

# ***In Situ* Generation of the Coates Catalyst: A Practical and Versatile Catalytic System for the Carbonylation of *Meso*-Epoxides**

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## Supporting Information

## General remarks

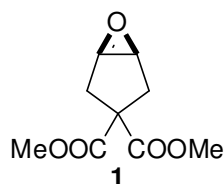
NMR spectra were recorded on Varian Inova 300 MHz and Varian 400 MHz FT spectrometers at room temperature with  $\text{CDCl}_3$  as the internal standard. The reference values used for  $\text{CDCl}_3$  were 7.26 and 77.0 ppm for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, respectively. The relative stereochemistry of the bicyclic 5- and 7-membered  $\beta$ -lactones was confirmed by NOESY studies. High resolution mass spectra were measured on a Waters/Micromass GCT and Waters 2996 Photodiode Array Detector instruments. Infrared spectra were recorded on a Varian 3100 FT-IR spectrometer at room temperature. Melting points were recorded in open capillaries on a digital Barnsted Electro Thermal 9300 melting point apparatus and are uncorrected. Elemental analysis was performed by UCD's School of Chemistry and Chemical Biology micro analytical service. All carbonylation reactions were carried out in a 100 mL custom built Parr reactor equipped with magnetic stirrer, which has an inlet, outlet, syringe port and pressure burst valve. Heating was performed in an oil bath.

## Materials

All reagents were obtained from commercial suppliers and used without further purification. Carbon monoxide gas (99.97% purity) was purchased from CK Gas Ltd. Tetraphenylporphyrinchromium(III) chloride and  $\text{Co}_2(\text{CO})_8$  were purchased from Strem Chemicals and used as received. 3-Chloroperoxybenzoic acid, *cis*-cyclooctene, 1,5-cyclooctadiene, cyclopentene, 2,5-dihydrofuran, *cis*-2-butene-1,4-diol, *cis*-2,3-dimethyloxirane were purchased from Fisher Scientific Ltd, and 1,2-epoxybutane was purchased from Sigma Aldrich. Dry THF was obtained from a solvent purification system and degassed prior to use. Thin layer chromatography was performed on Merck Aluminium sheets (silica gel 60 F<sub>254</sub>). Detection was carried out by UV and by coloration with ceric ammonium molybdate (CAM) or vanillin. Flash column chromatography was performed using Merck silica gel 60 (230-400 mesh).

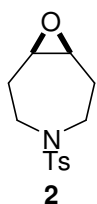
The following compounds were synthesized according to literature procedures: (TPP)CrCl,<sup>1</sup> (TPP)AlCl,<sup>1</sup> (TPP)CoCl,<sup>1</sup> (TPP)FeCl,<sup>2</sup> 1,2-epoxy-5-cyclooctene,<sup>3</sup> *cis*-cyclooctaneoxide,<sup>4</sup> *cis*-cyclohepteneoxide,<sup>5</sup> *cis*-cyclopenteneoxide,<sup>6</sup> *cis*-1,2-epoxycyclododecane,<sup>7</sup> *cis*-4-octeneoxide,<sup>8</sup> *cis*-2,3-dibenzylloxirane,<sup>9</sup> *cis*-2,3-bis(ethoxymethyl)oxirane,<sup>10</sup> *cis*-1,4-dibenzyl-2,3-epoxybutane,<sup>11</sup> 3,4-epoxytetrahydro-furan,<sup>12</sup> dimethyl cyclopent-3-ene-1,1-dicarboxylate<sup>13</sup> and 1-tosyl-2,3,6,7-tetrahydro-1H-azepine.<sup>14</sup> All epoxides were dried by either column chromatography or by distillation over  $\text{CaH}_2$  prior to use.

#### Dimethyl 6-oxa-bicyclo[3.1.0]hexane-3,3-dicarboxylate (1)



To a stirred solution of dimethyl cyclopent-3-ene-1,1-dicarboxylate (920 mg, 5.0 mmol) in dichloromethane (20 mL) was added at 0 °C *m*-CPBA (77% purity, 1.46 g, 6.5 mmol) portionwise over 10 min. The resulting reaction mixture was allowed to warm to room temperature and stirred for 24 h. The precipitate was filtered and the filtrate was diluted with dichloromethane (20 mL), washed with saturated aqueous NaHCO<sub>3</sub> solution and water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 80:20), to give the title compound (910 mg) as colorless liquid in 91% yield. IR (neat, cm<sup>-1</sup>): 2959, 2865, 1451, 1129, 919, 834; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.19 (d, *J* = 14.3 Hz, 2 H, CHH), 3.03 (d, *J* = 14.3 Hz, 2 H, CHH), 3.51 (s, 2 H, CH), 3.70 (s, 3 H, OCH<sub>3</sub>), 3.74 (s, 3 H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 36.0, 52.9, 53.1, 55.3, 55.6, 171.4, 171.5; HRMS (ESI): C<sub>9</sub>H<sub>12</sub>O<sub>5</sub> [M + Na]<sup>+</sup> calculated: 223.0582, found: 223.0589.

#### 4-Tosyl-8-oxa-4-azabicyclo[5.1.0]octane (2)

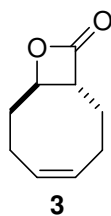


To a stirred solution of 1-tosyl-2,3,6,7-tetrahydro-1*H*-azepine (1.0 g, 3.98 mmol) in dichloromethane (20 mL) was added at 0 °C *m*-CPBA (77% purity, 1.46 g, 6.5 mmol) portionwise over 10 min. The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The precipitate was filtered and the filtrate was diluted with dichloromethane (20 mL), washed with saturated aqueous NaHCO<sub>3</sub> solution and water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (neutral Al<sub>2</sub>O<sub>3</sub>; pentane/Et<sub>2</sub>O, 50:50) to give the title compound (925 mg) as white solid in 87% yield. Mp: 55-58 °C; IR (neat, cm<sup>-1</sup>): 2949, 2865, 1441, 1129; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.20-2.35 (m, 4 H, CH<sub>2</sub>), 2.41 (s, 3 H, CH<sub>3</sub>), 2.65 (ddd, *J* = 14.0, 9.5, 4.6 Hz, 2 H, CHHN), 3.20 (d, *J* = 1.8 Hz, 2 H, CHO), 3.67 (ddd, *J* = 7.9, 4.4 Hz, 2 H, CHHN), 7.24-7.36 (m, 2 H, ArH), 7.64 (d, *J* = 8.2 Hz, 2 H, ArH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 21.4, 30.1, 45.0, 55.7, 126.8, 129.7, 136.8, 143.1; HRMS (ES): C<sub>13</sub>H<sub>17</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> calculated: 268.1007, found: 268.1017; Anal. cal. for C<sub>13</sub>H<sub>17</sub>NO<sub>3</sub>S (267.3): C 58.40, H 6.41, N 5.24; found: C 58.44, H 6.47, N 5.07.

### General procedure for carbonylation of *meso*-epoxides (Table 2)

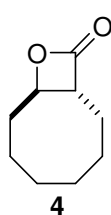
(TPP)CrCl (0.002-0.1 mmol), Co<sub>2</sub>(CO)<sub>8</sub> (0.003-0.15 mmol) were placed in an oven-dried Schlenk tube under N<sub>2</sub> atmosphere. Dry THF (3.0 mL) and the appropriate epoxide (2.0 mmol) were added and the reaction mixture was degassed by three vacuum/nitrogen cycles. The reaction mixture was injected *via* a syringe into an oven dried reactor under N<sub>2</sub>. The reactor was pressurized with CO gas to about 20 psi and vented. Subsequently, it was pressurized to 500 psi, placed in an oil bath and heated at 70 °C for 16 h. The reactor was allowed to cool to room temperature and the CO gas was vented off carefully. The reaction mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography to give the pure  $\beta$ -lactone.

#### 9-Oxabicyclo[6.2.0]dec-4-en-10-one (3)<sup>15</sup>



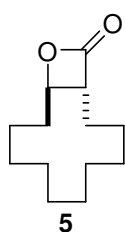
Isolated as colorless oil (276 mg) in 91% yield after purification by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 90:10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.54-1.61 (m, 1 H, CHHCH<sub>2</sub>), 1.73-1.96 (m, 2 H, CHHCHH), 2.11-2.39 (m, 5 H, CH<sub>2</sub>), 3.56 (dt, *J* = 12.5, 5.5 Hz, 1 H, CHCO), 4.35-4.40 (m, 1 H, CHO), 5.59-5.68 (m, 1 H, CH=CH), 5.71-5.78 (m, 1 H, CH=CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  22.0, 22.9, 24.3, 30.8, 55.9, 77.1, 129.7, 129.9, 171.3; HRMS (ESI): C<sub>9</sub>H<sub>12</sub>O<sub>2</sub> [M + H]<sup>+</sup> calculated: 153.0916, found: 153.0923.

#### 9-Oxabicyclo[6.2.0]decan-10-one (4)<sup>16</sup>



Isolated as colorless oil (267 mg) in 87% yield after purification by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 90:10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.85-1.02 (m, 1 H, CHHCH<sub>2</sub>), 1.03-1.17 (m, 1 H, CHHCH<sub>2</sub>), 1.23-1.56 (m, 2 H, CH<sub>2</sub>), 1.57-1.81 (m, 2 H, CH<sub>2</sub>), 1.83-2.16 (m, 5 H, CH<sub>2</sub>CH<sub>2</sub>CHH), 2.30 (m, 1 H, CHH), 3.35 (ddd, *J* = 12.8, 4.8, 2.8 Hz, 1 H, CHCO), 4.44 (ddd, *J* = 11.9, 4.8, 2.8 Hz, 1 H, CHO); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  27.1, 27.3, 27.5, 27.7, 29.0, 34.3, 57.1, 79.8, 171.4; HRMS (ESI): C<sub>9</sub>H<sub>14</sub>O<sub>2</sub> [M + H]<sup>+</sup> calculated: 155.1072, found: 155.1073.

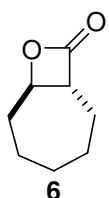
#### 13-Oxabicyclo[10.2.0]tetradecan-14-one (5)<sup>17</sup>



Isolated as colorless oil (382 mg) in 91% yield after purification by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 90:10). IR (neat, cm<sup>-1</sup>): 2938, 2860, 1830, 1450, 1110, 910, 824; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.10-1.63 (m, 18 H, CH<sub>2</sub>),

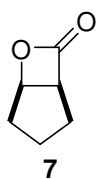
1.66-1.79 (m, 1 H, *CHHCH*<sub>2</sub>), 1.82-2.04 (m, 2 H, CH<sub>2</sub>), 2.12-2.26 (m, 1 H, *CHHCH*<sub>2</sub>), 3.30 (dt, *J* = 12.5, 3.9 Hz, 1 H, CHCO), 4.39 (dt, *J* = 11.0, 3.9 Hz, 1 H, CHO); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 22.80, 22.83, 23.4, 23.7, 24.8, 25.0, 27.3, 27.5, 27.6, 33.3, 54.2, 77.5, 172.3; HRMS (ESI): C<sub>13</sub>H<sub>22</sub>O<sub>2</sub> [M + H]<sup>+</sup> calculated: 211.1698, found: 211.1701.

### 8-Oxabicyclo[5.2.0]nonan-9-one (6)



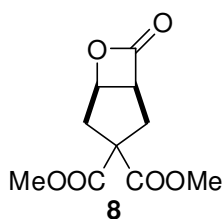
Isolated as colorless oil (249 mg) in 89% yield after purification by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 90:10). IR (neat, cm<sup>-1</sup>): 2939, 2865, 1839, 1451, 1129, 919, 834; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.37-1.73 (m, 5 H, CH<sub>2</sub>CH<sub>2</sub>CHH), 1.75-1.97 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 2.34 (dd, *J* = 11.7, 5.2 Hz, 1 H, CHHCH<sub>2</sub>), 3.44-3.50 (m, 1 H, CHCO), 4.30 (ddd, *J* = 11.0, 6.4, 4.3 Hz, 1 H, CHO); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.5, 24.2, 26.6, 28.0, 31.8, 57.1, 76.3, 171.1; HRMS (EI): C<sub>8</sub>H<sub>12</sub>O<sub>2</sub> [M]<sup>+</sup> calculated: 140.0837, found: 140.0843.

### 6-Oxabicyclo[3.2.0]heptan-7-one (7)<sup>18</sup>



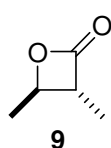
Isolated as colorless oil (188 mg) in 87% yield after purification by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 90:10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.46-1.71 (m, 2 H, CH<sub>2</sub>), 1.79 (m, 1 H, CH<sub>2</sub>), 1.82-2.01 (m, 1 H, CH<sub>2</sub>), 2.17 (dd, *J* = 13.4 6.2 Hz, 1 H, CHH), 2.24 (dd, *J* = 14.6, 6.1 Hz, 1 H, CHH), 3.89 (dd, *J* = 8.0, 3.9 Hz, 1 H, CHCO), 4.99 (virtual t, *J* = 3.8 Hz, 1 H, CHO); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 22.3, 26.5, 30.9, 55.8, 77.6, 171.5; HRMS (CI): C<sub>6</sub>H<sub>8</sub>O<sub>2</sub> [M + H]<sup>+</sup> calculated: 113.0603, found: 113.0606.

### Dimethyl 7-oxo-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (8)<sup>19</sup>



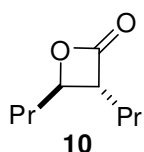
Isolated as colorless oil (337 mg) in 74% yield after purification by flash chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 50:50); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.11 (dd, *J* = 14.2, 9.1 Hz, 1 H, CHHCHCO), 2.46 (dd, *J* = 15.6, 4.2 Hz, 1 H, CHHCHO), 3.04 (d, *J* = 15.6 Hz, 1 H, CHHCHO), 3.17 (d, *J* = 14.2 Hz, 1 H, CHHCHO), 3.76 (s, 3 H, CH<sub>3</sub>), 3.78 (s, 3 H, CH<sub>3</sub>), 3.99 (dd, *J* = 9.0, 4.0 Hz, 1 H, CHCO), 5.04 (virtual t, *J* = 4.1 Hz, 1 H, CHO); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 34.0, 39.1, 53.1, 53.3, 55.9, 59.7, 76.9, 168.9, 170.4, 170.6; HRMS (ESI): C<sub>10</sub>H<sub>12</sub>O<sub>6</sub> [M + Na]<sup>+</sup> calculated: 251.0532, found: 251.0524.

### 3,4-Dimethyloxetan-2-one (**9**)<sup>20</sup>



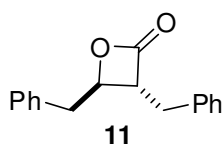
Isolated as a colorless oil (200 mg) in 95% yield after purification by flash chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 50:50); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.38 (d, *J* = 7.6 Hz, 3 H, CH<sub>3</sub>CHCO), 1.55 (d, *J* = 6.1 Hz, 3 H, CH<sub>3</sub>CHO), 3.17-3.24 (dq, *J* = 7.6, 3.9 Hz, 1 H, CHCO), 4.24-4.42 (dq, *J* = 6.1, 3.9 Hz, 1 H, CHO); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 12.2, 19.9, 52.2, 76.0, 171.7; HRMS (ESI): C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> [M + H]<sup>+</sup> calculated: 101.0603, found: 101.0598.

### 3,4-Dipropyloxetan-2-one (**10**)<sup>21</sup>



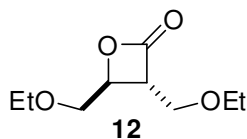
Isolated as colorless oil (293 mg) in 94% yield after purification by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 50:50). IR (neat, cm<sup>-1</sup>): 2962, 1822, 1466, 1382, 1129, 876, 724; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.95 (t, *J* = 7.4 Hz, 3 H, CH<sub>3</sub>), 0.99 (t, *J* = 7.4 Hz, 3 H, CH<sub>3</sub>), 1.35-1.54 (m, 4 H, CH<sub>2</sub>), 1.64-1.77 (m, 2 H, CH<sub>2</sub>), 1.78-1.90 (m, 2 H, CH<sub>2</sub>), 3.18 (ddd, *J* = 10.4, 6.6, 4.0 Hz, 1 H, CHCO), 4.15-4.33 (ddd, *J* = 13.0, 7.2, 4.0 Hz, 1 H, CHO); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 13.8, 18.4, 20.3, 29.9, 36.5, 56.0, 78.0, 171.6; HRMS (EI): C<sub>9</sub>H<sub>16</sub>O<sub>2</sub> [M]<sup>+</sup> calculated: 156.1150, found: 156.1146.

