

## Supporting Information for

### Pd-Catalyzed Borylative Cyclization of 1,6-Enynes

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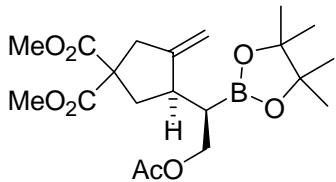
### Experimental details

Solvents were purified by standard methods, and commercially available reagents were used without additional purification. For the borylative cyclization reactions, toluene (SDS, anhydrous, analytical grade) was dried by standing with activated 4Å molecular sieves for several days prior to use. Anhydrous MeOH (Scharlau, HPLC grade) was also stored with 4Å molecular sieves. Bis(pinacolato)diboron (Aldrich) was used as received and stored under Ar at 4°C. Silicagel 60 (0.40-0.063 mm) purchased from Merck was used for column chromatography. Reagents were weighted on air, and reactions were performed under Ar. Subsequent work-up was performed on air.

### Preparation of alkylboronates

The corresponding enyne (*ca.* 100 mg), bis(pinacolato)diboron (1.1 equiv), and Pd(OAc)<sub>2</sub> (0.05 equiv) were sequentially added to a 5 mL flask. After purging with Ar, dry toluene (2 mL) and MeOH (1 equiv) were added. The mixture was heated at 50°C for the indicated time. After cooling to room temperature, Celite® was added and solvent was evaporated. Column chromatography (hexane-EtOAc) afforded the product. To obtain the highest possible yield, a 2 cm diameter column filled with 8.5 cm height of silicagel was used. Partial decomposition of the boronate was detected when using longer columns or retention times, probably due to hydrolysis, since boronates are stable in the presence of silicagel in dry toluene for 24 h at 23°C. Using pinacol (50 mol %) instead of MeOH made chromatographic separation more difficult.

**2a:** 2.5 h. Hexane-EtOAc 9:1. Colorless oil, 59%.



<sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>) δ 4.94 (m, 1H), 4.83 (m, 1H), 4.16 (d, *J* = 7.82, 2H), 3.69 (s, 6H), 2.94 (m, 2H), 2.82-2.71 (m, 1H), 2.53 (dd, *J* = 12.7, 7.7 Hz, 1H), 2.17 (dd, *J* = 12.7, 10.7 Hz, 1H), 2.00 (s, 3H), 1.80-1.73 (m, 1H), 1.18 (s, 12H).

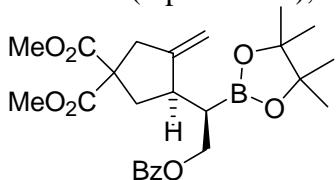
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 171.99 (C), 170.92 (C), 151.01 (C), 107.12 (CH<sub>2</sub>), 83.37 (C), 64.75 (CH<sub>2</sub>), 58.55 (C), 52.57 (CH<sub>3</sub>), 40.95 (CH<sub>2</sub>), 40.73 (CH), 38.02 (CH<sub>2</sub>), 24.71 (CH), 24.59 (CH<sub>3</sub>), 20.87 (CH<sub>3</sub>).

HRMS FAB+: Calc. 411.219024; found 411.217162.

Starting from the isomeric enyne with (*E*) configuration on the alkene, a diastereoisomer of **2a** is obtained:

<sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>) δ 8.01 (m, 2H), 7.51 (m, 1H), 7.39 (m, 2H), 4.93 (m, 2H), 4.45 (dd, *J* = 7.0, 1.2 Hz, 2H), 3.68 (s, 3H), 3.67 (s, 3H), 2.97 (m, 2H), 2.88 (m, 1H), 2.61 (m, 1H), 2.05 (dd, *J* = 12.9, 11.6 Hz, 1H), 1.74 (c, *J* = 6.4 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H).

**2b:** 3 h. Hexane-EtOAc 7:1. White solid (mp 75-78°C), 75%.



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.04 (m, 2H), 7.54 (m, 1H), 7.42 (m, 2H), 4.99 (d, *J* = 2.1 Hz, 1H), 4.90 (d, *J* = 2.1 Hz, 1H), 4.44 (m, 2H), 3.72 (s, 3H), 3.69 (s, 3H), 2.99 (s, 2H), 2.90 (m, 1H), 2.63 (dd, *J* = 7.7, 12.8 Hz, 1H), 2.29 (dd, *J* = 10.8, 12.8 Hz, 1H), 1.94 (c, *J* = 6.8 Hz, 1H), 1.19 (s, 12H).

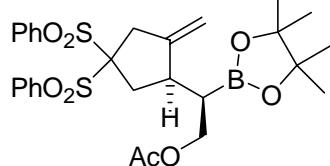
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 172.6 (C), 172.4 (C), 166.8 (C), 151.5 (C), 133.2 (CH), 130.9 (C), 130.0 (CH), 128.6 (CH), 107.7 (CH<sub>2</sub>), 83.9 (C), 65.8 (CH<sub>2</sub>), 59.1 (C), 53.1 (CH<sub>3</sub>), 53.0 (CH<sub>3</sub>), 41.4 (CH), 41.4 (CH<sub>2</sub>), 38.6 (CH<sub>2</sub>), 28.7 (CH), 25.1 (CH<sub>3</sub>).

HRMS ESI: Calc. 473.2341; found 473.2362

Starting from the isomeric enyne with (*E*) configuration on the alkene, a diastereoisomer of **2b** is obtained:

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.93 (m, 1H), 4.88 (m, 1H), 4.21 (dd, *J* = 7.5, 4.2 Hz, 2H), 3.71 (s, 6H), 2.95 (m, 2H), 2.79 (m, 1H), 2.54 (m, 1H), 2.01 (m, 1H), 2.00 (s, 3H), 1.61 (m, 1H), 1.22 (s, 12H).

**2c:** 3 h. Hexane-EtOAc 5:1. Sticky white solid, 47%.

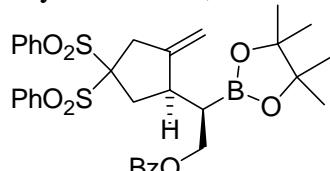


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (m, 2H), 8.04 (m, 2H), 7.70 (m, 2H), 7.58 (m, 4H), 4.95 (d,  $J = 2.2$  Hz, 1H), 4.90 (d,  $J = 2.2$  Hz, 1H), 4.13 (m, 2H), 3.50 (dd,  $J = 18.0, 2.0$  Hz, 1H), 3.05 (d,  $J = 18.0$  Hz, 1H), 2.96 (m, 1H), 2.89 (m, 1H), 2.56 (dd,  $J = 14.3, 7.6$  Hz, 1H), 2.01 (s, 3H), 1.84 (dd,  $J = 12.8, 6.6$  Hz), 1.25 (s, 6H), 1.24 (s, 6H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , DEPT-135)  $\delta$  171.2 (C), 149.3 (C), 137.5 (C), 136.3 (C), 134.9 (CH), 134.7 (CH), 131.7 (CH), 131.6 (CH), 129.0 (CH), 128.8 (CH), 108.1 (CH<sub>2</sub>), 91.9 (C), 84.1 (C), 65.1 (CH<sub>2</sub>), 42.1 (CH), 38.4 (CH<sub>2</sub>), 36.0 (CH<sub>2</sub>), 27.3 (CH), 25.1 (CH<sub>3</sub>), 25.0 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>).

HRMS FAB+: Calc. 575.194467; found 575.196300.

**2d:** 5 h. Hexane-EtOAc 9:1. Sticky white solid, 47%.

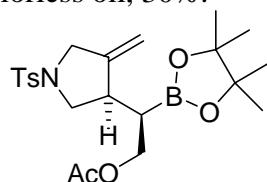


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (m, 2H), 8.02 (m, 4H), 7.65 (m, 2H), 7.55 (m, 3H), 7.46 (m, 4H), 4.98 (d,  $J = 2.2$  Hz, 1H), 4.95 (d,  $J = 2.2$  Hz, 1H), 4.38 (m, 2H), 3.53 (dd,  $J = 18.0, 2.0$  Hz, 1H), 3.10 (d,  $J = 18.0$  Hz, 1H), 3.06 (m, 1H), 3.00 (m, 1H), 2.62 (dd,  $J = 14.0, 7.4$  Hz, 1H), 2.01 (dd,  $J = 13.2, 6.2$  Hz, 1H), 1.25 (s, 12H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , DEPT-135)  $\delta$  166.8 (C), 149.4 (C), 137.5 (C), 136.3 (C), 134.9 (CH), 134.7 (CH), 133.4 (CH), 131.7 (CH), 131.6 (CH), 130.6 (C), 130.0 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 108.2 (CH<sub>2</sub>), 91.9 (C), 84.2 (C), 65.7 (CH<sub>2</sub>), 42.3 (CH), 38.5 (CH<sub>2</sub>), 35.9 (CH<sub>2</sub>), 25.2 (CH<sub>3</sub>), 25.1 (CH<sub>3</sub>), 21.4 (CH).

HRMS FAB+: Calc. 637.210118; found 637.210447.

**2e:** 2.5 h. Hexane-EtOAc 5:1. Colorless oil, 30%.



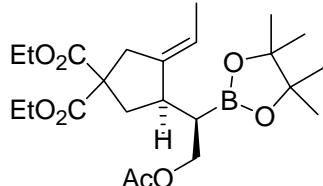
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 8.2$  Hz, 2H), 7.32 (d,  $J = 8.2$  Hz, 2H), 4.93 (dd,  $J = 4.3, 2.2$  Hz, 1H), 4.87 (dd,  $J = 4.6, 2.2$  Hz, 1H), 4.12 (d,  $J = 1.2$  Hz, 1H), 4.09

(s, 1H), 3.92 (dt,  $J = 13.8$  Hz, 1H), 3.65 (ddd,  $J = 13.8, 4.3, 2.2$  Hz, 1H), 3.50 (dd,  $J = 9.3, 7.8$  Hz, 1H), 3.15, dd,  $J = 9.3, 7.8$  Hz, 1H), 2.86 (m, 1H), 2.41 (s, 3H), 1.99 (s, 3H), 1.66 (dd,  $J = 13.2, 6.4$  Hz, 1H), 1.08 (s, 6H), 1.06 (s, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , DEPT-135)  $\delta$  171.2 (C), 147.7 (C), 143.8 (C), 132.9 (C), 129.9 (CH), 128.4 (CH), 107.6 ( $\text{CH}_2$ ), 83.9(C), 64.7 ( $\text{CH}_2$ ), 52.7 ( $\text{CH}_2$ ), 52.6 ( $\text{CH}_2$ ), 41.6 (CH), 25.0 (CH), 24.8 ( $\text{CH}_3$ ), 21.9 ( $\text{CH}_3$ ), 21.2 ( $\text{CH}_3$ ).

HRMS FAB+: Calc. 450.2116; found 450.2115.

**2f:** 4 h. Hexane-EtOAc 9:1. Colorless oil, 95%.

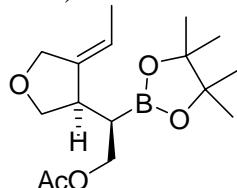


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.25 (m, 1H), 4.22 – 4.11 (m, 4H), 2.97 (d,  $J = 16.3$  Hz, 1H), 2.75 (m, 2H), 2.47 (dd,  $J = 11.4, 6.7$  Hz, 1H), 2.18 (dd,  $J = 11.4, 12.7$  Hz 1H), 1.99 (s, 3H), 1.81 (m, 1H), 1.57 (d,  $J = 6.7$  Hz, 3H), 1.25-1.19 (m, 6H), 1.17 (s, 6H), 1.16 (s, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , DEPT-135)  $\delta$  171.91 (C), 170.99 (C), 142.08 (C), 116.53 (CH), 83.20 (C), 64.86 ( $\text{CH}_2$ ), 61.30 ( $\text{CH}_2$ ), 58.67 (C), 40.66 (CH), 37.63 ( $\text{CH}_2$ ), 37.09 ( $\text{CH}_2$ ), 24.73 ( $\text{CH}_3$ ), 24.55 (CH), 20.91 ( $\text{CH}_3$ ), 14.47 ( $\text{CH}_3$ ), 14.01 ( $\text{CH}_3$ ), 13.99 ( $\text{CH}_3$ ).

HRMS FAB+: Calc. 453.265974; found 453.265249.

**2g:** 84 h. After 21 h,  $\text{Pd}(\text{OAc})_2$  (0.05 equiv) was added. Hexane-EtOAc 9:1. Colorless oil, 31% (corrected for 68% conversion).

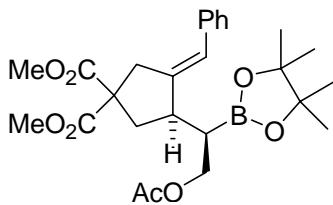


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.31 (m, 1H), 4.29 (m, 2H), 4.25 - 4.10 (m, 2H), 3.90 (dd,  $J = 6.3, 8.3$  Hz 1H), 3.80 (dd,  $J = 6.0, 8.3$  Hz 1H), 2.81 (m, 1H), 2.02 (s, 3H), 1.68-1.61 (m, 1H), 1.56 (dm,  $J = 7.0$  Hz, 3H), 1.20 (s, 12H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , DEPT-135)  $\delta$  170.99 (C), 142.28 (C), 114.98 (CH), 83.50 (C), 83.46 (C), 72.68 ( $\text{CH}_2$ ), 69.08 ( $\text{CH}_2$ ), 64.97 ( $\text{CH}_2$ ), 42.38 (CH), 25.04 (CH), 24.78 ( $\text{CH}_3$ ), 24.67 ( $\text{CH}_3$ ), 20.95 ( $\text{CH}_3$ ), 14.59 ( $\text{CH}_3$ ).

HRMS FAB+: Calc. 311.202980; found 311.202778.

**2h:** 3.5 h. Hexane-EtOAc 9:1. Colorless oil, 81%.

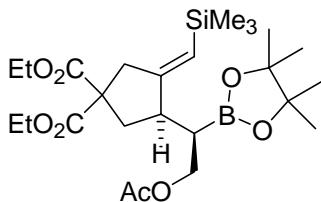


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.37 - 7.17 (m, 5H), 6.31 (m, 1H), 4.26 (d, *J* = 8.1 Hz, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 3.34 (d, *J* = 16.7 Hz, 1H), 3.24 (dt, *J* = 16.7, 2.9 Hz, 1H), 3.10-3.01 (m, 1H), 2.59 (dd, *J* = 7.7, 13.1 Hz, 1H), 2.24 (m, 1H), 2.05 (s, 3H), 1.97 (m, 1H), 1.26 (s, 6H), 1.24 (s, 6H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 172.14 (C), 172.11 (C), 171.07 (C), 144.55 (C), 138.00 (C), 128.34 (CH), 128.23 (CH), 126.21 (CH), 122.89 (CH), 83.48 (C), 83.24 (C), 64.78 (CH<sub>2</sub>), 59.52 (C), 59.79 (CH<sub>3</sub>), 59.77 (CH<sub>3</sub>), 42.62 (CH), 39.29 (CH<sub>2</sub>), 37.20 (CH<sub>2</sub>), 24.92 (CH<sub>3</sub>), 24.89 (CH<sub>3</sub>), 24.61 (CH), 20.99 (CH<sub>3</sub>).

HRMS ESI :Calc. 487.250324; found 487.251941.

**2i:** 50 h. Hexane-EtOAc 20:1 After 25 h, Pd(OAc)<sub>2</sub> (0.05 equiv) and MeOH (1 equiv) were added. Colorless oil, 79%.

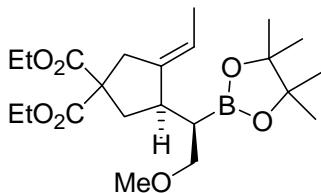


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.33 (m, 1H), 4.16 (m, 6H), 3.05 (dm, *J* = 16.6 Hz, 1H), 2.9 (dt, *J* = 16.6, 2.6 Hz, 1H), 2.80-2.70 (m, 1H), 2.50 (ddd, *J* = 1.6, 7.7, 12.6 Hz, 1H), 2.24 (dd, *J* = 11.5, 12.6 Hz, 1H), 2.00 (s, 3H), 1.86 (m, 1H), 1.23 (dt, *J* = 3.9, 7.1 Hz, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 0.07 (s, 9H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 171.71 (C), 171.02 (C), 160.39 (C), 149.53 (C), 119.87 (CH), 83.46 (C), 83.33 (C), 64.94 (CH<sub>2</sub>), 61.37 (CH<sub>2</sub>), 59.12 (C), 43.51 (CH), 40.61 (CH<sub>2</sub>), 36.99 (CH<sub>2</sub>), 27.72 (CH-B), 25.16 (CH<sub>3</sub>), 24.95 (CH<sub>3</sub>), 20.95 (CH<sub>3</sub>), 14.06 (CH<sub>3</sub>), -0.40 (CH<sub>3</sub>).

HRMS ESI: Calc. 511.2893; found 511.2904.

**2j:** 24 h. After 9 h, Pd(OAc)<sub>2</sub> (0.05 equiv) and MeOH (1 equiv) were added. Hexane-EtOAc 9:1. Colorless oil, 80%.



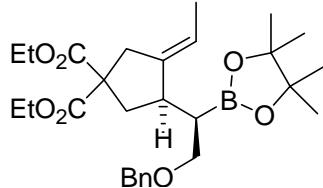
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.26 (m, 1H), 4.24 – 4.11 (m, 4H), 3.46 (d, *J* = 7.6 Hz, 2H), 3.29 (s, 3H), 2.97 (d, *J* = 16.4 Hz, 1H), 2.76 (dm, *J* = 15.8 Hz, 2H), 2.48 (dd, *J* =

7.6, 11.4Hz, 1H), 2.19 (dd,  $J = 11.4, 19.6$ Hz, 1H), 1.79 (m, 1H), 1.56 (d, 3H), 1.27-1.20 (m, 6H), 1.18 (s, 6H), 1.17 (s, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , DEPT-135)  $\delta$  172.10 (C), 172.08 (C), 142.71 (C), 116.07 (CH), 83.17 (C), 73.05 ( $\text{CH}_2$ ), 61.29 ( $\text{CH}_2$ ), 58.60 ( $\text{CH}_3$ ), 58.24 (C), 40.75 (CH), 37.86 ( $\text{CH}_2$ ), 37.17 ( $\text{CH}_2$ ), 28.55 (CH), 24.86 ( $\text{CH}_3$ ), 24.77 ( $\text{CH}_3$ ), 14.49 ( $\text{CH}_3$ ), 14.07 ( $\text{CH}_3$ ), 14.04 ( $\text{CH}_3$ ).

HRMS FAB+: Calc. 425.271059; found 425.70000.

**2k:** 4 h. Hexane-EtOAc 9:1. Colorless oil, 93%.

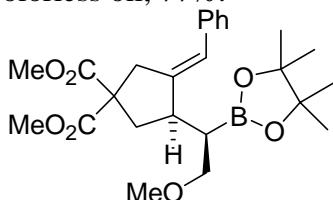


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.21 (m, 5H), 5.27 (m, 1H), 4.49 (d,  $J = 1.3$  Hz, 2H), 4.17 (m, 4H), 3.57 (m, 2H), 2.98 (d,  $J = 16.4$  Hz, 1H), 2.80 (m, 1H), 2.75 (dm,  $J = 16.4$  Hz, 1H), 2.48 (ddd,  $J = 12.6, 7.4, 1.6$  Hz, 1H), 2.22 (dd,  $J = 12.6, 1.2$  Hz, 1H), 1.80 (m, 1H), 1.57 (m, 3H), 1.23 (m, 6H), 1.17 (s, 6H), 1.16 (s, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , DEPT-135)  $\delta$  172.5 (C), 172.4 (C), 143.0 (C), 139.2 (C), 128.6 (CH), 127.8 (CH), 127.6 (CH), 116.5 (CH), 83.3 (C), 73.2 ( $\text{CH}_2$ ), 71.1 ( $\text{CH}_2$ ), 61.6 ( $\text{CH}_2$ ), 59.2 (C), 41.1 (CH), 38.2 ( $\text{CH}_2$ ), 37.6 ( $\text{CH}_2$ ), 29.2 (CH), 25.2 ( $\text{CH}_3$ ), 25.0 ( $\text{CH}_3$ ), 14.8 (CH<sub>3</sub>), 14.4 (CH<sub>3</sub>).

HRMS FAB+: Calc. 501.302359; found 501.303800.

**2l:** 3 h. Hexane-EtOAc 18:1. Colorless oil, 77%.

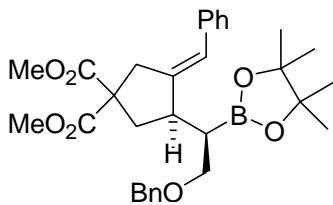


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.14 (m, 5H), 6.28 (d,  $J = 2.2$  Hz, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.53 (m, 2H), 3.32 (s, 3H), 3.28 (br s, 1H), 3.21 (dt,  $J = 17.1, 2.8$  Hz, 1H), 3.04 (m, 1H), 2.58 (dd,  $J = 12.8, 7.4$  Hz, 1H), 2.25 (dd,  $J = 12.8, 10.8$  Hz, 1H), 1.90 (m, 1H), 1.17 (s, 6H), 1.16 (s, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , DEPT-135)  $\delta$  172.6 (C), 172.5 (C), 145.6 (C), 138.5 (C), 128.6 (CH), 128.5 (CH), 126.3 (CH), 122.8 (CH), 83.5 (C), 73.1 ( $\text{CH}_2$ ), 59.9 (C), 58.9 ( $\text{CH}_3$ ), 53.0 ( $\text{CH}_3$ ), 52.9 ( $\text{CH}_3$ ), 43.0 (CH), 39.5 ( $\text{CH}_2$ ), 37.7 ( $\text{CH}_2$ ), 29.8 (CH), 25.2 ( $\text{CH}_3$ ), 24.9 ( $\text{CH}_3$ ).

HRMS FAB+: Calc. 459.255409; found 459.256545.

**2m:** 3h. Hexane-EtOAc 20:1. Colorless oil, 71%.

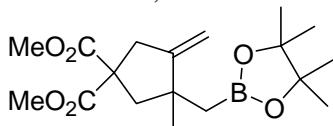


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34-7.10 (m, 10H), 6.26 (d, *J* = 2.5, 1H), 4.49 (m, 2H), 3.71 (s, 3H), 3.65 (s, 3H), 3.62 (m, 2H), 3.29 (d, *J* = 17.2 Hz, 1H), 3.17 (dt, *J* = 17.2, 2.8 Hz, 1H), 3.08 (m, 1H), 2.55 (ddd, *J* = 12.8, 7.6, 1.3 Hz, 1H), 2.25 (dd, *J* = 12.8, 10.8 Hz, 1H), 1.96 (m, 1H), 1.13 (s, 6H), 1.12 (s, 6H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 172.6 (C), 172.5 (C), 145.5 (C), 139.2 (C), 138.6 (C), 128.7 (CH), 128.6 (CH), 128.5 (CH), 127.9 (CH), 127.7 (CH), 126.4 (CH), 122.9 (CH), 83.6 (C), 73.3 (CH<sub>2</sub>), 70.8 (CH<sub>2</sub>), 59.9 (C), 53.1 (CH<sub>3</sub>), 53.0 (CH<sub>3</sub>), 43.1 (CH), 39.7 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 29.7 (CH), 25.3 (CH<sub>3</sub>), 25.0 (CH<sub>3</sub>).

