

**Supporting Information  
For**

**Catalytic Intermolecular Carbon Electrophile Induced Semipinacol  
Rearrangement**

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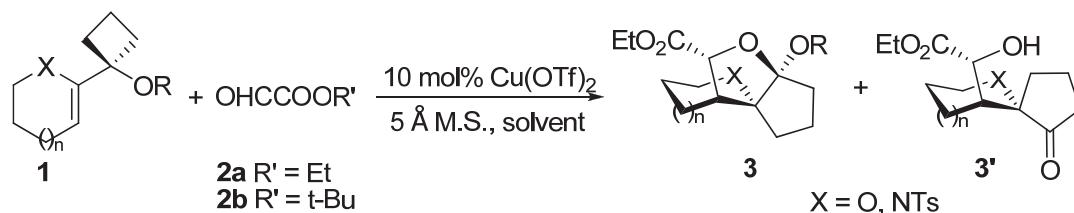
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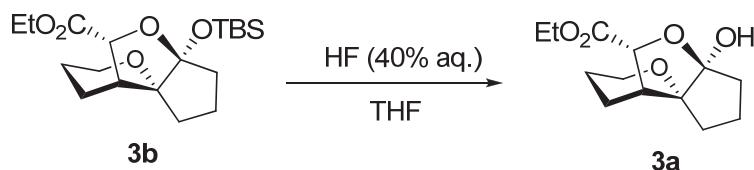
## General information

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F<sub>254</sub> plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petroleum was 60-90 °C. All other solvent were purified according to standard conditions. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or CD<sub>3</sub>COCD<sub>3</sub> solution on Bruker AX-400 MHz instruments and spectral data were reported in ppm with tetramethylsilane (TMS) as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the ESI technique. Enantioselectivities were determined by high performance liquid chromatography (HPLC) analysis employing a Darcel Chiracel AD column and optical rotation was detected on RUDOLPH A21202-J APTV/GW.

## General procedure of the catalytic intermolecular carbon electrophile induced semipinacol rearrangement (Table 2):

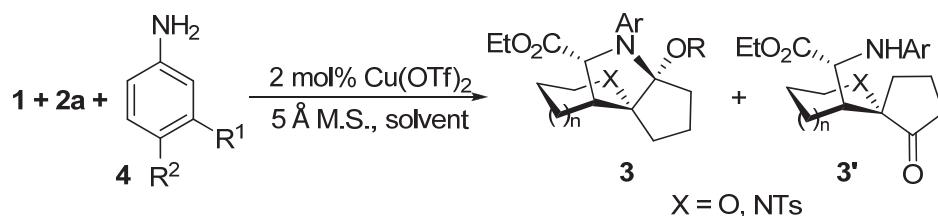


To an oven dried Schlenk tube charged with a magnetic stirring bar was sequentially added substrate (0.2 mmol), ethylglyoxalate (0.4 mmol.), 5Å molecular sieve (200 mg), THF (2 mL, acetone for the preparation of **3d**) and Cu(OTf)<sub>2</sub> (10 mol%) at room temperature (-10 °C for **3d**) (For synthesis of **3b**, the substrate **1b** was dissolved in half of the solvent and was added in 1 h with syringe pump). The reaction was monitored by TLC until all the substrate disappeared and the mixture was directly subjected to column chromatography on silica gel for purification.



The reaction system above containing **3b** was filtered and washed with additional THF (3 mL), HF (40% aq., 0.5 mL) was added and the mixture was stirred for 1h and quenched with K<sub>2</sub>CO<sub>3</sub>. The mixture was filtered with a short pad of Celite, concentrated and subjected to column chromatography on silica gel to afford **3a** (2 steps, 79% yield).

**General procedure of the three component reaction (Table 3):**



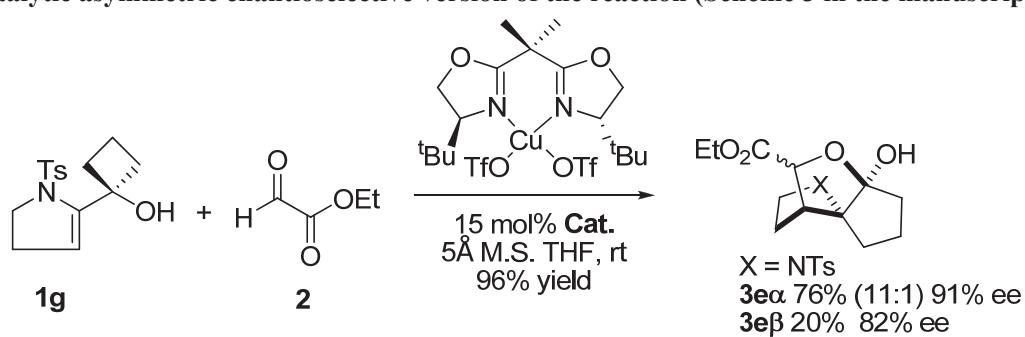
**For 3g-3i (entries 1-3):**

To an oven dried Schlenk tube charged with a magnetic stirring bar was sequentially added ethyl glyoxalate (2.0 mmol.) 5 Å molecular sieve (1 g), aniline derivatives (1.0 mmol), Cu(OTf)<sub>2</sub> (2 mol%) and acetone (5 mL). **1b** (1.0 mmol in 5 mL acetone) was then added to the system using syringe pump in 1 h at room temperature. The reaction was monitored by TLC until all the substrate disappeared and the mixture was directly subjected to column chromatography on silica gel for purification. (PE:DCM:EA = 25:75:1)

**For 3j (entry 4):**

To an oven dried Schlenk tube charged with a magnetic stirring bar was sequentially added substrate **1b** (0.2 mmol), ethyl glyoxalate (0.4 mmol), 5 Å molecular sieve (200 mg), aniline derivative **4b** (0.2 mmol), THF (2 mL) and Cu(OTf)<sub>2</sub> (15 mol%) at room temperature. The reaction was monitored by TLC until all the substrate disappeared and the mixture was directly subjected to column chromatography on silica gel for purification.

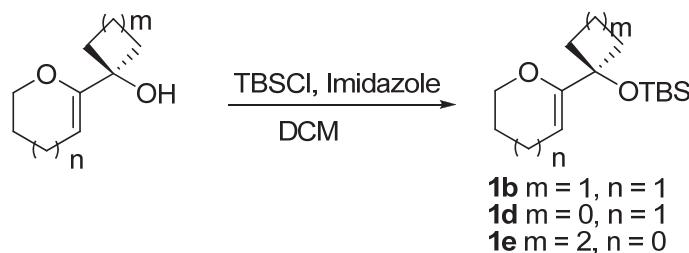
**Catalytic asymmetric enantioselective version of the reaction (Scheme 3 in the manuscript):**



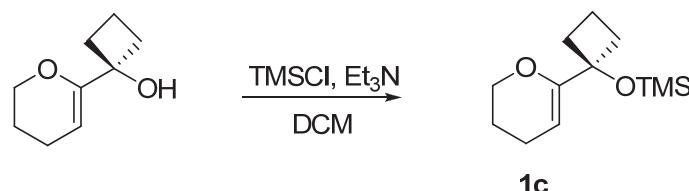
To an oven dried Schlenk tube charged with a magnetic stirring bar was sequentially added **1g** (0.2 mmol), ethyl glyoxalate **2** (0.4 mmol), 5 Å molecular sieve (100 mg/mL solvent), THF (2 mL) and (*S,S*)-*t*BuBOX (15 mol%), finally Cu(OTf)<sub>2</sub> (15 mol%) was added. The reaction was monitored by TLC until all the substrate disappeared and the mixture was directly subjected to column chromatography on silica gel for purification (PE:DCM:EA = 5:5:1, then PE:EA = 2:1). **3eα**: (60.0 mg, 76%, dr 11:1), **3eβ**: (15.8 mg, 20%).

## Preparation of substrates and spectroscopic data of key compounds:

### Preparation of substrates:

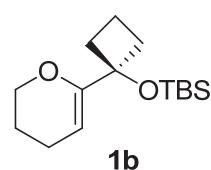


The tertiary alcohol substrates were dissolved in DCM followed by addition of imidazole. After being cooled to 0 °C TBSCl was added in one portion. After fully conversion of the substrates, the reaction was quenched with saturated NaHCO<sub>3</sub> (aq.) and extracted with DCM, the combined organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated under reduced pressure and purified by column chromatography on silica gel.



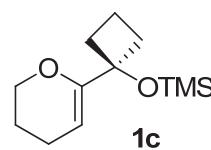
The tertiary alcohol substrate was dissolved in DCM followed by addition of Et<sub>3</sub>N. After being cooled to 0 °C TMSCl was added in one portion. After fully conversion of the substrates, the reaction was quenched with saturated NaHCO<sub>3</sub> (aq.) and extracted with DCM, the combined organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated under reduced pressure and purified by column chromatography on silica gel.

### Spectroscopic data of key compounds:



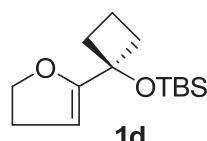
Colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm): δ 4.89 (t, J = 4.0 Hz, 1H), 4.02 (t, J = 5.2 Hz, 2H), 2.33 (tt, J<sub>1</sub> = 2.8 Hz, J<sub>2</sub> = 9.2 Hz, 2H), 2.14-2.02 (m, 4H), 1.81 (quint, J = 5.6 Hz, 2H), 1.75-1.60 (m, 1H), 1.51 (sext, J = 9.6 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 6H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm): δ 155.7, 94.9, 76.4, 66.0, 35.5, 25.9, 22.2, 20.2, 18.0, 13.2, 3.3; **HRMS (ESI)** calcd for C<sub>15</sub>H<sub>29</sub>O<sub>2</sub>Si [M+H]<sup>+</sup>: 269.1931, found 269.1934.



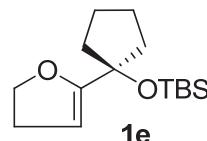
Colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 4.91 (t, *J* = 4.0 Hz, 1H), 4.00 (t, *J* = 5.2 Hz, 2H), 2.38-2.27 (m, 2H), 2.11-2.00 (m, 5H), 1.82-1.74 (m, 2H), 1.73-1.61 (m, 1H), 0.07 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 156.7, 95.8, 77.4, 66.7, 36.3, 23.0, 20.9, 13.9, 1.9; **HRMS** (ESI) calcd for C<sub>9</sub>H<sub>15</sub>O<sub>2</sub><sup>+</sup>[M-TMS+H]<sup>+</sup>: 155.1067, found 155.1070.



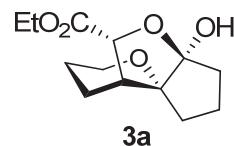
Colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 4.97 (t, *J* = 2.0 Hz, 1H), 4.34 (t, *J* = 9.2 Hz, 2H), 2.64 (dt, *J*<sub>1</sub> = 2.4 Hz, *J*<sub>2</sub> = 9.2 Hz, 2H), 2.32 (tt, *J*<sub>1</sub> = 2.8 Hz, *J*<sub>2</sub> = 8.8 Hz, 2H), 2.13 (dq, *J*<sub>1</sub> = 2.8 Hz, *J*<sub>2</sub> = 9.6 Hz, 2H), 1.69 (tq, *J*<sub>1</sub> = 2.8 Hz, *J*<sub>2</sub> = 9.6 Hz, 1H), 1.55 (sext, *J* = 9.2 Hz, 1H), 0.88 (s, 9H), 0.06 (s, 6H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 161.9, 95.8, 73.7, 70.7, 37.0, 30.6, 26.3, 18.6, 13.8, -3.1; **HRMS** (ESI) calcd for C<sub>14</sub>H<sub>27</sub>O<sub>2</sub>Si [M+H]<sup>+</sup>: 255.1775, found 255.1773.



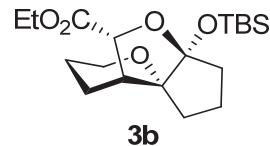
Colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 4.84 (t, *J* = 2.4 Hz, 1H), 4.31 (t, *J* = 9.2 Hz, 2H), 2.61 (dt, *J*<sub>1</sub> = 2.4 Hz, *J*<sub>2</sub> = 9.6 Hz, 2H), 1.88-1.72 (m, 6H), 1.70-1.56 (m, 2H), 0.87 (s, 9H), 0.08 (s, 6H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 162.5, 95.1, 81.6, 70.3, 39.9, 30.6, 26.3, 23.9, 18.9, -3.0; **HRMS** (ESI) C<sub>15</sub>H<sub>29</sub>O<sub>2</sub>Si [M+H]<sup>+</sup>: 269.1931, found 269.1937.



Colorless crystal, **MP** 65-67 °C.

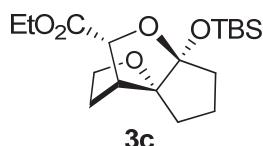
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm): δ 4.85 (brs, 1H), 4.44 (d, *J* = 8.8 Hz, 1H), 4.33-4.20 (m, 1H), 4.20-4.05 (m, 1H), 3.32-3.81 (m, 1H), 3.48 (dt, *J*<sub>1</sub> = 3.6 Hz, *J*<sub>2</sub> = 7.2 Hz, 1H), 2.32-2.23 (m, 1H), 2.13-2.02 (m, 2H), 2.02-1.92 (m, 1H), 1.89-1.75 (m, 2H), 1.75-1.65 (m, 1H), 1.63-1.53 (m, 1H), 1.48-1.30 (m, 3H), 2.02-1.92 (t, *J* = 6.0 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm): δ 174.2, 116.3, 84.4, 79.1, 63.1, 61.6, 43.8, 37.2, 34.9, 20.6, 20.3, 19.0, 14.0; **HRMS** (ESI) calcd for C<sub>13</sub>H<sub>24</sub>NO<sub>5</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 274.1649, found 274.1653.



Colorless oil.

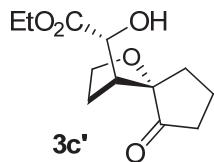
**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 4.50 (d, *J* = 5.6 Hz, 1H), 4.40-4.28 (m, 1H),

4.20 (q,  $J = 7.2$  Hz, 2H), 3.68-3.55 (m, 1H), 2.25-2.12 (m, 1H), 2.01-1.82 (m, 4H), 1.81-1.70 (m, 1H), 1.68-1.57 (m, 1H), 1.57-1.33 (m, 4H), 1.26 (t,  $J = 7.2$  Hz, 1H), 0.93 (s, 9H), 0.28 (s, 3H), 0.24 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{COCD}_3$ , ppm):  $\delta$  170.6, 115.4, 85.6, 79.1, 64.3, 61.1, 44.4, 41.3, 39.8, 26.5, 24.5, 22.0, 21.6, 18.6, 14.8, -2.6, -2.8; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{34}\text{NaO}_5\text{Si} [\text{M}+\text{Na}]^+$ : 393.2068, found 393.2072.



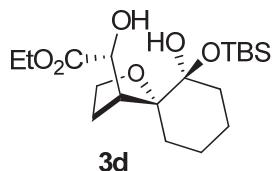
Colorless oil, inseparable mixture ( $\text{dr} = 5:1$ ), for major isomer:

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  4.55 (d,  $J = 6.0$  Hz, 1H), 4.21 (q,  $J = 7.2$  Hz, 2H), 4.06 (q,  $J = 8.0$  Hz, 1H), 3.93 (q,  $J = 8.0$  Hz, 1H), 2.78 (dt,  $J_1 = 6.4$  Hz,  $J_2 = 9.2$  Hz, 1H), 2.10-1.94 (m, 5H), 1.80-1.58 (m, 2H), 1.49-1.32 (m, 1H), 1.28 (t,  $J = 7.2$  Hz, 1H), 0.91 (s, 9H), 0.23 (s, 3H), 0.17 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  170.4, 113.4, 96.4, 76.9, 69.2, 60.8, 50.6, 39.3, 35.3, 28.9, 25.7, 21.1, 17.8, 14.2, -3.3; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{32}\text{NaO}_5\text{Si} [\text{M}+\text{Na}]^+$ : 379.1911, found 379.1915.



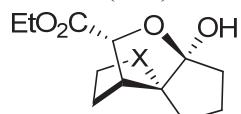
Colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  4.29 (d,  $J = 7.2$  Hz, 1H), 4.28-4.22 (m, 2H), 3.97 (dt,  $J_1 = 4.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 3.70 (q,  $J = 8.0$  Hz, 1H), 2.97 (brs, 1H), 2.80-2.70 (m, 1H), 2.53-2.42 (m, 1H), 2.33-2.25 (m, 1H), 2.21-2.12 (m, 1H), 2.12-1.88 (m, 5H), 1.32 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  215.8, 174.2, 87.2, 69.9, 66.6, 62.3, 42.6, 34.9, 32.2, 26.5, 18.8, 14.1; HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{18}\text{NaO}_5 [\text{M}+\text{Na}]^+$ : 265.1046, found 265.1041.



Colorless crystal, MP 76-78.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.65 (s, 1H), 4.35-4.22 (m, 3H), 3.98 (dd,  $J_1 = 7.2$  Hz,  $J_2 = 15.2$  Hz, 1H), 3.83 (dt,  $J_1 = 5.6$  Hz,  $J_2 = 8.0$  Hz, 1H), 3.61 (d,  $J = 3.2$  Hz, 1H), 3.01-2.87 (m, 1H), 2.22-2.18 (m, 1H), 2.06-1.94 (m, 2H), 1.85-1.58 (m, 8H), 1.30 (t,  $J = 7.1$  Hz, 3H), 0.88 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  173.2, 108.7, 89.5, 70.2, 66.2, 61.8, 44.3, 36.1, 36.0, 26.0, 24.9, 24.7, 24.7, 18.4, 14.1, -2.7, -2.7; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{36}\text{NaO}_6\text{Si} [\text{M}+\text{Na}]^+$ : 411.2173, found 411.2179.

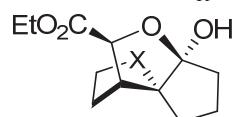


**3e $\alpha$** , X = NTs

Colorless viscous oil. Column chromatography (PE:DCM:EA = 5:5:1).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 5.24 (s, 1H), 4.64 (d, *J* = 8.4 Hz, 1H), 4.20 (dq, *J*<sub>1</sub> = 3.8, *J*<sub>2</sub> = 10.8 Hz, 2H), 3.38-3.30 (m, 2H), 3.21 – 3.03 (m, 1H), 2.91 (dt, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 12.4 Hz, 1H), 2.41 (s, 3H), 2.15 – 2.06 (m, 1H), 1.97 – 1.79 (m, 4H), 1.79 – 1.66 (m, 1H), 1.55 – 1.40 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 174.1, 143.6, 140.2, 130.3, 128.2, 116.2, 83.6, 78.5, 62.3, 57.9, 50.6, 38.1, 36.9, 25.0, 21.4, 21.4, 14.5; **HRMS** (ESI) calcd for C<sub>19</sub>H<sub>25</sub>NNaO<sub>6</sub>S [M+Na]<sup>+</sup>: 418.1295, found 418.1263.

**HPLC** Enantiomeric excess is 91.5% determined by HPLC (Chiralcel AD, Hexane/Isopropanol 60/40, flow rate=1.0 mL/min, 240 nm): major isomer: t<sub>R</sub> = 16.9 min; minor isomer: t<sub>R</sub> = 17.8 min, [a]<sub>D</sub><sup>25</sup> -26° (*c* 1.0, CHCl<sub>3</sub>).

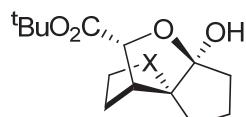


**3eβ, X = NTs**

Colorless crystal MP 148-149 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.38 (d, *J* = 10.0 Hz, 1H), 4.22 (q, *J* = 7.2, 2H), 3.71 (brs, 1H), 3.68-3.52 (m, 2H), 2.67 (dd, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 9.6 Hz, 1H), 2.91 (dt, *J*<sub>1</sub> = 7.2 Hz, *J*<sub>2</sub> = 12.8 Hz, 1H), 2.43 (s, 3H), 2.21 (dd, *J*<sub>1</sub> = 6.0 Hz, *J*<sub>2</sub> = 12.8 Hz, 1H), 1.99 – 1.82 (m, 3H), 1.79 – 1.63 (m, 2H), 1.63 – 1.48 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) 170.1, 143.3, 138.7, 129.7, 126.7, 113.7, 83.3, 77.7, 61.3, 58.9, 49.1, 37.6, 35.5, 25.0, 21.4, 20.6, 14.1; **HRMS** (ESI) calcd for C<sub>19</sub>H<sub>25</sub>NO<sub>6</sub>S [M+NH<sub>4</sub>]<sup>+</sup>: 395.1403, found 395.1697.

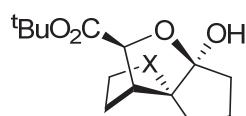
**HPLC** Enantiomeric excess is 82% determined by HPLC (Chiralcel AD, Hexane/Isopropanol 60/40, flow rate=1.0 mL/min, 246 nm): major isomer: t<sub>R</sub> = 15.2 min; minor isomer: t<sub>R</sub> = 16.8 min, [a]<sub>D</sub><sup>25</sup> +53° (*c* 1.0, CHCl<sub>3</sub>).



**3fα, X = NTs**

Colorless amorphous solid.

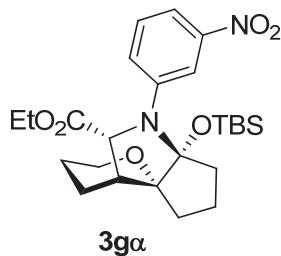
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.06 (s, 1H), 4.50 (d, *J* = 9.2 Hz, 1H), 3.40-3.35 (m, 2H), 3.05-2.87 (m, 2H), 2.40 (s, 3H), 2.16 (dt, *J*<sub>1</sub> = 6.8 Hz, *J*<sub>2</sub> = 12.8 Hz 1H), 2.09 – 2.03 (m, 1H), 1.95-1.83 (m, 2H), 1.77 (dt, *J*<sub>1</sub> = 6.8 Hz, *J*<sub>2</sub> = 13.2 Hz, 2H), 1.44 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 173.0, 142.8, 138.1, 129.3, 127.3, 116.0, 83.6, 83.3, 78.9, 57.7, 49.3, 37.2, 36.9, 27.9, 23.9, 21.4, 20.4; **HRMS** (ESI) calcd for C<sub>21</sub>H<sub>33</sub>N<sub>2</sub>O<sub>6</sub>S [M+NH<sub>4</sub>]<sup>+</sup>: 441.2054, found 441.2050.



**3fβ, X = NTs**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.27 (d, *J* = 10.4 Hz, 1H), 3.70 -3.52 (m, 2H), 2.67-2.58 (m, 1H), 2.58-2.50 (m, 1H), 2.44

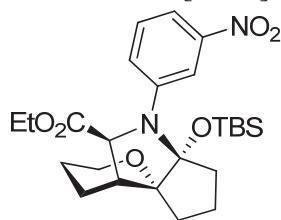
(s, 3H), 2.22 (dd,  $J_1 = 5.6$  Hz,  $J_2 = 12.4$  Hz, 1H), 1.97-1.86 (m, 2H), 1.78-1.63 (m, 2H), 1.63-1.52 (m, 2H), 1.48 (s, 9H). **HRMS** (ESI) calcd for  $C_{21}H_{33}N_2O_6S$  [ $M+NH_4$ ]<sup>+</sup>: 441.2054, found 441.2050. (together with **3fa**)



**3g $\alpha$**

Yellowish oil.

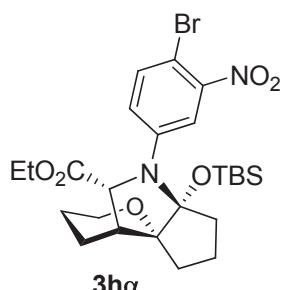
**$^1H$  NMR** (400 MHz,  $CD_3COCD_3$ , ppm):  $\delta$  7.63 (d,  $J = 2.4$  Hz, 1H), 7.54 (dd,  $J_1 = 1.2$  Hz,  $J_2 = 8.8$  Hz, 1H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.11 (dd,  $J_1 = 2.4$  Hz,  $J_2 = 8.4$  Hz, 1H), 4.66 (d,  $J = 10.0$  Hz, 1H), 4.13 (q,  $J = 7.2$  Hz, 2H), 3.94 (dd,  $J_1 = 3.2$  Hz,  $J_2 = 10.0$  Hz, 1H), 3.53 (t,  $J = 4.0$  Hz, 1H), 2.52-2.38 (m, 2H), 2.27 (d,  $J = 9.6$  Hz, 1H), 2.23-2.12 (m, 1H), 2.10-1.98 (m, 1H), 1.96-1.92 (m, 3H), 1.92-1.70 (m, 2H), 1.61-1.49 (m, 1H), 1.14 (t,  $J = 7.2$  Hz, 3H), 0.70 (s, 9H), 0.09 (s, 3H), -0.18 (s, 3H);  **$^{13}C$  NMR** (100 MHz,  $CD_3COCD_3$ , ppm):  $\delta$  171.3, 149.6, 146.7, 130.1, 122.4, 113.5, 111.4, 104.4, 88.0, 64.6, 63.1, 61.5, 41.5, 38.5, 36.2, 26.8, 22.8, 21.5, 20.9, 19.8, 14.7, -1.0, -1.8; **HRMS** (ESI) calcd for  $C_{25}H_{39}N_2O_6Si$  [ $M+H$ ]<sup>+</sup>: 491.2572, found 491.2568.



**3g $\beta$**

Yellowish crystal, **MP** 110-111 °C.

