

## Supporting Information

### Stannylated allyl carbonates as versatile building blocks for the diversity oriented synthesis of allylic amines and amides

Christian Bukovec and Uli Kazmaier\*

*Institut für Organische Chemie, Universität des Saarlandes, D-66123 Saarbrücken, Germany.  
Fax: +49 681 302 2409; Tel: +49 681 302 3409; E-mail: [u.kazmaier@mx.uni-saarland.de](mailto:u.kazmaier@mx.uni-saarland.de)*

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**Ethyl 2-(tributylstannyl)allyl carbonate (1a):** In a flame-dried 100 mL three-necked flask equipped with a reflux condenser with connection to high vacuum and nitrogen via a Schlenk line, a dropping funnel, a septum and a magnetic stir bar were placed tris-(*tert*-butylisonitri)-tricarbonyl-molybdän (258 mg, 0.6 mmol, 3 mol%) and hydroquinone (220 mg, 2.0 mmol, 10 mol%) under nitrogen. Then the nitrogen atmosphere was evacuated and CO was added via a balloon and a syringe. Subsequently THF and ethyl propargyl carbonate (2.56 g, 20 mmol, 1 equiv) were added and the resulting mixture was stirred for 15 min vigorously. Tributyl tin hydride (11.6g, 40 mmol, 2 equiv) was then added via the dropping funnel and the reaction mixture was heated to 60° C for 4 h. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/NEt<sub>3</sub> 99:0:1–98:1:1) the pure product was obtained in 89 % yield (7.46 g, 17.8 mmol) with a regioisomeric ratio:  $\alpha/\beta$ -(*E*)/ $\beta$ -(*Z*) = 95/4/1. <sup>1</sup>H NMR:  $\delta$  = 5.91 (ddt,  $J_{\text{Sn}}$  = 122.2 Hz,  $J$  = 1.9 Hz,  $J$  = 1.9 Hz, 1 H), 5.31 (ddt,  $J_{\text{Sn}}$  = 58.9 Hz,  $J$  = 2.1 Hz,  $J$  = 1.7 Hz, 1 H), 4.74 (ddd,  $J_{\text{Sn}}$  = 28.4 Hz,  $J$  = 1.7 Hz, 2 H), 4.20 (q,  $J$  = 7.1 Hz, 2 H), 1.60 – 1.40 (m, 6 H), 1.36 – 1.27 (m, 9 H), 0.96 – 0.92 (m, 6 H), 0.89 (t,  $J$  = 7.3 Hz, 9 H). <sup>13</sup>C NMR:  $\delta$  = 155.1, 148.8, 125.6, 74.0, 63.8, 29.0 ( $J_{\text{Sn}}$  = 20.2 Hz), 27.3 ( $J_{\text{Sn}}$  = 58.3 Hz), 14.3, 13.6, 9.5 ( $J_{\text{Sn}}$  = 335.3 Hz). <sup>119</sup>Sn NMR:  $\delta$  = –41.9. (***E*-Ethyl 3-(tributylstannyl)allyl carbonate ( $\beta$ -*E*-1)** (selected signals): <sup>1</sup>H NMR:  $\delta$  = 6.31 (dt,  $J$  = 19.1 Hz,  $J$  = 1.4 Hz, 1H), 6.05 (dt,  $J$  = 19.1 Hz,  $J$  = 5.3 Hz, 1H), 4.63 (dd,  $J$  = 5.3 Hz,  $J$  = 1.4 Hz, 2H). HRMS (CI)  $m/z$  calcd for C<sub>14</sub>H<sub>27</sub>O<sub>3</sub>Sn (M-Bu)<sup>+</sup>: 363.0982, found: 363.0986.

**1-(2-(Tributylstannyl)allyl)morpholine (2b):** Following the general procedure for allylic aminations **2b** was obtained from morpholine (24 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after 2 h at 0° C. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/NEt<sub>3</sub> 99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 87 % yield (91 mg, 0.219 mmol) as a colorless oil. <sup>1</sup>H NMR:  $\delta$  = 5.79 (dt,  $J_{\text{Sn}}$  = 135.6 Hz,  $J$  = 2.8,  $J$  = 1.4 Hz, 1 H), 5.22 (dt,  $J_{\text{Sn}}$  = 61.5 Hz,  $J$  = 2.8,  $J$  = 1.4 Hz, 1 H), 3.67 (t,  $J$  = 4.6 Hz, 4 H), 3.05 (dd,  $J_{\text{Sn}}$  = 46.5 Hz,  $J$  = 1.2 Hz,  $J$  = 1.2 Hz, 2 H), 2.36 (m, 4 H), 1.47 (m, 6 H), 1.32 (tq,  $J$  = 7.4,  $J$  = 7.2 Hz, 6 H), 0.81 – 0.98 (m, 15 H). <sup>13</sup>C NMR:  $\delta$  = 154.1, 126.3, 69.4, 67.1, 53.7, 29.2 ( $J_{\text{Sn}}$  = 19.4 Hz), 27.5 ( $J_{\text{Sn}}$  = 57.3 Hz), 13.7, 9.6 ( $J_{\text{Sn}}$  = 328.8 Hz). <sup>119</sup>Sn NMR:  $\delta$  = –48.9. HRMS (CI)  $m/z$  calcd for C<sub>19</sub>H<sub>39</sub>NOSn<sup>120</sup> [M]<sup>+</sup>: 417.2054, found: 417.2044.

**1-(2-(Tributylstannyl)allyl)pyrrolidine (2c):** Following the general procedure for allylic aminations **2c** was obtained from pyrrolidine (20 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after 2 h at 0° C. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/NEt<sub>3</sub> 99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 86 % yield (86 mg, 0.215 mmol) as a colorless oil. <sup>1</sup>H NMR:  $\delta$  = 5.79 (dt,  $J_{\text{Sn}}$  = 139.1 Hz,  $J$  = 2.7,  $J$  = 1.3 Hz, 1 H), 5.14 (dt,  $J_{\text{Sn}}$  = 63.3 Hz,  $J$  = 2.6 Hz,  $J$  = 1.3 Hz, 1 H), 3.17 (m,  $J_{\text{Sn}}$  = 44.9 Hz, 2 H), 2.39 (m, 4 H), 1.71 (m, 4

H), 1.49 (m, 6 H), 1.31 (tq,  $J = 7.4$ ,  $J = 7.2$  Hz, 6 H), 0.79–0.96 (m, 15 H).  $^{13}\text{C}$  NMR:  $\delta = 152.5$ , 123.8, 66.1, 54.0, 29.2, 27.5, 23.6, 13.7, 9.5.  $^{119}\text{Sn}$  NMR:  $\delta = -49.0$ . HRMS (CI) calcd for  $\text{C}_{19}\text{H}_{39}\text{NSn}^{120} [\text{M}]^+$ : 401.2104, found: 401.2152.

***N,N*-Diethyl-1-(2-(Tributylstannyl)allyl)-amine (2d)**: Following the general procedure for allylic aminations **2d** was obtained from diethylamine (20 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after 2 h at 0° C. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/NEt<sub>3</sub> 99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 90 % yield (90 mg, 0.224 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta = 5.79$  (m,  $J_{\text{Sn}} = 138.7$  Hz, 1 H), 5.18 (m,  $J_{\text{Sn}} = 63.0$  Hz, 1 H), 3.11 (dd,  $J_{\text{Sn}} = 47.1$  Hz,  $J = 1.4$  Hz = 1.4 Hz, 2 H), 2.43 (q,  $J = 7.1$  Hz, 4 H), 1.49 (m, 6 H), 1.31 (tq,  $J = 7.3$ , 7.2 Hz, 6 H), 0.96 (t,  $J = 7.1$  Hz, 6 H), 0.80–0.94 (m, 15 H).  $^{13}\text{C}$  NMR:  $\delta = 156.2$ , 124.9 ( $J_{\text{Sn}} = 27$  Hz), 64.1 ( $J_{\text{Sn}} = 34$  Hz), 45.9, 29.2 ( $J_{\text{Sn}} = 19$  Hz), 27.5 ( $J_{\text{Sn}} = 58$  Hz), 13.7, 11.0, 9.5 ( $J_{\text{Sn}} = 328$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -49.4$ . HRMS (CI) calcd for  $\text{C}_{19}\text{H}_{41}\text{NSn}^{120} [\text{M}]^+$ : 403.2261, found: 403.2265.

***N,N*-Diallyl-1-(2-(Tributylstannyl)allyl)-amine (2e)**: Following the general procedure for allylic aminations **2e** was obtained from diallylamine (27 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after 2 h at 0° C. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/NEt<sub>3</sub> 99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 84 % yield (90 mg, 0.211 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta = 5.64 - 5.98$  (m, 3 H), 5.22 (dt,  $J_{\text{Sn}} = 60.5$  Hz,  $J = 2.9$ ,  $J = 1.5$  Hz, 1 H), 5.10–5.15 (m, 4 H), 3.13 (dd,  $J_{\text{Sn}} = 46.4$  Hz,  $J = 1.3$  Hz = 1.3 Hz, 2 H), 2.00 (ddd,  $J = 6.5$ ,  $J = 1.6$ ,  $J = 1.6$  Hz, 4 H), 1.49 (m, 6 H), 1.31 (tq,  $J = 7.3$ ,  $J = 7.2$  Hz, 6 H), 0.81 – 0.98 (m, 15 H).  $^{13}\text{C}$  NMR:  $\delta = 155.2$ , 135.9, 126.0, 117.2, 64.1 ( $J_{\text{Sn}} = 34$  Hz), 56.3, 29.2 ( $J_{\text{Sn}} = 19$  Hz), 27.5 ( $J_{\text{Sn}} = 58$  Hz), 13.7, 9.5 ( $J_{\text{Sn}} = 329$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -48.3$ . HRMS (CI) calcd for  $\text{C}_{21}\text{H}_{41}\text{NSn}^{120} [\text{M}]^+$ : 427.2261, found: 427.2293.

***N,N*-Dibenzyl-1-(2-(Tributylstannyl)allyl)-amine (2f)**: Following the general procedure for allylic aminations **2f** was obtained from dibenzylamine (54 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after warming up from 0° C to r.t. over 16 h. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/NEt<sub>3</sub> 99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 53 % yield (70 mg, 0.133 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta = 7.41 - 7.30$  (m, 8 H), 7.26 (m, 2 H), 6.01 (dt,  $J_{\text{Sn}} = 134.2$  Hz,  $J = 2.9$ , 1.4 Hz, 1 H), 5.34 (m,  $J_{\text{Sn}} = 61.6$  Hz, 1 H), 3.53 (s, 4 H), 3.20 (m,  $J_{\text{Sn}} = 43.5$  Hz, 2 H), 1.45 (m, 6 H), 1.28 (tq,  $J = 7.3$ , 7.1 Hz, 6 H), 0.97 – 0.81 (m, 15 H).  $^{13}\text{C}$  NMR:  $\delta = 153.8$ , 139.0, 129.1, 128.1, 127.2 ( $J_{\text{Sn}} = 25$  Hz), 126.8 ( $J_{\text{Sn}} = 27$  Hz), 64.2 ( $J_{\text{Sn}} = 34$  Hz), 57.9, 29.1 ( $J_{\text{Sn}} = 19$  Hz), 27.4 ( $J_{\text{Sn}} = 58$  Hz), 13.7, 9.5 ( $J_{\text{Sn}} = 335$

Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -46.0$ . HRMS (CI) calcd for  $\text{C}_{29}\text{H}_{45}\text{NSn}^{120}$   $[\text{M}]^+$ : 527.2574, found: 527.2602.

***N,N*-Dicyclohexyl-1-(2-(Tributylstannyl)allyl)-amine (2g)**: Following the general procedure for allylic aminations **2g** was obtained from dicyclohexylamine (50 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after warming up from 0° C to r.t. over 16 h. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/ $\text{NEt}_3$  99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 17 % yield (22 mg, 0.043 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta = 5.88$  (dt,  $J_{\text{Sn}} = 139.2$  Hz,  $J = 3.1$ ,  $J = 1.5$  Hz, 1 H), 5.17 (dt,  $J_{\text{Sn}} = 63.2$  Hz,  $J = 3.1$ ,  $J = 1.5$  Hz, 1 H), 3.33 (dd,  $J_{\text{Sn}} = 43.8$  Hz,  $J = 1.4 = 1.4$  Hz, 2 H), 2.49 (m, 2 H), 1.80 – 1.54 (m, 12 H), 1.46 (m, 6 H), 1.31 (tq,  $J = 7.3$ ,  $J = 7.2$  Hz, 6 H), 1.19 (m, 8 H), 0.98 – 0.81 (m, 15 H).  $^{13}\text{C}$  NMR:  $\delta = 156.2$ , 125.2, 56.8, 55.7 ( $J_{\text{Sn}} = 41$  Hz), 31.6, 29.2 ( $J_{\text{Sn}} = 19$  Hz), 27.5 ( $J_{\text{Sn}} = 58$  Hz), 26.5, 26.3, 13.7, 9.5 ( $J_{\text{Sn}} = 332$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -46.7$ . HRMS (CI) calcd for  $\text{C}_{27}\text{H}_{53}\text{NSn}^{120}$   $[\text{M}]^+$ : 511.3200, found: 511.3161.

**1-(2-(Tributylstannyl)allyl)aniline (2h)**: Following the general procedure for allylic aminations **2h** was obtained from aniline (26 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after warming up from 0° C to r.t. over 16 h. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/ $\text{NEt}_3$  99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 25 % yield (26 mg, 0.062 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta = 7.16$  (m, 2 H), 6.69 (tt,  $J = 7.3$ ,  $J = 1.0$  Hz, 1 H), 6.60 (m, 2H), 5.95 (dt,  $J_{\text{Sn}} = 131.0$  Hz,  $J = 2.2$ ,  $J = 1.7$  Hz, 1 H), 5.29 (dt,  $J_{\text{Sn}} = 60.9$  Hz,  $J = 2.3$ ,  $J = 1.5$  Hz, 1 H), 3.90 (dd,  $J_{\text{Sn}} = 32.8$  Hz,  $J = 1.6 = 1.6$  Hz, 2 H), 3.77 (bs, 1 H), 1.49 (m, 6 H), 1.30 (tq,  $J = 7.3$ , 7.2 Hz, 6 H), 1.00 – 0.83 (m, 15 H).  $^{13}\text{C}$  NMR:  $\delta = 153.0$ , 148.3, 129.1, 125.3 ( $J_{\text{Sn}} = 23$  Hz), 117.3, 113.0, 53.1, 29.2 ( $J_{\text{Sn}} = 20$  Hz), 27.4 ( $J_{\text{Sn}} = 58$  Hz), 13.7, 9.5 ( $J_{\text{Sn}} = 329$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -44.9$ . HRMS (CI) calcd for  $\text{C}_{21}\text{H}_{37}\text{NSn}^{120}$   $[\text{M}]^+$ : 366.1244, found: 366.1252.

**1-(2-(Tributylstannyl)allyl)-4-methoxy-aniline (2i)**: Following the general procedure for allylic aminations **2i** was obtained from 4-methoxyaniline (34 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after warming up from 0° C to r.t. over 16 h. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/ $\text{NEt}_3$  99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 58 % yield (66 mg, 0.146 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta = 6.77$  (m, 2 H), 6.57 (m, 2H), 5.95 (dt,  $J_{\text{Sn}} = 131.7$  Hz,  $J = 2.2$ , 1.8 Hz, 1 H), 5.29 (dt,  $J_{\text{Sn}} = 61.2$  Hz,  $J = 2.3$ , 1.6 Hz, 1 H), 3.86 (dd,  $J_{\text{Sn}} = 33.6$  Hz,  $J = 1.6$ , 1.6 Hz, 2 H), 3.75 (s, 3 H), 3.63 (bs, 1 H), 1.48 (m, 6 H), 1.30 (tq,  $J = 7.3$ , 7.2 Hz, 6 H), 0.99 – 0.82 (m, 15 H).  $^{13}\text{C}$  NMR:  $\delta = 153.6$ ; 152.1, 142.5, 125.1 ( $J_{\text{Sn}} = 23$  Hz), 114.8, 114.3, 55.8, 54.1 ( $J_{\text{Sn}} = 42$  Hz), 29.1 ( $J_{\text{Sn}} = 20$  Hz), 27.4

( $J_{\text{Sn}} = 58$  Hz), 13.7, 9.6 ( $J_{\text{Sn}} = 330$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -45.2$ . HRMS (CI) calcd for  $\text{C}_{22}\text{H}_{39}\text{NOSn}^{120}$   $[\text{M}]^+$ : 453.2054, found: 453.2060.

***N*-Benzyl-1-(2-(Tributylstannyl)allyl)-amine (2k)**: Following the general procedure for allylic aminations **2k** was obtained from benzylamine (29 mg, 0.275 mmol, 1.1 equiv) and 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after warming up from 0° C to r.t. over 16 h. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/ $\text{NEt}_3$  99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 51 % yield (56 mg, 0.128 mmol) as a colorless oil. In addition 34 % (32 mg, 0.042 mmol) of the diallylated product **2k'** were obtained as a colorless oil. Analysis data **2k**:  $^1\text{H}$  NMR:  $\delta = 7.29 - 7.34$  (m, 4 H), 7.24 (m, 1 H), 5.84 (dt,  $J_{\text{Sn}} = 135.8$  Hz,  $J = 2.6$ ,  $J = 1.6$  Hz, 1 H), 5.23 (dt,  $J_{\text{Sn}} = 62.6$  Hz,  $J = 2.6$ ,  $J = 1.4$  Hz, 1 H), 3.76 (s, 2 H), 3.41 (dd,  $J_{\text{Sn}} = 39.7$  Hz,  $J = 1.5 = 1.5$  Hz, 2 H), 1.49 (m, 6 H), 1.31 (tq,  $J = 7.3$ ,  $J = 7.1$  Hz, 6 H), 0.96 – 0.83 (m, 15 H).  $^{13}\text{C}$  NMR:  $\delta = 154.8$ , 140.6, 128.2, 128.1, 126.8, 124.6 ( $J_{\text{Sn}} = 25$  Hz), 58.7, 53.5, 29.2 ( $J_{\text{Sn}} = 20$  Hz), 27.4 ( $J_{\text{Sn}} = 57$  Hz), 13.7, 9.5 ( $J_{\text{Sn}} = 329$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -47.2$ . HRMS (CI) calcd for  $\text{C}_{22}\text{H}_{39}\text{NSn}^{120}$   $[\text{M}]^+$ : 437.2104, found: 437.2117. Analysis data **2k'**:  $\delta = 7.33 - 7.27$  (m, 4 H), 7.22 (m, 1 H), 6.07 (dt,  $J_{\text{Sn}} = 137.3$  Hz,  $J = 3.0$ ,  $J = 1.5$  Hz, 2 H), 5.31 (dt,  $J_{\text{Sn}} = 64.6$  Hz,  $J = 3.0$ ,  $J = 1.5$  Hz, 2 H), 3.54 (s, 2 H), 3.11 (m,  $J_{\text{Sn}} = 31.0$  Hz, 4 H), 1.44 (m, 12 H), 1.29 (tq,  $J = 7.3$ ,  $J = 7.1$  Hz, 12 H), 0.96 – 0.79 (m, 30 H).  $^{13}\text{C}$  NMR:  $\delta = 152.4$ , 139.2, 129.2, 128.0, 126.7, 125.8 ( $J_{\text{Sn}} = 25$  Hz), 62.8, 58.2, 29.1 ( $J_{\text{Sn}} = 20$  Hz), 27.4 ( $J_{\text{Sn}} = 57$  Hz), 13.7, 9.3 ( $J_{\text{Sn}} = 329$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -45.8$ . HRMS (CI) calcd for  $\text{C}_{37}\text{H}_{69}\text{NSn}_2^{120}$   $[\text{M}]^+$ : 767.3474, found: 767.3474.

***N*-Cyclohexyl-1-(2-(Tributylstannyl)allyl)-amine (2l)**: Following the general procedure for allylic aminations **2l** was obtained from cyclohexylamine (27 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after warming up from 0° C to r.t. over 16 h. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/ $\text{NEt}_3$  99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 65 % yield (70 mg, 0.163 mmol) as a colorless oil. In addition 19 % (18 mg, 0.024 mmol) of the diallylated product **2l'** were obtained as a colorless oil. Analysis data **2l**:  $^1\text{H}$  NMR:  $\delta = 5.79$  (dt,  $J_{\text{Sn}} = 137.8$  Hz,  $J = 2.6$ ,  $J = 1.7$  Hz, 1 H), 5.17 (dt,  $J_{\text{Sn}} = 63.6$  Hz,  $J = 2.7$ ,  $J = 1.4$  Hz, 1 H), 3.39 (m,  $J_{\text{Sn}} = 39.9$  Hz, 2 H), 1.88 – 1.57 (m, 6 H), 2.41 (m, 1 H), 1.49 (m, 6 H), 1.31 (tq,  $J = 7.3$ ,  $J = 7.2$  Hz, 6 H), 1.24 – 1.00 (m, 4 H), 0.98 – 0.81 (m, 15 H), 0.76 (m, 1 H).  $^{13}\text{C}$  NMR:  $\delta = 155.5$ , 123.7 ( $J_{\text{Sn}} = 25$  Hz), 56.0, 56.0 ( $J_{\text{Sn}} = 20$  Hz), 33.7, 29.2 ( $J_{\text{Sn}} = 20$  Hz), 27.4 ( $J_{\text{Sn}} = 57$  Hz), 26.3, 25.0, 13.7, 9.8 ( $J_{\text{Sn}} = 328$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -47.8$ . HRMS (CI) calcd for  $\text{C}_{21}\text{H}_{43}\text{NSn}^{120}$   $[\text{M}]^+$ : 429.2417, found: 429.2463. Analysis data **2l'**:  $\delta = 5.95$  (m,  $J_{\text{Sn}} = 139.2$  Hz, 2 H), 5.22 (m,  $J_{\text{Sn}} = 64.9$  Hz, 2 H), 3.16 (m,  $J_{\text{Sn}} = 33.0$  Hz, 4 H), 2.56 (m, 1 H), 1.88 – 1.75 (m, 4 H), 1.48 (m, 12 H), 1.30 (tq,  $J = 7.3$ ,  $J = 7.2$  Hz, 12 H), 1.21 – 1.03 (m, 6 H), 0.98 – 0.81 (m, 30 H).  $^{13}\text{C}$  NMR:  $\delta = 153.3$ , 125.2 ( $J_{\text{Sn}} = 25$  Hz), 58.6, 57.8 ( $J_{\text{Sn}} = 20$

Hz), 29.2 ( $J_{\text{Sn}} = 20$  Hz), 28.2, 27.4 ( $J_{\text{Sn}} = 57$  Hz), 26.6, 26.4, 13.7, 9.4 ( $J_{\text{Sn}} = 325$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -46.3$ . HRMS (CI) calcd for  $\text{C}_{36}\text{H}_{73}\text{NSn}_2^{120} [\text{M}]^+$ : 759.3787, found: 759.3780.

***N*-(1-Phenylethyl)-1-(2-(Tributylstannyl)allyl)-amine (2m):** Following the general procedure for allylic aminations **2m** was obtained from 1-phenylethyl amine (33 mg, 0.275 mmol, 1.1 equiv) and methyl 2-(tributylstannyl)allyl carbonate **1b** (101 mg, 0.25 mmol, 1 equiv) after warming up from 0° C to r.t. over 16 h. After evaporation of the solvent *in vacuo* and flash chromatography (hexanes/EtOAc/NEt<sub>3</sub> 99 : 0 : 1 – 97 : 2 : 1) the desired product could be isolated in 84 % yield (94 mg, 0.209 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta = 7.34 - 7.29$  (m, 4 H), 7.23 (m, 1 H), 5.77 (dt,  $J_{\text{Sn}} = 136.5$  Hz,  $J = 2.5$ ,  $J = 1.5$  Hz, 1 H), 5.18 (dt,  $J_{\text{Sn}} = 62.8$  Hz,  $J = 2.6$ ,  $J = 1.3$  Hz, 1 H), 3.75 (q,  $J = 6.6$  Hz, 1 H), 3.23 (dd,  $J_{\text{Sn}} = 40.7$  Hz,  $J = 1.3 = 1.3$  Hz, 2 H), 1.49 (m, 6 H), 1.35 – 1.27 (m, 9 H), 0.99 – 0.82 (m, 15 H).  $^{13}\text{C}$  NMR:  $\delta = 154.9, 145.9, 128.3, 126.8, 126.6, 124.4$  ( $J_{\text{Sn}} = 25$  Hz), 57.8, 57.2, 29.2 ( $J_{\text{Sn}} = 20$  Hz), 27.4 ( $J_{\text{Sn}} = 57$  Hz), 24.2, 13.7, 9.7 ( $J_{\text{Sn}} = 329$  Hz).  $^{119}\text{Sn}$  NMR:  $\delta = -46.8$ . HRMS (CI) calcd for  $\text{C}_{23}\text{H}_{41}\text{NSn}^{120} [\text{M}]^+$ : 451.2261, found: 451.2271.

***N*-(2-Benzylallyl)piperidin (3c):** In a Schlenk flask [allylPdCl]<sub>2</sub> (2.0 mg, 5.0  $\mu\text{mol}$ , 2 mol%) and PPh<sub>3</sub> (3.0 mg, 11  $\mu\text{mol}$ , 4 mol%) were dissolved in dry THF (1 mL) under nitrogen and stirred for 15 min at r.t. after which a yellow solution was obtained. In a second Schlenk flask compound **2a** (83 mg, 0.20 mmol, 1 equiv) and benzylbromide (86 mg, 0.4 mmol, 2 equiv) were dissolved in dry THF (1 mL). This solution was heated to 60 °C, then the catalyst solution was added and the resulting mixture was stirred at 60 °C for 3 d. The reaction mixture was allowed to cool to r.t. before KF (58 mg, 1 mmol, 4 equiv) and water (5 mL) were added. The mixture was stirred for 16 h and then diluted with ethylacetate. The organic phase was separated, the aqueous phase was extracted with ethylacetate (3 times) and the combined organic phase were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The desired product could be isolated after flash chromatography (hexanes/EtOAc 95 : 5 – 80 : 20) in 37 % yield (20 mg, 0.093 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta = 7.28$  (m, 2 H), 7.17–7.23 (m, 3 H), 4.97 (m, 1 H), 4.82 (m, 1 H), 3.39 (s, 2 H), 2.77 (s, 2 H), 2.30 (m, 4 H), 1.58 (tt,  $J = 5.5$  Hz = 5.5 Hz, 4 H), 1.43 (m, 2 H).  $^{13}\text{C}$  NMR:  $\delta = 146.8, 140.0, 129.2, 128.1, 125.9, 113.1, 63.9, 54.5, 41.0, 26.1, 24.5$ . MS (CI)  $m/z$  216 (100, M<sub>+1</sub>), 137 (2), 124 (9), 98 (91), 84 (4). HRMS (CI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{21}\text{N} (\text{M})^+$ : 215.1674, found: 215.1676.