HRMS FAB+: Calc. 535.286709; found 535.287900.

**2n:** 3 h. Hexane-EtOAc, 10:1 Colorless oil, 74%. It contains traces of **6** (98:2).

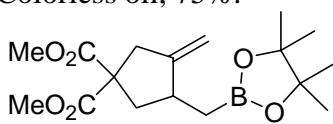


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.80 (m, 1H), 4.76 (m, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.06 (m, 2H), 2.48 (d, *J* = 13.80 Hz, 1H), 2.32 (d, *J* = 13.80 Hz, 1H), 1.20 (s, 12H), 1.10 (s, 3H), 0.98 (d, *J* = 4.60, Hz, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 172.88 (C), 172.68 (C), 158.96 (C), 104.52 (CH<sub>2</sub>), 83.06 (C), 82.94 (C), 57.67 (C), 52.76 (CH<sub>3</sub>), 52.68 (CH<sub>3</sub>), 47.87 (CH<sub>2</sub>), 40.80 (CH<sub>2</sub>), 38.11 (CH), 29.21 (CH<sub>3</sub>), 24.87 (CH<sub>3</sub>), 24.83 (CH<sub>3</sub>).

HRMS FAB+: Calc. 353.213544; found 353.215100.

**2o:** 3.5 h. Hexane-EtOAc 9:1. Colorless oil, 75%.

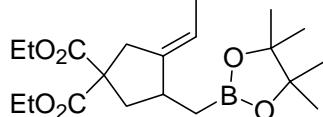


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.87 (m, 1H), 4.82 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.04 (dm, *J* = 16.95 Hz, 1H), 2.94 (dm, *J* = 16.95 Hz, 1H), 2.74-2.57 (m, 2H), 1.84 (dd, *J* = 10.3, 11.94 Hz, 1H), 1.24 (s, 12H), 1.08 (dd, *J* = 5.6, 15.71 Hz, 1H), 0.87 (dd, *J* = 7.77, 15.7 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 172.47 (C), 172.38 (C), 153.64 (C), 105.58 (CH<sub>2</sub>), 83.15 (C), 58.20 (C), 52.72 (CH<sub>3</sub>), 52.67 (CH<sub>3</sub>), 42.02 (CH<sub>2</sub>), 40.60 (CH<sub>2</sub>), 38.66 (CH), 24.90 (CH<sub>3</sub>), 24.76 (CH<sub>3</sub>), 15.73 (CH).

HRMS FAB+: Calc. 339.197894; found 339.198600.

**2p:** 6 h. Hexane-EtOAc 9:1. Colorless oil, 93%.

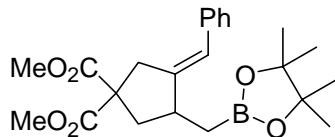


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.87 (m, 1H), 4.82 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.04 (dm, *J* = 16.95 Hz, 1H), 2.94 (dm, *J* = 16.95 Hz, 1H), 2.74-2.57 (m, 2H), 1.84 (dd, *J* = 10.3, 11.94 Hz, 1H), 1.24 (s, 12H), 1.08 (dd, *J* = 5.6, 15.71 Hz, 1H), 0.87 (dd, *J* = 7.77, 15.7 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 172.47 (C), 172.38 (C), 153.64 (C), 105.58 (CH<sub>2</sub>), 83.15 (C), 58.20 (C), 52.72 (CH<sub>3</sub>), 52.67 (CH<sub>3</sub>), 42.02 (CH<sub>2</sub>), 40.60 (CH<sub>2</sub>), 38.66 (CH), 24.90 (CH<sub>3</sub>), 24.76 (CH<sub>3</sub>), 15.73 (CH).

HRMS FAB+: Calc. 339.197894; found 339.198600.

**2q:** 70 h. After 23 h, Pd(OAc)<sub>2</sub> (0.05 equiv) and MeOH (1 equiv) were added. Hexane-EtOAc 9:1. Colorless oil. 86%.



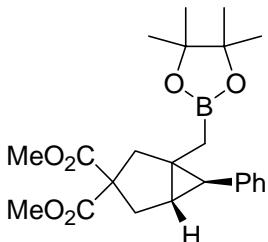
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.28 (m, 4H), 7.15 (m, 1H), 6.23 (d, *J* = 2.5 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.34 (d, *J* = 17.5 Hz, 1H), 3.19 (dt, *J* = 17.5, 2.5 Hz, 1H), 2.88 (m, 1H), 2.63 (ddd, *J* = 12.7, 7.2, 1.4 Hz, 1H), 1.87 (dd, *J* = 12.7, 11.6 Hz, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 1.18 (dd, *J* = 15.7, 5.8 Hz, 1H), 0.99 (dd, *J* = 15.7, 7.7 Hz, 1H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, DEPT-135) δ 172.7 (C), 172.6 (C), 147.0 (C), 138.4 (C), 128.7 (CH), 128.6 (CH), 126.5 (CH), 121.9 (CH), 83.5 (C), 59.4 (C), 53.1 (CH<sub>3</sub>), 53.0 (CH<sub>3</sub>), 41.5 (CH<sub>2</sub>), 40.8 (CH), 39.3 (CH<sub>2</sub>), 25.3 (CH<sub>3</sub>), 25.1 (CH<sub>3</sub>), 16.0 (CH<sub>2</sub>).

HRMS FAB+: Calc. 414.221369; found 414.222722.

Compounds **5** and **6** were obtained in the same conditions from the corresponding Ph-substituted enynes:

**5:** 8 h. Hexane-EtOAc 12:1. Colorless oil, 36%. It is obtained along with traces (93:7) of a different compound which seems to be the corresponding alkylboronate of the general structure reported in this work.

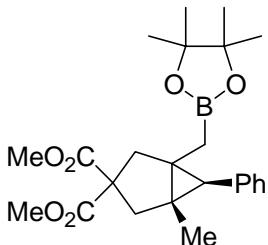


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.23-7.08 (m, 6H), 3.74 (s, 3H), 3.70 (s, 3H), 2.86 (d, *J* = 13.9 Hz, 1H), 2.74 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.66 (d, *J* = 13.5 Hz, 1H), 2.47 (d, *J* = 14.0 Hz, 1H), 1.73 (d, *J* = 4.2 Hz, 1H), 1.66 (m, 1H), 1.18 (s, 6H), 1.17 (s, 6H), 0.74 (m, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 173.51 (C), 172.68 (C), 139.03 (C), 129.00 (CH), 127.86 (CH), 125.61 (CH), 83.01 (C), 60.68 (C), 52.85 (CH<sub>3</sub>), 52.81 (CH<sub>3</sub>), 43.61 (CH<sub>2</sub>), 37.40 (CH<sub>2</sub>), 33.82 (C), 31.92 (CH), 29.08 (CH), 25.05 (CH<sub>3</sub>), 24.89 (CH<sub>3</sub>), 14.13 (CH<sub>2</sub>).

HRMS ESI: Calc. 415.2286; found 415.2303.

**6:** 30 h. After 8 h, Pd(OAc)<sub>2</sub> (0.05 equiv) and MeOH (1 equiv) were added. Hexane-EtOAc 15:1. Colorless oil, 30%.



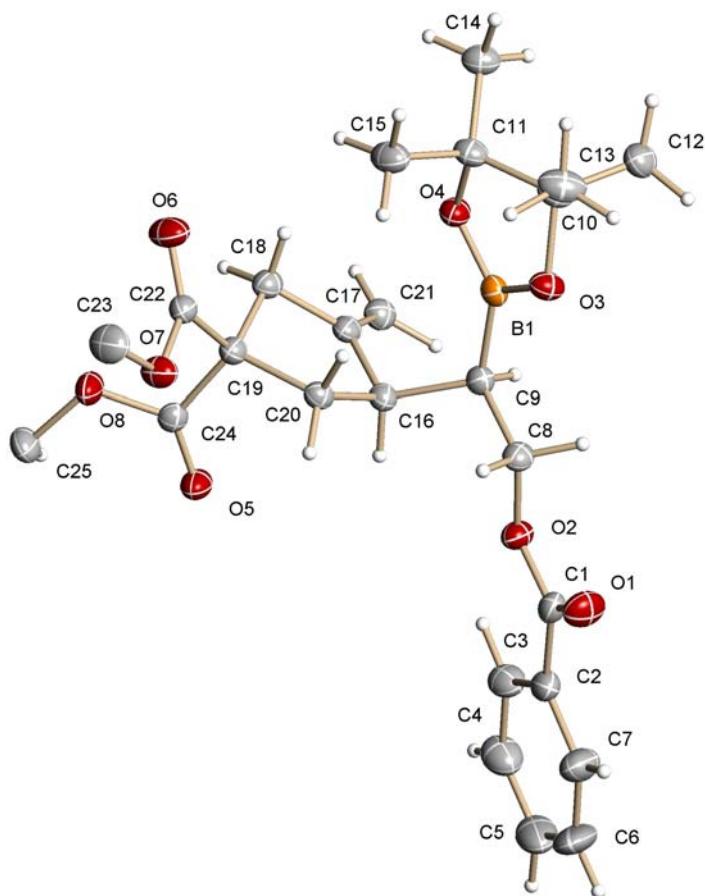
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.24-7.02 (m, 5H), 3.62 (s, 3H), 3.61 (s, 3H), 2.83 (d, *J* = 13.7 Hz, 1H), 2.77 (d, *J* = 13.6 Hz, 1H), 2.47 (d, *J* = 13.7 Hz, 1H), 2.38 (d, *J* = 13.6 Hz, 1H), 1.56 (s, 1H), 1.16 (s, 12H), 0.96 (s, 3H), 0.81 (d, *J* = 16.5 Hz, 1H), 0.59 (d, *J* = 16.5 Hz, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, DEPT-135) δ 173.9 (C), 173.1 (C), 138.3 (C), 131.6 (CH), 128.2 (CH), 126.0 (CH), 83.8 (C), 83.5 (C), 59.1 (C), 53.1 (CH<sub>3</sub>), 53.0 (CH<sub>3</sub>), 45.3 (CH<sub>2</sub>), 44.4 (CH<sub>2</sub>), 33.1 (C), 32.2 (CH), 31.9 (C), 25.4 (CH<sub>3</sub>), 25.2 (CH<sub>3</sub>), 15.7 (CH<sub>3</sub>), 11.8 (CH<sub>2</sub>).

HRMS FAB+: Calc. 428.237019; found 428.236600.

### X-ray diffraction analysis of **2b**

Single crystals of **2b** suitable for X-ray diffraction were obtained by slow evaporation of a solution of the compound in hexane at room temperature. Details of the crystal structure, data acquisition and refining are given in the following tables.



**Table 1.** Crystal data and structure refinement for **2b**.

Empirical formula	C <sub>25</sub> H <sub>33</sub> B <sub>1</sub> O <sub>8</sub>
Formula weight	472.32
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P2(1)/c

Unit cell dimensions	$a = 11.9275(3) \text{ \AA}$	$\alpha = 90^\circ$ .
	$b = 6.0749(2) \text{ \AA}$	$\beta = 93.038(2)^\circ$ .
	$c = 34.4730(8) \text{ \AA}$	$\gamma = 90^\circ$ .
Volume	$2494.35(12) \text{ \AA}^3$	
Z	4	
Density (calculated)	$1.258 \text{ Mg/m}^3$	
Absorption coefficient	$0.761 \text{ mm}^{-1}$	
F(000)	1008	
Crystal size	$0.10 \times 0.08 \times 0.04 \text{ mm}^3$	
Theta range for data collection	2.57 to 67.70°.	
Index ranges	-12≤h≤14, -6≤k≤6, -40≤l≤37	
Reflections collected	13510	
Independent reflections	4403 [R(int) = 0.0675]	
Completeness to theta = 67.70°	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	4403 / 0 / 439	
Goodness-of-fit on $F^2$	0.983	
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0444, wR_2 = 0.0997$	
R indices (all data)	$R_1 = 0.0748, wR_2 = 0.1146$	
Largest diff. peak and hole	0.239 and -0.227 e. $\text{\AA}^{-3}$	

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**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
C(1)	-373(2)	-585(4)	1282(1)	25(1)
C(2)	-845(2)	-1401(4)	1649(1)	29(1)
C(3)	-620(2)	-370(4)	2003(1)	33(1)
C(4)	-1074(2)	-1198(5)	2335(1)	44(1)
C(5)	-1755(2)	-3047(6)	2311(1)	52(1)
C(6)	-1976(2)	-4073(6)	1958(1)	59(1)
C(7)	-1522(2)	-3257(5)	1627(1)	44(1)
C(8)	780(2)	2074(4)	1000(1)	24(1)
C(9)	1416(2)	4141(4)	1115(1)	22(1)

C(10)	1876(2)	6323(4)	102(1)	27(1)
C(11)	2909(2)	7305(4)	340(1)	24(1)
C(12)	938(2)	7979(4)	31(1)	31(1)
C(13)	2131(3)	5146(4)	-272(1)	36(1)
C(14)	3128(2)	9717(4)	269(1)	28(1)
C(15)	3985(2)	6005(4)	296(1)	33(1)
C(16)	2370(2)	3689(4)	1426(1)	20(1)
C(17)	2911(2)	5773(3)	1596(1)	22(1)
C(18)	4153(2)	5743(4)	1521(1)	23(1)
C(19)	4433(2)	3292(4)	1473(1)	21(1)
C(20)	3343(2)	2344(4)	1271(1)	20(1)
C(21)	2369(2)	7314(4)	1782(1)	25(1)
C(22)	5427(2)	2852(4)	1222(1)	22(1)
C(23)	6497(2)	-25(5)	964(1)	37(1)
C(24)	4673(2)	2271(3)	1871(1)	21(1)
C(25)	6103(2)	1575(5)	2358(1)	32(1)
B(1)	1831(2)	5330(4)	740(1)	22(1)
O(1)	-531(1)	-1448(3)	968(1)	37(1)
O(2)	257(1)	1219(2)	1341(1)	25(1)
O(3)	1469(1)	4691(2)	375(1)	26(1)
O(4)	2591(1)	7022(2)	741(1)	24(1)
O(5)	3986(1)	1498(3)	2074(1)	28(1)
O(6)	5980(1)	4205(3)	1069(1)	34(1)
O(7)	5571(1)	678(3)	1186(1)	28(1)
O(8)	5762(1)	2451(3)	1980(1)	29(1)

**Table 3.** Bond lengths [Å] and angles [°]

C(1)-O(2)	1.339(3)	C(5)-C(6)	1.380(5)
C(1)-C(2)	1.494(3)	C(5)-H(5)	0.99(3)
C(2)-C(3)	1.386(4)	C(6)-C(7)	1.382(4)
C(2)-C(7)	1.387(4)	C(6)-H(6)	0.92(4)
C(3)-C(4)	1.388(4)	C(7)-H(7)	0.96(3)
C(3)-H(3)	0.98(3)	C(8)-O(2)	1.456(2)
C(4)-C(5)	1.386(5)	C(8)-C(9)	1.509(3)
C(4)-H(4)	0.96(4)	C(8)-H(8A)	0.98(2)

C(8)-H(8B)	1.02(2)	C(22)-O(6)	1.193(3)
C(9)-C(16)	1.547(3)	C(22)-O(7)	1.338(3)
C(9)-B(1)	1.583(3)	C(23)-O(7)	1.442(3)
C(9)-H(9A)	1.00(2)	C(24)-O(5)	1.200(3)
C(10)-O(3)	1.466(3)	C(24)-O(8)	1.337(2)
C(10)-C(12)	1.515(3)	C(25)-O(8)	1.448(3)
C(10)-C(13)	1.521(3)	B(1)-O(3)	1.367(3)
C(10)-C(11)	1.562(3)	B(1)-O(4)	1.371(3)
C(11)-O(4)	1.462(2)	O(1)-C(1)-O(2)	123.4(2)
C(11)-C(14)	1.511(3)	O(1)-C(1)-C(2)	124.5(2)
C(11)-C(15)	1.522(3)	O(2)-C(1)-C(2)	112.11(19)
C(12)-H(12B)	0.98(3)	C(3)-C(2)-C(1)	122.1(2)
C(12)-H(12A)	0.95(3)	C(7)-C(2)-C(1)	117.9(2)
C(12)-H(12C)	1.00(3)	O(2)-C(8)-C(9)	108.36(17)
C(13)-H(13A)	1.01(3)	O(2)-C(8)-H(8A)	106.2(14)
C(13)-H(13B)	0.97(3)	C(9)-C(8)-H(8A)	112.8(13)
C(13)-H(13C)	0.96(3)	O(2)-C(8)-H(8B)	106.8(13)
C(14)-H(14A)	0.98(2)	C(9)-C(8)-H(8B)	109.7(13)
C(14)-H(14C)	0.99(3)	H(8A)-C(8)-H(8B)	112.7(19)
C(14)-H(14B)	0.94(3)	C(8)-C(9)-C(16)	112.05(18)
C(15)-H(15C)	0.97(3)	C(8)-C(9)-B(1)	109.82(18)
C(15)-H(15B)	0.97(3)	C(16)-C(9)-B(1)	113.39(17)
C(15)-H(15A)	0.98(3)	C(8)-C(9)-H(9A)	108.4(13)
C(16)-C(17)	1.524(3)	C(16)-C(9)-H(9A)	106.5(13)
C(16)-C(20)	1.538(3)	B(1)-C(9)-H(9A)	106.3(14)
C(16)-H(16)	0.98(2)	O(3)-C(10)-C(12)	106.66(17)
C(17)-C(21)	1.322(3)	O(3)-C(10)-C(13)	108.30(18)
C(17)-C(18)	1.518(3)	C(12)-C(10)-C(13)	110.7(2)
C(18)-C(19)	1.537(3)	O(3)-C(10)-C(11)	101.54(16)
C(18)-H(18B)	0.94(2)	C(12)-C(10)-C(11)	112.77(19)
C(18)-H(18A)	0.96(3)	C(13)-C(10)-C(11)	116.0(2)
C(19)-C(24)	1.521(3)	O(4)-C(11)-C(14)	108.86(17)
C(19)-C(22)	1.529(3)	O(4)-C(11)-C(15)	107.22(17)
C(19)-C(20)	1.551(3)	C(14)-C(11)-C(15)	109.46(19)
C(20)-H(20B)	0.97(2)	O(4)-C(11)-C(10)	102.42(16)
C(20)-H(20A)	0.97(3)	C(14)-C(11)-C(10)	115.04(19)
C(21)-H(21B)	0.96(3)	C(15)-C(11)-C(10)	113.27(19)
C(21)-H(21A)	1.01(3)	C(17)-C(16)-C(20)	105.23(16)

C(17)-C(16)-C(9)	113.58(17)	C(16)-C(20)-H(20B)	109.4(13)
C(20)-C(16)-C(9)	113.26(17)	C(19)-C(20)-H(20B)	106.2(13)
C(17)-C(16)-H(16)	107.1(14)	C(16)-C(20)-H(20A)	114.2(14)
C(20)-C(16)-H(16)	109.2(13)	C(19)-C(20)-H(20A)	114.0(14)
C(9)-C(16)-H(16)	108.2(13)	H(20B)-C(20)-H(20A)	106.6(19)
C(21)-C(17)-C(18)	126.8(2)	C(17)-C(21)-H(21B)	122.9(14)
C(21)-C(17)-C(16)	124.49(19)	C(17)-C(21)-H(21A)	120.9(14)
C(18)-C(17)-C(16)	108.75(17)	H(21B)-C(21)-H(21A)	116(2)
C(17)-C(18)-C(19)	104.45(17)	O(6)-C(22)-O(7)	124.33(19)
C(17)-C(18)-H(18B)	111.2(12)	O(6)-C(22)-C(19)	126.3(2)
C(19)-C(18)-H(18B)	107.2(13)	O(7)-C(22)-C(19)	109.34(17)
C(17)-C(18)-H(18A)	111.9(14)	O(5)-C(24)-O(8)	123.6(2)
C(19)-C(18)-H(18A)	114.1(15)	O(5)-C(24)-C(19)	125.65(19)
H(18B)-C(18)-H(18A)	108(2)	O(8)-C(24)-C(19)	110.69(17)
C(24)-C(19)-C(22)	108.97(17)	O(3)-B(1)-O(4)	113.06(19)
C(24)-C(19)-C(18)	109.20(17)	O(3)-B(1)-C(9)	121.8(2)
C(22)-C(19)-C(18)	114.21(17)	O(4)-B(1)-C(9)	125.13(19)
C(24)-C(19)-C(20)	111.50(17)	C(1)-O(2)-C(8)	115.49(16)
C(22)-C(19)-C(20)	109.79(17)	B(1)-O(3)-C(10)	107.45(17)
C(16)-C(20)-C(19)	106.10(17)	B(1)-O(4)-C(11)	106.88(16)

**Table 4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^{*} b^{*} U^{12} ]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C(1)	19(1)	25(1)	32(1)	1(1)	-2(1)	-1(1)
C(2)	21(1)	30(1)	35(1)	8(1)	2(1)	1(1)
C(3)	30(1)	34(2)	35(1)	5(1)	10(1)	1(1)
C(4)	42(2)	52(2)	38(2)	11(1)	12(1)	7(1)
C(5)	36(1)	70(2)	50(2)	28(2)	14(1)	0(1)
C(6)	41(2)	63(2)	71(2)	31(2)	-1(2)	-26(2)
C(7)	40(1)	47(2)	46(2)	12(1)	-4(1)	-16(1)
C(8)	25(1)	27(1)	20(1)	2(1)	2(1)	-2(1)
C(9)	21(1)	21(1)	24(1)	1(1)	1(1)	1(1)
C(10)	37(1)	24(1)	20(1)	2(1)	1(1)	-2(1)