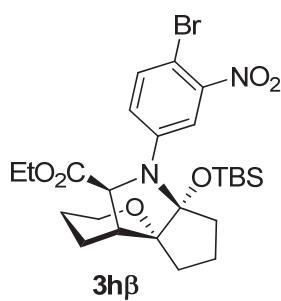
**$^1H$  NMR** (400 MHz,  $CD_3COCD_3$ , ppm):  $\delta$  7.85 (t,  $J = 2.4$  Hz, 1H), 7.60 (dd,  $J_1 = 1.6$  Hz,  $J_2 = 8.0$  Hz, 1H), 7.43 (t,  $J = 8.4$  Hz, 1H), 7.18 (dd,  $J_1 = 2.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 4.53 (d,  $J = 8.4$  Hz, 1H), 4.16 (q,  $J = 7.2$  Hz, 2H), 4.04-3.96 (m, 1H), 3.68-3.59 (m, 1H), 2.60-2.48 (m, 1H), 2.43-2.33 (m, 1H), 2.25-2.02 (m, 3H), 1.95-1.83 (m, 1H), 1.80-1.67 (m, 2H), 1.67-1.55 (m, 1H), 1.55-1.41 (m, 1H), 1.32-1.23 (m, 1H), 1.20 (t,  $J = 7.2$  Hz, 3H), 0.95 (s, 9H), 0.34 (s, 3H), 0.22 (s, 3H);  **$^{13}C$  NMR** (100 MHz,  $CD_3COCD_3$ , ppm):  $\delta$  173.5, 149.7, 146.2, 130.3, 122.8, 112.8, 111.3, 105.1, 88.9, 65.0, 63.6, 61.8, 43.6, 40.5, 29.8, 27.0, 22.2, 21.3, 20.1, 19.8, 14.6, -1.3, -2.4; **HRMS** (ESI) calcd for  $C_{19}H_{23}N_2O_5$  [ $M-OTBS$ ]<sup>+</sup>: 359.1601, found 359.1597.



**3h $\alpha$**

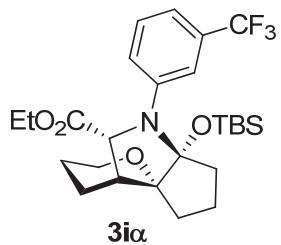
Yellowish oil.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 7.57 (d, *J* = 8.8 Hz, 1H), 7.27 (d, *J* = 2.8 Hz, 1H), 6.90 (dd, *J*<sub>1</sub> = 2.8 Hz, *J*<sub>2</sub> = 9.2 Hz, 1H), 4.63 (d, *J* = 10.0 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.97-3.90 (m, 1H), 3.38-3.50 (m, 1H), 2.46-2.32 (m, 2H), 2.26 (dt, *J*<sub>1</sub> = 4.0 Hz, *J*<sub>2</sub> = 10.0 Hz, 1H), 2.18-2.10 (m, 1H), 2.04-1.97 (m, 1H), 1.97-1.87 (m, 3H), 1.87-1.78 (m, 1H), 1.78-1.69 (m, 1H), 1.58-1.49 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.74 (s, 9H), 0.10 (s, 3H), -0.14 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 173.2, 151.0, 145.4, 135.2, 121.6, 113.4, 105.1, 100.1, 88.8, 64.8, 63.6, 62.0, 43.5, 40.1, 29.7, 27.1, 22.1, 21.2, 20.1, 19.9, 14.6, -1.3, -2.4; **HRMS** (ESI) calcd for C<sub>25</sub>H<sub>38</sub>BrN<sub>2</sub>O<sub>6</sub>Si [M+H]<sup>+</sup>: 569.1677, found 569.1670.



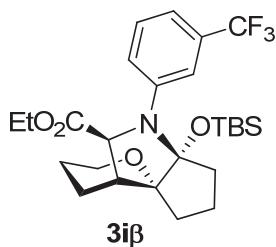
Yellowish crystal, **MP** 145-147 °C.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 7.59 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 3.2 Hz, 1H), 6.95 (dd, *J*<sub>1</sub> = 3.2 Hz, *J*<sub>2</sub> = 8.8 Hz, 1H), 4.50 (d, *J* = 8.8 Hz, 1H), 4.23-4.10 (m, 2H), 4.00-3.90 (m, 1H), 3.65-3.55 (m, 1H), 2.60-2.50 (m, 1H), 2.42-2.32 (m, 1H), 2.21-2.00 (m, 3H), 1.92-1.70 (m, 3H), 1.63-1.44 (m, 2H), 1.40-1.25 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.92 (s, 9H), 0.27 (s, 3H), 0.20 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 171.1, 151.0, 145.9, 135.1, 121.0, 113.1, 104.5, 100.6, 88.2, 64.5, 62.9, 61.6, 41.3, 38.2, 35.5, 26.8, 22.6, 21.6, 20.6, 19.7, 14.6, -1.1, -1.9; **HRMS** (ESI) calcd for C<sub>25</sub>H<sub>38</sub>BrN<sub>2</sub>O<sub>6</sub>Si [M+H]<sup>+</sup>: 569.1677, found 569.1664.



Yellowish oil.

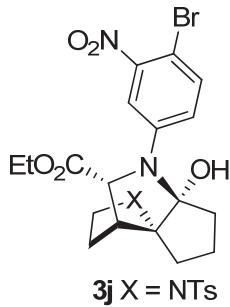
**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 7.48 (t, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 7.13 (dd, *J*<sub>1</sub> = 3.2 Hz, *J*<sub>2</sub> = 8.0 Hz, 2H), 4.77 (d, *J* = 10.0 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 4.08 (dd, *J*<sub>1</sub> = 3.6 Hz, *J*<sub>2</sub> = 6.4 Hz, 1H), 3.69 (dd, *J*<sub>1</sub> = 9.6 Hz, *J*<sub>2</sub> = 11.6 Hz, 1H), 2.68-2.56 (m, 1H), 2.56-2.47 (m, 1H), 2.43-2.35 (m, 1H), 2.33-2.22 (m, 1H), 2.22-2.10 (m, 1H), 2.10-1.93 (m, 4H), 1.93-1.82 (m, 1H), 1.73-1.60 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.84 (s, 9H), 0.21 (s, 3H), 0.03 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm): δ 173.6, 145.6, 131.5 (q, *J*<sub>F</sub> = 31.0 Hz), 130.1, 125.7 (d, *J*<sub>F</sub> = 270 Hz), 120.6, 114.9 (*J*<sub>F</sub> = 3.8 Hz), 113.5 (*J*<sub>F</sub> = 4.0 Hz), 105.0, 88.8, 65.1, 63.5, 61.6, 43.6, 40.8, 30.0, 27.1, 22.3, 21.4, 20.2, 19.8, 14.5, -1.4, -2.3; **HRMS** (ESI) calcd for C<sub>20</sub>H<sub>25</sub>F<sub>3</sub>NO<sub>4</sub> [M-TBS+H]<sup>+</sup>: 400.1730, found 400.1758.



**3i $\beta$**

Yellowish crystal, **MP** 48-52 °C.

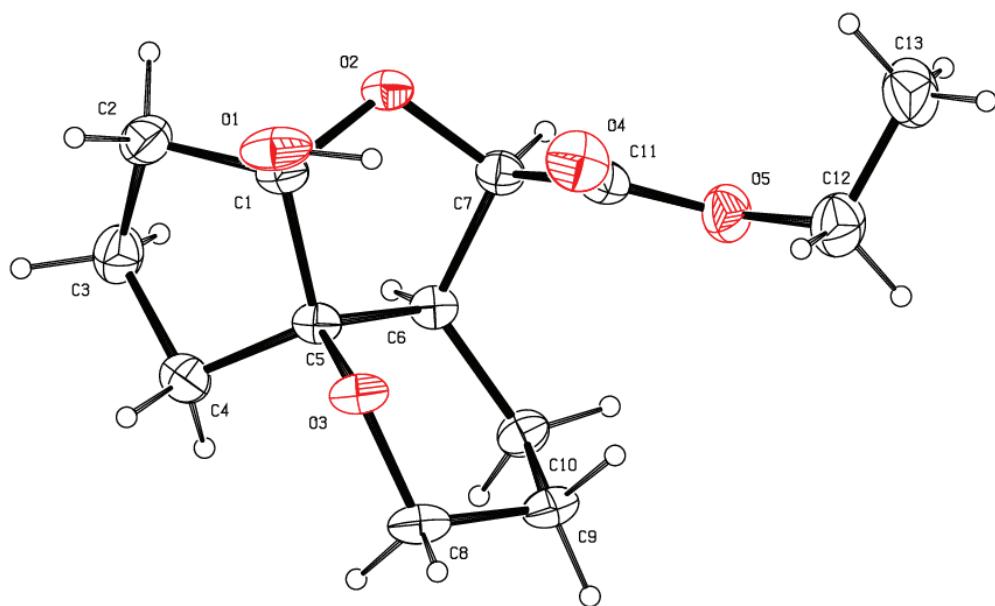
**$^1\text{H}$  NMR** (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm):  $\delta$  7.37 (t,  $J$  = 8.0 Hz, 1H), 7.32 (s, 1H), 7.10-7.02 (m, 2H), 4.50 (d,  $J$  = 8.4 Hz, 1H), 4.14 (q,  $J$  = 7.2 Hz, 2H), 4.07-3.97 (m, 1H), 3.68-3.58 (m, 1H), 2.55-2.45 (m, 1H), 2.41-2.30 (m, 1H), 2.18-2.00 (m, 3H), 1.95-1.84 (m, 1H), 1.75-1.57 (m, 3H), 1.57-1.43 (m, 1H), 1.28-1.15 (m, 1H), 1.18 (t,  $J$  = 7.2 Hz, 3H), 0.96 (s, 9H), 0.30 (s, 3H), 0.22 (s, 3H);  **$^{13}\text{C}$  NMR** (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm):  $\delta$  171.4, 146.2, 131.0 (q,  $J_F$  = 31.0 Hz), 130.0, 125.8 (d,  $J_F$  = 270 Hz), 120.1, 115.5 ( $J_F$  = 2.9 Hz), 113.8 ( $J_F$  = 3.6 Hz), 104.2, 87.9, 64.5, 63.1, 61.3, 41.6, 38.0, 36.6, 26.8, 23.0, 21.5, 21.0, 19.7, 14.6, -1.0, -1.8; **HRMS** (ESI) calcd for C<sub>20</sub>H<sub>23</sub>F<sub>3</sub>NO<sub>3</sub> [M-OTBS]<sup>+</sup>: 382.1625, found 382.1626.



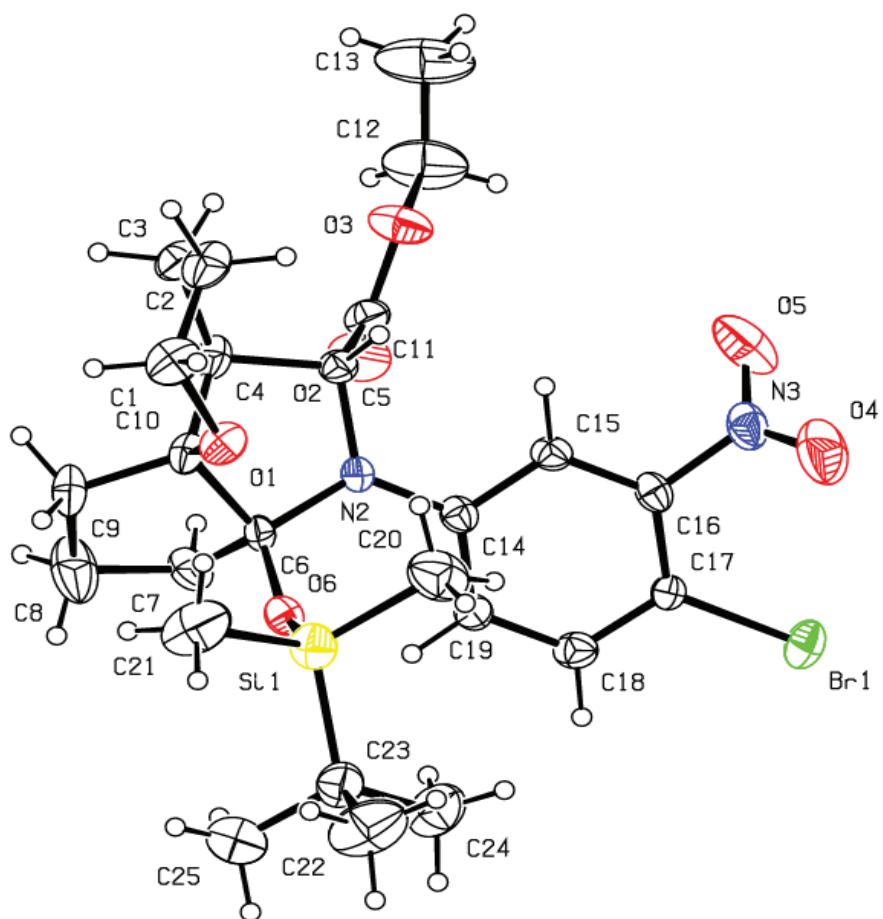
**3j X = NTs**

Yellowish viscous oil.

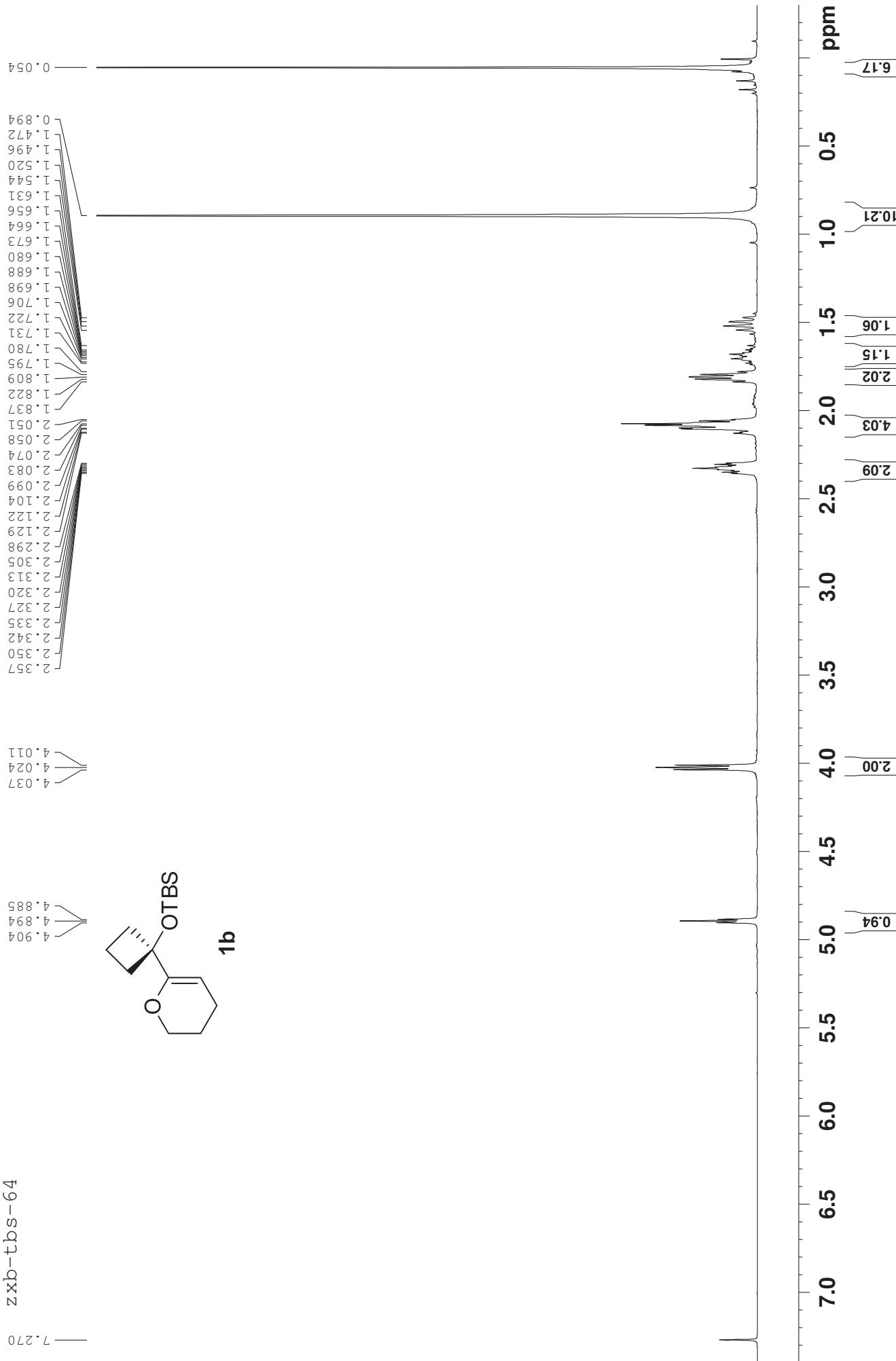
**$^1\text{H}$  NMR** (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm)  $\delta$  7.81 (d,  $J$  = 8.4 Hz, 2H), 7.64 (d,  $J$  = 6.4 Hz, 1H), 7.62 (s, 1H), 7.41 (d,  $J$  = 8.0 Hz, 2H), 7.27 (dd,  $J_1$  = 2.8 Hz,  $J_2$  = 8.8 Hz, 1H), 4.69 (d,  $J$  = 8.4 Hz, 1H), 4.16 (q,  $J$  = 7.2 Hz, 2H), 3.63 (dt,  $J_1$  = 4.0 Hz,  $J_2$  = 8.8 Hz, 1H), 3.39 (td,  $J_1$  = 6.8 Hz,  $J_2$  = 8.8 Hz, 1H), 3.11 (dd,  $J_1$  = 3.6 Hz,  $J_2$  = 12.8 Hz, 1H), 2.97 (dt,  $J_1$  = 8.0 Hz,  $J_2$  = 12.8 Hz, 1H), 2.82 (s, 1H), 2.43 (s, 3H), 2.36 (dd,  $J_1$  = 6.0 Hz,  $J_2$  = 12.8 Hz, 1H), 2.29-2.10 (m, 2H), 1.93-1.79 (m, 2H), 1.69-1.57 (m, 1H), 1.20 (t,  $J$  = 7.2 Hz, 3H);  **$^{13}\text{C}$  NMR** (101 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm)  $\delta$  171.3, 151.2, 146.2, 144.0, 140.0, 135.2, 130.5, 128.1, 123.0, 114.6, 102.3, 101.9, 83.6, 62.6, 62.2, 53.2, 50.6, 35.8, 35.2, 26.0, 21.5, 21.4, 21.4, 14.6; **HRMS** (ESI) calcd for C<sub>25</sub>H<sub>27</sub>BrN<sub>3</sub>O<sub>6</sub>S [M-OH]<sup>+</sup>: 576.0798, found 576.0780.

