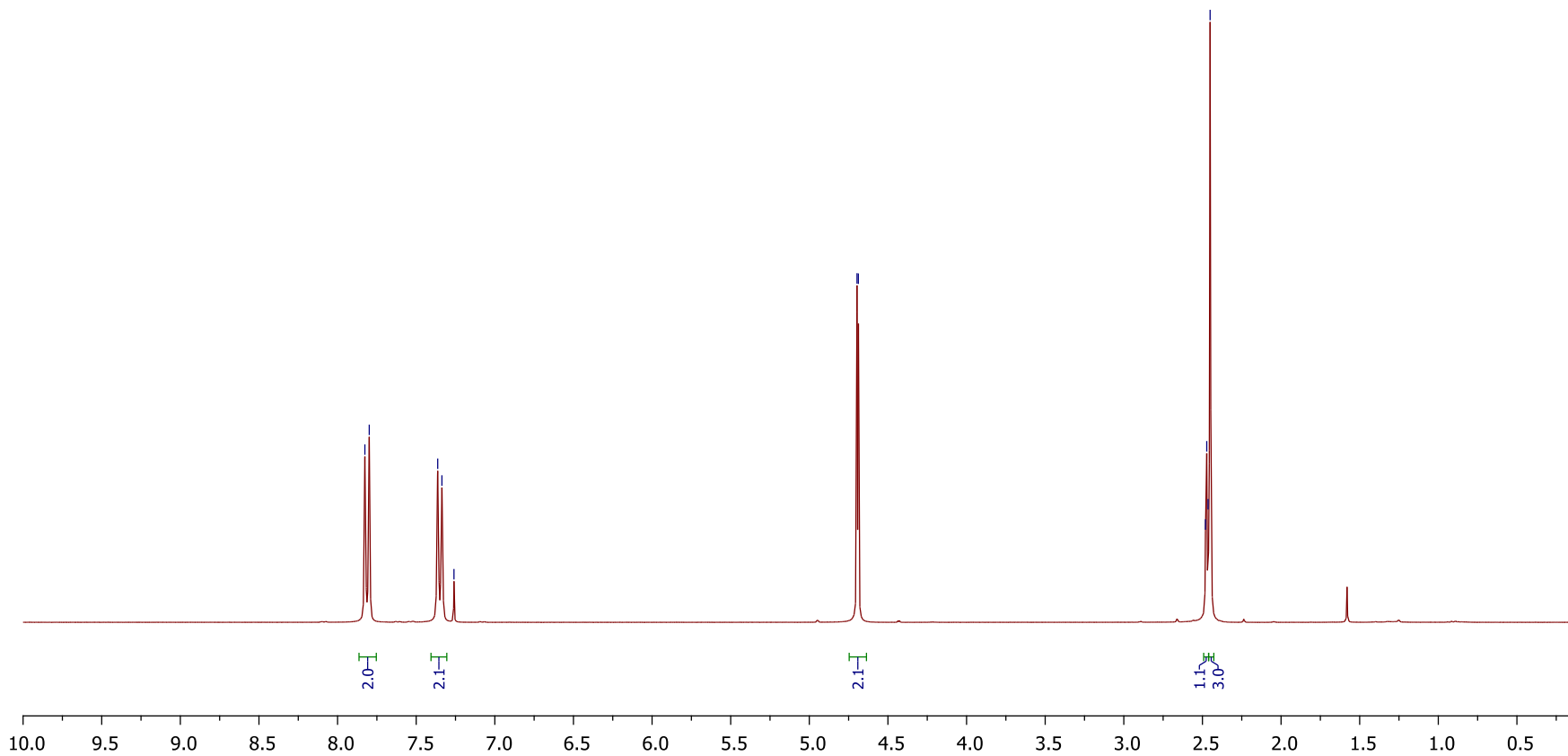
7.826  
7.799

7.363  
7.336  
7.260

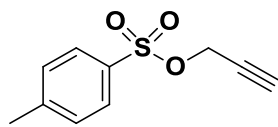
CDCl<sub>3</sub>, 300 MHz

4.697  
4.688

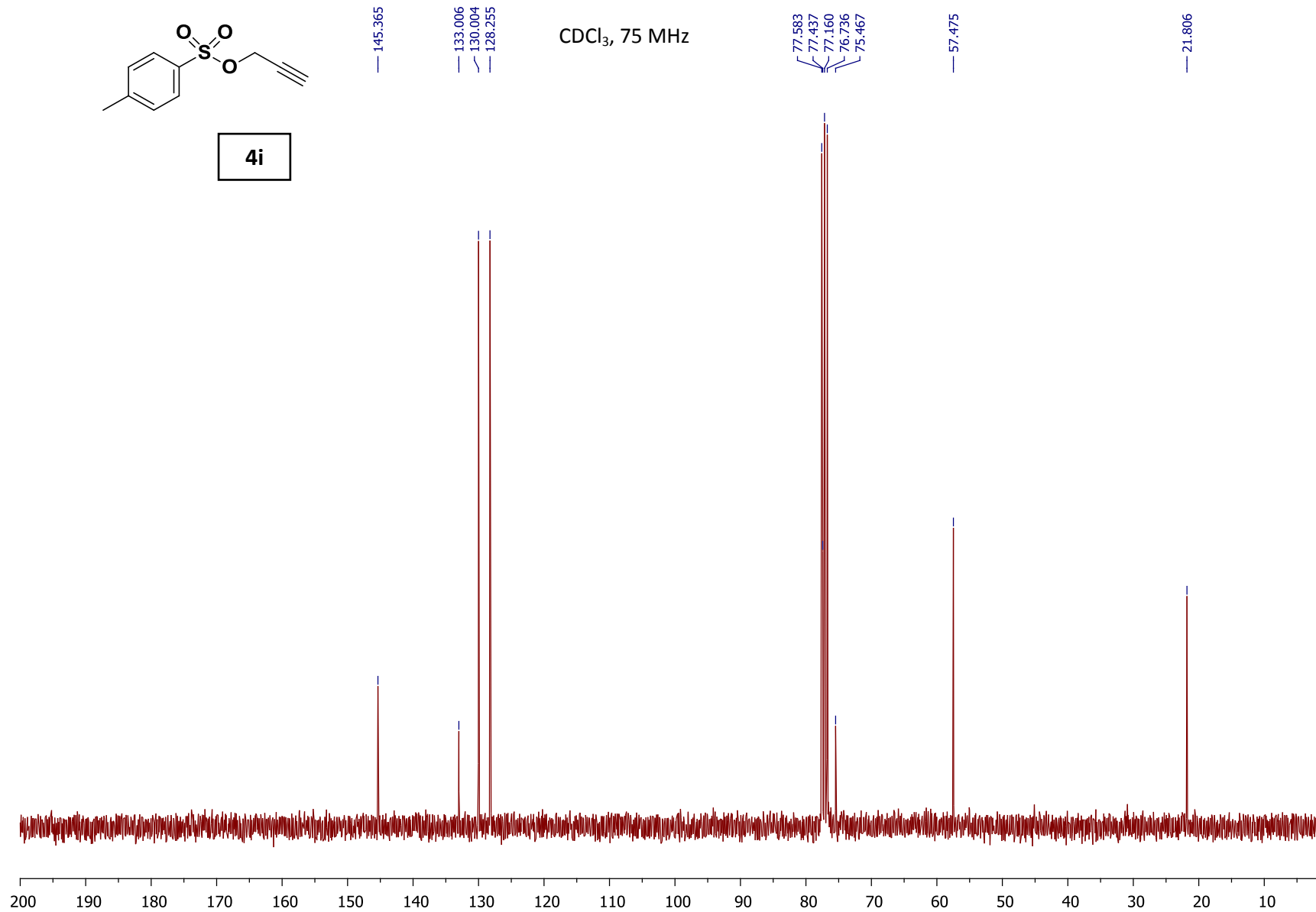
2.481  
2.473  
2.464  
2.451

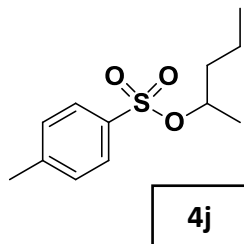


S26



4i





7.808  
7.780

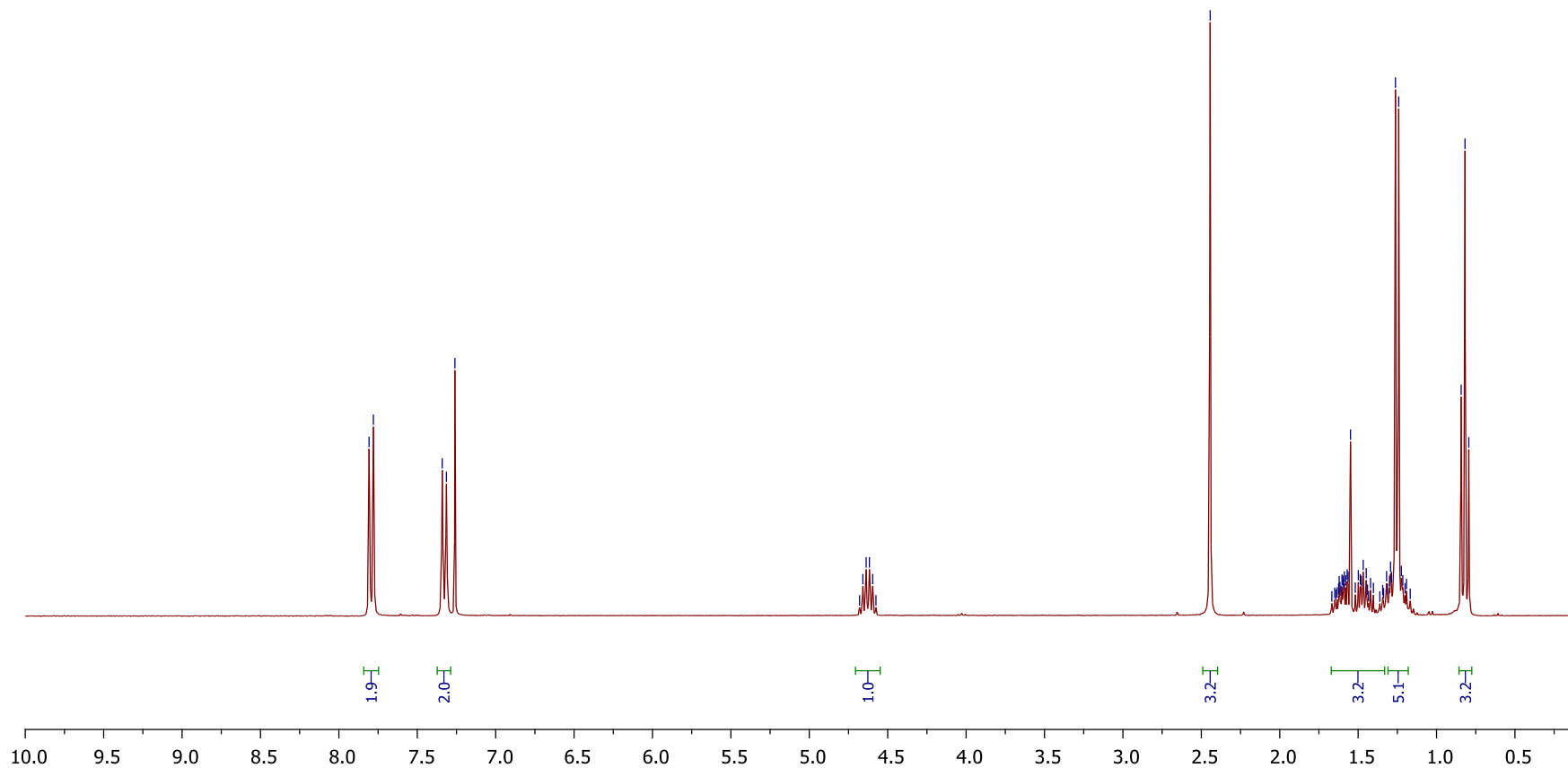
7.341  
7.314  
7.260

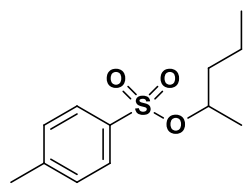
CDCl<sub>3</sub>, 300 MHz

4.679  
4.658  
4.637  
4.617  
4.596  
4.575

2.444

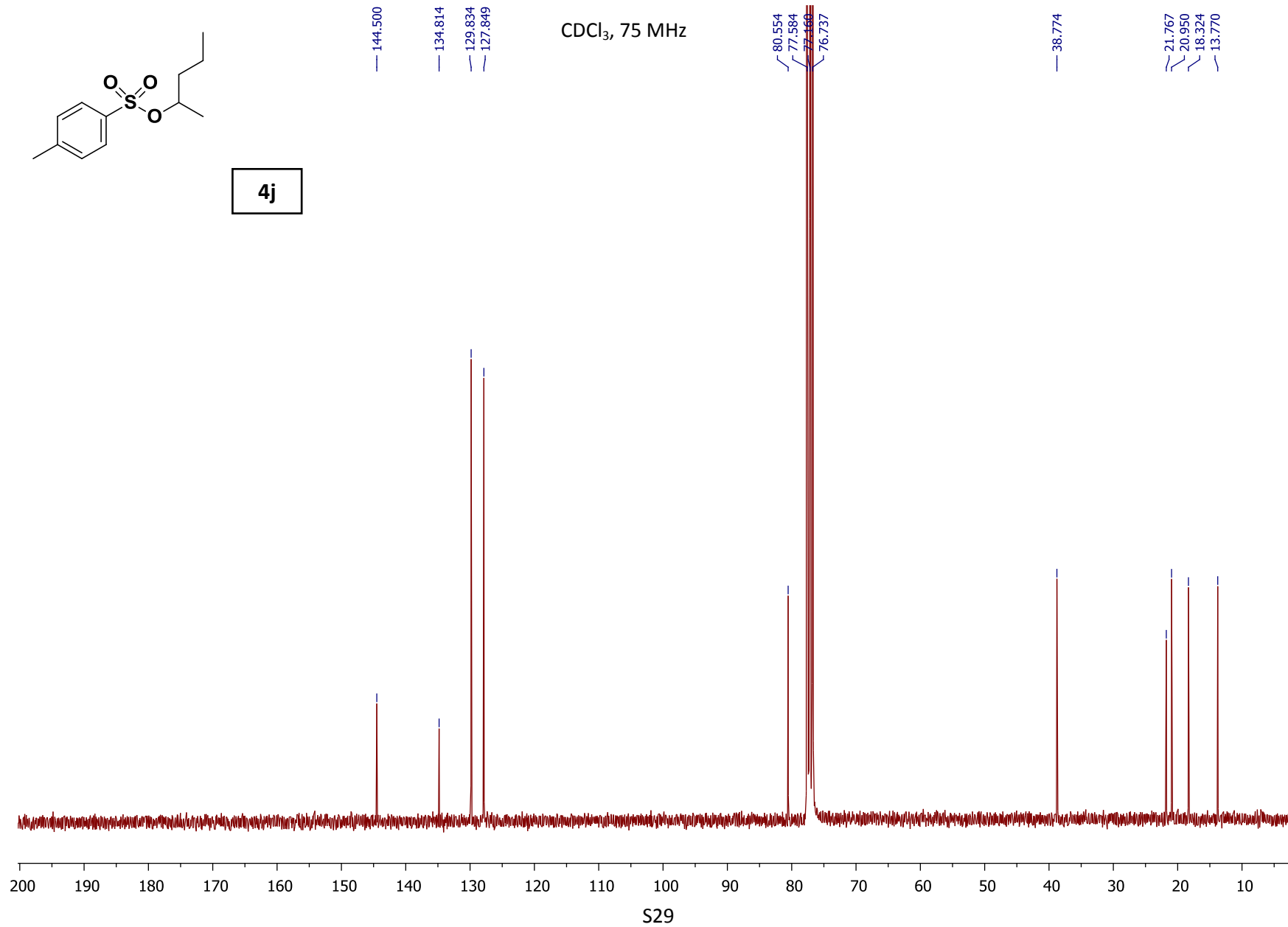
1.588  
1.570  
1.549  
1.499  
1.468  
1.448  
1.319  
1.293  
1.262  
1.241  
0.823  
0.818  
0.794