C(11)	30(1)	22(1)	21(1)	3(1)	5(1)	1(1)
C(12)	32(1)	33(2)	27(1)	4(1)	-3(1)	-1(1)
C(13)	58(2)	28(2)	23(1)	-1(1)	10(1)	-4(1)
C(14)	35(1)	23(1)	25(1)	0(1)	7(1)	-2(1)
C(15)	32(1)	29(2)	40(2)	7(1)	12(1)	4(1)
C(16)	21(1)	21(1)	19(1)	2(1)	1(1)	0(1)
C(17)	23(1)	24(1)	19(1)	5(1)	-1(1)	-2(1)
C(18)	24(1)	24(1)	21(1)	2(1)	0(1)	-3(1)
C(19)	21(1)	22(1)	21(1)	2(1)	0(1)	-2(1)
C(20)	24(1)	18(1)	19(1)	0(1)	0(1)	-1(1)
C(21)	27(1)	26(1)	22(1)	1(1)	0(1)	-1(1)
C(22)	21(1)	23(1)	22(1)	2(1)	0(1)	-1(1)
C(23)	33(1)	35(2)	43(2)	0(1)	14(1)	9(1)
C(24)	22(1)	18(1)	24(1)	-3(1)	0(1)	-1(1)
C(25)	29(1)	40(2)	26(1)	9(1)	-4(1)	1(1)
B(1)	21(1)	21(1)	24(1)	0(1)	0(1)	4(1)
O(1)	43(1)	35(1)	32(1)	-6(1)	-1(1)	-13(1)
O(2)	25(1)	27(1)	23(1)	2(1)	2(1)	-6(1)
O(3)	33(1)	23(1)	20(1)	2(1)	1(1)	-4(1)
O(4)	24(1)	26(1)	21(1)	3(1)	2(1)	-2(1)
O(5)	24(1)	36(1)	24(1)	7(1)	1(1)	-5(1)
O(6)	32(1)	28(1)	43(1)	6(1)	14(1)	-1(1)
O(7)	29(1)	24(1)	33(1)	1(1)	10(1)	3(1)
O(8)	22(1)	40(1)	25(1)	8(1)	-4(1)	-5(1)

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**Table 5.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

	x	y	z	U(eq)
H(18B)	4292(16)	6440(40)	1286(6)	13(5)
H(14A)	2481(19)	10640(40)	328(7)	21(6)
H(15C)	3875(19)	4430(50)	324(7)	26(6)
H(16)	2051(18)	2890(40)	1642(7)	21(6)
H(13A)	2680(20)	3900(50)	-223(8)	39(7)
H(14C)	3310(20)	9920(40)	-5(8)	31(7)

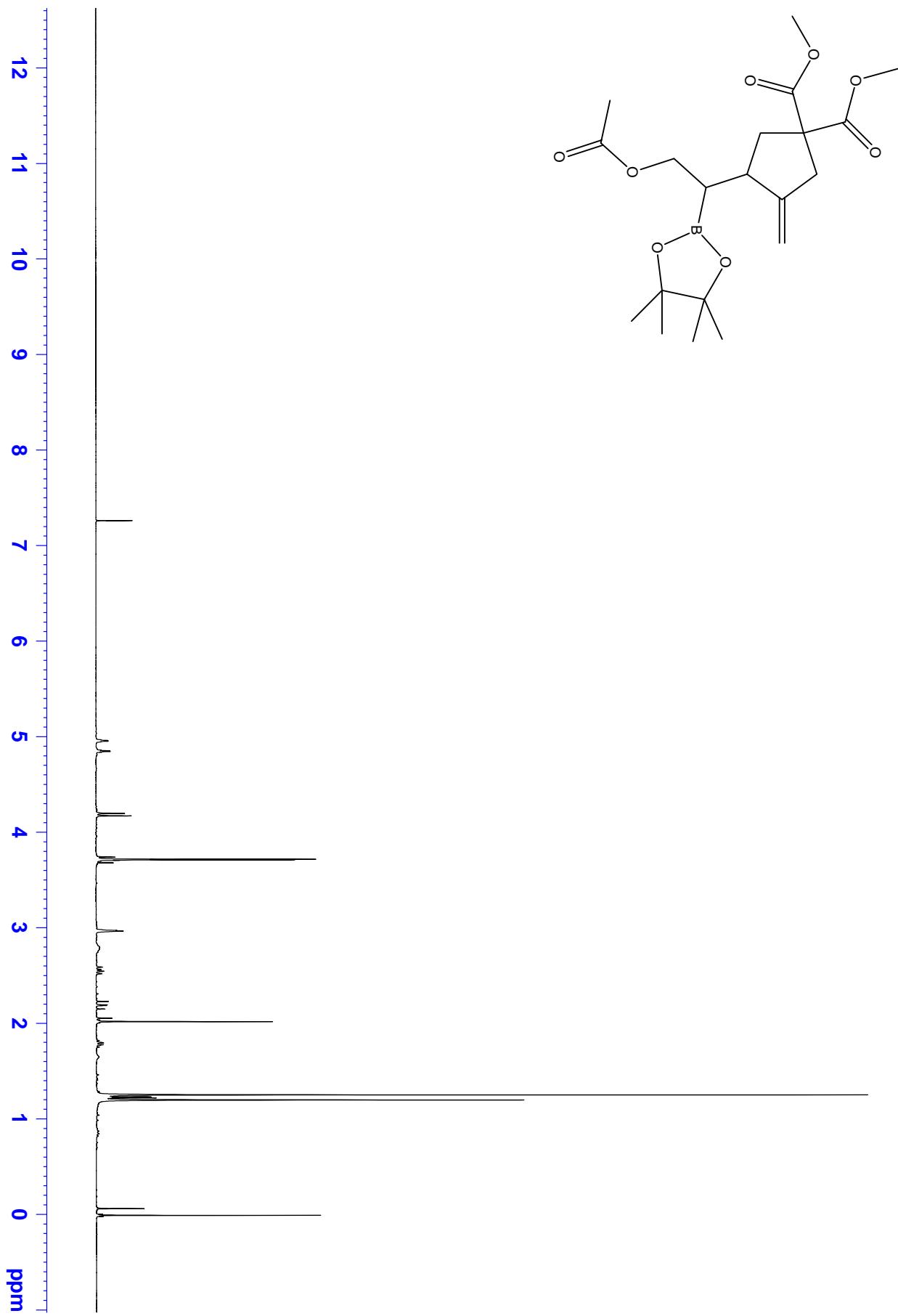
H(20B)	3393(17)	2630(40)	995(7)	16(5)
H(8A)	1270(19)	900(40)	912(7)	21(6)
H(9A)	885(19)	5180(40)	1235(7)	24(6)
H(18A)	4600(20)	6470(40)	1724(8)	29(6)
H(13B)	2430(20)	6170(50)	-457(8)	39(7)
H(21B)	2733(19)	8610(40)	1890(7)	25(6)
H(20A)	3263(19)	760(40)	1300(7)	26(6)
H(25A)	5700(20)	2290(40)	2563(8)	31(7)
H(12B)	270(20)	7140(40)	-62(8)	35(7)
H(5)	-2060(20)	-3570(50)	2556(9)	50(8)
H(12A)	1130(19)	9030(40)	-159(7)	25(6)
H(21A)	1530(20)	7220(40)	1806(7)	30(6)
H(12C)	750(20)	8730(40)	278(8)	33(7)
H(14B)	3760(20)	10280(50)	414(8)	37(7)
H(3)	-140(20)	940(50)	2010(7)	33(7)
H(8B)	150(20)	2440(40)	802(7)	23(6)
H(23B)	7190(20)	560(40)	1087(7)	27(6)
H(4)	-910(30)	-460(60)	2578(11)	68(11)
H(23A)	6500(20)	-1660(60)	976(8)	46(8)
H(13C)	1460(20)	4460(50)	-382(9)	48(8)
H(25B)	5940(20)	0(60)	2356(8)	44(8)
H(25C)	6920(30)	1710(50)	2380(9)	52(9)
H(15B)	4540(20)	6630(50)	480(8)	42(8)
H(15A)	4230(20)	6240(50)	31(8)	37(7)
H(23C)	6380(20)	460(50)	694(9)	48(8)
H(6)	-2420(30)	-5310(60)	1936(10)	65(10)
H(7)	-1660(30)	-4060(50)	1388(10)	54(9)

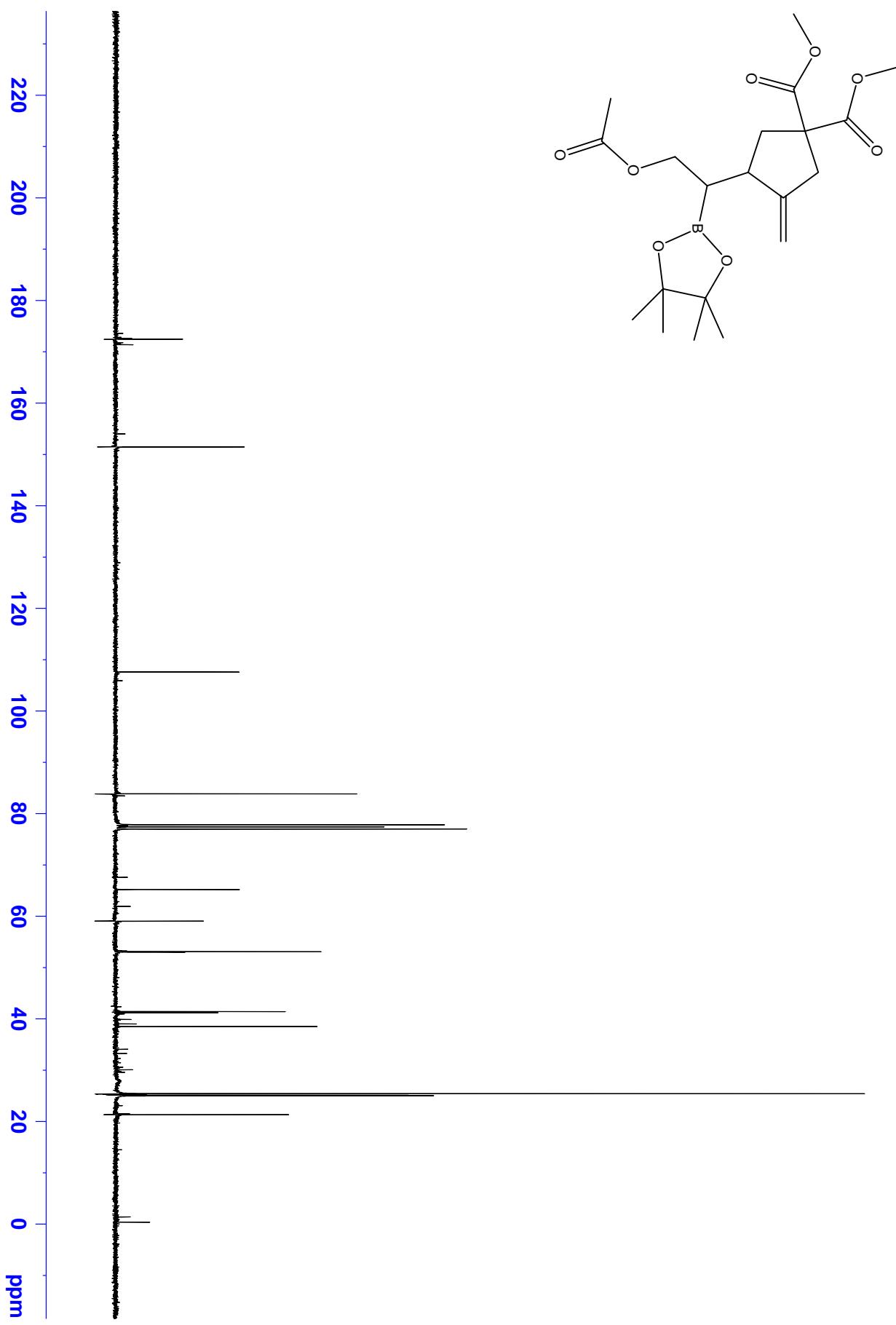
**Table 6.** Torsion angles [°]

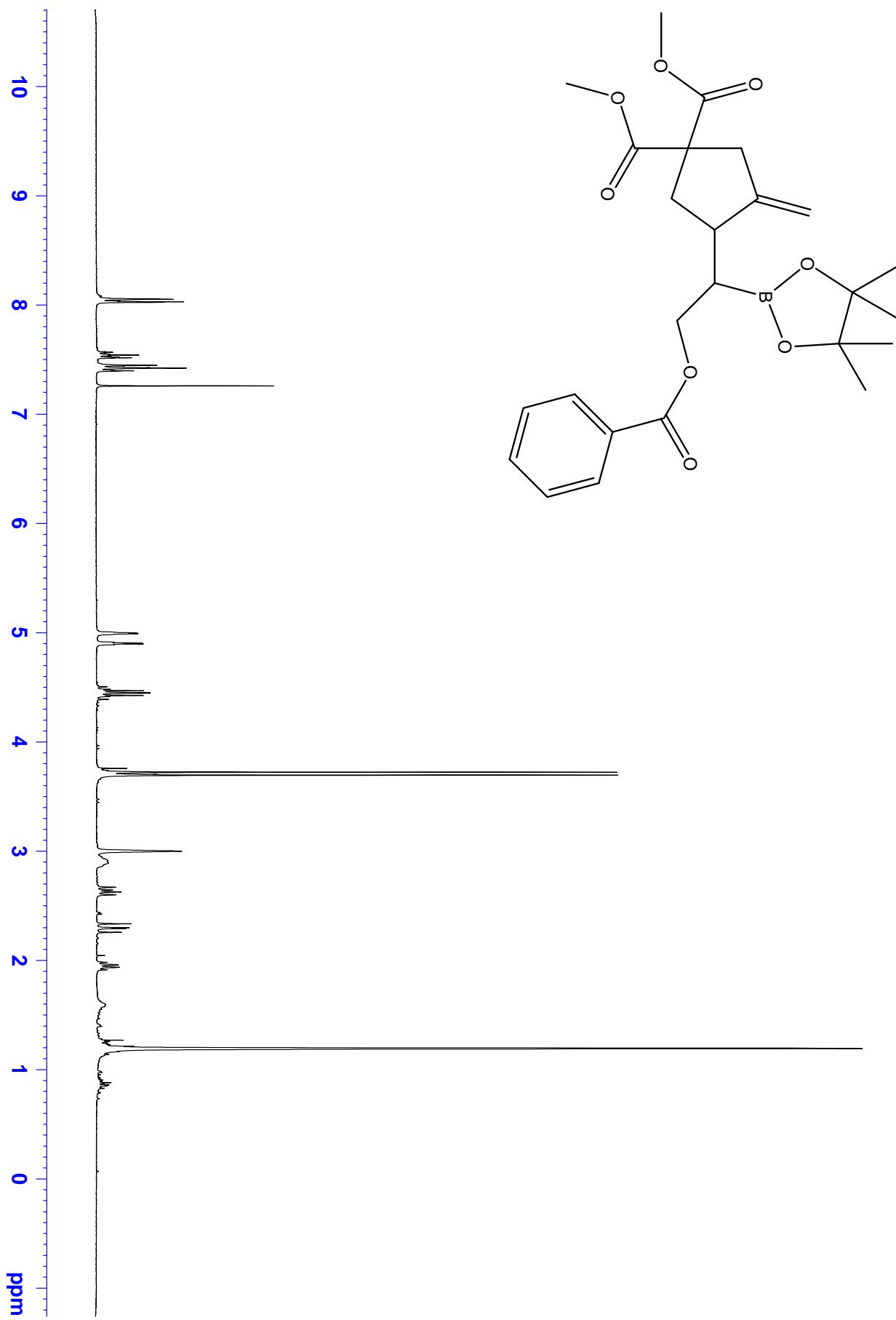
O(1)-C(1)-C(2)-C(3)	178.8(2)	C(2)-C(3)-C(4)-C(5)	-0.3(4)
O(2)-C(1)-C(2)-C(3)	-0.7(3)	C(3)-C(4)-C(5)-C(6)	0.4(4)
O(1)-C(1)-C(2)-C(7)	-0.9(4)	C(4)-C(5)-C(6)-C(7)	-0.1(5)
O(2)-C(1)-C(2)-C(7)	179.6(2)	C(5)-C(6)-C(7)-C(2)	-0.2(5)
C(7)-C(2)-C(3)-C(4)	0.0(4)	C(3)-C(2)-C(7)-C(6)	0.3(4)
C(1)-C(2)-C(3)-C(4)	-179.7(2)	C(1)-C(2)-C(7)-C(6)	180.0(3)

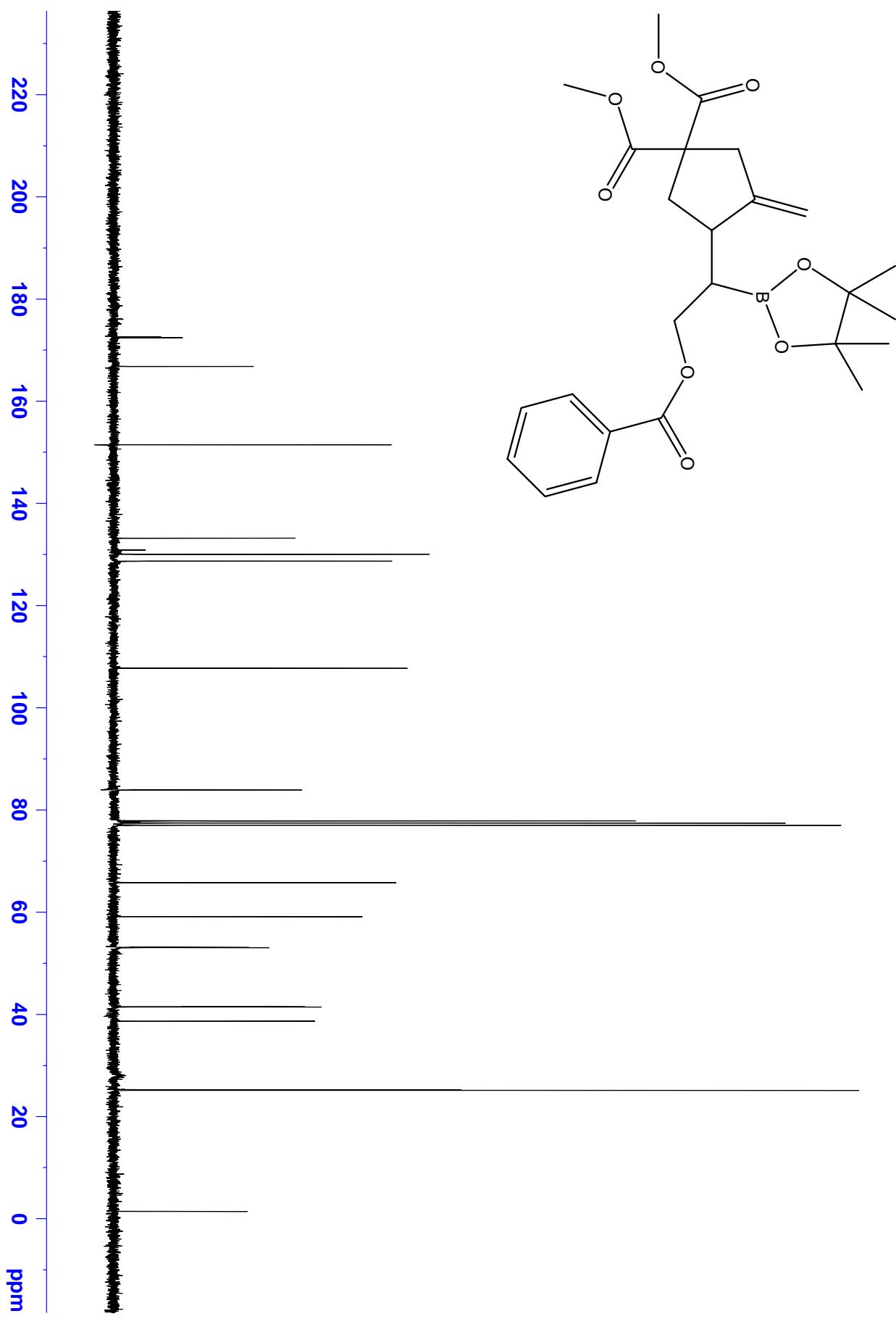
O(2)-C(8)-C(9)-C(16)	62.2(2)	C(20)-C(19)-C(22)-O(6)	115.6(2)
O(2)-C(8)-C(9)-B(1)	-170.89(16)	C(24)-C(19)-C(22)-O(7)	59.9(2)
O(3)-C(10)-C(11)-O(4)	-28.70(19)	C(18)-C(19)-C(22)-O(7)	-177.67(17)
C(12)-C(10)-C(11)-O(4)	85.1(2)	C(20)-C(19)-C(22)-O(7)	-62.4(2)
C(13)-C(10)-C(11)-O(4)	-145.83(19)	C(22)-C(19)-C(24)-O(5)	-147.2(2)
O(3)-C(10)-C(11)-C(14)	-146.62(18)	C(18)-C(19)-C(24)-O(5)	87.4(3)
C(12)-C(10)-C(11)-C(14)	-32.9(3)	C(20)-C(19)-C(24)-O(5)	-25.9(3)
C(13)-C(10)-C(11)-C(14)	96.3(2)	C(22)-C(19)-C(24)-O(8)	36.2(2)
O(3)-C(10)-C(11)-C(15)	86.4(2)	C(18)-C(19)-C(24)-O(8)	-89.1(2)
C(12)-C(10)-C(11)-C(15)	-159.81(19)	C(20)-C(19)-C(24)-O(8)	157.56(17)
C(13)-C(10)-C(11)-C(15)	-30.7(3)	C(8)-C(9)-B(1)-O(3)	10.2(3)
C(8)-C(9)-C(16)-C(17)	-170.93(17)	C(16)-C(9)-B(1)-O(3)	136.4(2)
B(1)-C(9)-C(16)-C(17)	64.1(2)	C(8)-C(9)-B(1)-O(4)	-168.0(2)
C(8)-C(9)-C(16)-C(20)	69.1(2)	C(16)-C(9)-B(1)-O(4)	-41.8(3)
B(1)-C(9)-C(16)-C(20)	-55.9(2)	O(1)-C(1)-O(2)-C(8)	-1.5(3)
C(20)-C(16)-C(17)-C(21)	-175.5(2)	C(2)-C(1)-O(2)-C(8)	177.97(18)
C(9)-C(16)-C(17)-C(21)	60.0(3)	C(9)-C(8)-O(2)-C(1)	177.79(17)
C(20)-C(16)-C(17)-C(18)	3.6(2)	O(4)-B(1)-O(3)-C(10)	-9.9(2)
C(9)-C(16)-C(17)-C(18)	-120.80(18)	C(9)-B(1)-O(3)-C(10)	171.65(19)
C(21)-C(17)-C(18)-C(19)	155.0(2)	C(12)-C(10)-O(3)-B(1)	-94.4(2)
C(16)-C(17)-C(18)-C(19)	-24.1(2)	C(13)-C(10)-O(3)-B(1)	146.4(2)
C(17)-C(18)-C(19)-C(24)	-84.2(2)	C(11)-C(10)-O(3)-B(1)	23.9(2)
C(17)-C(18)-C(19)-C(22)	153.50(17)	O(3)-B(1)-O(4)-C(11)	-10.0(2)
C(17)-C(18)-C(19)-C(20)	34.4(2)	C(9)-B(1)-O(4)-C(11)	168.30(19)
C(17)-C(16)-C(20)-C(19)	18.2(2)	C(14)-C(11)-O(4)-B(1)	146.28(19)
C(9)-C(16)-C(20)-C(19)	142.80(17)	C(15)-C(11)-O(4)-B(1)	-95.4(2)
C(24)-C(19)-C(20)-C(16)	84.3(2)	C(10)-C(11)-O(4)-B(1)	24.1(2)
C(22)-C(19)-C(20)-C(16)	-154.84(17)	O(6)-C(22)-O(7)-C(23)	3.3(3)
C(18)-C(19)-C(20)-C(16)	-32.7(2)	C(19)-C(22)-O(7)-C(23)	-178.61(19)
C(24)-C(19)-C(22)-O(6)	-122.0(2)	O(5)-C(24)-O(8)-C(25)	2.3(3)
C(18)-C(19)-C(22)-O(6)	0.4(3)	C(19)-C(24)-O(8)-C(25)	178.97(19)