### 3,4-Dibenzoyloxetan-2-one (**11**)



Isolated as a white solid (342 mg) in 68% yield after purification by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 50:50) yield; Mp: 78-81 °C; IR (KBr, cm<sup>-1</sup>): 2360, 1821, 1610, 1457; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.90-3.10 (m, 4 H, CH<sub>2</sub>Ph), 3.55 (ddd, *J* = 10.1, 6.0, 4.2 Hz, 1 H, CHCO), 4.49 (ddd, *J* = 12.4, 6.2, 4.2 Hz, 1 H, CHO), 6.87-7.10 (m, 4 H, ArH), 7.12-7.45 (m, 6 H, ArH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 33.5, 40.0, 56.6, 76.7, 127.0, 127.2, 128.5, 128.7, 128.8, 129.1, 134.8, 136.8, 170.2; HRMS (ESI): C<sub>17</sub>H<sub>16</sub>O<sub>2</sub> [M + Na]<sup>+</sup> calculated: 275.1048, found 275.1053.

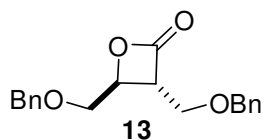
### 3,4-Bis(ethoxymethyl)oxetan-2-one (**12**)



Isolated as colorless oil (315 mg) in 84% yield after purification by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 80:20). IR (neat, cm<sup>-1</sup>): 2977, 2871, 1829, 1378, 1126, 840; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.20 (q, *J* = 6.9 Hz, 6 H, OCH<sub>2</sub>CH<sub>3</sub>), 3.47-3.63 (m, 4 H, OCH<sub>2</sub>CH<sub>3</sub>), 3.64-3.71 (m, 1 H, CHCO), 3.72-3.83 (m, 4 H, CH<sub>2</sub>OEt), 4.69 (m, 1 H, CHO); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 14.9, 15.0, 53.3, 64.9, 66.9, 67.4, 69.4, 73.4, 169.1; HRMS (EI): C<sub>9</sub>H<sub>16</sub>O<sub>4</sub>

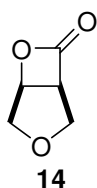
[M]<sup>+</sup> calculated: 188.1049, found 188.1057; Anal. cal. for C<sub>9</sub>H<sub>16</sub>O<sub>4</sub> (188.10): C 57.43, H 8.57; found: C 57.23, H 8.70.

### 3,4-Bis(benzyloxymethyl)oxetan-2-one (13)



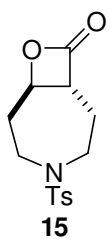
Isolated as a white solid (293 mg) in 47% yield after purification by flash column chromatography (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O, 80:20). Mp: 43-45 °C; IR (KBr, cm<sup>-1</sup>): 2962, 1822, 1466, 1382, 1293; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.64-3.73 (m, 1 H, CHCO), 3.76-3.81 (m, 4 H, OCH<sub>2</sub>CH), 4.65-4.49 (m, 4 H, OCH<sub>2</sub>Ph), 4.72 (dd, *J* = 7.2, 3.7 Hz, 1 H, CHO), 7.26-7.40 (m, 10 H, ArH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 53.4, 64.4, 68.8, 73.2, 73.3, 73.7, 127.6, 127.7, 127.8, 127.9, 128.5, 128.6, 137.4, 137.5, 168.7; HRMS (ESI): C<sub>19</sub>H<sub>20</sub>O<sub>4</sub> [M + Na]<sup>+</sup> calculated: 335.1259, found 335.1248; Anal. cal. for C<sub>19</sub>H<sub>20</sub>O<sub>4</sub> (312.35): C 73.06, H 6.45; found: C 72.88, H 6.56.

### 3,6-Dioxabicyclo[3.2.0]heptan-7-one (14)



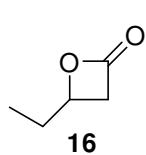
Isolated as a colorless oil (207 mg) in 91% yield after purification by flash column chromatography (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 50:50); IR (neat, cm<sup>-1</sup>): 2363, 1831, 1624, 1566, 1118; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.50 (dd, *J* = 11.8, 2.4 Hz, 1 H, CHHCHO), 3.56 (dd, *J* = 10.1, 5.6 Hz, 1 H, CHHCHCO), 4.14 (dd, *J* = 4.5, 2.8 Hz, 1 H, CHCO), 4.34 (d, *J* = 11.8 Hz, 1 H, CHHCHO), 4.42 (d, *J* = 10.1 Hz, CHHCHCO), 5.15 (dd, *J* = 4.3, 2.4 Hz, 1 H, CHO); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 57.1, 67.3, 70.3, 75.1, 168.7; HRMS (CI): C<sub>5</sub>H<sub>6</sub>O<sub>3</sub> [M + H]<sup>+</sup> calculated: 115.0395, found 115.0391.

### 4-Tosyl-8-oxa-4-azabicyclo[5.2.0]nonan-9-one (15)



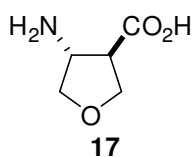
Isolated as a white solid (513.0 mg) in 87 % yield after flash column chromatography (SiO<sub>2</sub>; 70:30, pentane/EtOAc); Mp: 127-131 °C; IR (KBr, cm<sup>-1</sup>): 2964, 2255, 1829, 1599; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 50 °C): δ 1.90-2.03 (m, 2 H, CHHCHCO, CHHCHO), 2.15-2.19 (m, 1 H, CHHCHCO), 2.42 (s, 3 H, CH<sub>3</sub>), 2.44-2.49 (m, 1 H, CHHCHO), 3.18 (bs, 1 H, NCHHCH<sub>2</sub>CHO), 3.25 (bs, 1 H, NCHHCH<sub>2</sub>CHCO), 3.52 (bs, 1 H, NCHHCH<sub>2</sub>CHCO), 3.71 (m, 2 H, CHCO, NCHCH<sub>2</sub>CHO), 4.33-4.49 (m, 1 H, CHO), 7.30 (d, *J* = 8.0 Hz, 2 H, ArH), 7.66 (d, *J* = 8.3 Hz, 2 H, ArH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.5, 23.8, 32.6, 48.8, 50.7, 56.2, 74.7, 126.6, 129.9, 136.7, 143.7, 169.5; HRMS (ES<sup>-</sup>): C<sub>17</sub>H<sub>14</sub>NO<sub>4</sub>S [M + H]<sup>+</sup> calculated: 294.0800, found 294.0811.

#### 4-Ethyloxetan-2-one (16)<sup>20</sup>



(TPP)CrCl (7.0 mg,  $1 \times 10^{-8}$  mmol),  $\text{Co}_2(\text{CO})_8$  (5.0 mg,  $1.5 \times 10^{-8}$  mmol) were placed in an oven-dried Schlenk tube under  $\text{N}_2$  atmosphere. Dry THF (10 mL) and 1,2-epoxybutane (7.2 g, 100.0 mmol) were added and the reaction mixture was degassed by three vacuum/nitrogen cycles. The reaction mixture was injected *via* a syringe into an oven dried reactor under  $\text{N}_2$ . The reactor was pressurized with CO gas to about 20 psi and vented. Subsequently, it was pressurized to 500 psi, placed in an oil bath and heated at 70 °C for 16 h. The reactor was allowed to cool to room temperature and the CO gas was vented off carefully. The product was isolated by fractional distillation of the reaction mixture (65 °C, 15 mm/Hg) to give the title compound (9.1 g) in 92% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.95 (t,  $J$  = 7.4 Hz, 3 H,  $\text{CH}_3$ ), 1.61-1.9 (m, 2 H,  $\text{CH}_2$ ), 2.99 (dd,  $J$  = 16.3, 4.3 Hz, 1 H,  $\text{CHHCO}$ ), 3.43 (dd,  $J$  = 16.3, 5.8 Hz,  $\text{CHHCO}$ ), 4.39 (dt,  $J$  = 11.7, 6.1 Hz, 1 H,  $\text{CHO}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.7, 27.6, 42.2, 72.2, 168.3.

#### *Trans*-4-aminotetrahydrofuran-3-carboxylic acid (17)<sup>22</sup>



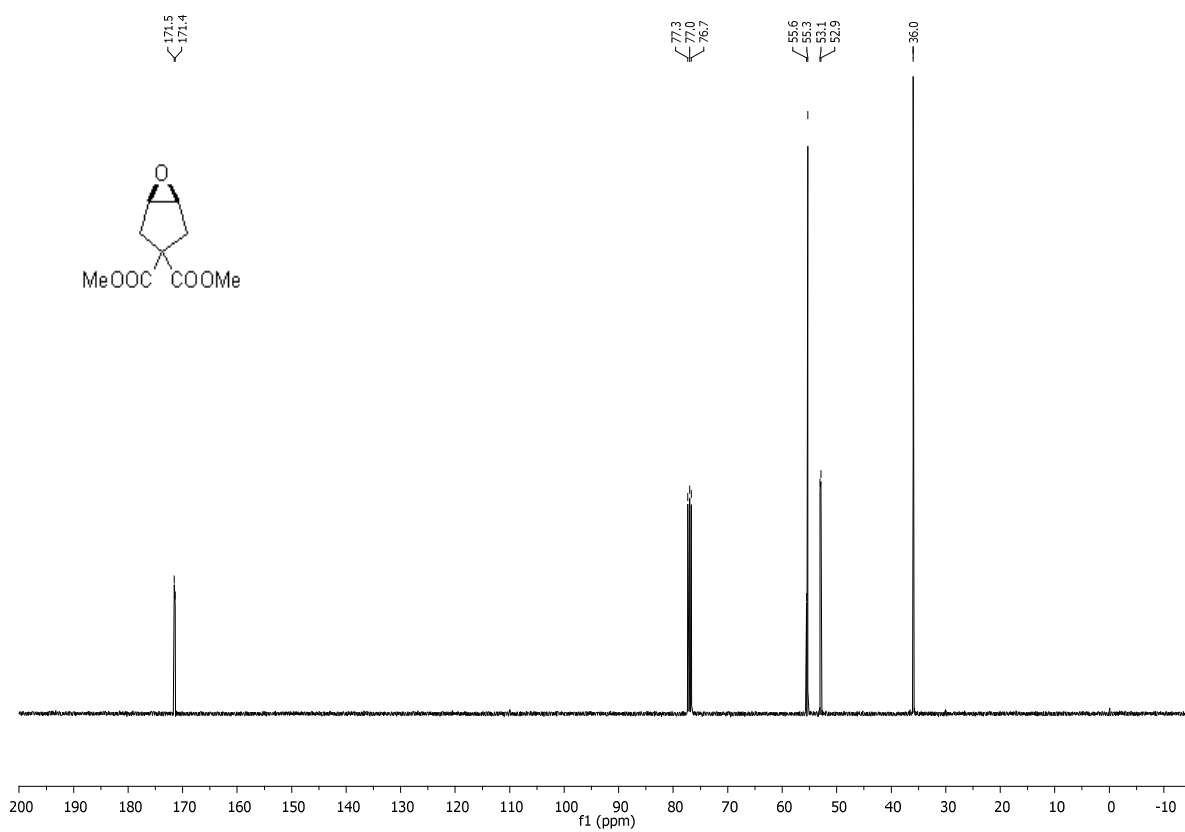
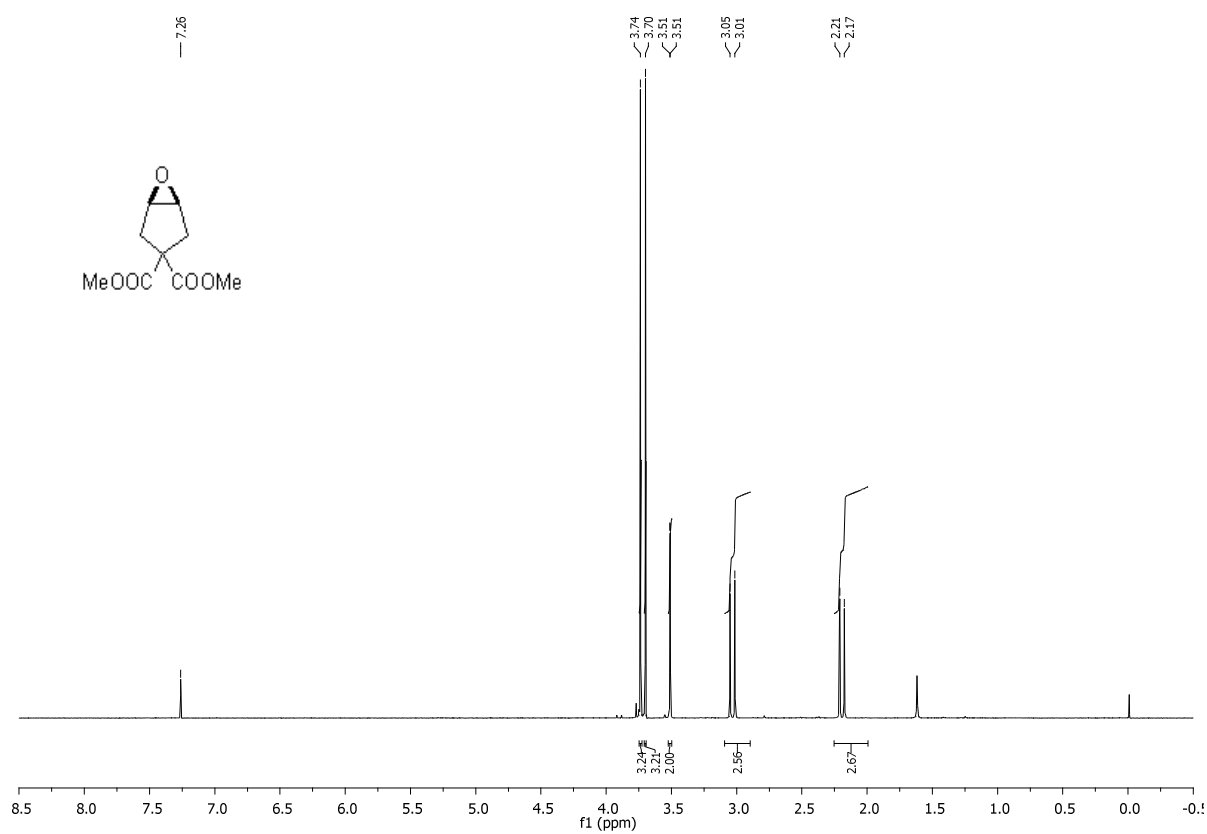
To a stirred solution of 3,6-dioxabicyclo[3.2.0]heptan-7-one (150 mg, 1.3 mmol) in dry DMF (5 mL) was added  $\text{NaN}_3$  (427 mg, 6.5 mmol) under  $\text{N}_2$  atm. The reaction mixture was stirred at room temperature for 48 h and diluted with water (10 mL). The pH was adjusted to 8 with saturated aqueous  $\text{NaHCO}_3$  solution and extracted with EtOAc (10 mL). The aqueous layer was acidified to a pH of 2 with 1 M HCl and then extracted with  $\text{Et}_2\text{O}$  (3 x 30 mL). The combined  $\text{Et}_2\text{O}$  layers were washed with brine (2 x 20 mL), dried over  $\text{Na}_2\text{SO}_4$  and evaporated to dryness to yield the crude azide. The crude azide was dissolved in methanol (3 mL) and 10 % Pd/C (10 mg) was added and the reaction mixture stirred under a  $\text{H}_2$  atmosphere (1 atm,  $\text{H}_2$  balloon) for 12 h. The reaction mixture was filtered through a pad of celite using methanol as the eluent and evaporated to dryness to afford the crude amino acid, which was triturated with  $\text{Et}_2\text{O}$  (5 mL) and dried under high vacuum to afford the title compound as white solid (73 mg) in 56 % yield.  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  2.96-3.03 (m, 1 H,  $\text{CHCOOH}$ ), 3.71-3.76 (m, 1 H,  $\text{CHHO}$ ), 3.80-3.88 (m, 2 H,  $\text{CH}_2\text{CHNH}_2$ ), 3.97-4.14 (m,  $\text{CHNH}_2$ ), 4.18 (virtual t,  $J$  = 8.8 Hz, 1 H,  $\text{CHHO}$ ).