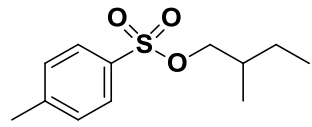




4j

CDCl<sub>3</sub>, 75 MHz





4k

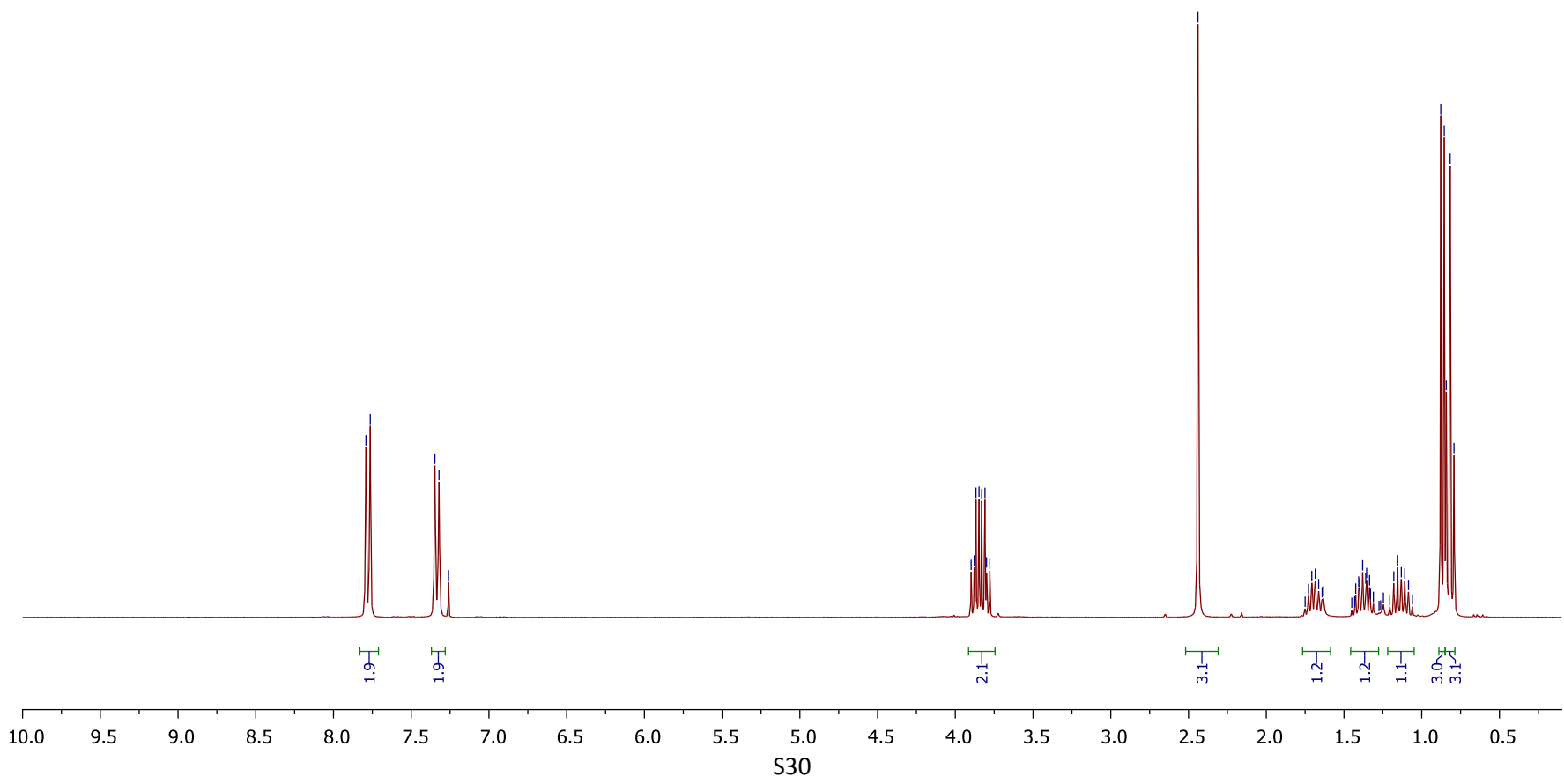
7.791  
7.763

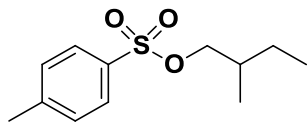
7.348  
7.321  
7.260

CDCl<sub>3</sub>, 300 MHz

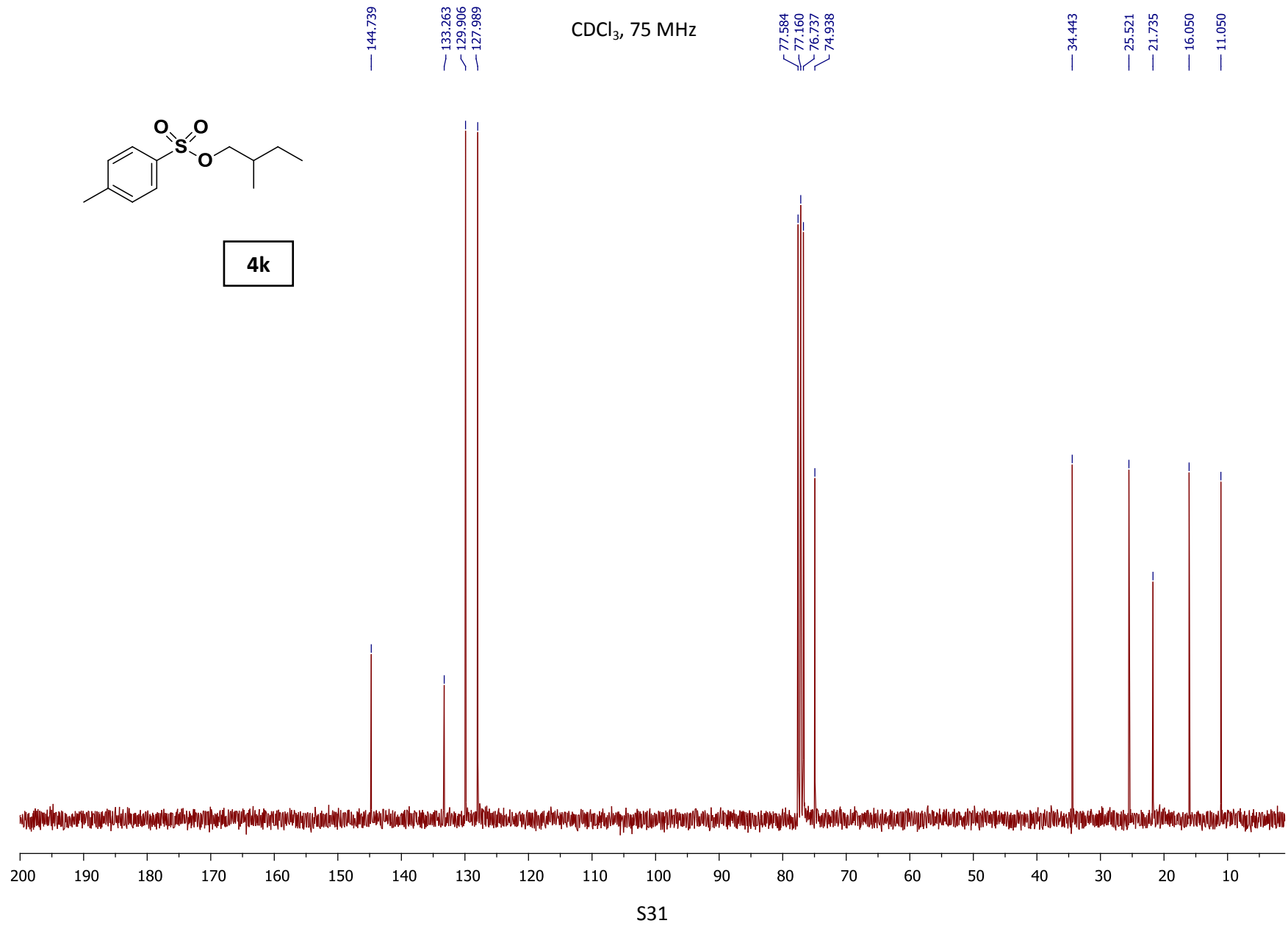
3.898  
3.879  
3.867  
3.847  
3.830  
3.809  
3.799  
3.778

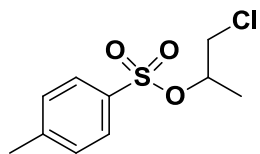
2.439  
1.707  
1.685  
1.663  
1.405  
1.400  
1.380  
1.360  
1.354  
1.335  
1.180  
1.155  
1.131  
1.109  
1.085  
0.878  
0.855  
0.842  
0.817  
0.792





4k





4I

7.820  
7.792

7.359  
7.332

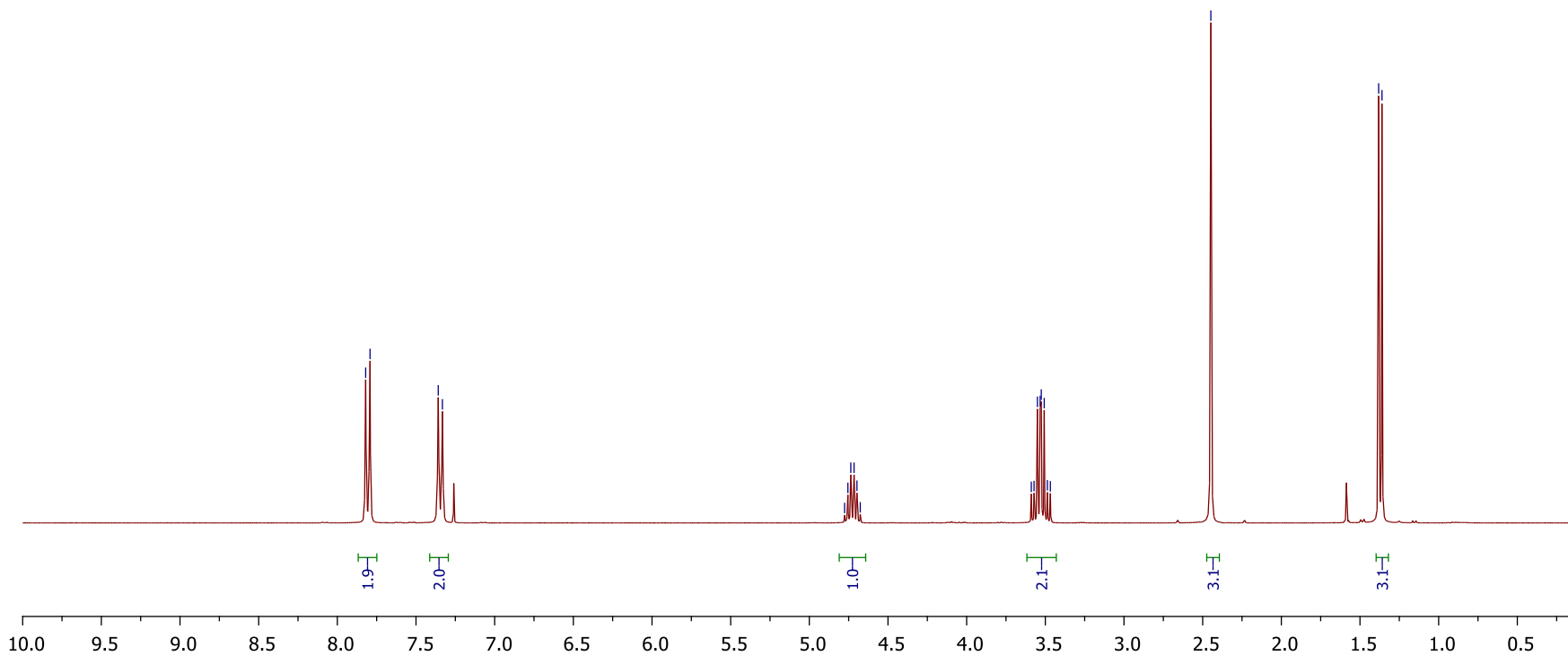
CDCl<sub>3</sub>, 300 MHz

4.776  
4.755  
4.736  
4.716  
4.697  
4.676

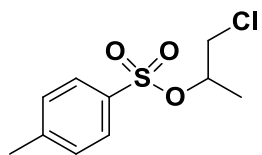
3.589  
3.572  
3.550  
3.533  
3.526  
3.507  
3.487  
3.468