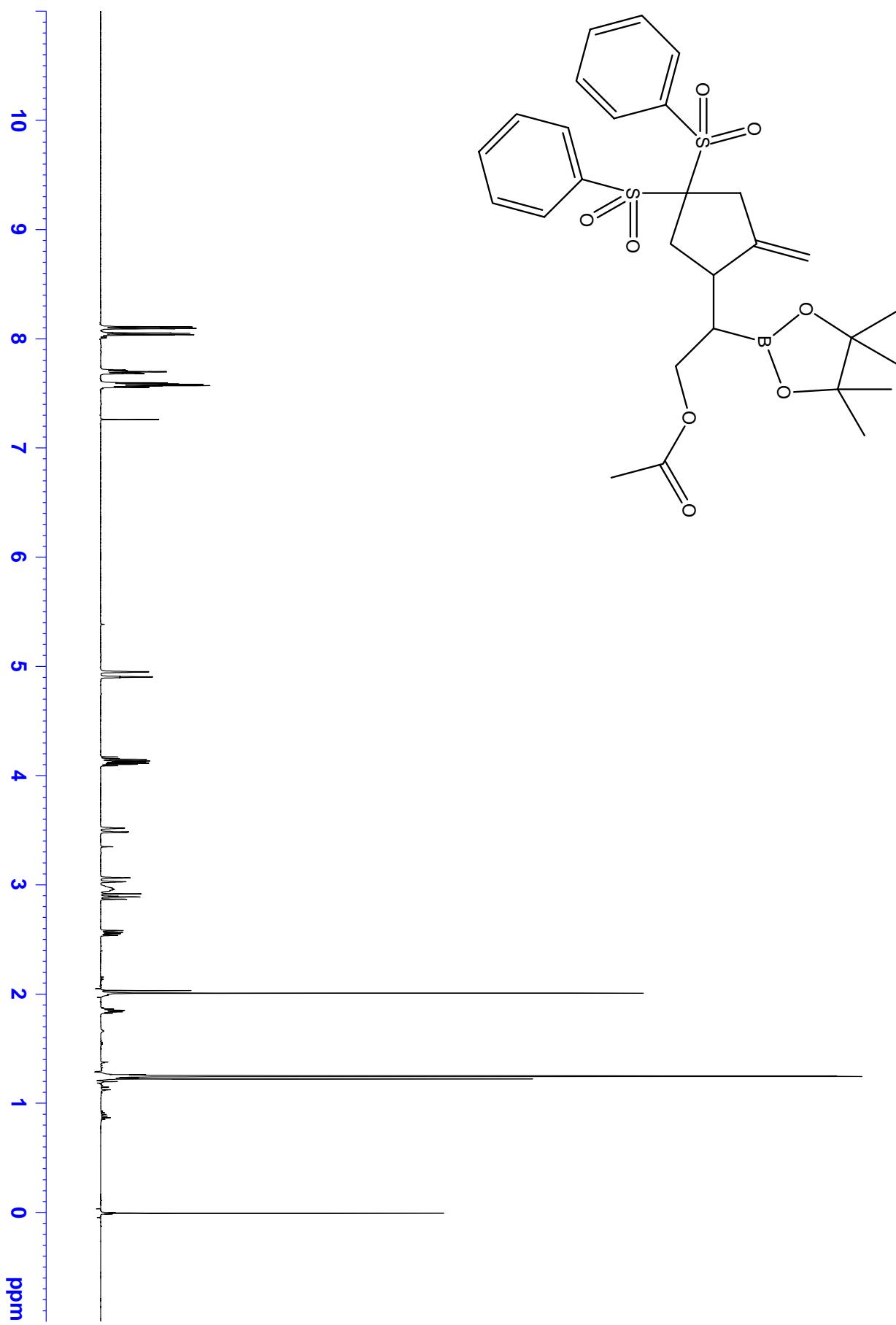
### **<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for alkylboronates**

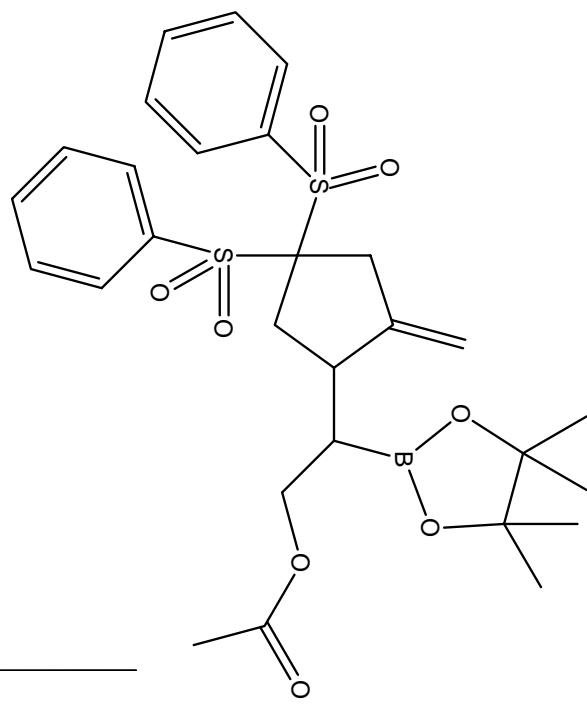


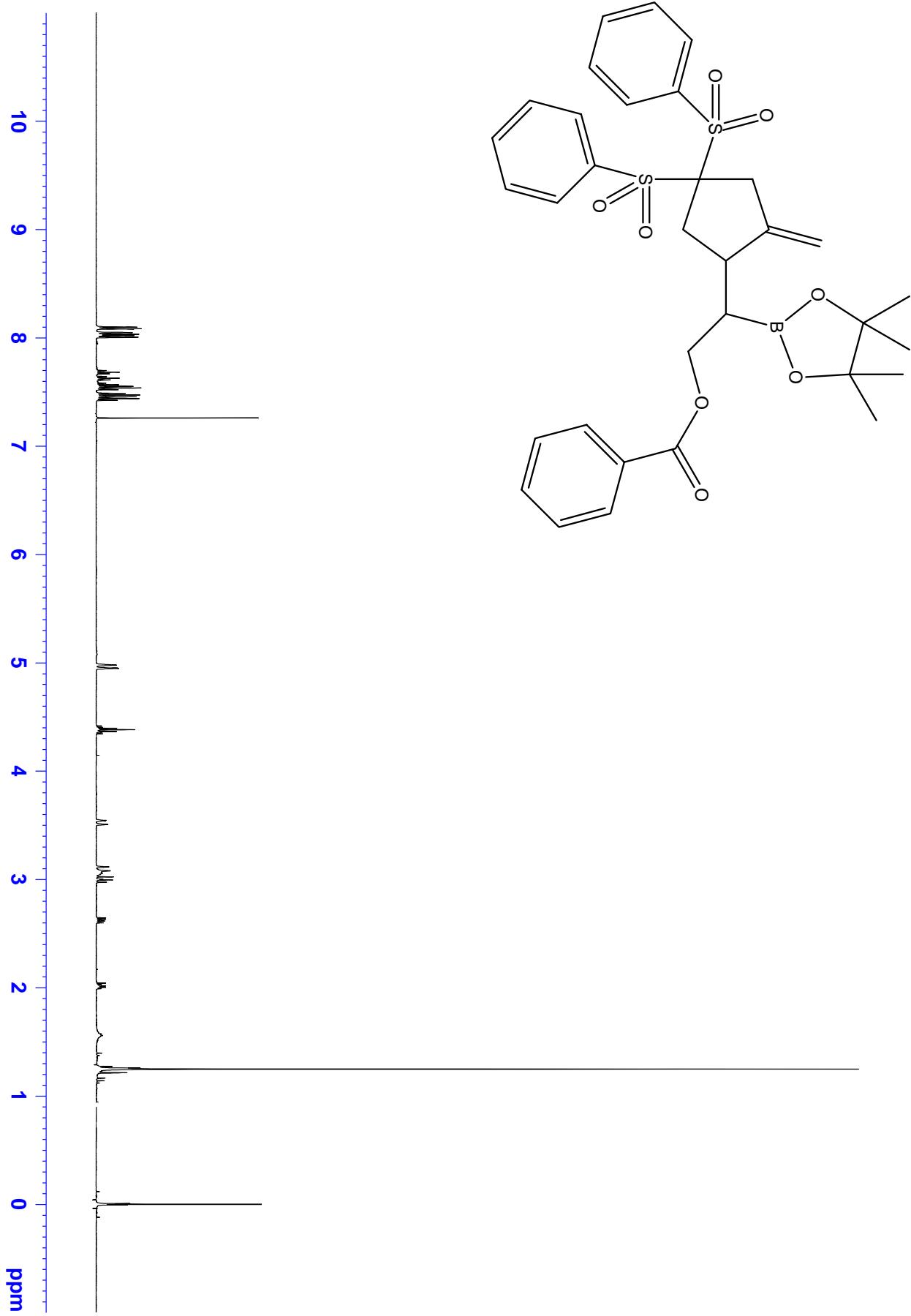


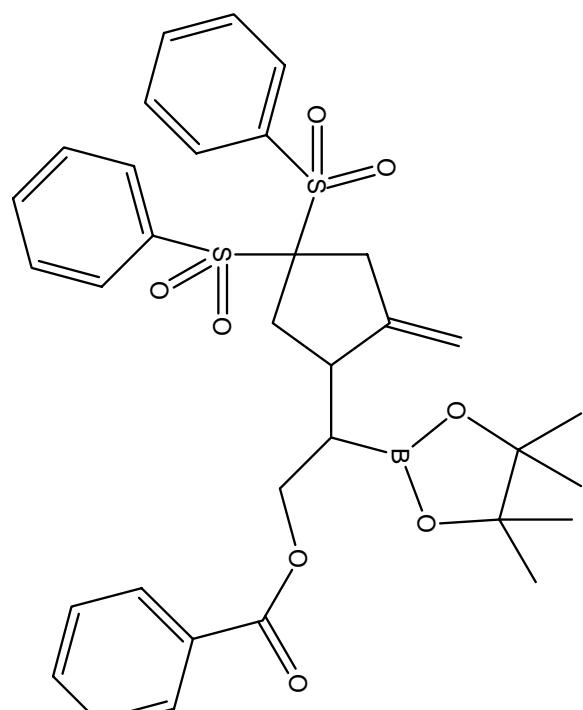


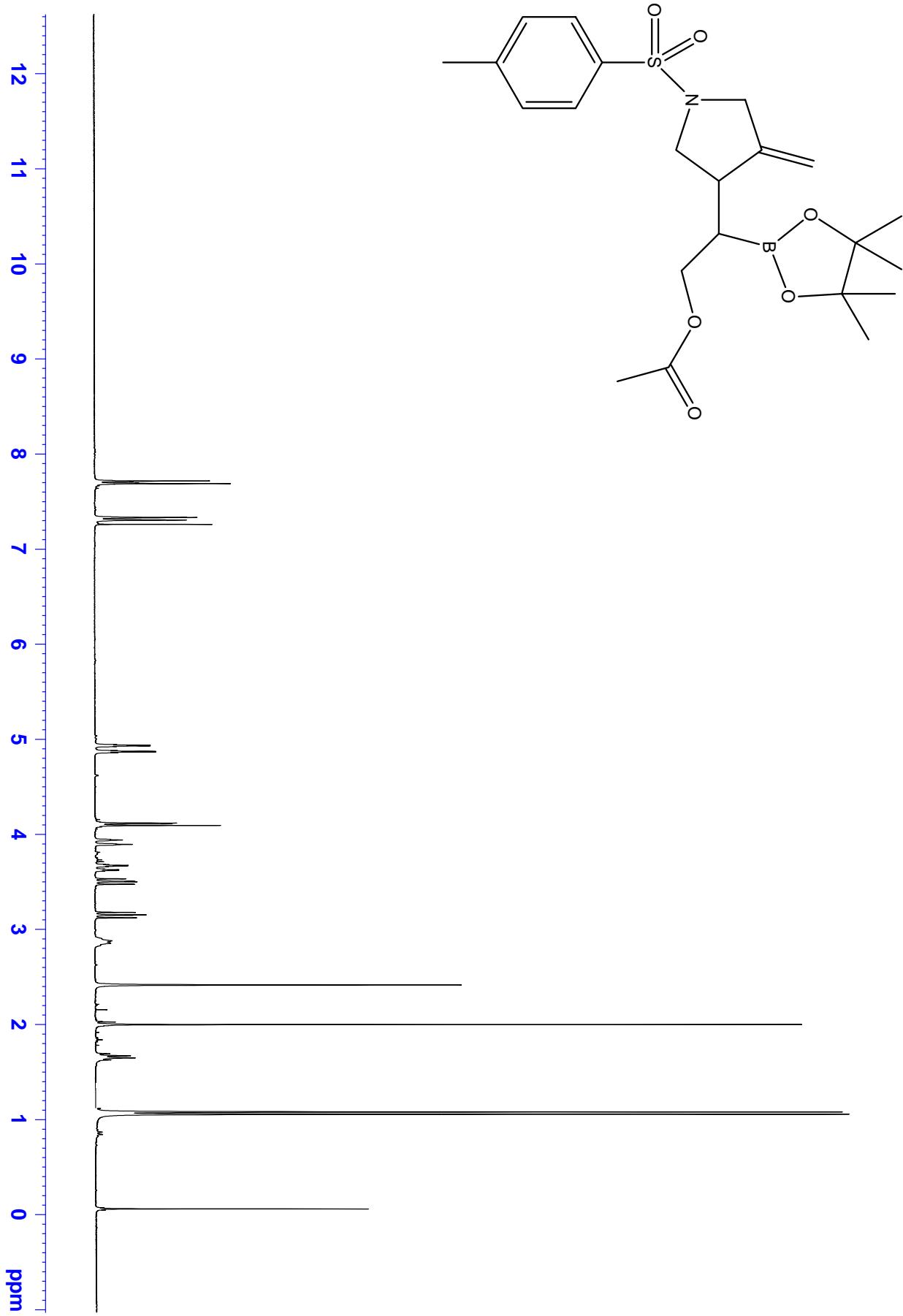


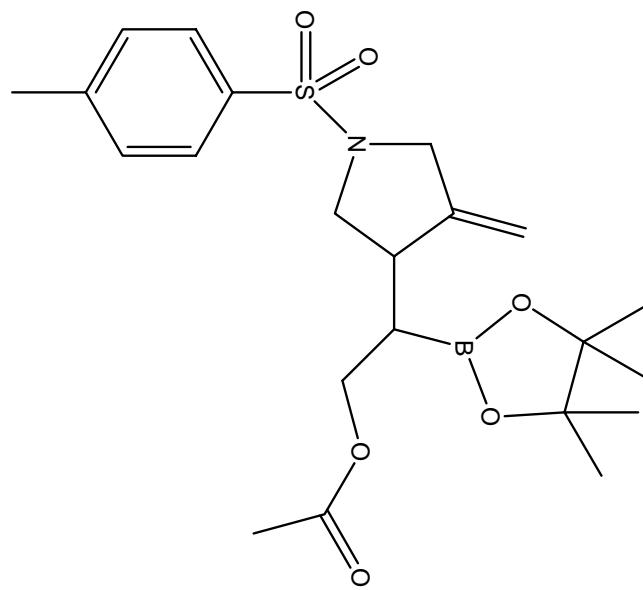
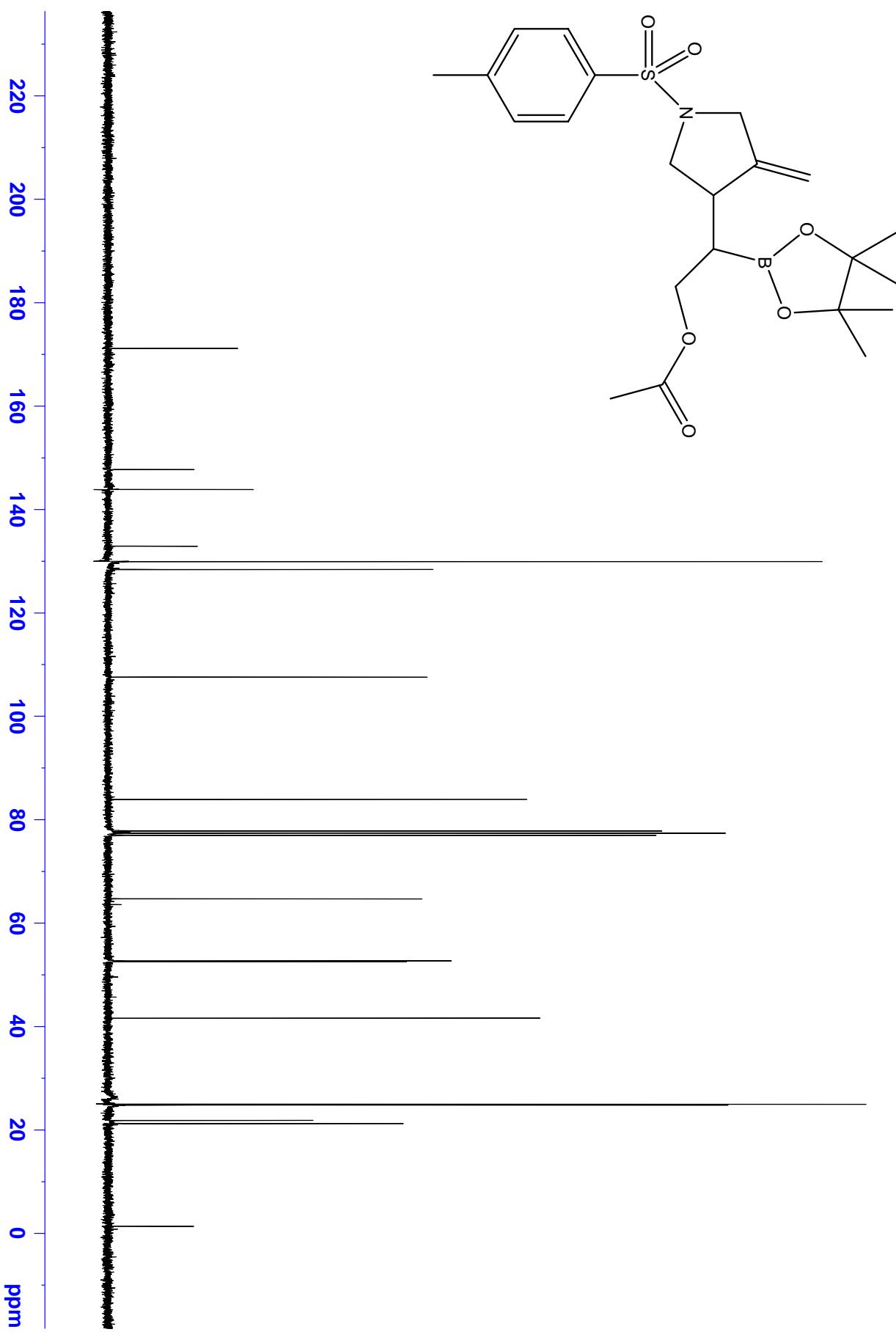