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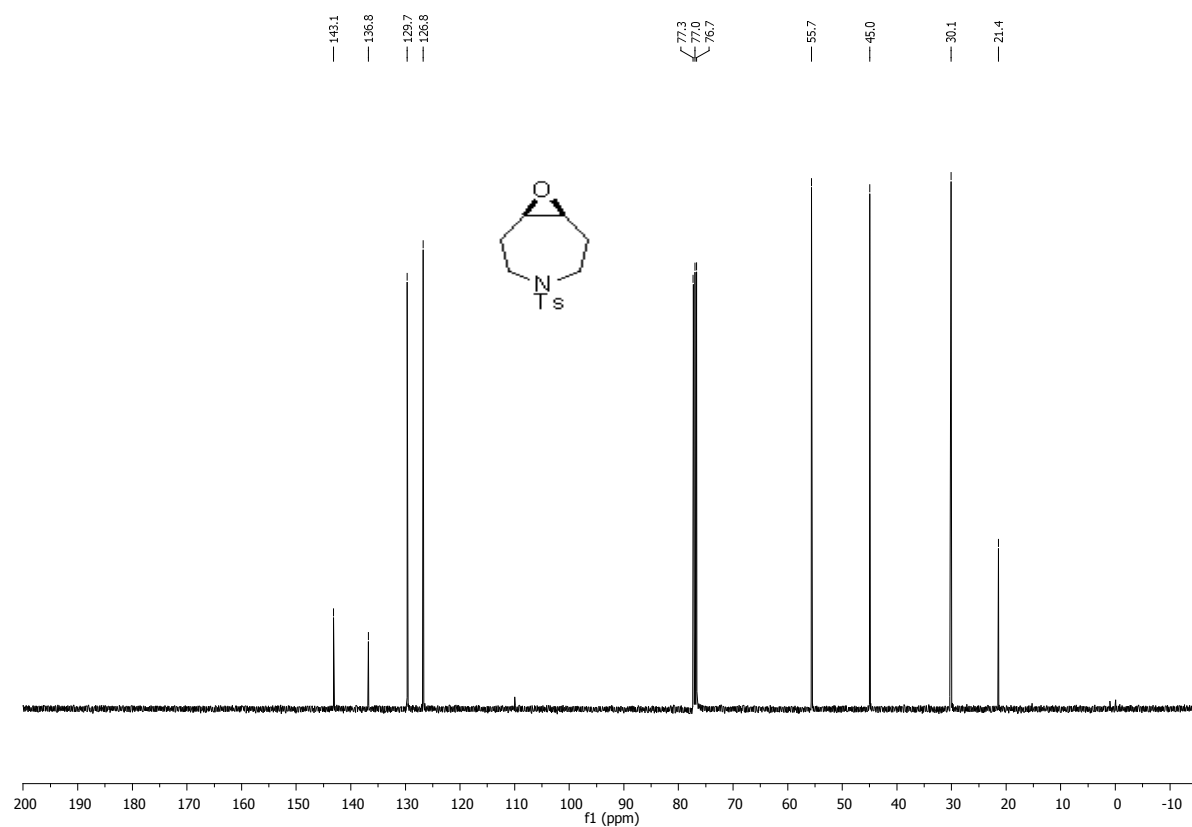
# <sup>1</sup>H and <sup>13</sup>C Spectra of Dimethyl 6-oxa-bicyclo[3.1.0]hexane-3,3-dicarboxylate (1)



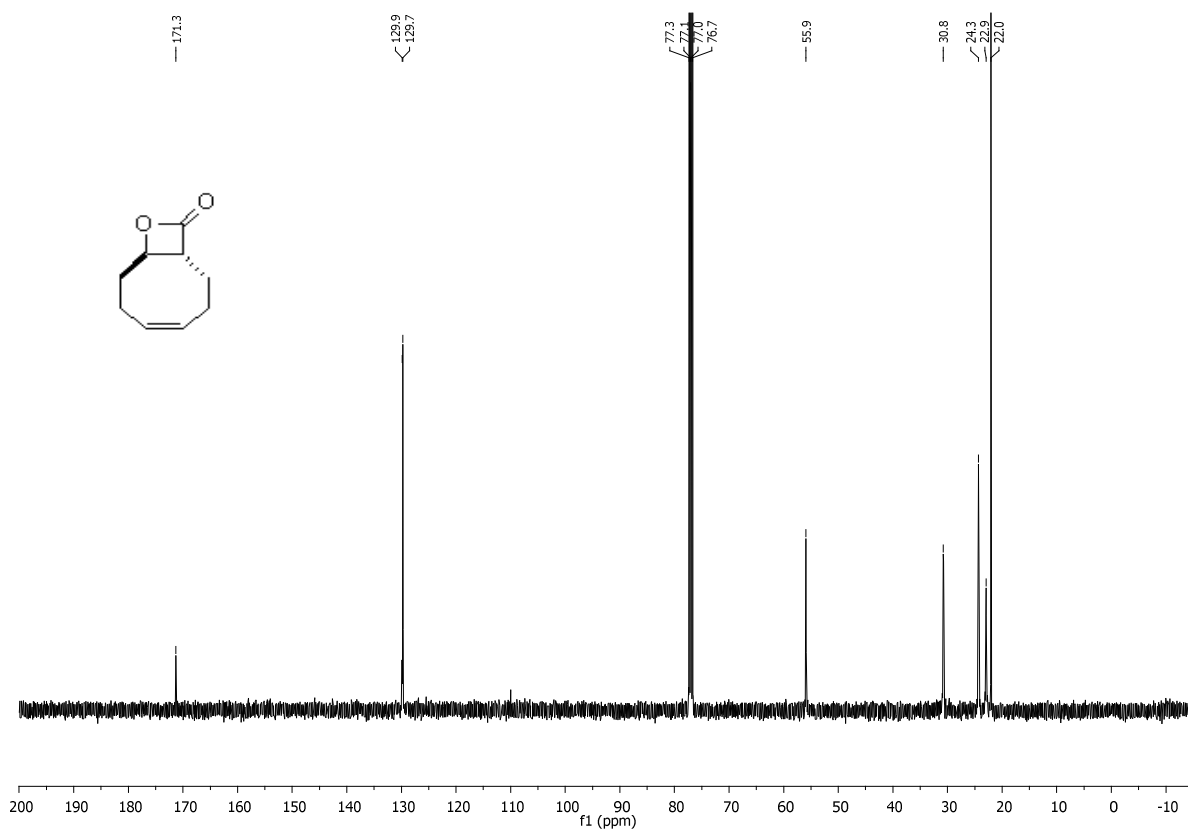
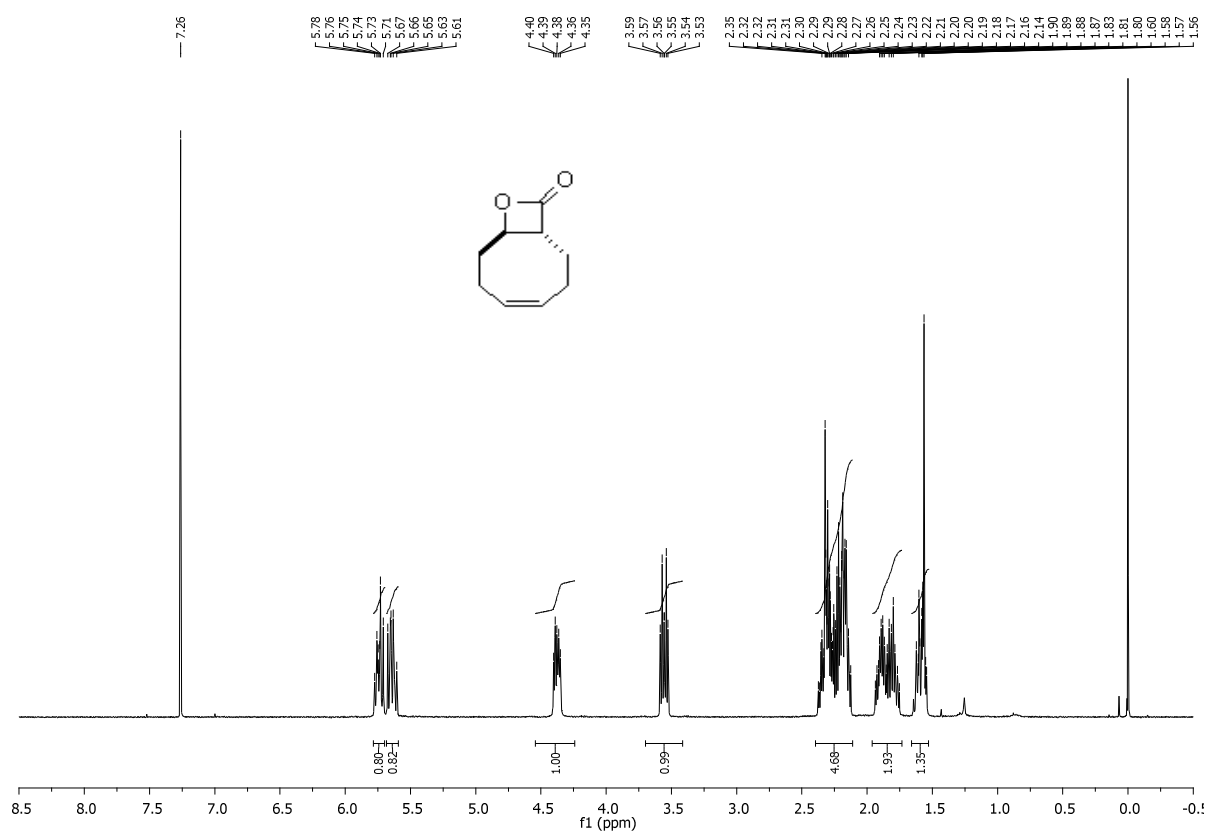
Chemical structure: C1CN2CCCC2C1

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of 2,3-dihydro-2H-indole. The spectrum shows peaks in the aromatic region (7.25-7.65 ppm) and aliphatic region (1.25-3.68 ppm). Integration values are provided below the peaks.

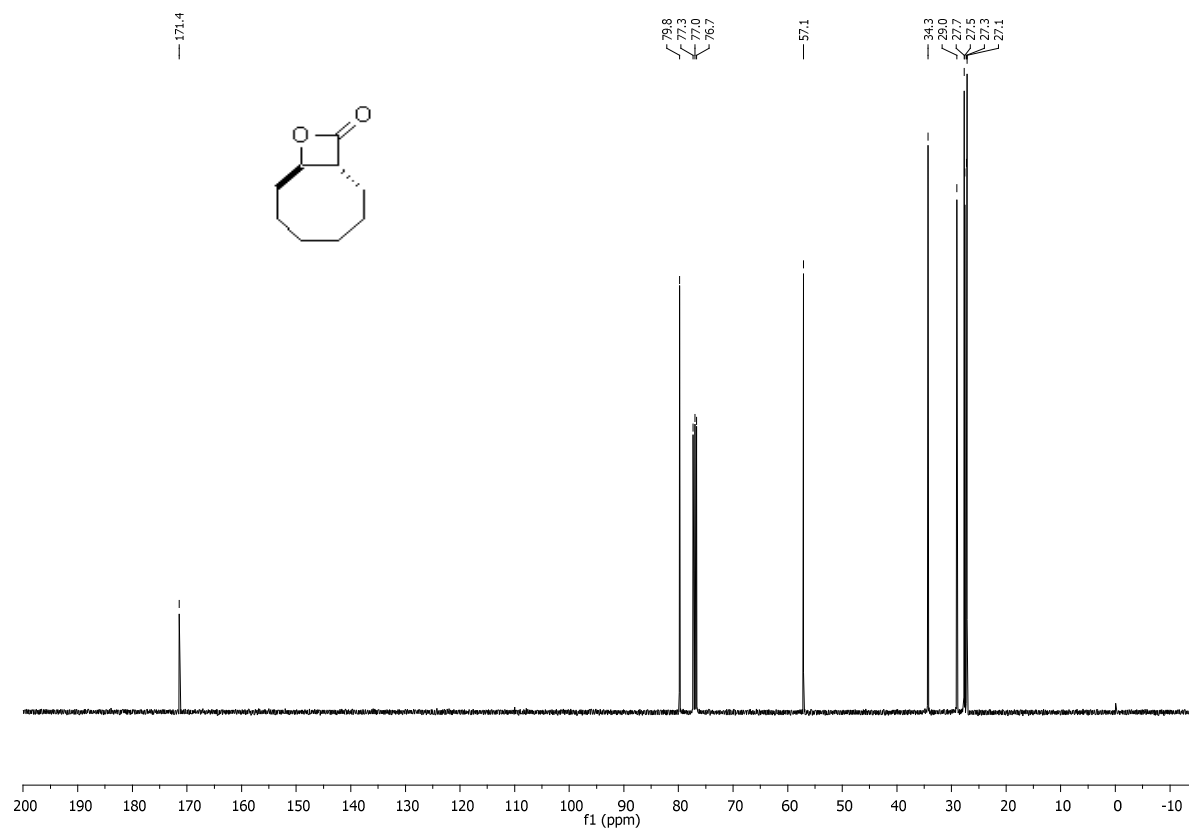
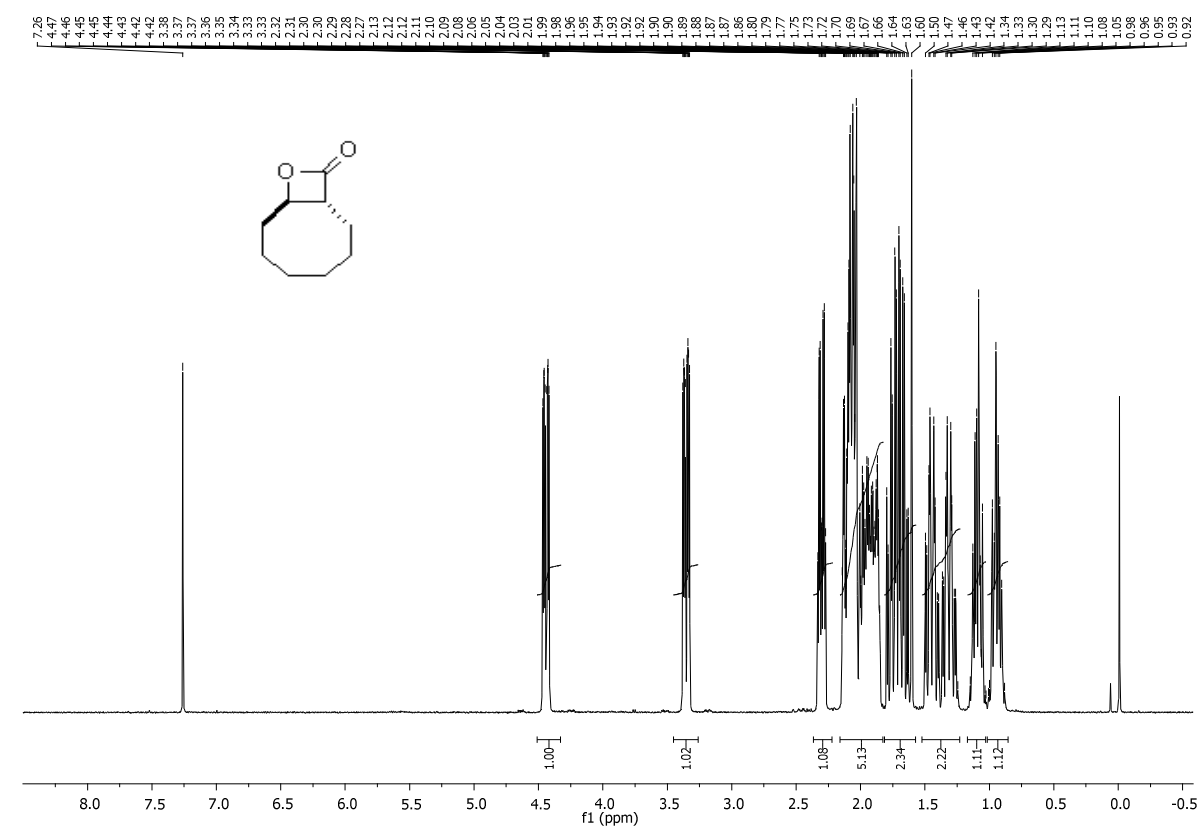
| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| 7.65                 | 1.00        |
| 7.29                 | 1.10        |
| 7.27                 |             |
| 7.26                 |             |
| 3.68                 | 0.99        |
| 3.67                 |             |
| 3.66                 |             |
| 3.65                 |             |
| 3.64                 |             |
| 3.20                 | 1.10        |
| 2.68                 | 0.96        |
| 2.66                 |             |
| 2.65                 |             |
| 2.64                 |             |
| 2.63                 | 1.73        |
| 2.62                 |             |
| 2.41                 | 1.99        |
| 2.41                 |             |
| 2.30                 |             |
| 2.29                 |             |
| 2.28                 |             |
| 1.27                 |             |
| 1.25                 |             |