2.448

1.381  
1.360

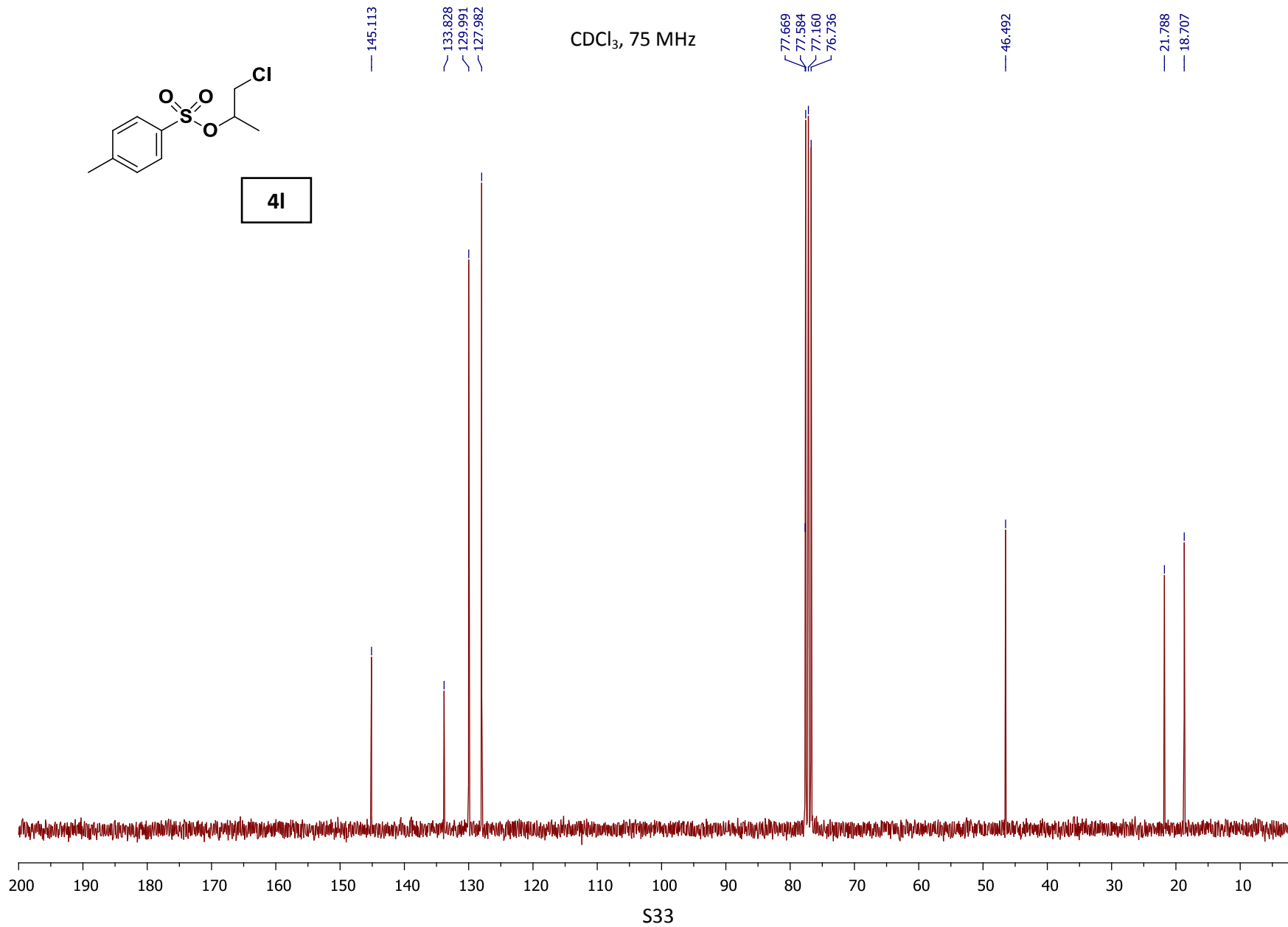


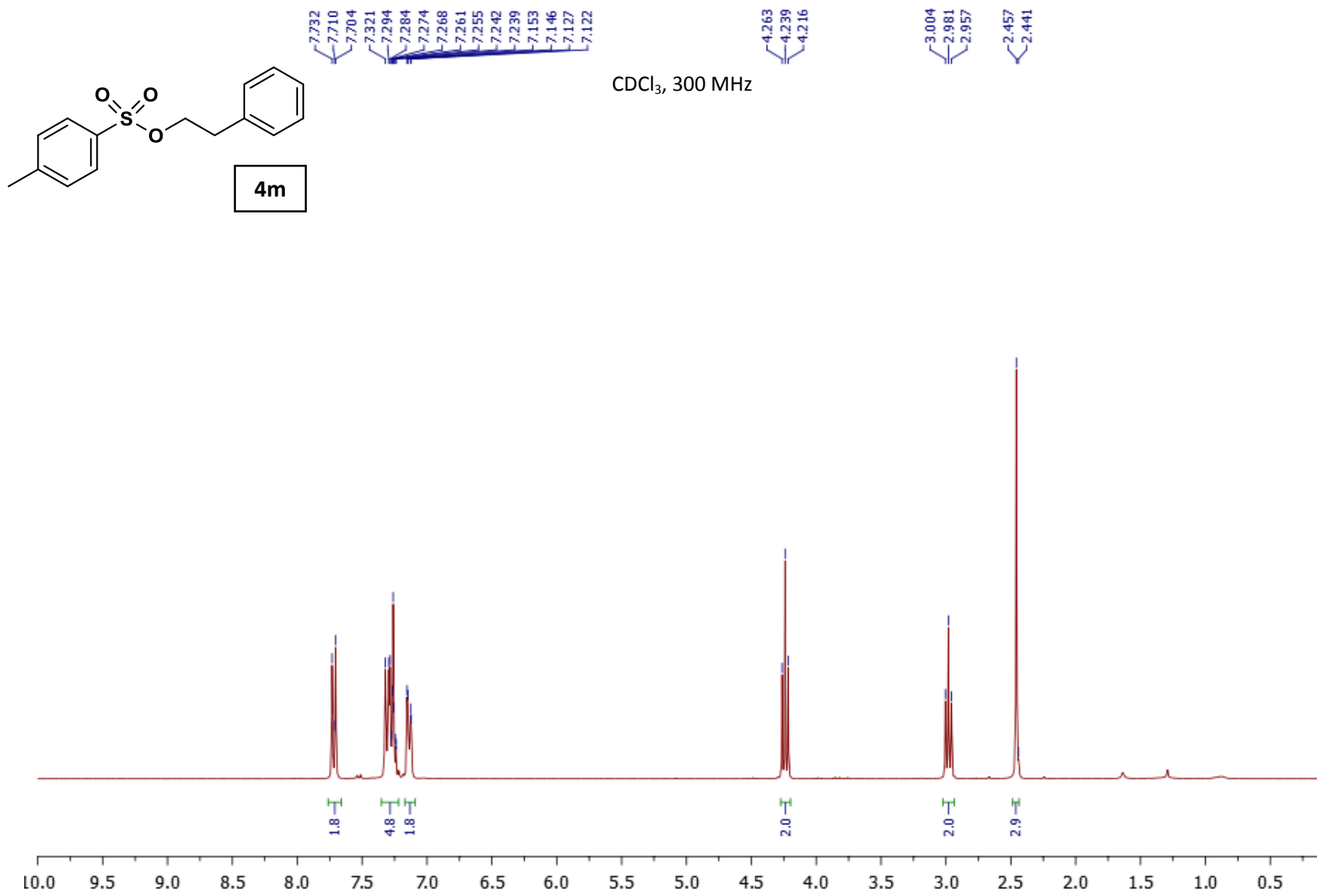


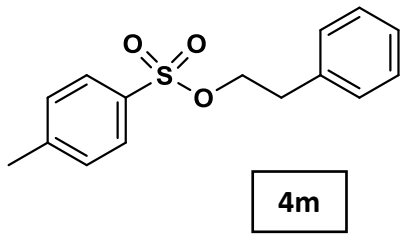


4I

CDCl<sub>3</sub>, 75 MHz







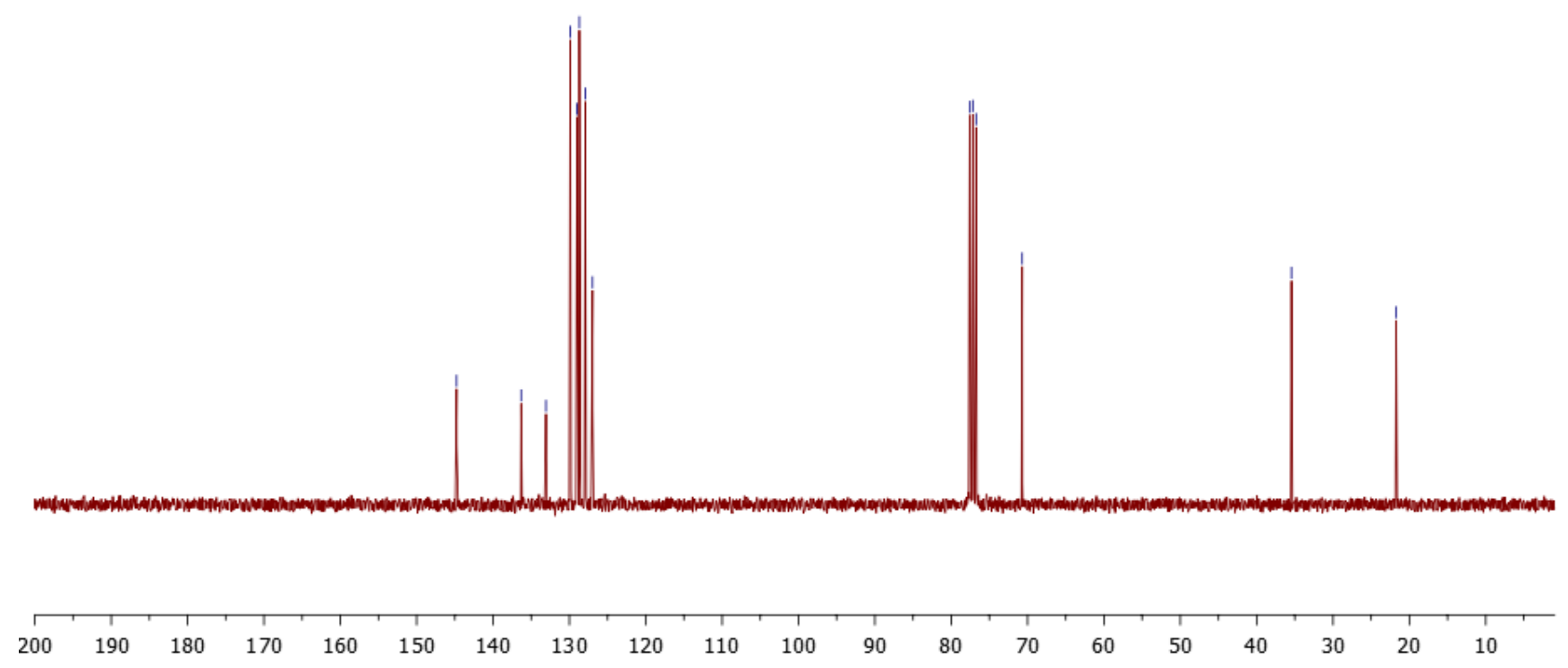
144.770  
136.316  
133.072  
129.892  
129.005  
128.695  
127.926  
126.970