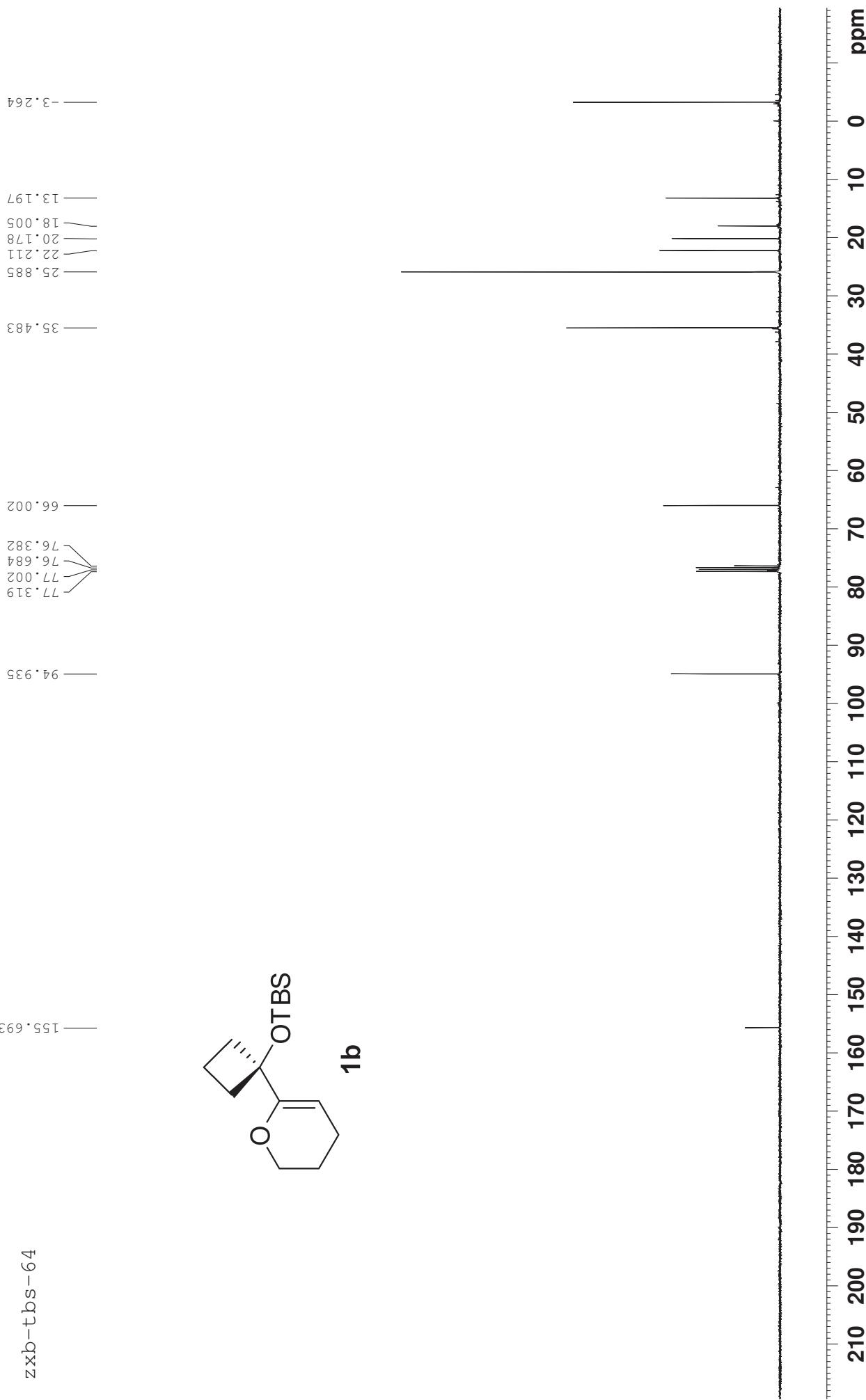


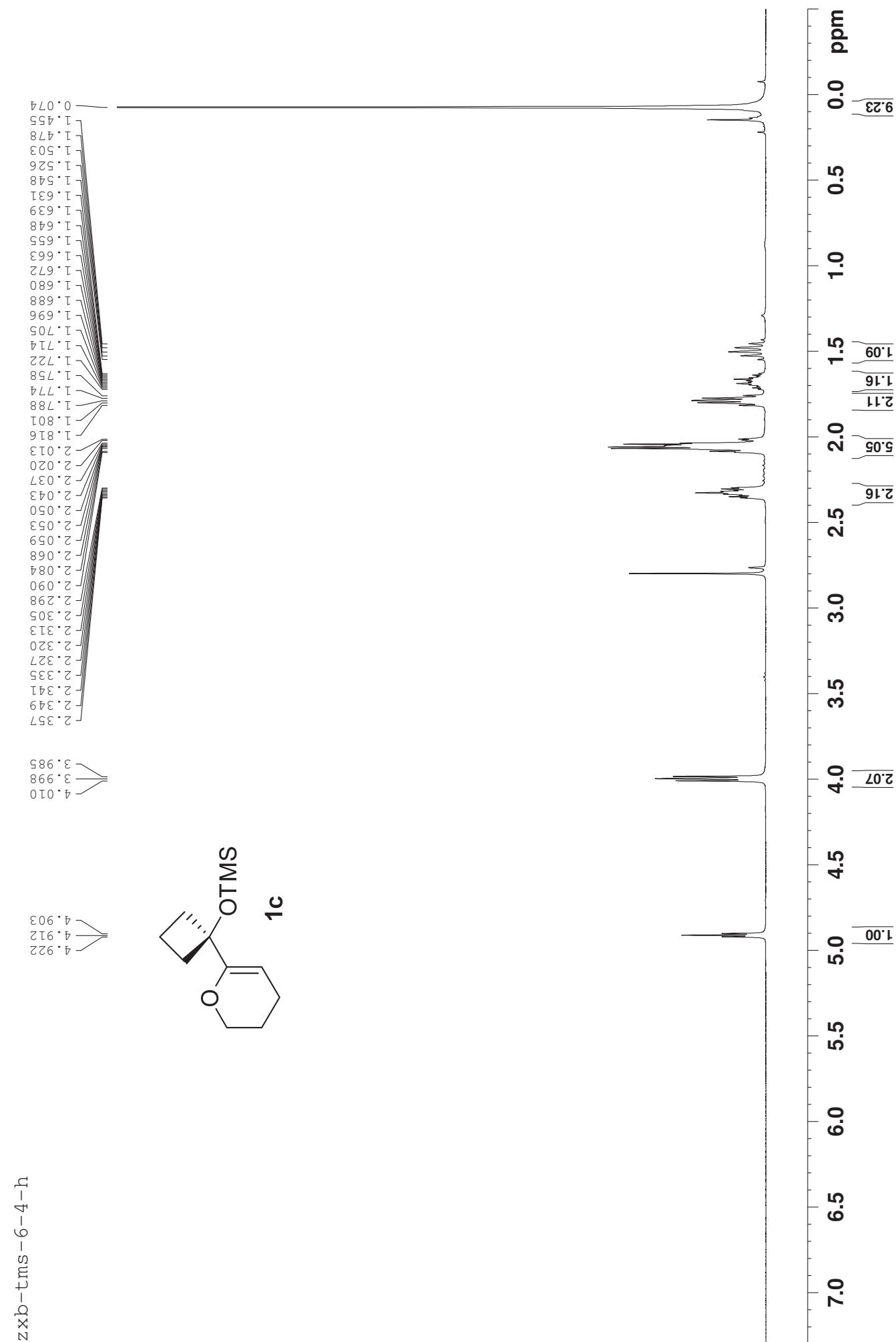
ORTEP drawing of 3a

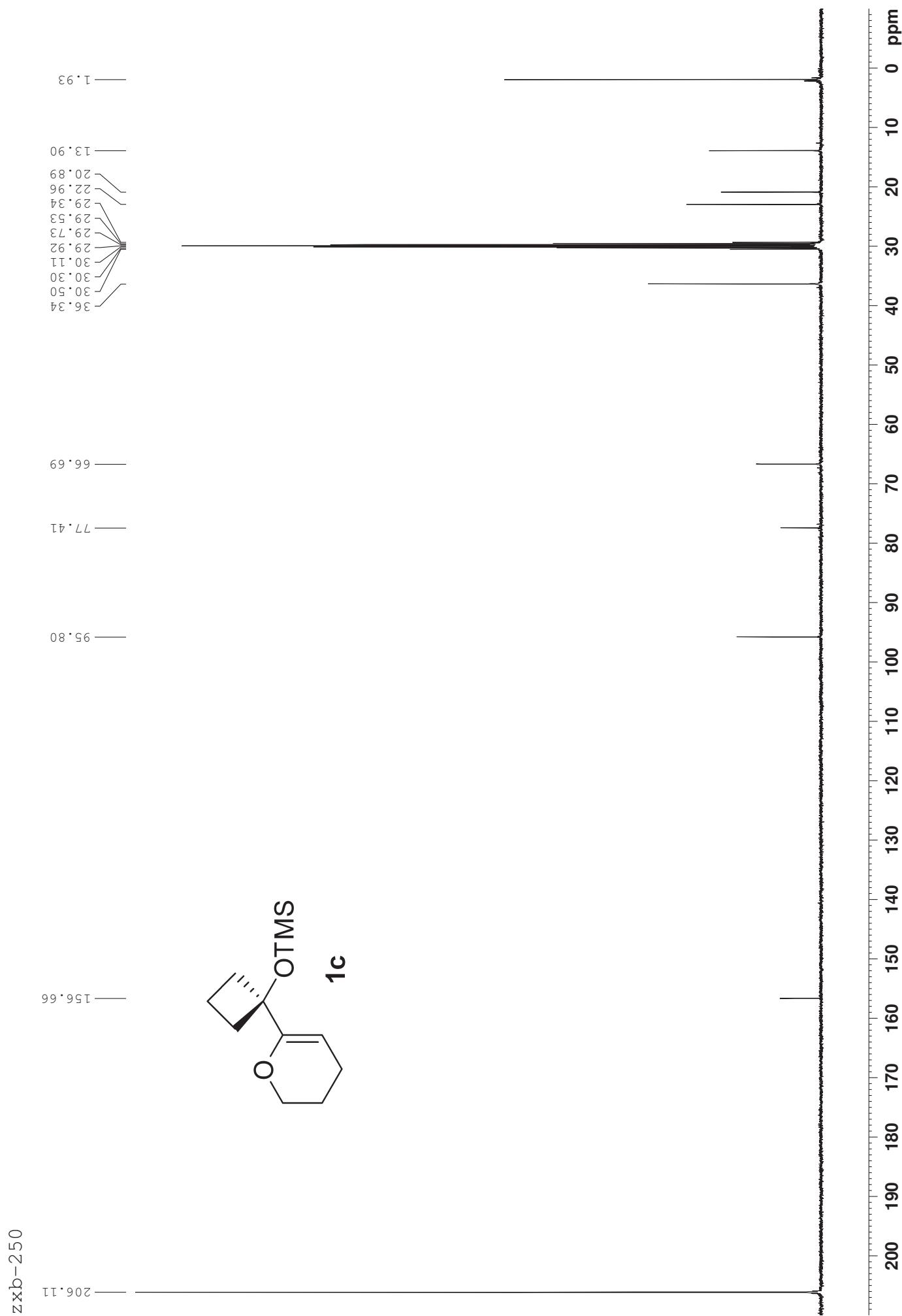


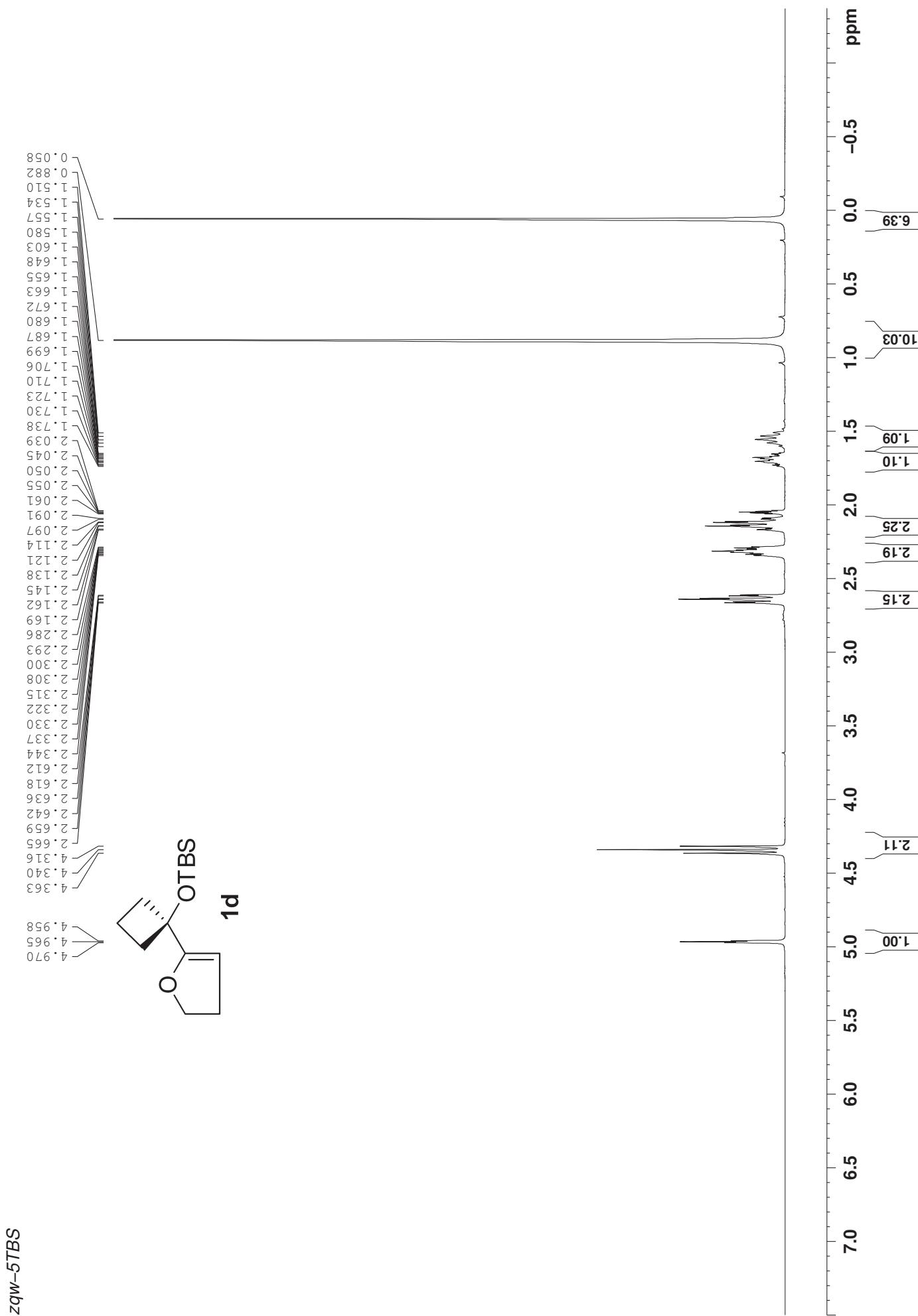
ORTEP drawing of 3hb

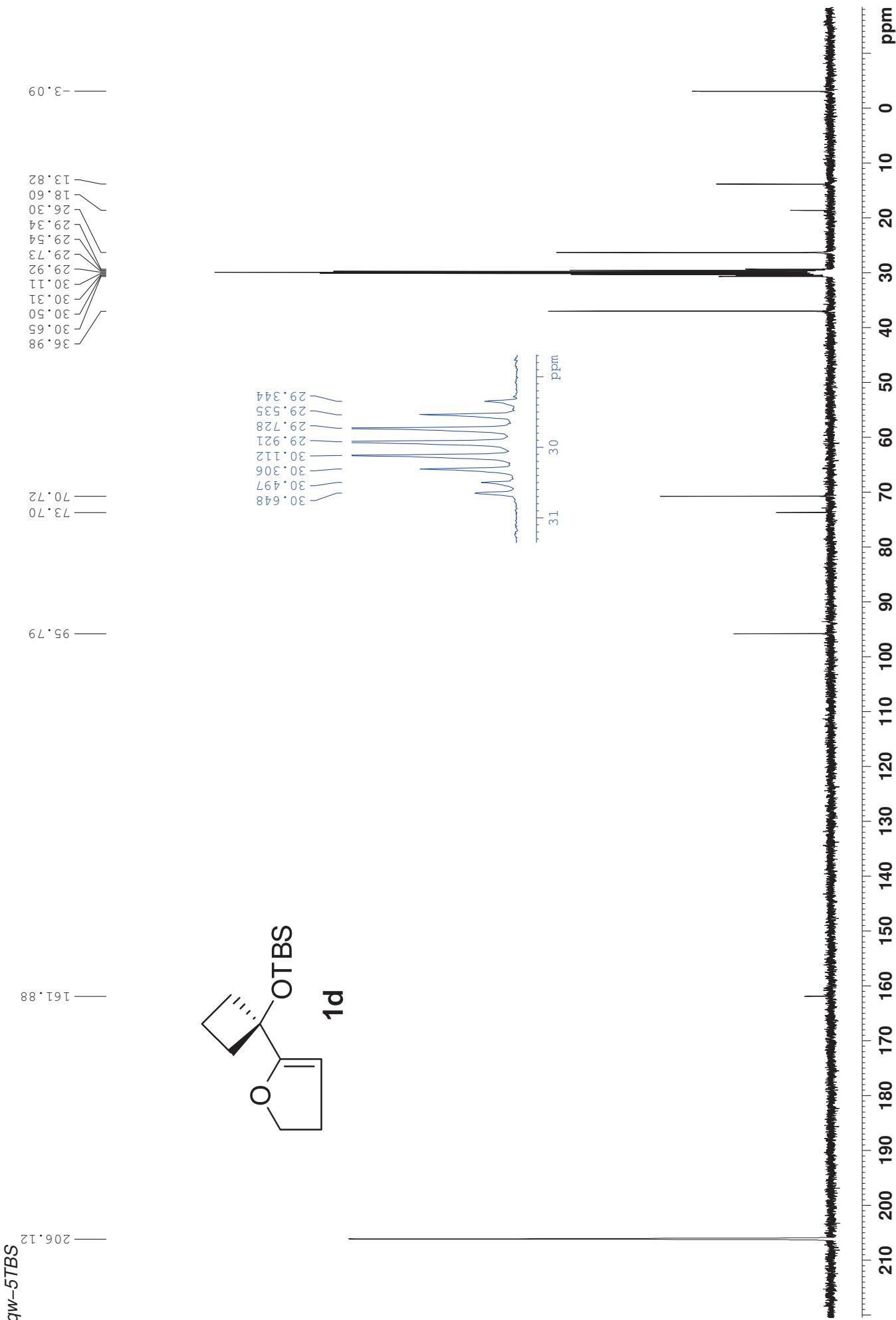


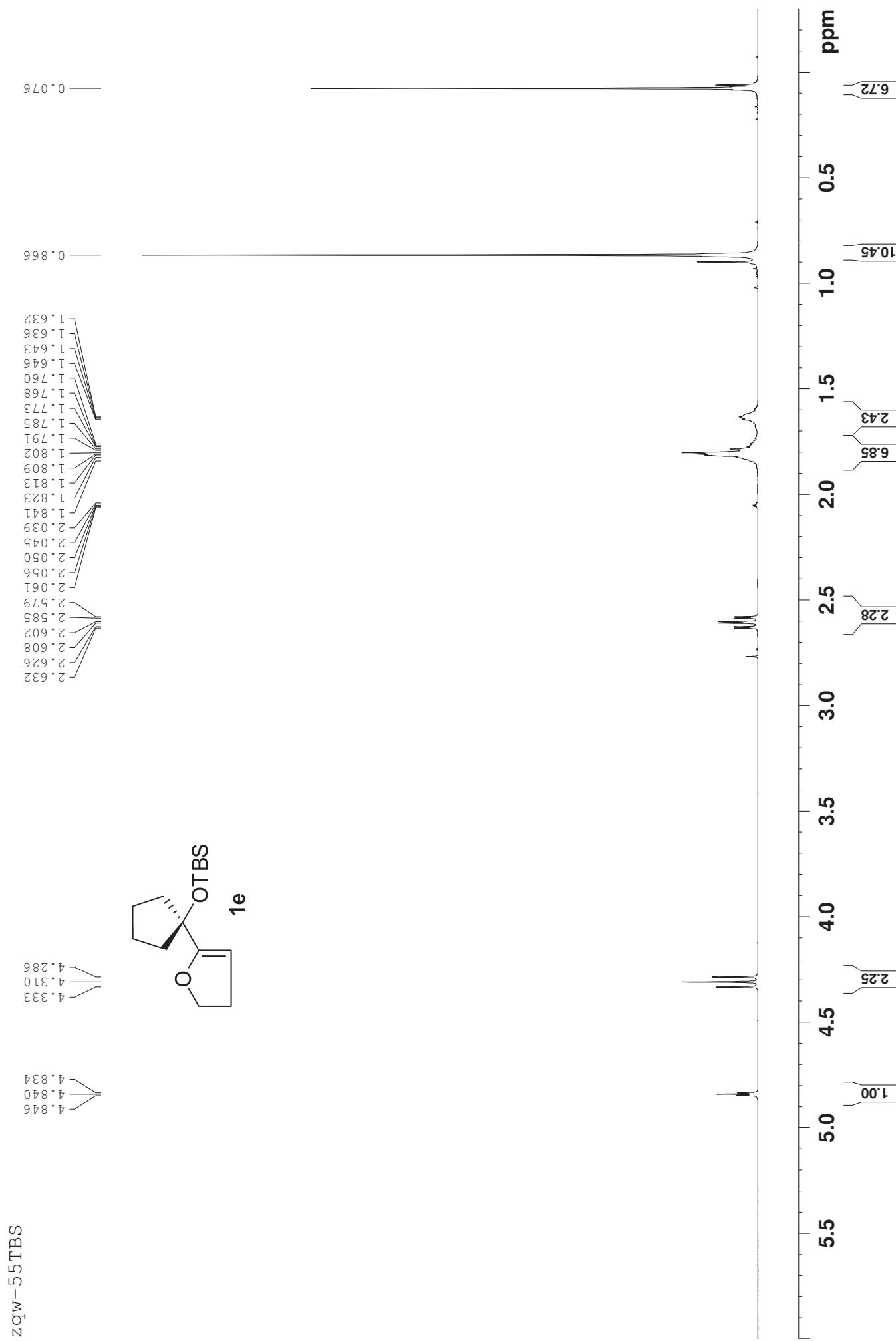


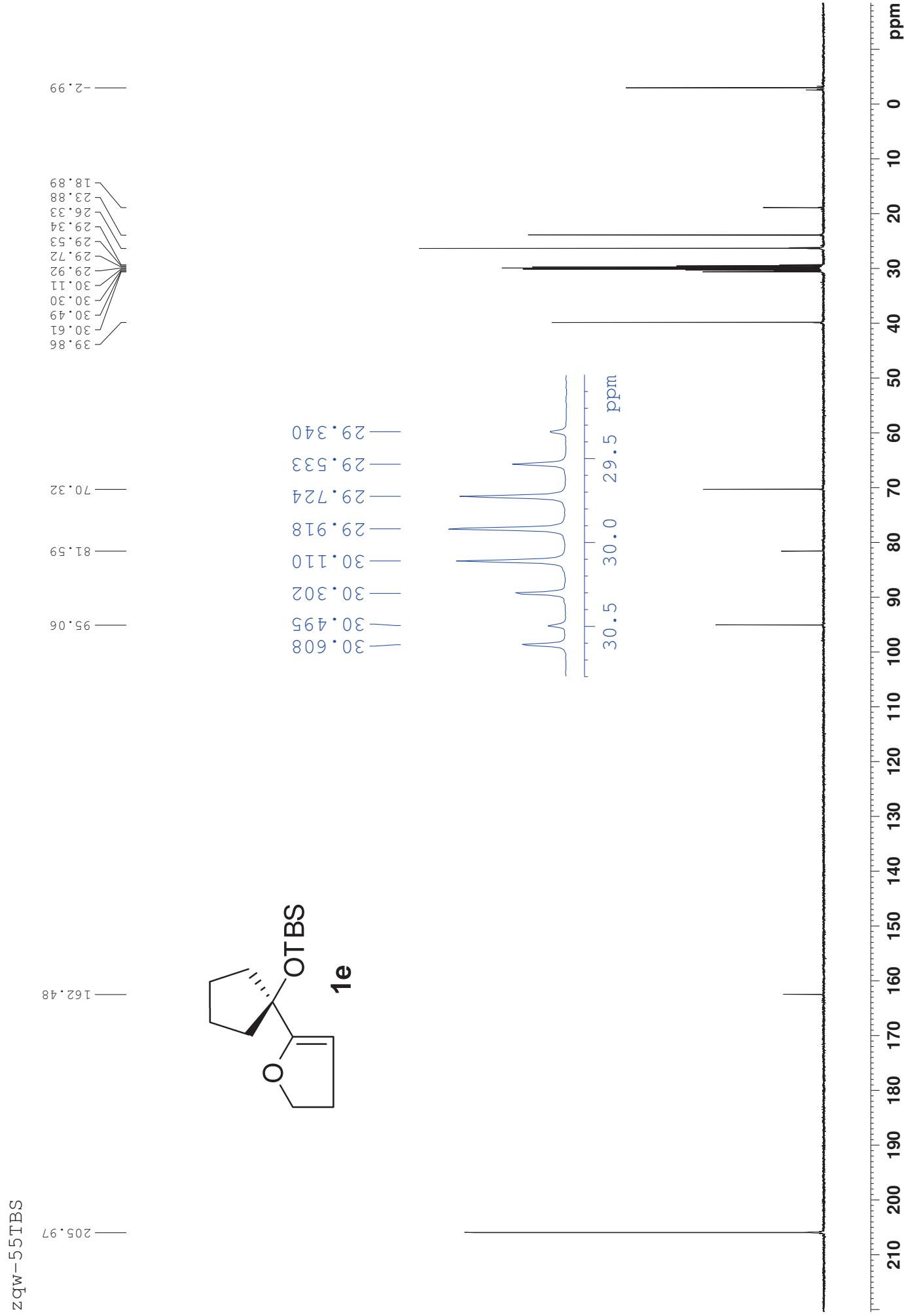


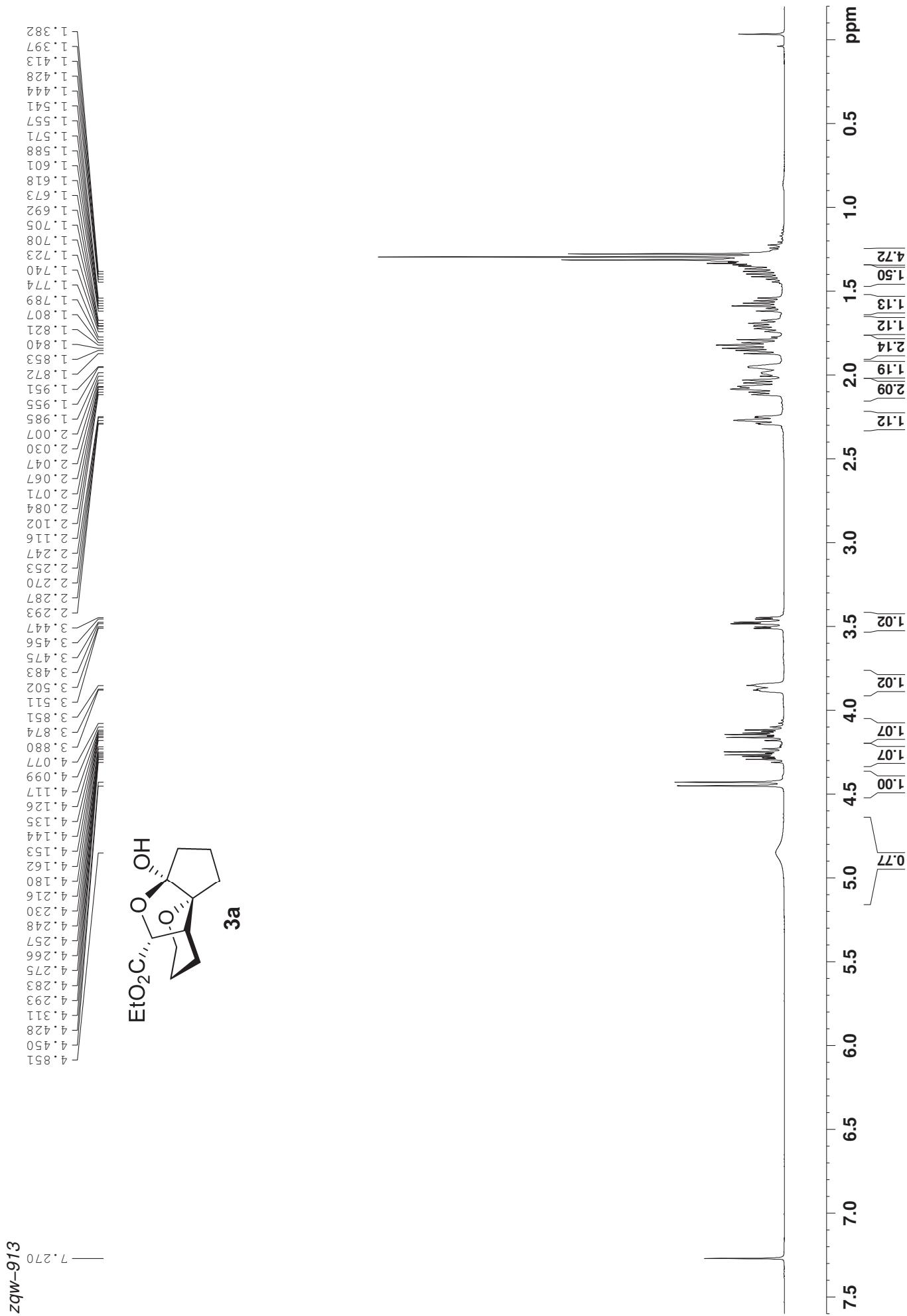




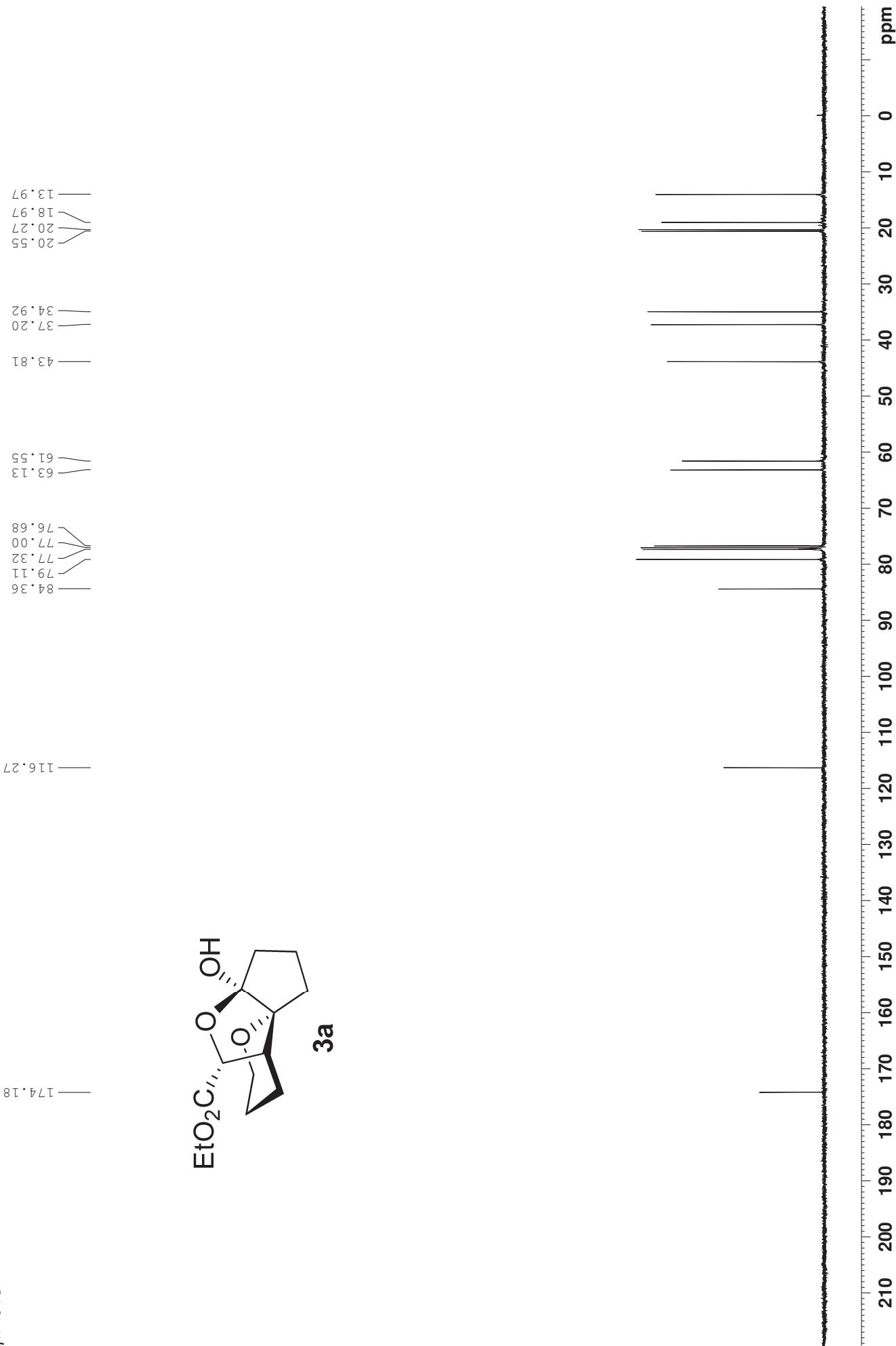


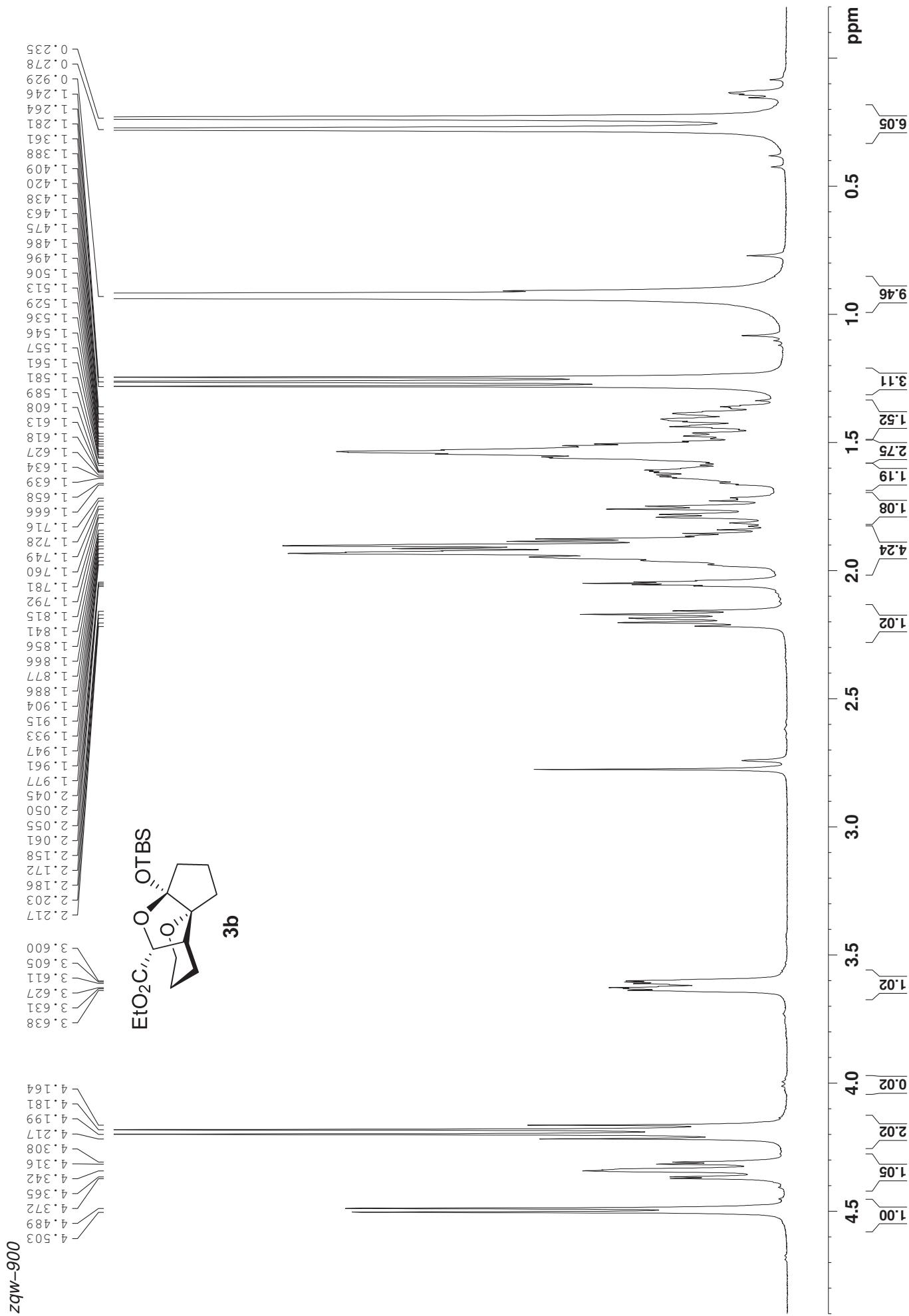


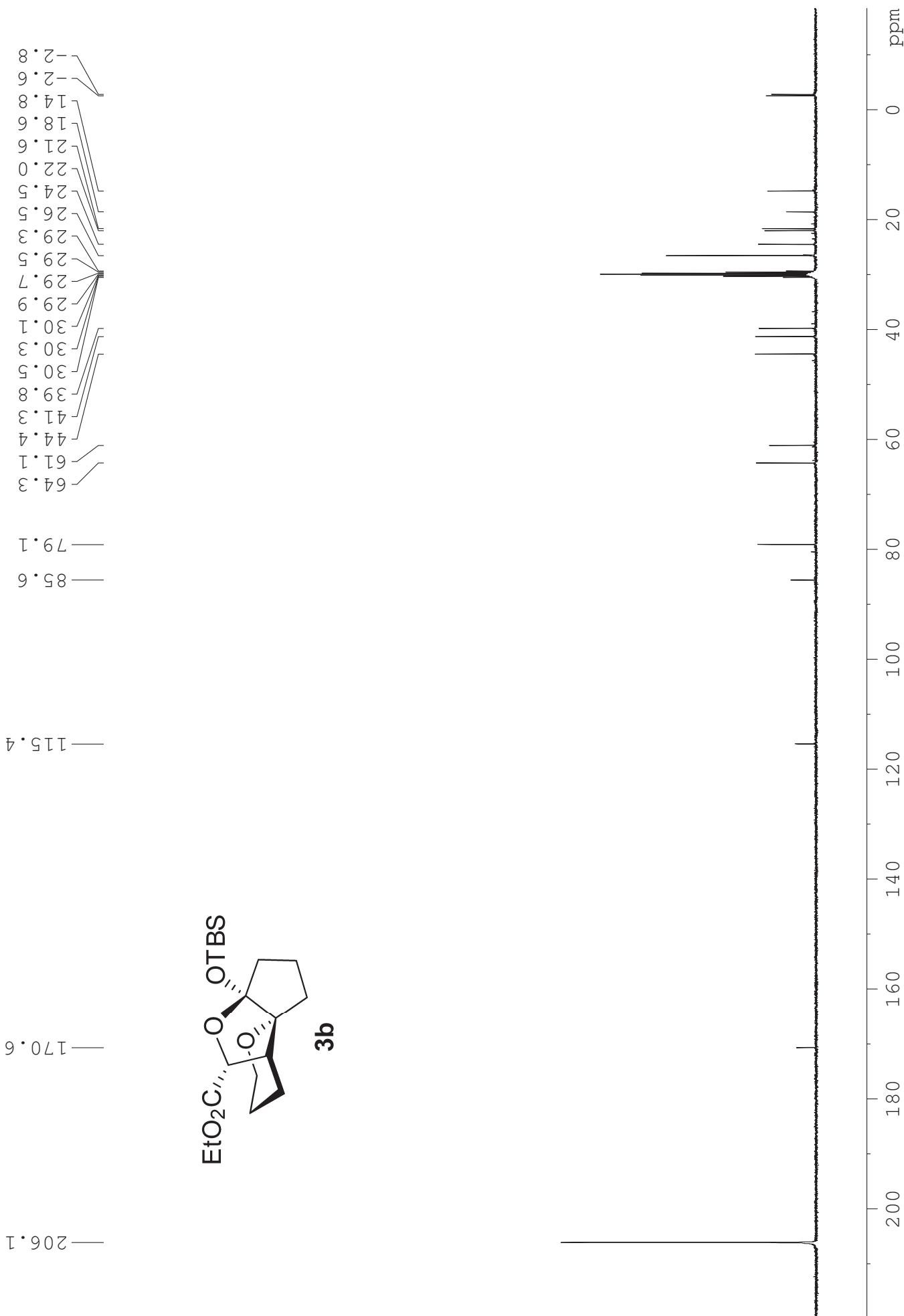


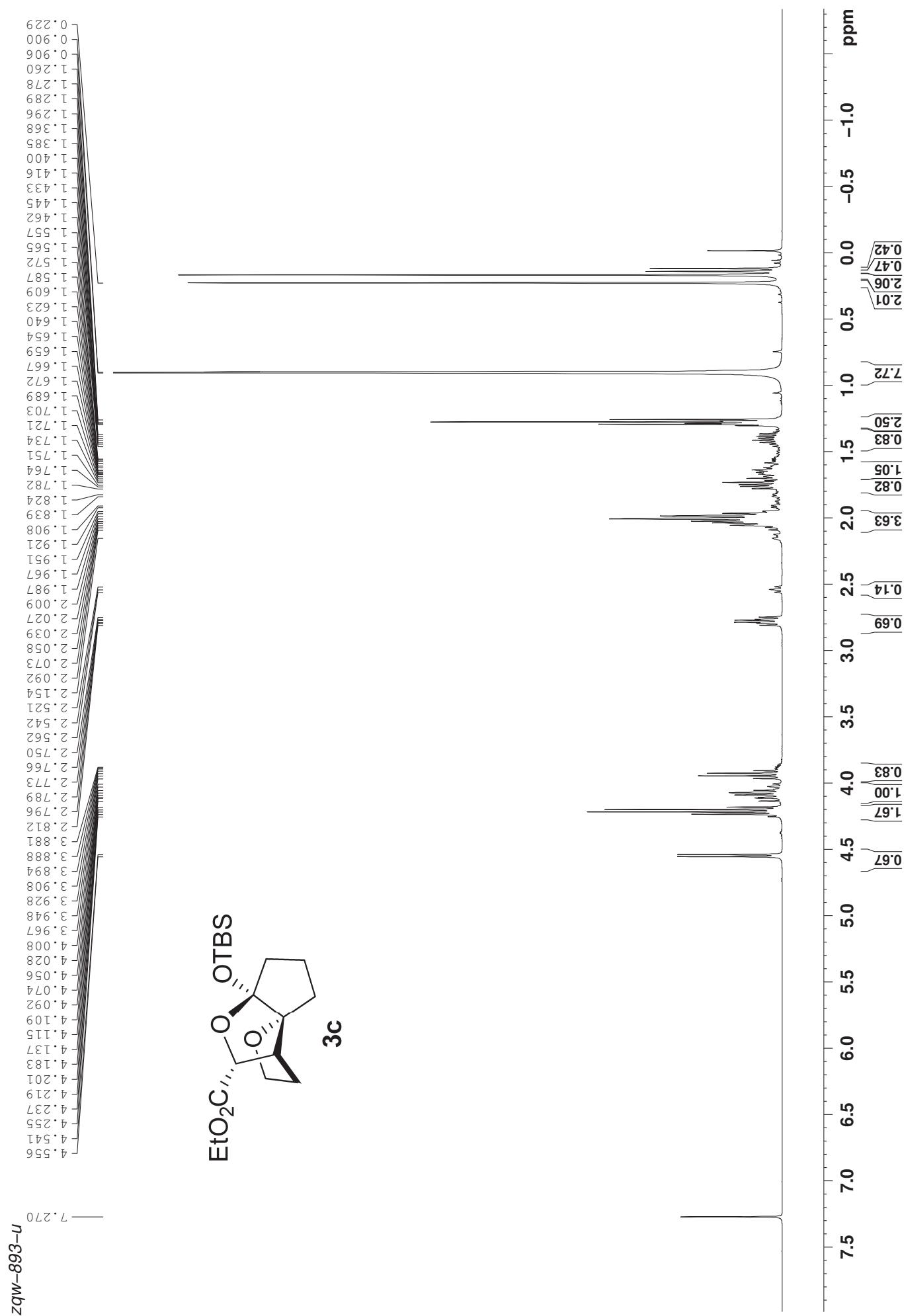


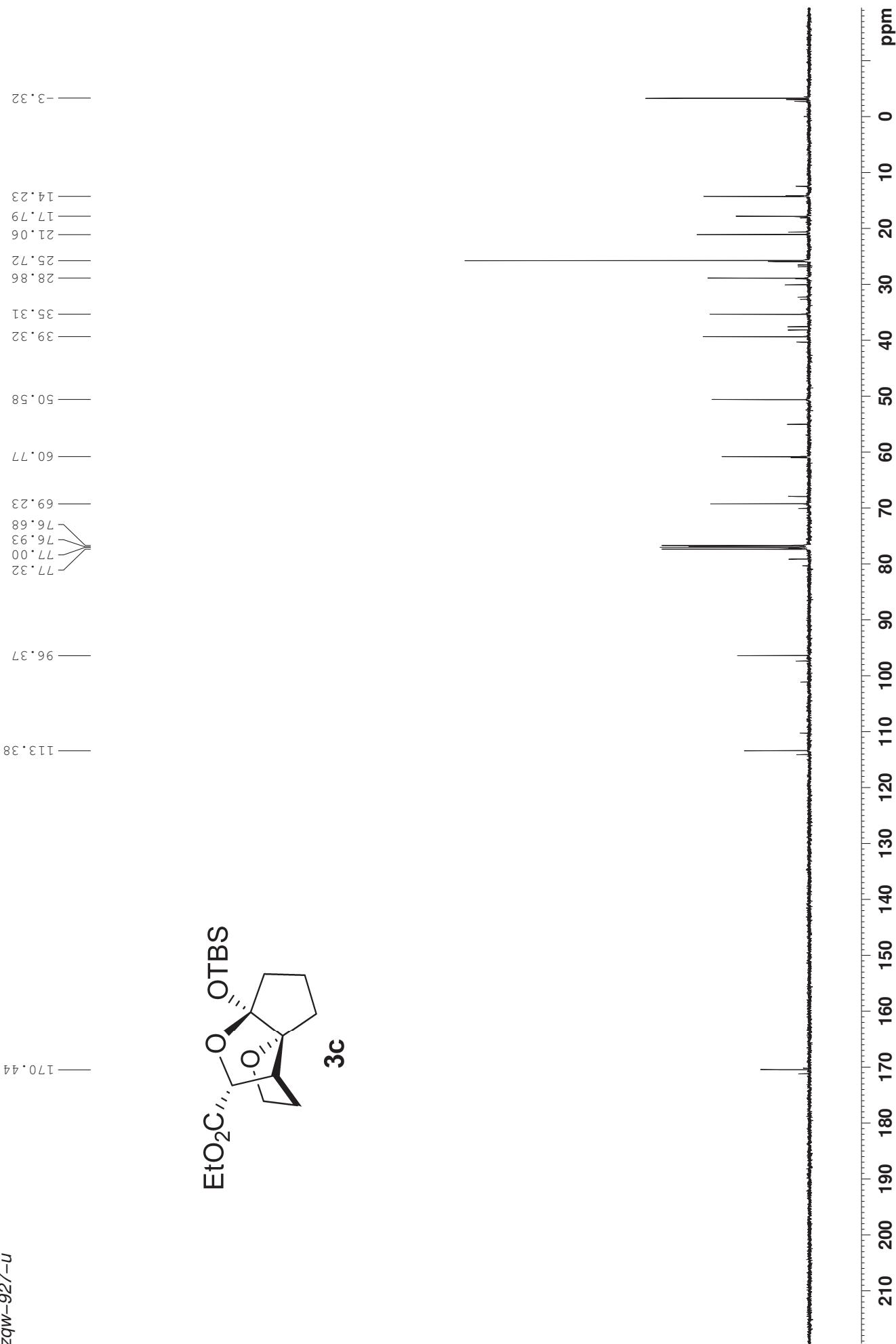
zqw-913

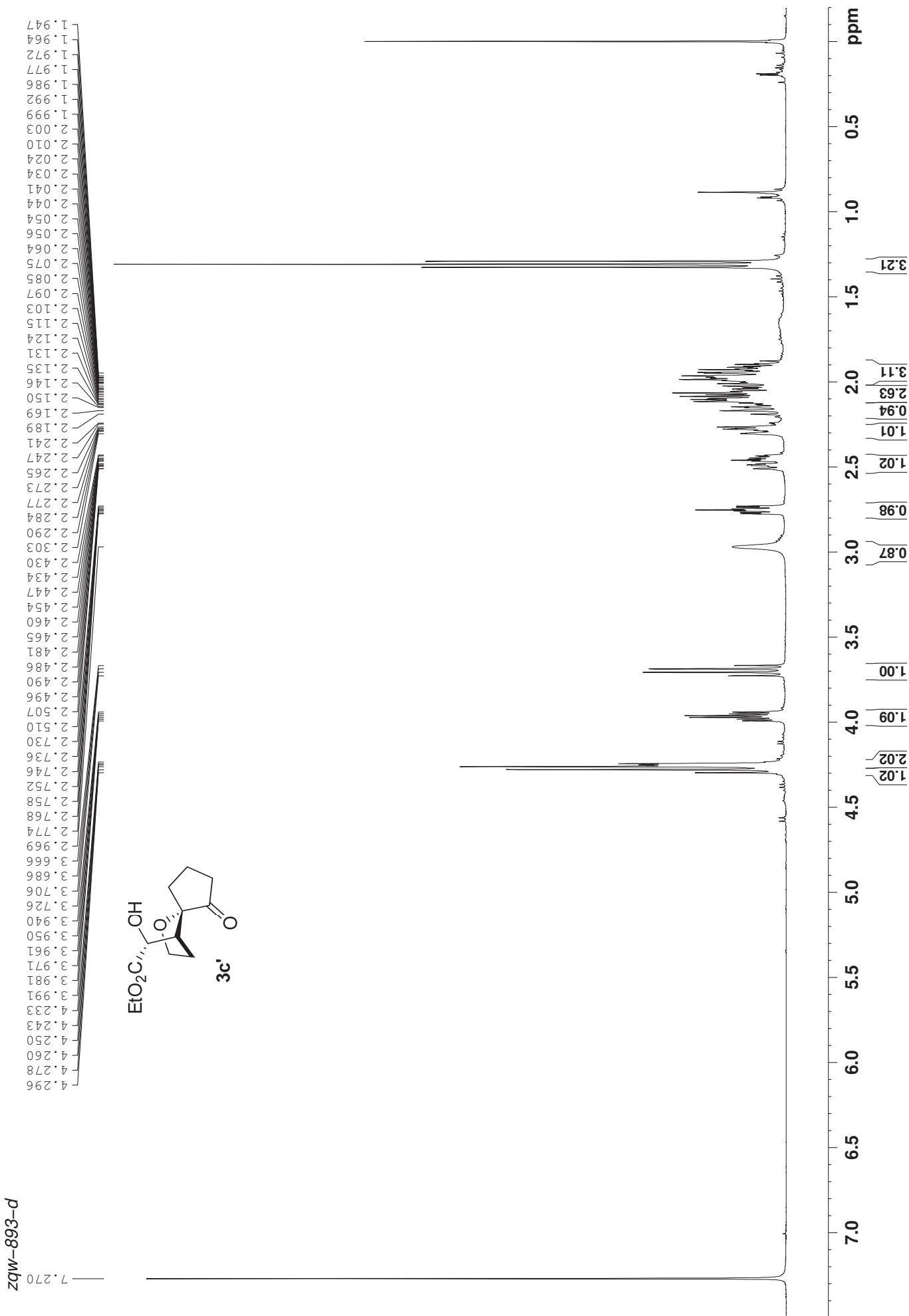


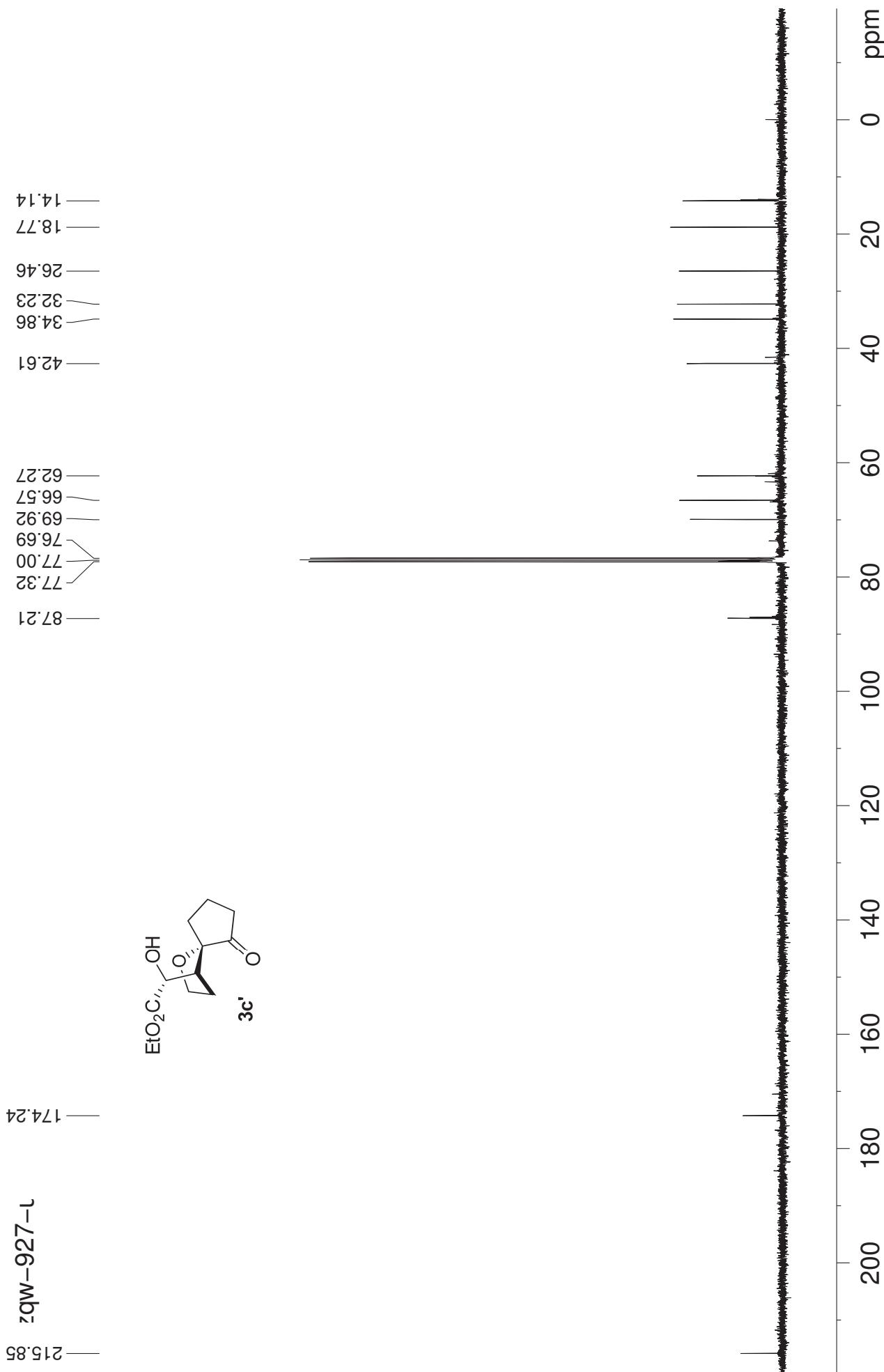


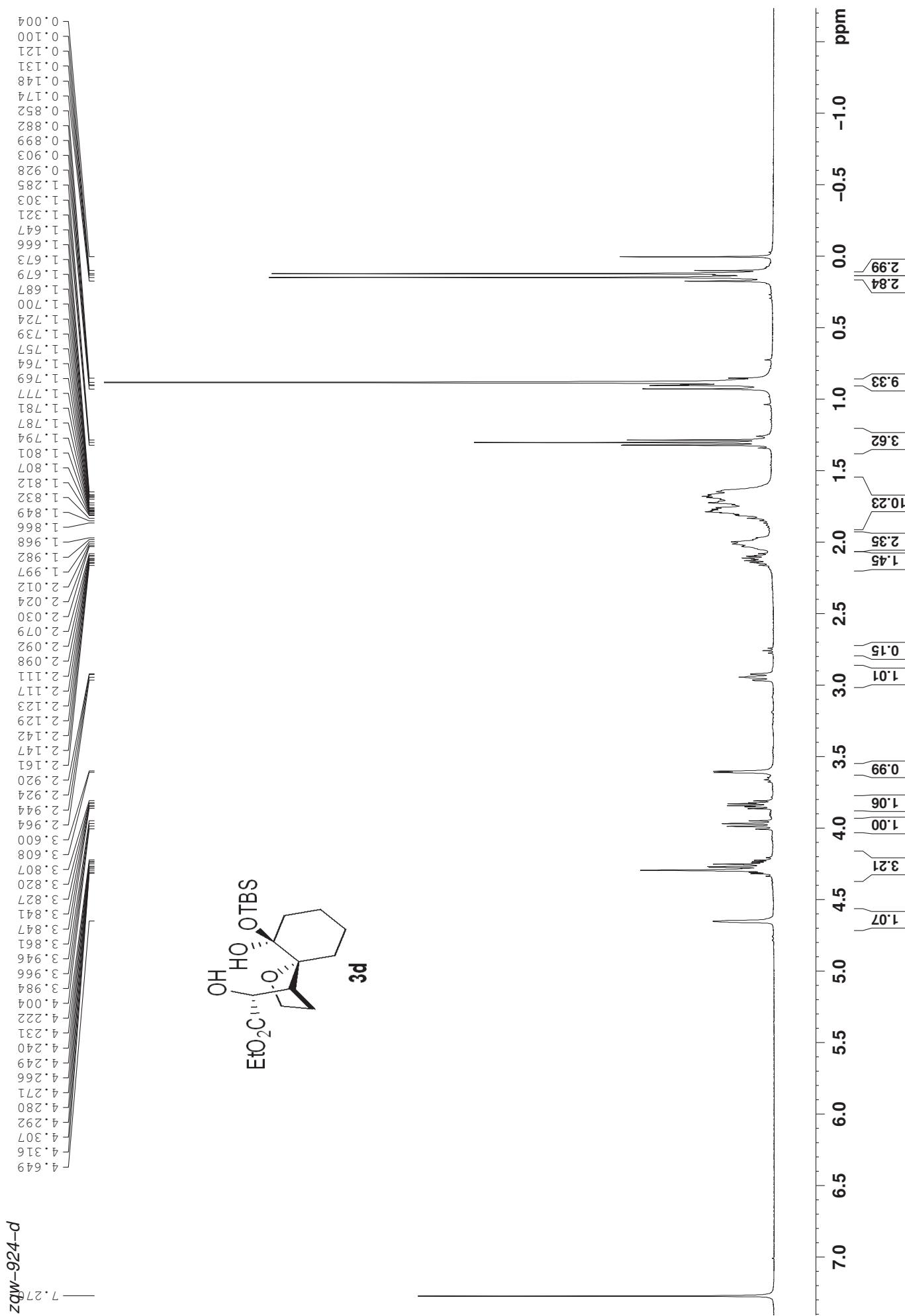


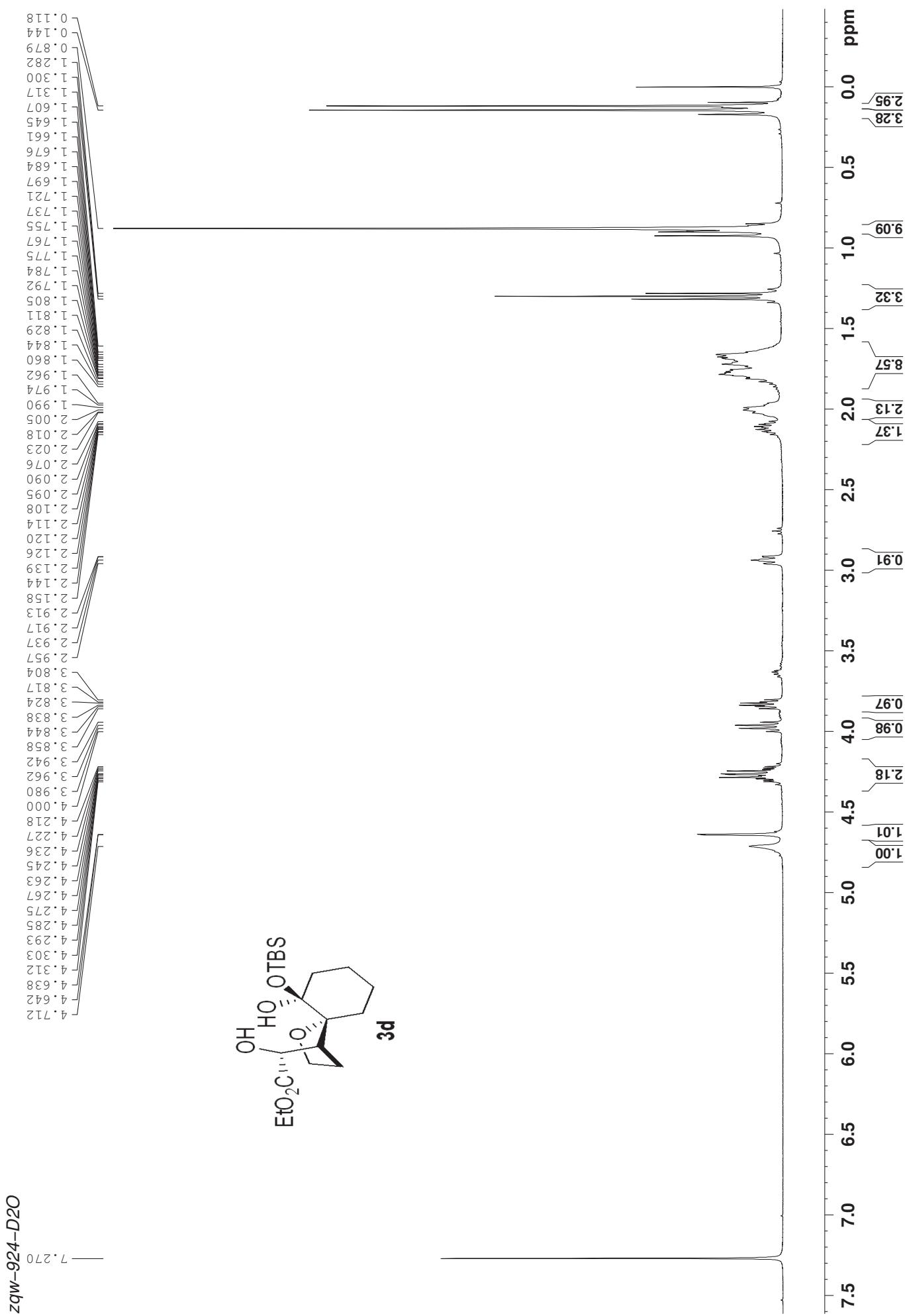


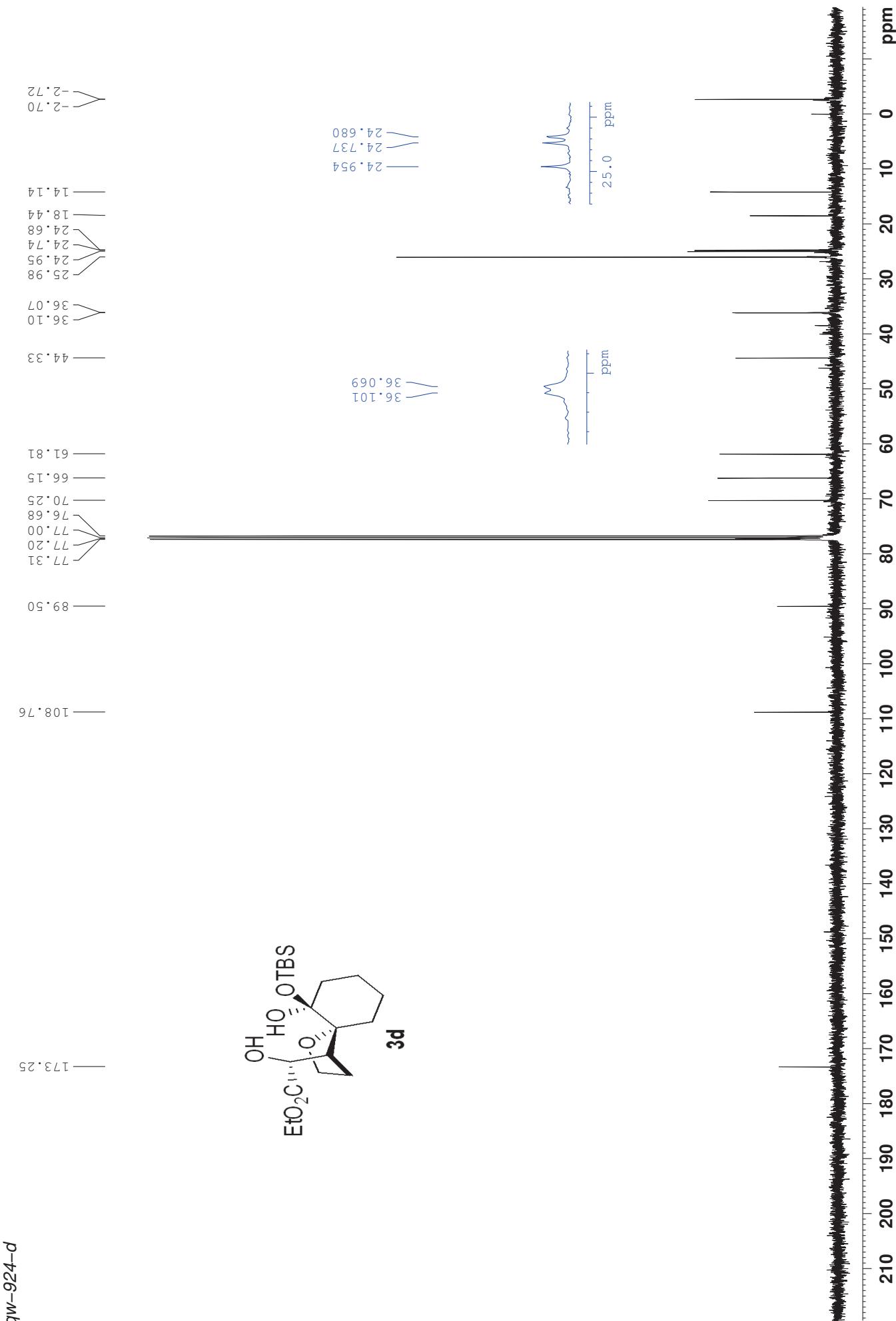


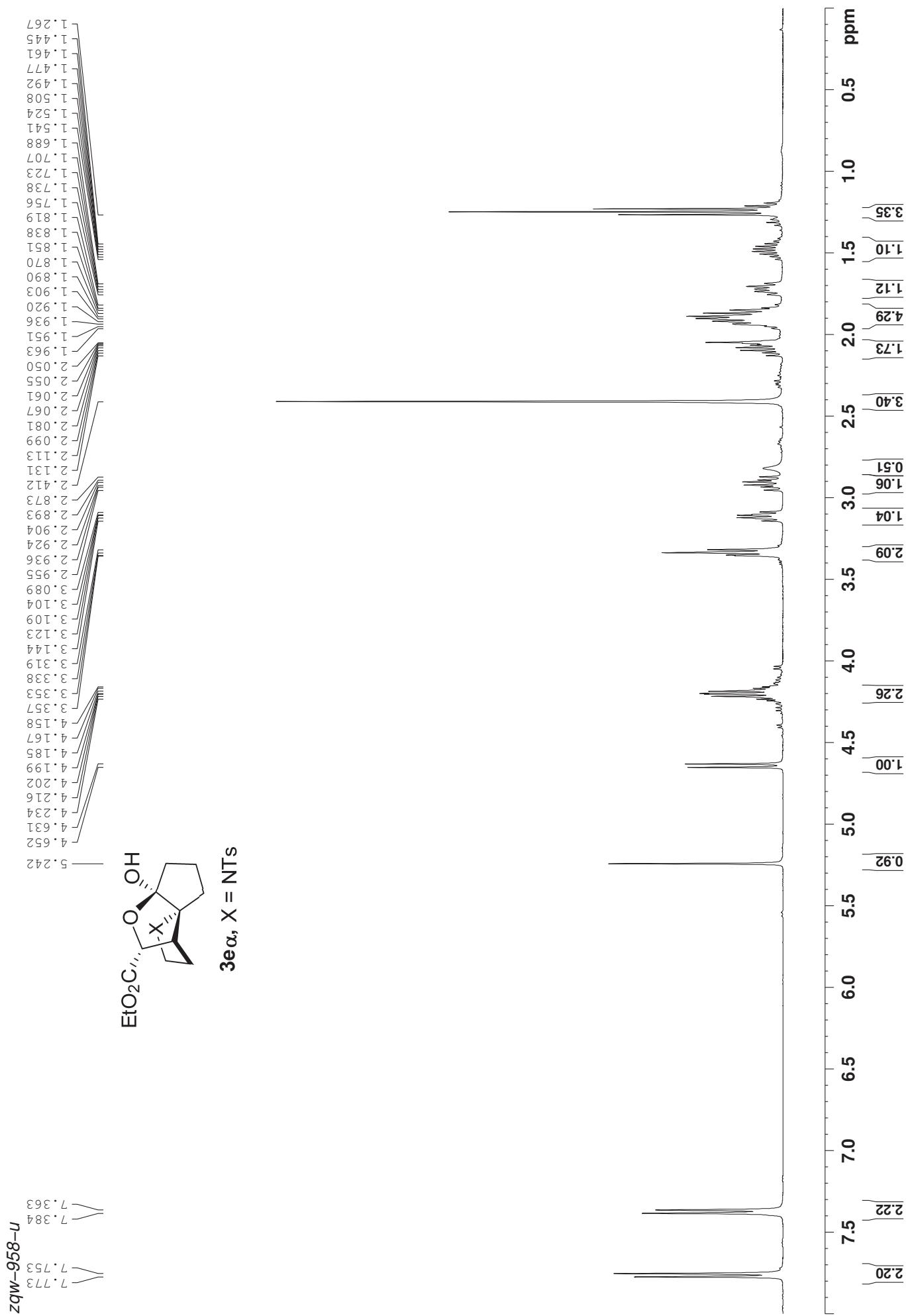


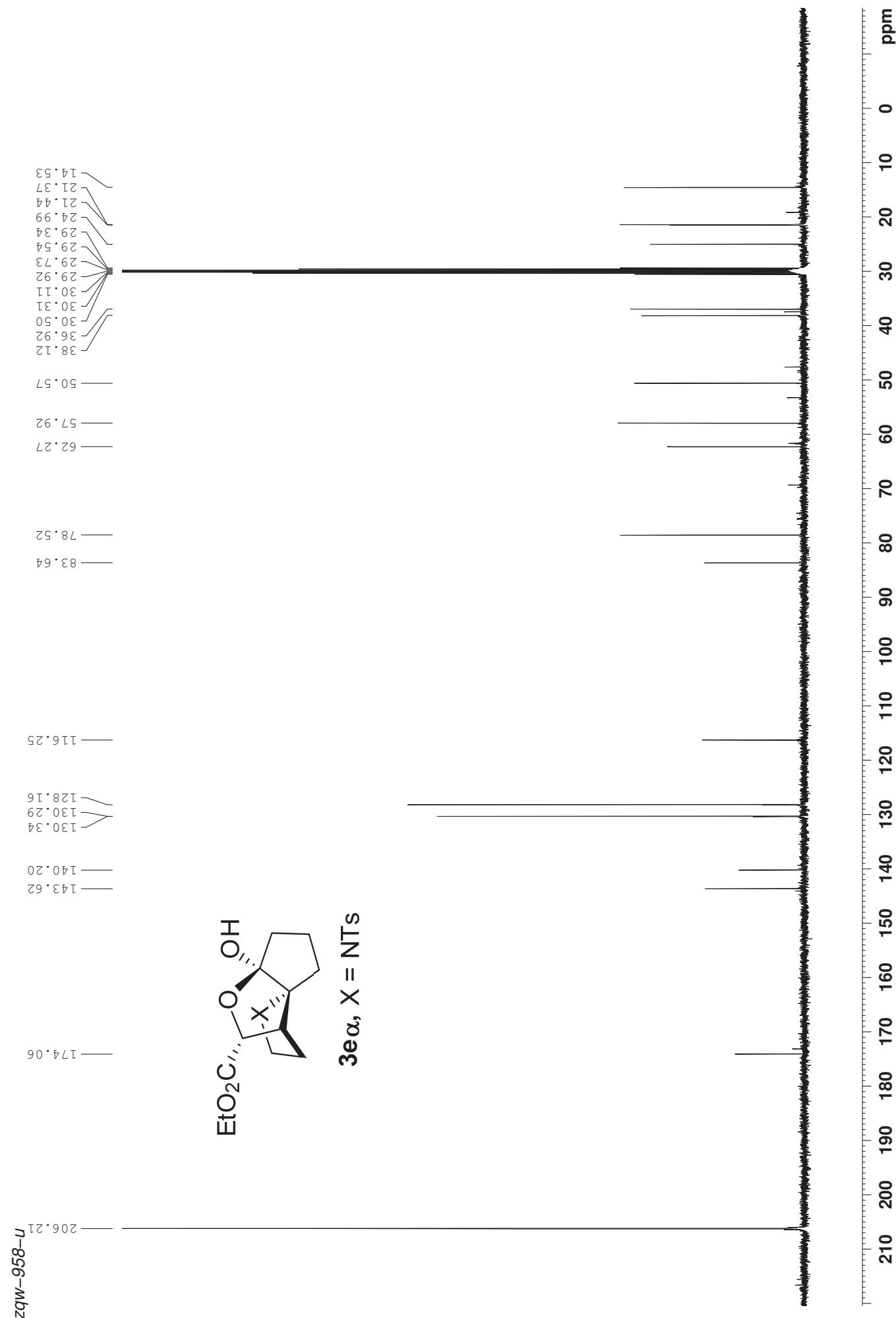


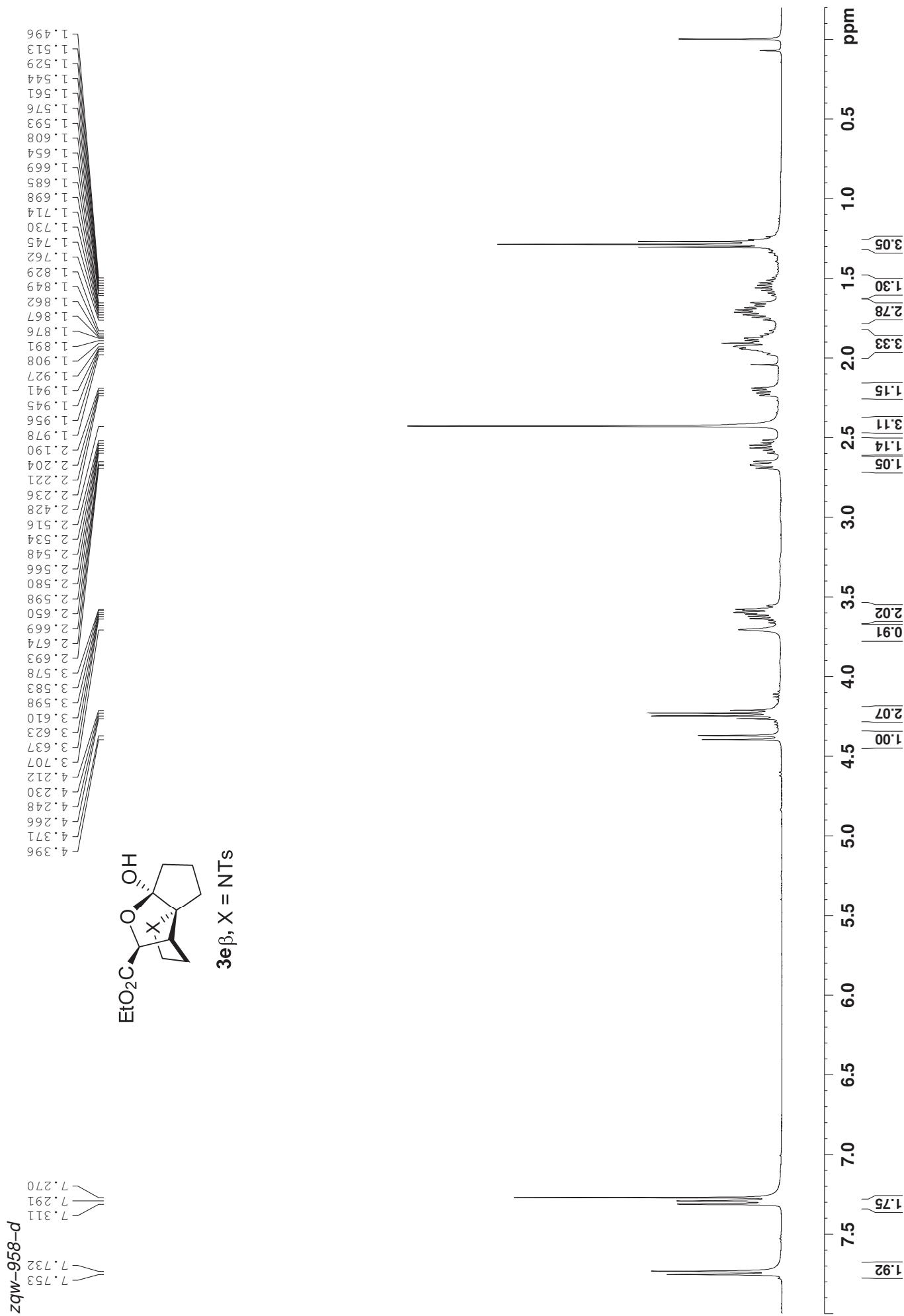




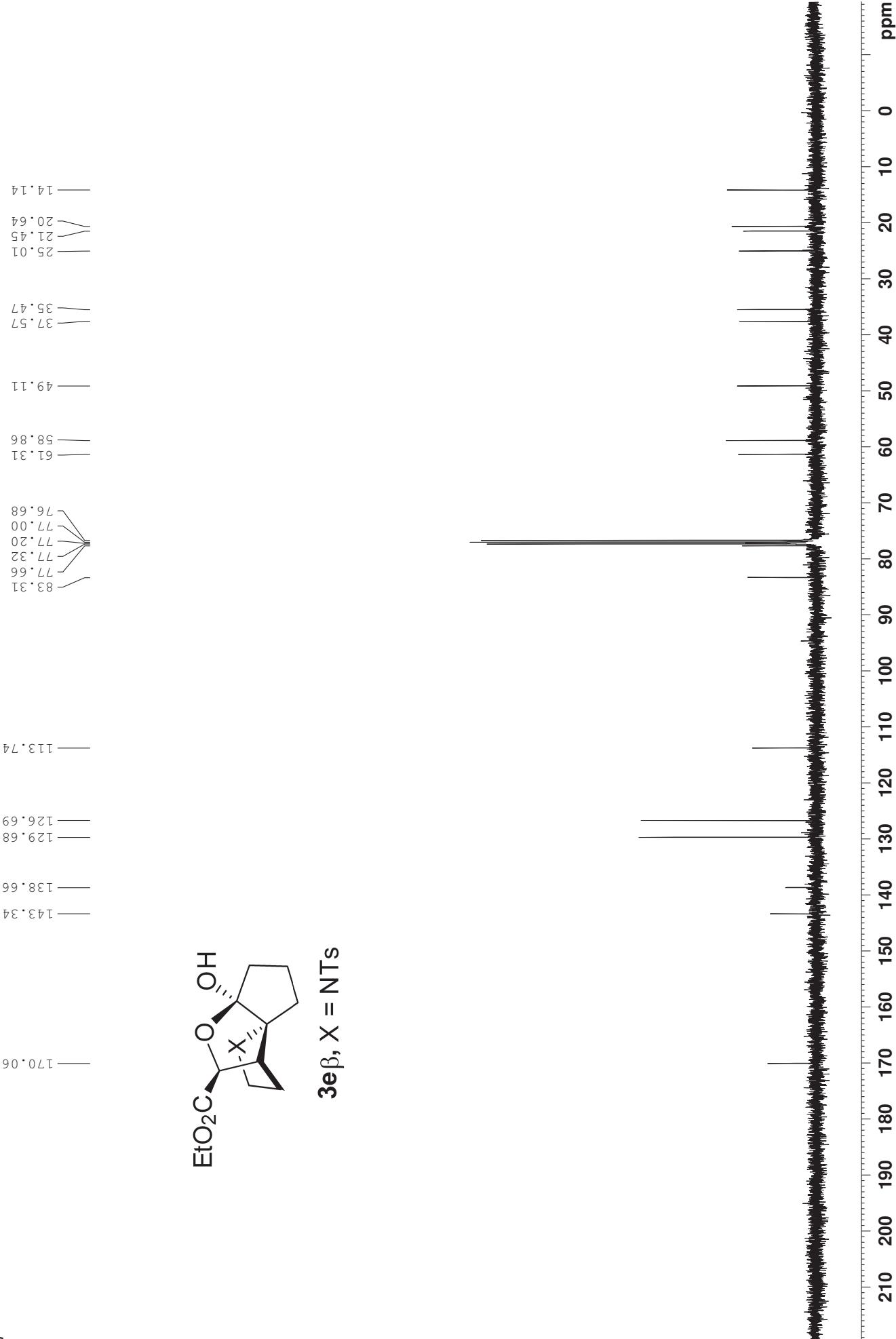


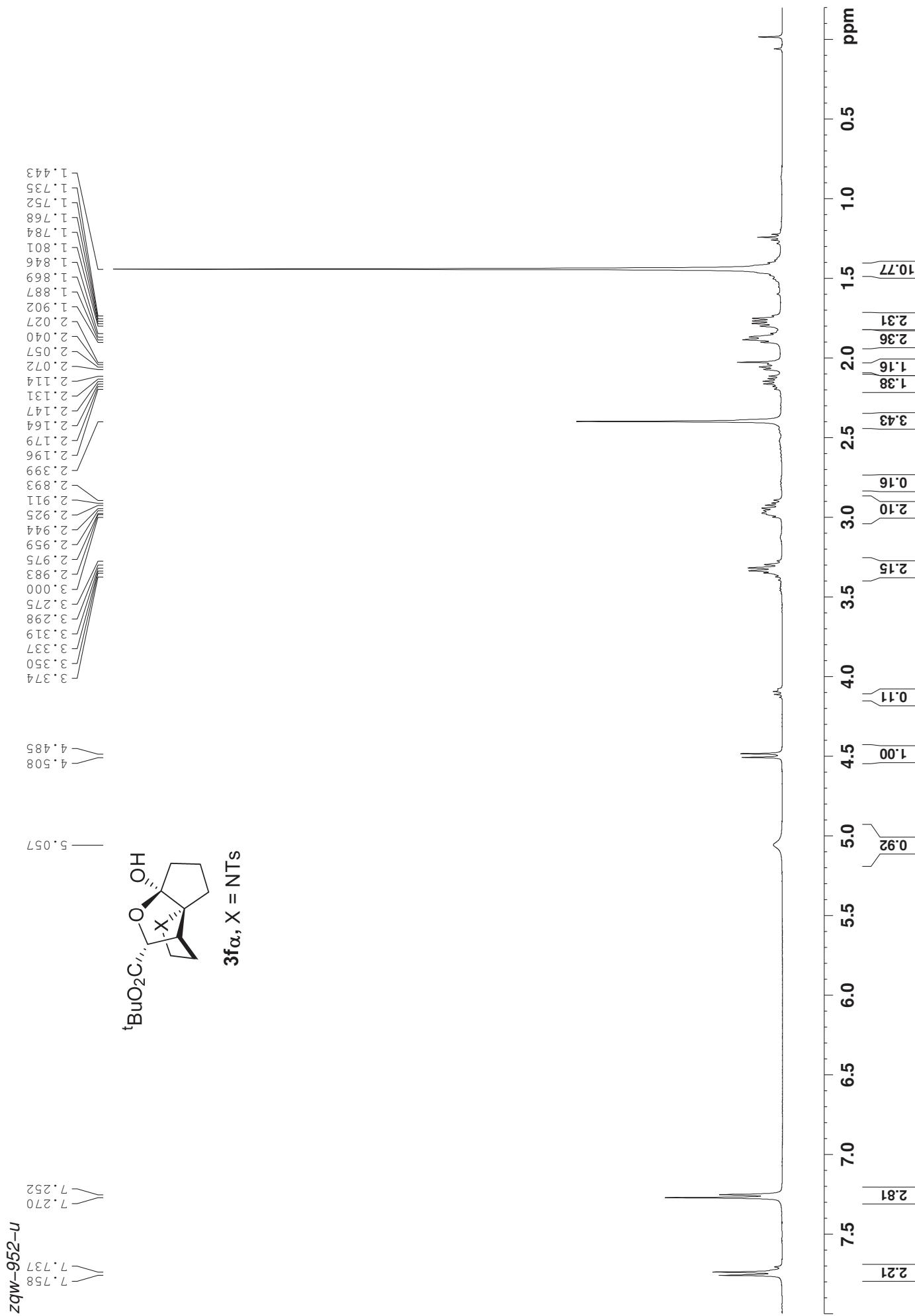


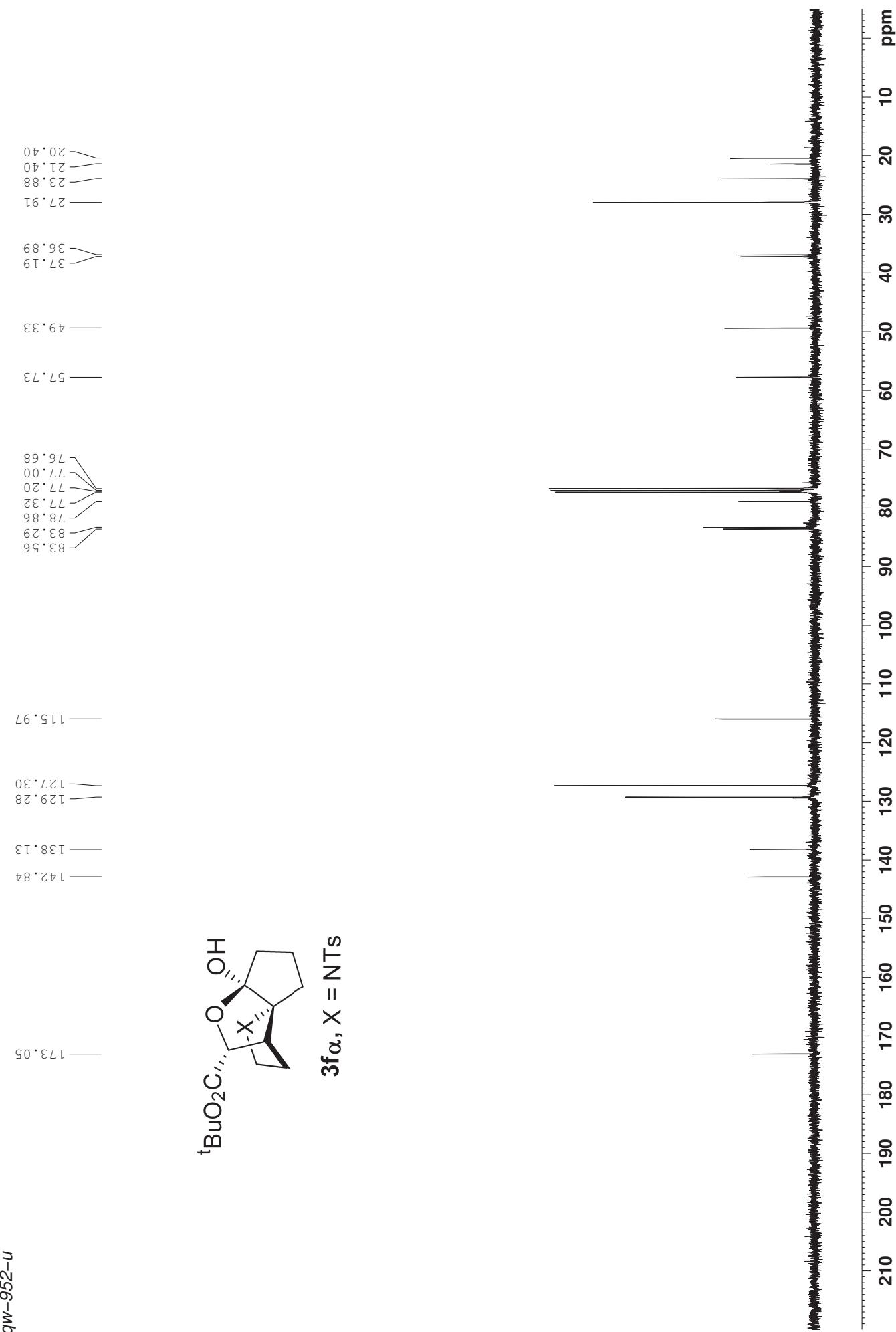


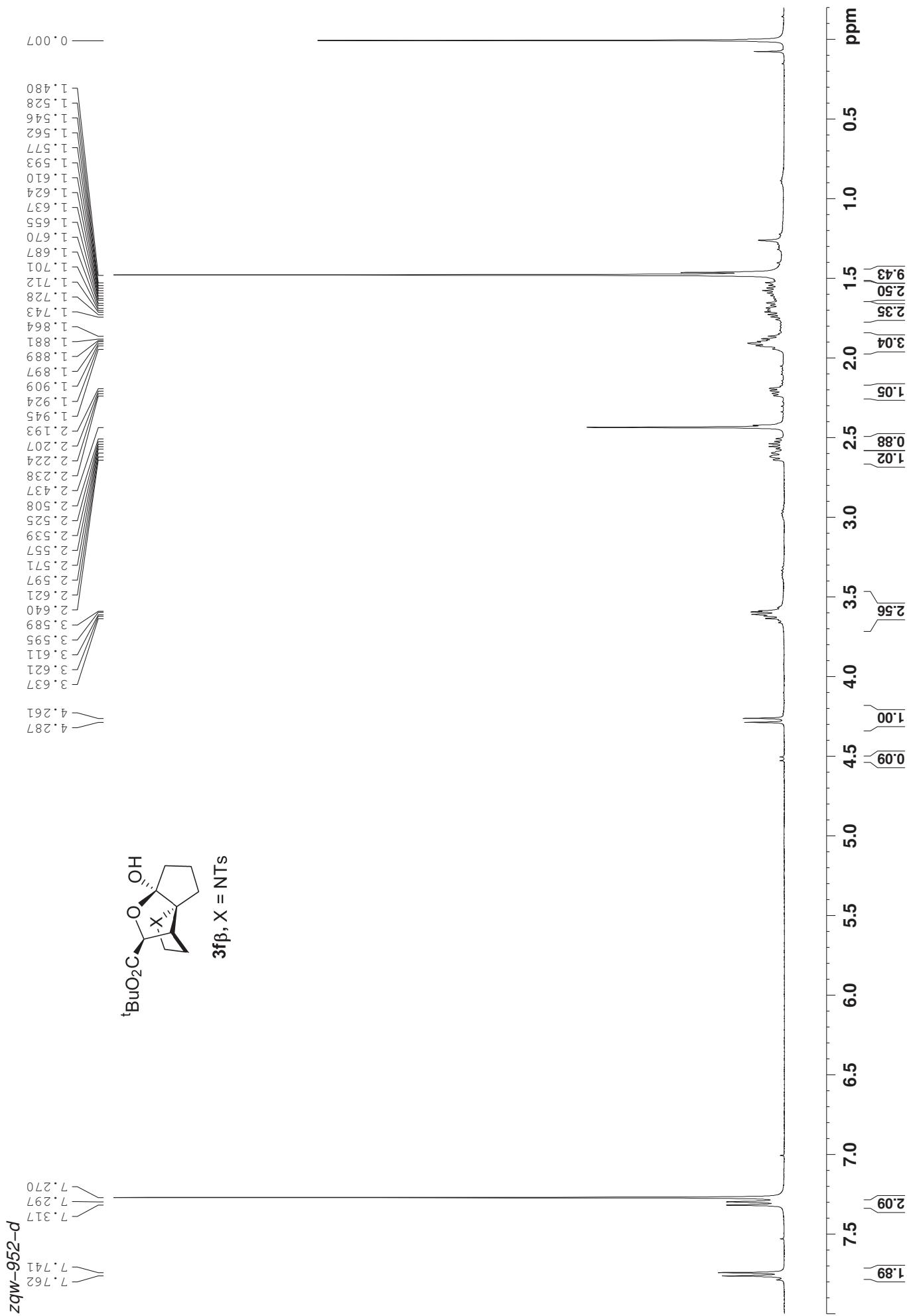


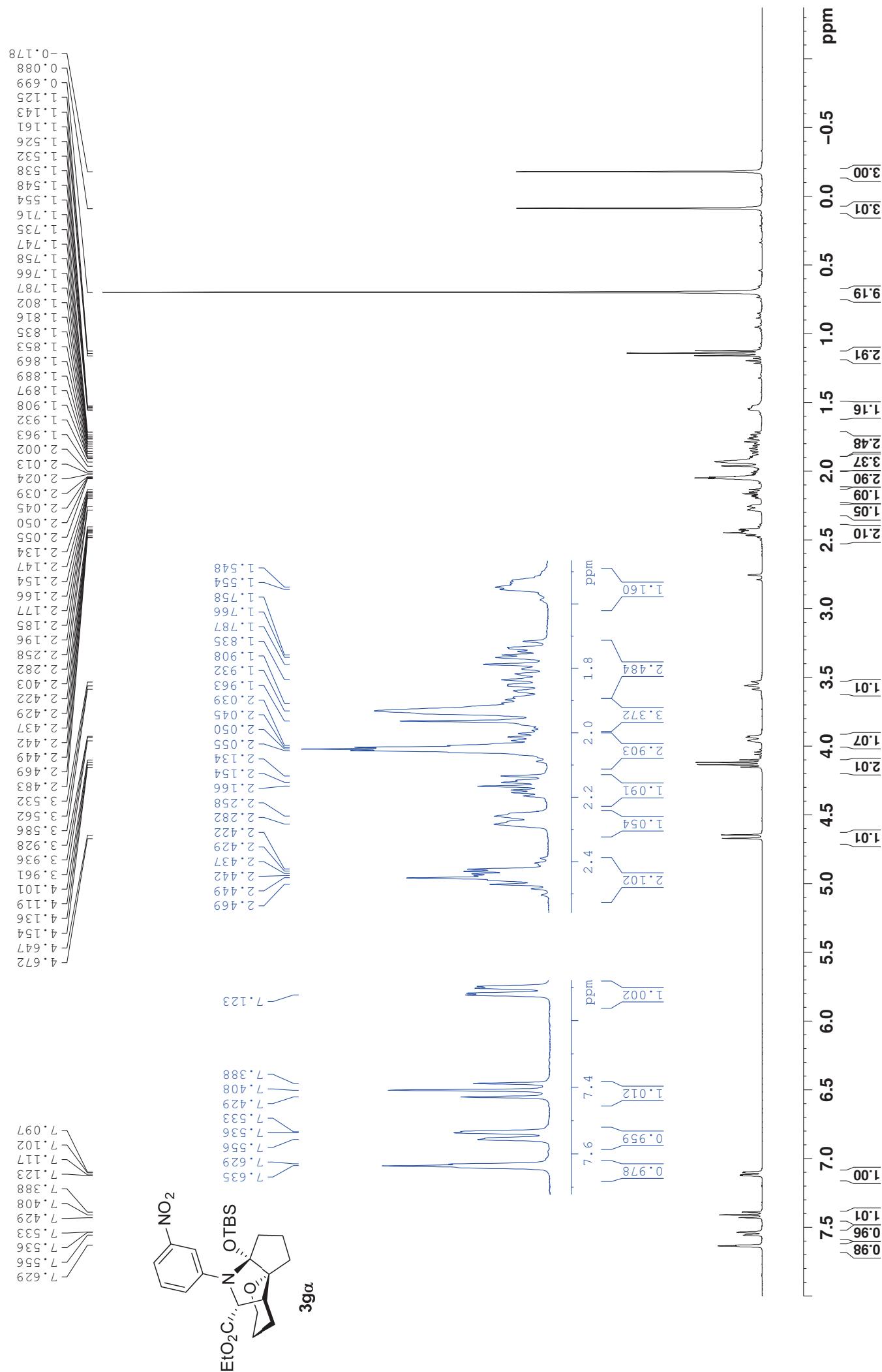