***Z*-Ethyl 4-(piperidin-1-ylmethyl)penta-2,4-dienoate (3d):** Following the general procedure for one-pot allylic aminations/Stille couplings **3d** was obtained from piperidine (21.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and *cis*-3-iodoacrylate (59 mg, 0.26 mmol, 1.05 equiv) with Pd(PPh<sub>3</sub>)<sub>4</sub> (5.2 mg, 20  $\mu\text{mol}$ , 8 mol%) as catalyst and dry DMF as solvent. For the Stille coupling the reaction mixture was stirred at room temperature for 3 h. After work-up and flash chromatography

(hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 96 % yield (50 mg, 0.240 mmol) as a colorless oil with an (*E/Z*)-ratio of 9:1. <sup>1</sup>H NMR: δ = 6.45 (dd, *J* = 12.5 Hz, *J* = 1.0 Hz, 1H), 5.80 (d, *J* = 12.5 Hz, 1H), 5.33 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.10 (s, 2H), 2.32 (m, 4H), 1.52 (m, 4H), 1.40 (m, 2H, 1-H), 1.29 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR: δ = 167.4, 145.4, 141.4, 124.7, 119.2, 61.0, 60.3, 54.6, 26.0, 24.4, 14.3. Selected signals of the *E*-isomer: <sup>1</sup>H NMR: δ = 7.30 (d, *J* = 15.9 Hz, 1H), 6.21 (d, *J* = 15.9 Hz, 1H), 5.46 (s, 2H). MS (CI) *m/z* 223 (30, M<sub>+</sub>), 194 (2), 178 (7), 136 (17), 98 (100). HRMS (CI) *m/z* calcd for C<sub>13</sub>H<sub>21</sub>NO<sub>2</sub> (M)<sup>+</sup>: 223.1572, found: 223.1526.

**1-(2-(4-Nitrophenyl)allyl)piperidine (3e):** Following the general procedure for one-pot allylic aminations/Stille couplings **3e** was obtained from piperidine (21.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and 1-bromo-4-nitrobenzene (101 mg, 0.50 mmol, 2 equiv) with Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 1 h and then to 90 °C for 1h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 80 % yield (49 mg, 0.199 mmol) as a yellow oil. <sup>1</sup>H NMR: δ = 8.16 (m, 2H), 7.70 (m, 2H), 5.59 (d, *J* = 1.1, 1H), 5.38 (dd, *J* = 1.1 Hz = 1.1 Hz, 1H), 3.30 (d, *J* = 1.1, 2H), 2.37 (m, 4H), 1.52 (m, 4H), 1.41 (m, 2H). <sup>13</sup>C NMR: δ = 147.1, 147.0, 143.2, 127.2, 123.3, 118.5, 63.7, 54.4, 26.0, 24.4. MS (CI) *m/z* 246 (10, M<sub>+</sub>), 199 (1), 148 (2), 115 (2), 98 (100). HRMS (CI) *m/z* calcd for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> (M)<sup>+</sup>: 246.1368, found: 246.1362. Elemental analysis calcd (%) for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C 68.27, H 7.37, N 11.37 and found: C 67.83, H 7.27, N 11.37.

**4-(3-(Piperidin-1-yl)prop-1-en-2-yl)benzaldehyde (3f):** Following the general procedure for one-pot allylic aminations/Stille couplings **3f** was obtained from piperidine (21.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and 4-bromobenzaldehyde (56 mg, 0.30 mmol, 1.2 equiv) with [allylPdCl]<sub>2</sub> (0.9 mg, 2.5 μmol, 1 mol%) and PPh<sub>3</sub> (5.2 mg, 20 μmol, 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 16 h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 95 % yield (54 mg, 0.238 mmol) as a colorless oil. <sup>1</sup>H NMR: δ = 10.00 (s, 1H), 7.84 – 7.81 (m, 2H), 7.71 – 7.68 (m, 2H), 5.58 (d, *J* = 1.3 Hz, 1H), 5.37 (d, *J* = 1.2 Hz, 1H), 3.32 (s, 2H), 2.40 (bs, 4H), 1.56 – 1.51 (m, 4H), 1.44 – 1.39 (m, 2H). <sup>13</sup>C NMR: δ = 191.9, 146.8, 143.8, 135.3, 129.6, 127.0, 117.7, 63.5, 54.4, 25.9, 24.4. MS (CI) *m/z* 229 (10, M<sub>+</sub>), 201 (1), 115 (3), 98 (100). HRMS (CI) *m/z* calcd for C<sub>15</sub>H<sub>19</sub>NO (M)<sup>+</sup>: 229.1467, found: 229.1446.

**1-(2-(Naphthalen-2-yl)allyl)piperidine (3g):** Following the general procedure for one-pot allylic aminations/Stille couplings **3g** was obtained from piperidine (21.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and 4-bromobenzaldehyde (104 mg, 0.50 mmol, 2 equiv) with [allylPdCl]<sub>2</sub> (0.9 mg, 2.5 μmol, 1



mol%) and PPh<sub>3</sub> (5.2 mg, 20 μmol, 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 16 h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 62 % yield (39 mg, 0.155 mmol) as a colorless oil. <sup>1</sup>H NMR: δ = 8.00 (m, 1H), 7.85 – 7.77 (m, 3H), 7.67 (dd, *J* = 8.6 Hz, *J* = 1.8 Hz, 1H), 7.48 – 7.42 (m, 2H), 5.60 (m, 1H), 5.35 (m, 1H), 3.41 (s, 2H), 2.46 (m, 4H), 1.56 (m, 4H), 1.43 (m, 2H). <sup>13</sup>C NMR: δ = 144.4,; 138.0, 133.3, 132.8, 128.2, 127.4, 125.9, 125.6, 125.0, 124.8, 115.4, 63.7, 54.6, 26.0, 24.4. MS (CI) *m/z* 251 (25, M<sub>+</sub>), 168 (14), 152 (6), 98 (100). HRMS (CI) *m/z* calcd for C<sub>18</sub>H<sub>21</sub>N (M)<sup>+</sup>: 251.1674, found: 251.1662.

**5-(3-(Piperidin-1-yl)prop-1-en-2-yl)pyrimidine (3h):** Following the general procedure for one-pot allylic aminations/Stille couplings **3h** was obtained from piperidine (21.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and 5-bromopyrimidine (79 mg, 0.50 mmol, 2 equiv) with [allylPdCl]<sub>2</sub> (0.9 mg, 2.5 μmol, 1 mol%) and PPh<sub>3</sub> (5.2 mg, 20 μmol, 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 90 °C for 16 h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 97 % yield (49 mg, 0.243 mmol) as a colorless oil. <sup>1</sup>H NMR: δ = 9.09 (s, 1H), 8.91 (s, 2H), 5.55 (m, 1H), 5.34 (m, 1H), 3.27 (m, 2H), 2.37 (m, 4H), 1.50 (m, 4H), 1.41 (m, 2H). <sup>13</sup>C NMR: δ = 157.4, 154.6, 139.4, 133.3, 117.8, 63.4, 54.1, 25.9, 24.3. MS (CI) *m/z* 204 (43, M<sub>++</sub>), 98 (100). HRMS (CI) *m/z* calcd for C<sub>12</sub>H<sub>17</sub>N<sub>3</sub> (M)<sup>+</sup>: 203.1422, found: 203.1400. Elemental analysis calcd (%) for C<sub>12</sub>H<sub>17</sub>N<sub>3</sub>: C 70.90, H 8.43, N 20.67 and found: C 70.54, H 8.31, N 20.25.

**1-(2-(4-Methoxyphenyl)allyl)piperidine (3i):** Following the general procedure for one-pot allylic aminations/Stille couplings **3i** was obtained from piperidine (21.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and 1-bromo-4-methoxybenzene (94 mg, 0.50 mmol, 2 equiv) with [allylPdCl]<sub>2</sub> (0.9 mg, 2.5 μmol, 1 mol%) and PPh<sub>3</sub> (5.2 mg, 20 μmol, 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 100 °C for 6 h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 69 % yield (40 mg, 0.173 mmol) as a slightly yellow oil. <sup>1</sup>H NMR: δ = 7.49 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.38 (m, 1H), 5.14 (m, 1H), 3.81 (s, 3H), 3.26 (s, 2H), 2.40 (m, 4H), 1.55 (m, 4H), 1.41 (m, 2H). <sup>13</sup>C NMR: δ = 158.9, 133.2, 128.0, 127.4, 126.3, 113.3, 63.9, 55.2, 54.5, 26.0, 24.4. MS (CI) *m/z* 232 (100, M<sub>++</sub>), 201 (19), 148 (14), 98 (100). HRMS (CI) *m/z* calcd for C<sub>15</sub>H<sub>21</sub>NO (M)<sup>+</sup>: 231.1623, found: 231.1636. Elemental analysis calcd (%) for C<sub>15</sub>H<sub>21</sub>NO: C 77.88, H 9.15, N 6.05 and found: C 77.70, H 9.04, N 5.72.

**1-(2-Methylene-4-phenylbut-3-enyl)piperidine (3k):** Following the general procedure for one-pot allylic aminations/Stille couplings **3k** was obtained from piperidine (21.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv)

and  $\beta$ -bromostyrene (55 mg, 0.30 mmol, 1.2 equiv) with  $[\text{allylPdCl}]_2$  (0.9 mg, 2.5  $\mu\text{mol}$ , 1 mol%) and  $\text{PPh}_3$  (5.2 mg, 20  $\mu\text{mol}$ , 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 16h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product was isolated in 95 % yield (54 mg, 0.238 mmol) as a yellow oil.  $^1\text{H}$  NMR:  $\delta$  = 7.44 (m, 2H), 7.33 (m, 2H), 7.23 (m, 1H), 6.90 (d,  $J$  = 16.3 Hz, 1H), 6.82 (d,  $J$  = 16.3 Hz, 1H), 5.26 (m, 1H), 5.24 (m, 1H), 3.18 (s, 2H), 2.41 (m, 4H), 1.59 (m, 4H), 1.45 (m, 2H).  $^{13}\text{C}$  NMR:  $\delta$  = 142.3, 137.6, 130.0, 128.9, 128.5, 127.4, 126.5, 118.1, 61.2, 54.6, 25.9, 24.4. MS (CI)  $m/z$  228 (50,  $\text{M}^+$ ), 136 (14), 98 (100). HRMS (CI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{21}\text{N}$  ( $\text{M}^+$ ): 227.1674, found: 227.1662.

**Ethyl 2-(3-(piperidin-1-yl)prop-1-en-2-yl)benzoate (3p):** Following the general procedure for one-pot allylic aminations/Stille couplings **3p** was obtained from piperidine (21.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and ethyl 2-iodobenzoate (138 mg, 0.50 mmol, 2 equiv)  $[\text{allylPdCl}]_2$  (0.9 mg, 2.5  $\mu\text{mol}$ , 1 mol%) and  $\text{PPh}_3$  (5.2 mg, 20  $\mu\text{mol}$ , 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 100 °C for 5 h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 60 % yield (41 mg, 0.150 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta$  = 7.76 (dd,  $J$  = 7.7 Hz,  $J$  = 1.2 Hz, 1H), 7.42 (dt,  $J$  = 7.5 Hz = 7.5 Hz,  $J$  = 1.4 Hz, 1H), 7.31 (dt,  $J$  = 7.6 Hz = 7.6 Hz,  $J$  = 1.3 Hz, 1H), 7.26 (dd,  $J$  = 7.7 Hz,  $J$  = 1.1 Hz, 1H), 5.30 (s, 1H), 5.06 (s, 1H), 4.30 (q,  $J$  = 7.1, 2H), 3.20 (s, 2H), 2.40 (m, 4H), 1.52 (m, 4H), 1.42 (m, 2H), 1.35 (t,  $J$  = 7.1, 3H).  $^{13}\text{C}$  NMR:  $\delta$  = 168.1, 143.2, 131.0, 130.5, 130.2, 129.4, 126.8, 115.0, 64.5, 60.9, 54.6, 26.0, 24.4, 14.1. MS (CI)  $m/z$  273 (60,  $\text{M}^+$ ), 200 (10), 110 (19), 98 (100). HRMS (CI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{23}\text{NO}_2$  ( $\text{M}^+$ ): 273.1729, found: 273.1696. Elemental analysis calcd (%) for  $\text{C}_{17}\text{H}_{23}\text{NO}_2$ : C 74.69, H 8.48, N 5.12 and found: C 74.68, H 8.21, N 5.50.

**1-(2-Phenylallyl)morpholine (4a):** Following the general procedure for one-pot allylic aminations/Stille couplings **4a** was obtained from morpholine (21.8 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and phenyliodide (102 mg, 0.5 mmol, 2 equiv) with  $[\text{allylPdCl}]_2$  (0.9 mg, 2.5  $\mu\text{mol}$ , 1 mol%) and  $\text{PPh}_3$  (5.2 mg, 20  $\mu\text{mol}$ , 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 16 h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 96 % yield (48 mg, 0.235 mmol) as a colorless oil.  $^1\text{H}$  NMR:  $\delta$  = 7.54 (m, 2H), 7.35 – 7.27 (m, 3H), 5.50 (m, 1H), 5.25 (m, 1H), 3.68 (t,  $J$  = 4.6 Hz, 4H), 3.34 (s, 2H), 2.48 (m, 4H).  $^{13}\text{C}$  NMR:  $\delta$  = 143.6, 140.2, 128.1, 127.5, 126.2, 115.5, 67.0, 63.5, 53.5. MS (CI)  $m/z$  203 (34,  $\text{M}^+$ ), 118 (13), 100 (100). HRMS (CI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{17}\text{NO}$  ( $\text{M}^+$ ): 203.1310, found: 203.1300.

**1-(2-Phenylallyl)pyrrolidine (5a):** Following the general procedure for one-pot allylic aminations/Stille couplings **5a** was obtained from pyrrolidine (17.8 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and phenyliodide (102 mg, 0.5 mmol, 2 equiv) with [allylPdCl]<sub>2</sub> (0.9 mg, 2.5 μmol, 1 mol%) and PPh<sub>3</sub> (5.2 mg, 20 μmol, 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 16 h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 91 % yield (43 mg, 0.228 mmol) as a colorless oil. <sup>1</sup>H NMR: δ = 7.51 (m, 2H), 7.34 – 7.24 (m, 3H), 5.42 (m, 1H), 5.28 (m, 1H), 3.48 (s, 2H), 2.54 (m, 4H), 1.76 (m, 4H). <sup>13</sup>C NMR: δ = 143.7, 140.6, 128.2, 127.4, 126.2, 114.6, 60.6, 54.2, 23.6. MS (CI) *m/z* 187 (23, M<sub>+</sub>+1), 118 (9), 84 (100), 70 (4). HRMS (CI) *m/z* calcd for C<sub>13</sub>H<sub>17</sub>N (M)<sup>+</sup>: 187.1361, found: 187.1385.

**N,N-Diethyl-2-phenylprop-2-en-1-amine (6a):** Following the general procedure for one-pot allylic aminations/Stille couplings **6a** was obtained from diethylamine (18.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and phenyliodide (102 mg, 0.5 mmol, 2 equiv) with [allylPdCl]<sub>2</sub> (0.9 mg, 2.5 μmol, 1 mol%) and PPh<sub>3</sub> (5.2 mg, 20 μmol, 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 16 h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 74 % yield (35 mg, 0.185 mmol) as a colorless oil. <sup>1</sup>H NMR: δ = 7.50 (m, 2H), 7.33 – 7.24 (m, 3H), 5.42 (m, 1H), 5.28 (m, 1H), 3.41 (s, 2H), 2.54 (q, *J* = 7.1 Hz, 4H), 1.01 (t, *J* = 7.1 Hz, 6H). <sup>13</sup>C NMR: δ = 146.0, 140.7, 128.0, 127.3, 126.3, 114.6, 57.6, 46.7, 11.5. MS (CI) *m/z* 189 (14, M<sub>+</sub>), 172 (30), 86 (100). HRMS (CI) *m/z* calcd for C<sub>13</sub>H<sub>19</sub>N (M)<sup>+</sup>: 189.1517, found: 189.1497.

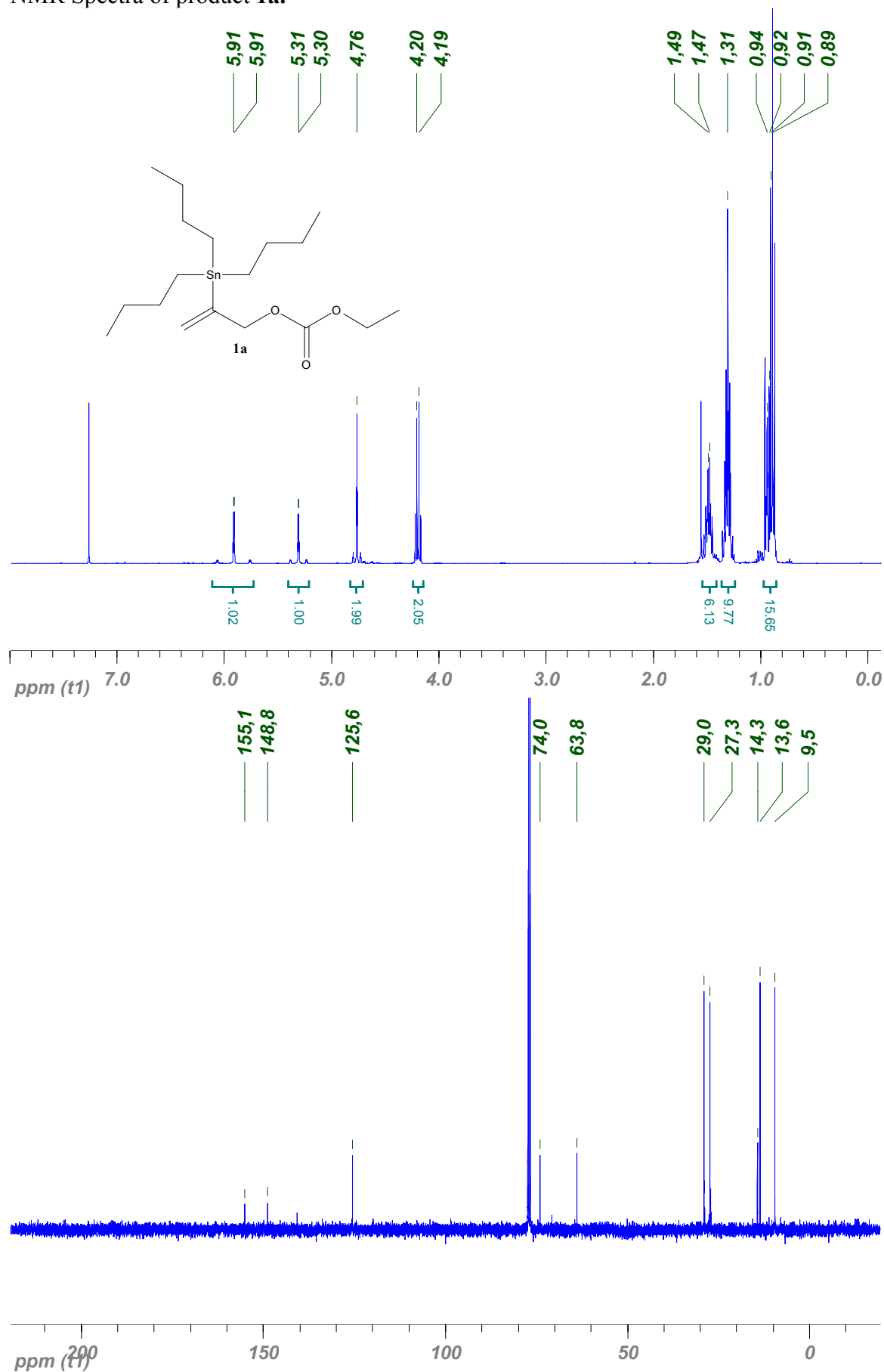
**N,N-Diallyl-2-phenylprop-2-en-1-amine (7a):** Following the general procedure for one-pot allylic aminations/Stille couplings **7a** was obtained from diallylamine (24.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and phenyliodide (102 mg, 0.5 mmol, 2 equiv) with [allylPdCl]<sub>2</sub> (0.9 mg, 2.5 μmol, 1 mol%) and PPh<sub>3</sub> (5.2 mg, 20 μmol, 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 16 h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product could be isolated in 66 % yield (35 mg, 0.165 mmol) as a colorless oil. <sup>1</sup>H NMR: δ = 7.47 (m, 2H), 7.33 – 7.24 (m, 3H), 5.84 (ddt, *J* = 17.1 Hz, *J* = 10.3 Hz, *J* = 6.4 Hz, 2H), 5.43 (m, 1H), 5.29 (m, 1H), 5.18 (m, 1H), 5.14 (m, 1H), 3.42 (s, 2H), 3.10 (m, 4H). <sup>13</sup>C NMR: δ = 145.6, 140.5, 135.8, 128.0, 127.3, 126.4, 117.2, 114.9, 57.6, 56.4. MS (CI) *m/z* 213 (24, M<sub>+</sub>), 110 (100). HRMS (CI) *m/z* calcd for C<sub>15</sub>H<sub>19</sub>N (M)<sup>+</sup>: 213.1517, found: 213.1542.

**N-tert-Butyl-2-phenylprop-2-en-1-amine (8a):** Following the general procedure for one-pot allylic aminations/Stille couplings **8a** was obtained from *tert*-butylamine (18.3 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv)

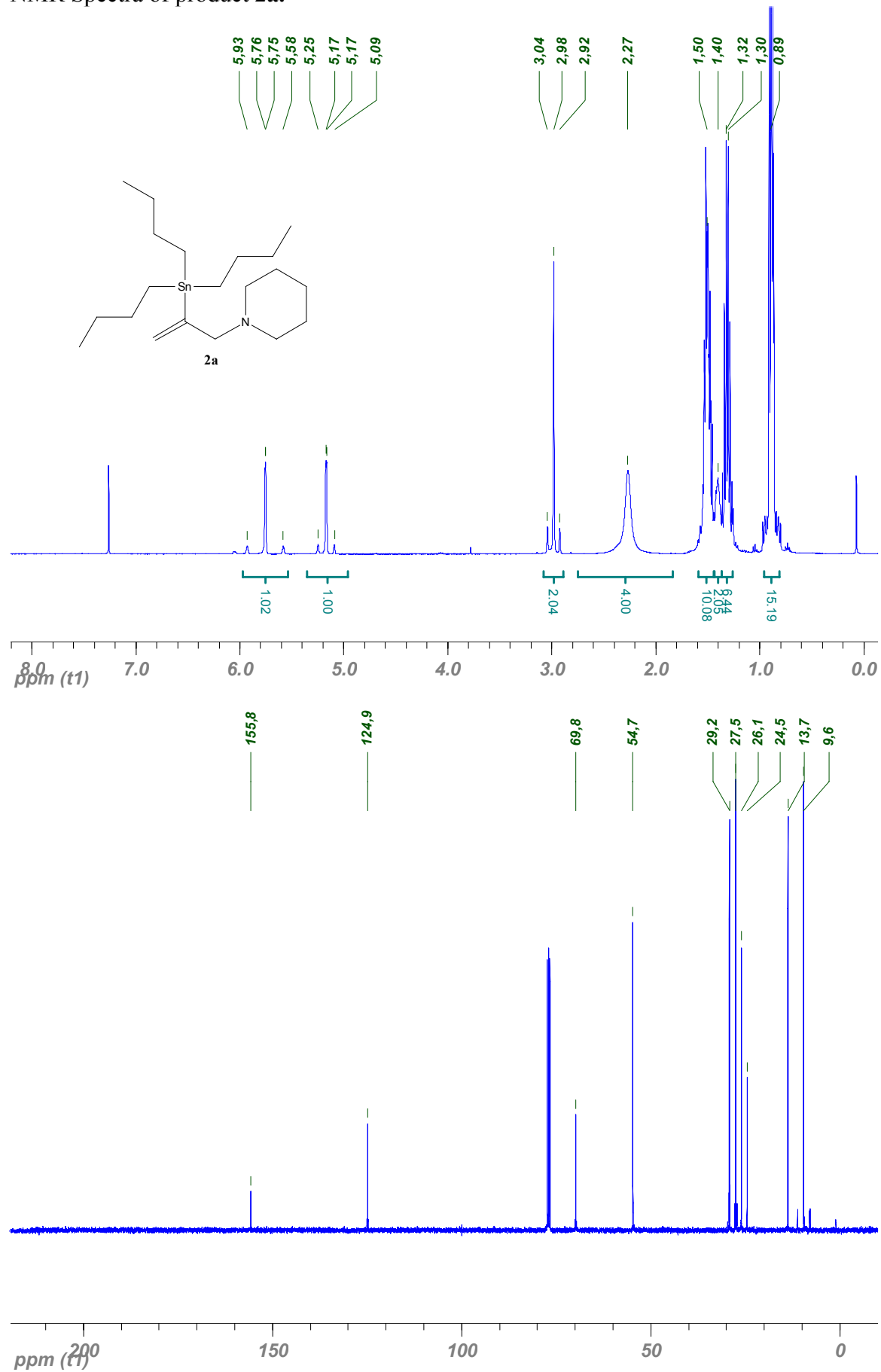
and phenyliodide (102 mg, 0.5 mmol, 2 equiv) with [allylPdCl]<sub>2</sub> (0.9 mg, 2.5 μmol, 1 mol%) and PPh<sub>3</sub> (5.2 mg, 20 μmol, 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 16h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product was isolated in 89 % yield (42 mg, 0.223 mmol) as a colorless oil. <sup>1</sup>H NMR: δ = 7.47 (m, 2H), 7.36 (m, 2H), 7.30 (m, 1H), 5.39 (m, 1H), 5.25 (m, 1H), 3.64 (m, 2H), 1.15 (s, 9H), 1.12 (bs, 1H). <sup>13</sup>C NMR: δ = 147.2, 140.2, 128.3, 127.5, 126.1, 113.0, 50.5, 46.6, 29.0. MS (CI) *m/z* 190 (42, M<sub>+</sub>+2), 174 (100), 117 (11), 86 (6). HRMS (CI) *m/z* calcd for C<sub>13</sub>H<sub>19</sub>N (M)<sup>+</sup>: 189.1517, found: 189.1500.