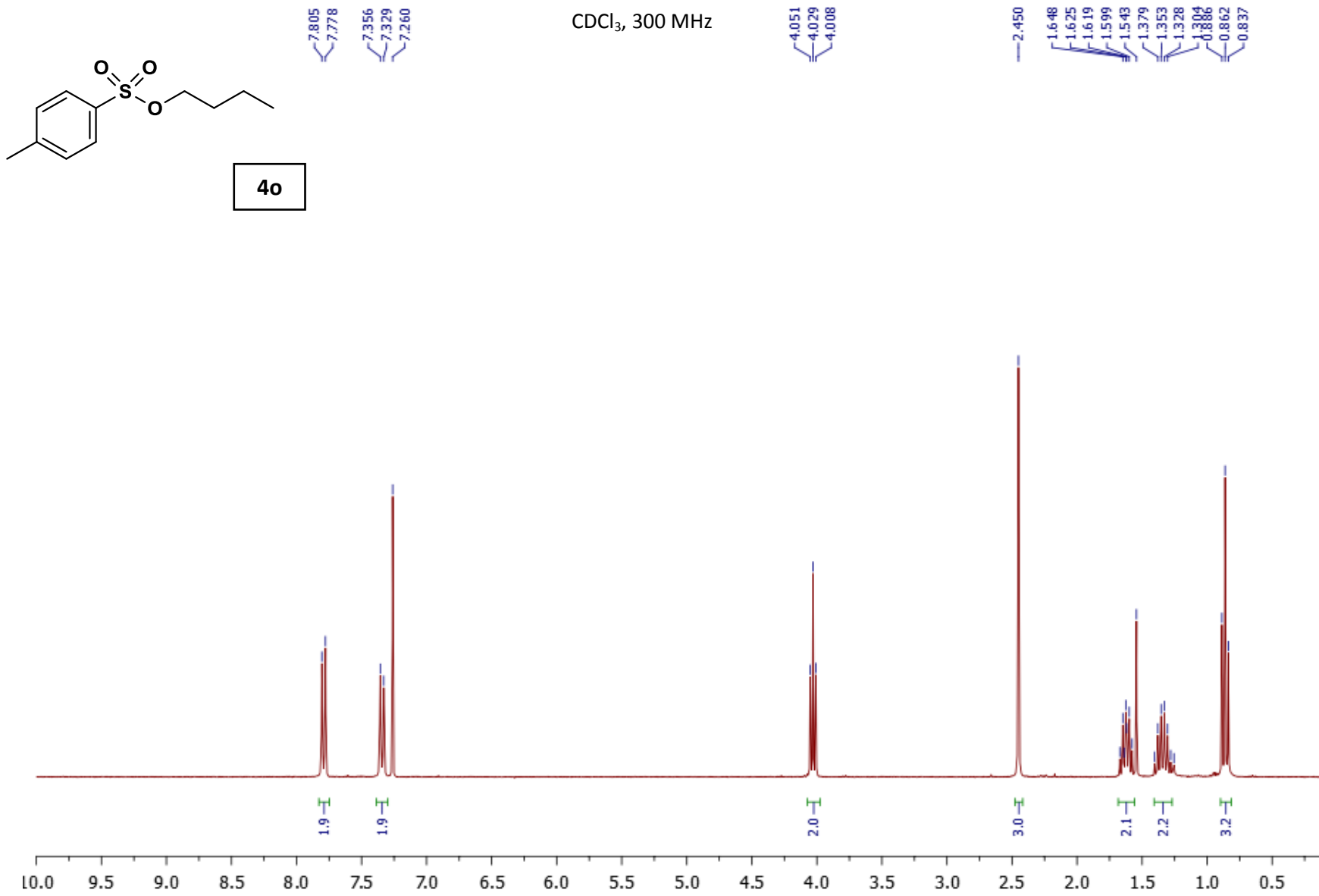
CDCl<sub>3</sub>, 75 MHz

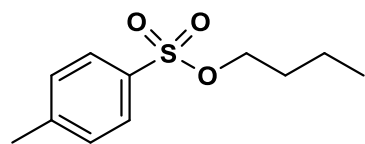
77.584  
77.160  
76.736  
70.710

35.443

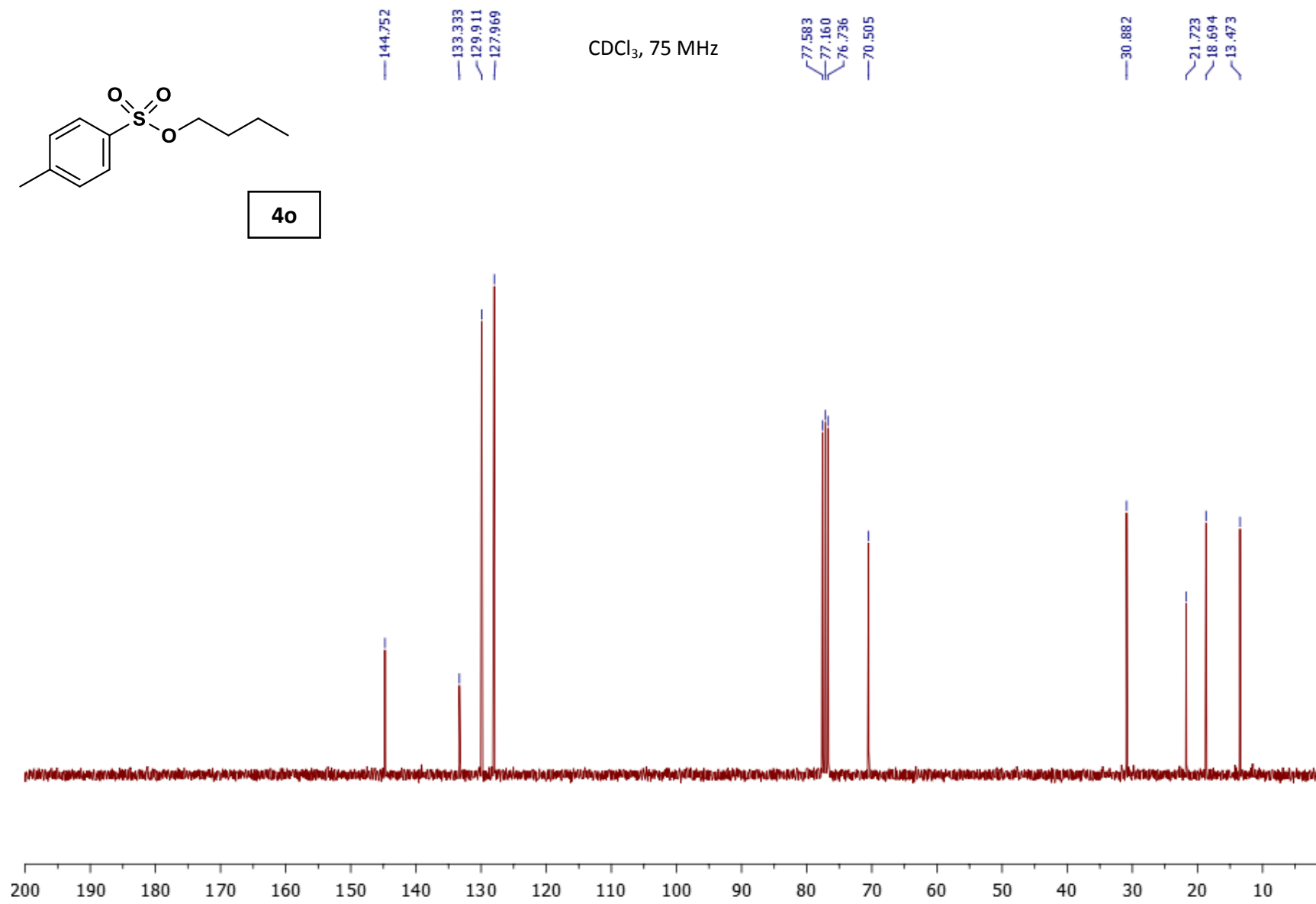
21.722

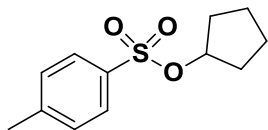






4o





4p

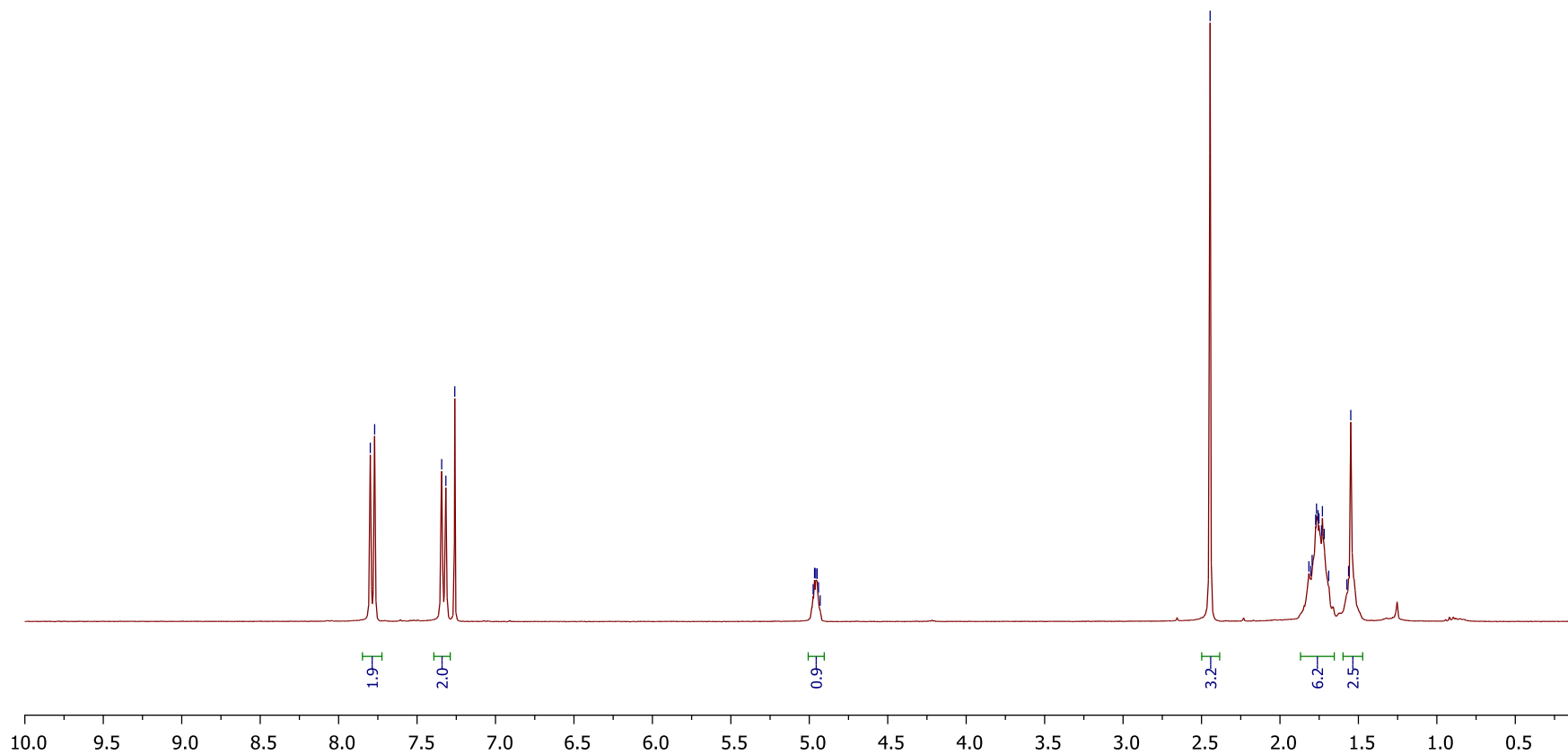
7.798  
7.770

7.343  
7.316  
7.260

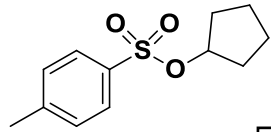
CDCl<sub>3</sub>, 300 MHz

4.975  
4.967  
4.959  
4.950  
4.941  
4.930

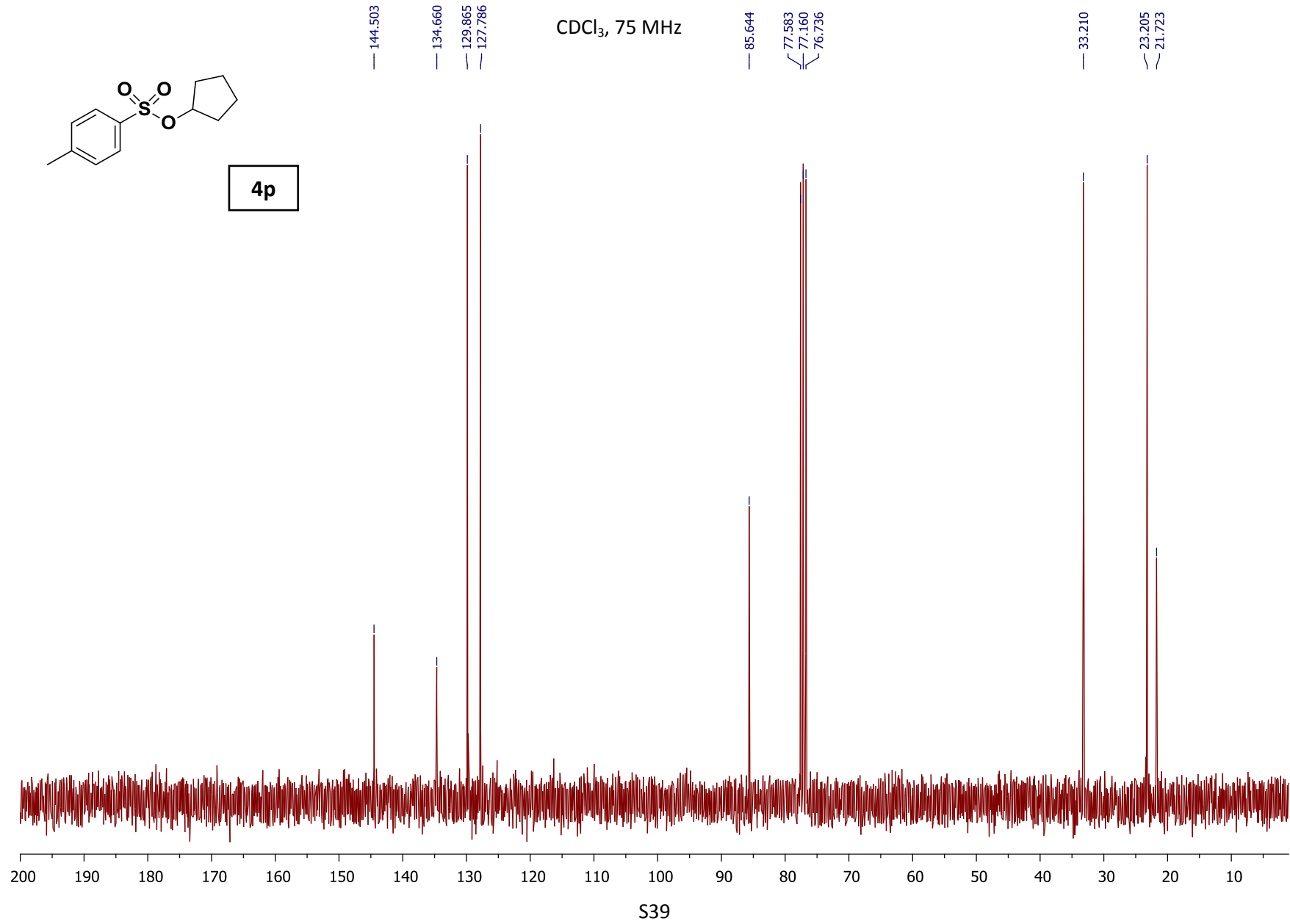
2.445  
1.816  
1.803  
1.795  
1.772  
1.767  
1.757  
1.752  
1.735  
1.729  
1.718  
1.689  
1.573  
1.563  
1.549