zqw-958-d

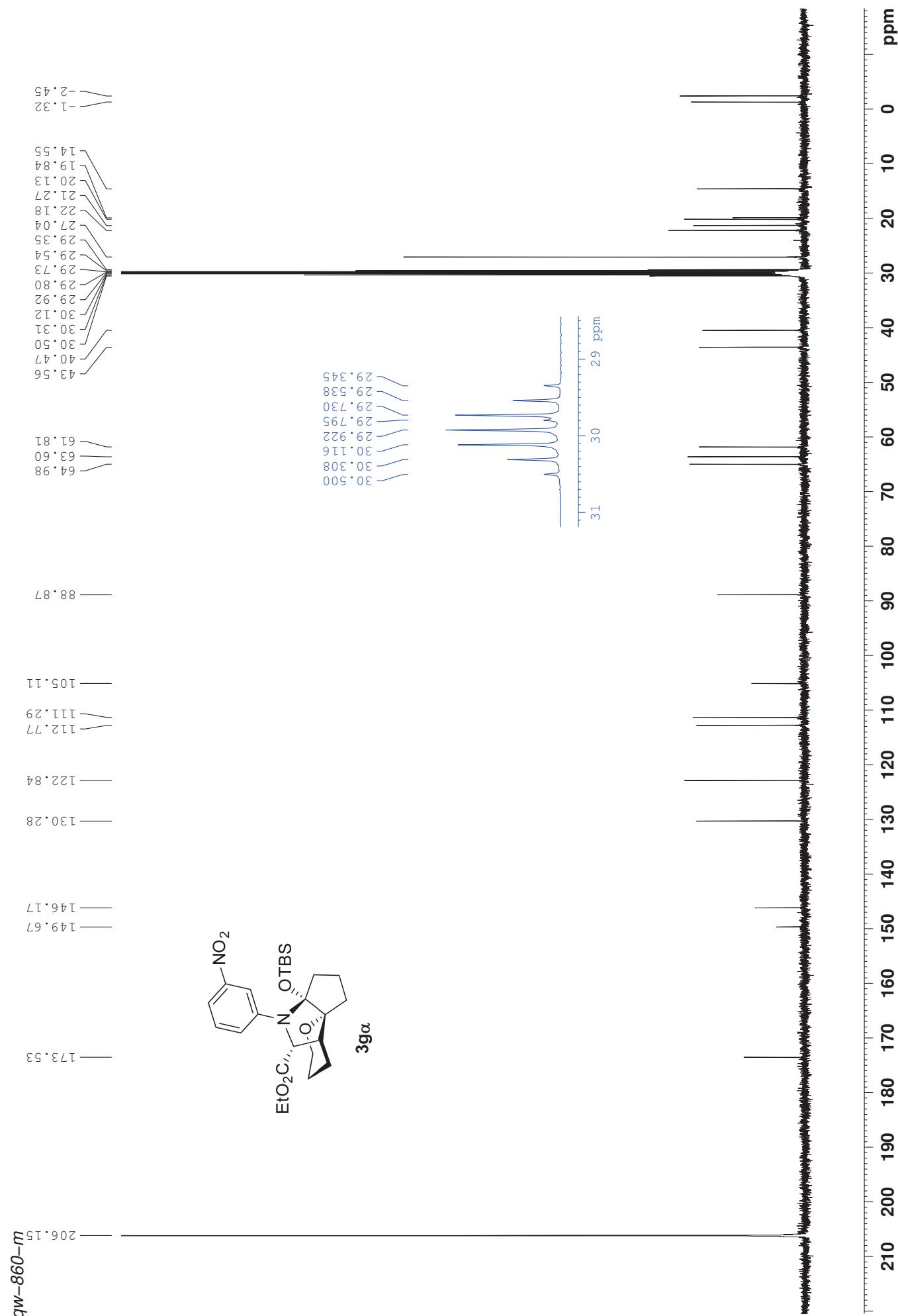


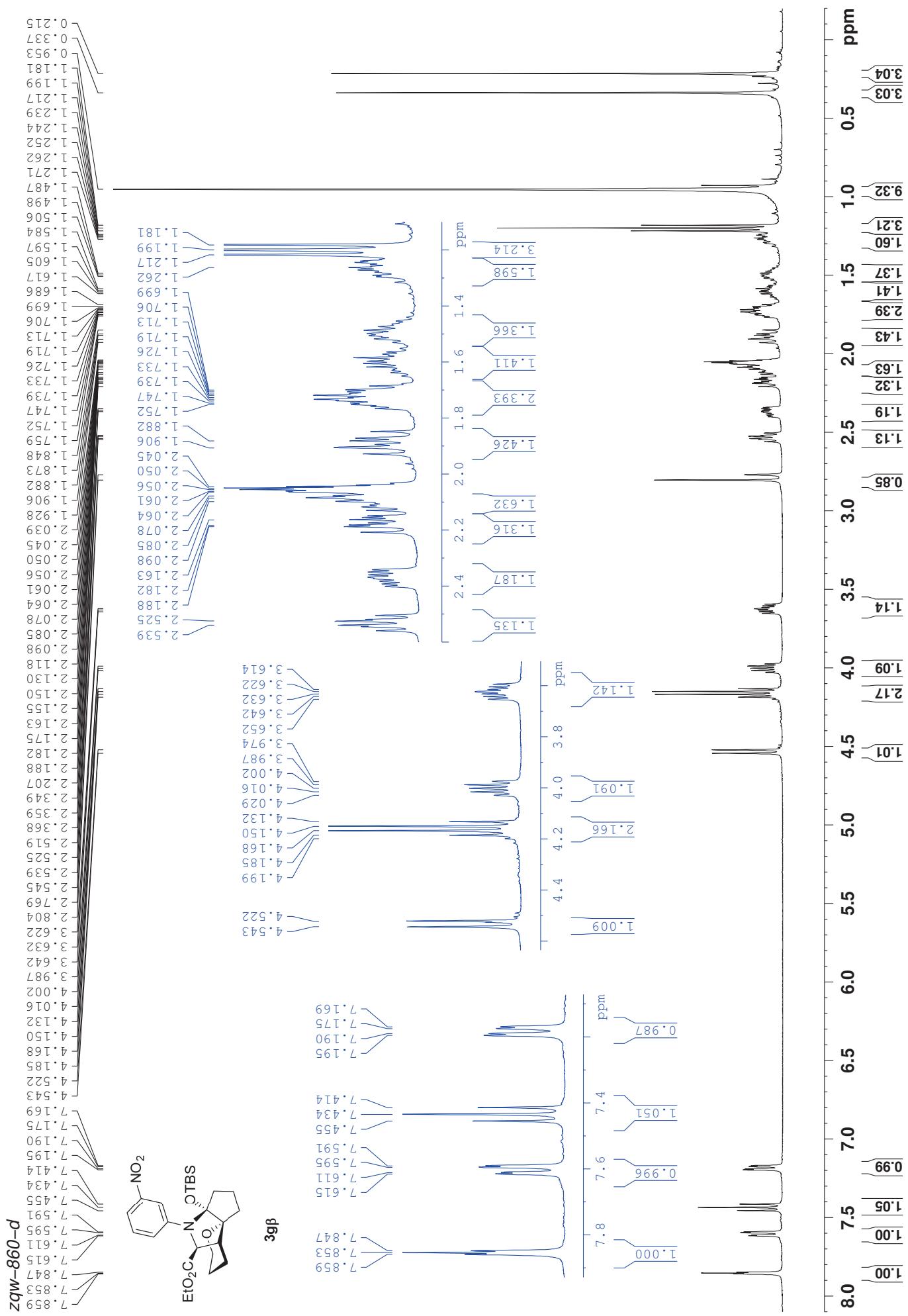


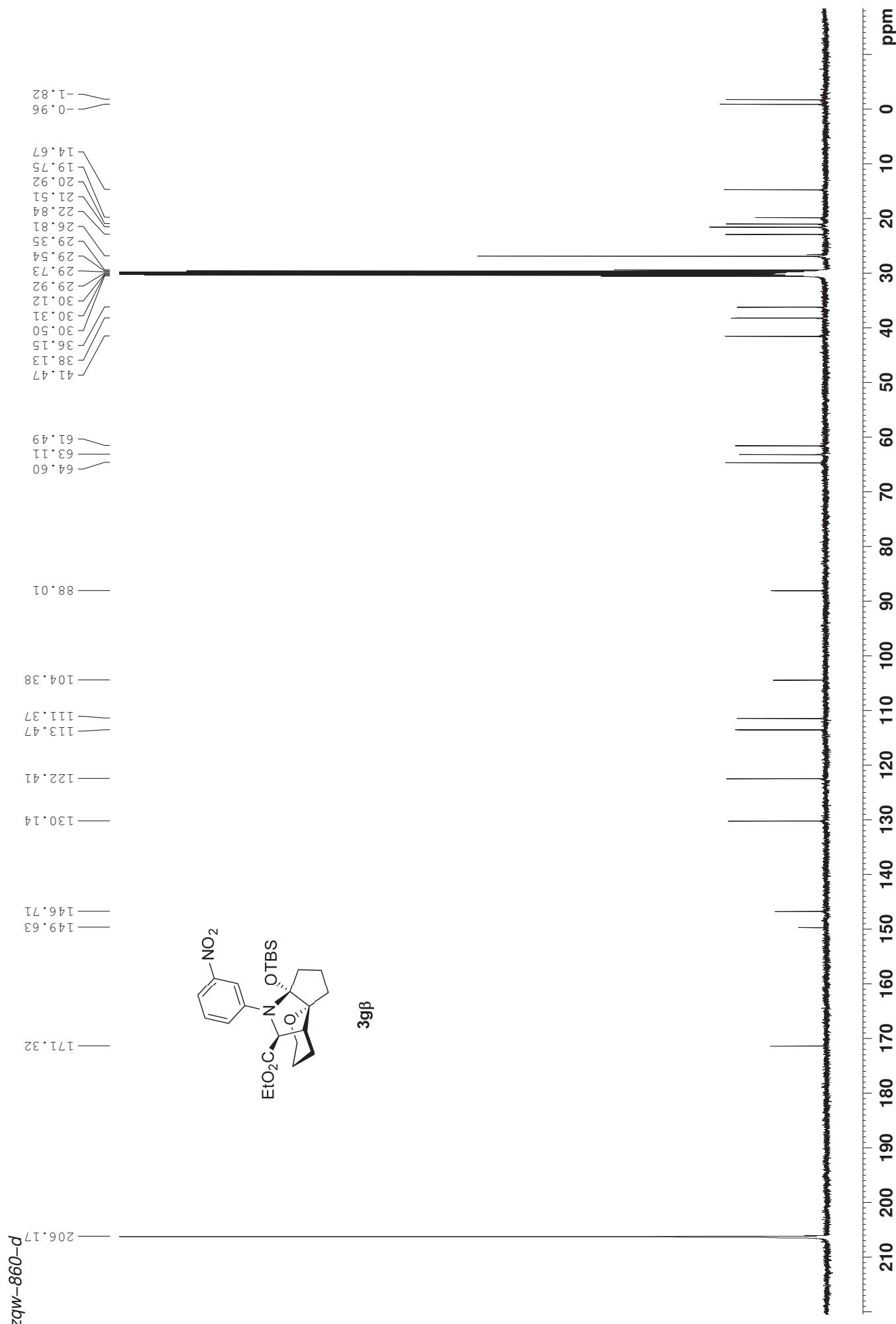


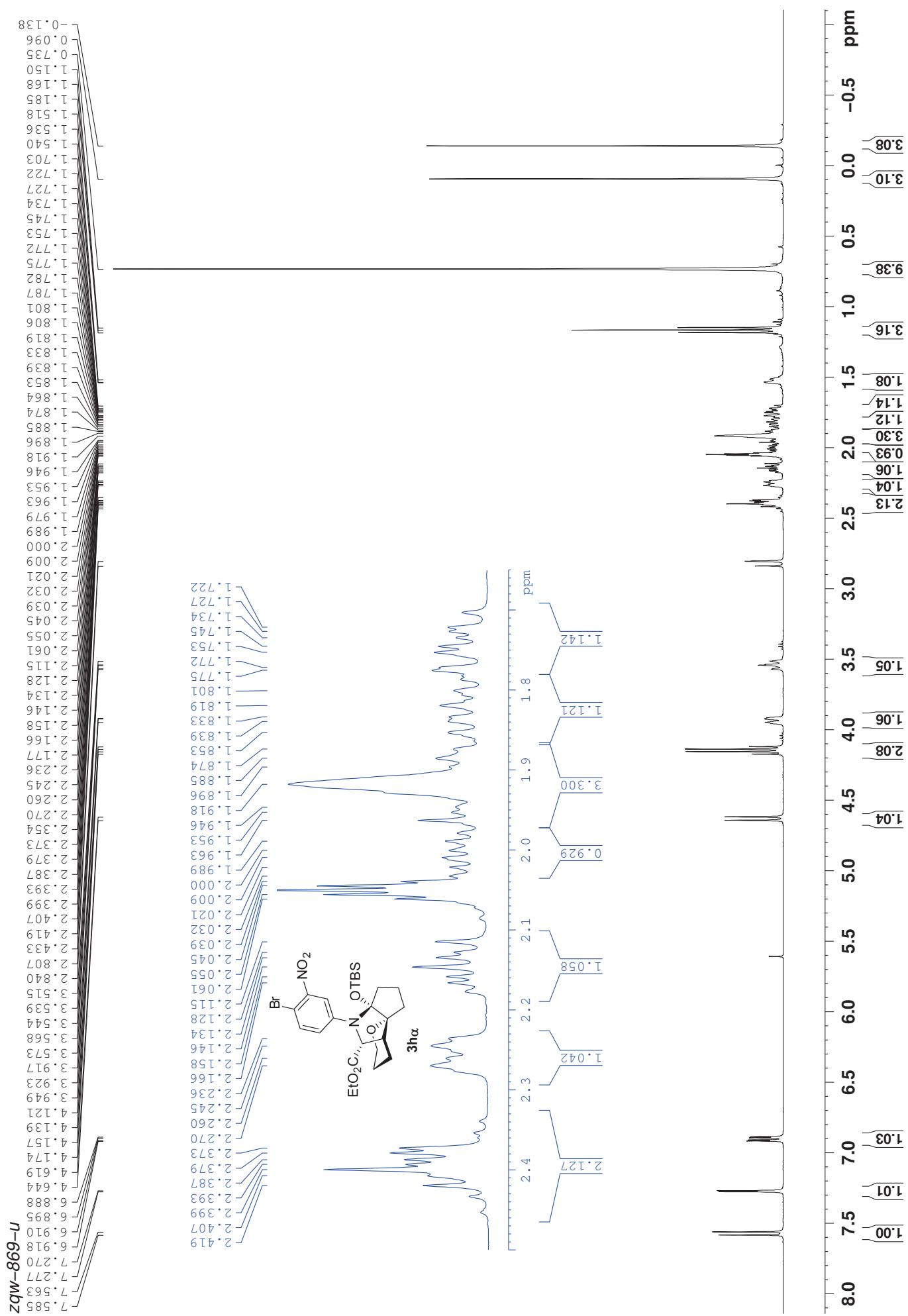


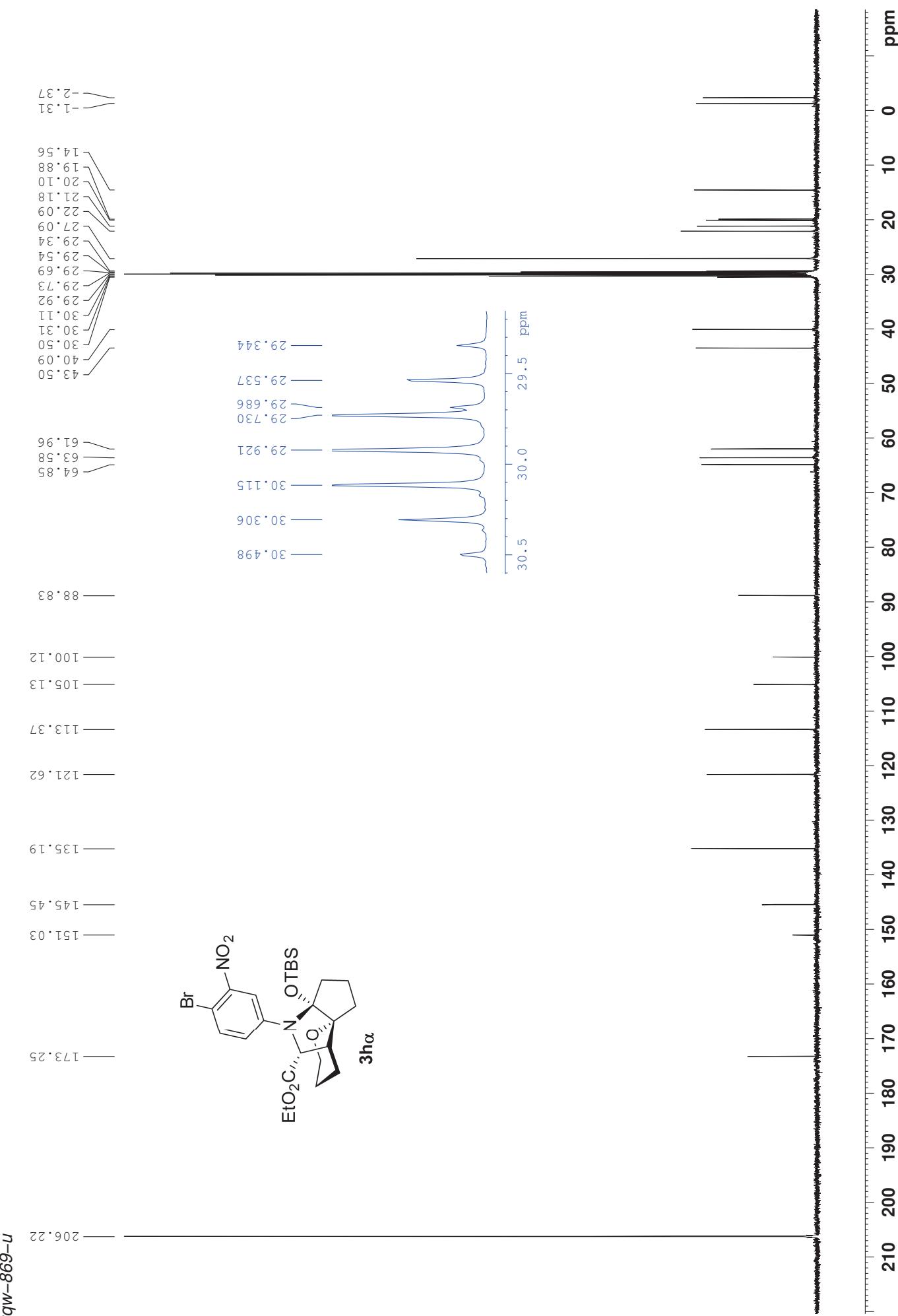


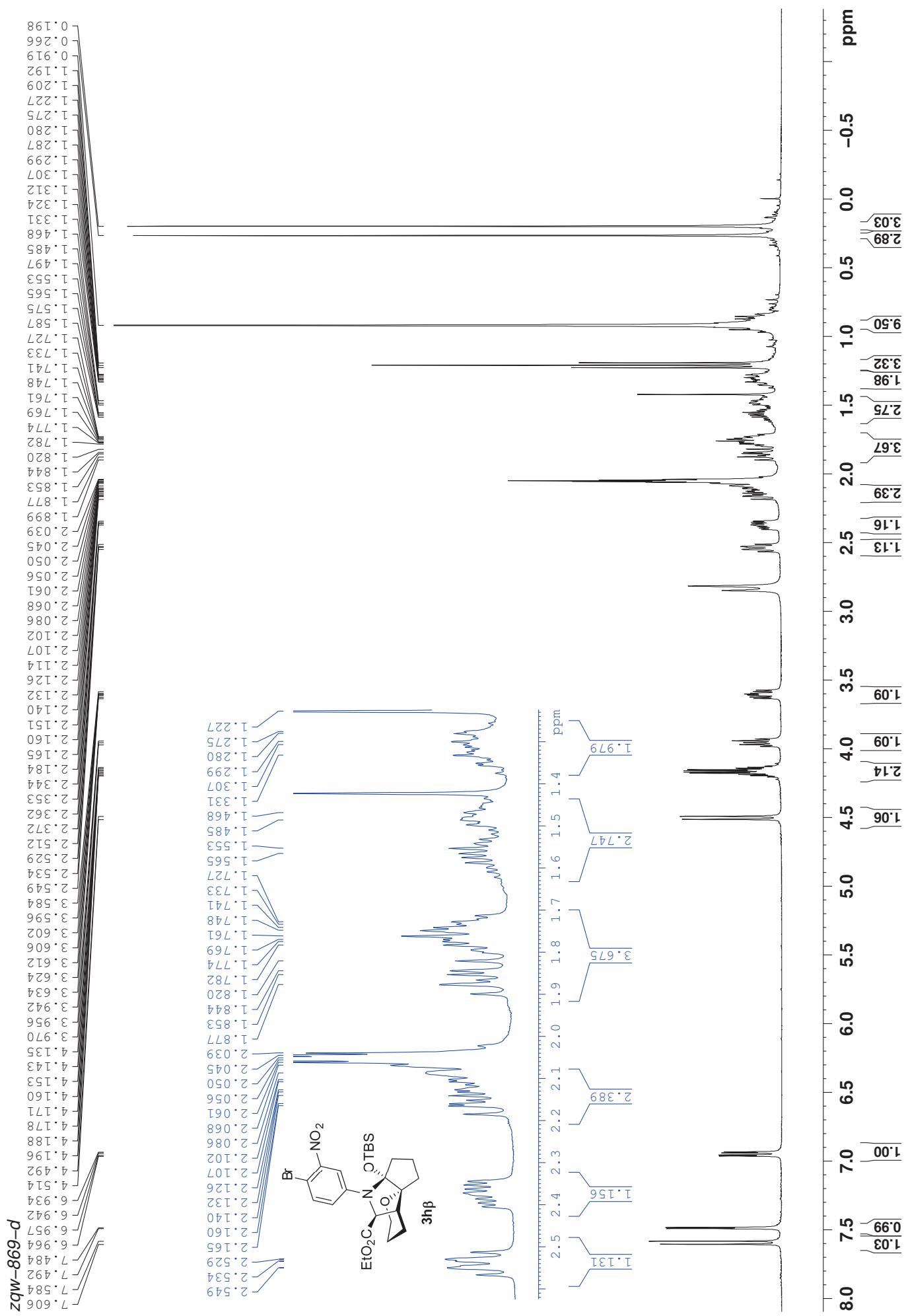


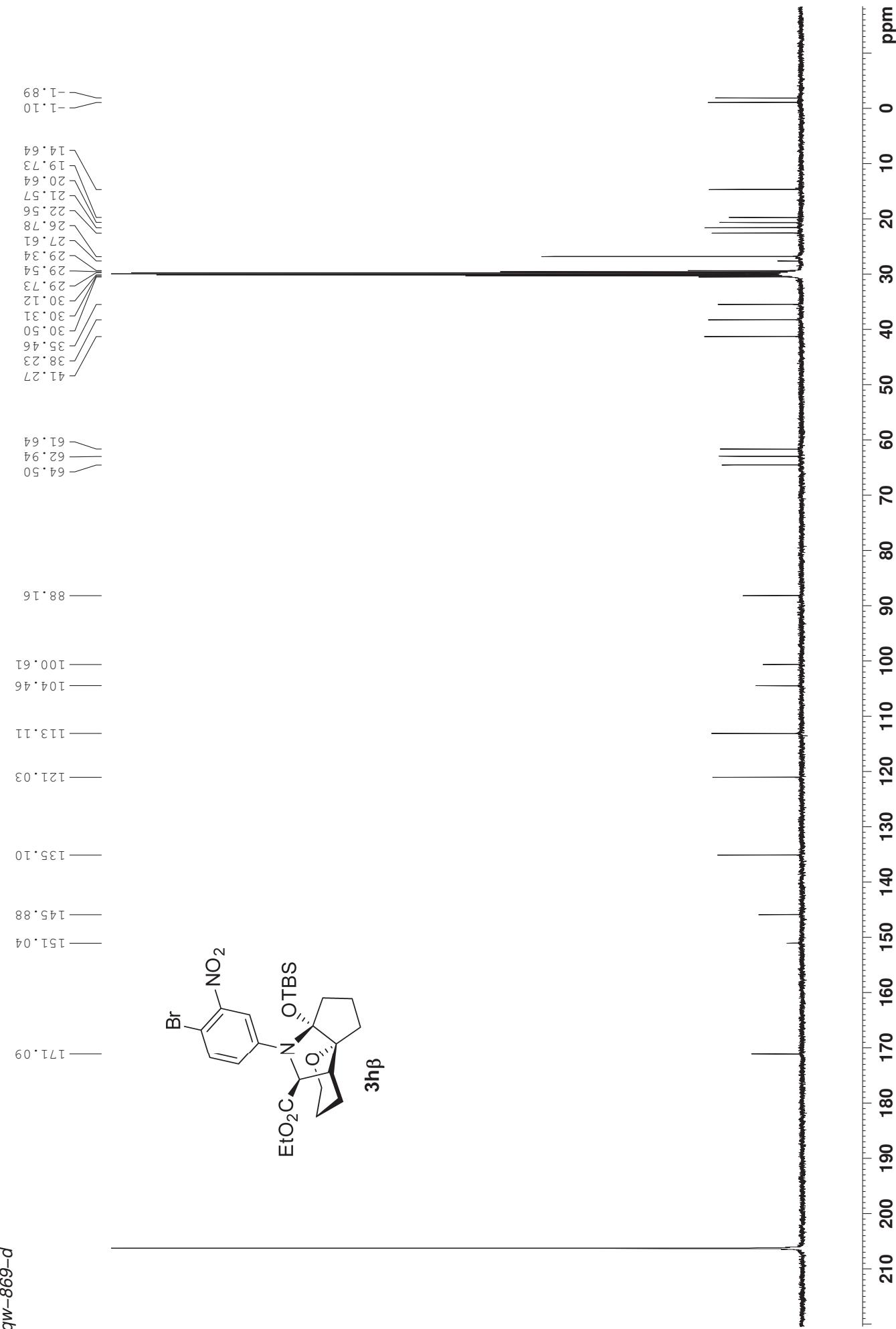


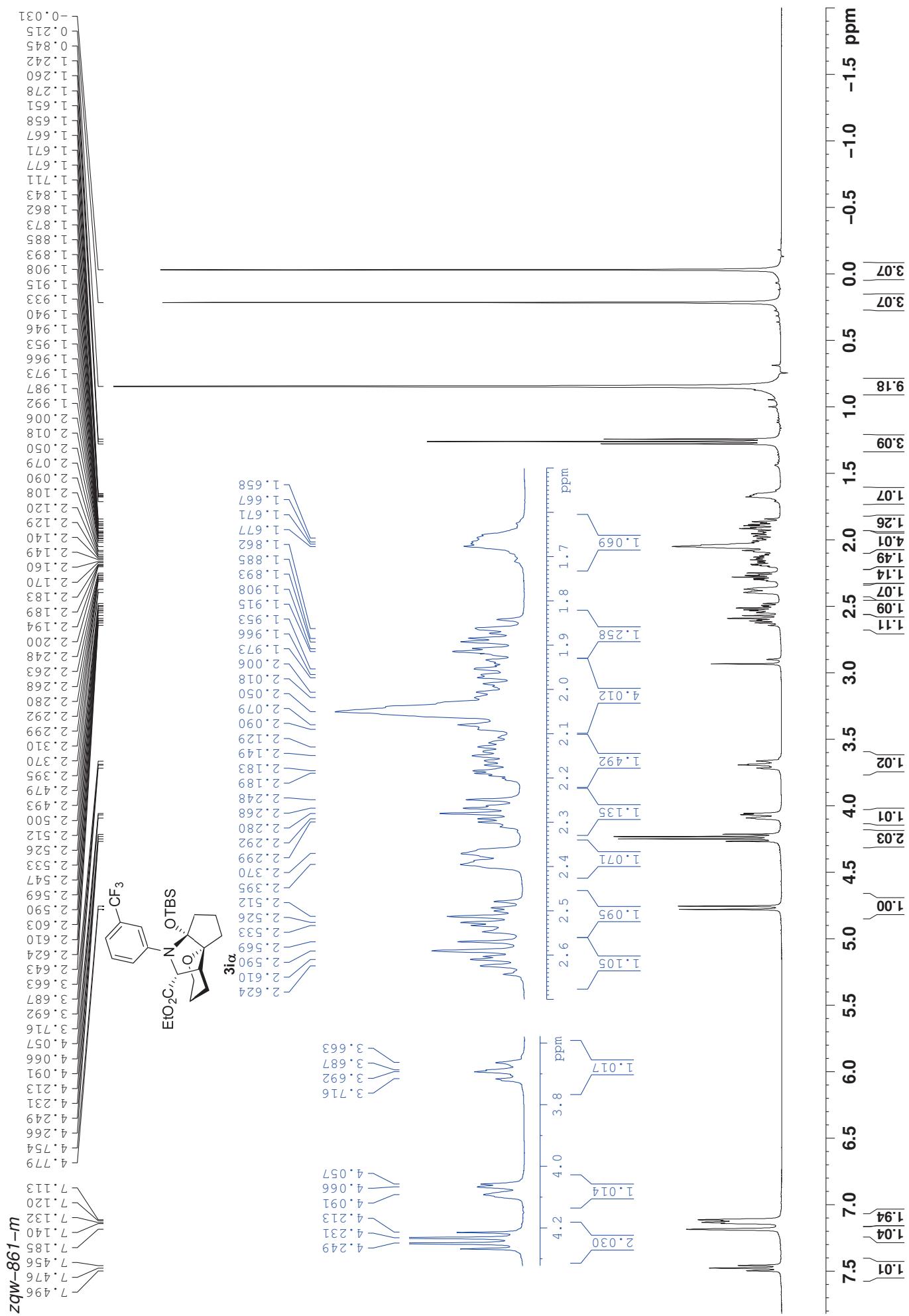


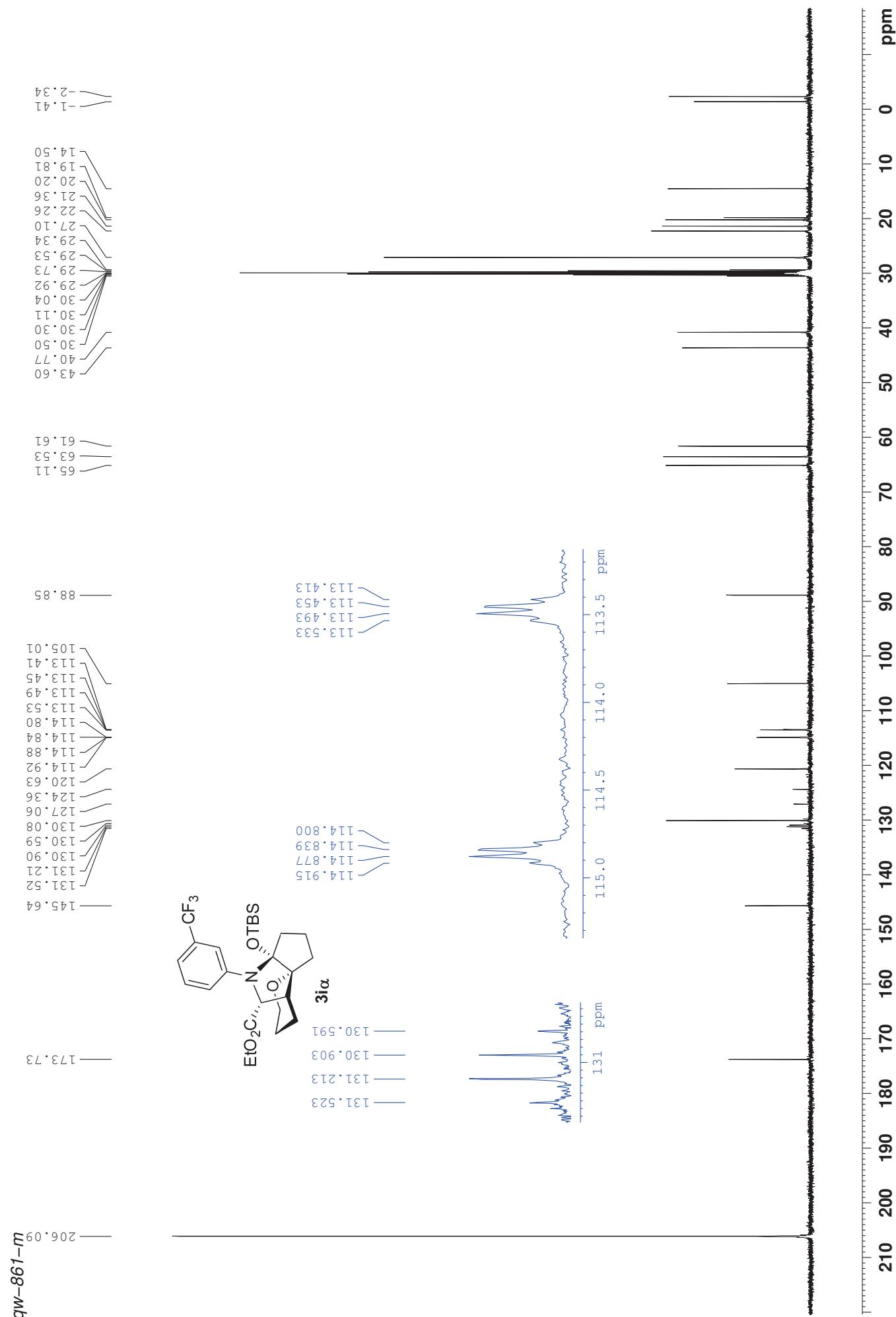


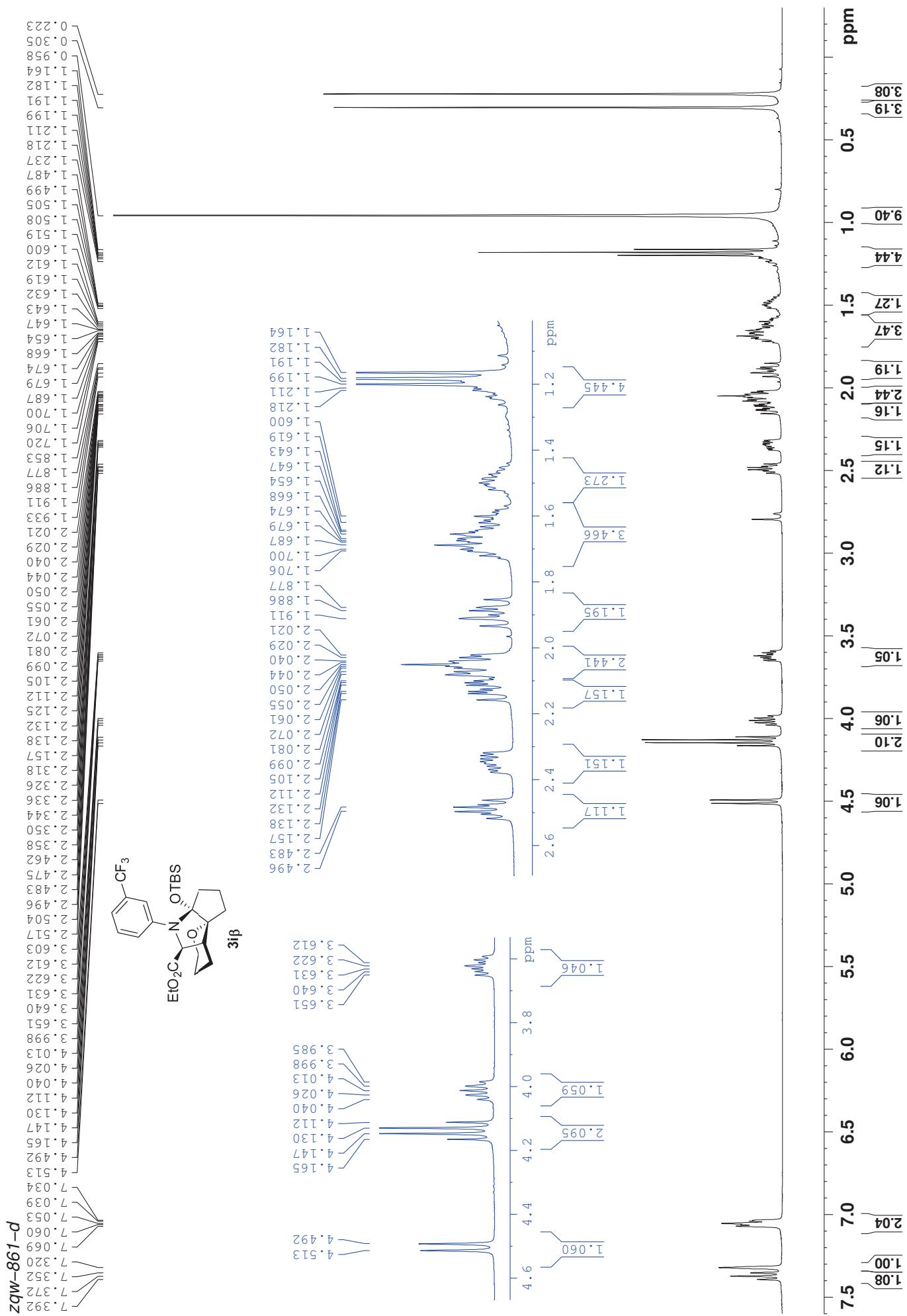


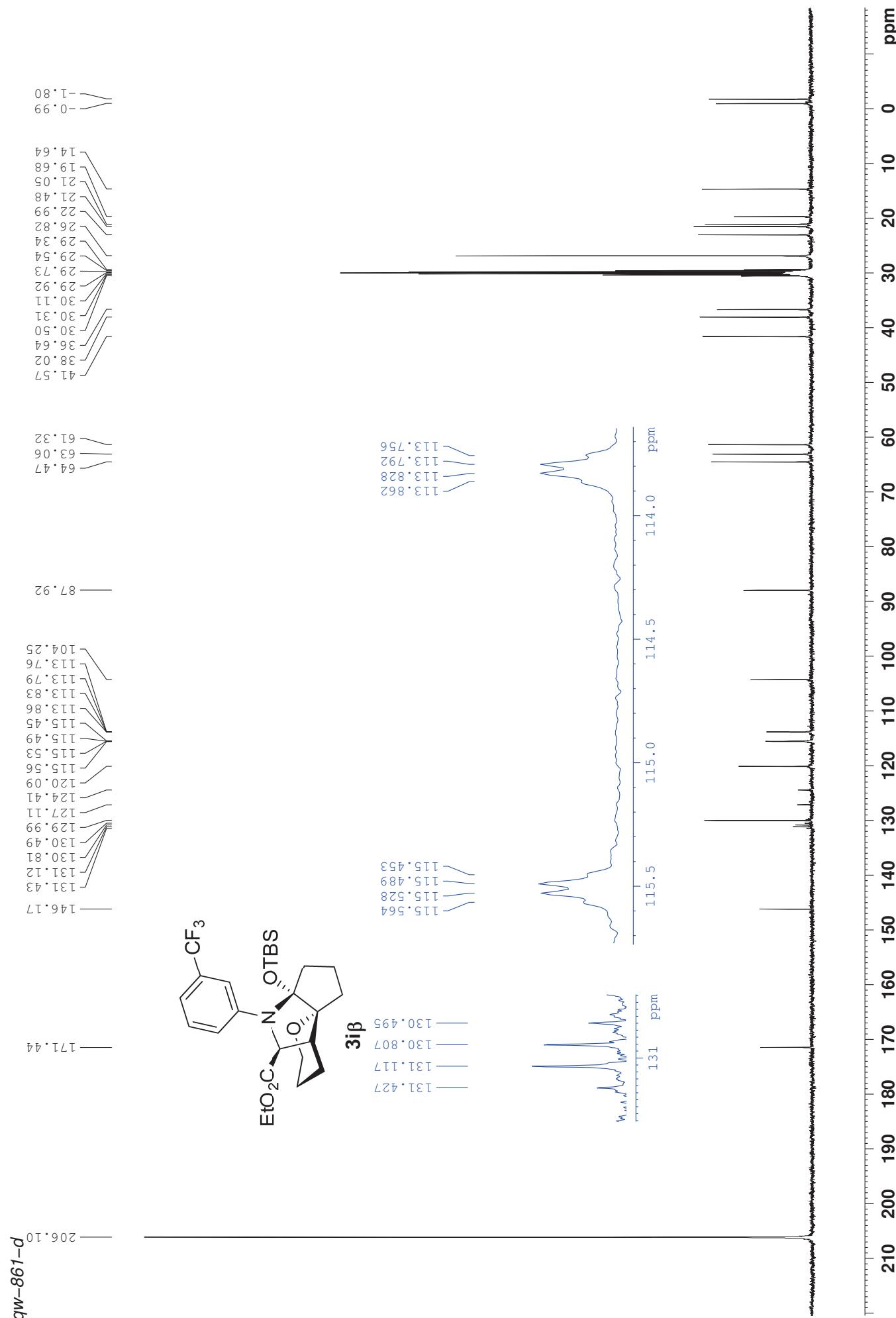


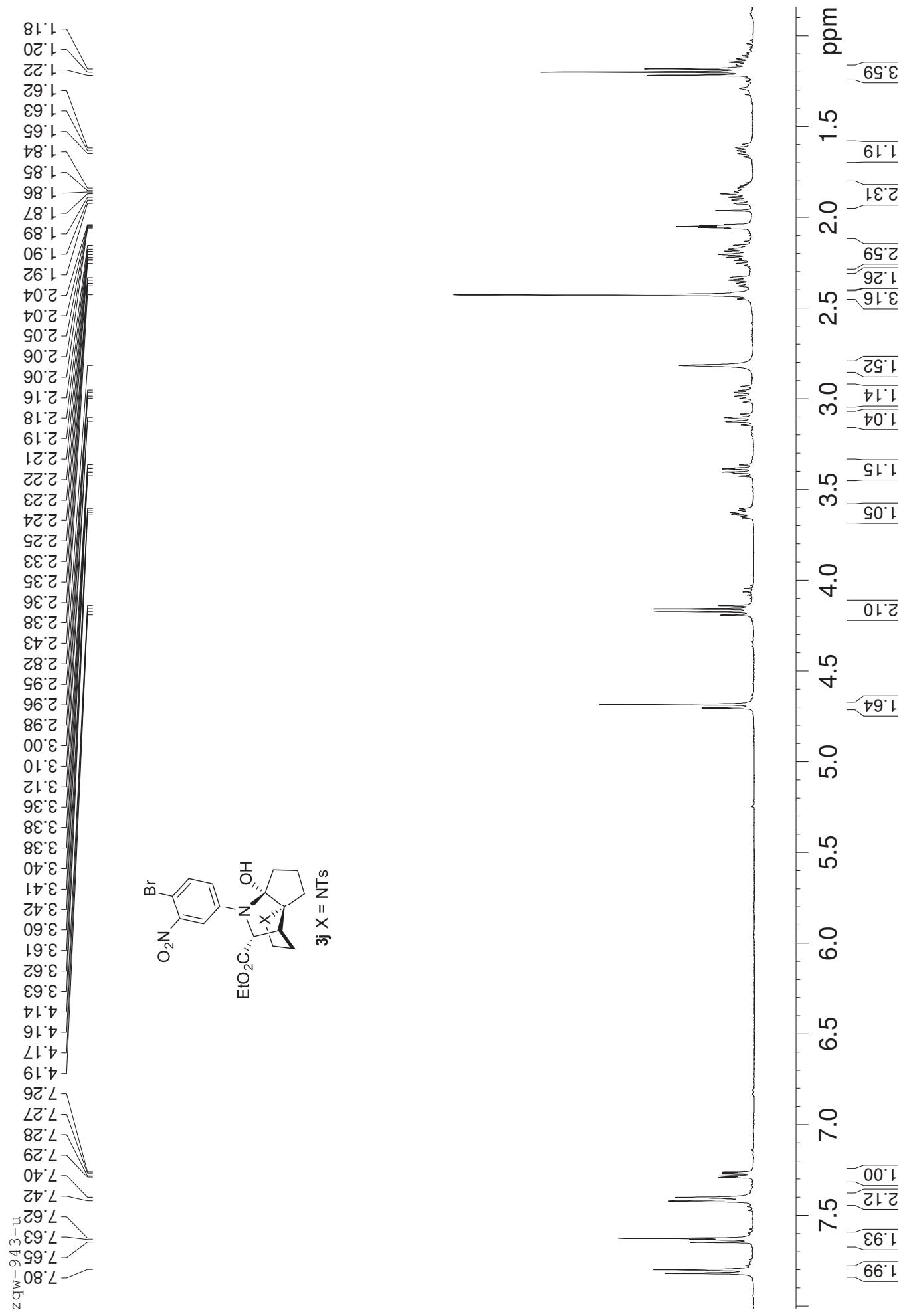


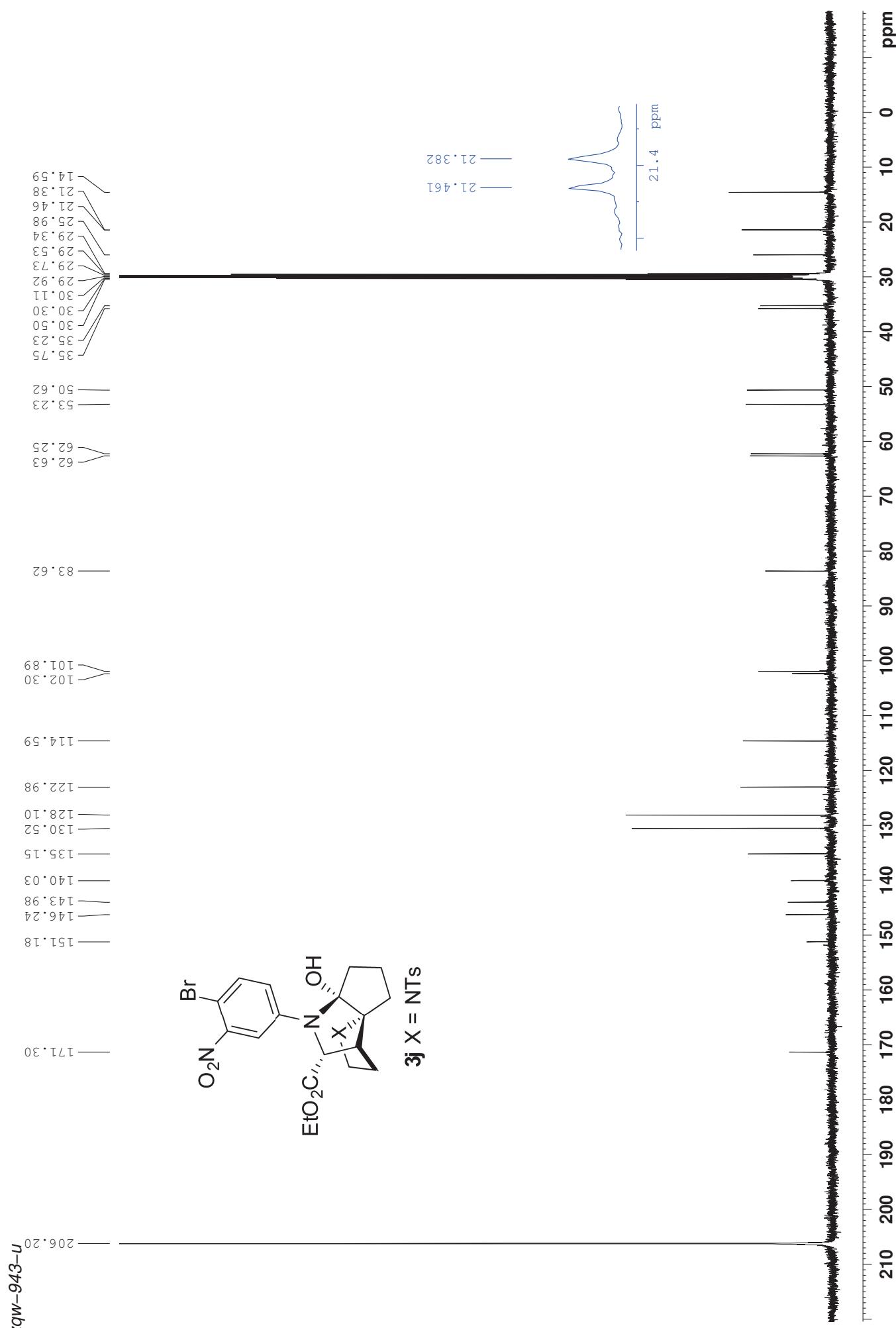












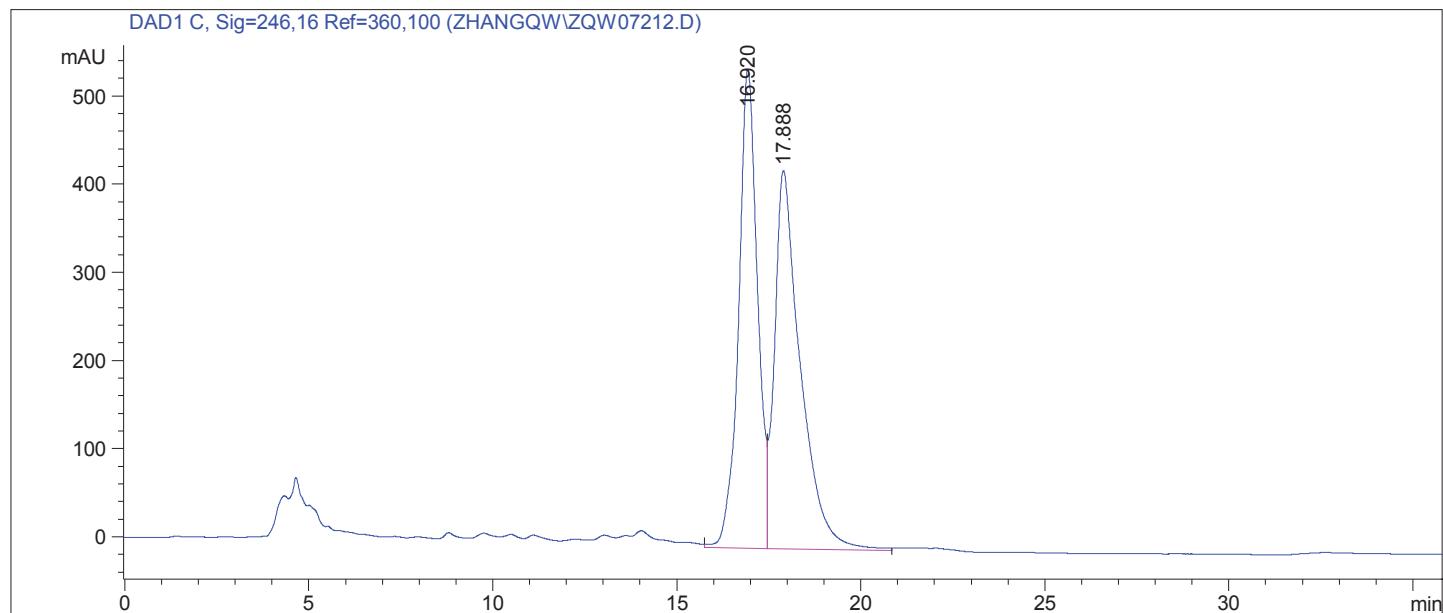
Data File C:\HPCHEM\1\DATA\ZHANGQW\ZQW07212.D  
AD hex:ipr=60:40 1ml/min

Sample Name: zqw-N

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Injection Date : 7/25/2002 1:00:54 AM  
Sample Name : zqw-N Location : Vial 1  
Acq. Operator : zhangqw  
Acq. Method : C:\HPCHEM\1\METHODS\ZHANGQW.M  
Last changed : 7/25/2002 12:59:11 AM by zhangqw  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\ZHANGQW.M  
Last changed : 7/25/2002 2:05:55 AM by ZDY

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Area Percent Report