**2-Phenyl-*N*-(1-phenylethyl)prop-2-en-1-amine (9a):** Following the general procedure for one-pot allylic aminations/Stille couplings **9a** was obtained from 1-phenylethanamine (43 mg, 0.25 mmol, 1.0 equiv), ethyl 2-(tributylstannyl)allyl carbonate **1a** (109 mg, 0.26 mmol, 1.05 equiv) and phenyliodide (102 mg, 0.5 mmol, 2 equiv) with [allylPdCl]<sub>2</sub> (0.9 mg, 2.5 μmol, 1 mol%) and PPh<sub>3</sub> (5.2 mg, 20 μmol, 8 mol%) as catalyst. For the Stille coupling the reaction mixture was heated up to 65 °C for 16h. After work-up and flash chromatography (hexanes/EtOAc 9 : 1 – 1 : 1) the product was isolated in 73 % yield (43 mg, 0.183 mmol) as a colorless oil. <sup>1</sup>H NMR: δ = 7.40 – 7.22 (m, 10H), 5.39 (m, 1H), 5.21 (m, 1H), 3.82 (q, *J* = 6.6 Hz, 1H), 3.56 (d, *J* = 14.3 Hz, 1H), 3.47 (d, *J* = 14.1 Hz, 1H), 1.75 (bs, 1H), 1.33 (d, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR: δ = 146.5, 145.4, 139.9, 128.4, 128.4, 127.6, 126.9, 126.8, 126.2, 113.3, 57.4, 51.3, 24.2. MS (CI) *m/z* 238 (88, M<sub>+</sub>+1), 222 (100), 134 (17), 105 (70), 98 (82). HRMS (CI) *m/z* calcd for C<sub>17</sub>H<sub>19</sub>N (M)<sup>+</sup>: 237.1517, found: 237.1538.

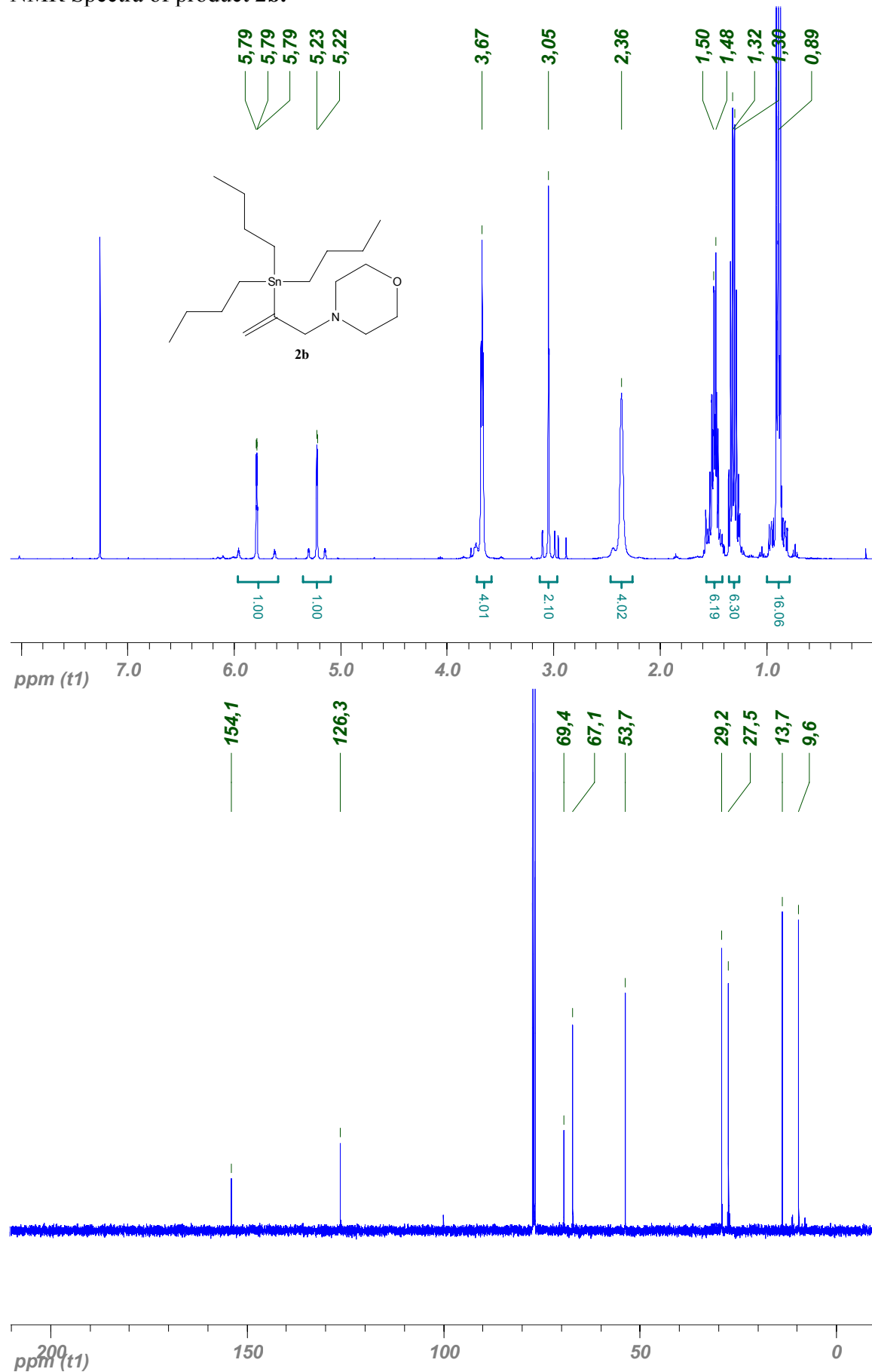
NMR Spectra of product **1a**.



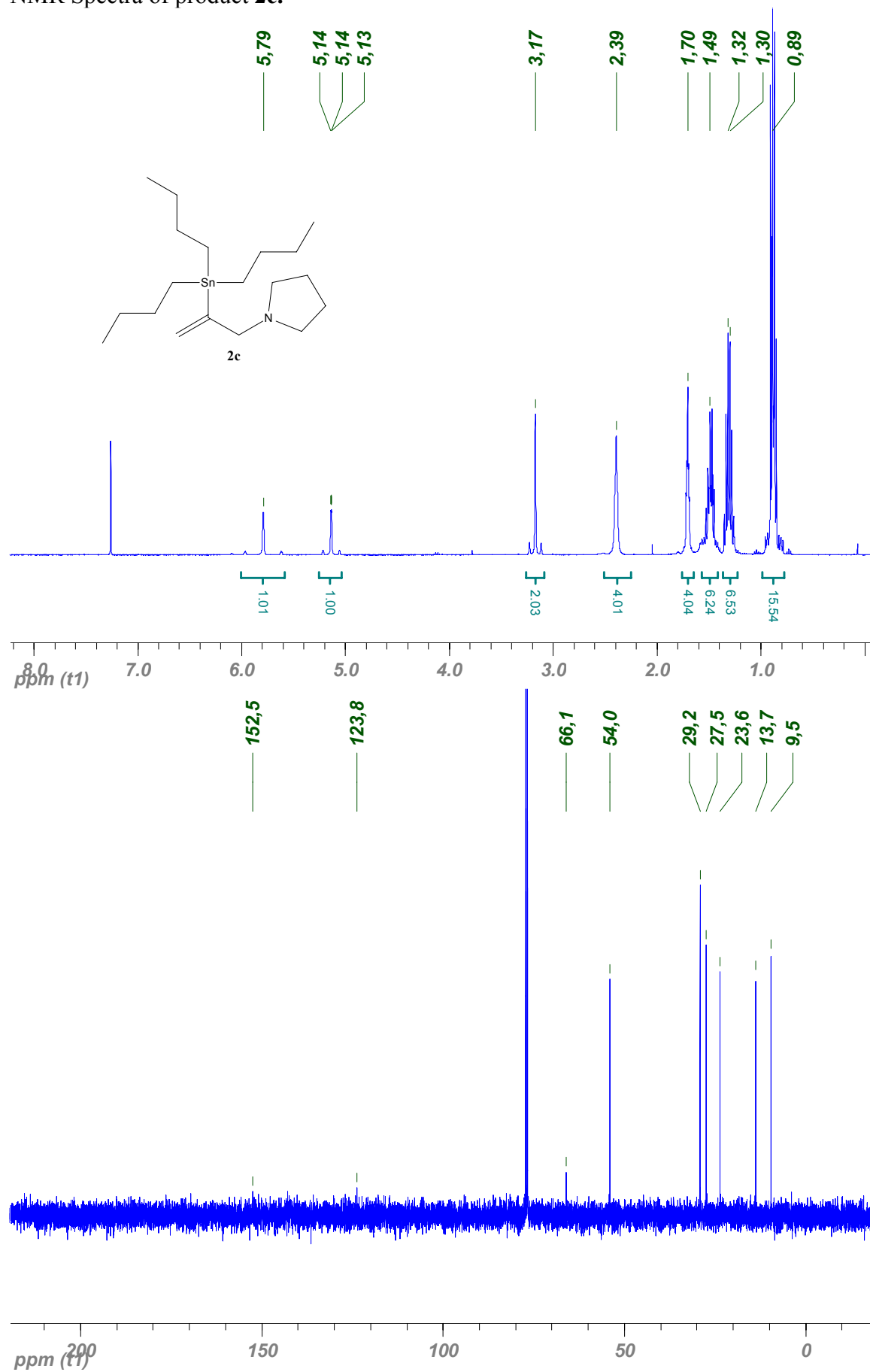
### NMR Spectra of product **2a**.



NMR Spectra of product **2b**.

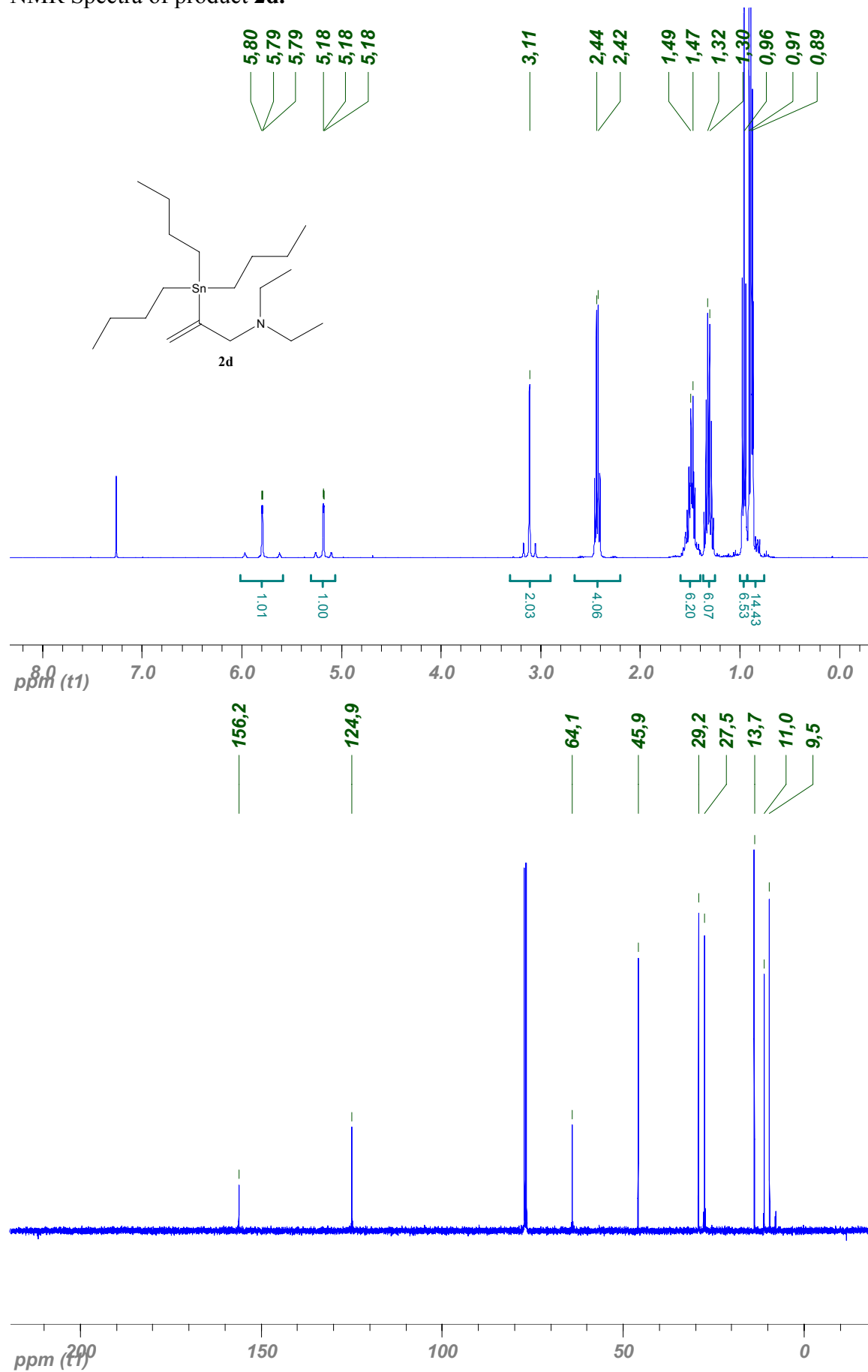


NMR Spectra of product **2c**.

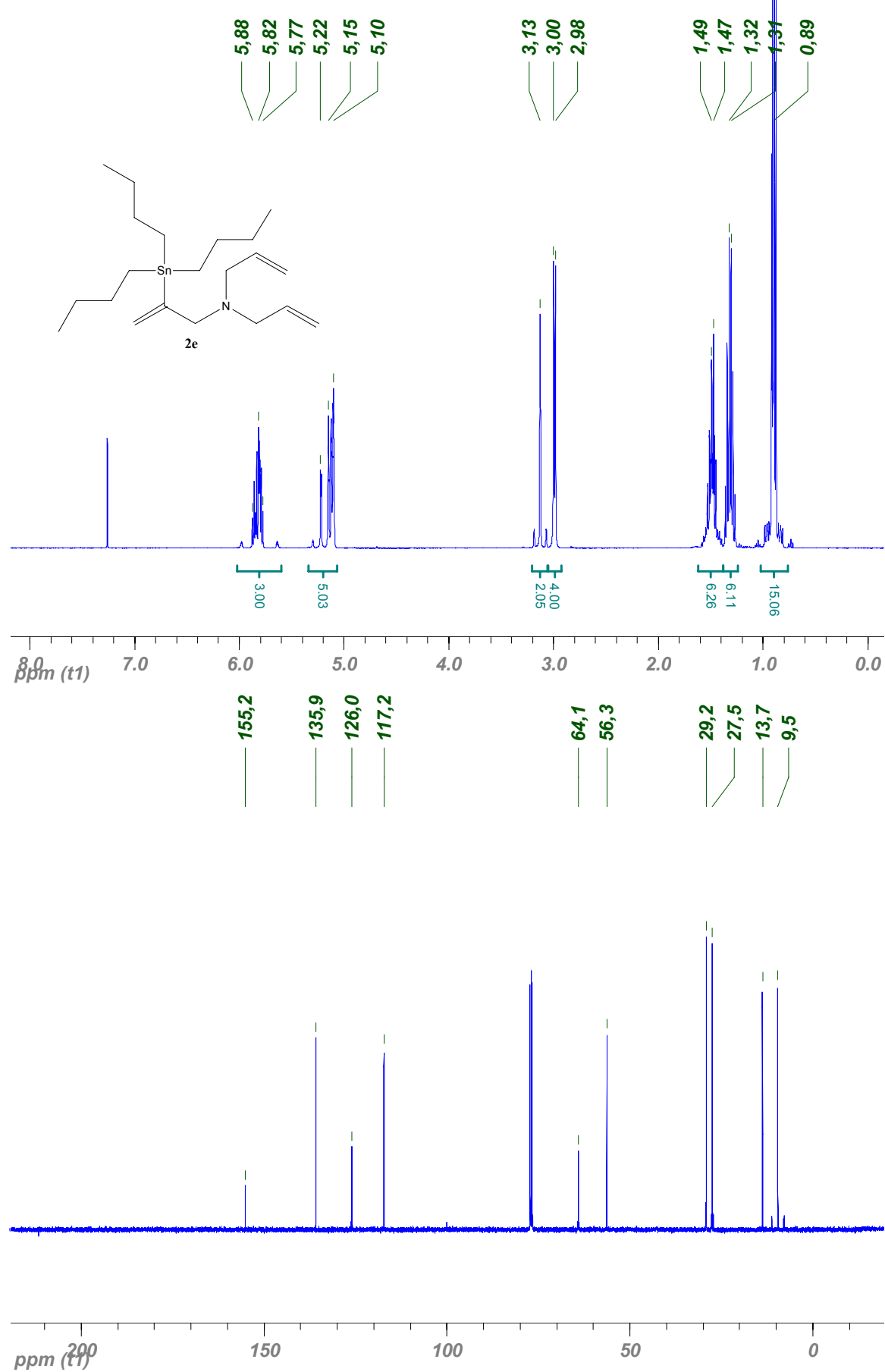




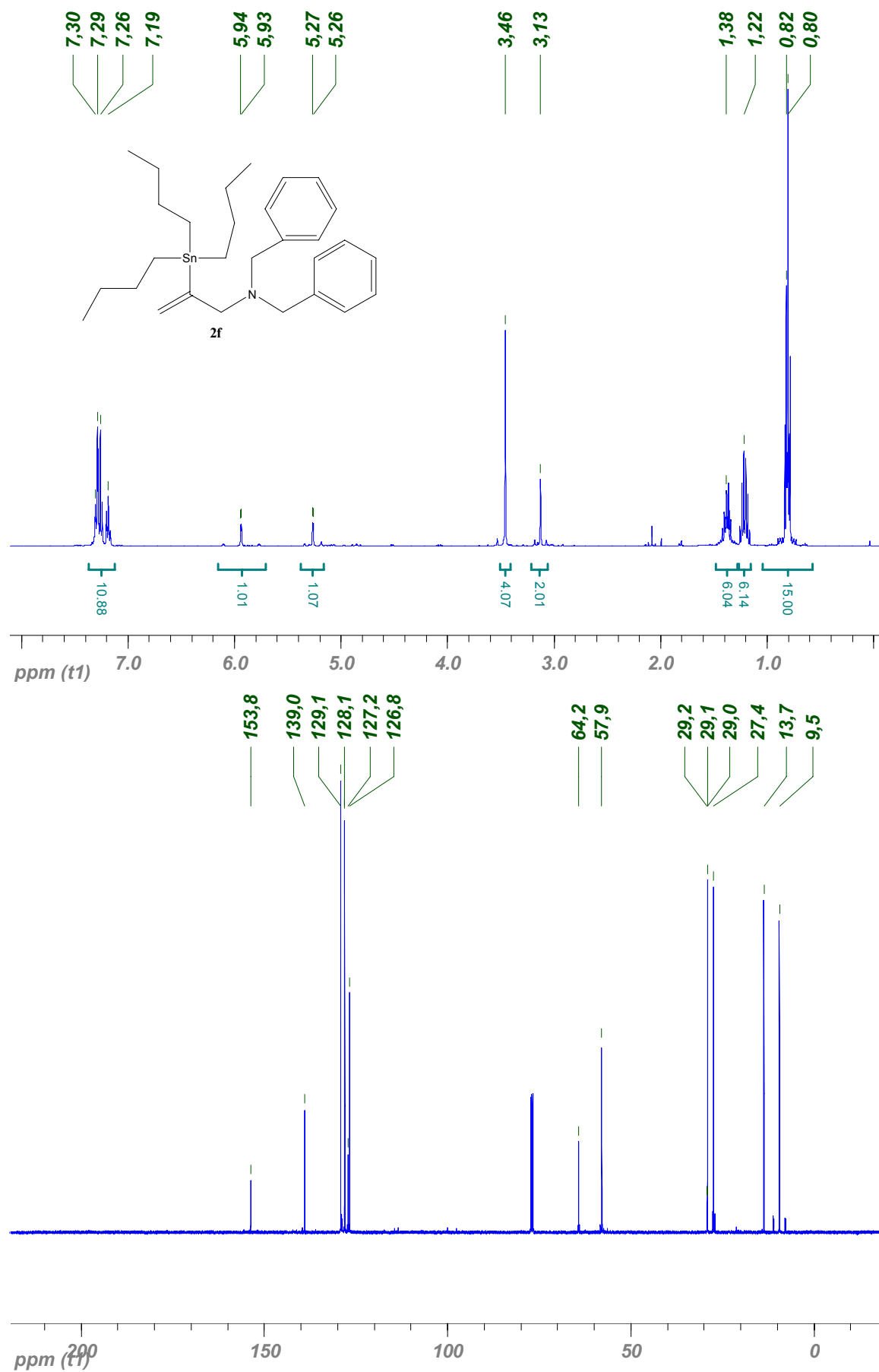
NMR Spectra of product **2d**.



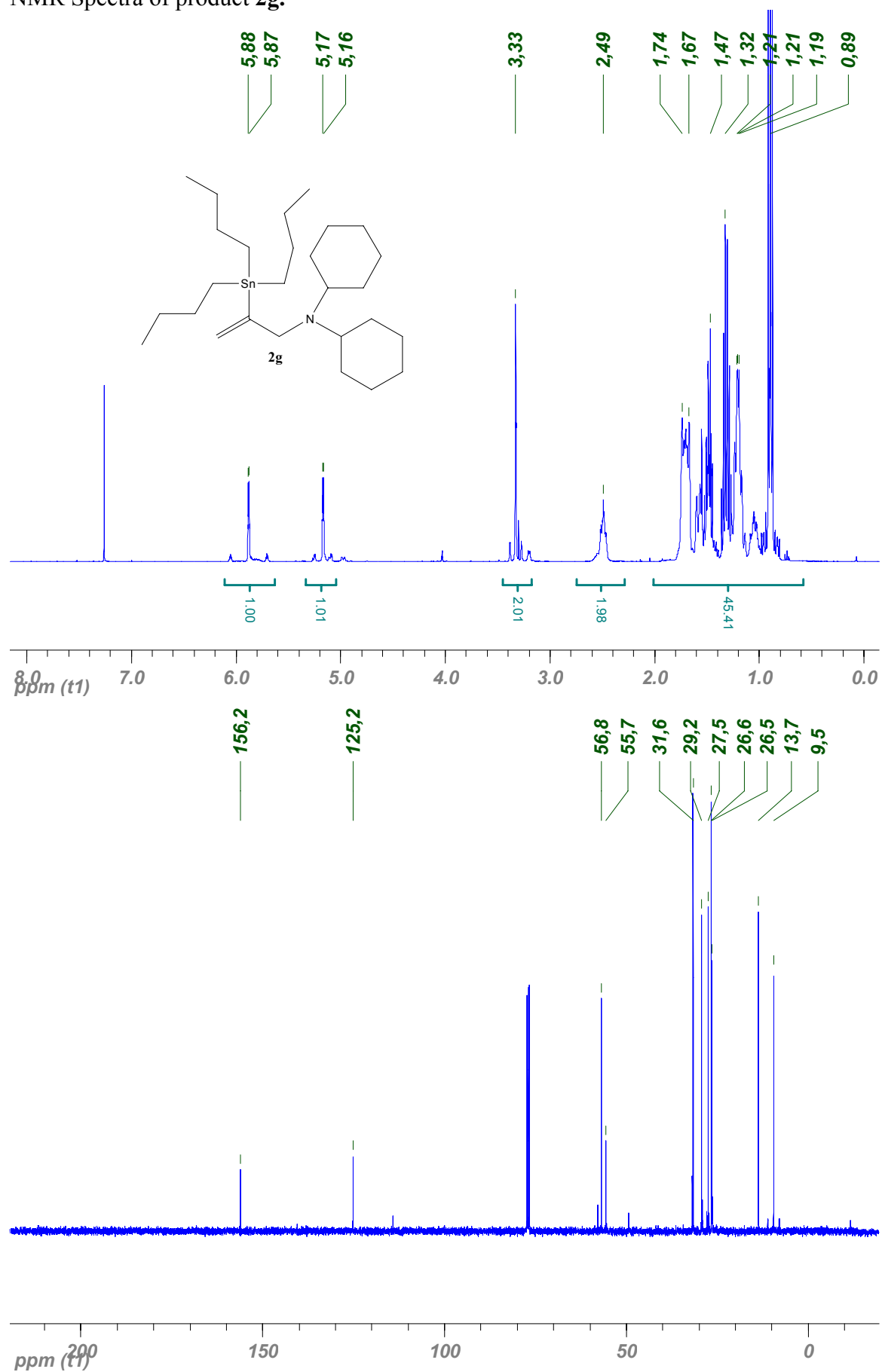
NMR Spectra of product **2e**.