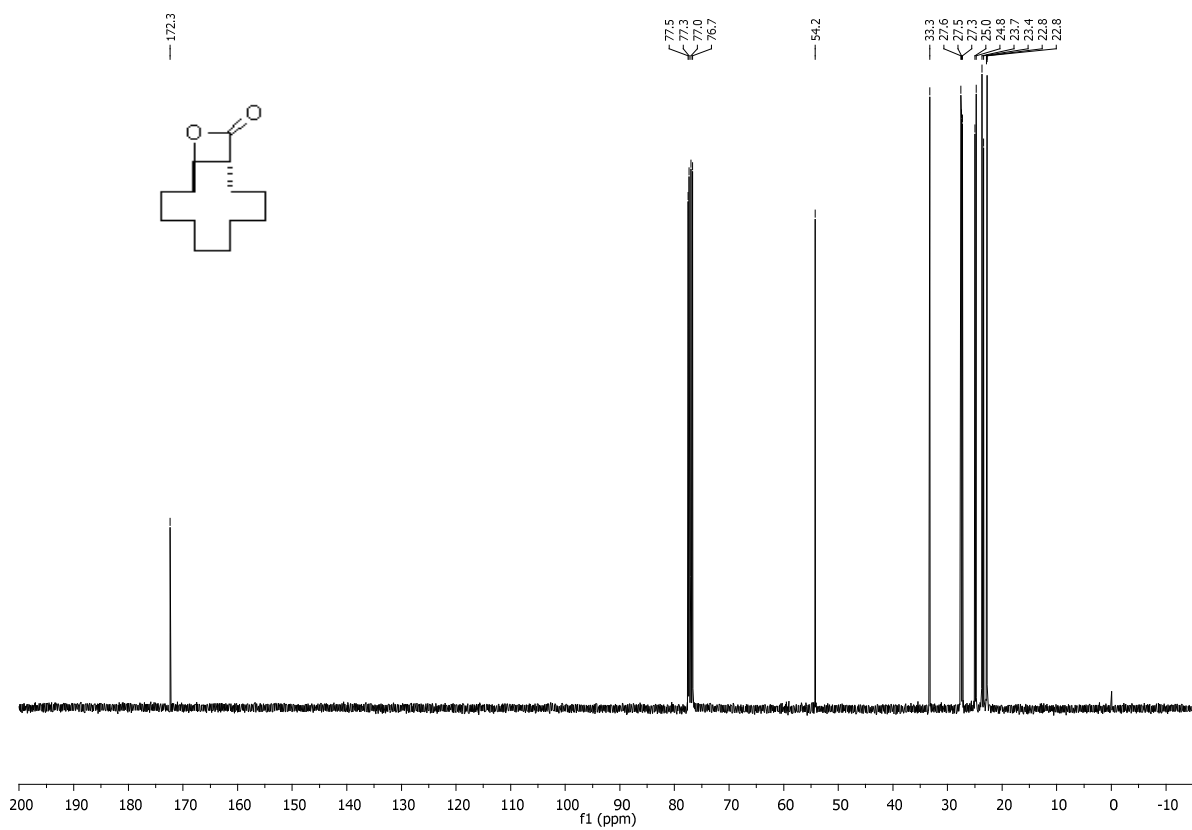
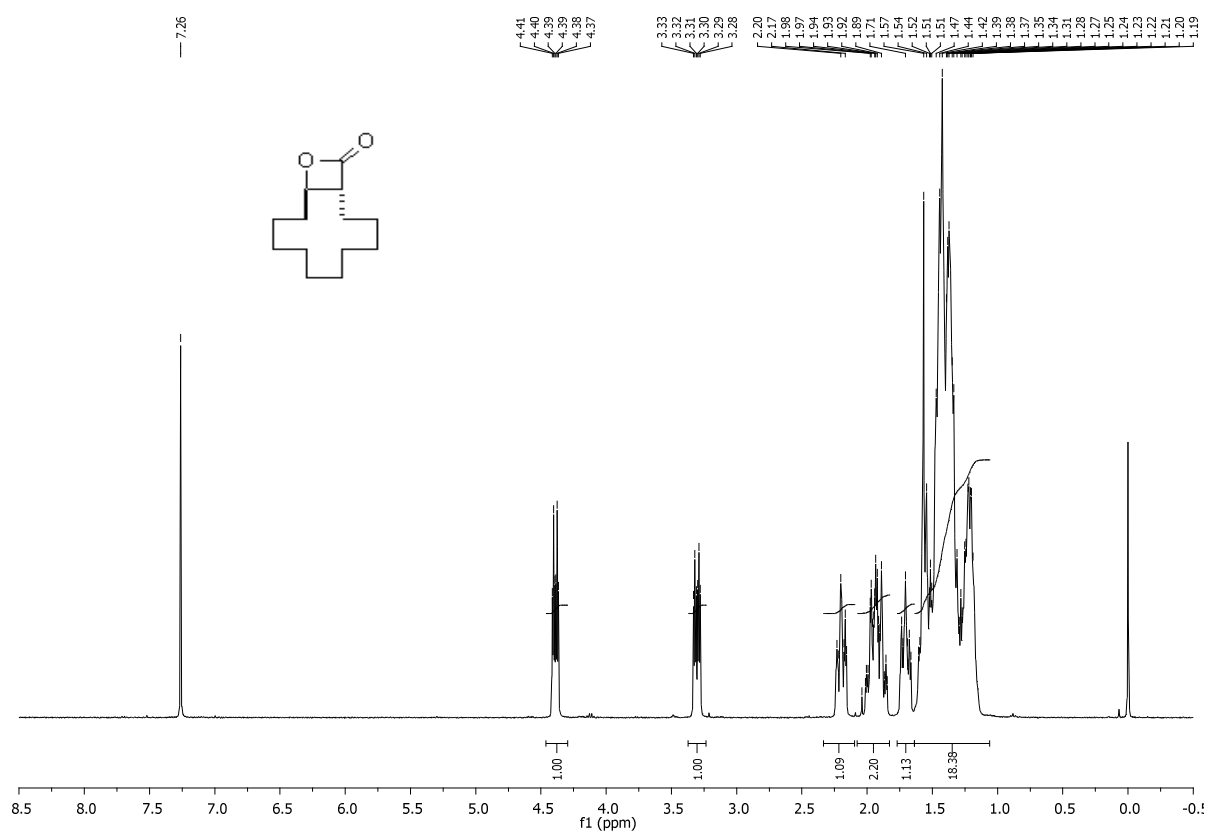
# <sup>1</sup>H and <sup>13</sup>C Spectra of 9-Oxabicyclo[6.2.0]dec-4-en-10-one (3)



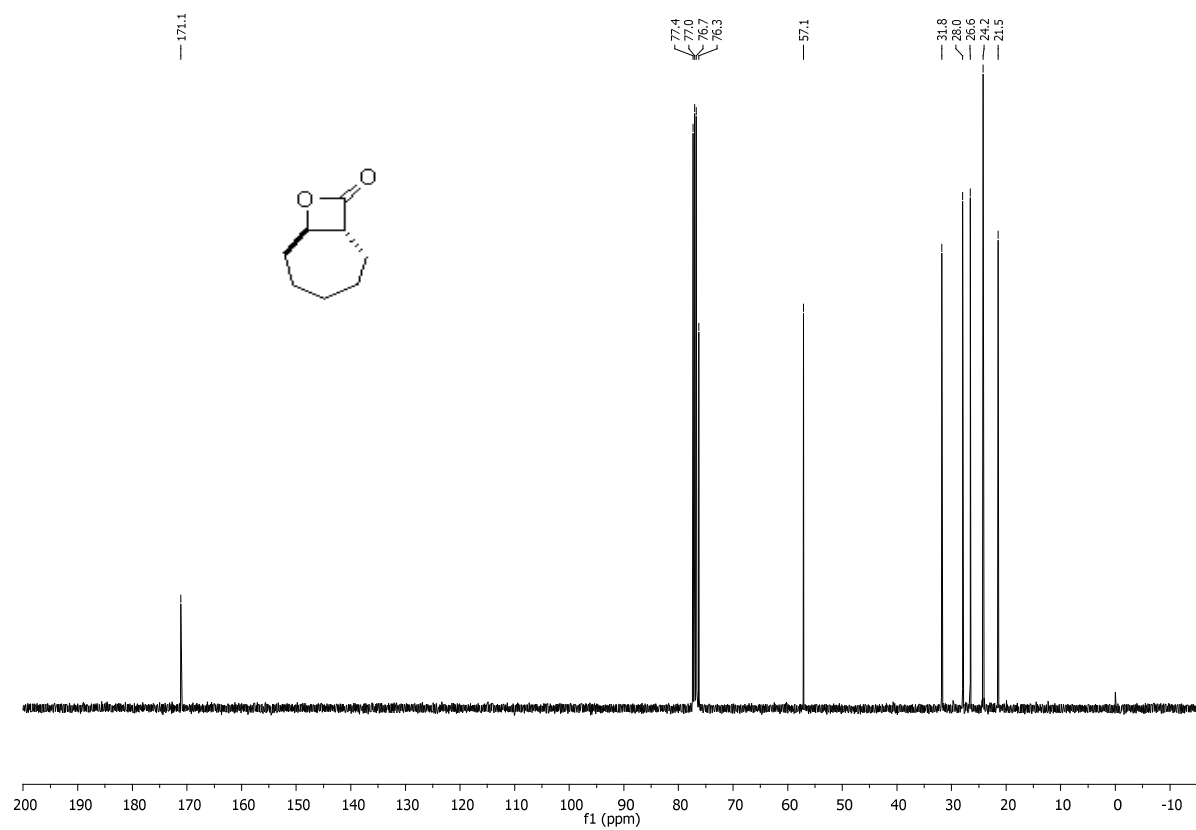
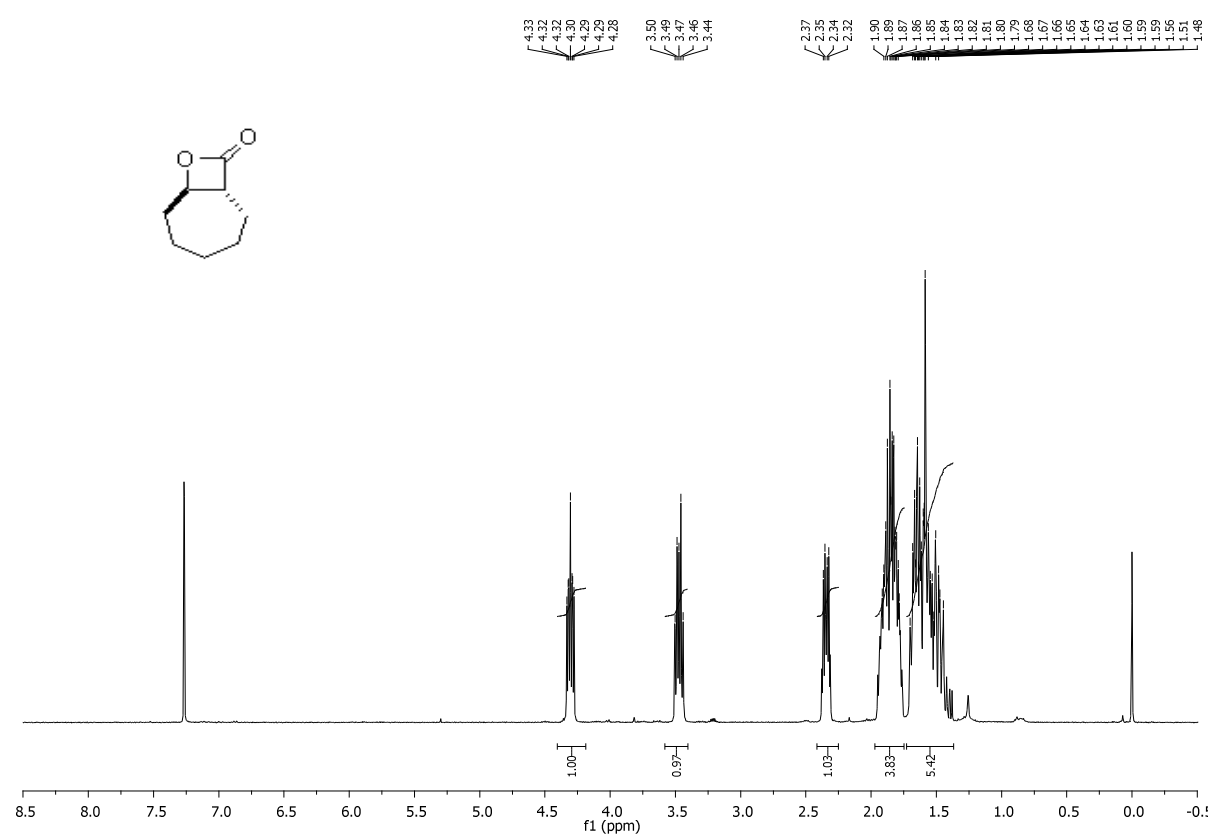
# <sup>1</sup>H and <sup>13</sup>C Spectra of 9-Oxabicyclo[6.2.0]decan-10-one (4)