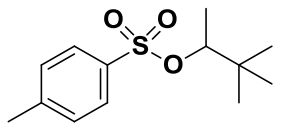


S38



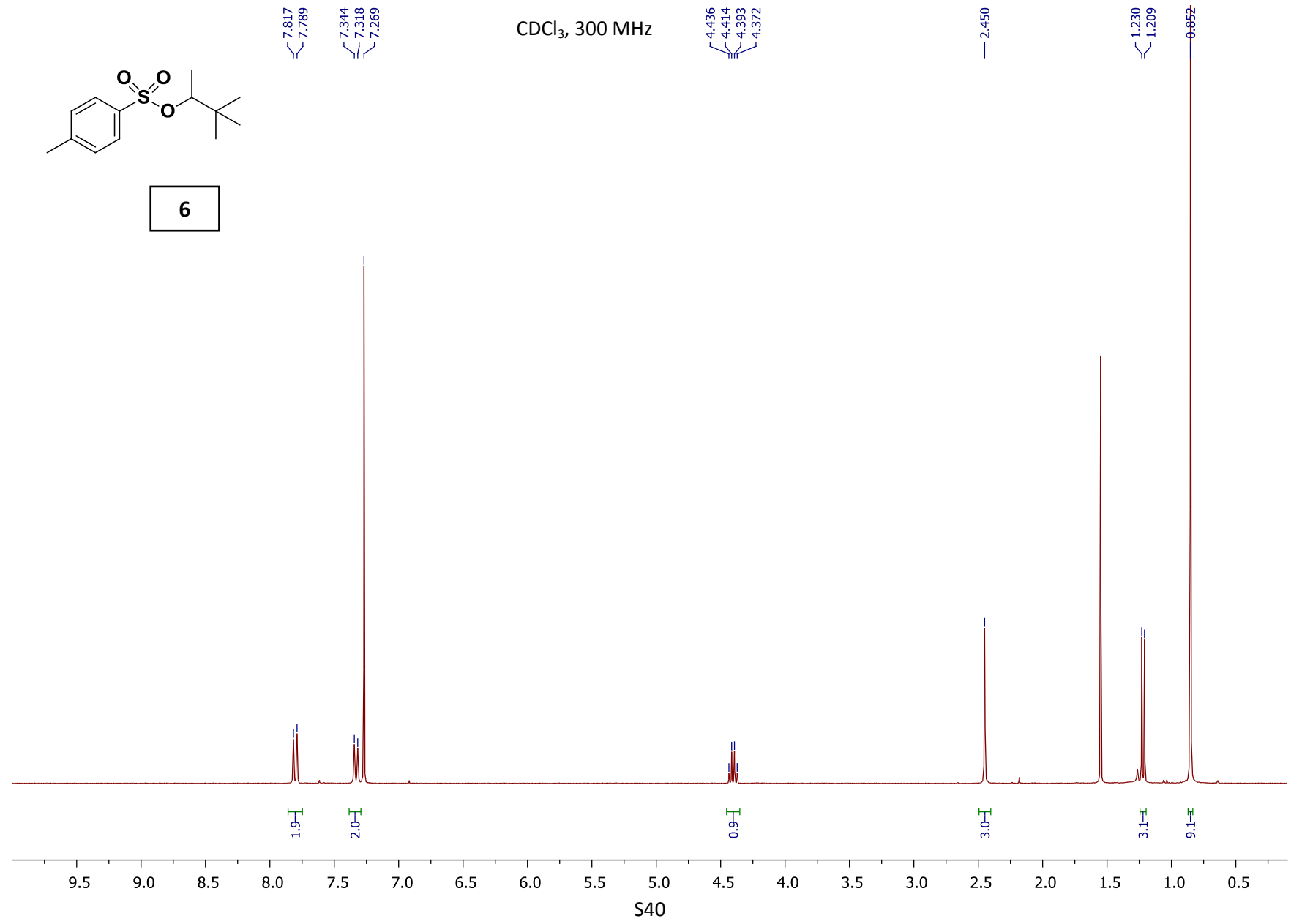
4p



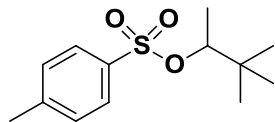


6

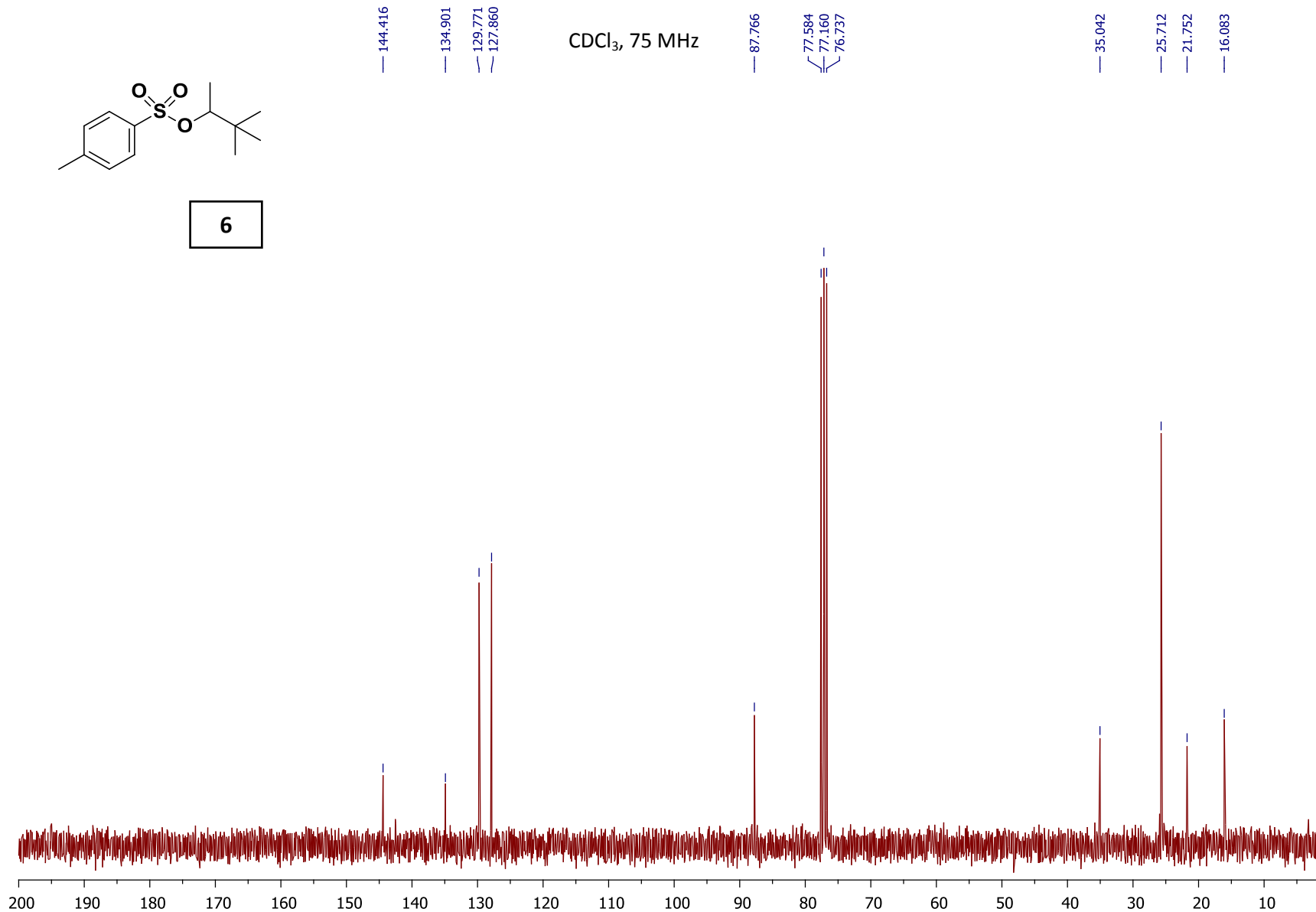
CDCl<sub>3</sub>, 300 MHz

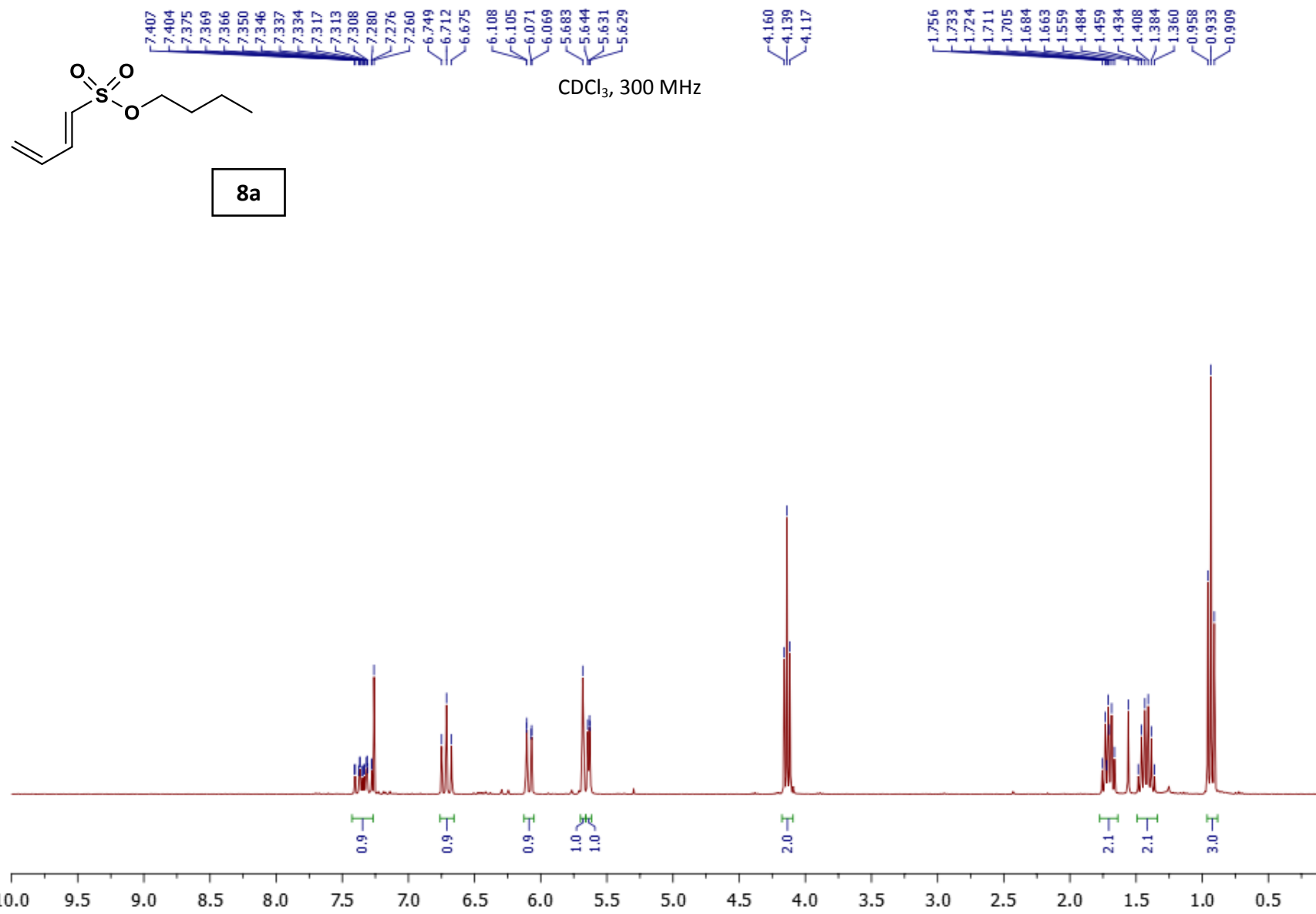


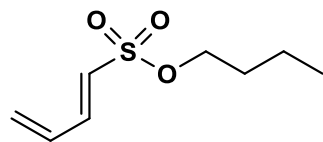




6







8a

143.151

130.379

129.111

122.577

CDCl<sub>3</sub>, 75 MHz

77.584

77.160

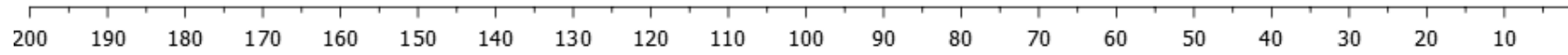
76.737

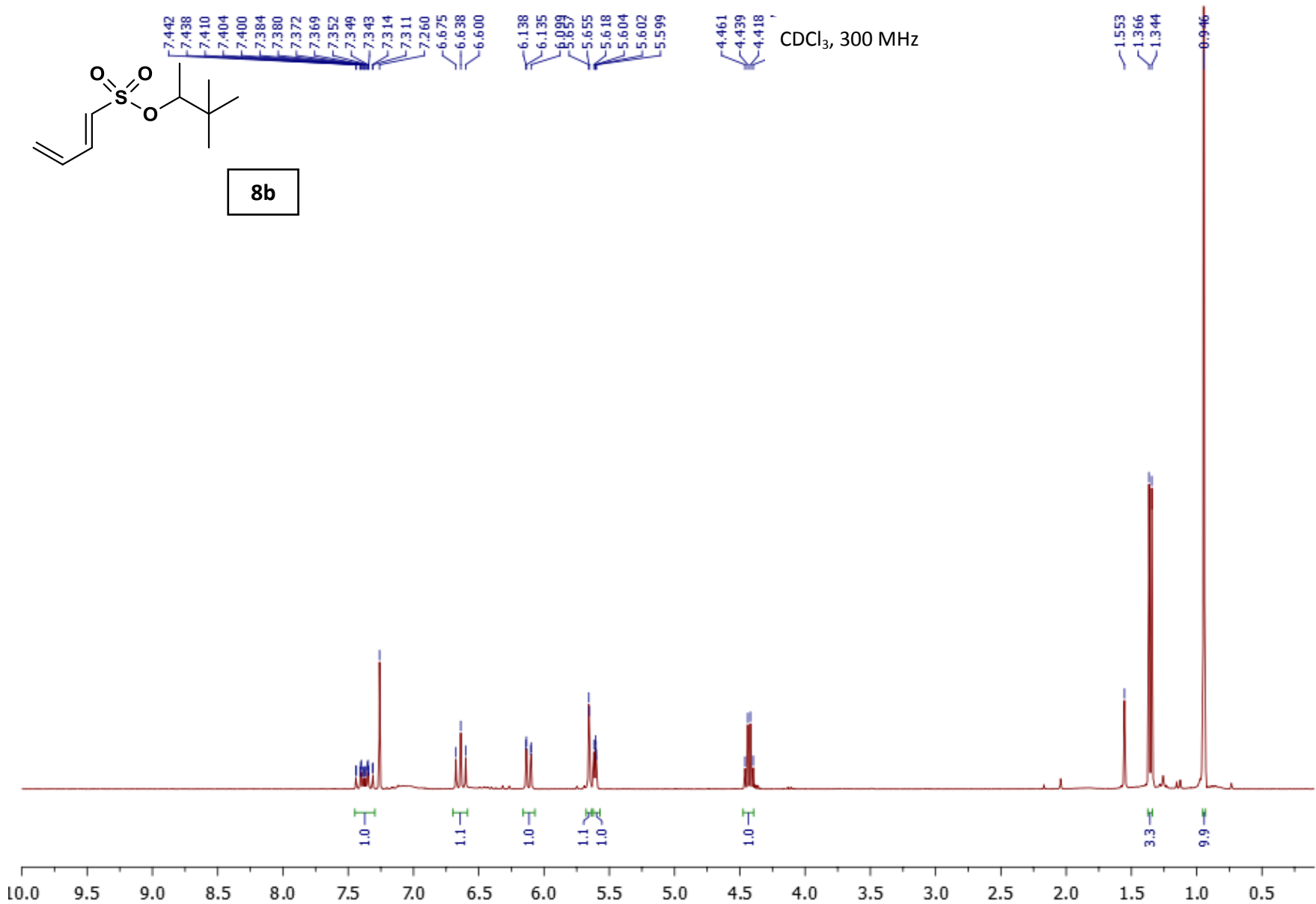
70.489

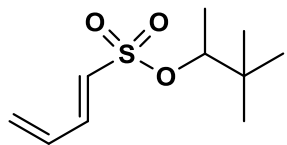
31.059

18.827

13.587

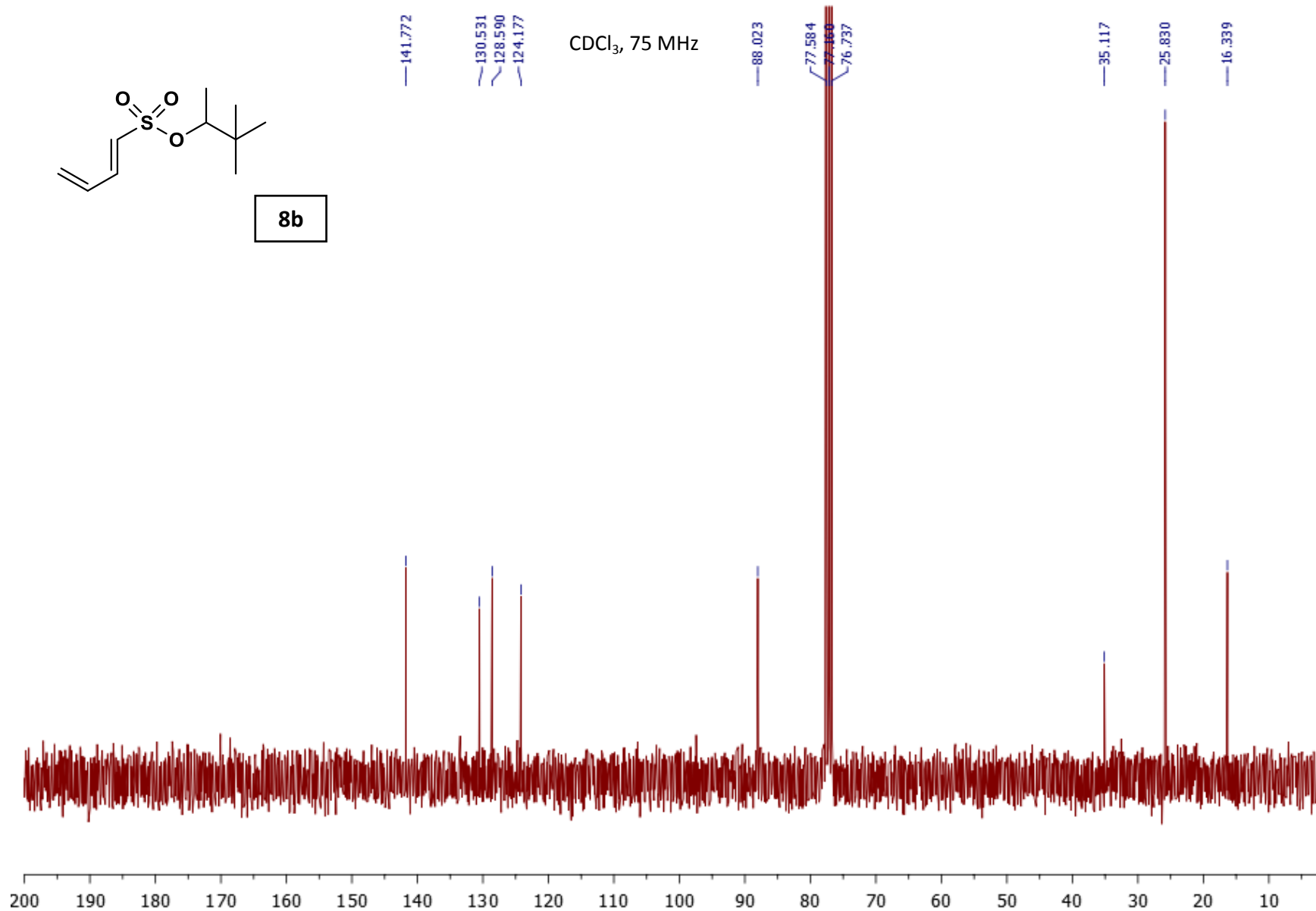




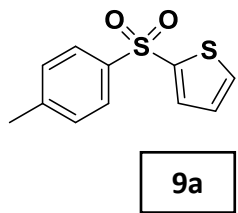


8b

CDCl<sub>3</sub>, 75 MHz



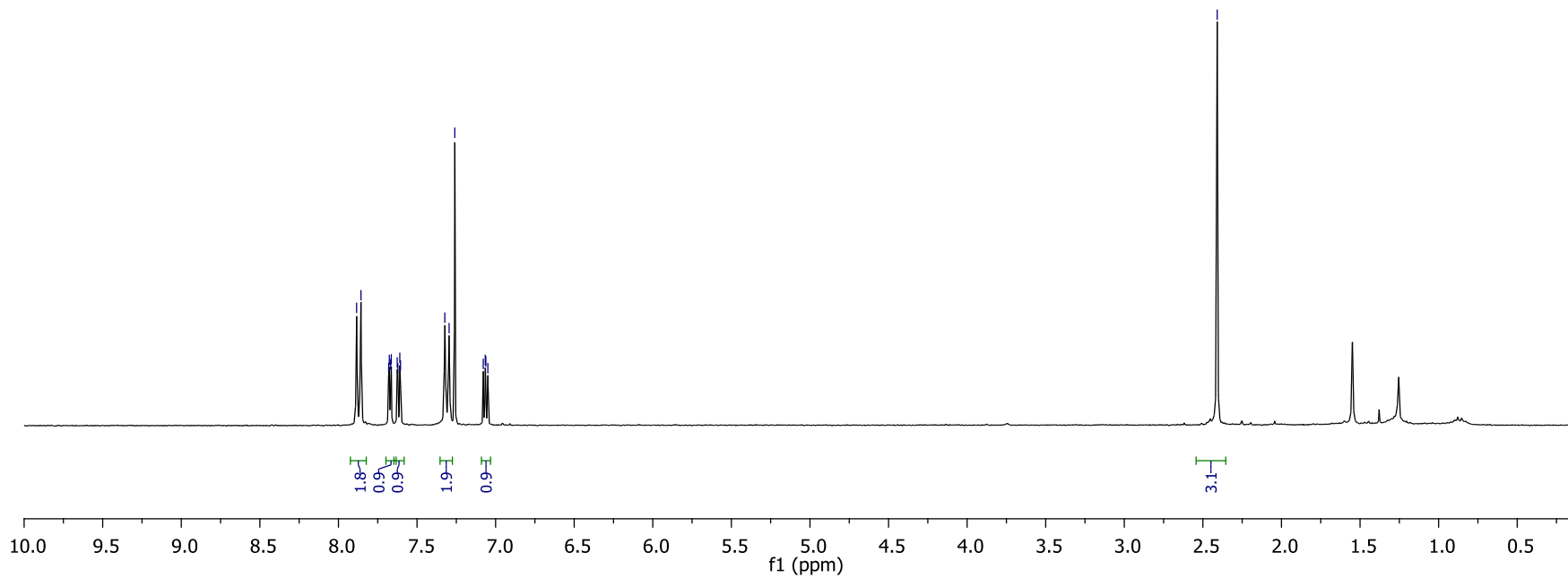
S45

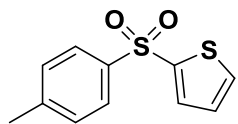


7.884  
7.857  
7.681  
7.676  
7.668  
7.664  
7.626  
7.622  
7.610  
7.605  
7.323  
7.296  
7.260  
7.079  
7.066  
7.062  
7.049