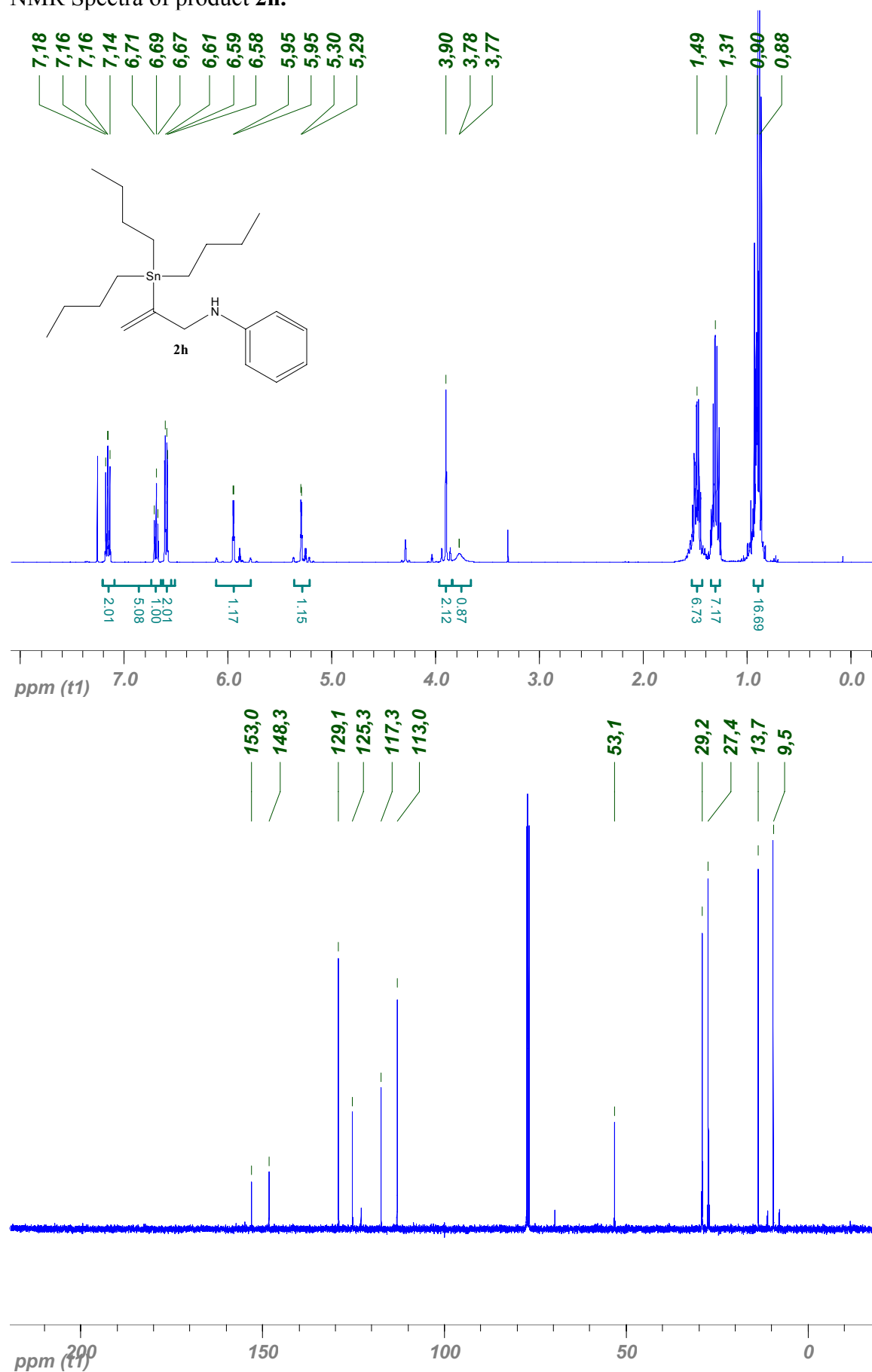
NMR Spectra of product **2f**.



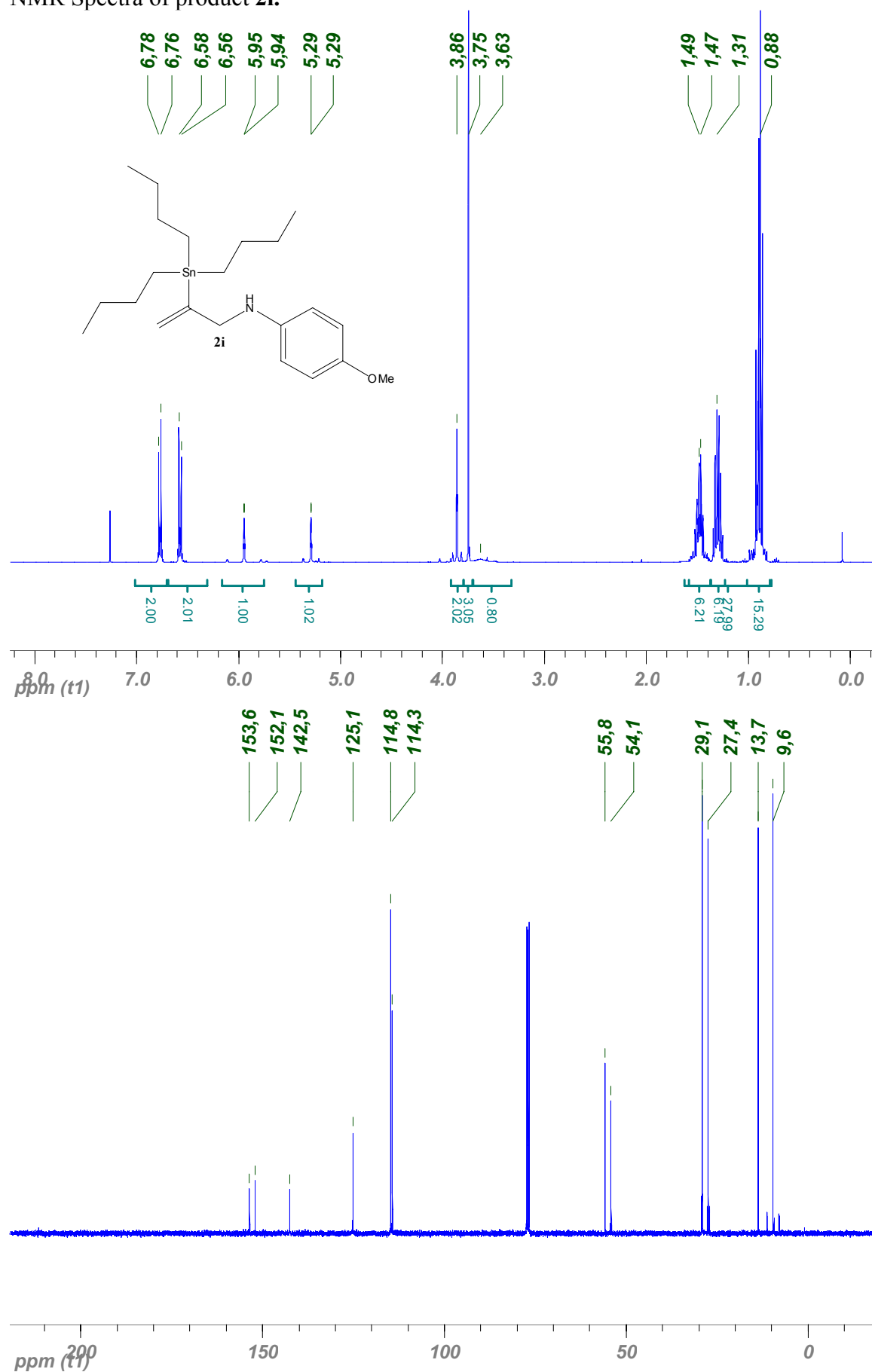
NMR Spectra of product **2g**.



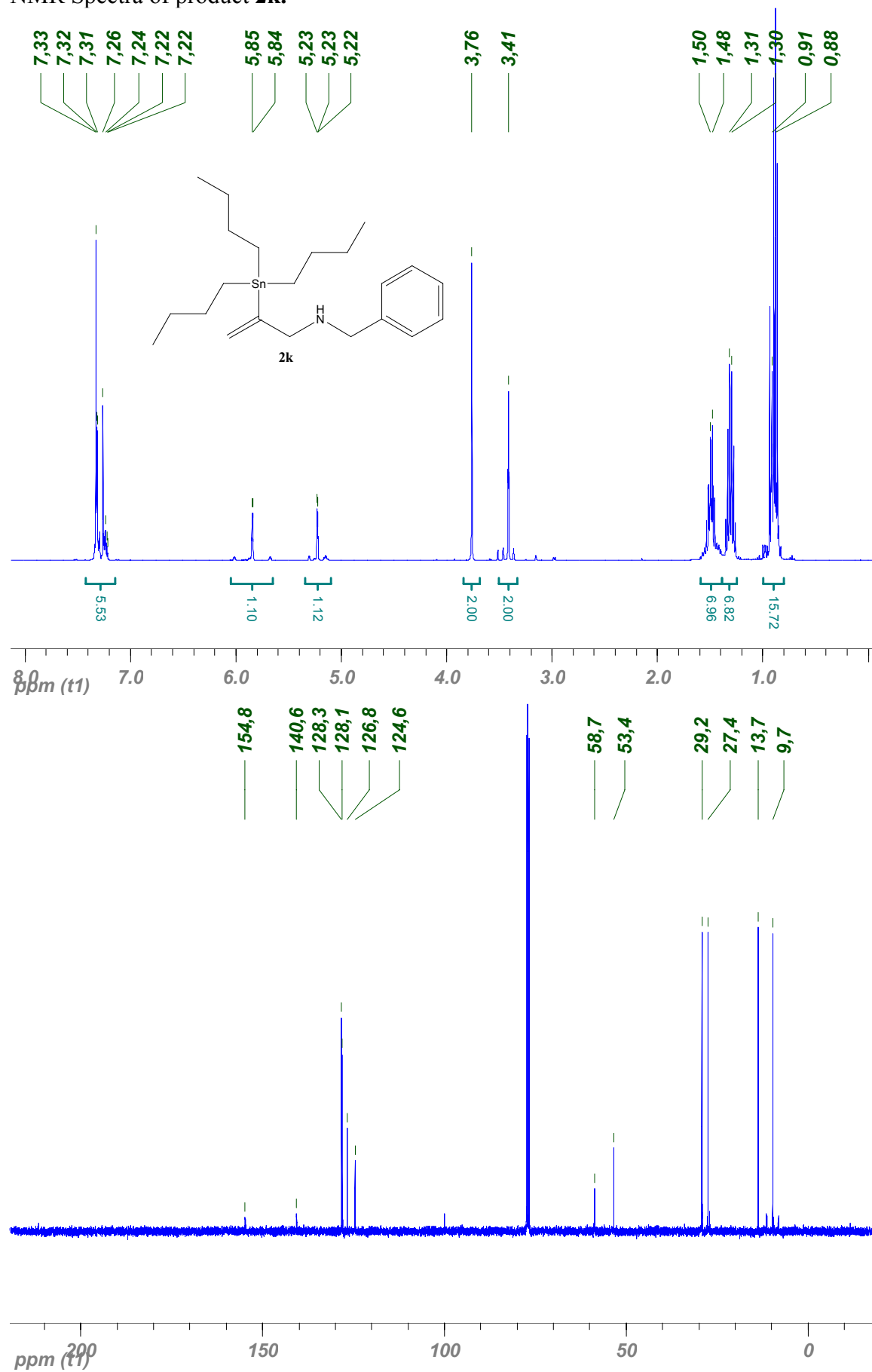
### NMR Spectra of product **2h**.



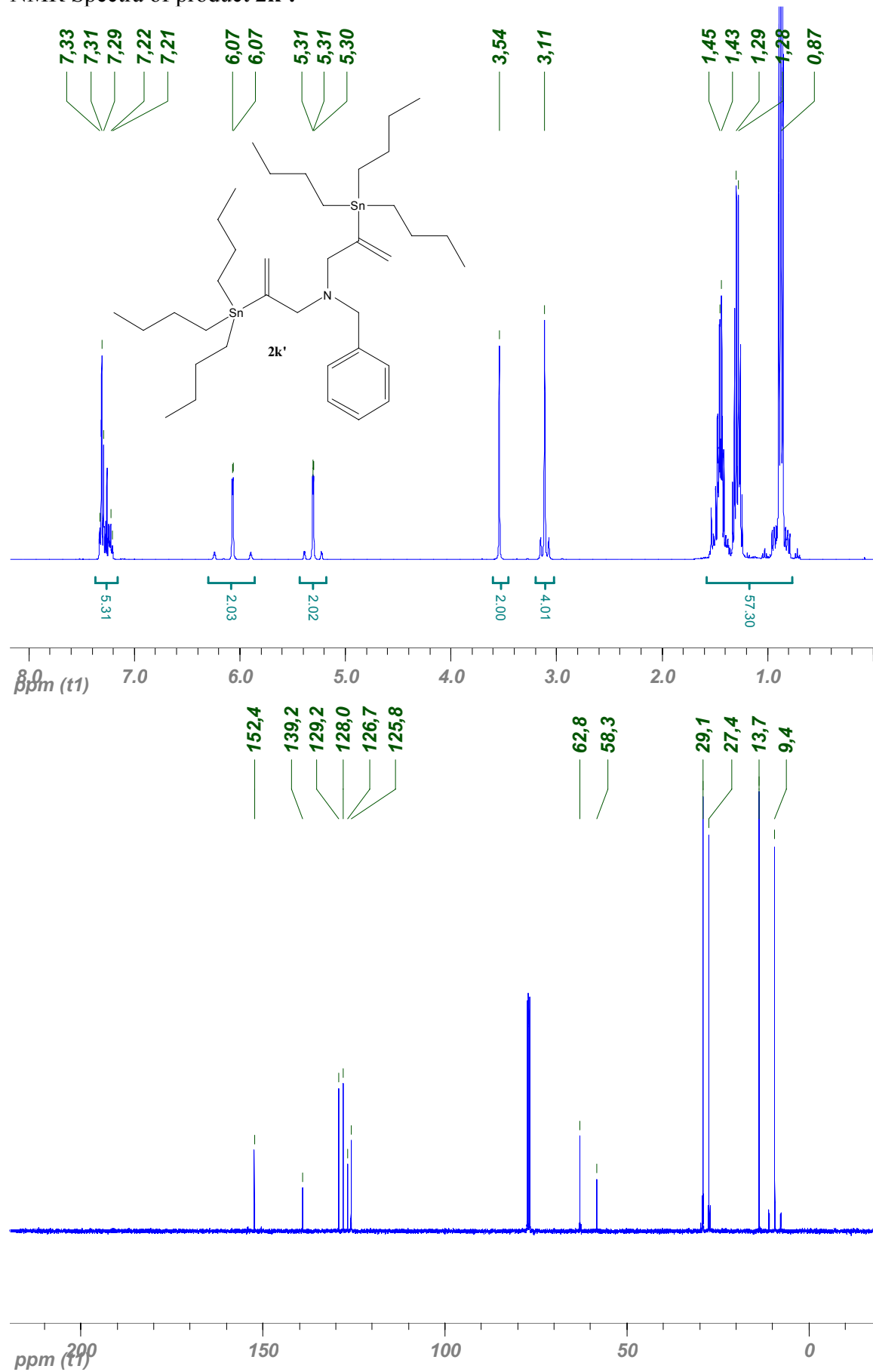
### NMR Spectra of product **2i**.



NMR Spectra of product **2k**.

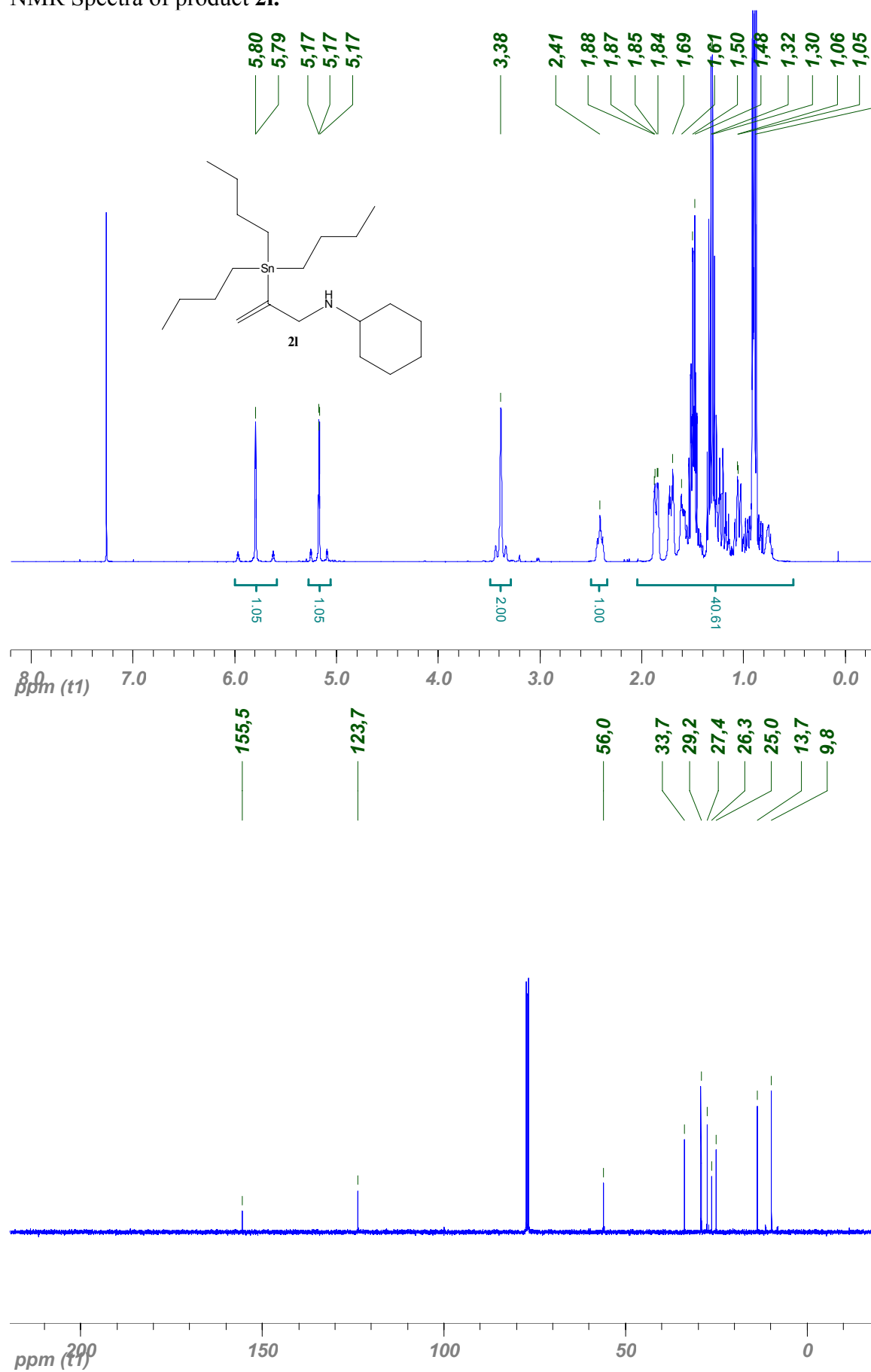


NMR Spectra of product **2k'**.

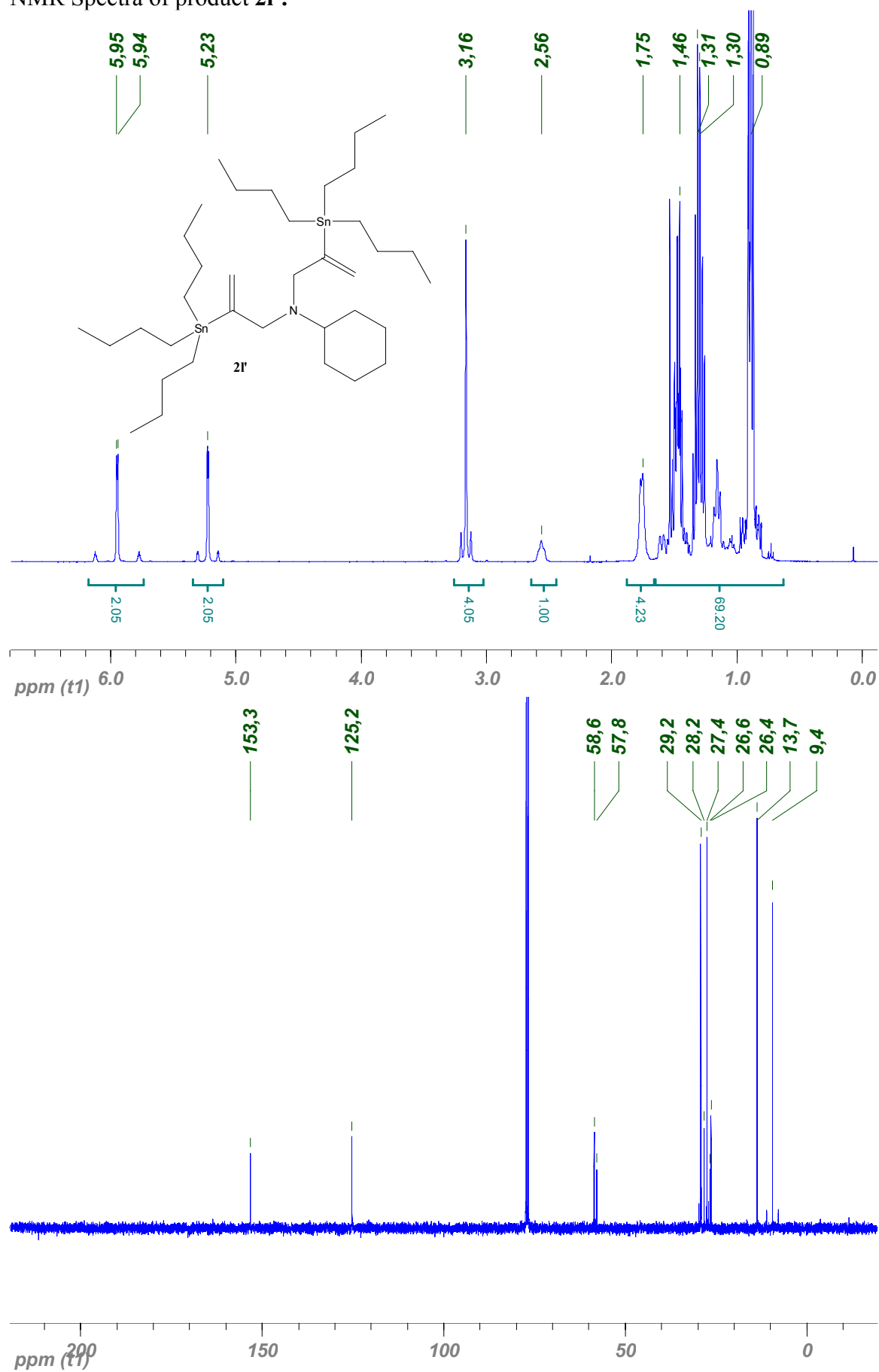




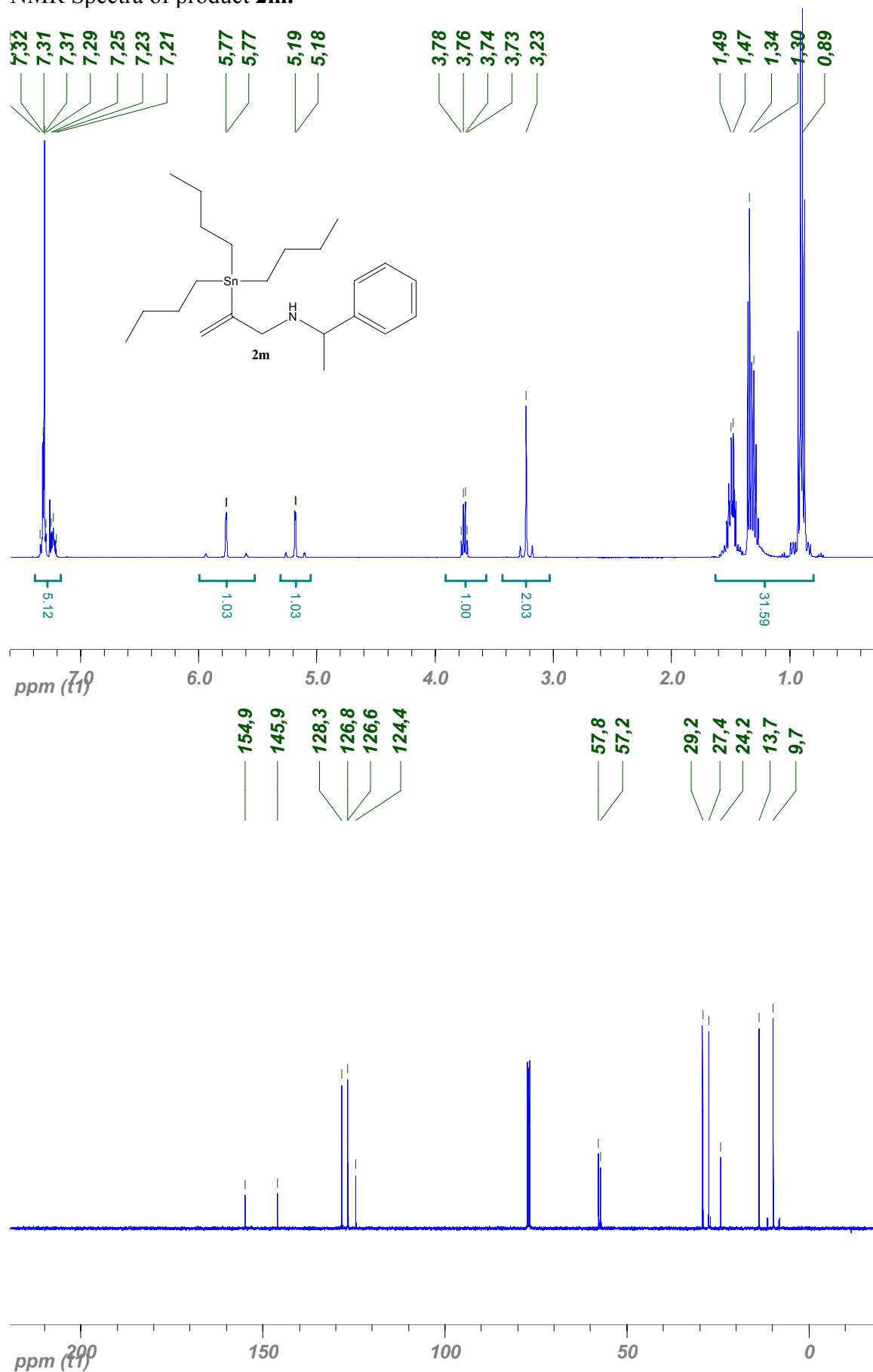
NMR Spectra of product **21**.