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Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000

Signal 1: DAD1 C, Sig=246,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.920	VV	0.5288	1.93985e4	542.99091	48.0985
2	17.888	VB	0.6812	2.09323e4	429.04163	51.9015

Totals : 4.03309e4 972.03253

Results obtained with enhanced integrator!

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Summed Peaks Report

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Signal 1: DAD1 C, Sig=246,16 Ref=360,100

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Final Summed Peaks Report

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Signal 1: DAD1 C, Sig=246,16 Ref=360,100

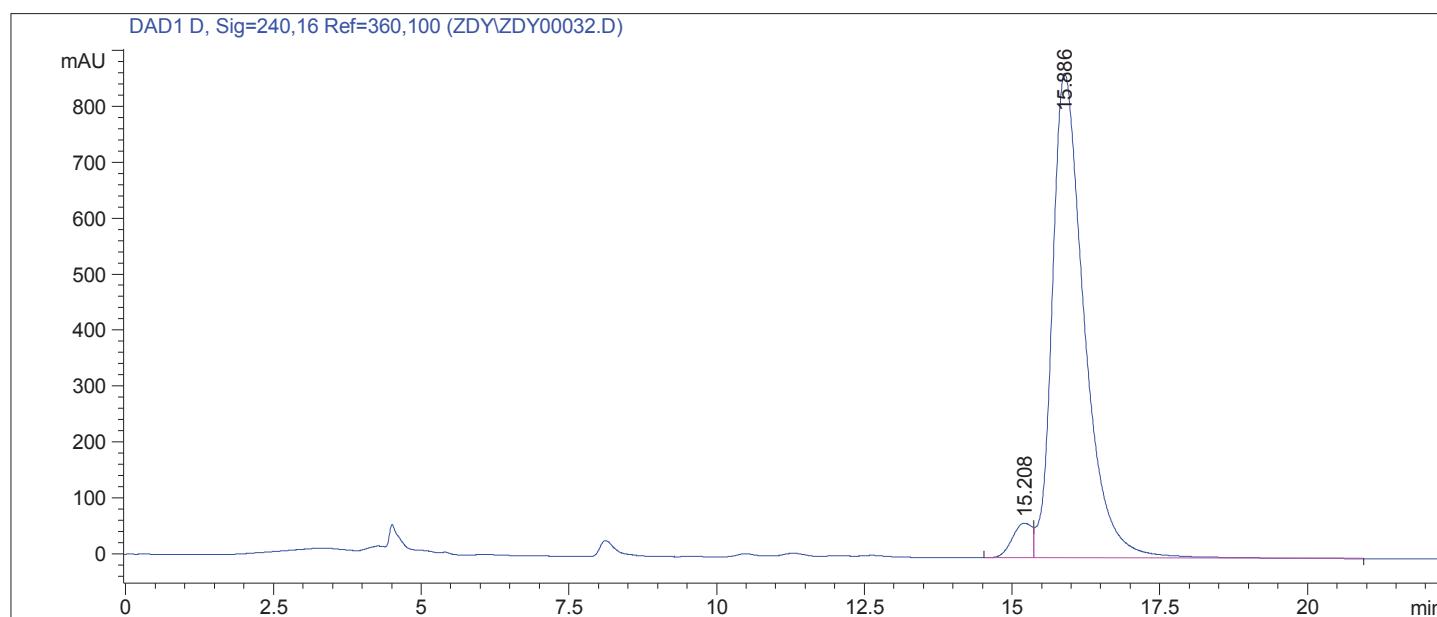
Data File C:\HPCHEM\1\DATA\ZDY\ZDY00032.D  
AD hex:ipr=90:10 1ml/min

Sample Name: zqw-Box-tBu-u

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Injection Date : 7/25/2002 12:40:41 AM  
Sample Name : zqw-Box-tBu-u Location : Vial 1  
Acq. Operator : ZDY  
Acq. Method : C:\HPCHEM\1\METHODS\ZHANGQW.M  
Last changed : 7/25/2002 12:41:15 AM by ZDY  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\ZHANGQW.M  