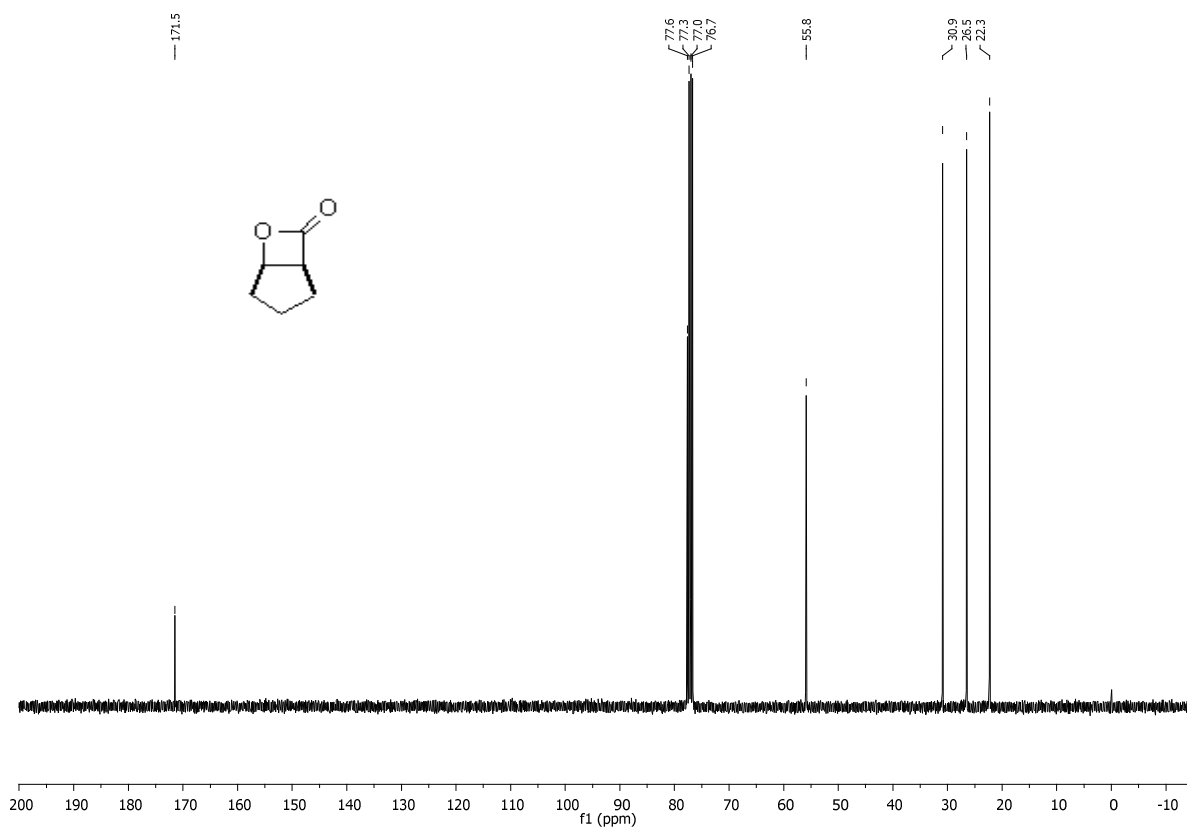
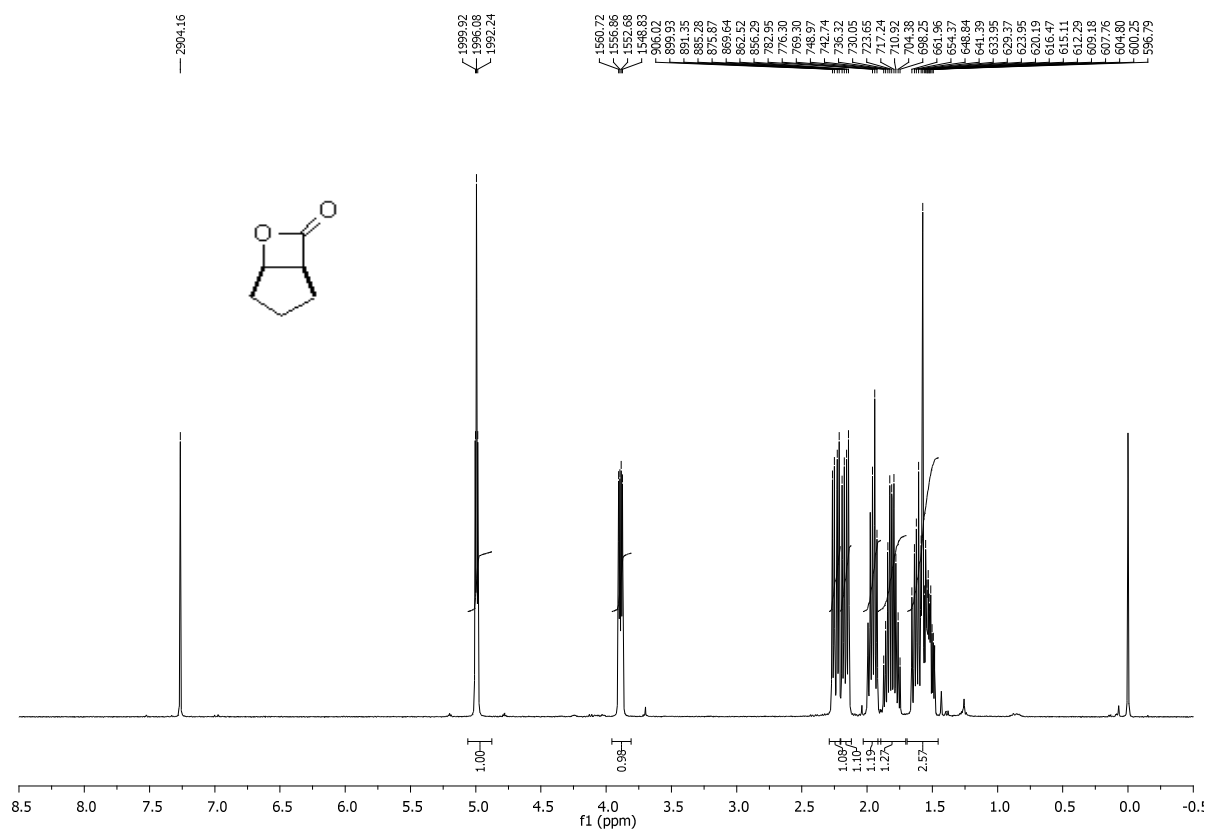
# <sup>1</sup>H and <sup>13</sup>C Spectra of 13-Oxabicyclo[10.2.0]tetradecan-14-one (5)



# <sup>1</sup>H and <sup>13</sup>C Spectra of 8-Oxabicyclo[5.2.0]nonan-9-one (6)

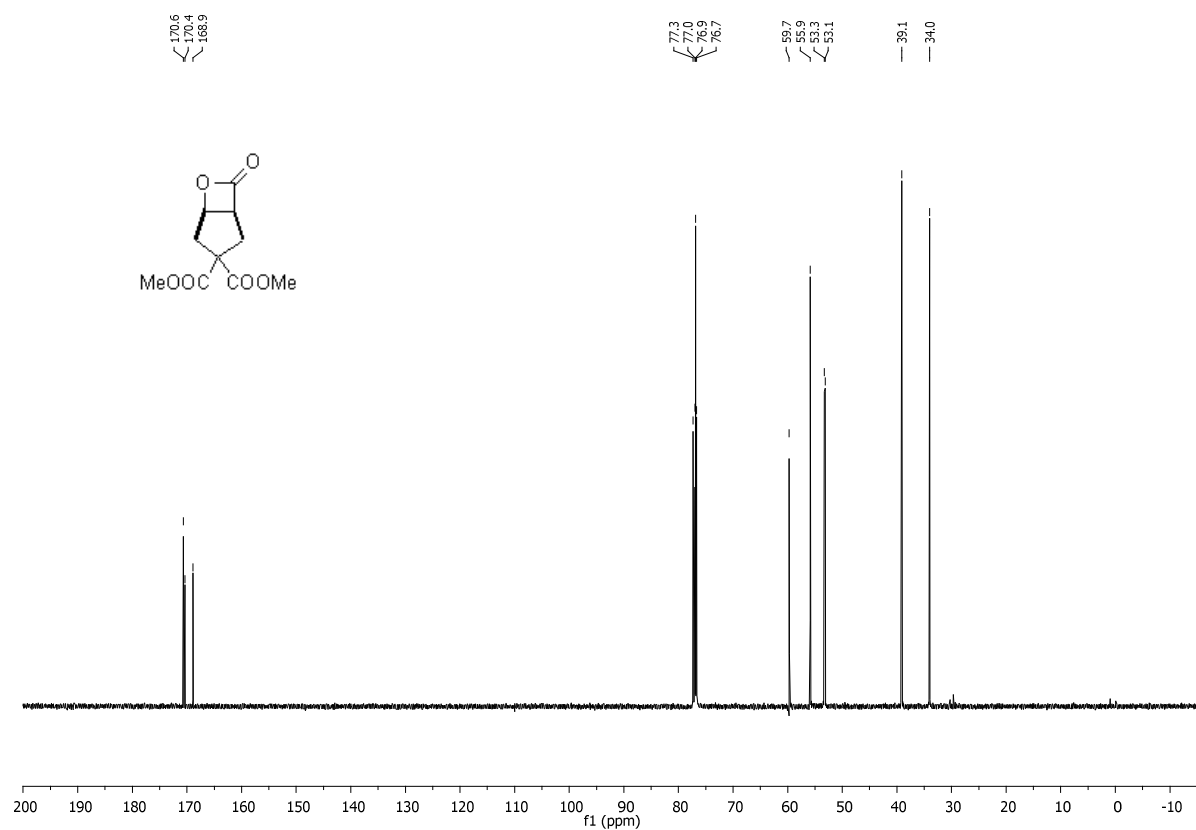
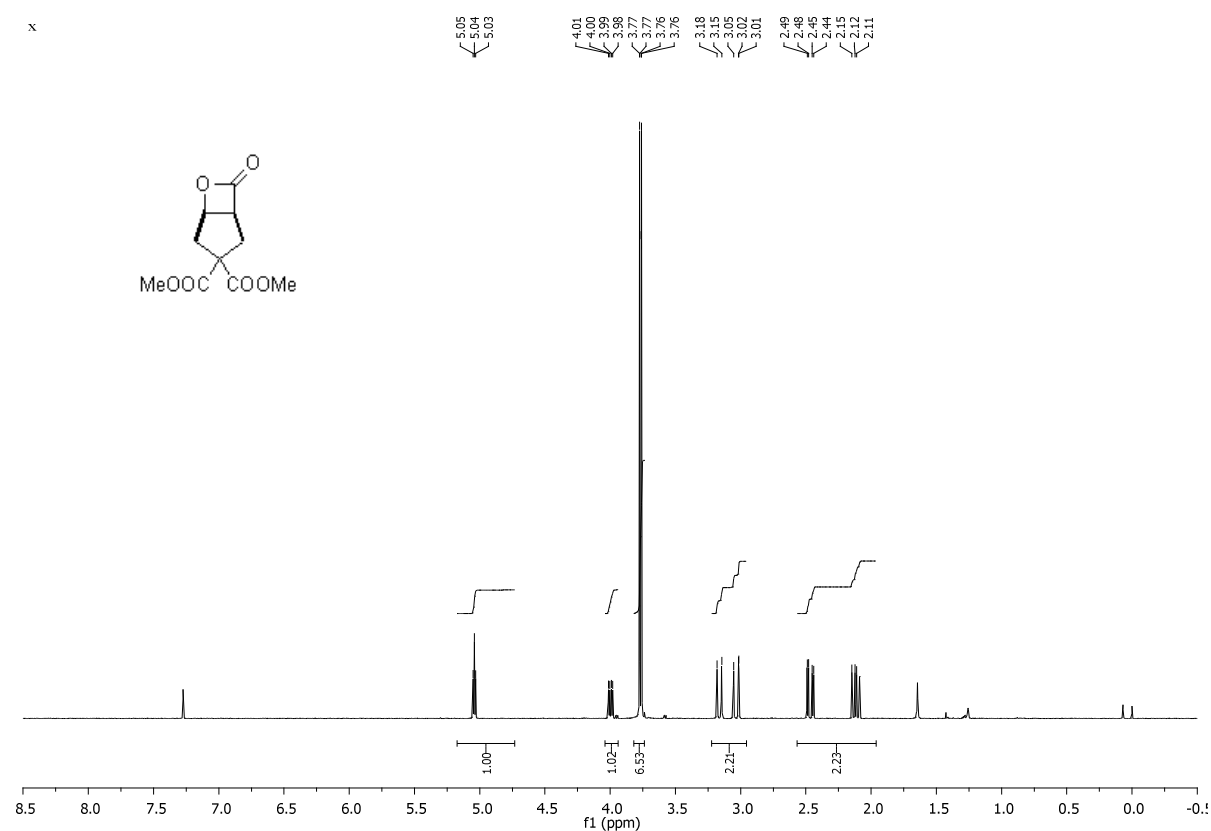


# <sup>1</sup>H and <sup>13</sup>C Spectra of 6-Oxabicyclo[3.2.0]heptan-7-one (7)

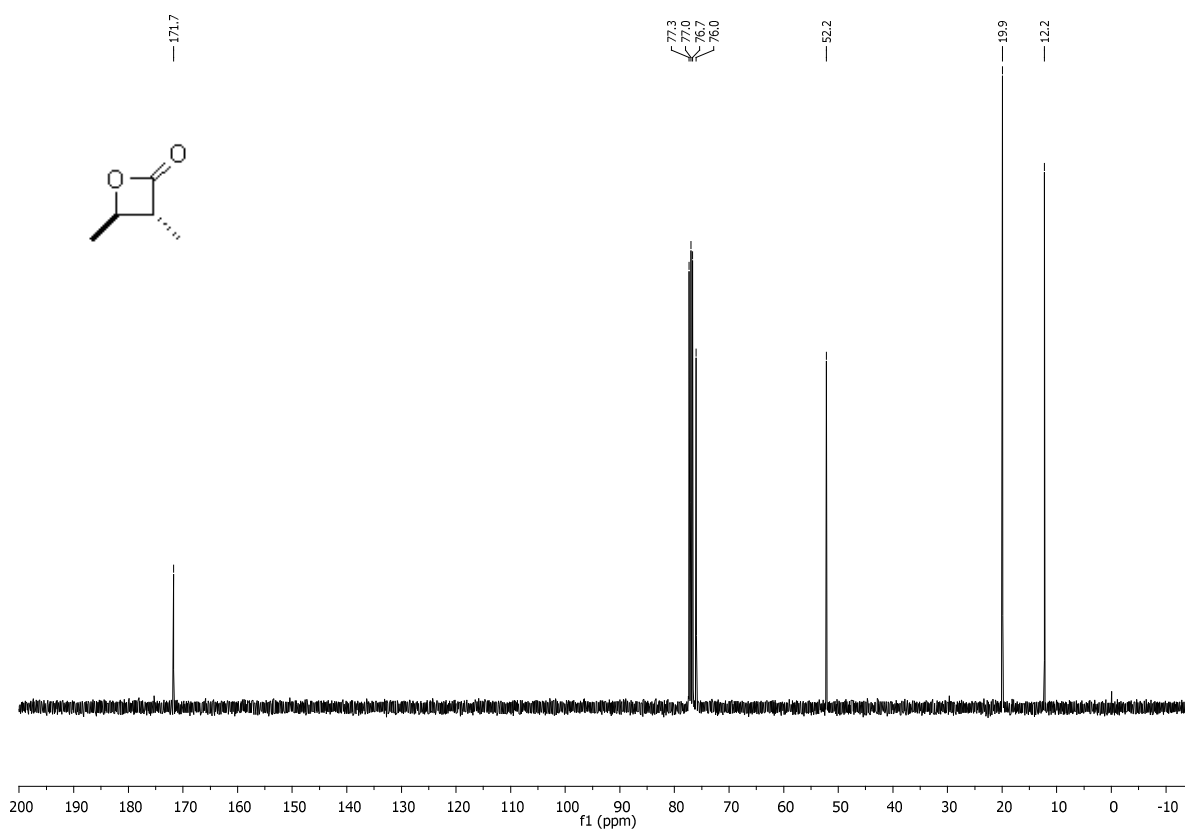
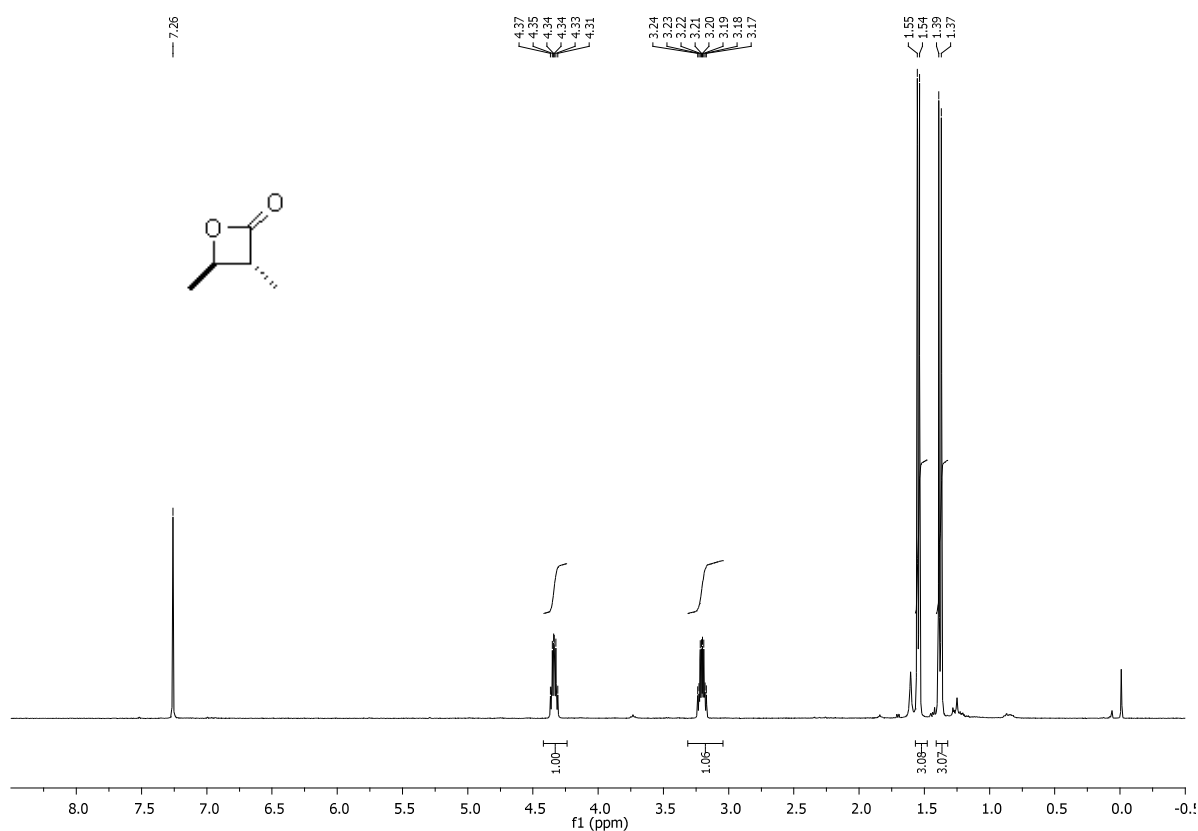