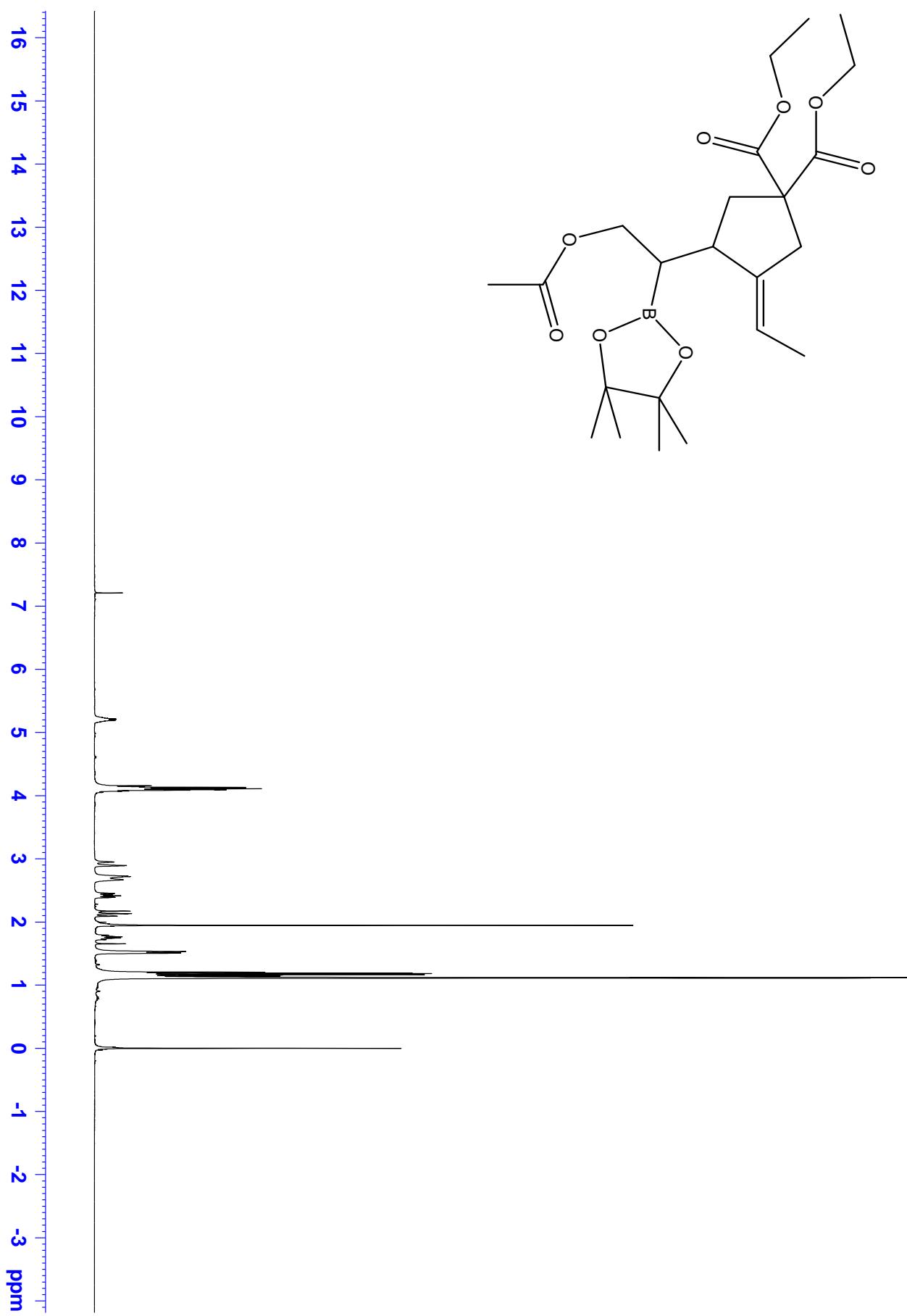


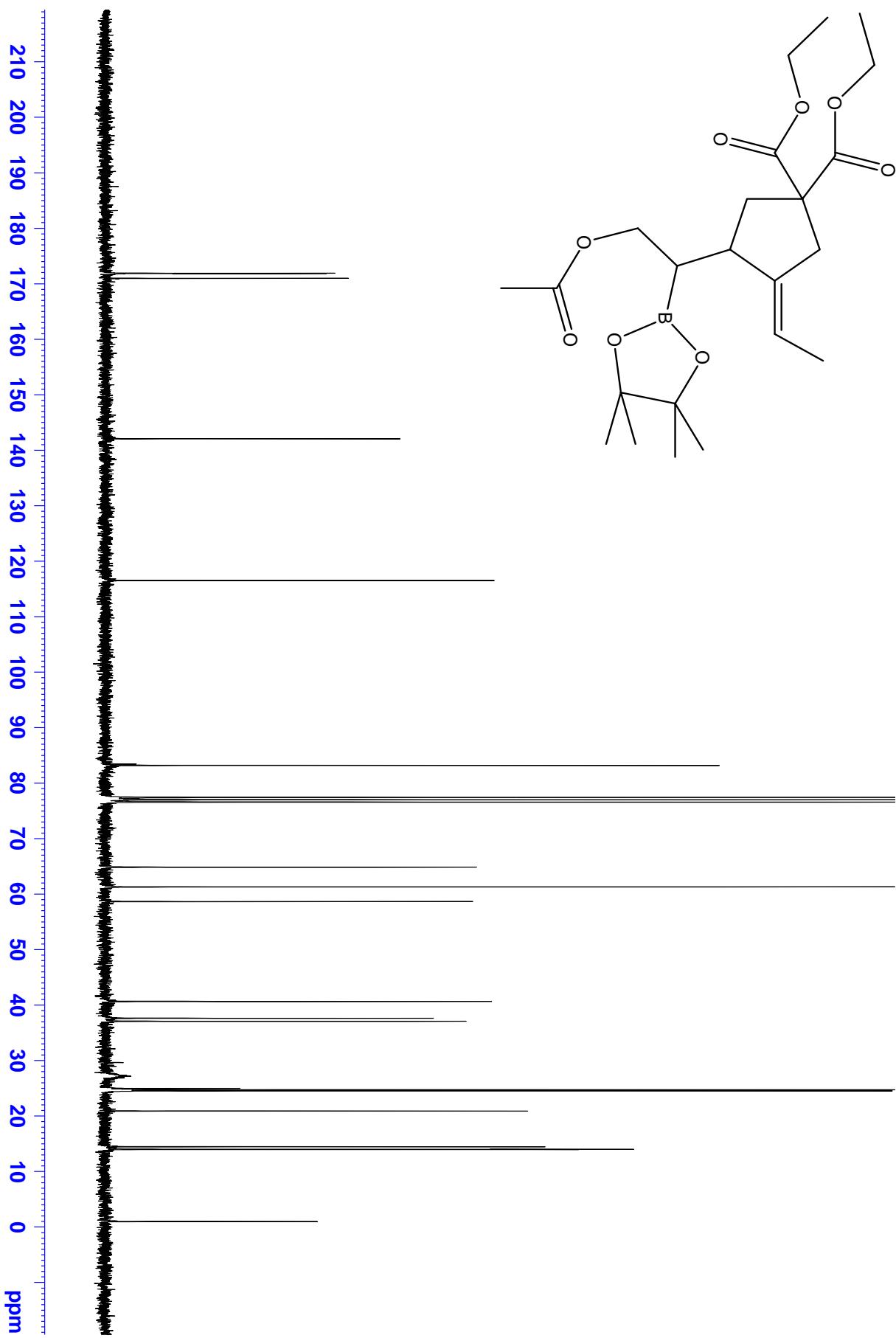


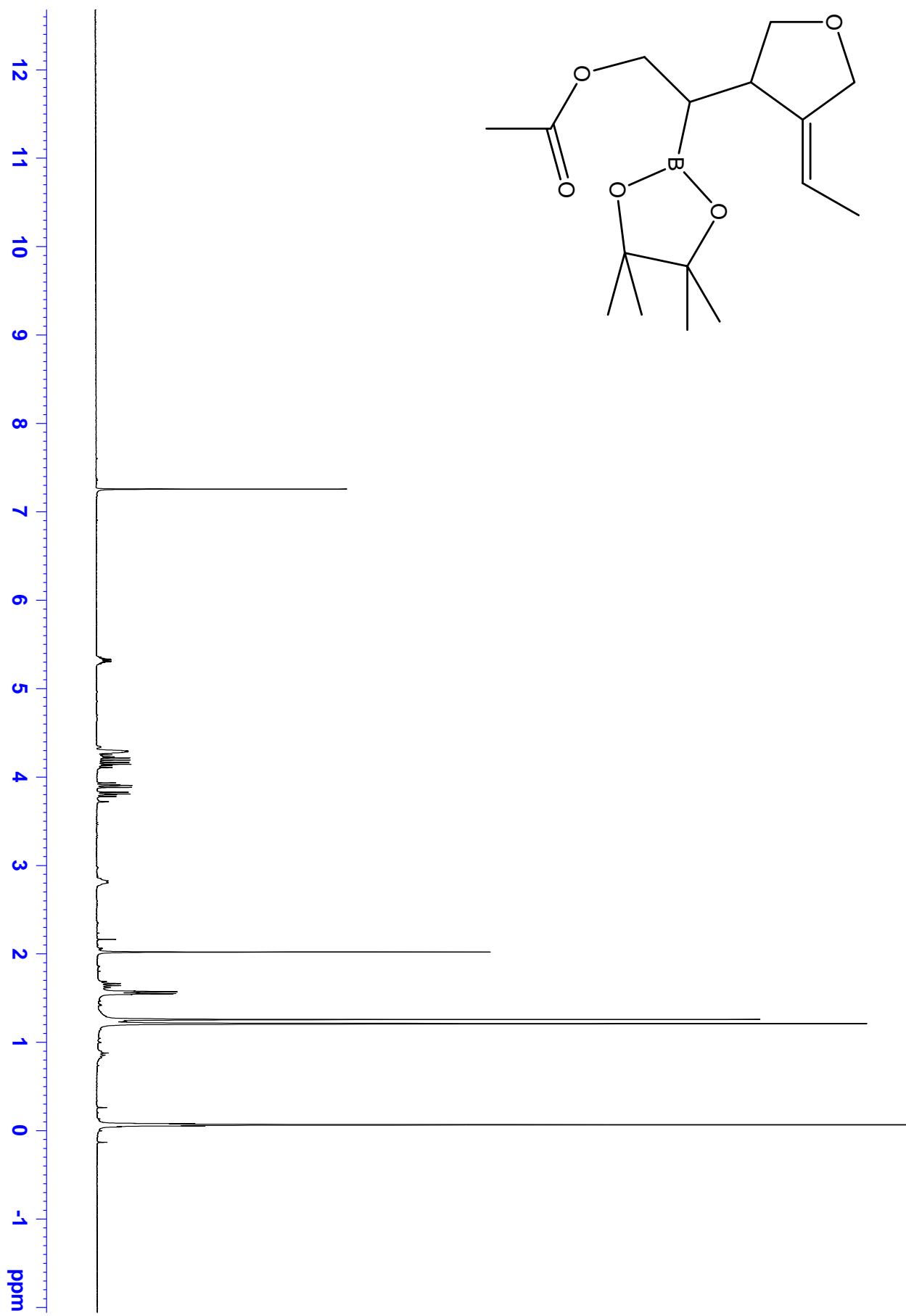


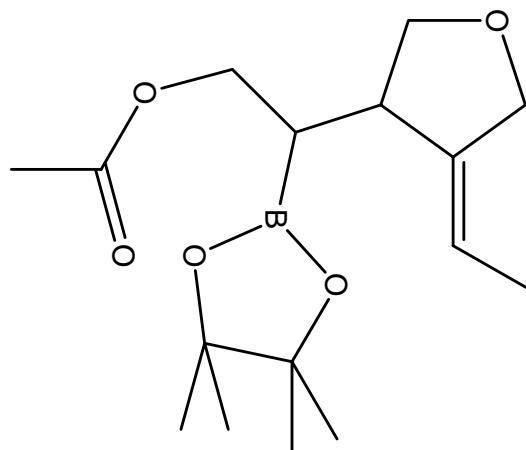
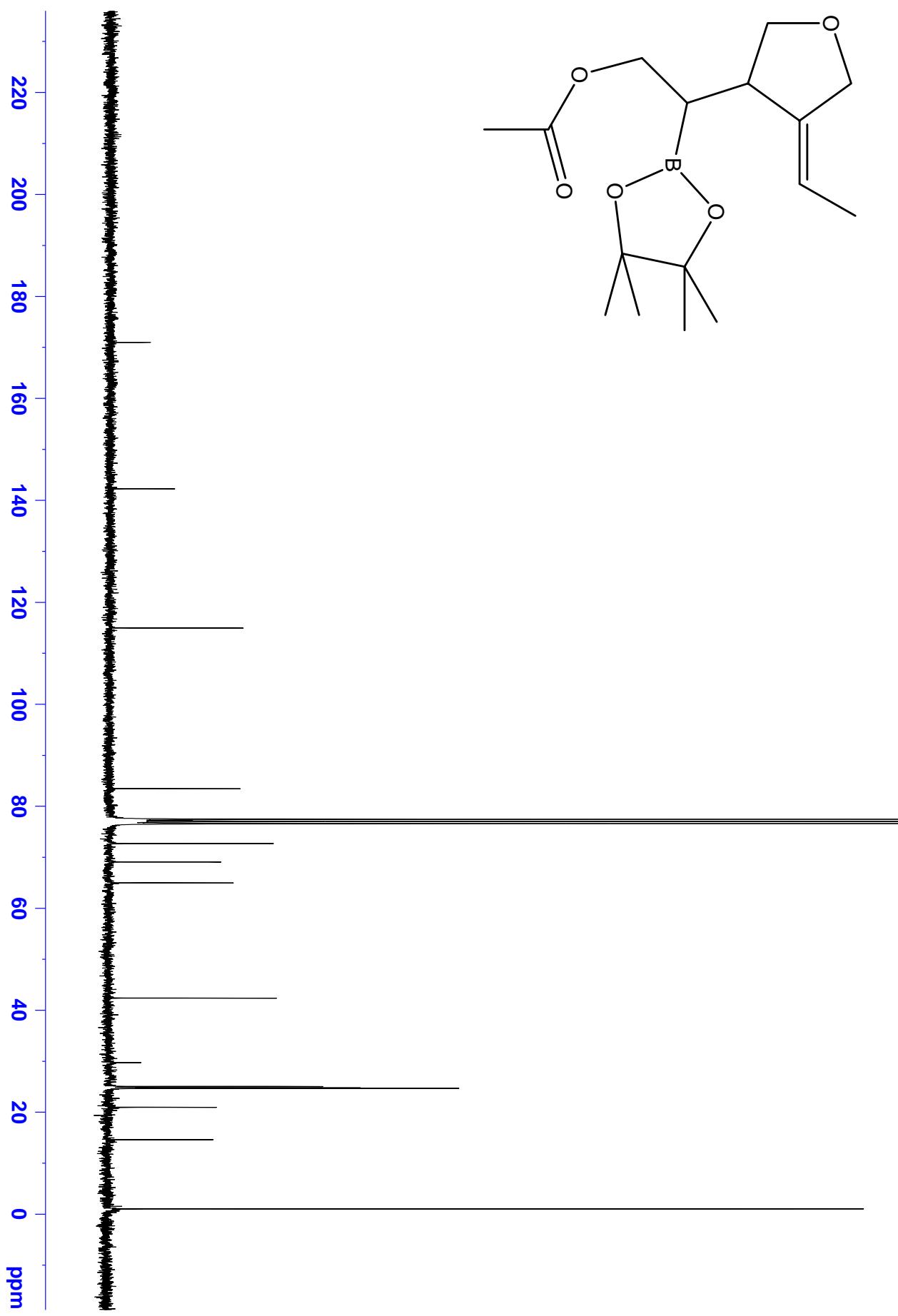