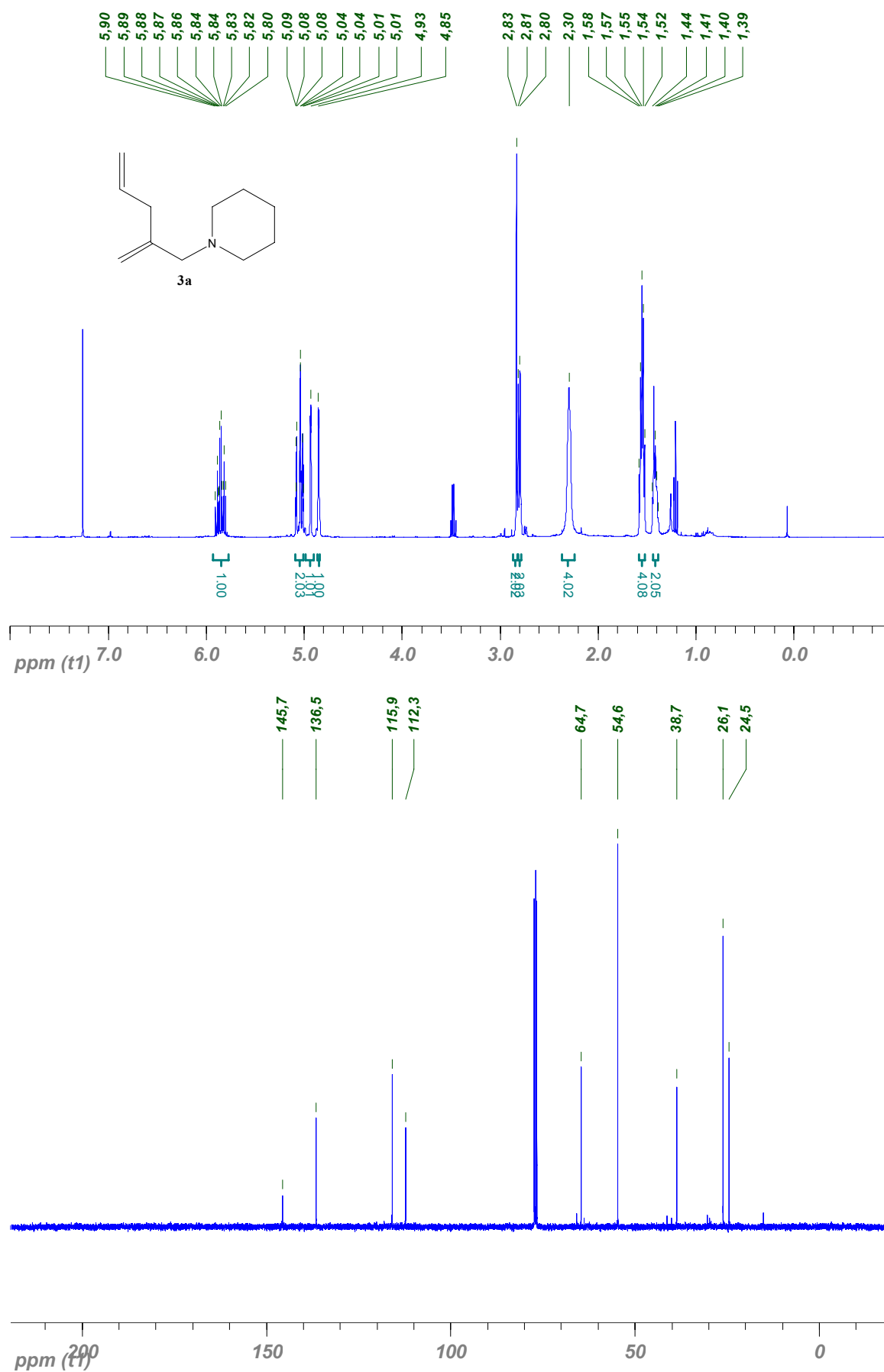
NMR Spectra of product **21'**.



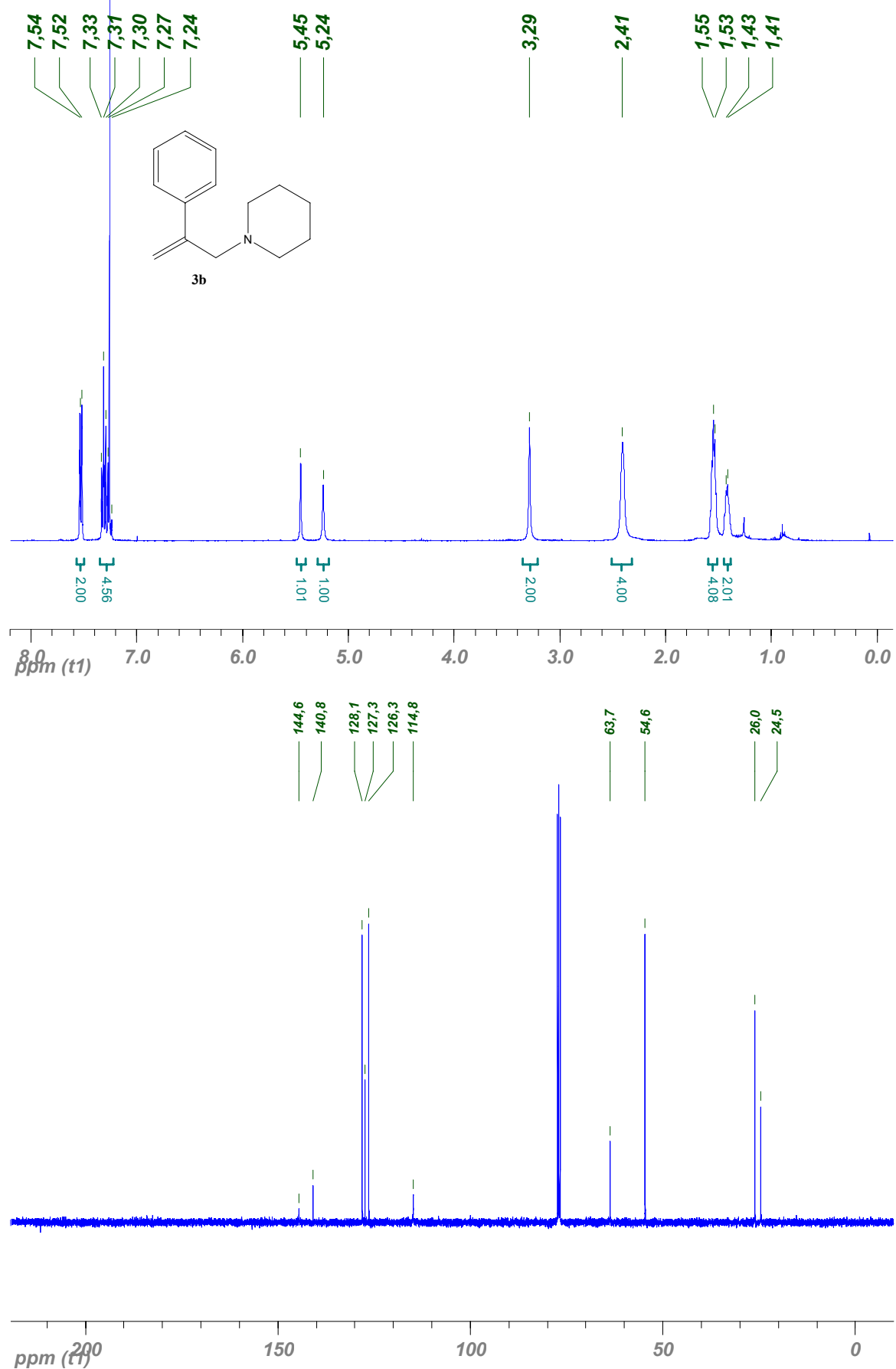
NMR Spectra of product **2m**.



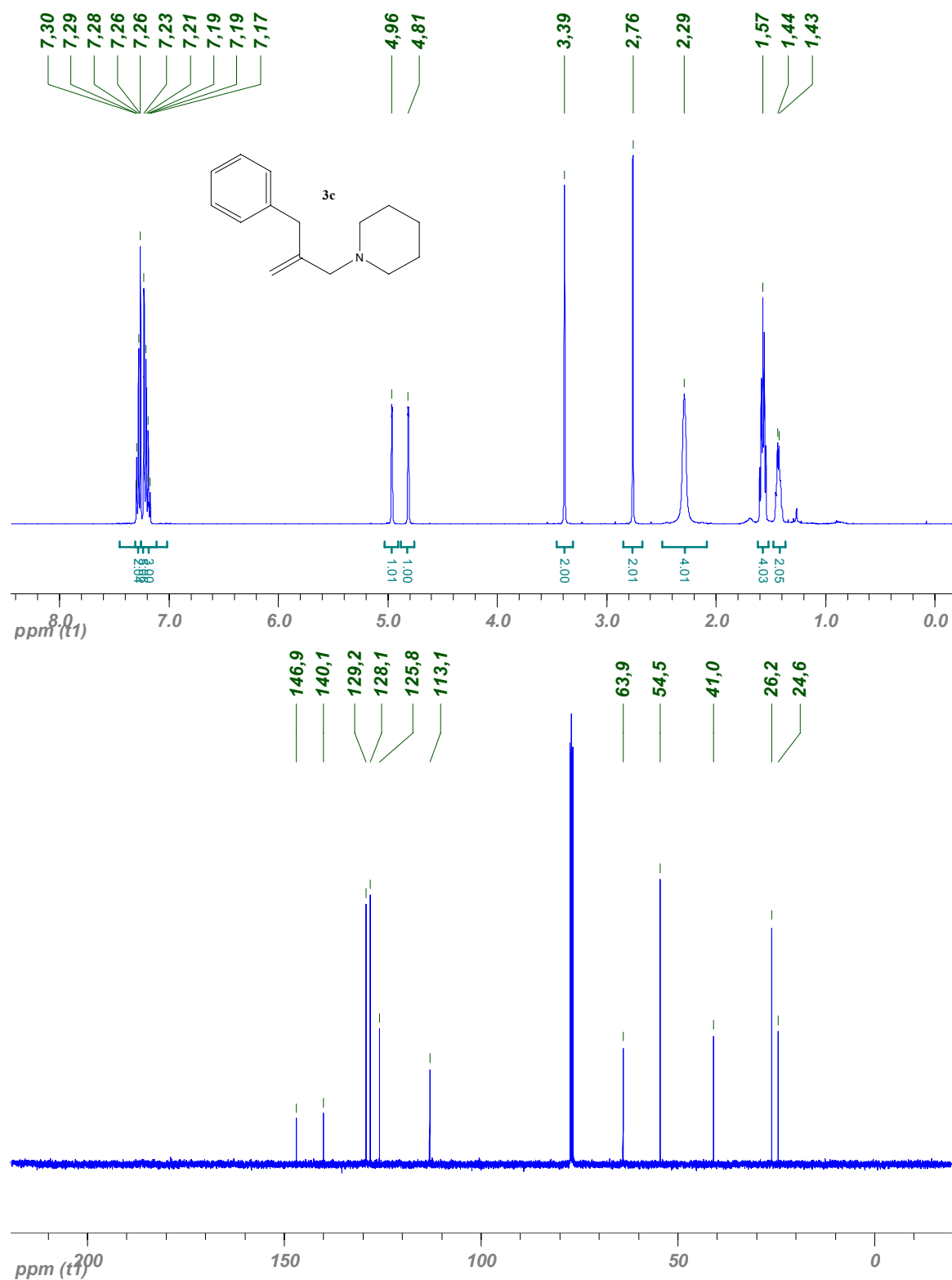
### NMR Spectra of product **3a**.



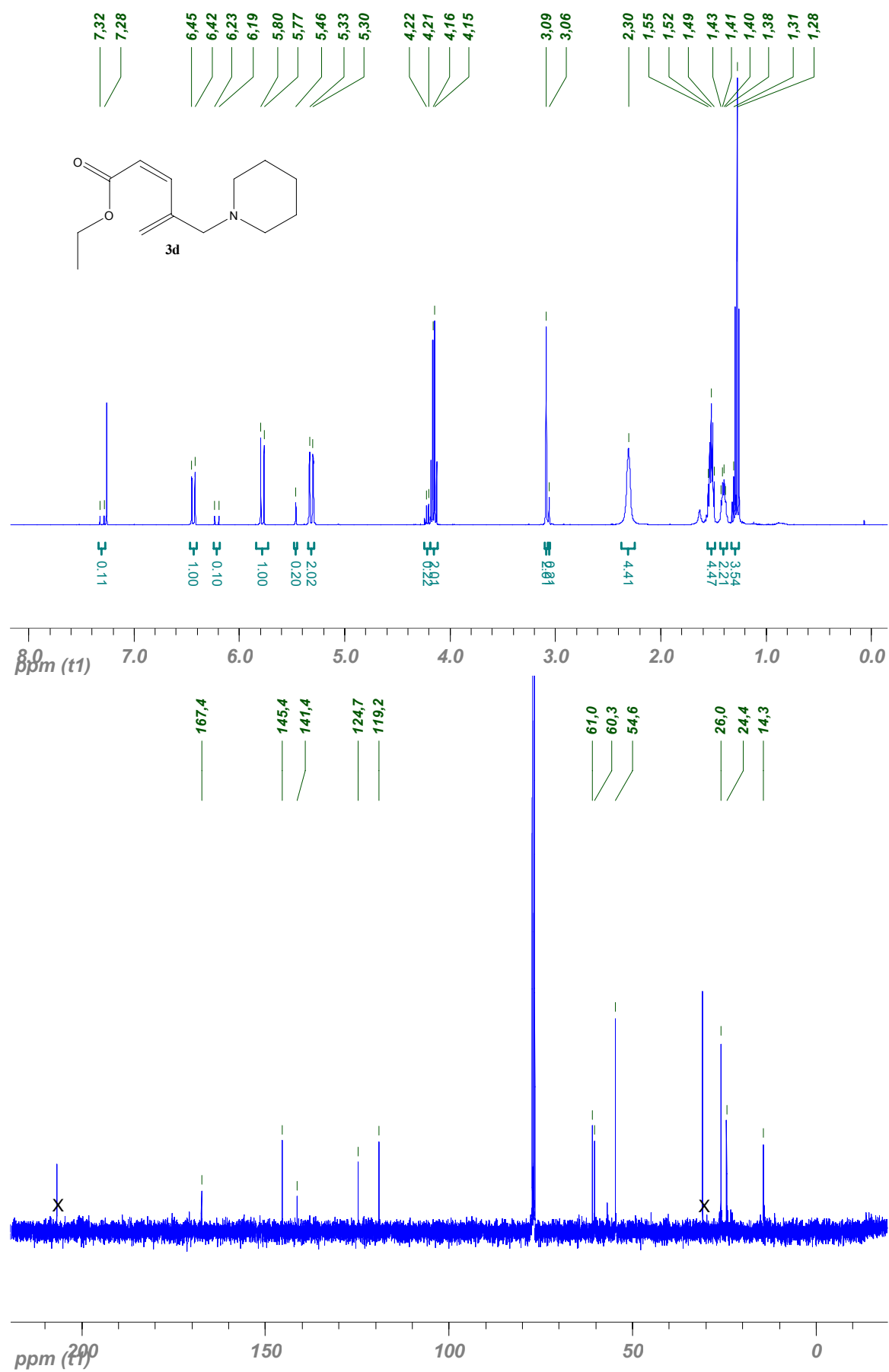
NMR Spectra of product **3b**.



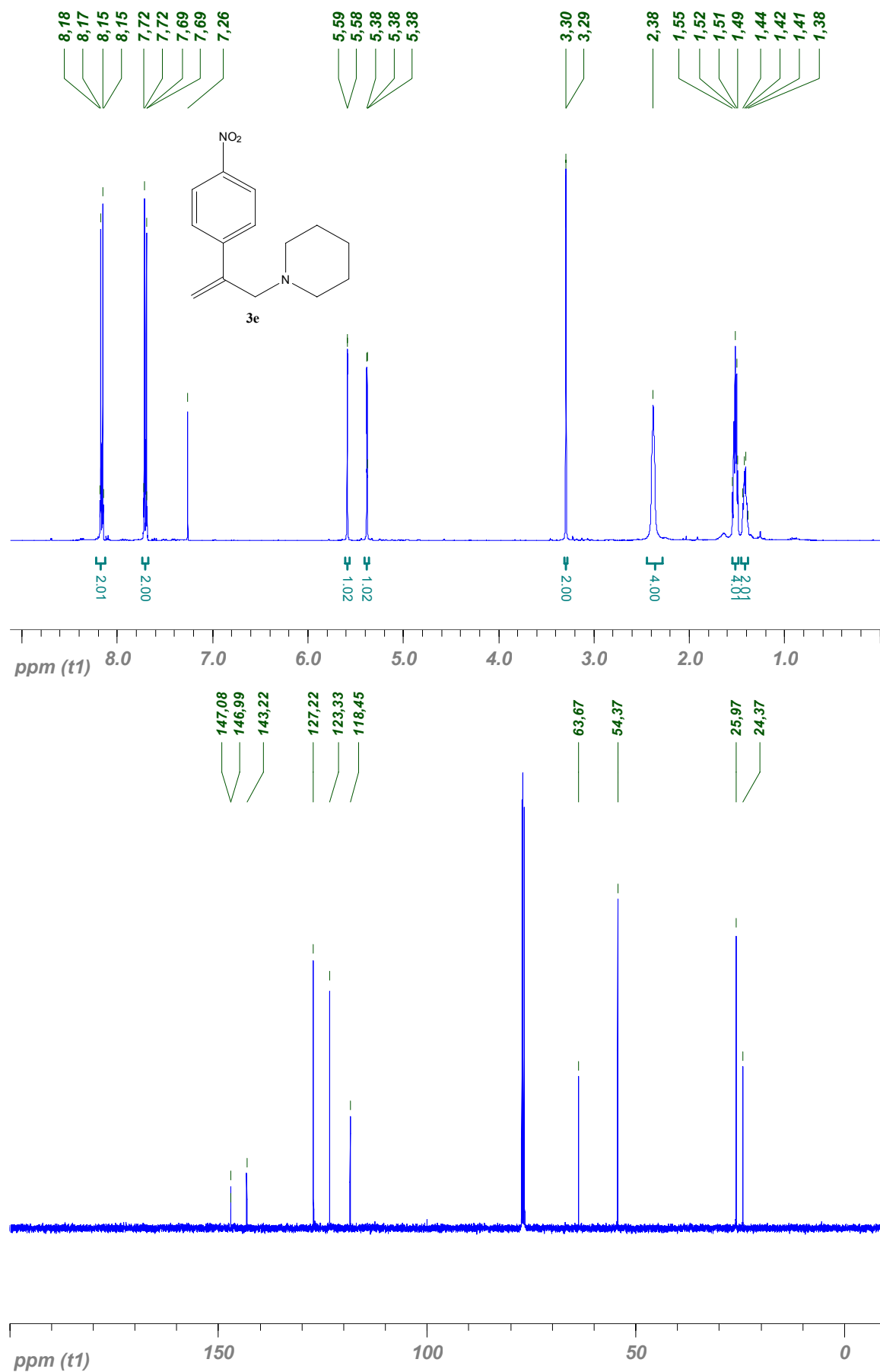
### NMR Spectra of product **3c**.



### NMR Spectra of product **3d**.

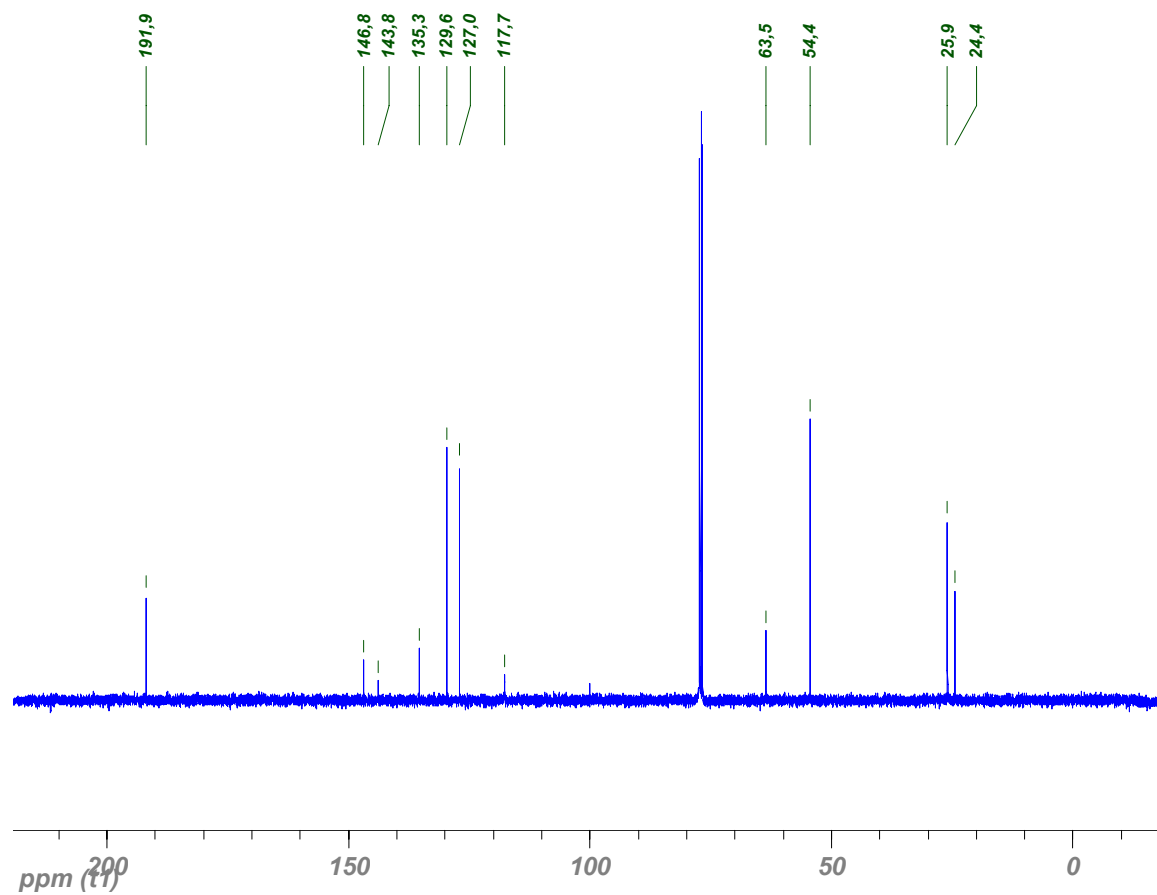
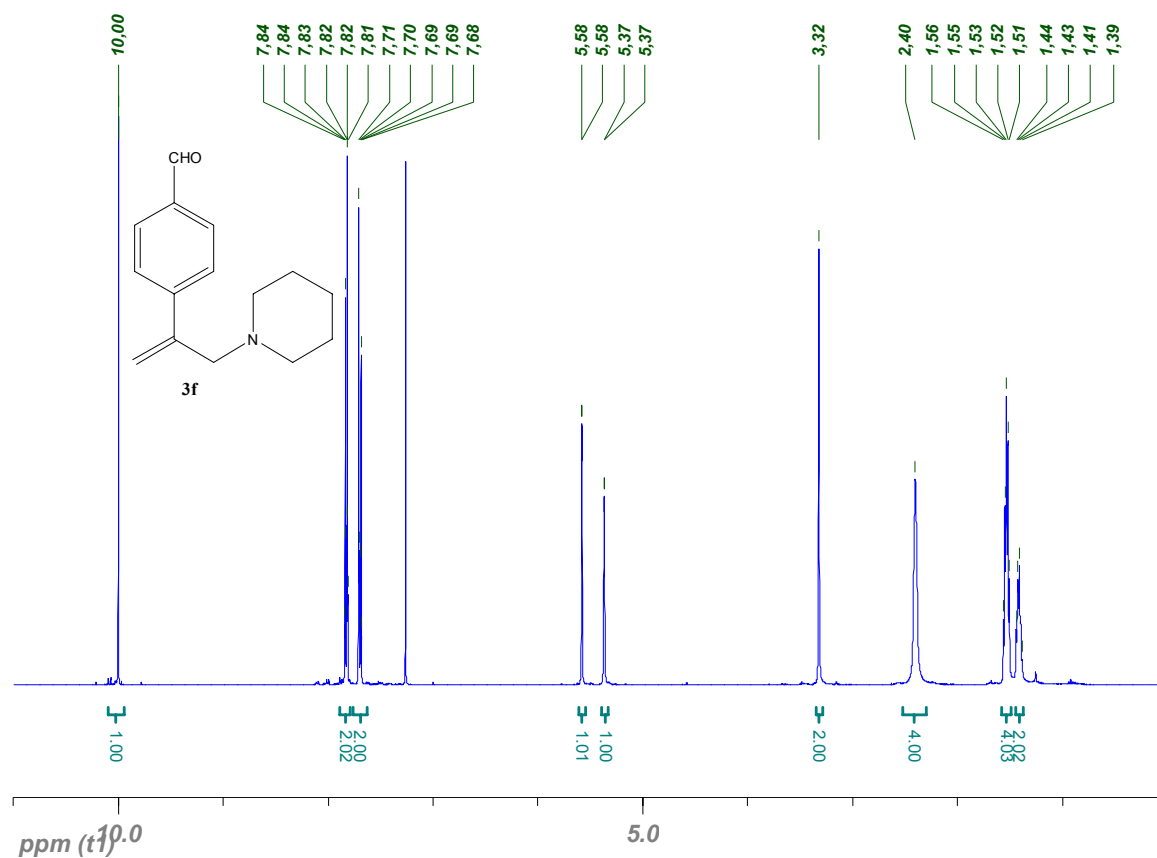