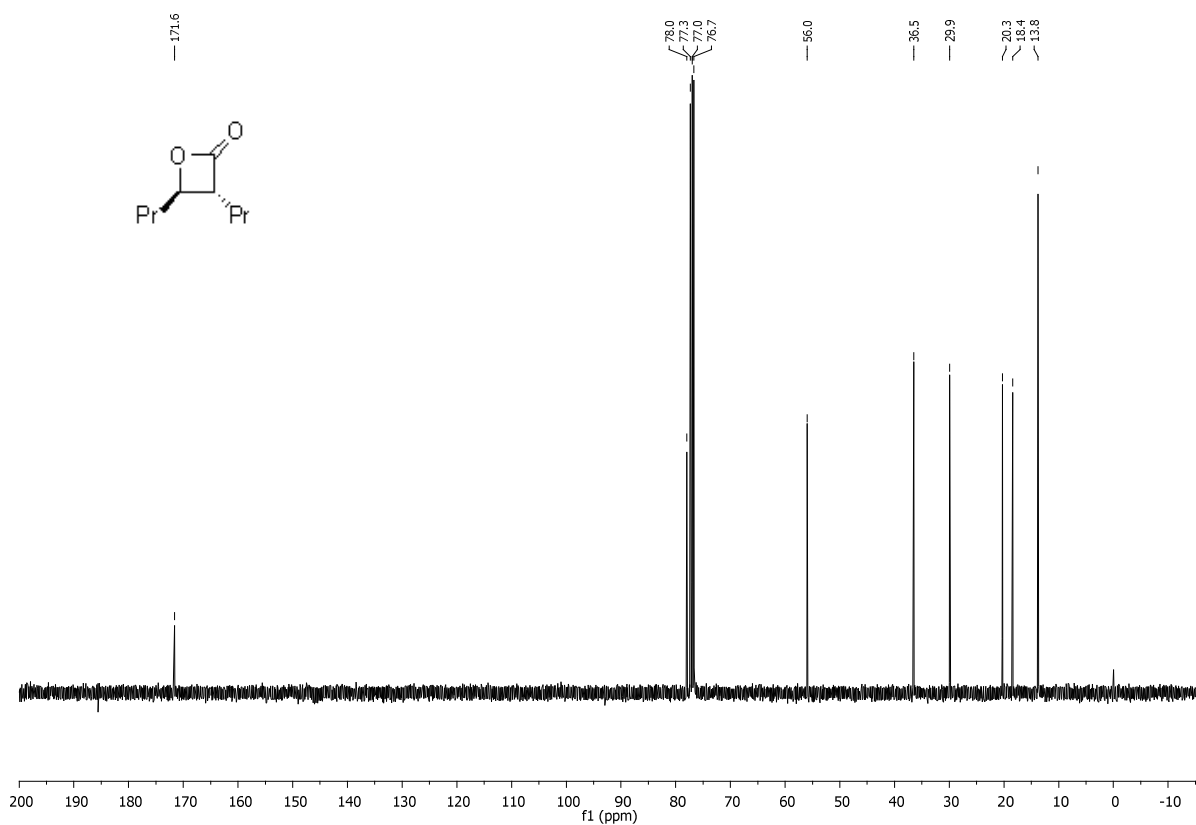
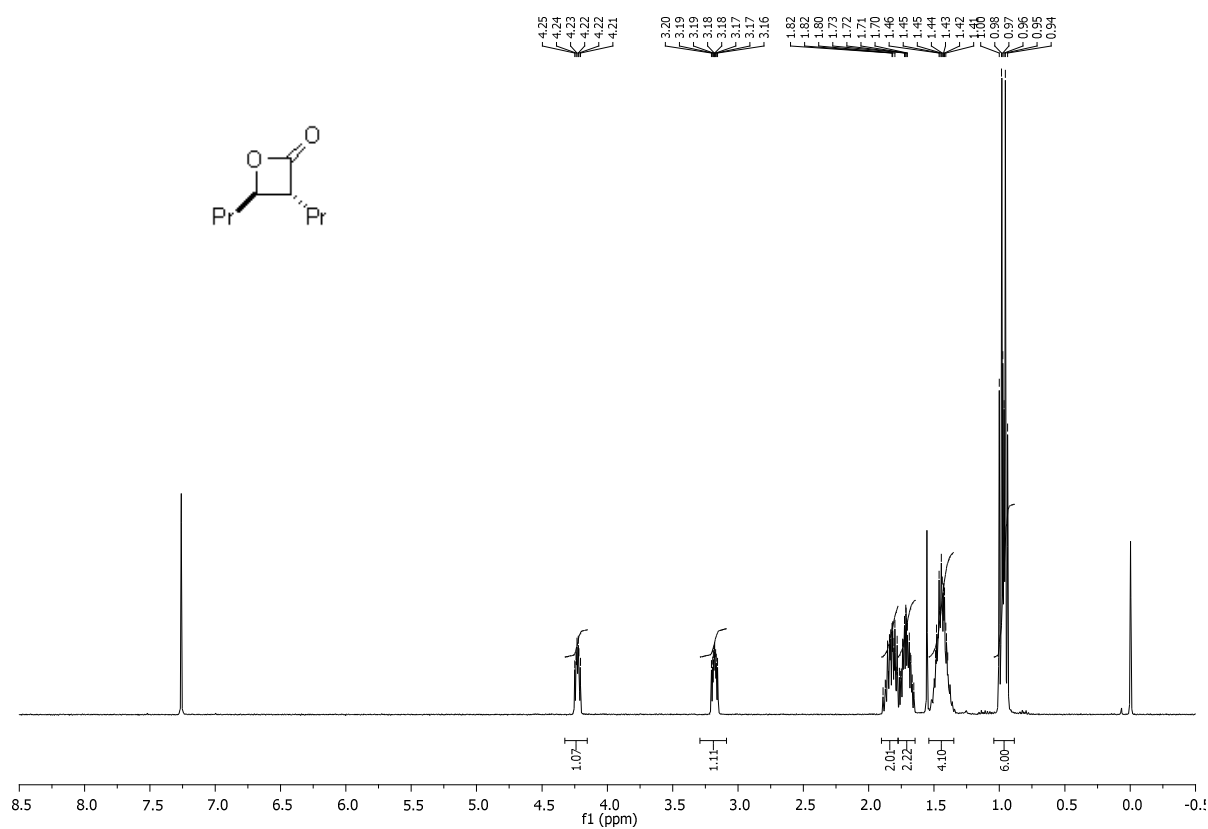
# <sup>1</sup>H and <sup>13</sup>C Spectra of Dimethyl 7-oxo-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (8)



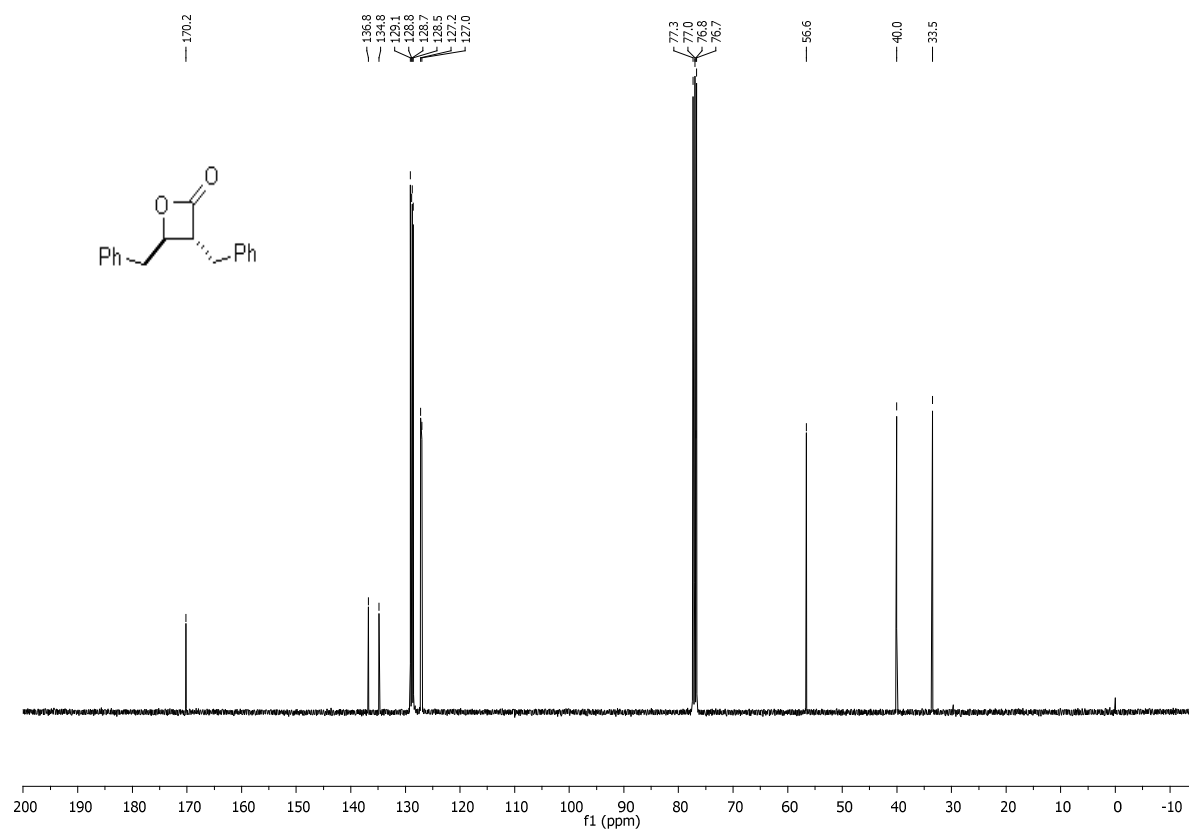
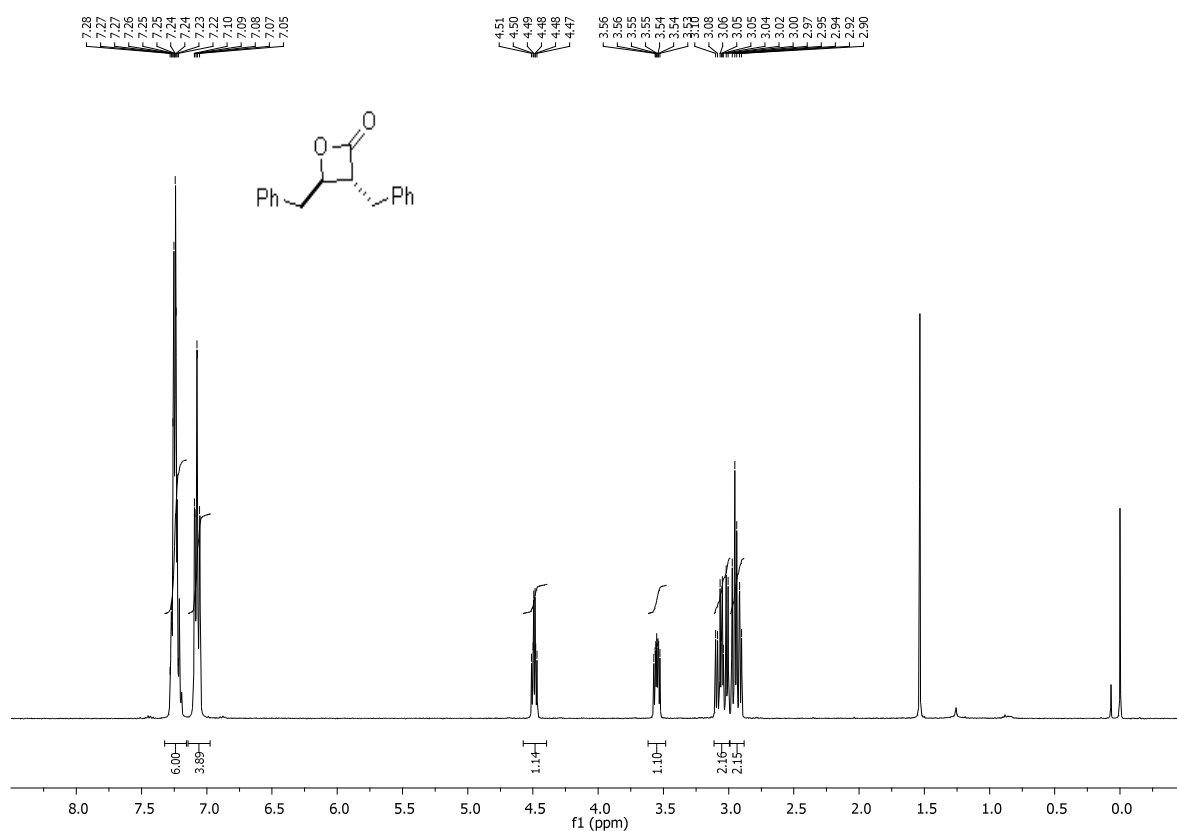
# <sup>1</sup>H and <sup>13</sup>C Spectra of 3,4-Dimethyloxetan-2-one (9)