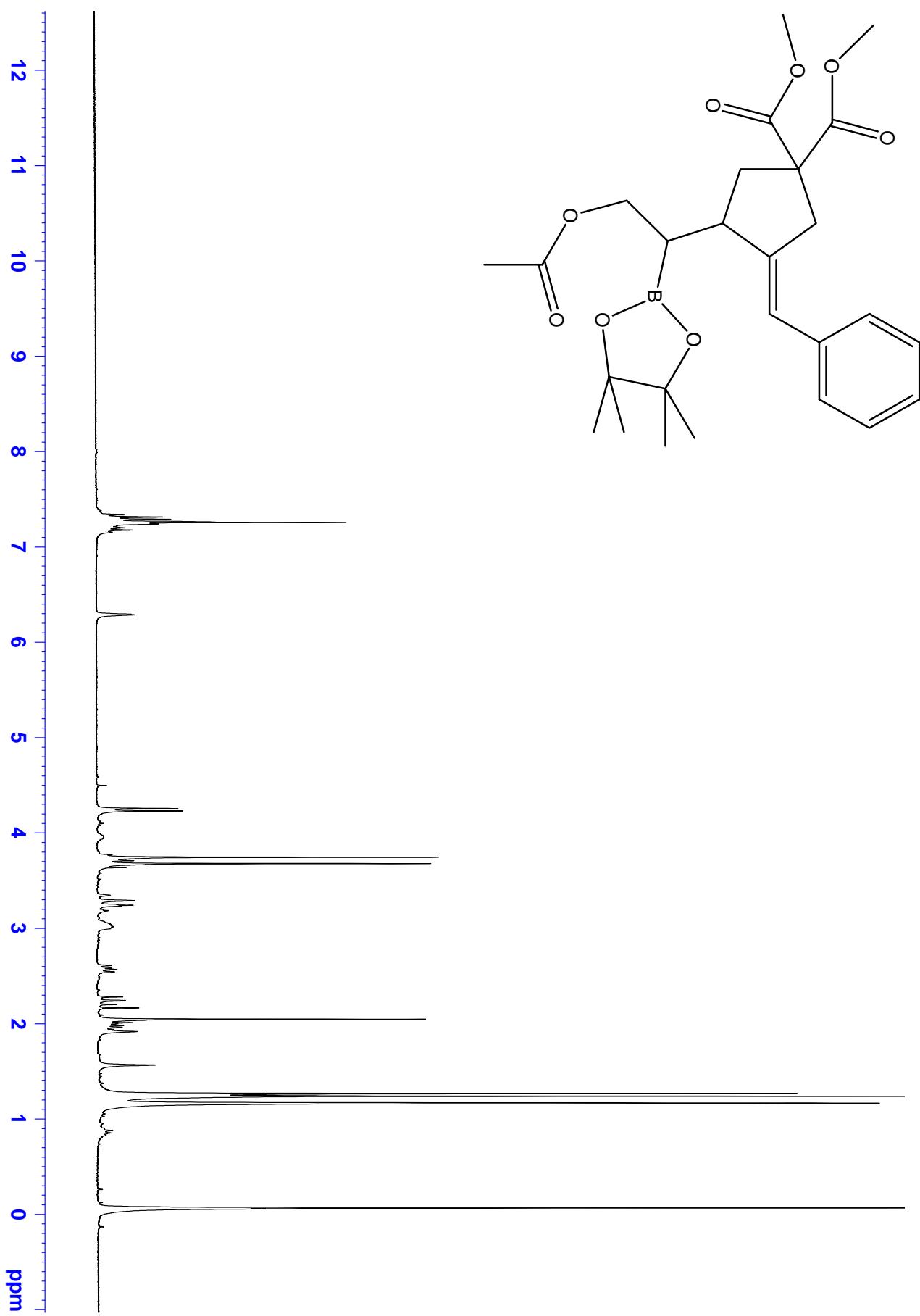




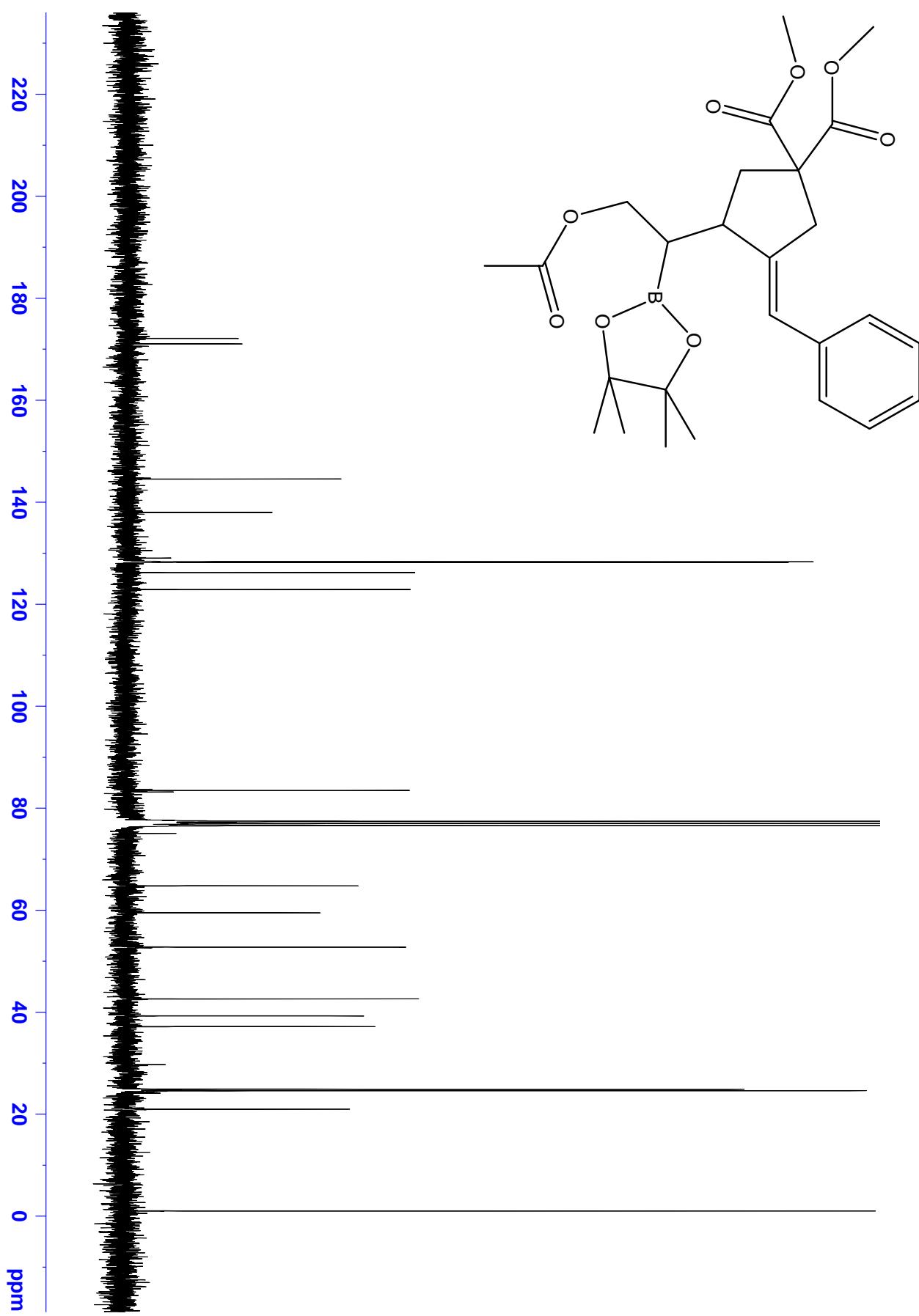


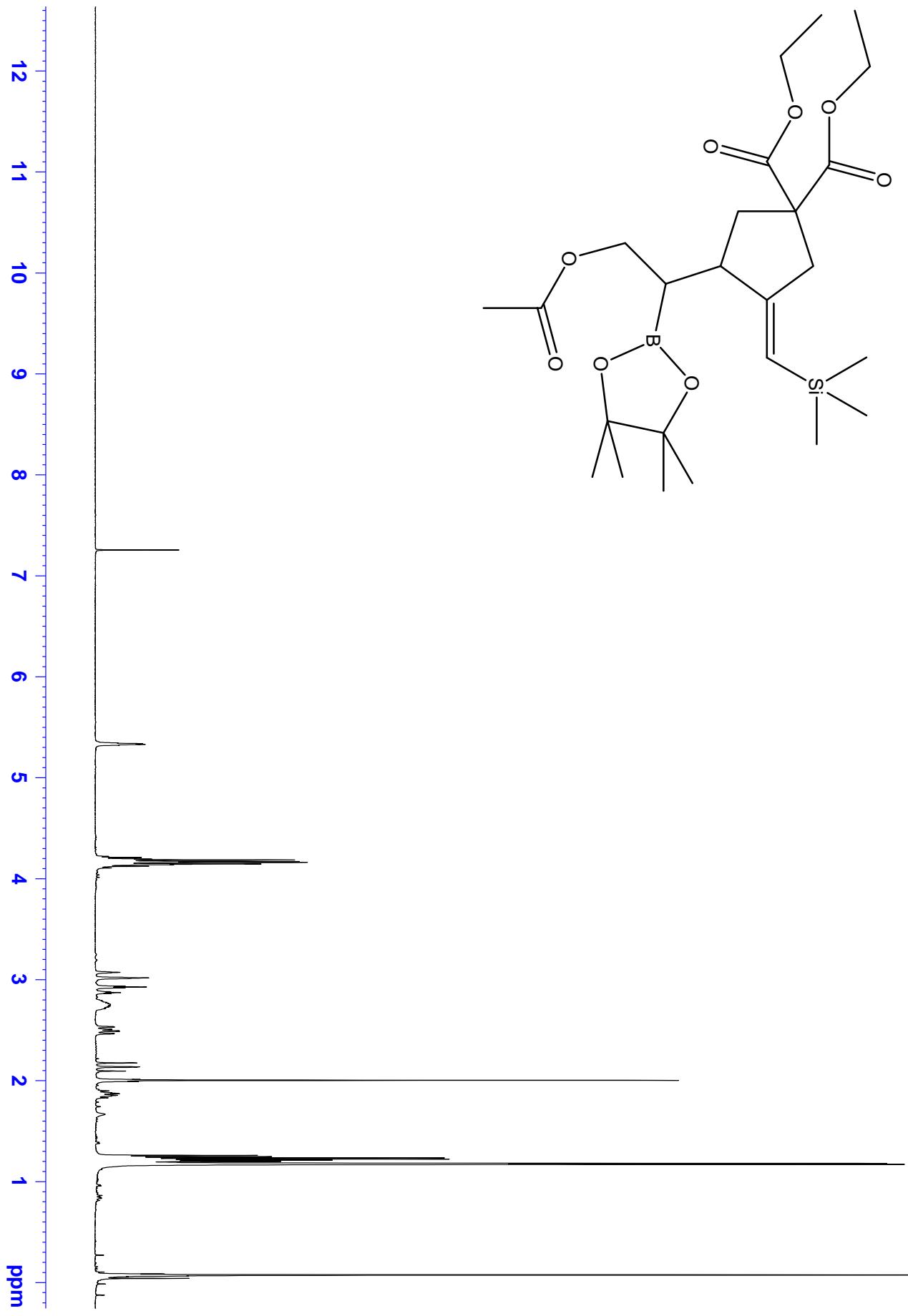


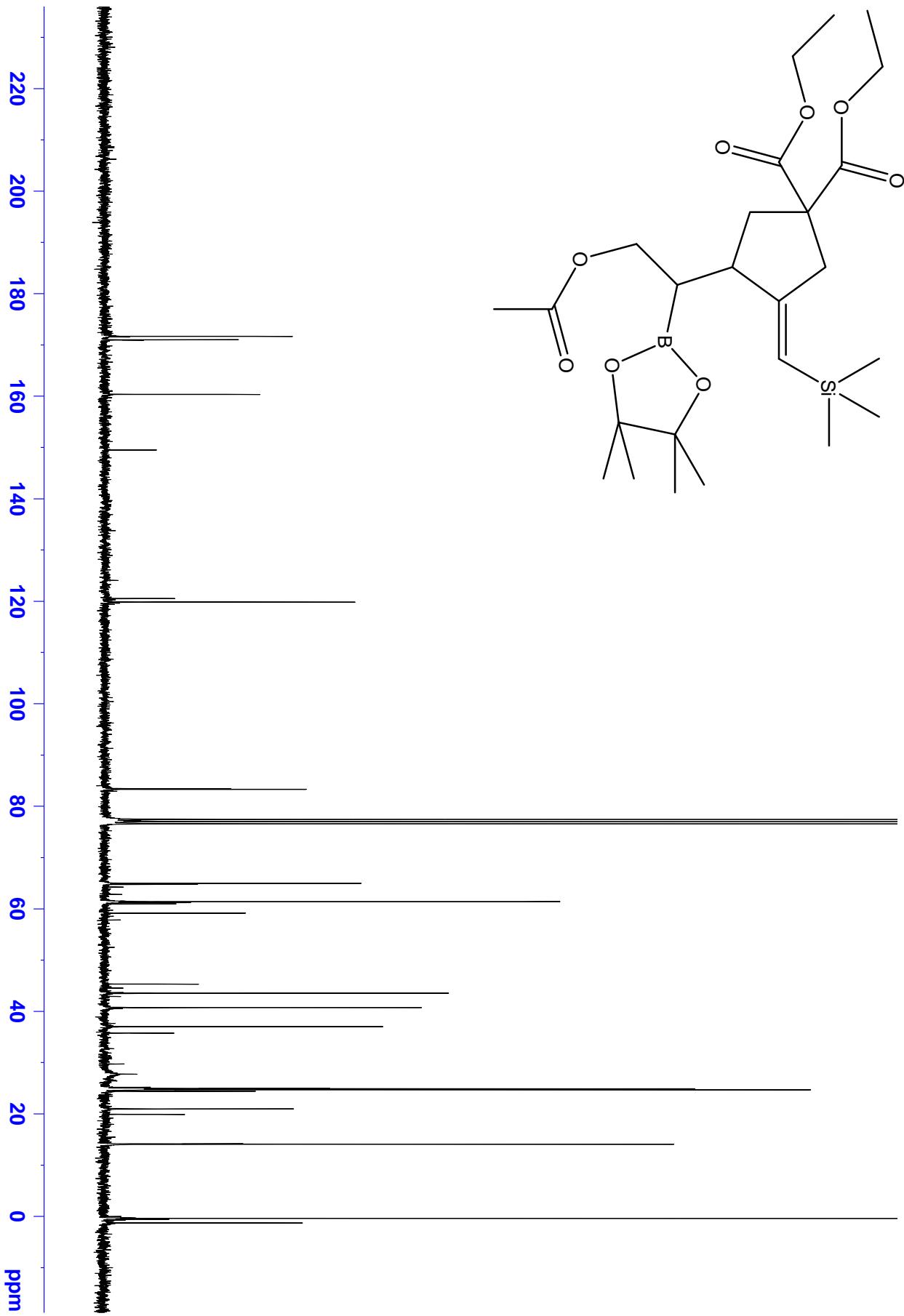
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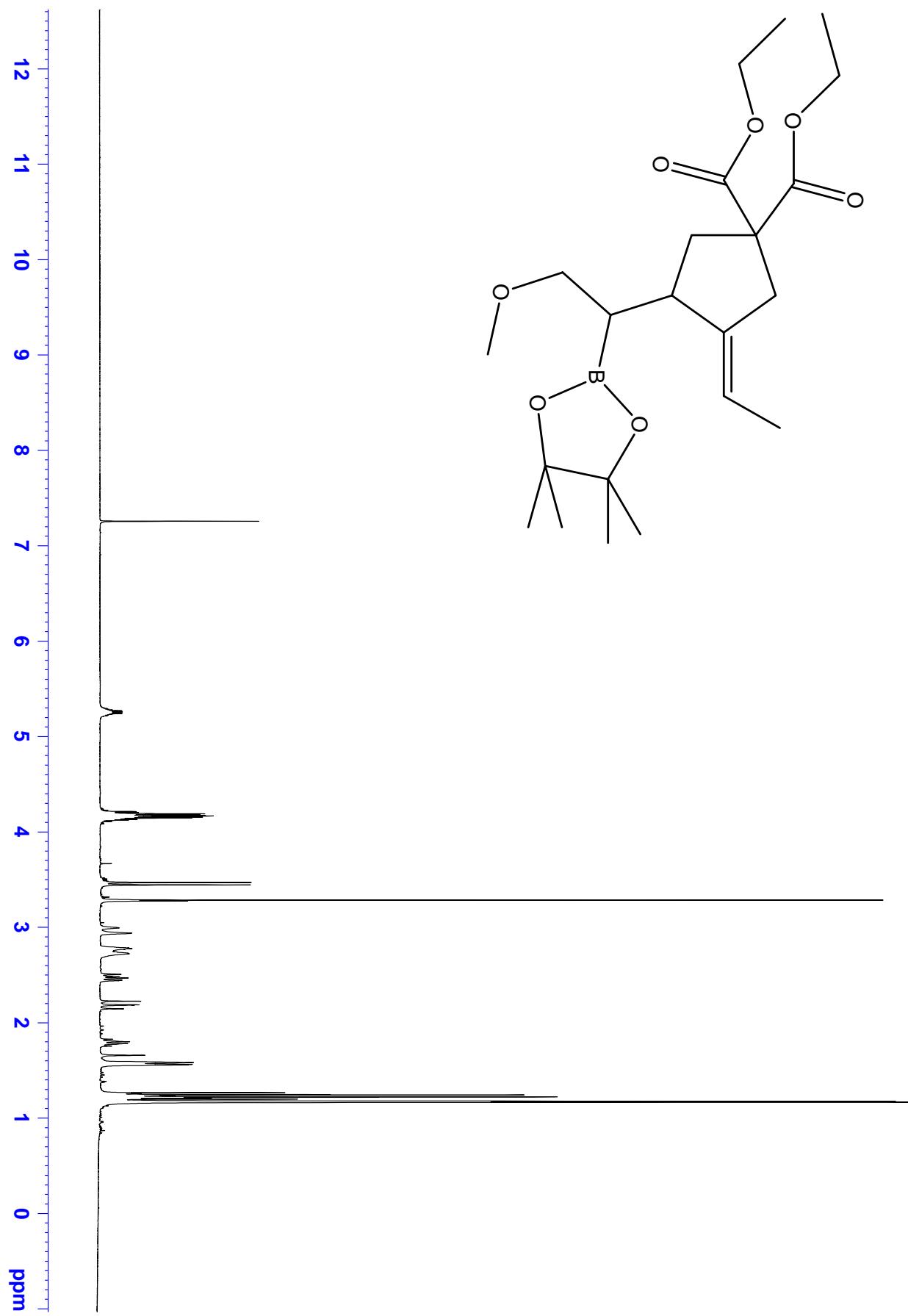


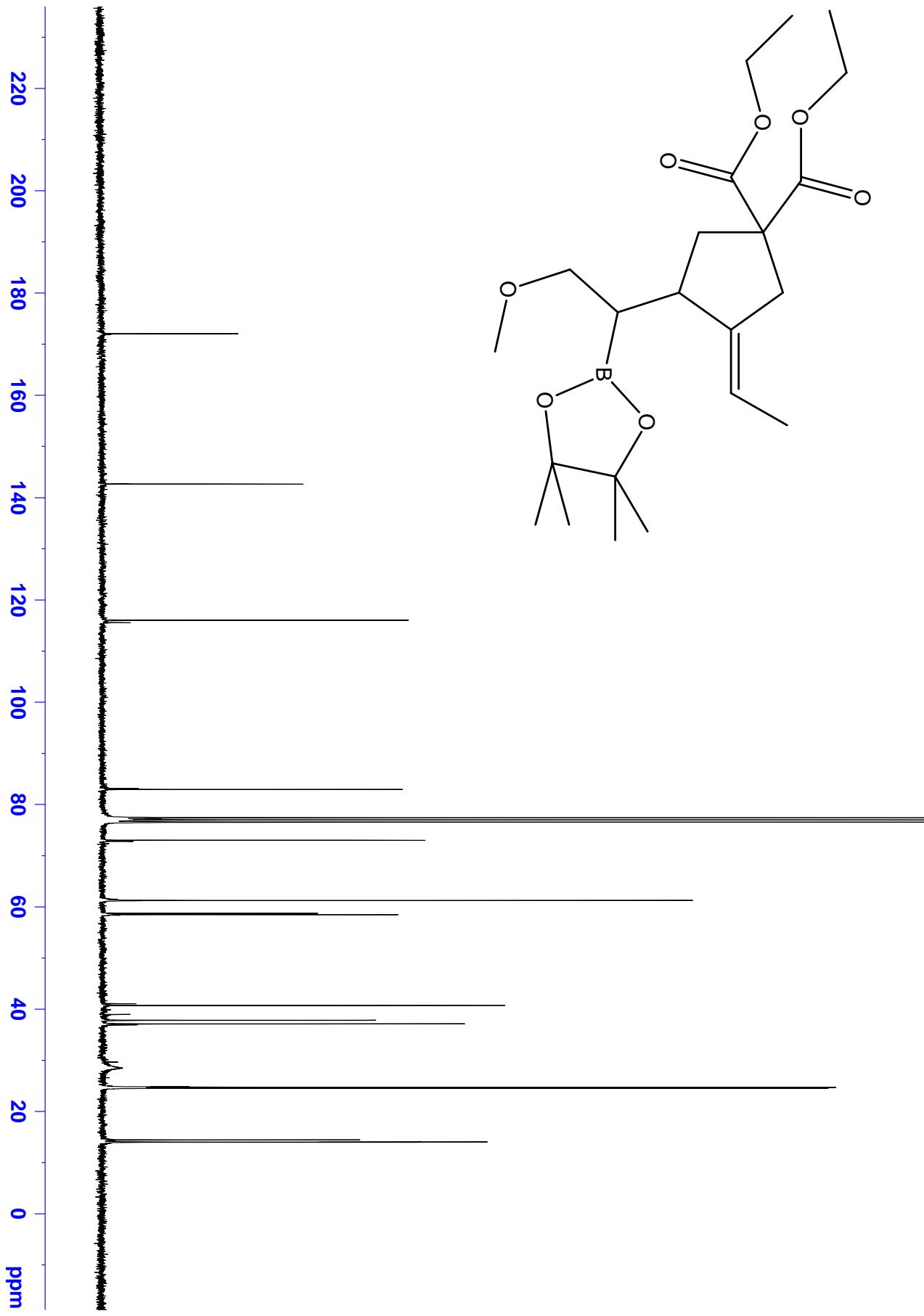
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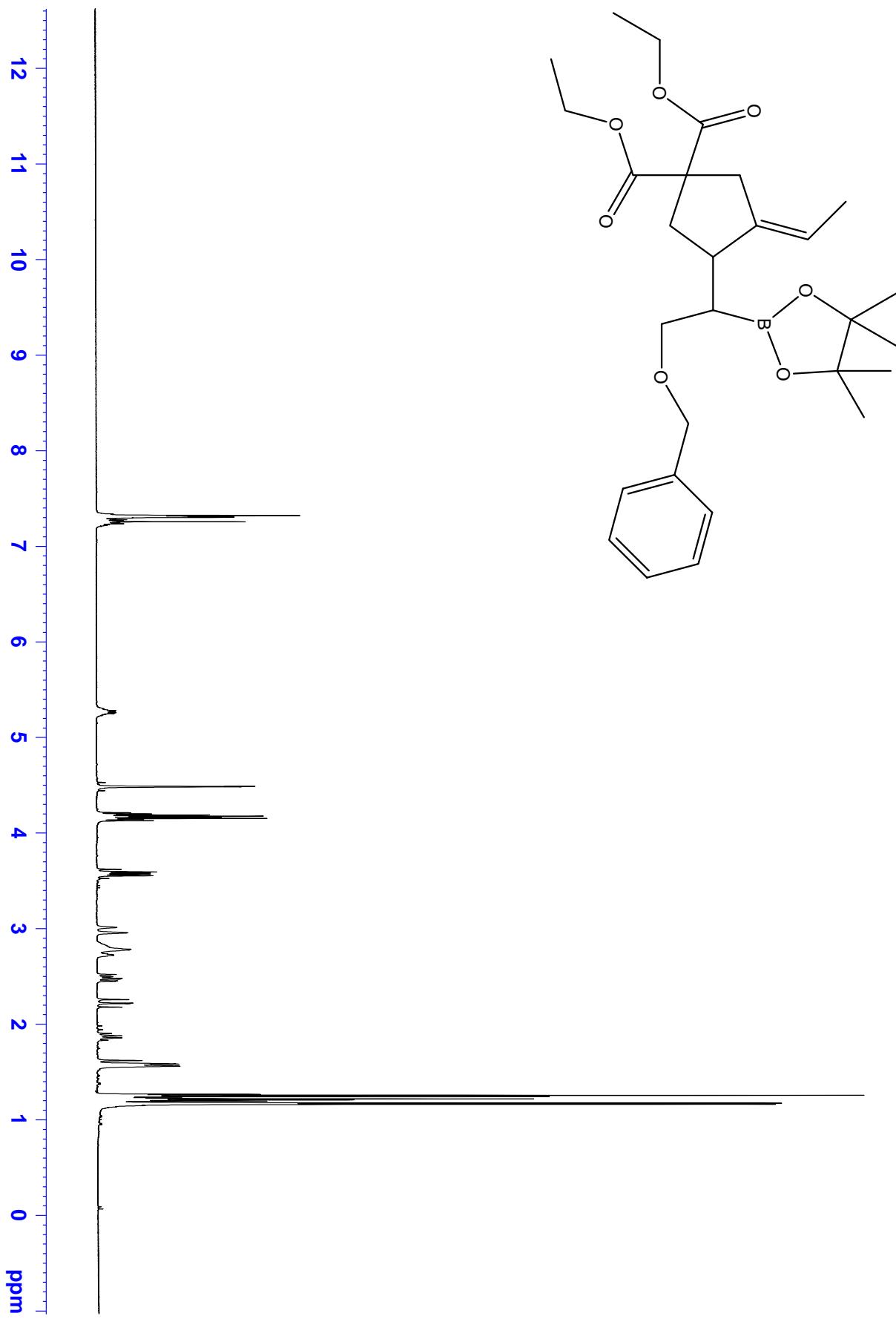