CDCl<sub>3</sub>, 300 MHz

— 2.409



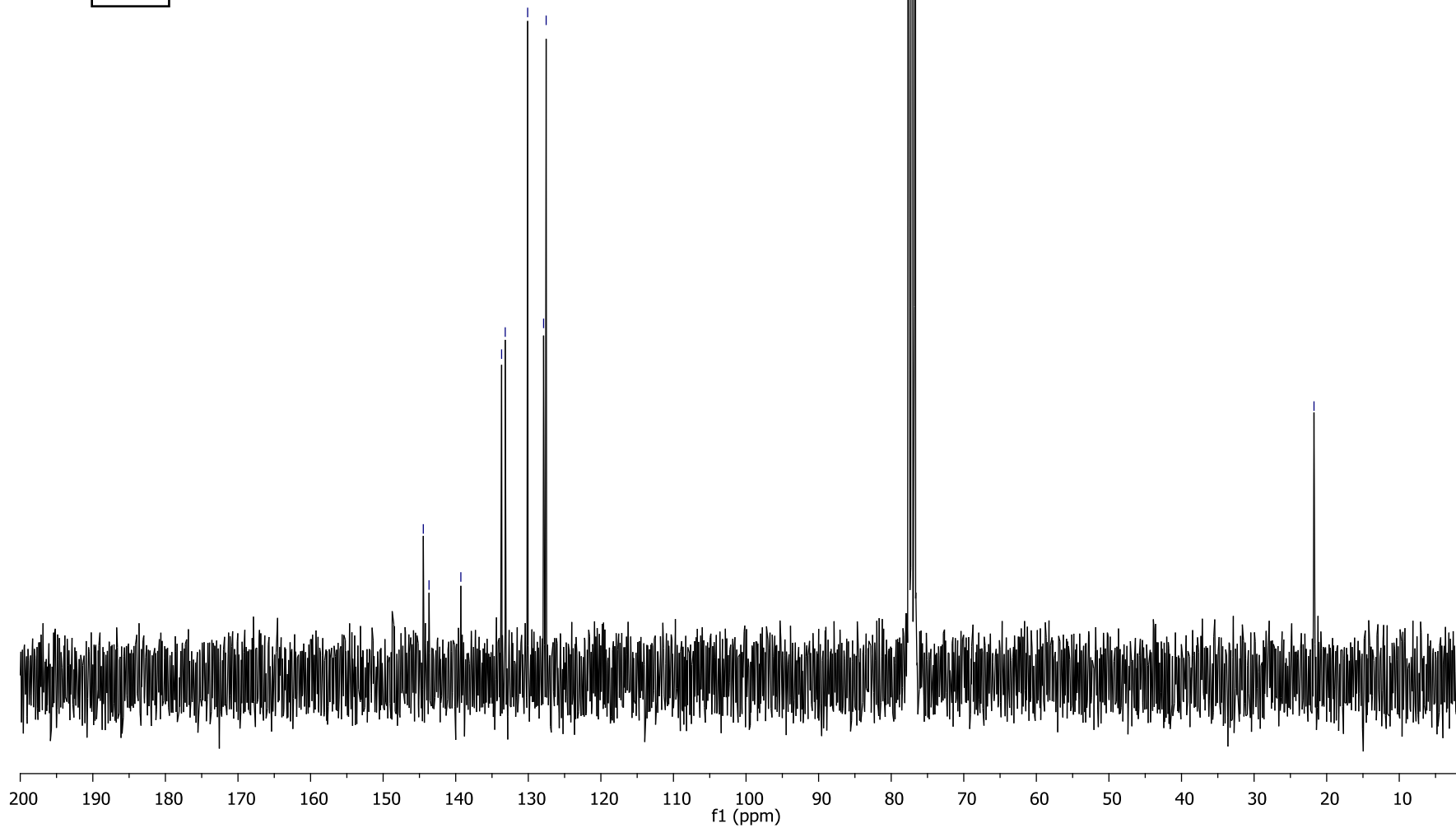


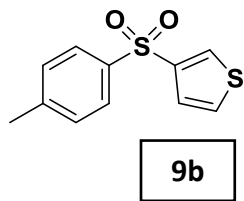
9a

144.467  
143.677  
139.293  
133.679  
133.178  
130.088  
127.892  
127.539  
CDCl<sub>3</sub>, 75 MHz