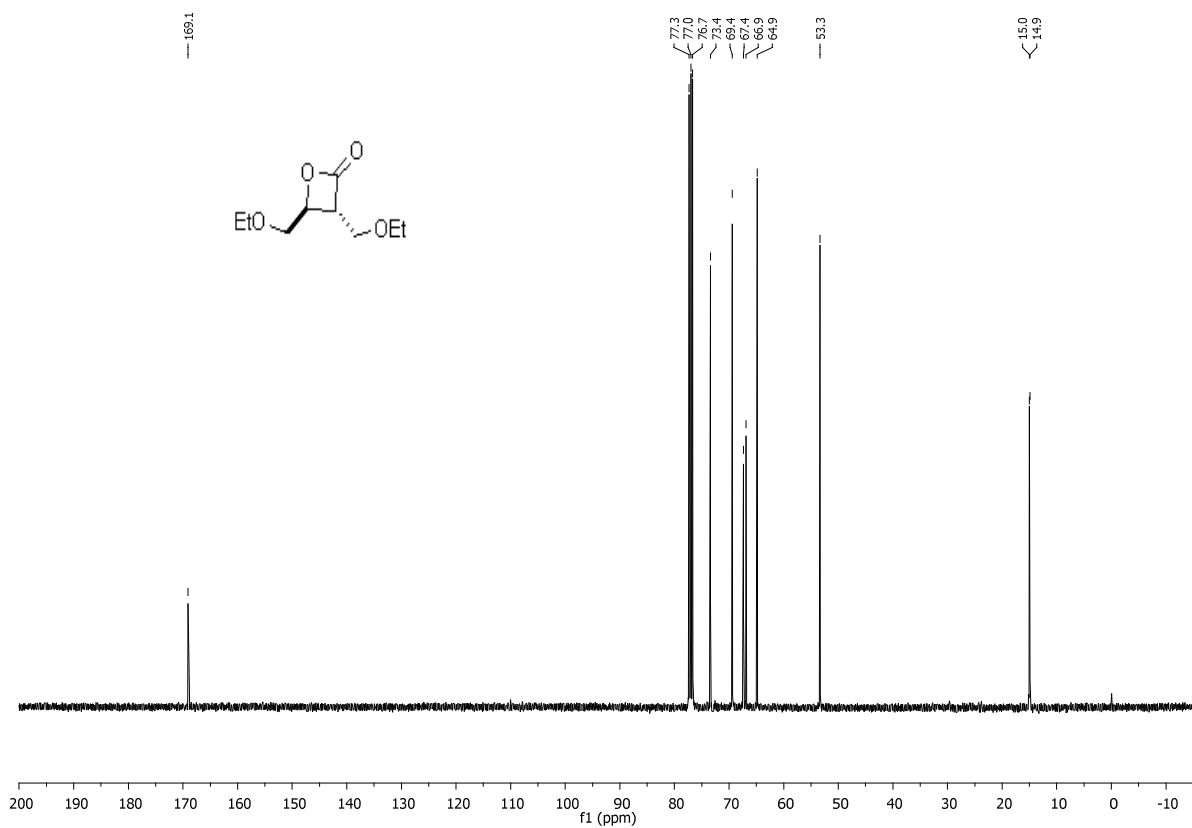
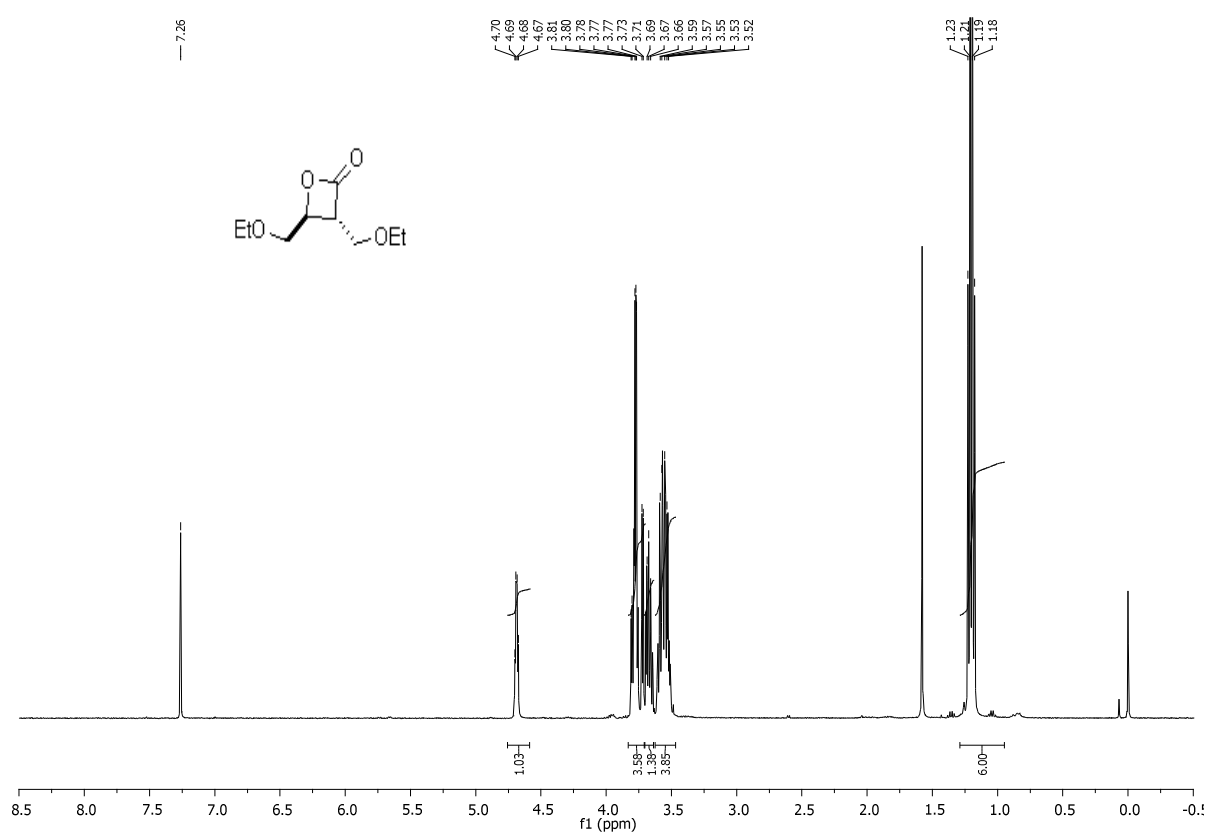
# <sup>1</sup>H and <sup>13</sup>C Spectra of 3,4-Dipropyloxetan-2-one (10)



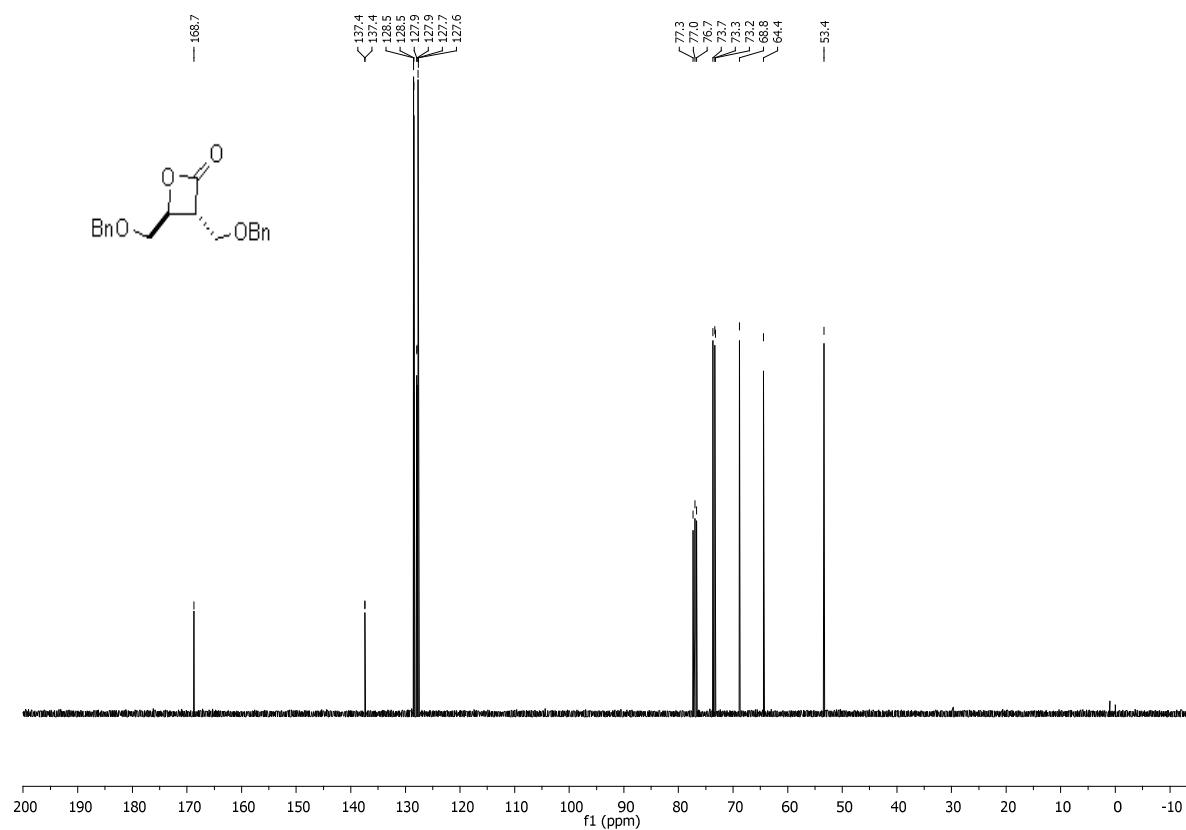
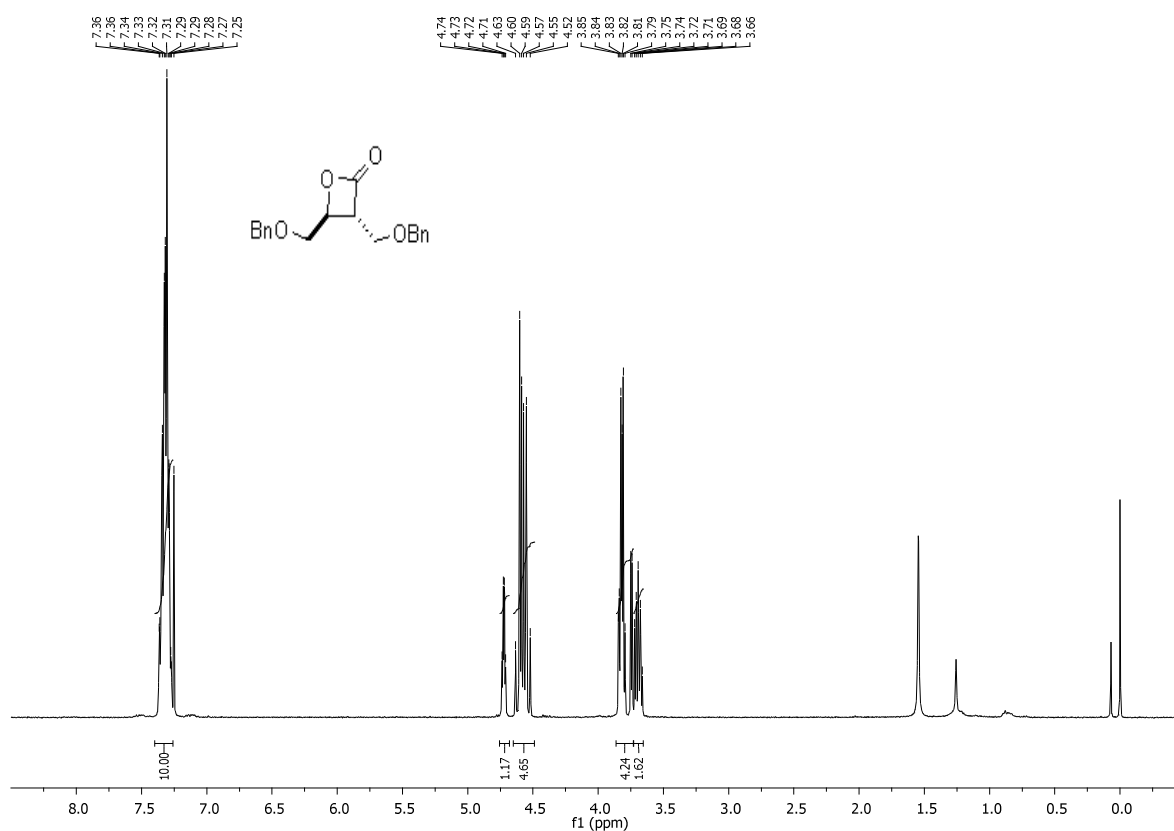
# <sup>1</sup>H and <sup>13</sup>C Spectra of 3,4-Dibenzylloxetan-2-one (11)



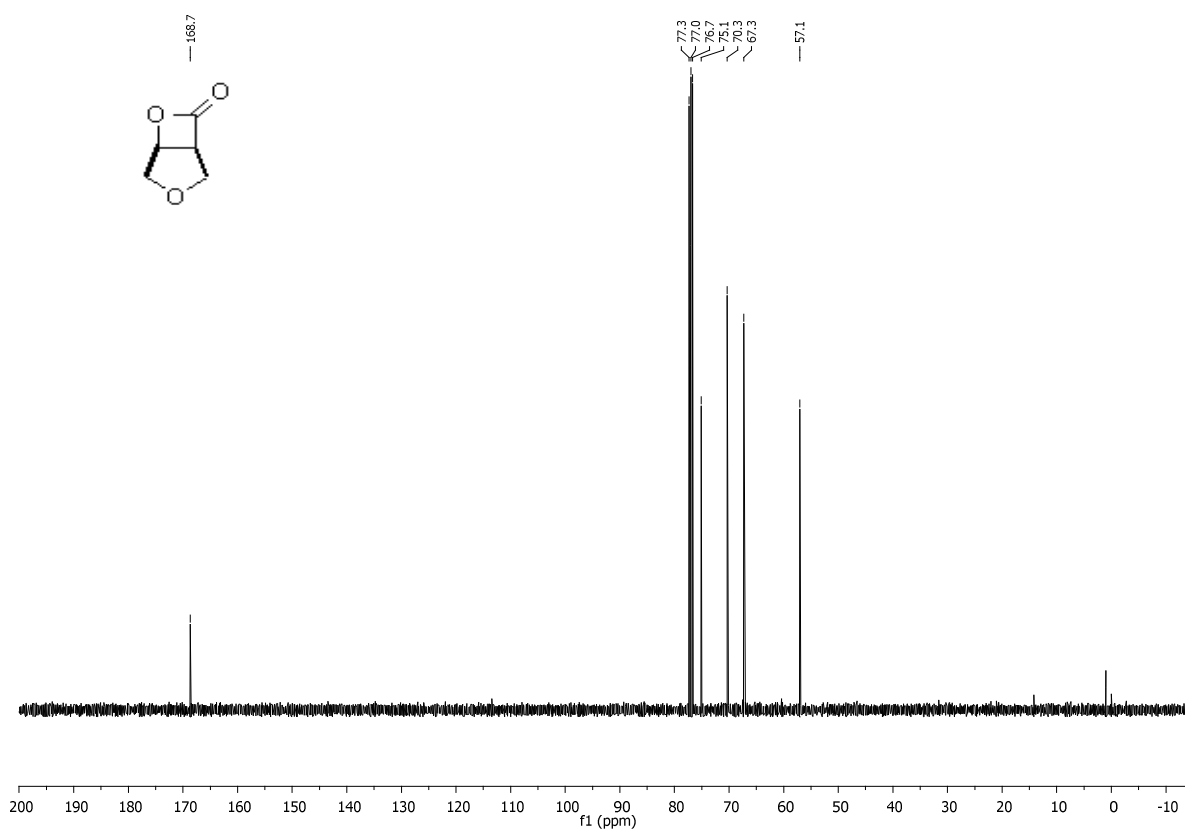
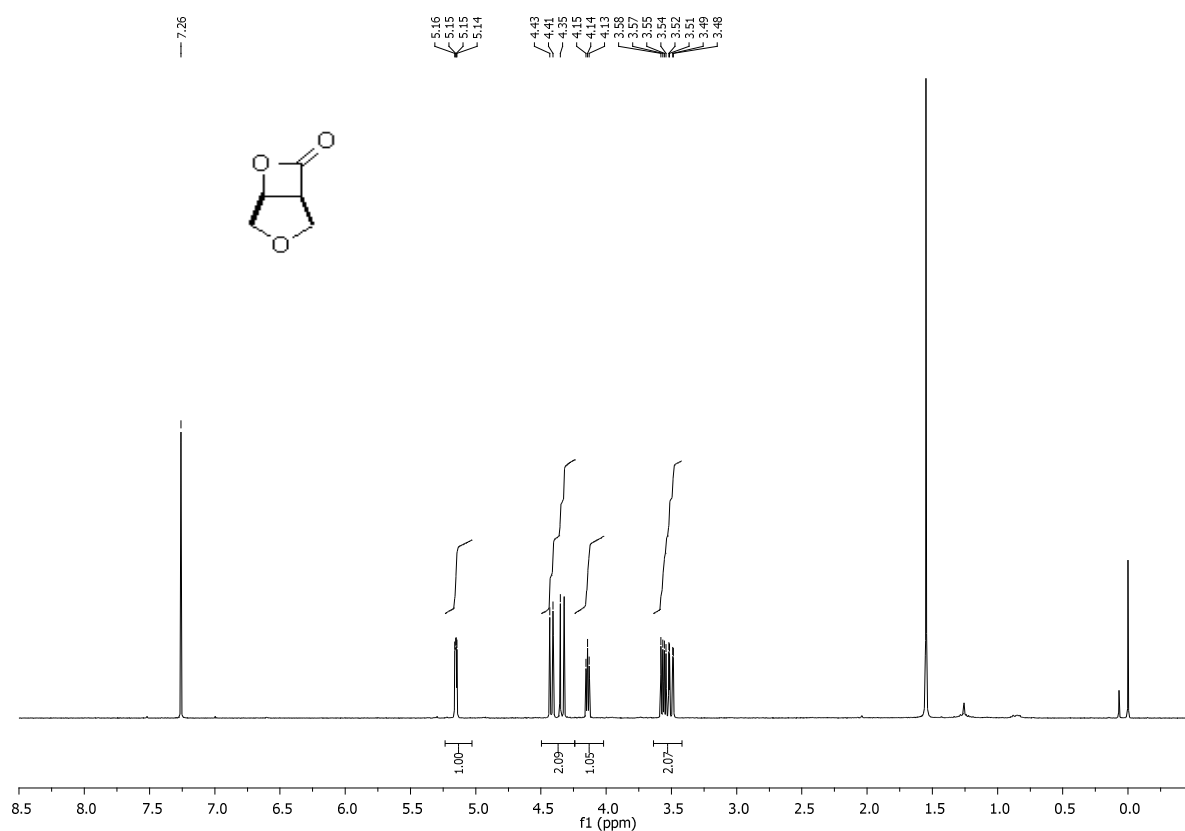
# <sup>1</sup>H and <sup>13</sup>C Spectra of 3,4-Bis(ethoxymethyl)oxetan-2-one (12)