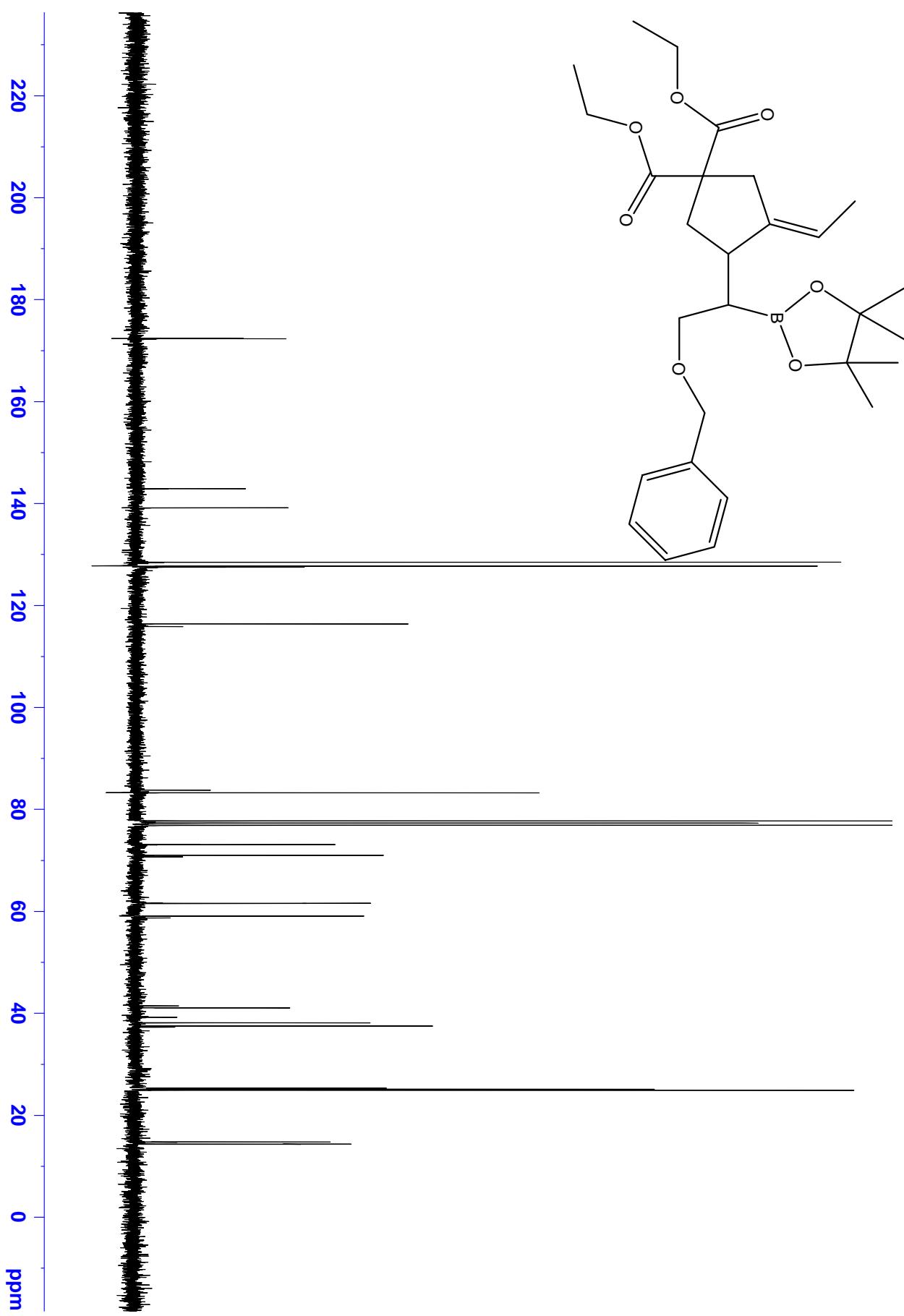


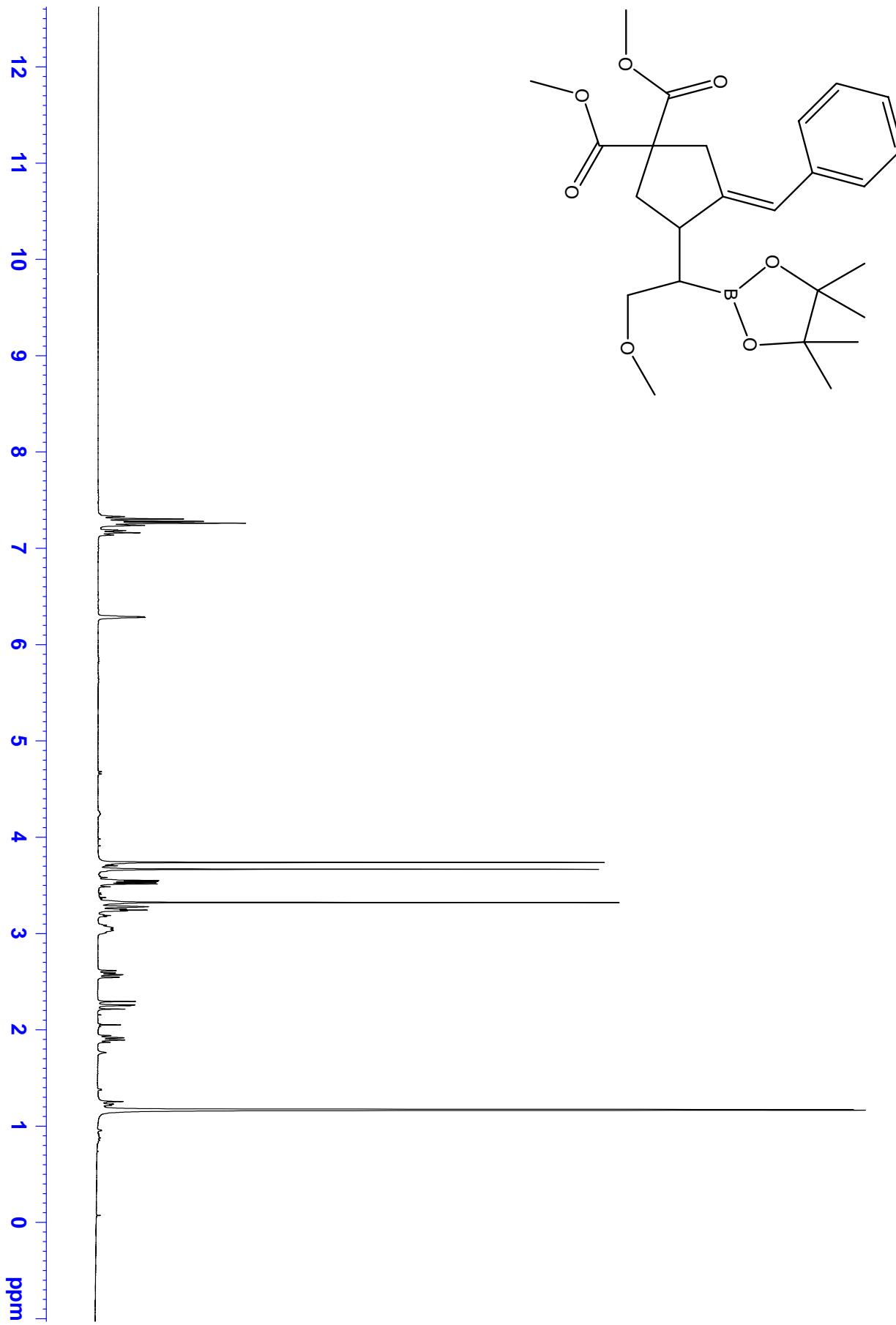


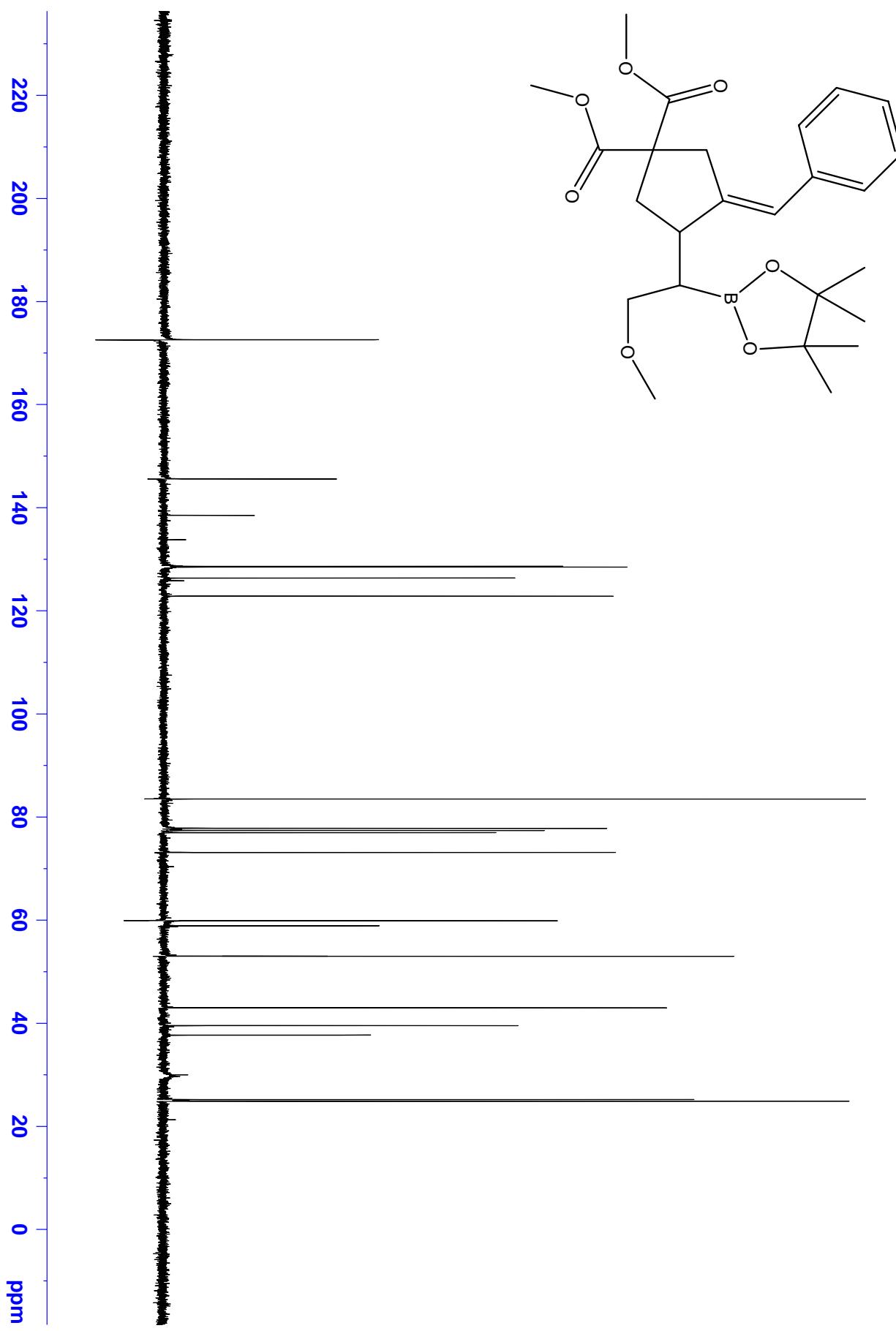


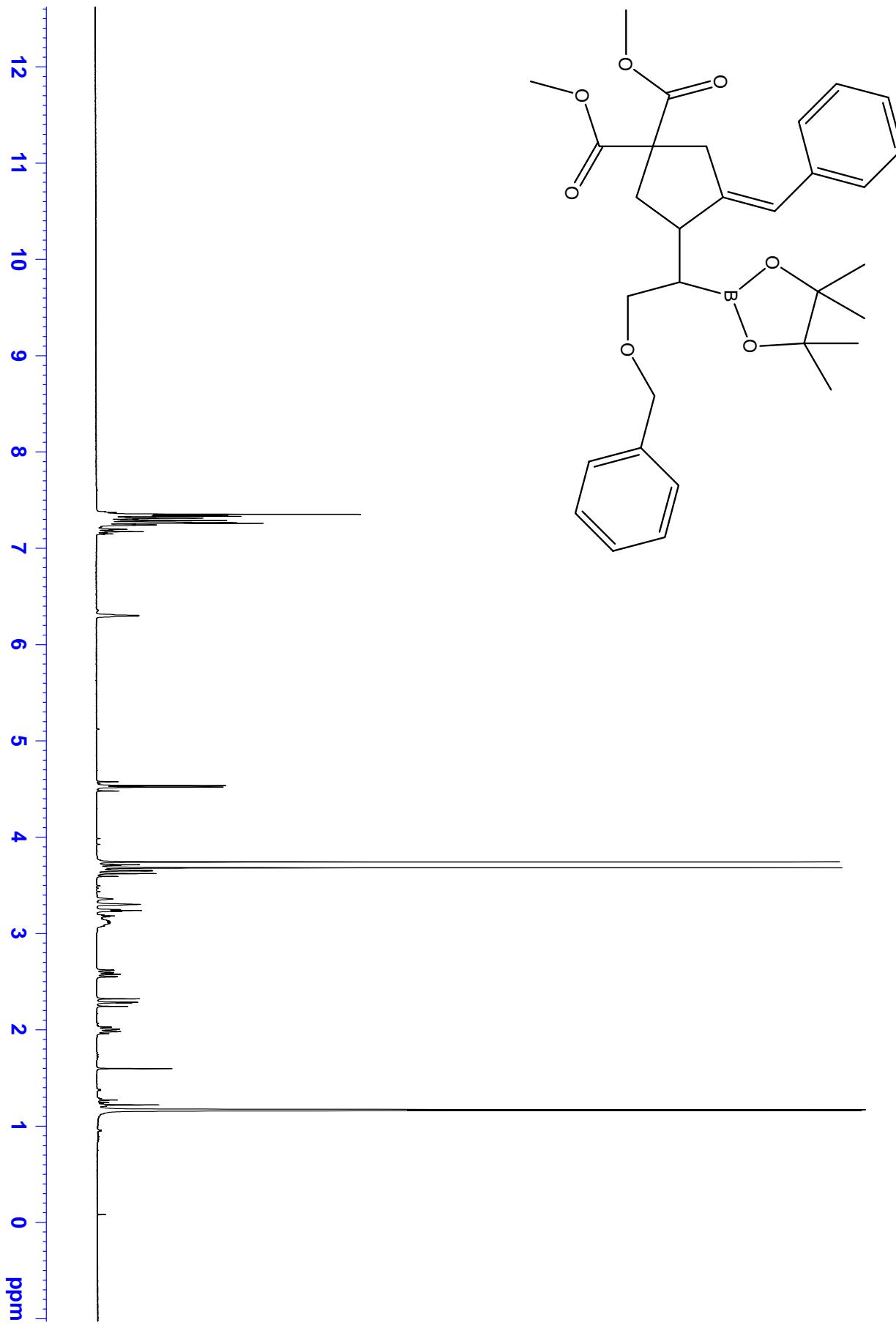


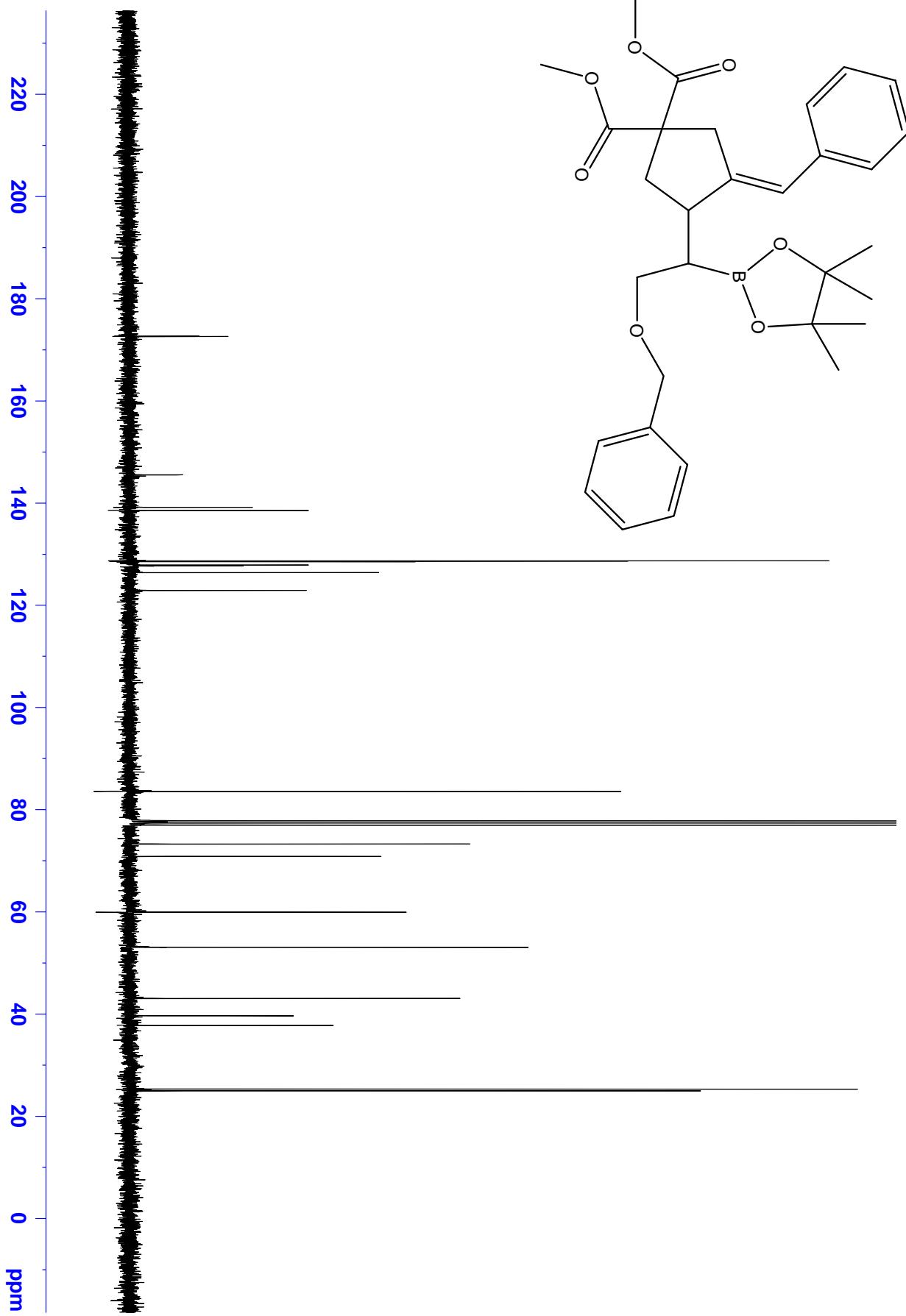


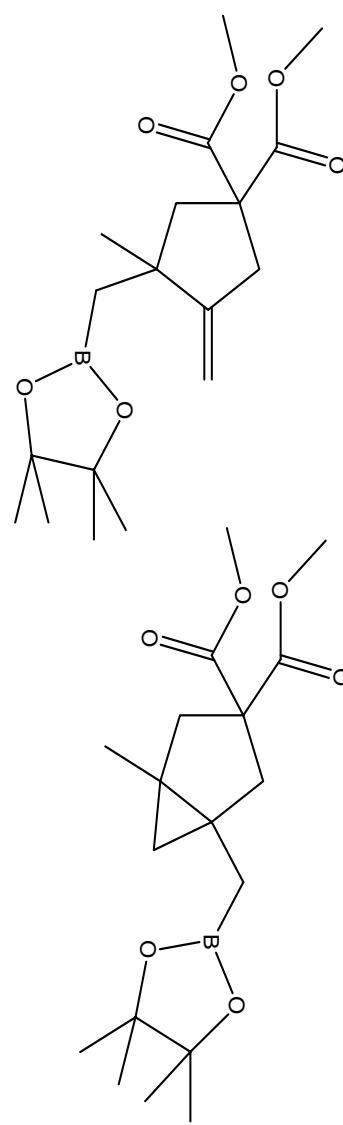
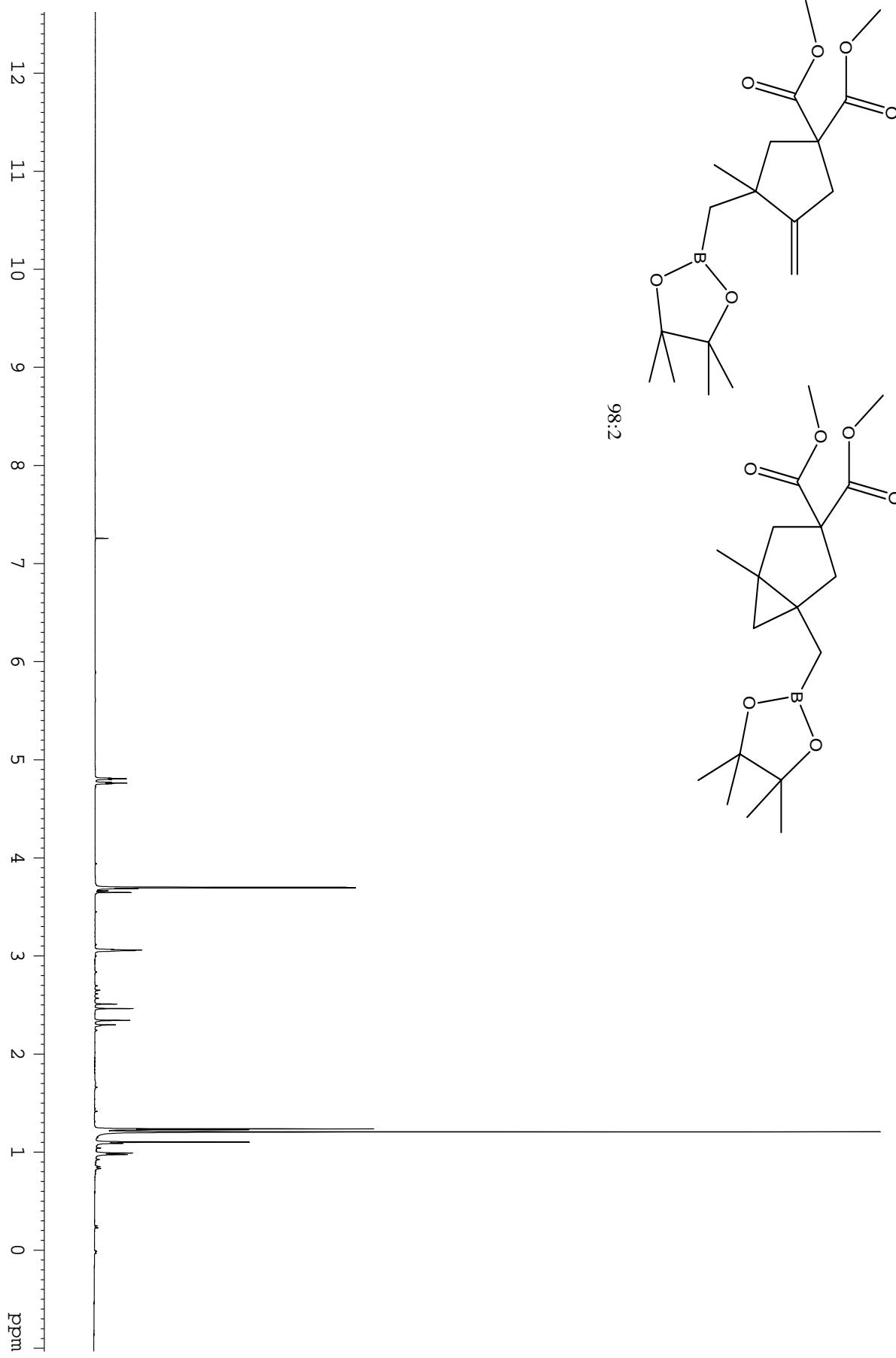