77.584  
77.169  
76.737

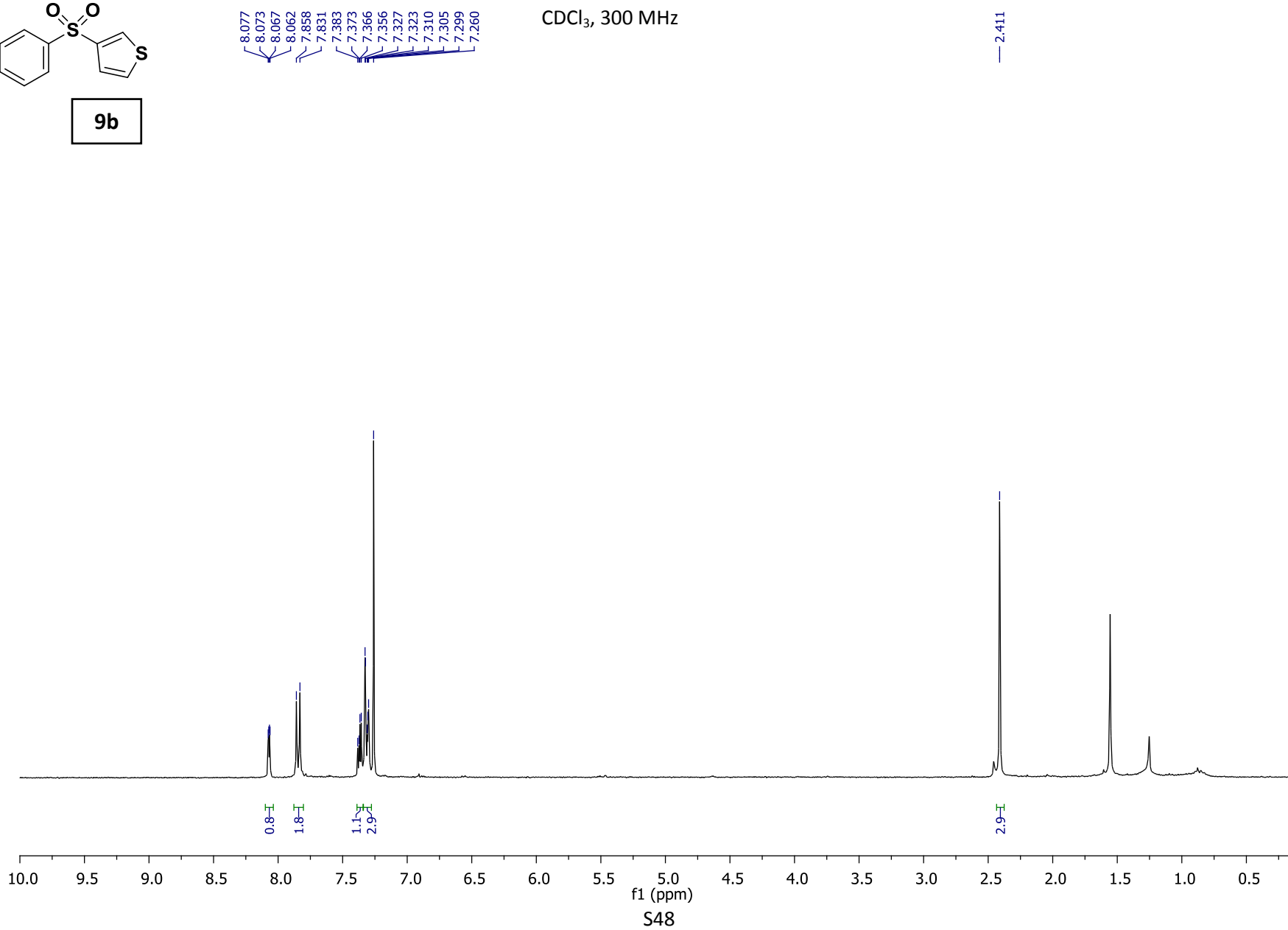
21.746



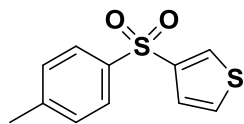


CDCl<sub>3</sub>, 300 MHz

— 2.411

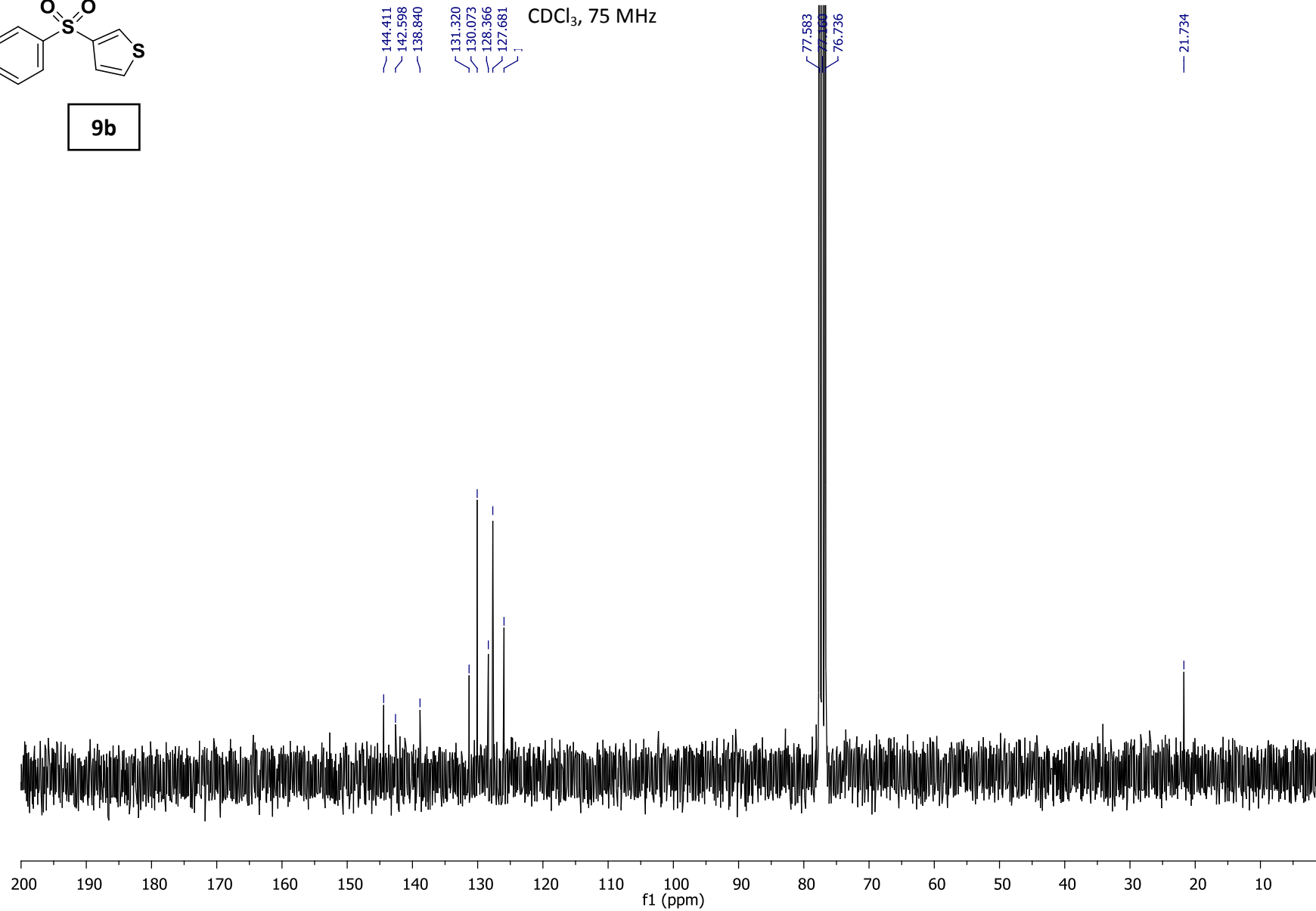


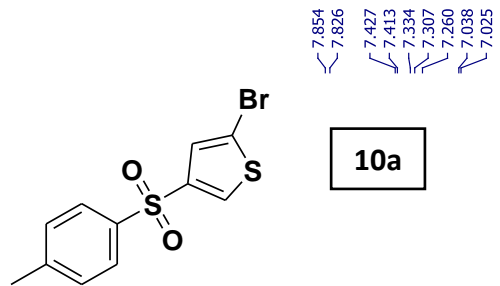




9b

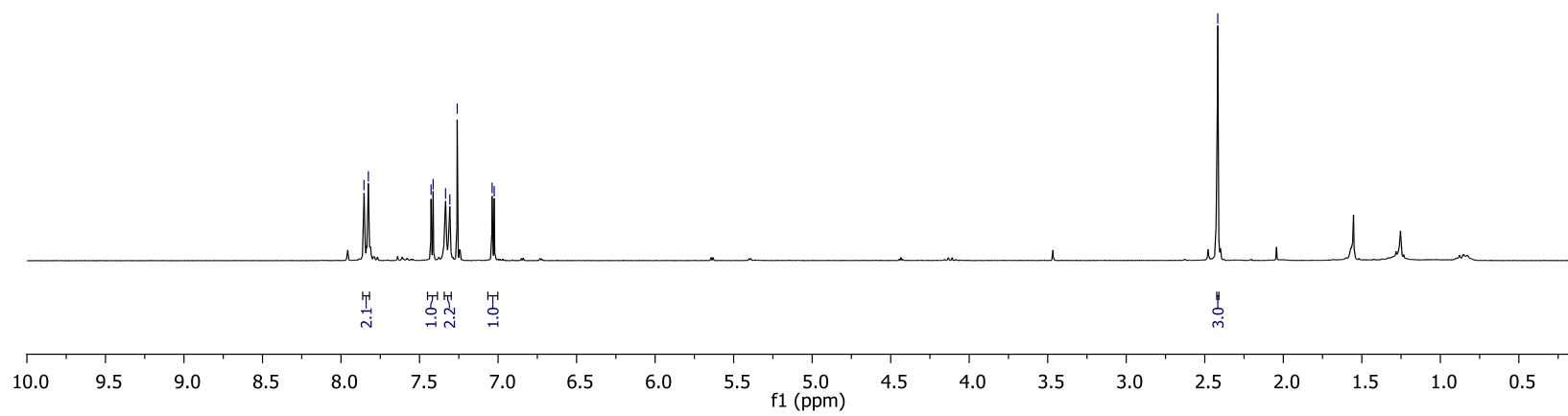
CDCl<sub>3</sub>, 75 MHz

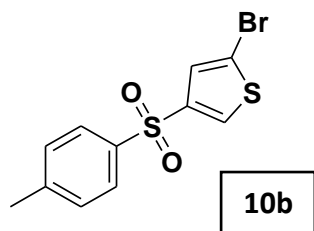




CDCl<sub>3</sub>, 300 MHz

— 2.417

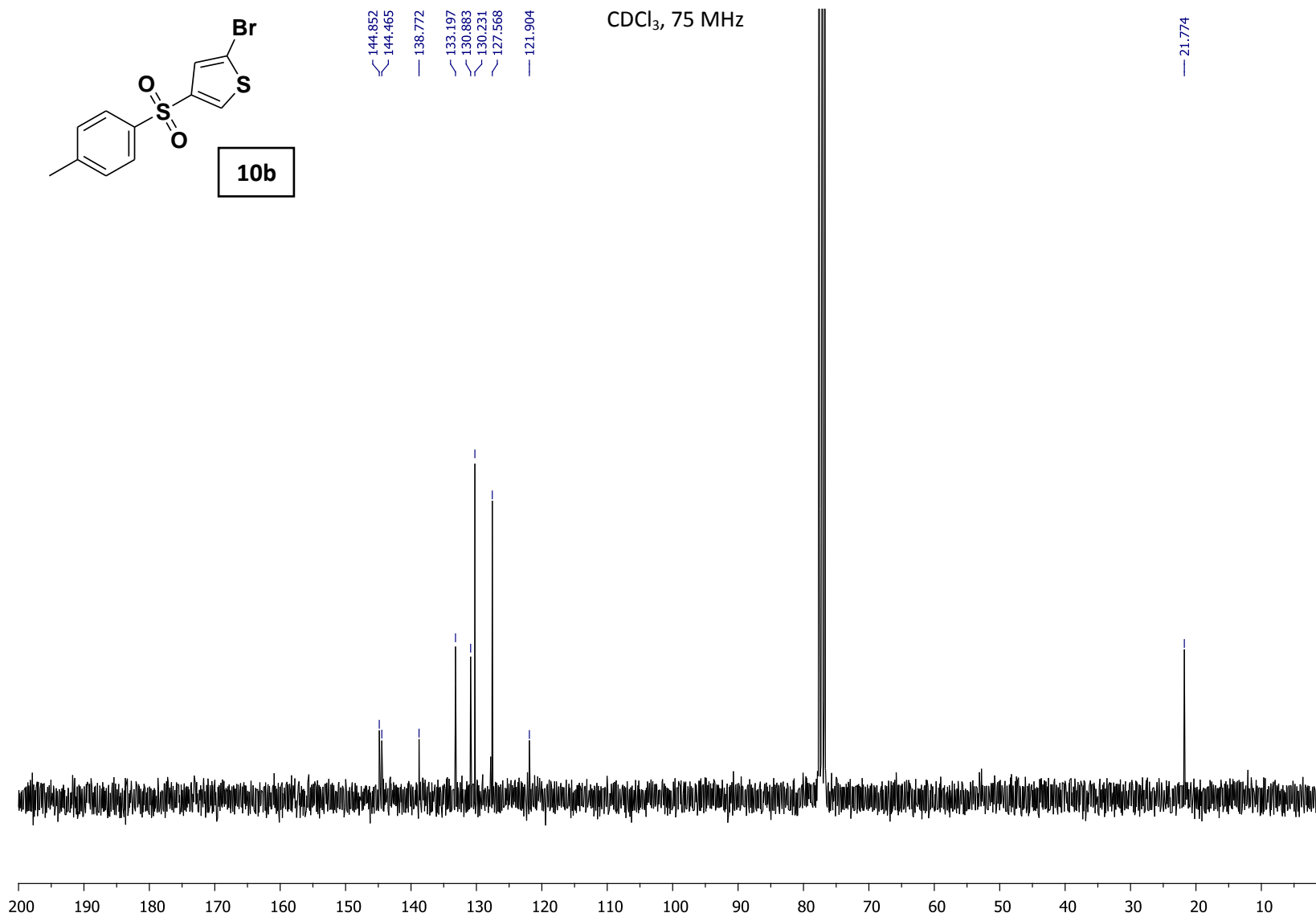


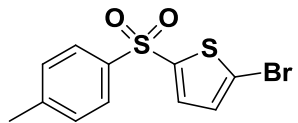


144.852  
144.465  
138.772  
133.197  
130.883  
130.231  
127.568  
121.904

CDCl<sub>3</sub>, 75 MHz

21.774



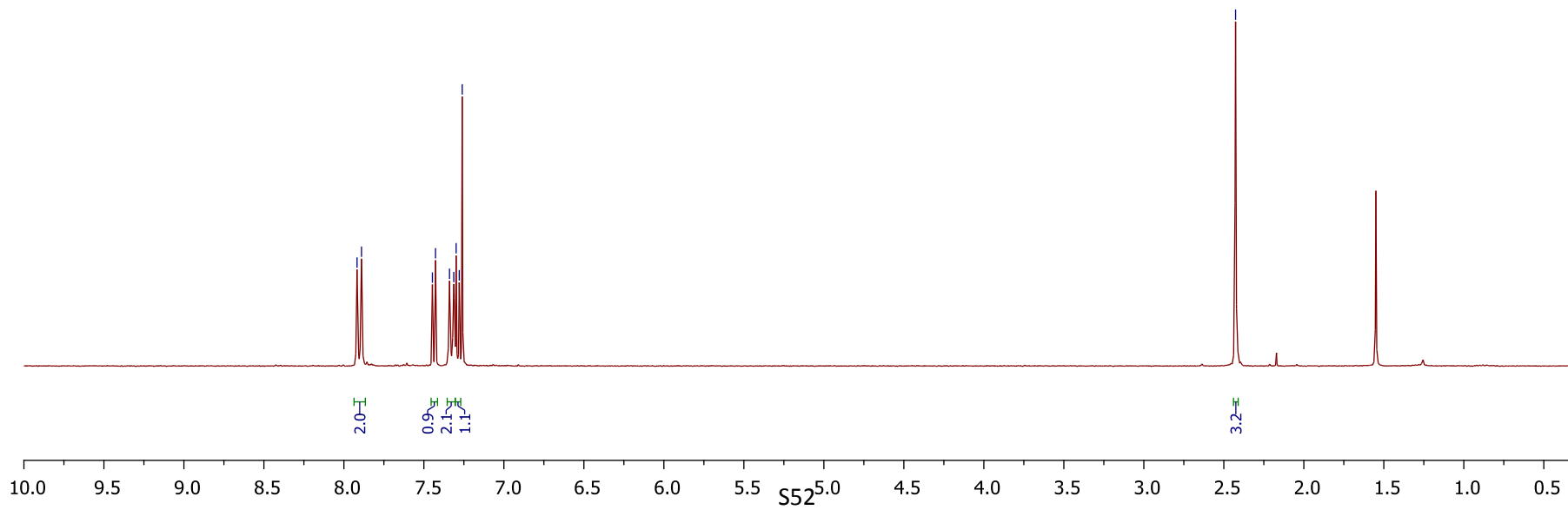


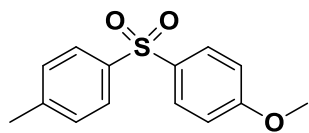
10b

7.918  
7.890  
7.447  
7.427  
7.340  
7.313  
7.298  
7.279  
7.260

CDCl<sub>3</sub>, 300 MHz

2.427





11b

7.873  
7.844  
7.808  
7.780

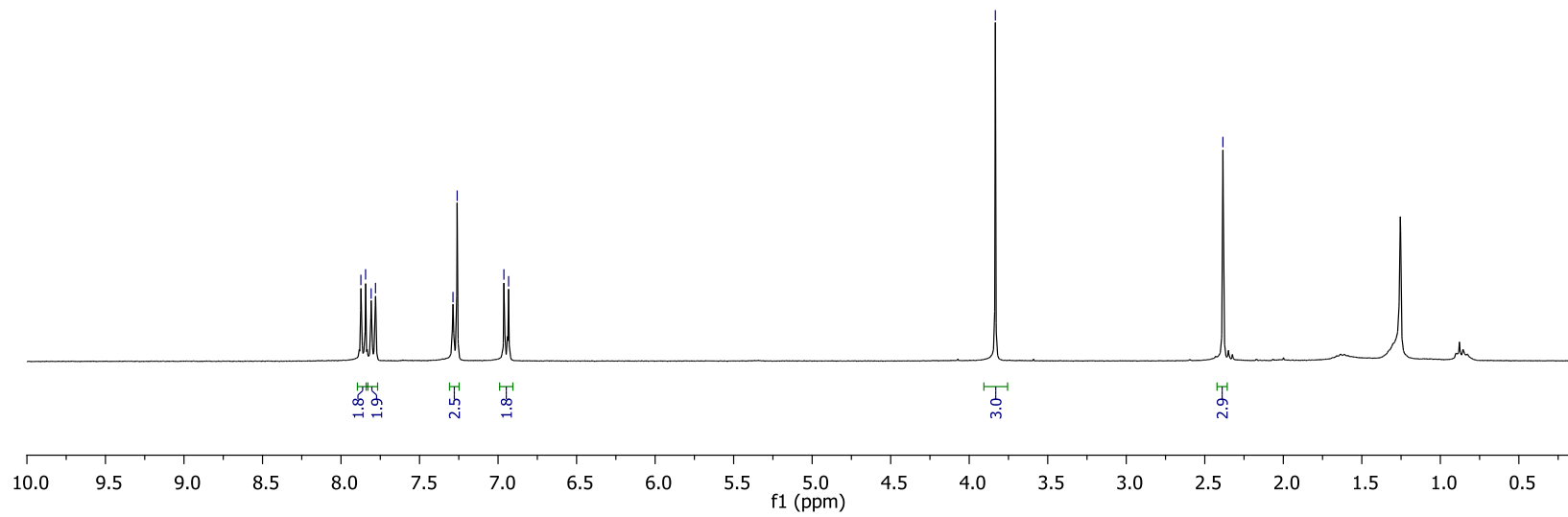
7.287  