Last changed : 7/25/2002 2:05:55 AM by ZDY

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Area Percent Report

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Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000

Signal 1: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.208	VV	0.3608	1452.43188	62.11741	4.2630
2	15.886	VP	0.5634	3.26179e4	866.06079	95.7370

Totals : 3.40703e4 928.17820

Results obtained with enhanced integrator!

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Summed Peaks Report

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Signal 1: DAD1 D, Sig=240,16 Ref=360,100

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Final Summed Peaks Report

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Signal 1: DAD1 D, Sig=240,16 Ref=360,100

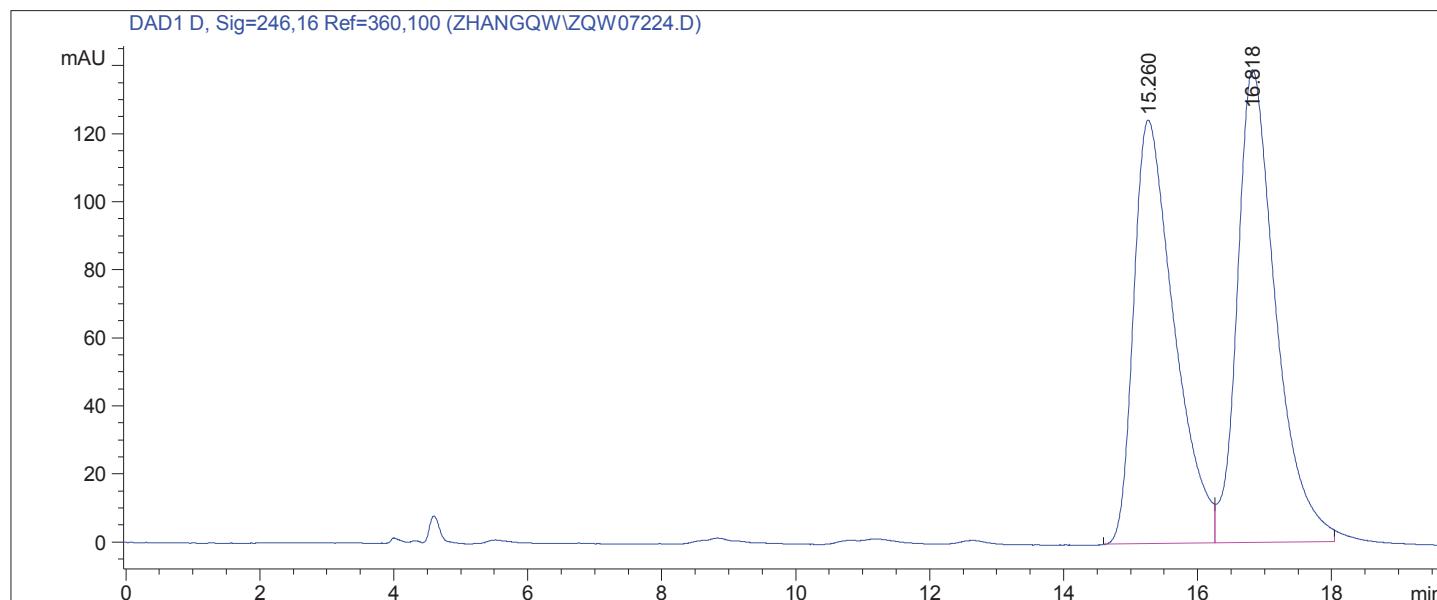
Data File C:\HPCHEM\1\DATA\ZHANGQW\ZQW07224.D  
AD hex:ipr=60:40 1ml/min

Sample Name: zqw-N-d-race

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Injection Date : 7/25/2002 4:03:09 AM  
Sample Name : zqw-N-d-race Location : Vial 1  
Acq. Operator : zhangqw  