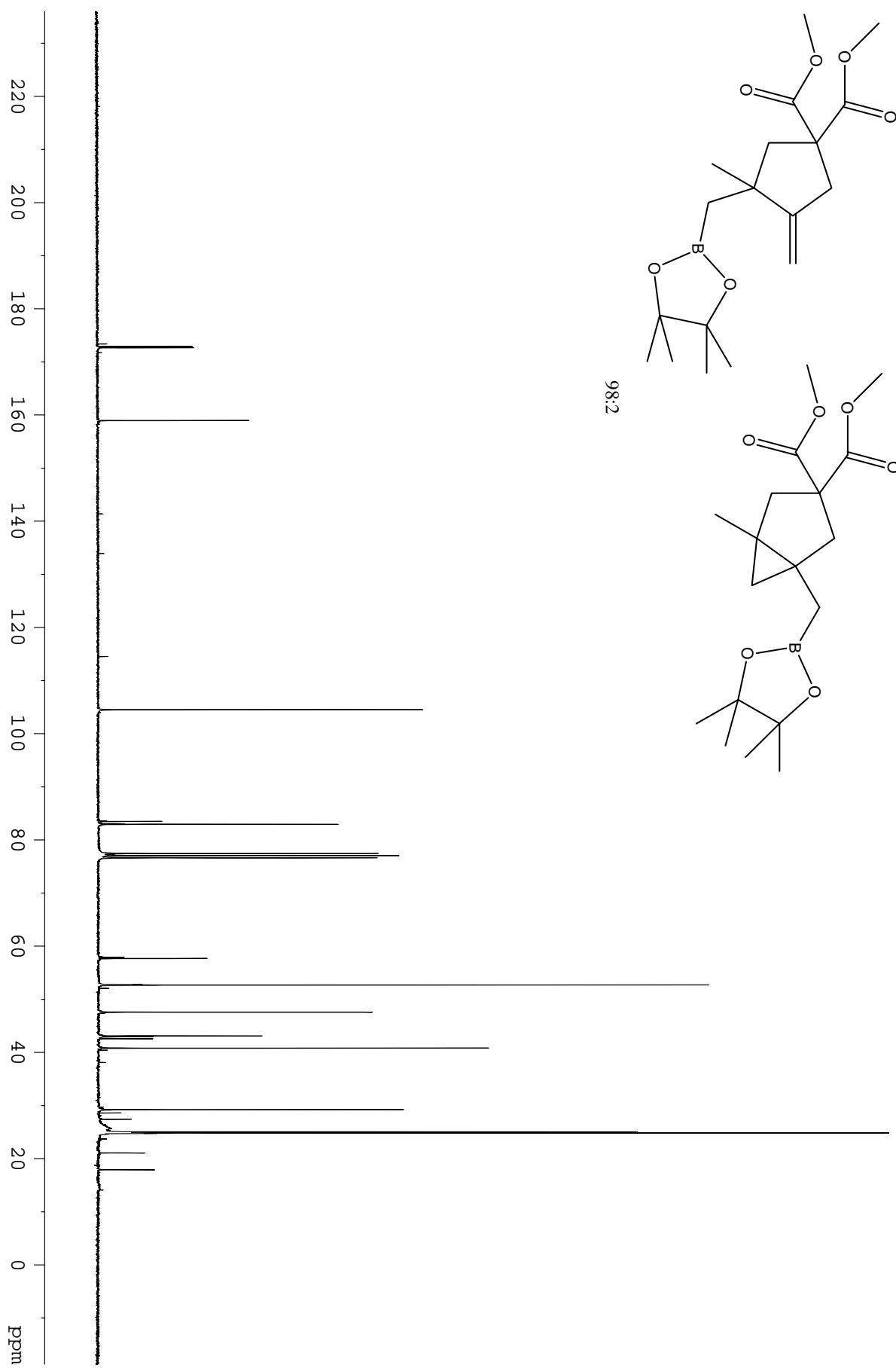


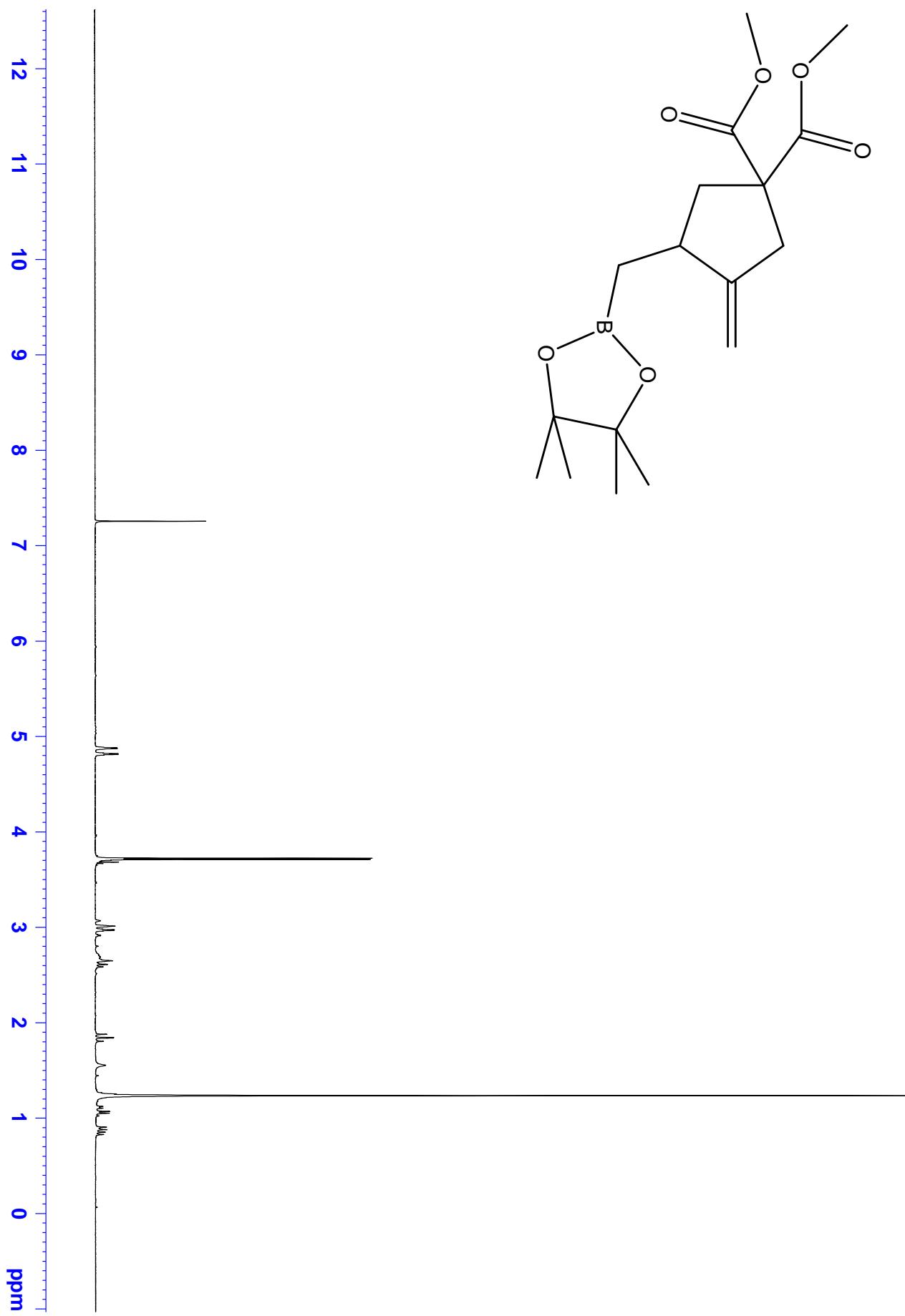


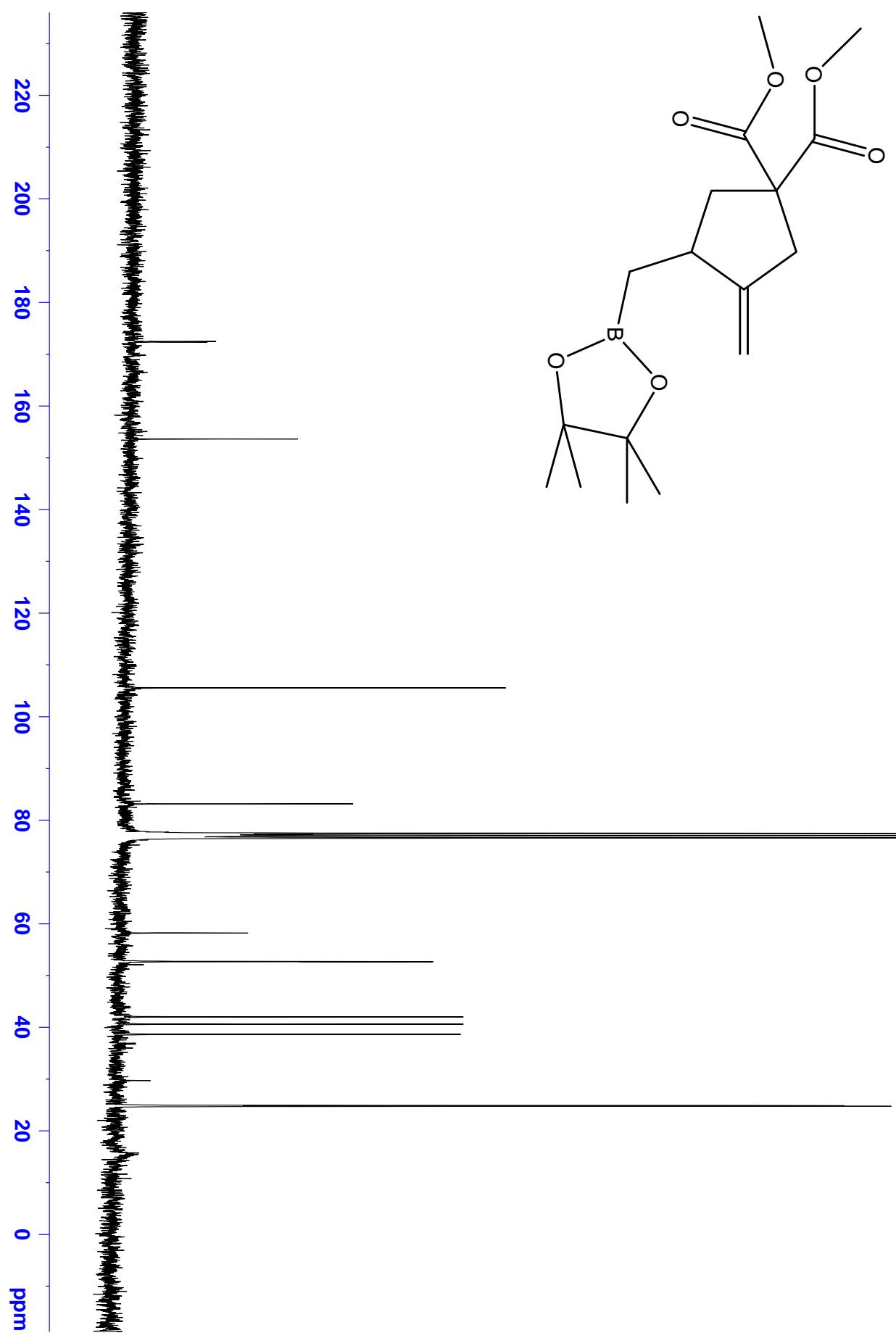


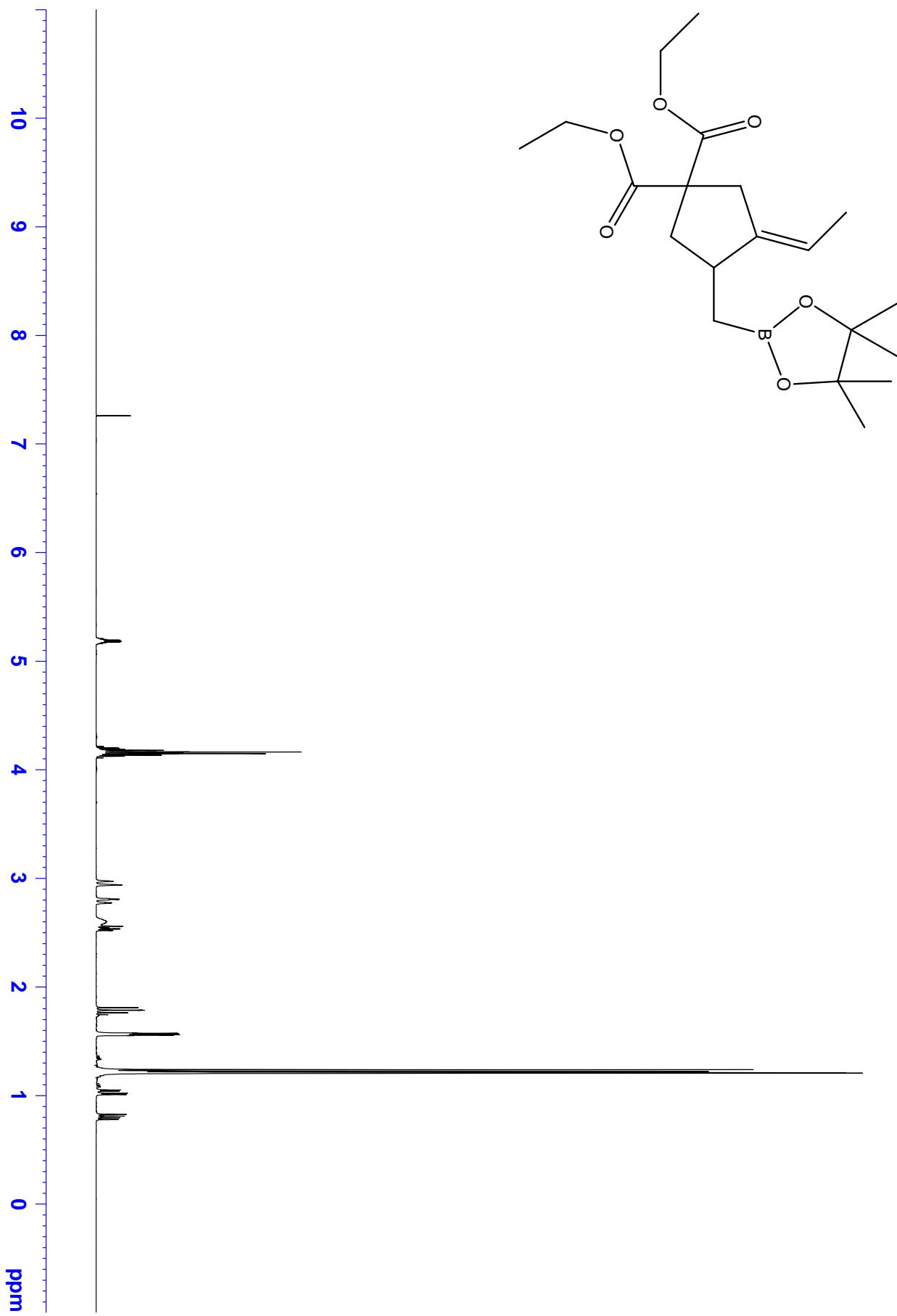


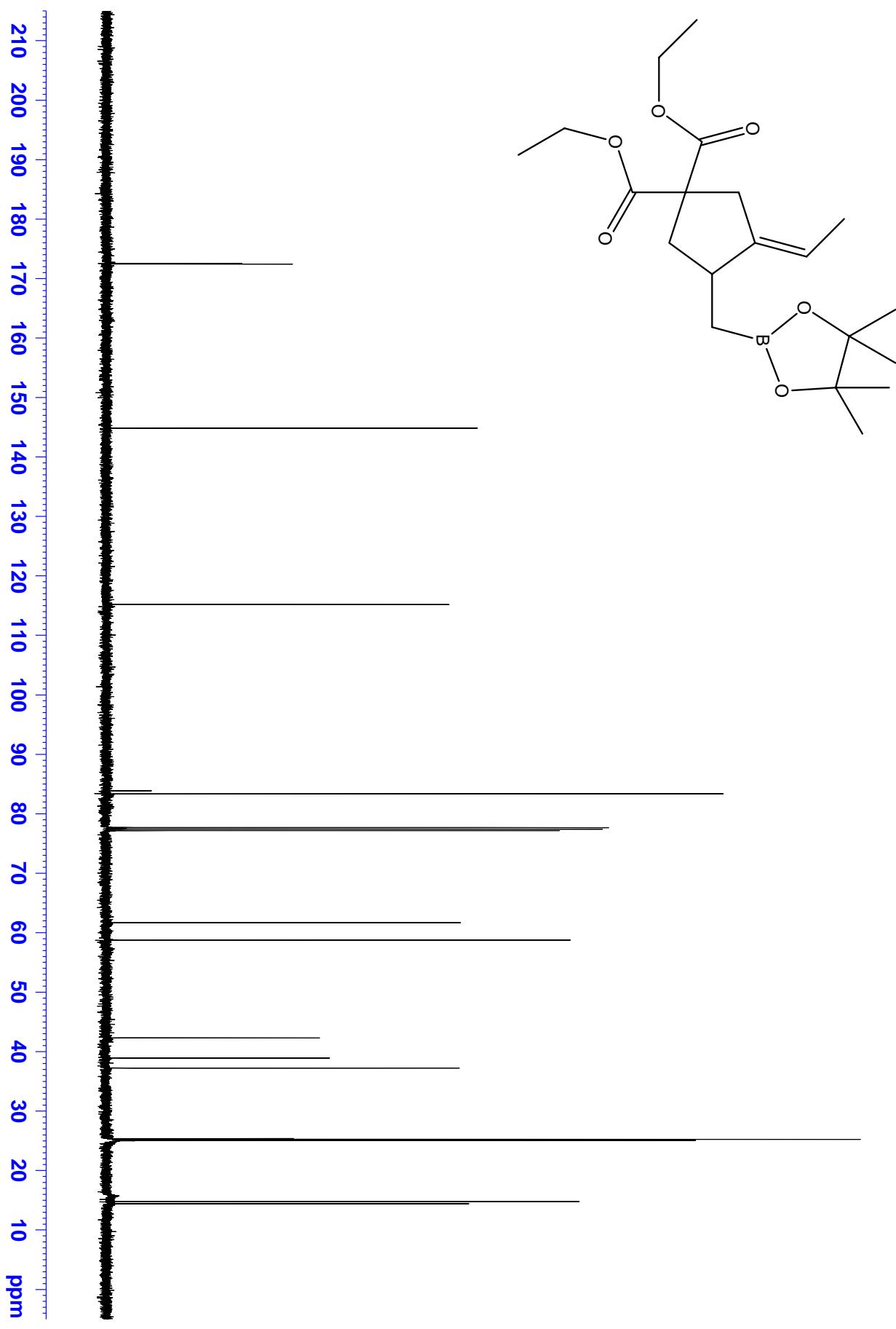


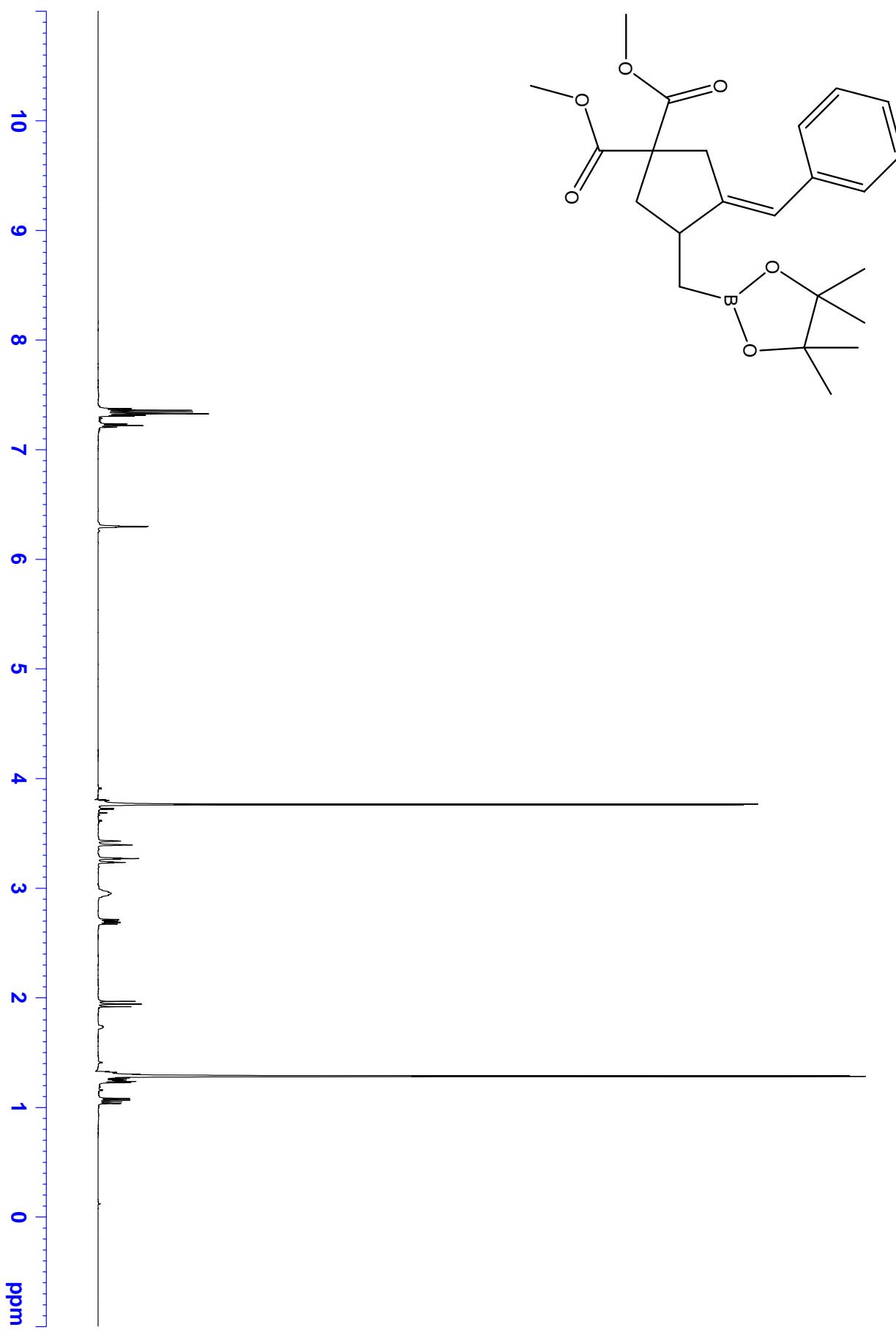


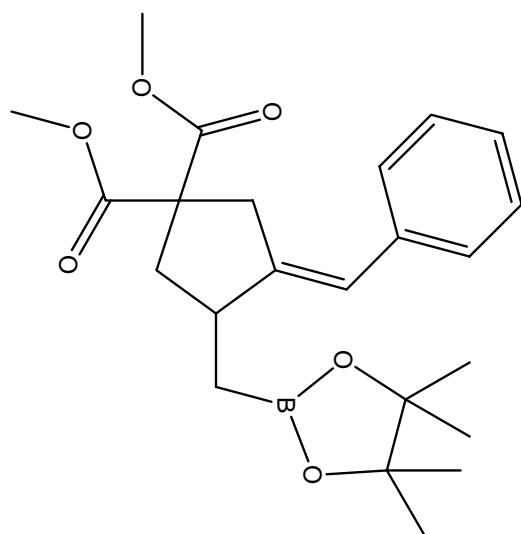


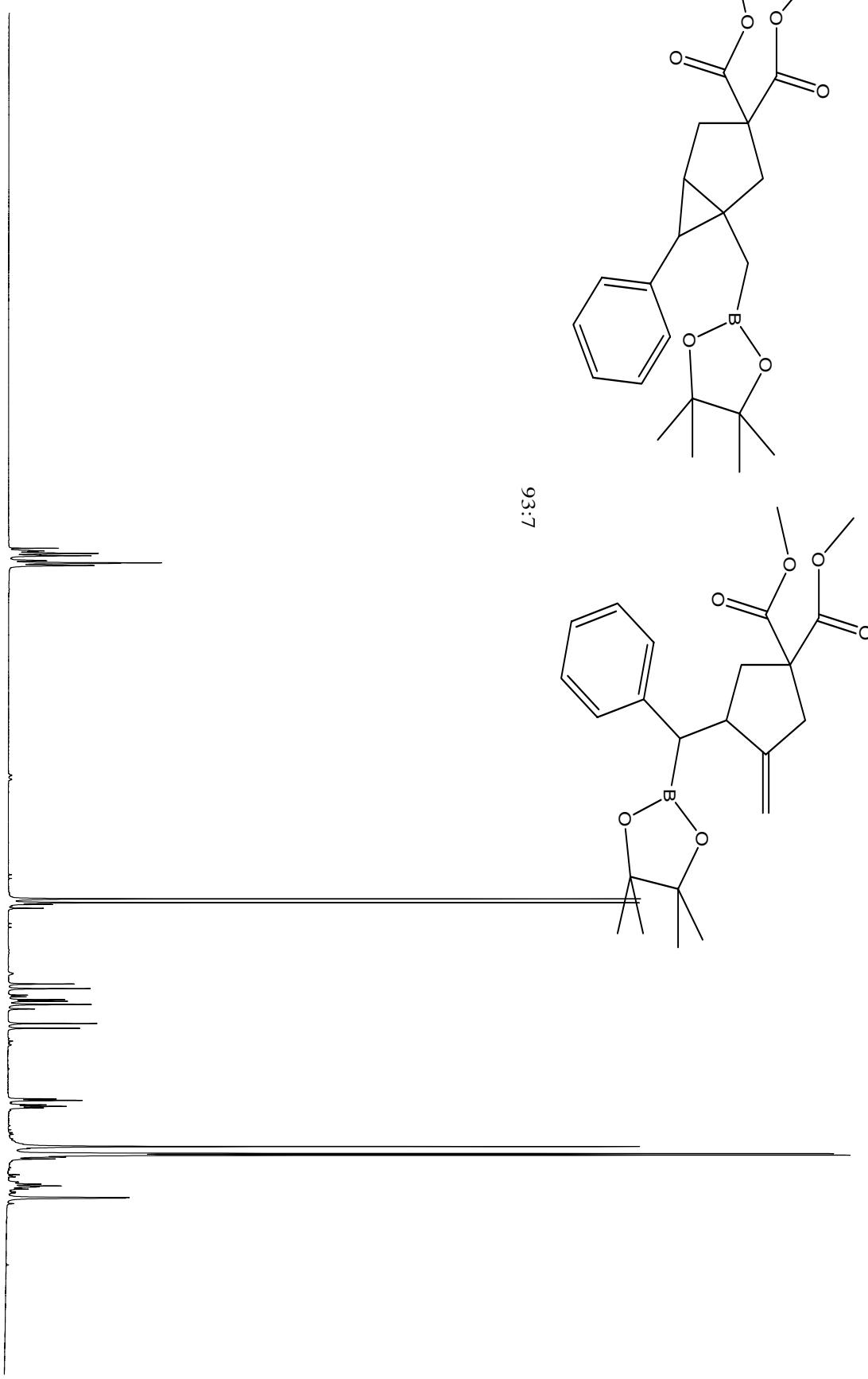
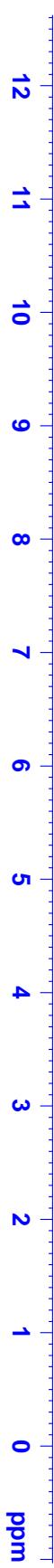












220  
200  
180  
160  
140  
120  
100  
80  
60  
40  
20  
0 ppm