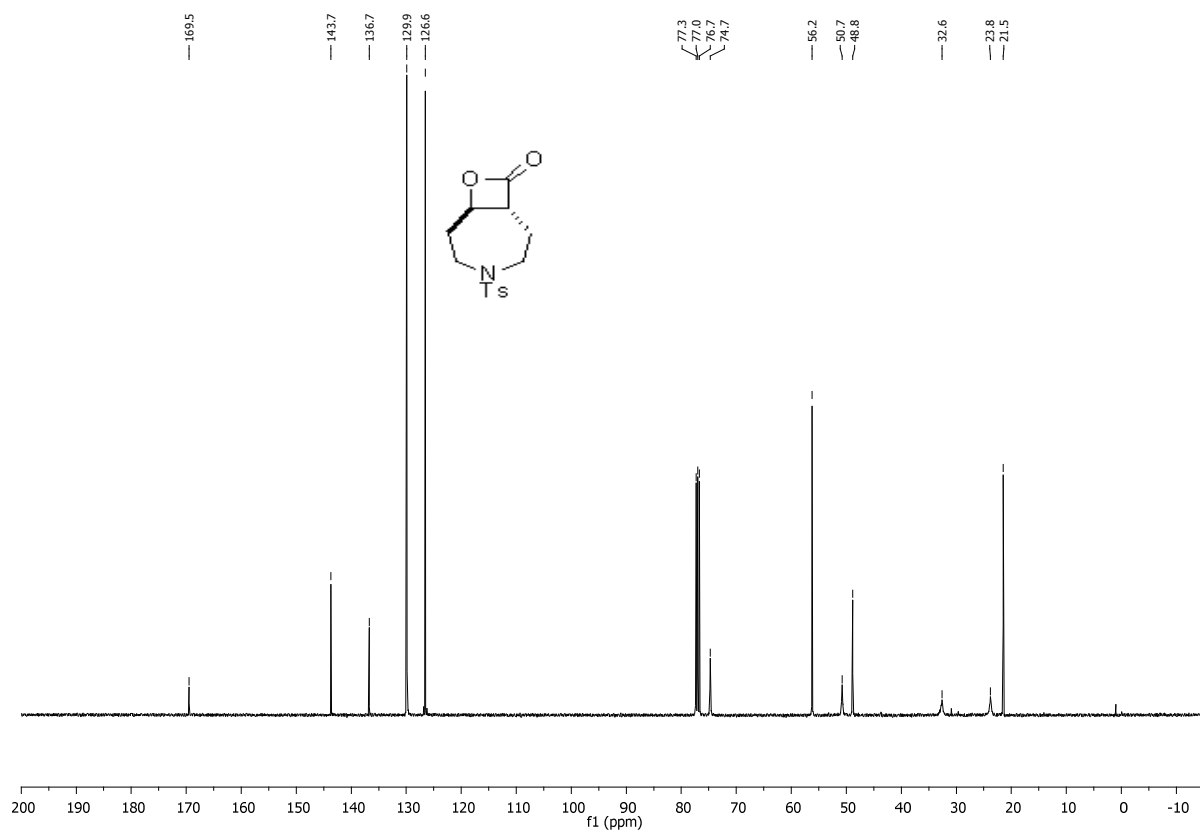
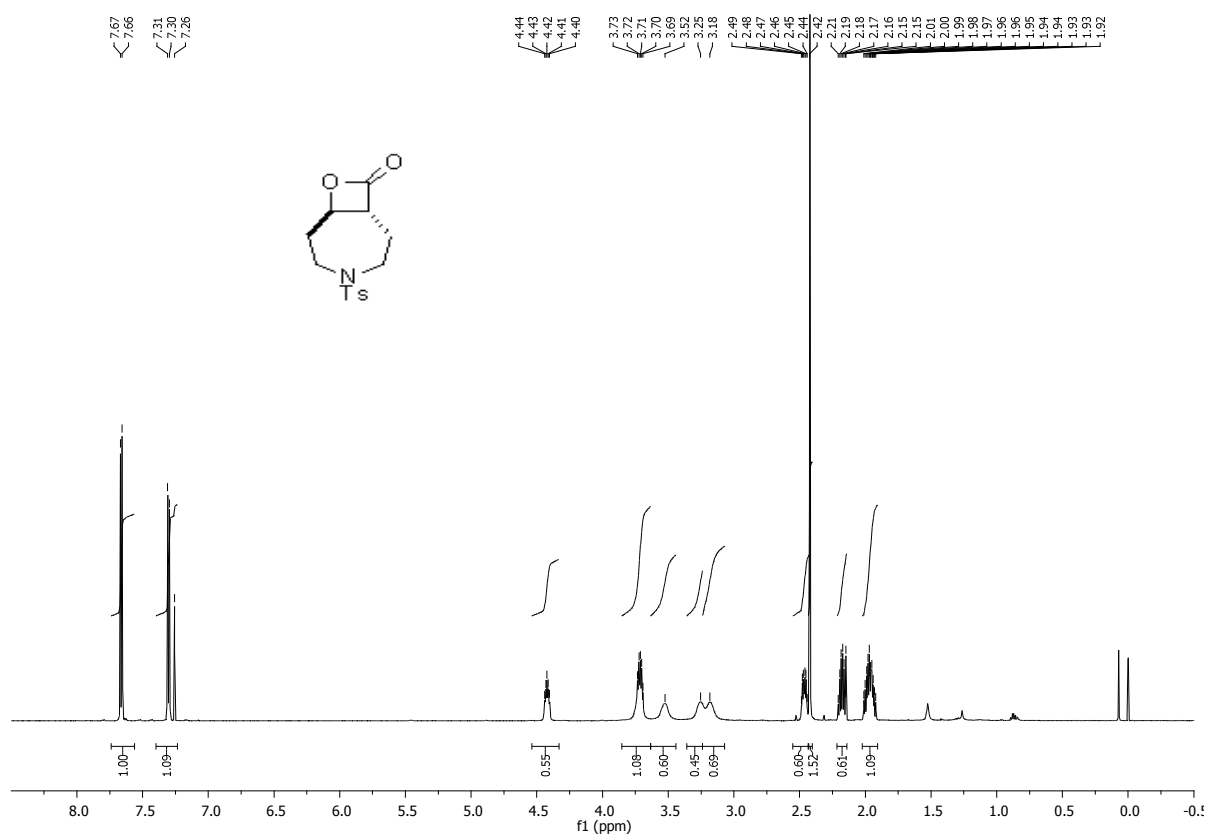
# <sup>1</sup>H and <sup>13</sup>C Spectra of 3,4-Bis(benzyloxymethyl)oxetan-2-one (13)



# <sup>1</sup>H and <sup>13</sup>C Spectra of 3,6-Dioxabicyclo[3.2.0]heptan-7-one (14)

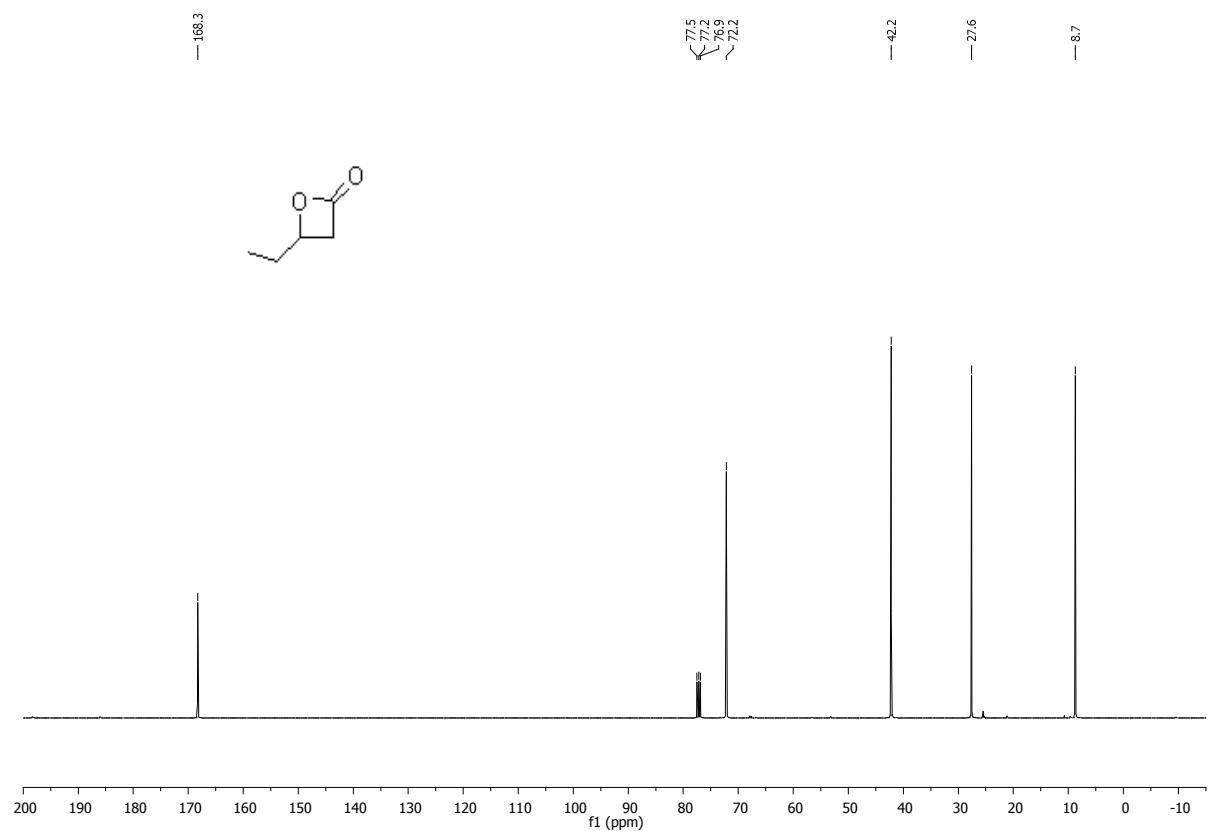
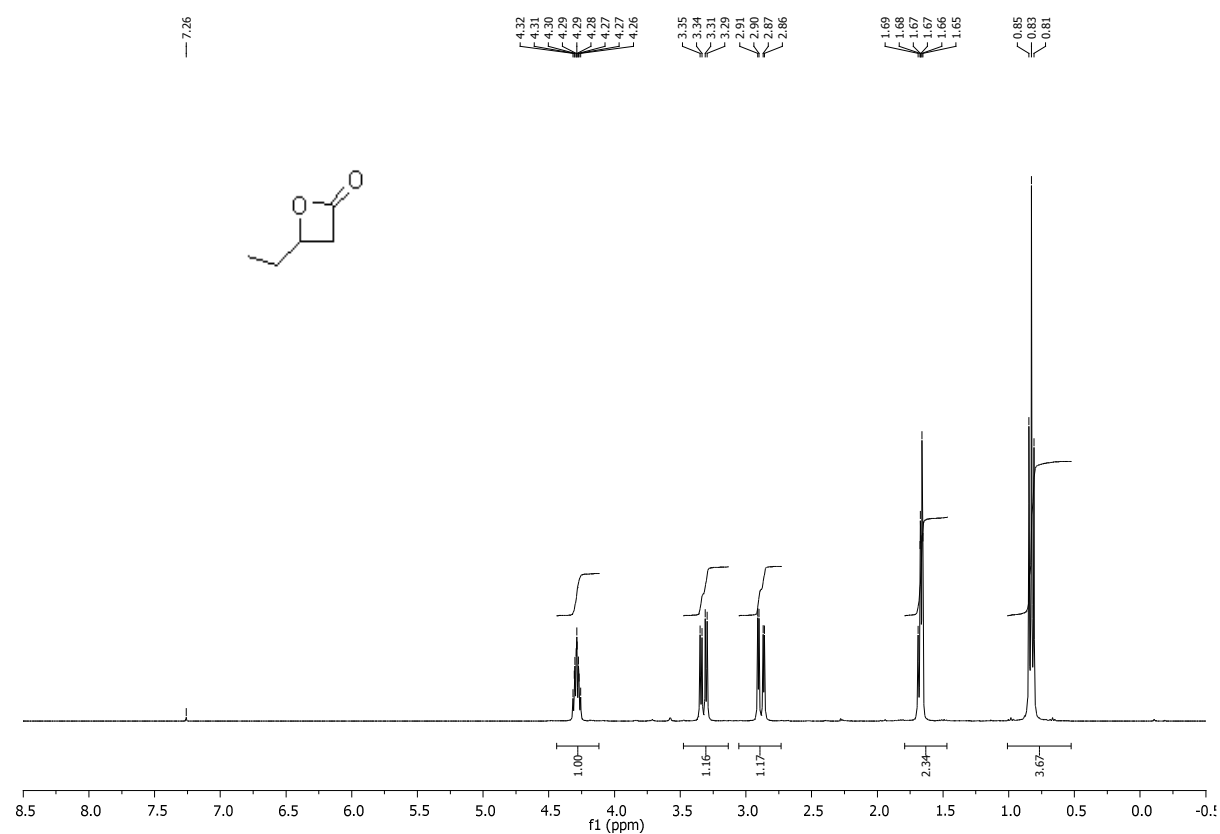


# <sup>1</sup>H and <sup>13</sup>C Spectra of 4-Tosyl-8-oxa-4-azabicyclo[5.2.0]nonan-9-one (15)





# <sup>1</sup>H and <sup>13</sup>C Spectra of 4-Ethyloxetan-2-one (16)



**<sup>1</sup>H Spectrum of *Trans*-4-aminotetrahydrofuran-3-carboxylic acid (17)**