Acq. Method : C:\HPCHEM\1\METHODS\ZHANGQW.M  
Last changed : 7/25/2002 3:45:21 AM by zhangqw  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\ZHANGQW.M  
Last changed : 7/25/2002 4:24:59 AM by zhangqw  
(modified after loading)

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Area Percent Report

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Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000

Signal 1: DAD1 D, Sig=246,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.260	BV	0.6259	5231.52295	124.59288	48.5024
2	16.818	VB	0.5982	5554.58740	139.00560	51.4976

Totals : 1.07861e4 263.59848

Results obtained with enhanced integrator!

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Summed Peaks Report

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Signal 1: DAD1 D, Sig=246,16 Ref=360,100

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Final Summed Peaks Report

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Signal 1: DAD1 D, Sig=246,16 Ref=360,100

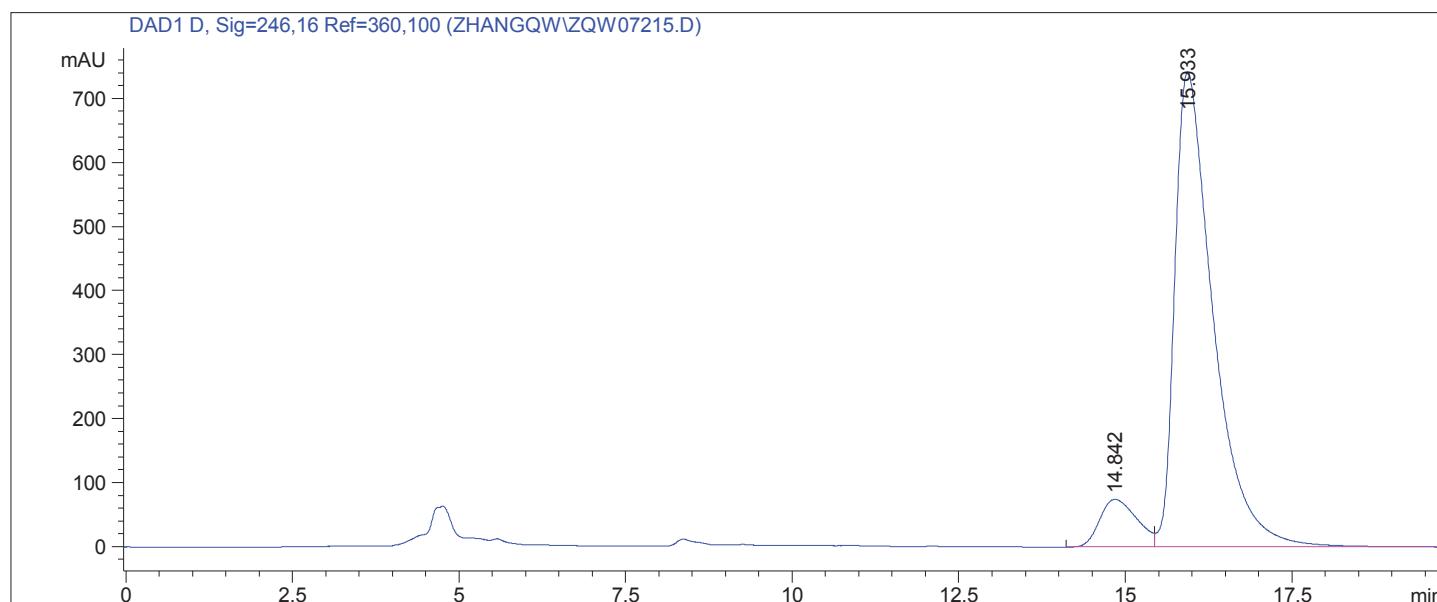
Data File C:\HPCHEM\1\DATA\ZHANGQW\ZQW07215.D  
AD hex:ipr=60:40 1ml/min

Sample Name: zqw-N-chiral-d

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Injection Date : 7/25/2002 1:45:47 AM  
Sample Name : zqw-N-chiral-d Location : Vial 1  
Acq. Operator : zhangqw  
Acq. Method : C:\HPCHEM\1\METHODS\ZHANGQW.M  
Last changed : 7/25/2002 12:41:15 AM by ZDY  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\ZHANGQW.M  
Last changed : 7/25/2002 1:48:54 AM by ZDY  
(modified after loading)

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Area Percent Report

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Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000

Signal 1: DAD1 D, Sig=246,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.842	VV	0.6101	2905.15674	74.64555	8.8810
2	15.933	VBA	0.6005	2.98069e4	742.27356	91.1190

Totals : 3.27121e4 816.91911

Results obtained with enhanced integrator!

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Summed Peaks Report

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Signal 1: DAD1 D, Sig=246,16 Ref=360,100

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Final Summed Peaks Report

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Signal 1: DAD1 D, Sig=246,16 Ref=360,100