### NMR Spectra of product **3e**.

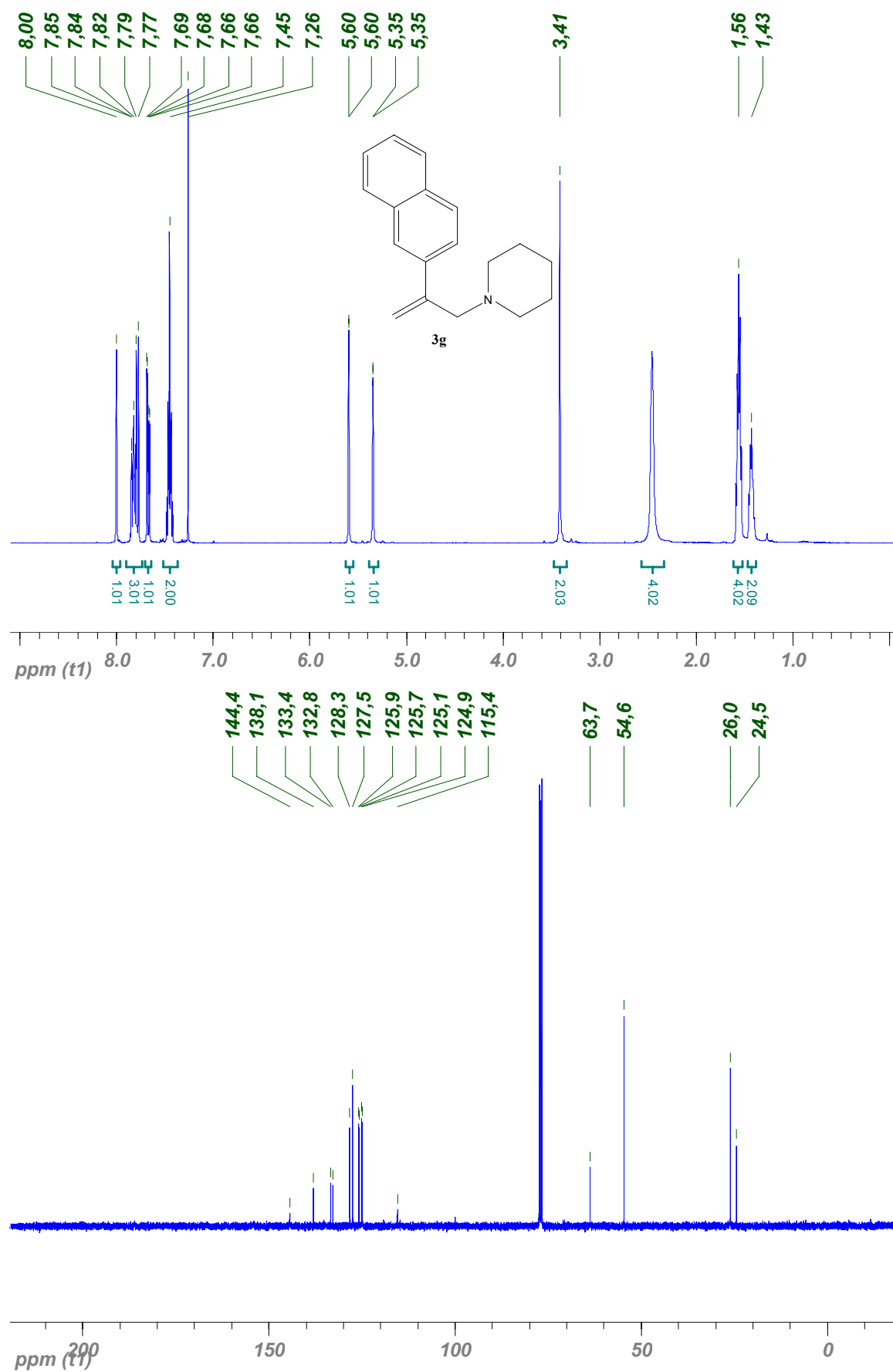




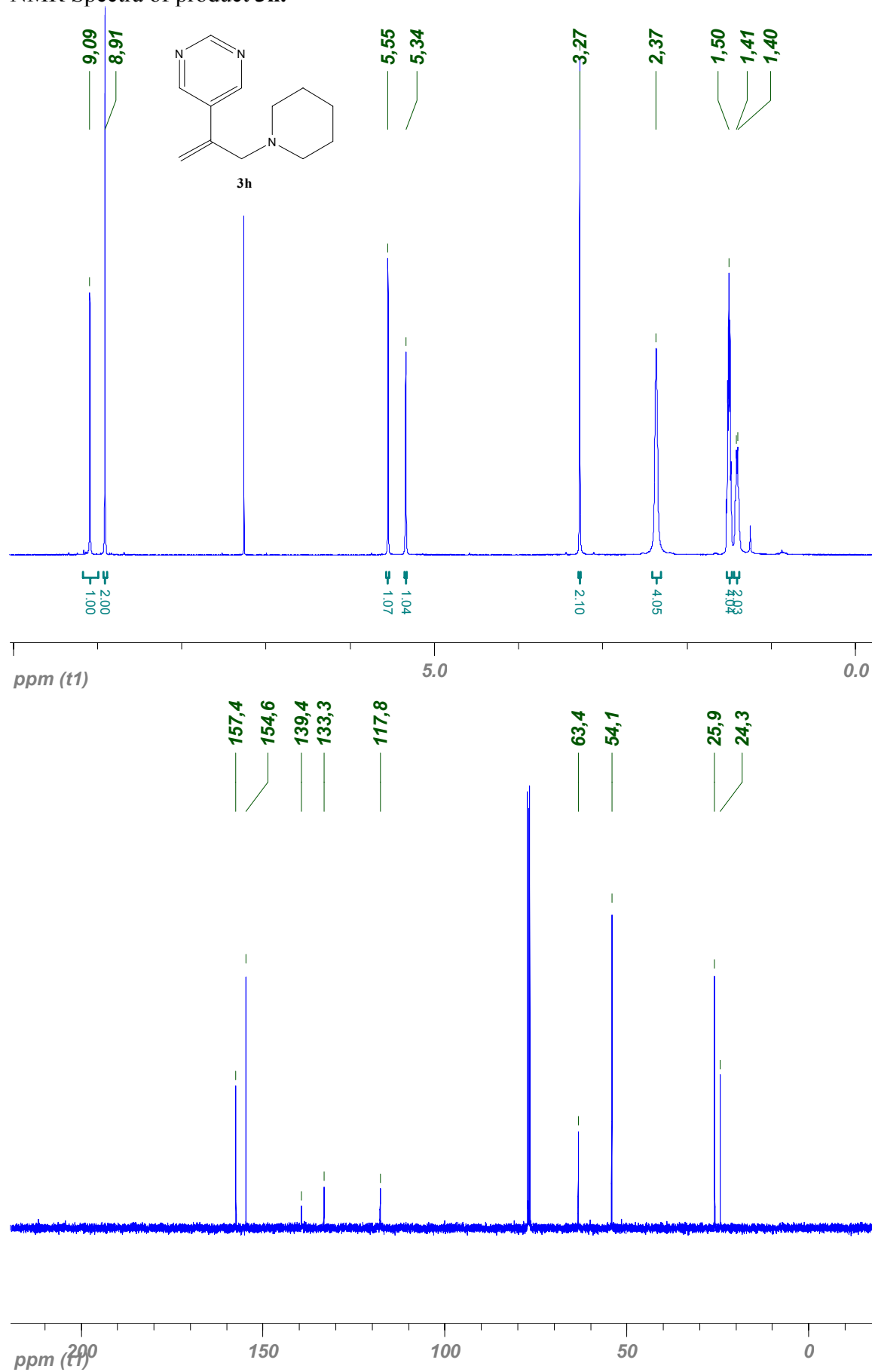
### NMR Spectra of product **3f**.



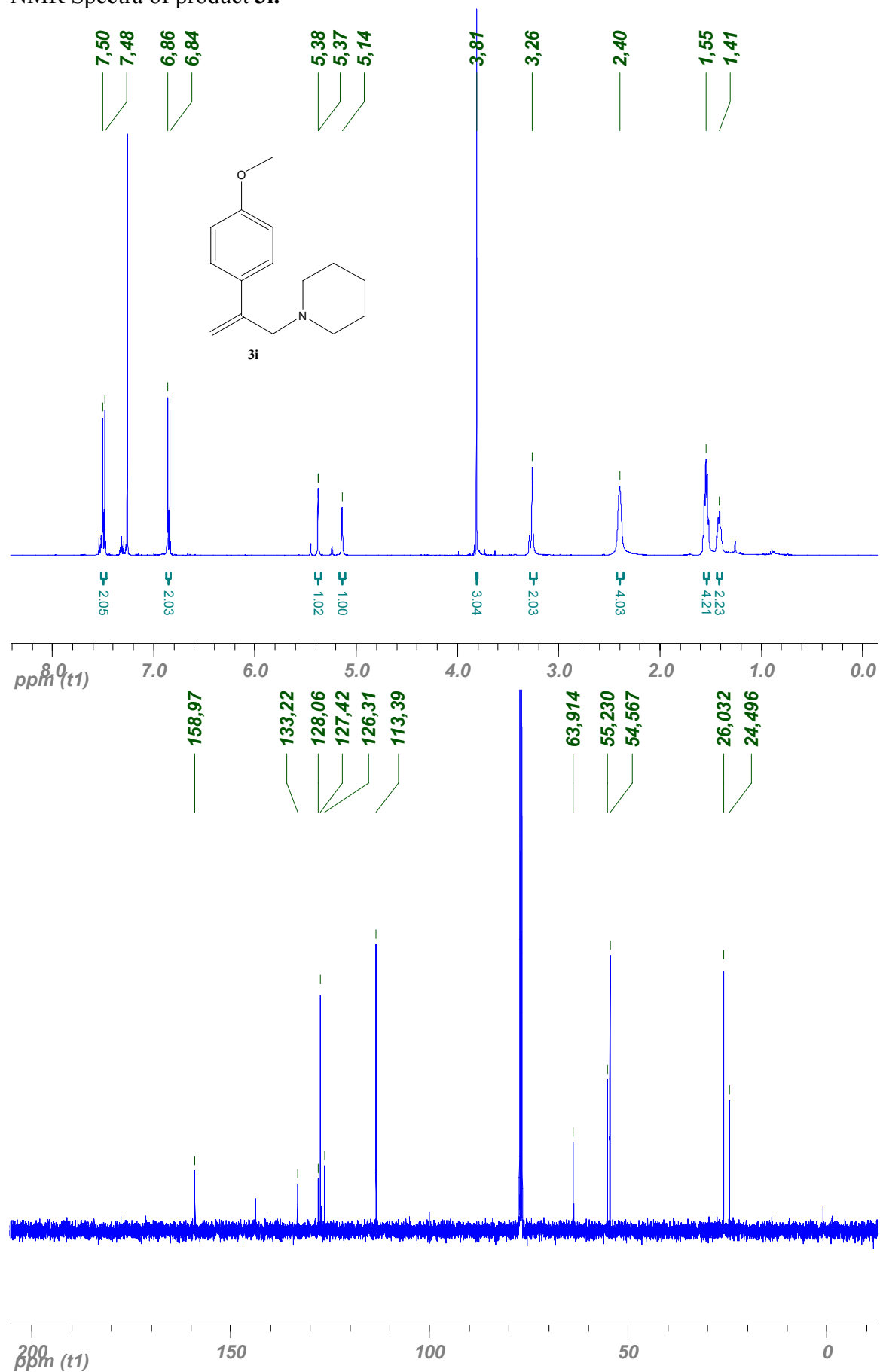
NMR Spectra of product **3g**.



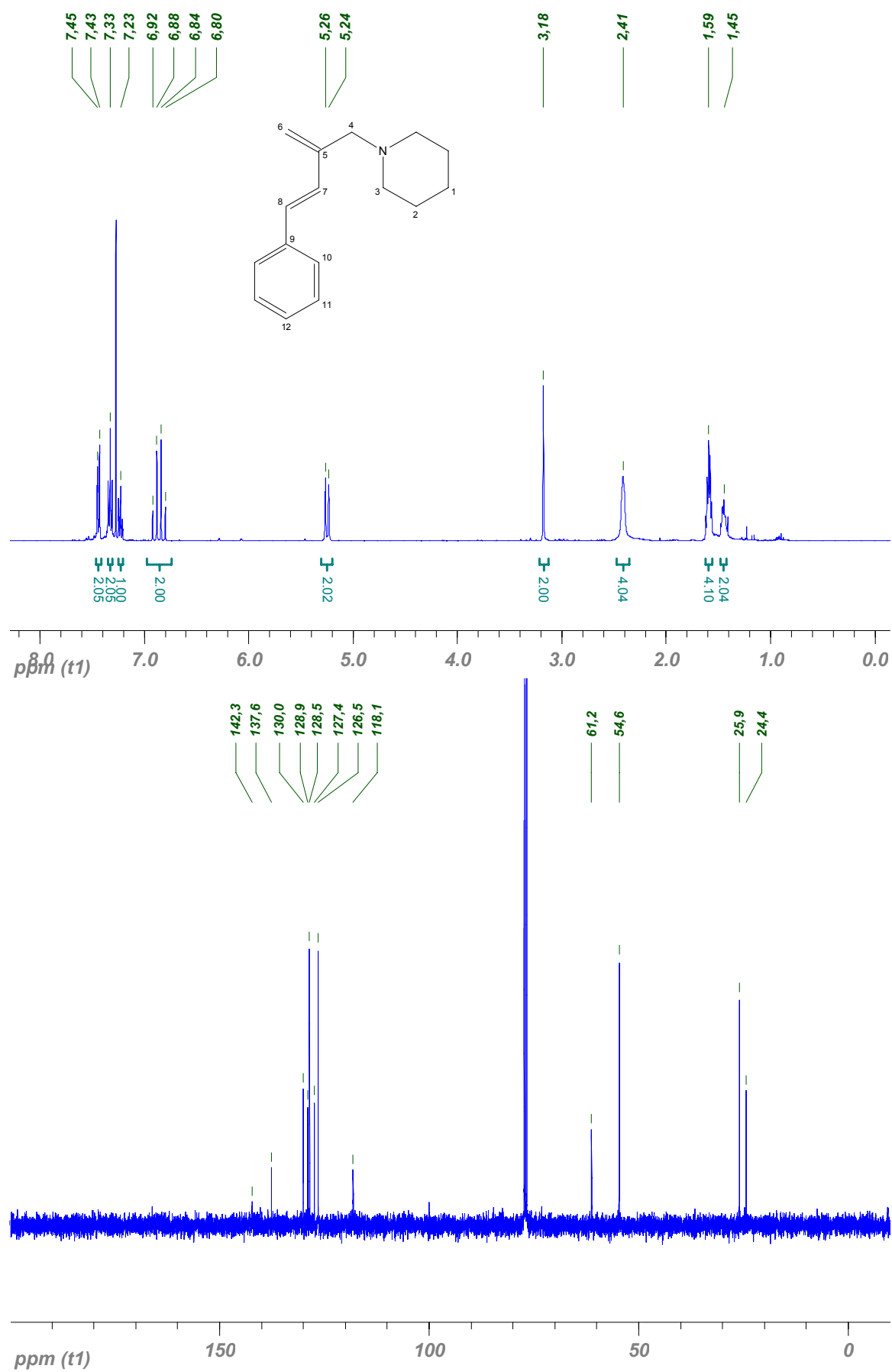
NMR Spectra of product **3h**.



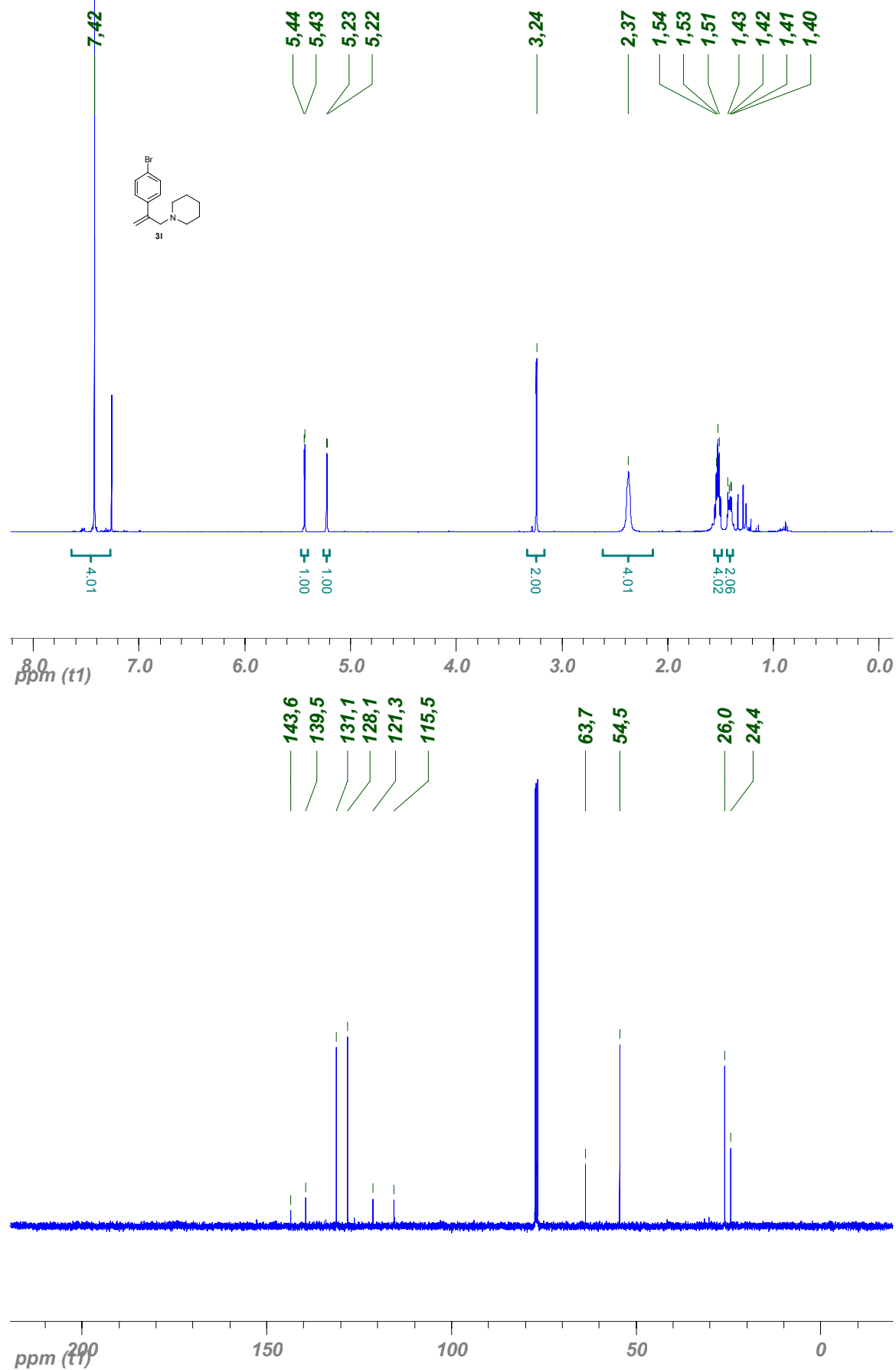
NMR Spectra of product **3i**.



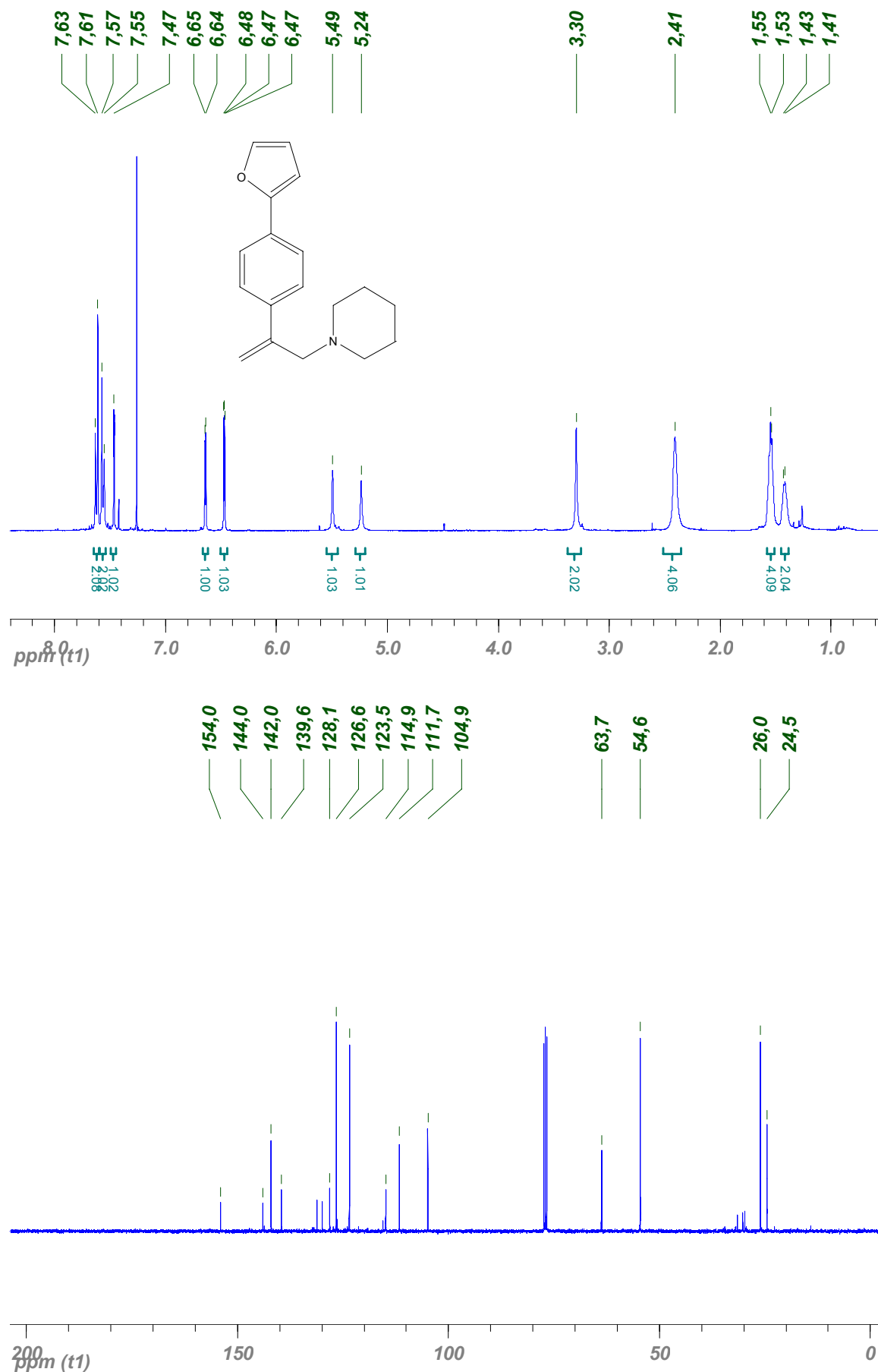
### NMR Spectra of product **3k**.



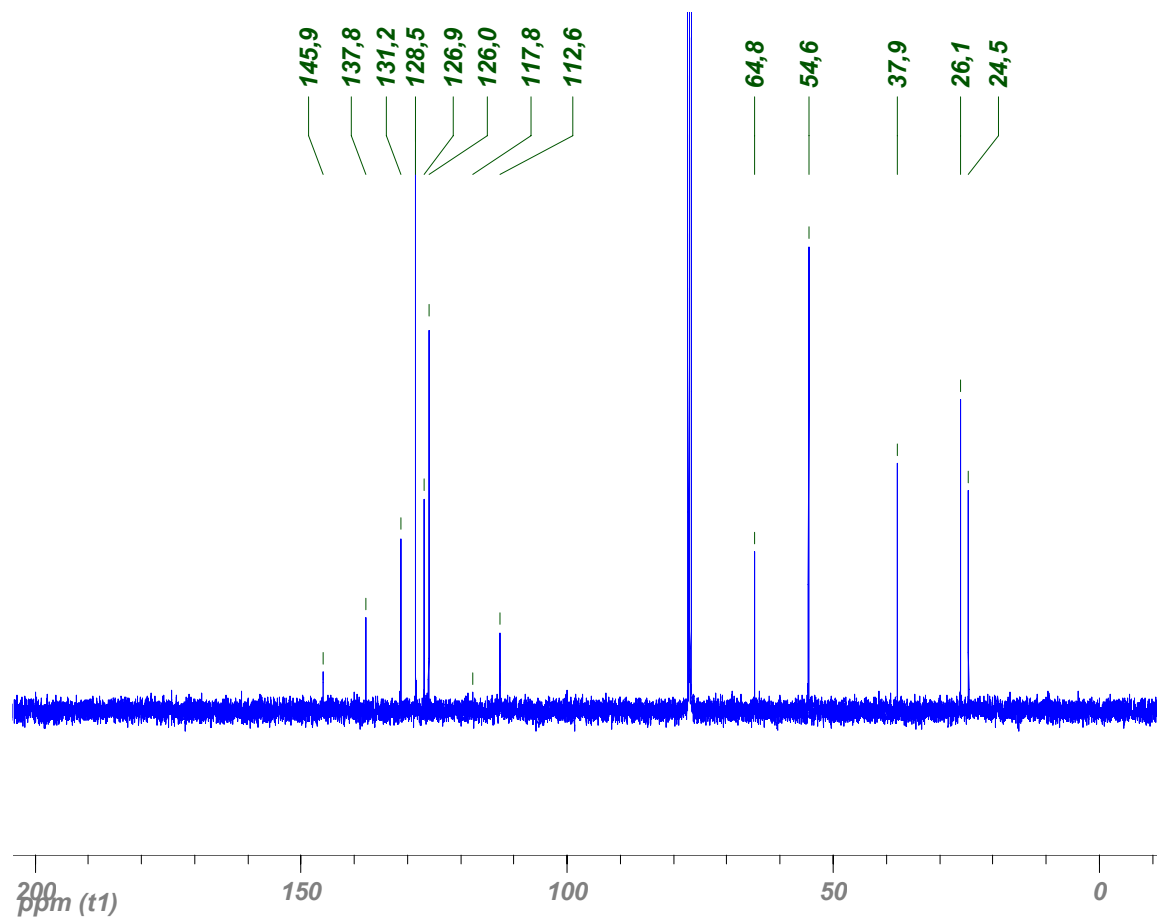
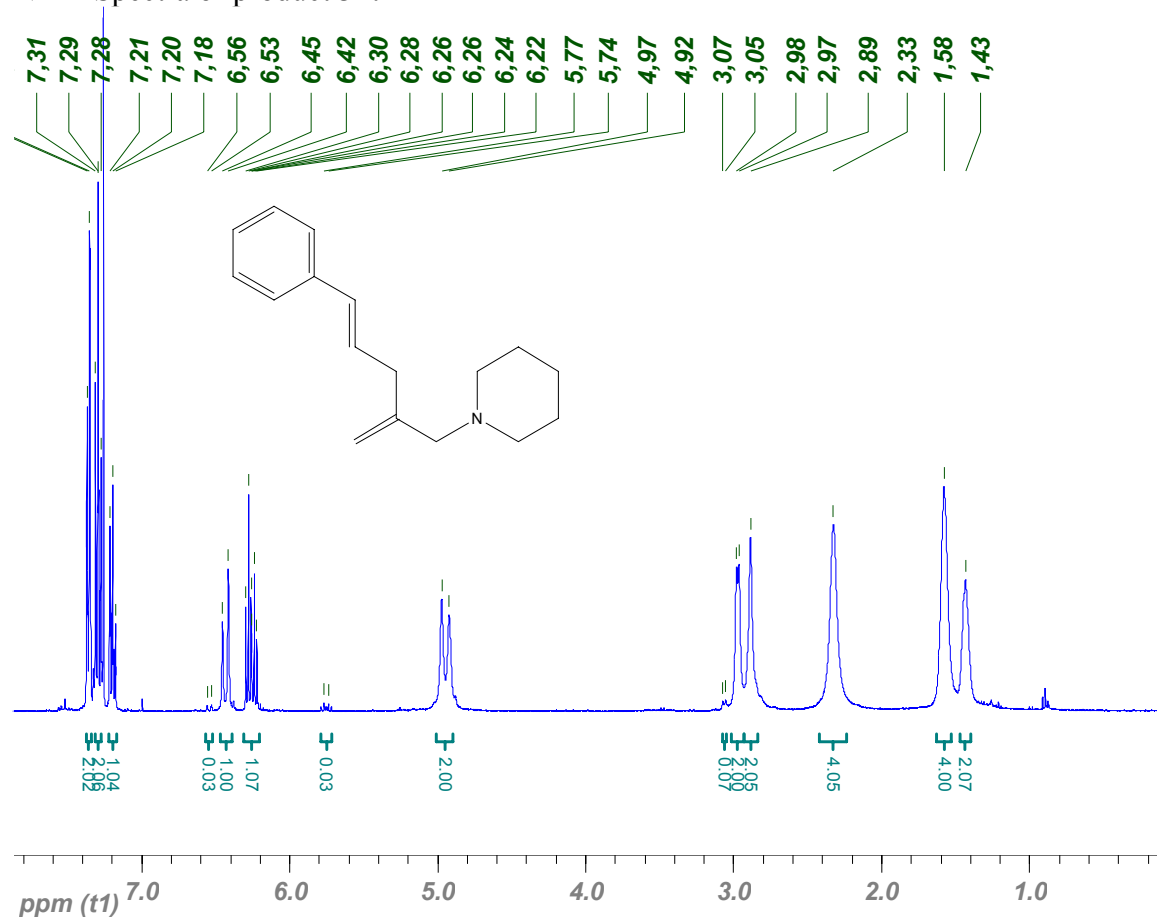
NMR Spectra of product **31**.