7.260

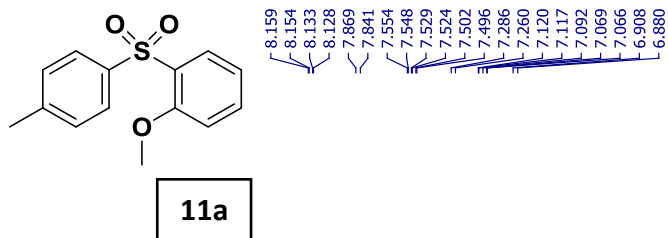
6.963  
6.933

CDCl<sub>3</sub>, 300 MHz

3.833

2.385

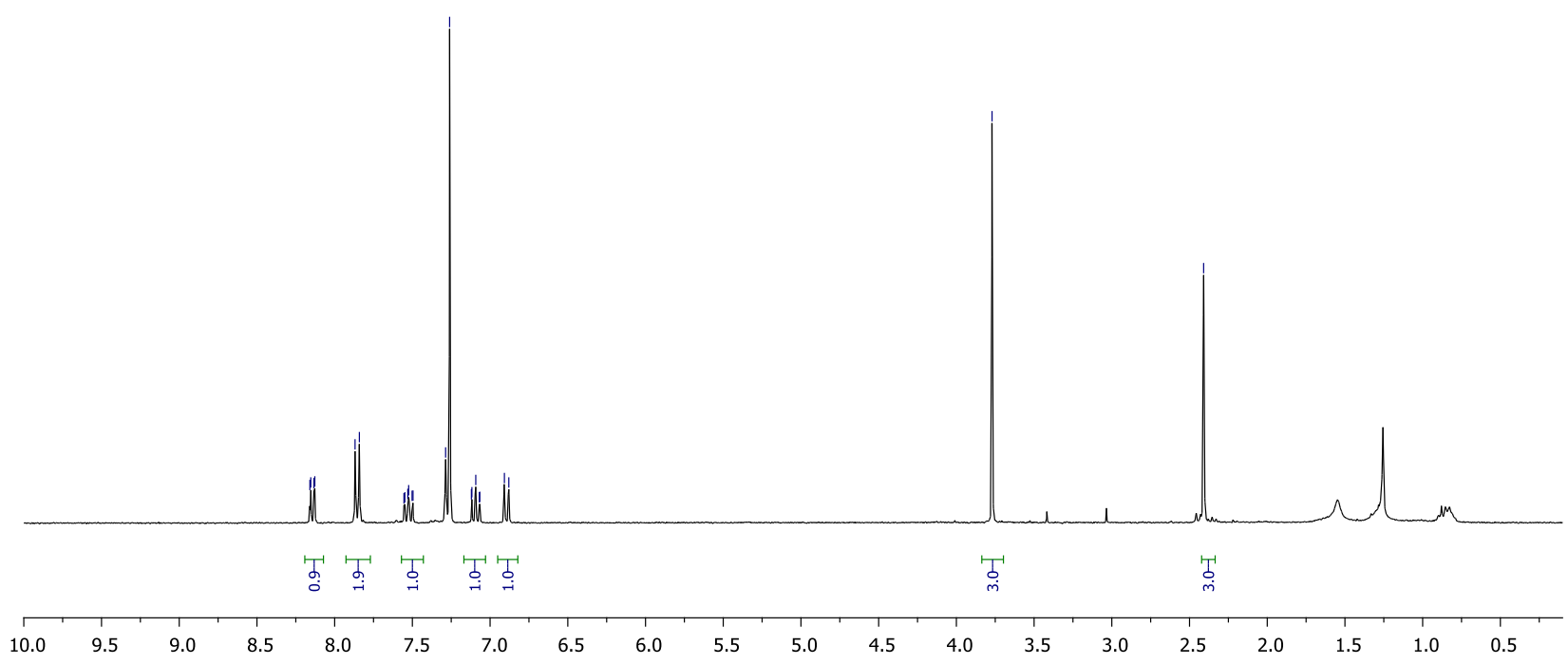


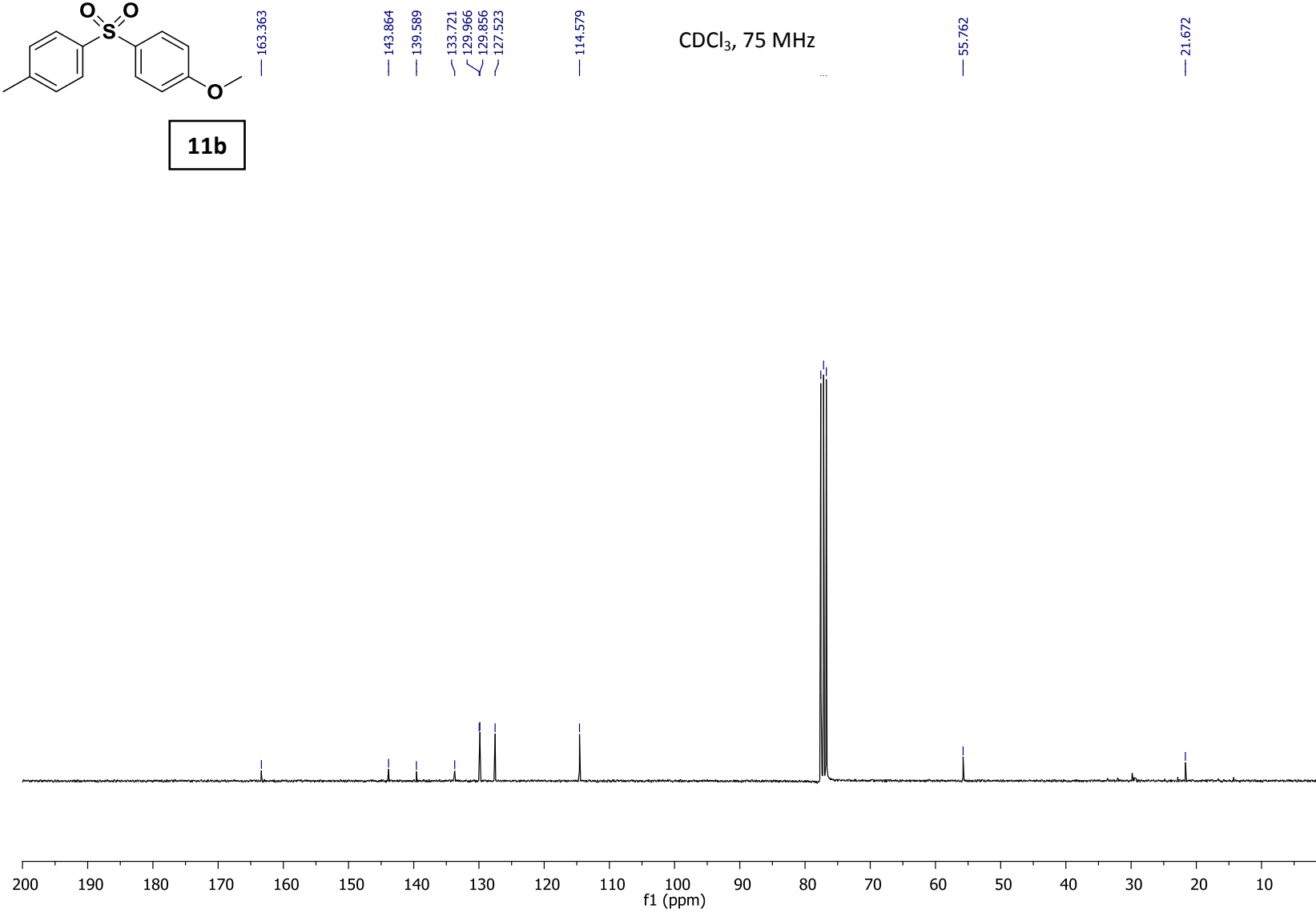
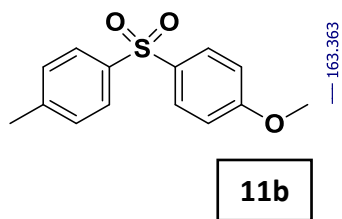


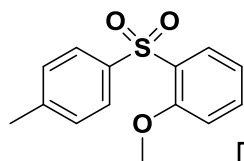
CDCl<sub>3</sub>, 300 MHz

— 3.771  
— 2.409

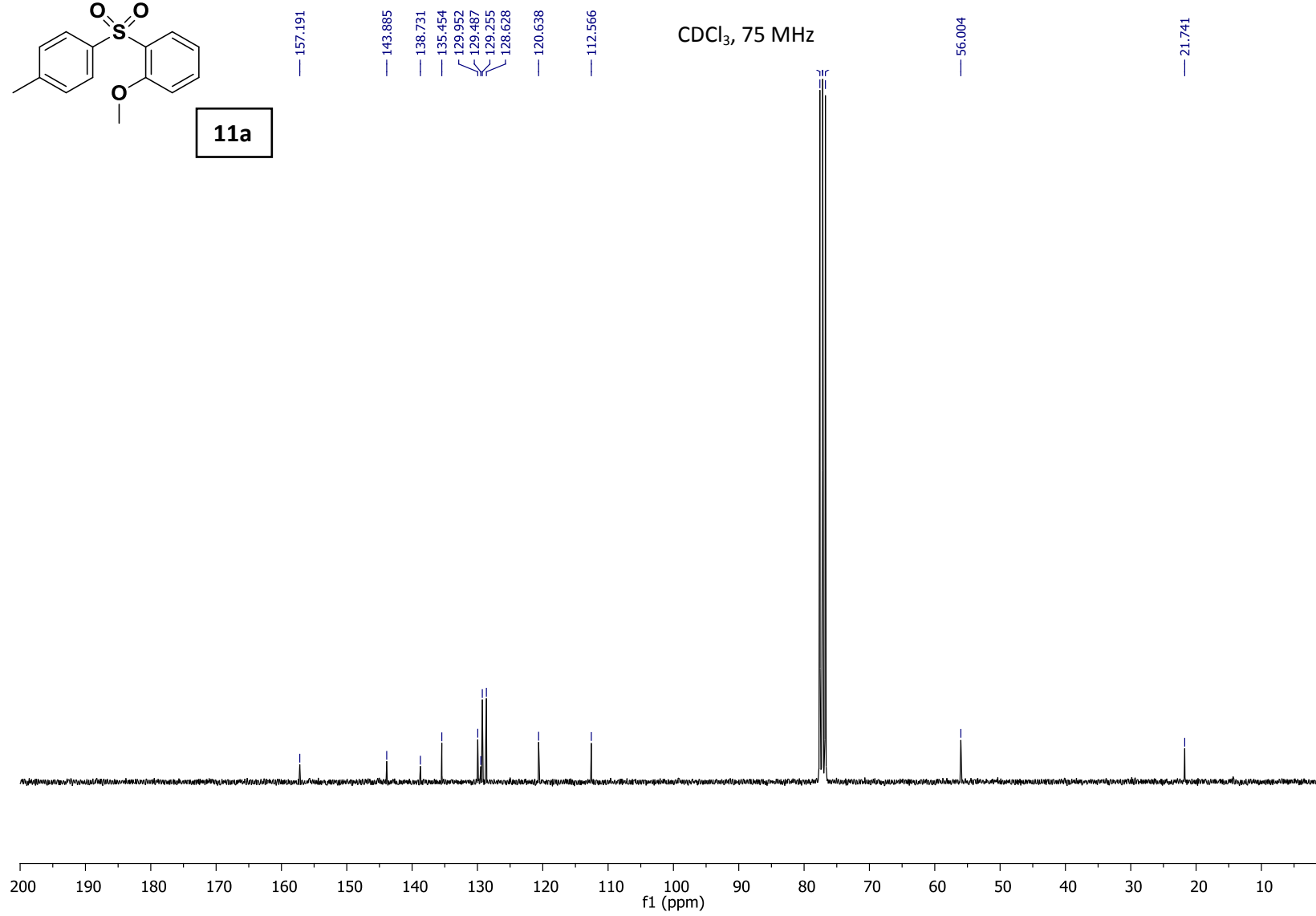
8.159  
8.154  
8.133  
8.128  
7.869  
7.841  
7.554  
7.548  
7.524  
7.502  
7.496  
7.286  
7.260  
7.120  
7.117  
7.092  
7.069  
7.066  
6.908  
6.880



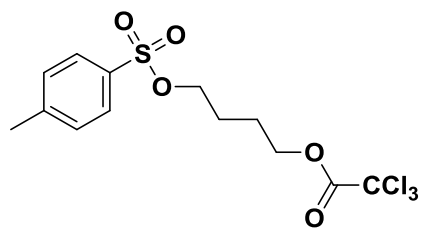




**11a**







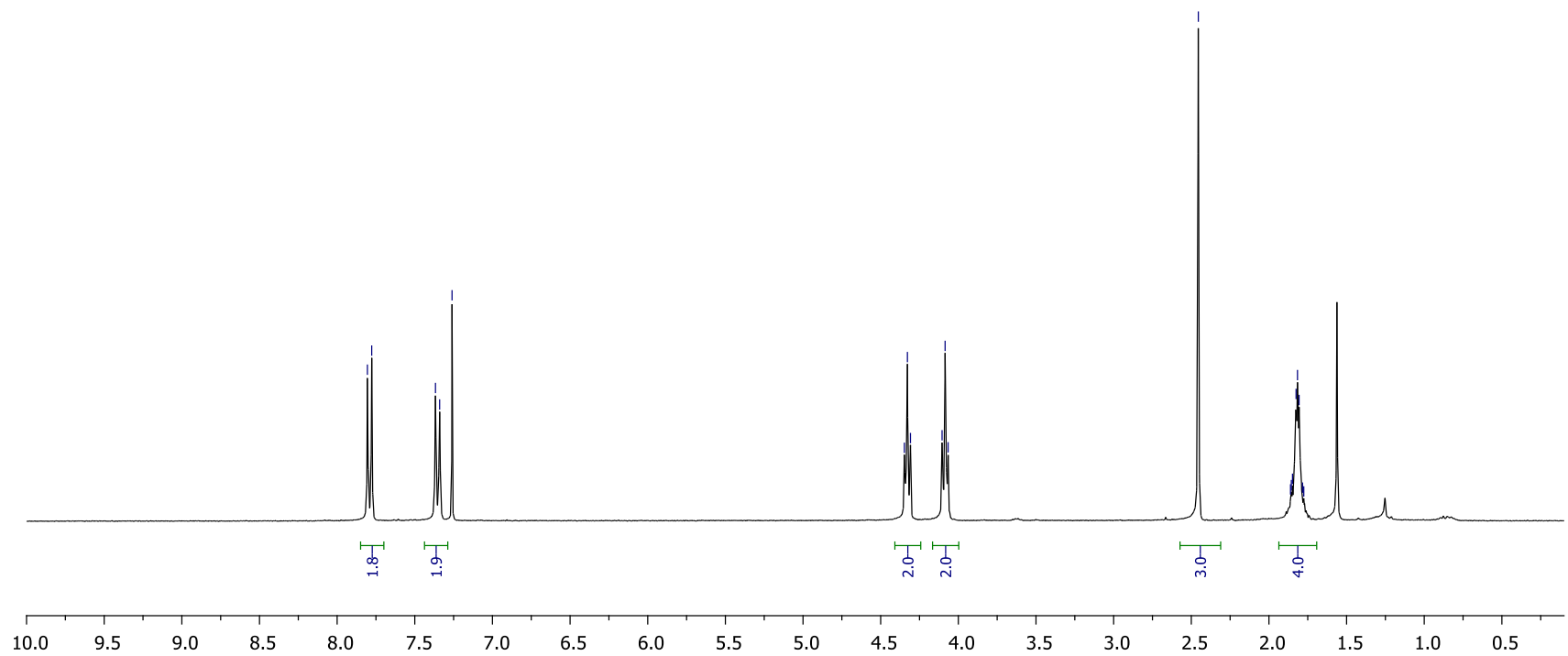
12

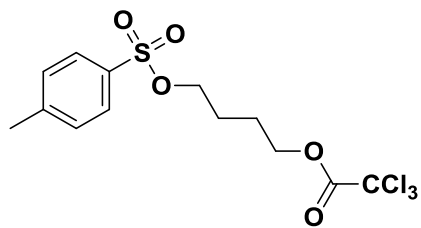
7.805  
7.777

7.367  
7.340  
7.260

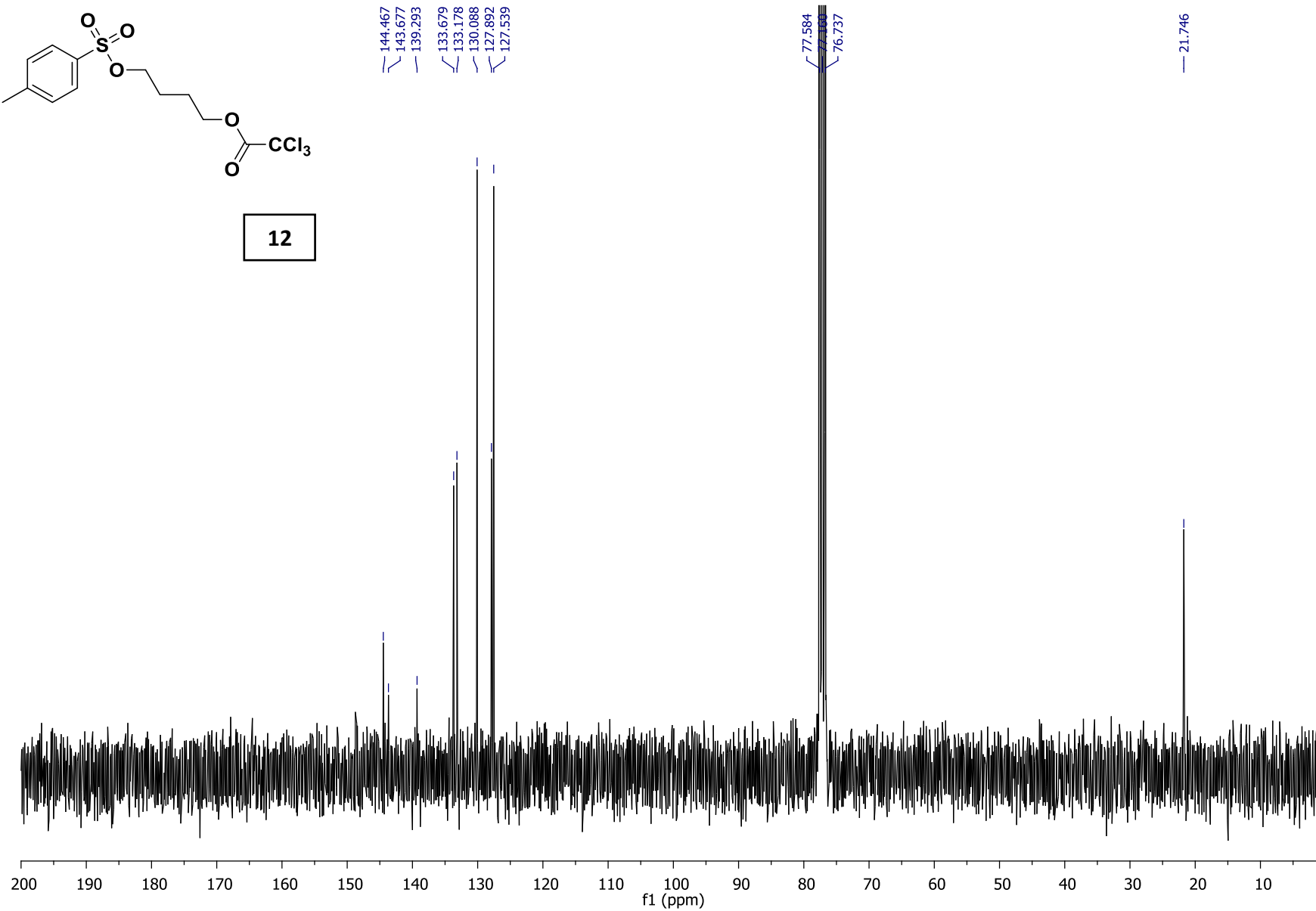
4.348  
4.328  
4.308  
4.105  
4.085  
4.066

2.455  
1.861  
1.856  
1.848  
1.825  
1.816  
1.806  
1.783  
1.776





12



S58