NMR Spectra of product **3m**.

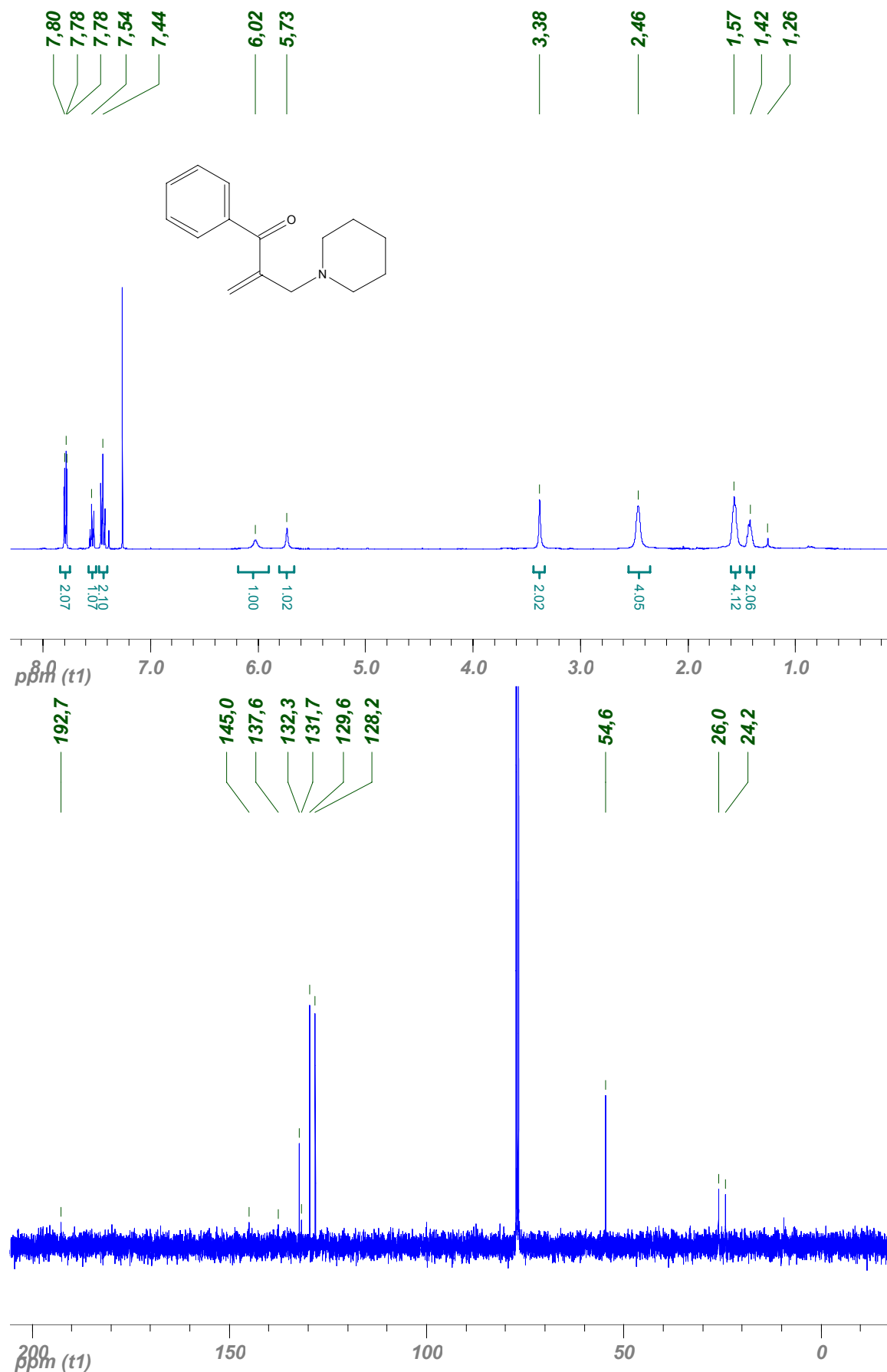


NMR Spectra of product **3n**.

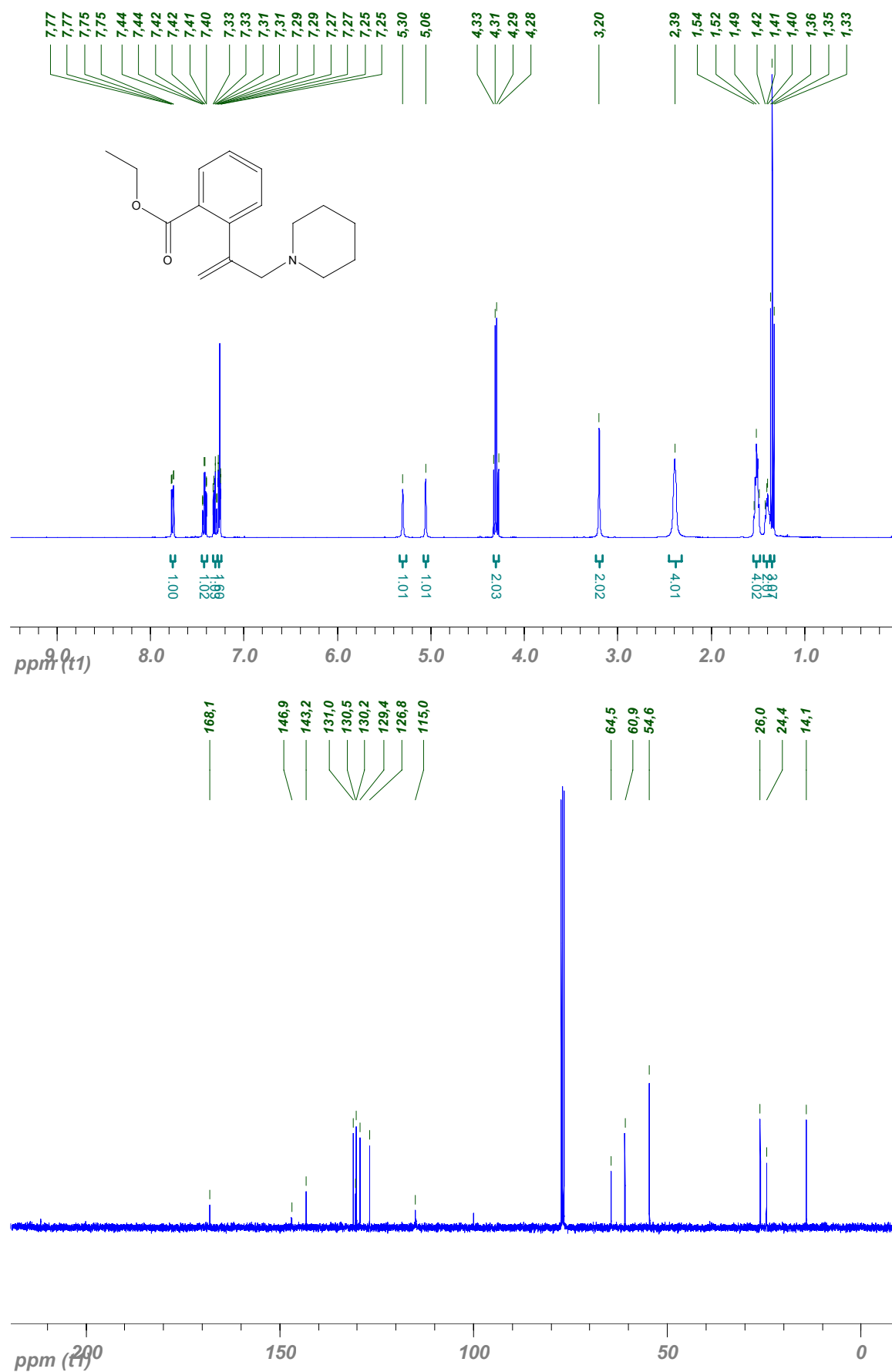




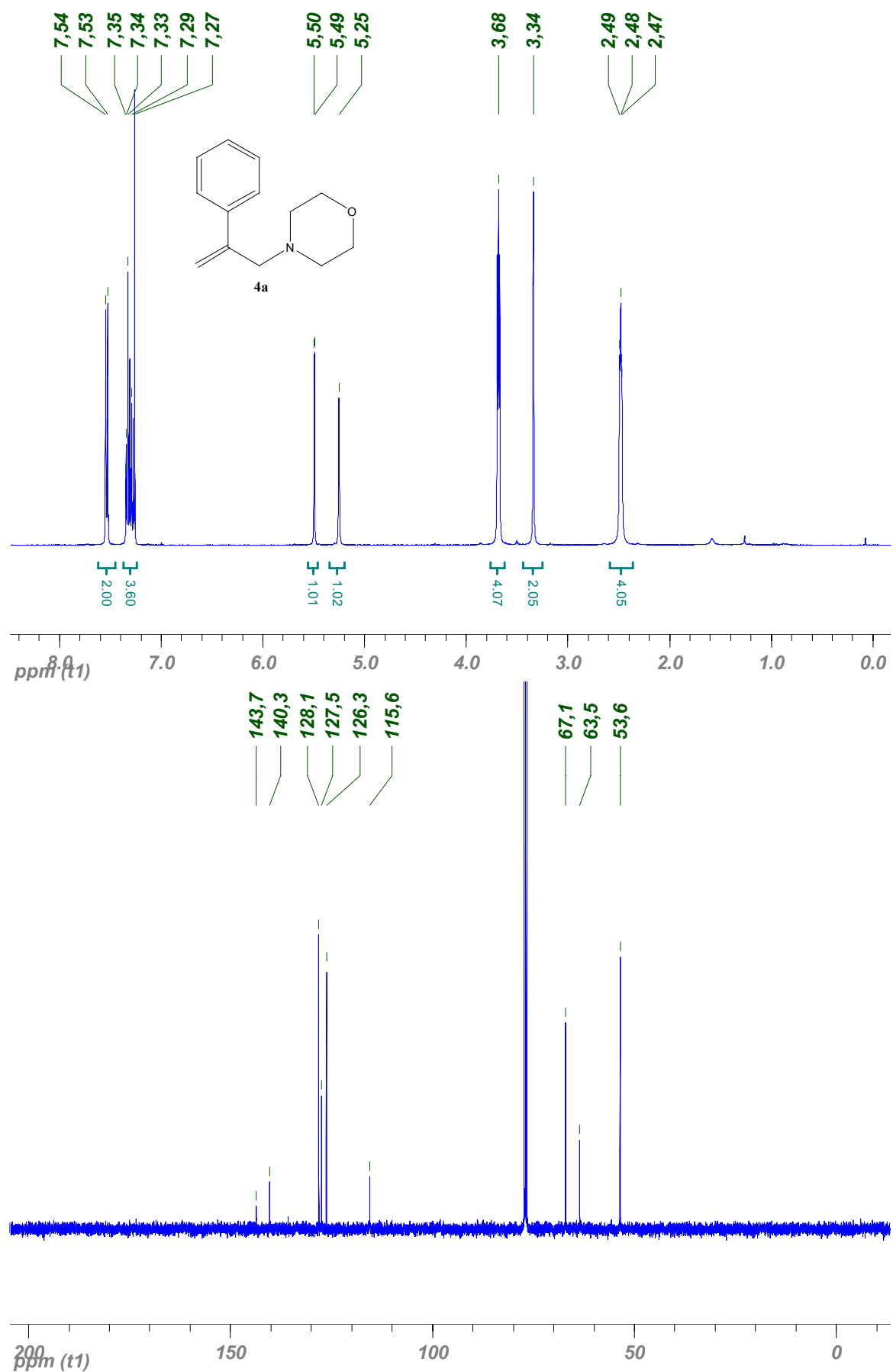
NMR Spectra of product **30**.



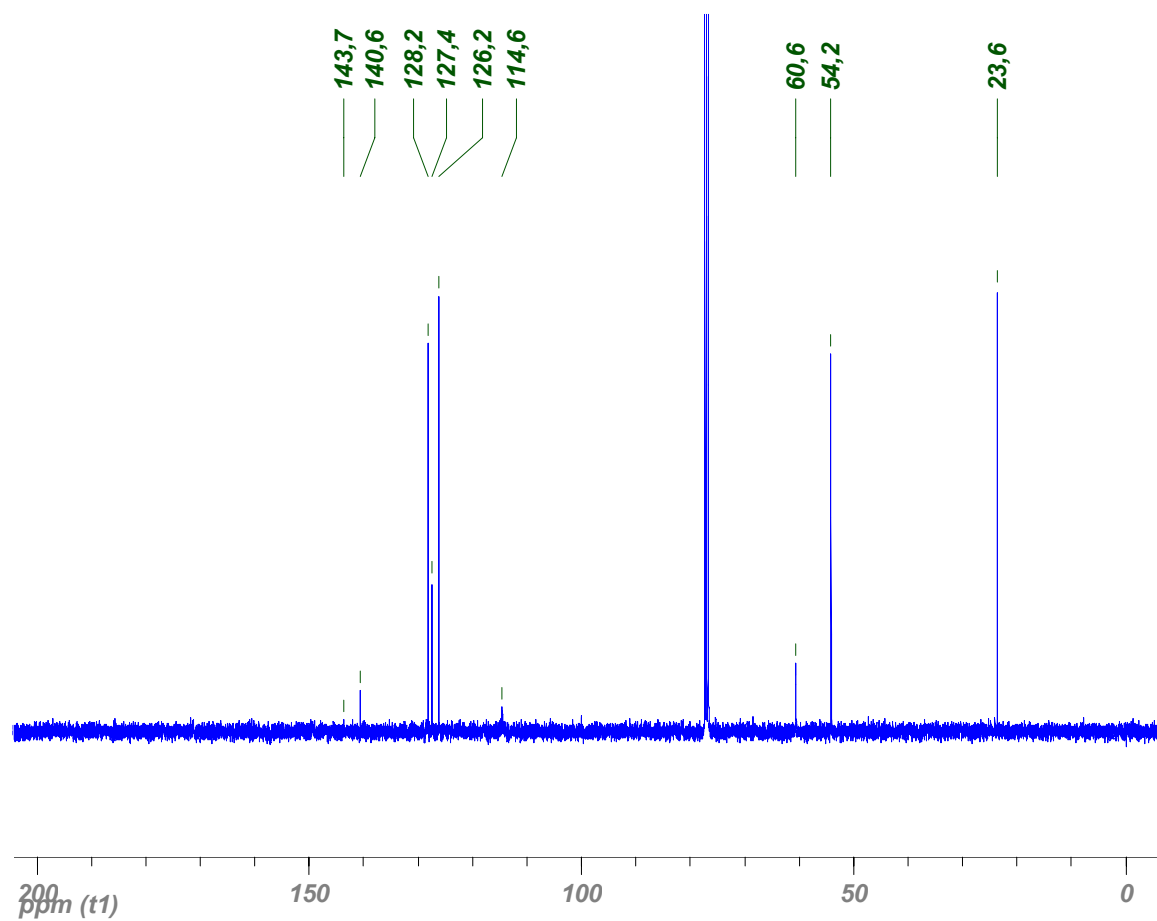
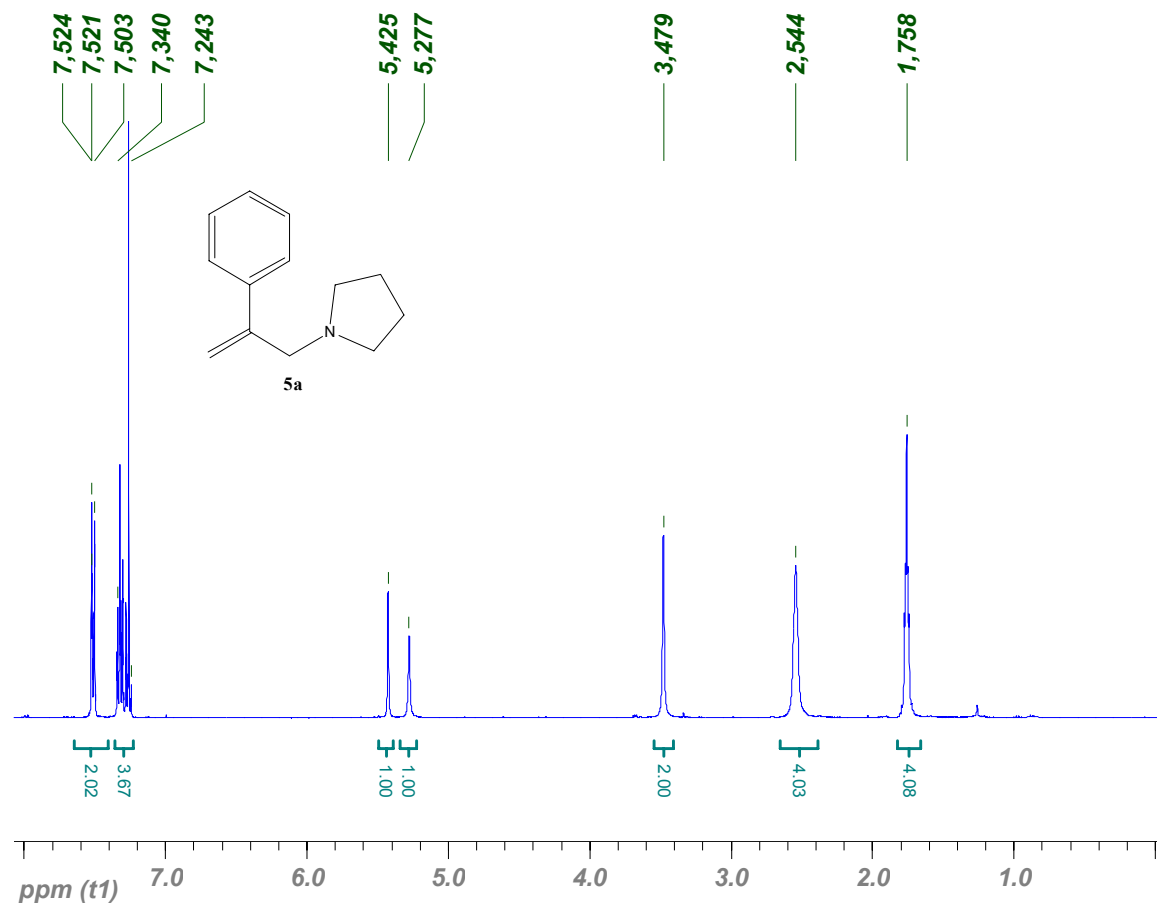
### NMR Spectra of product **3p**.



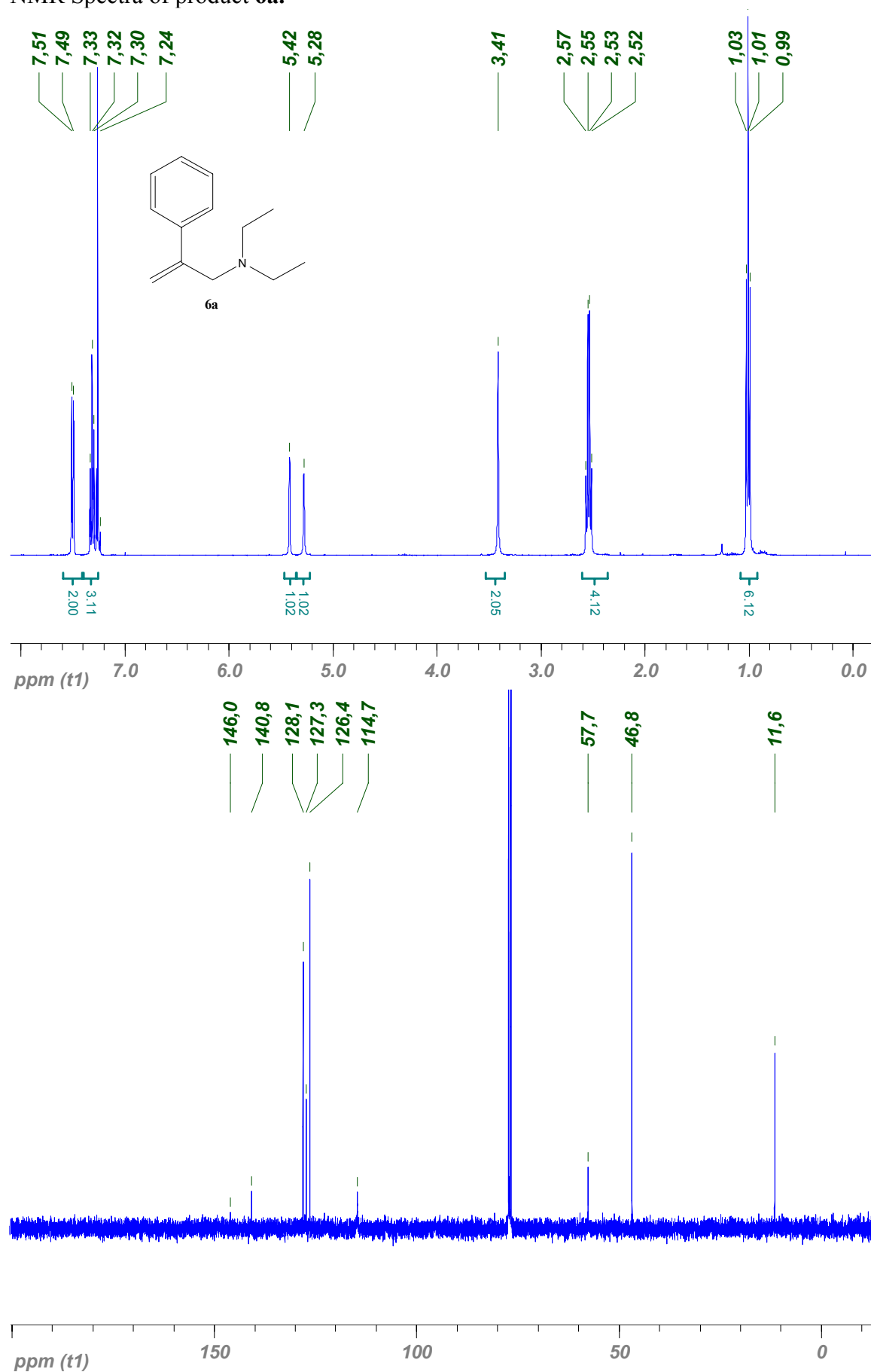
NMR Spectra of product **4a**.



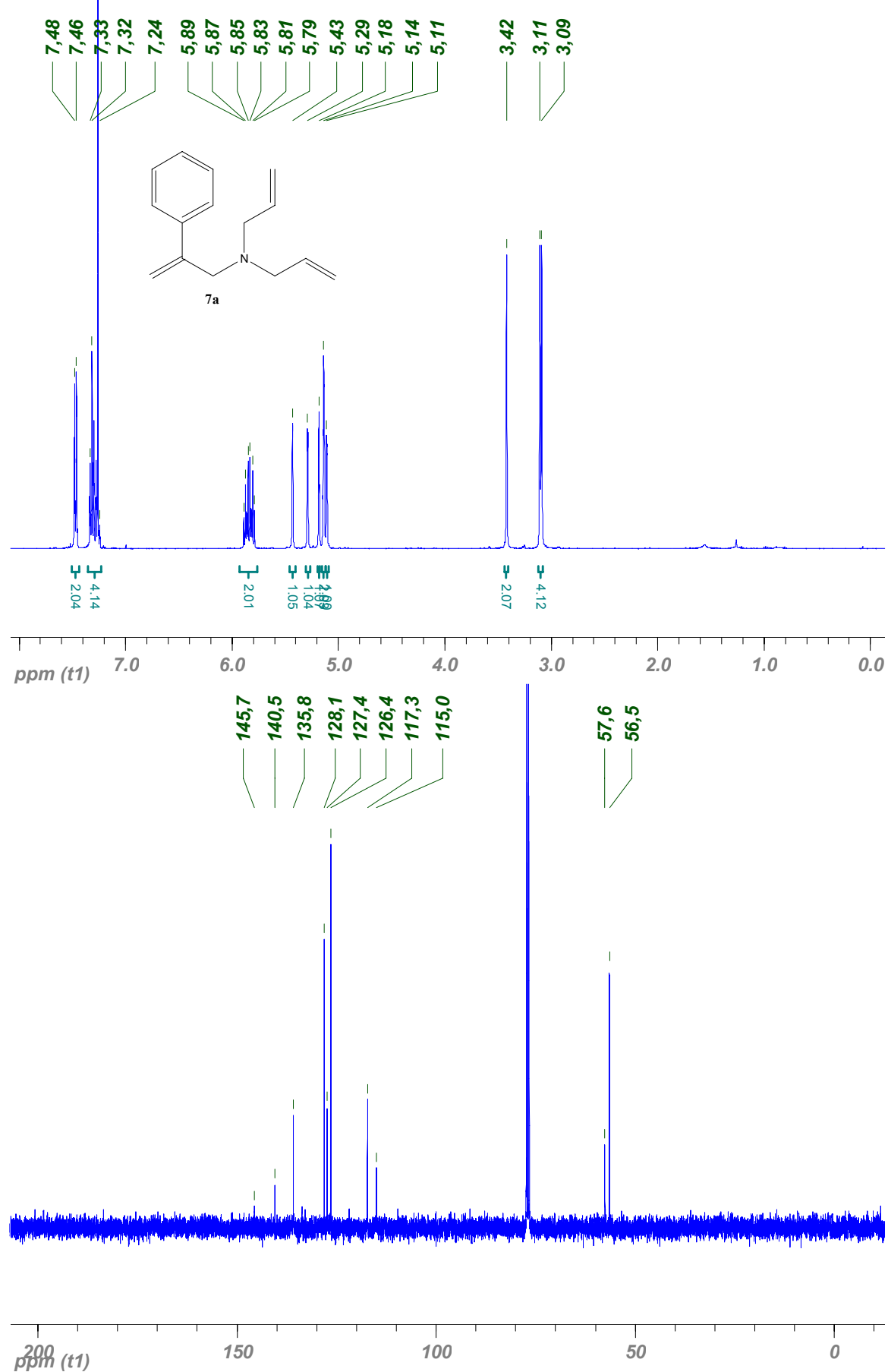
NMR Spectra of product **5a**.



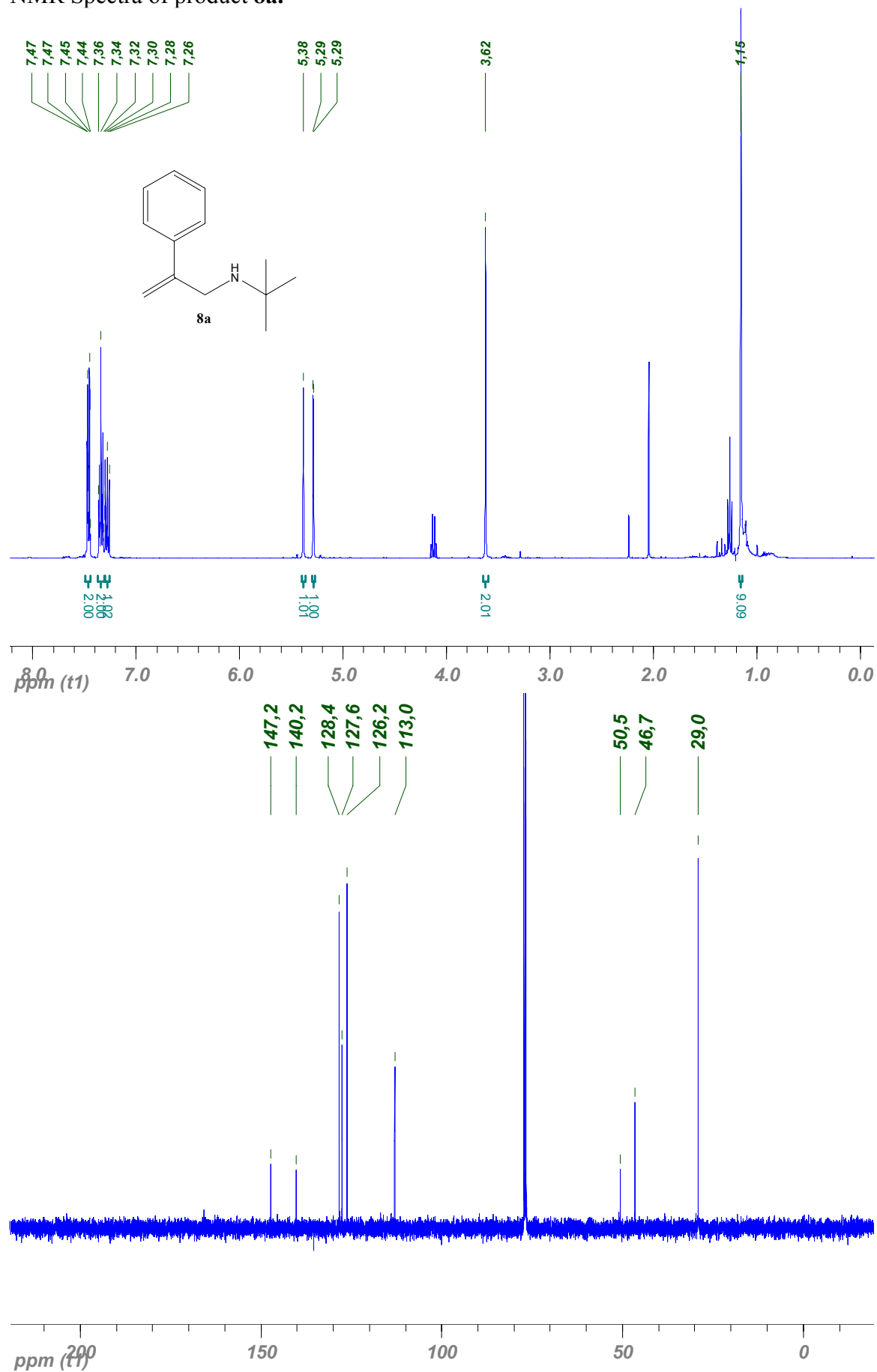
NMR Spectra of product **6a**.



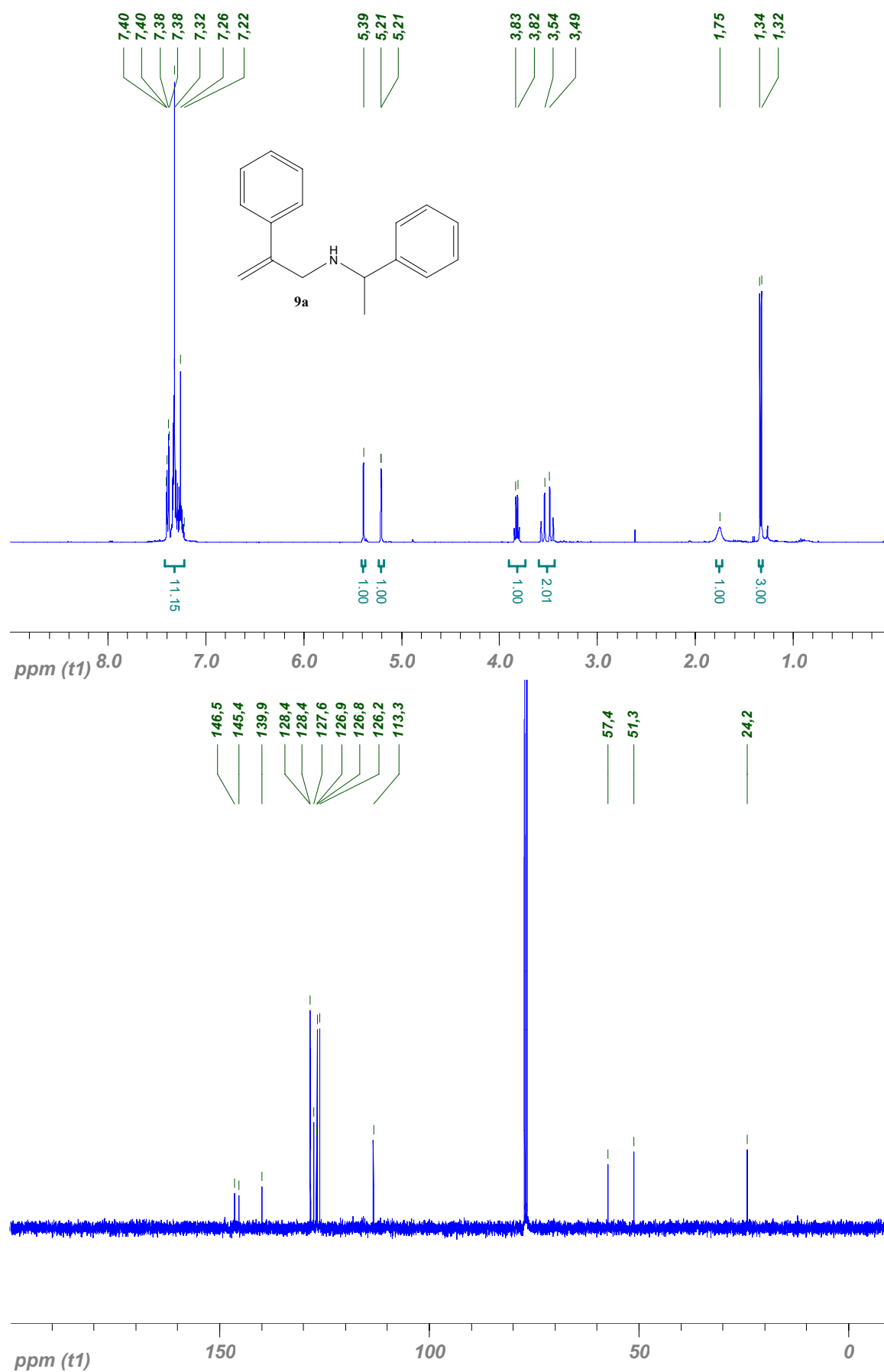
NMR Spectra of product **7a**.



### NMR Spectra of product **8a**.

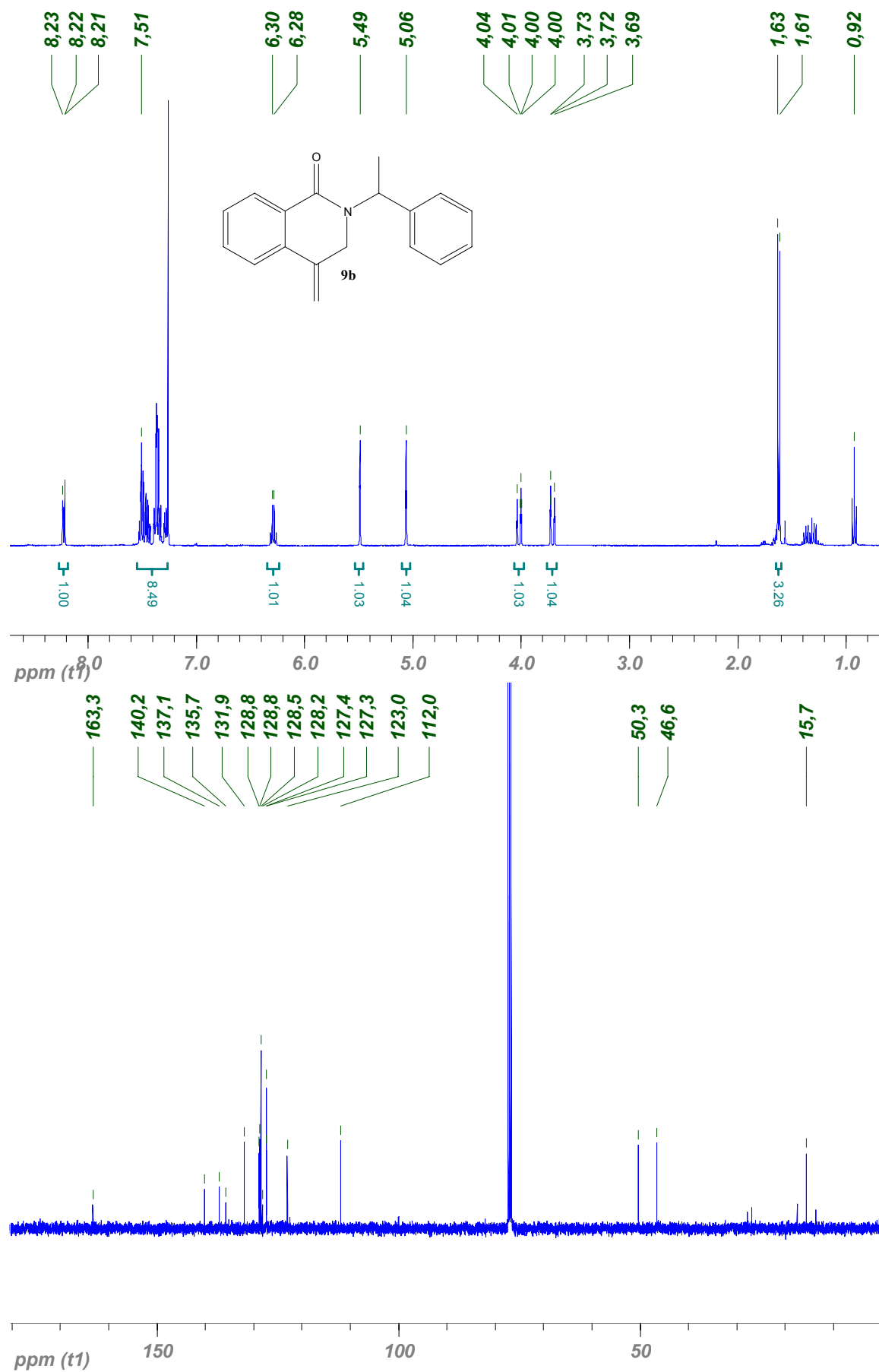


### NMR Spectra of product **9a**.

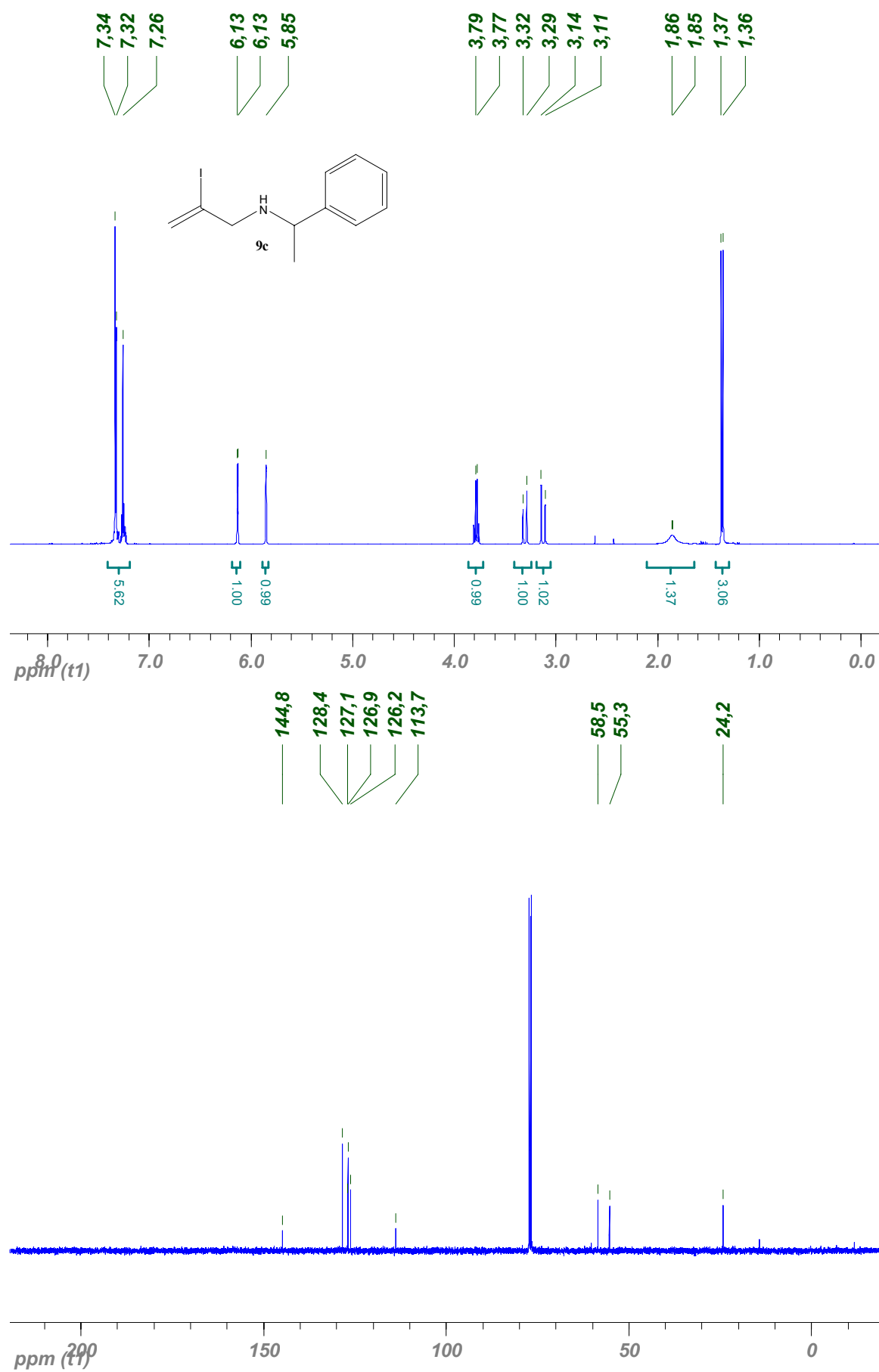




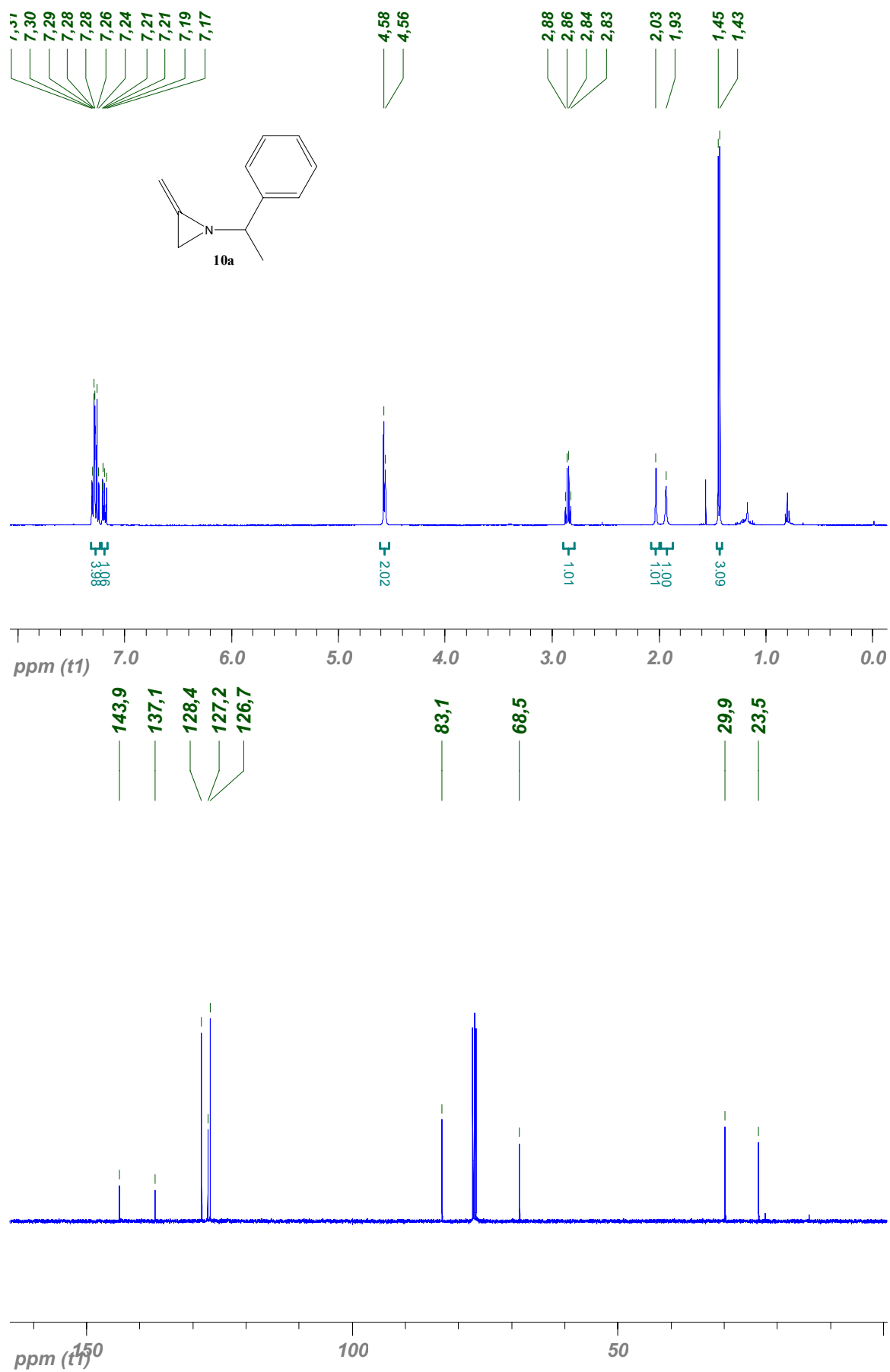
NMR Spectra of product **9b**.



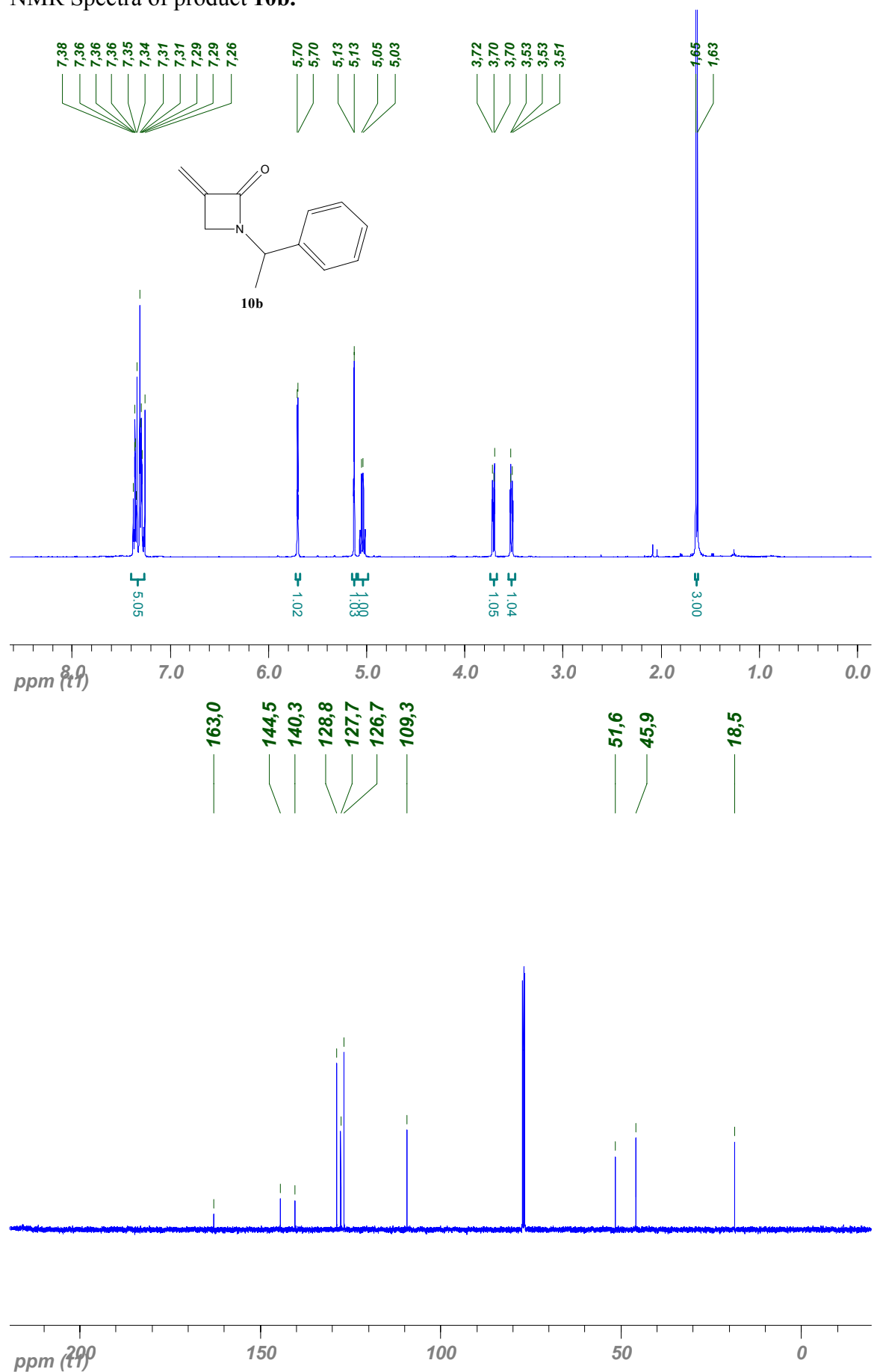
NMR Spectra of product **9c**.



### NMR Spectra of product **10a**.



### NMR Spectra of product **10b**.



### NMR Spectra of product **11a**.

