

# Nucleophilic Additions to Fused Bicyclic Five-Membered Ring Oxocarbenium Ions: Evidence for Preferential Attack on the Inside Face

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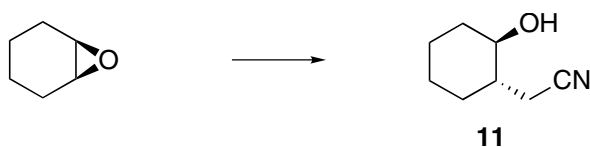
## Supporting Information

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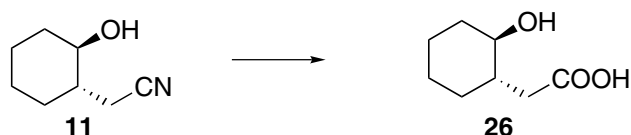
**General.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at ambient temperature at 500 MHz and 125 MHz, respectively, using a Nicolet Omega 500 or a GN 500 spectrometer. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the  $\delta$  scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Infrared (IR) spectra were obtained using a MIDAC Prospect FT-IR spectrometer. High resolution mass spectra were acquired on a VG Analytical 7070E or Fisons Autospec spectrometer, and were obtained by peak matching. Microanalyses were performed by Atlantic Microlab, Atlanta, GA. Analytical gas-liquid chromatography (GC) analyses were performed on a Hewlett Packard 5890 Level 4 Chromatograph, equipped with a split-mode injection system and a flame ionization detector. Fused silica capillary column (30 m x 0.32 mm) wall coated with DB-1 (J & W Scientific) was used with helium as the carrier gas (16 psi column head pressure). Melting points are reported uncorrected. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on EM Reagents silica gel ( $\text{SiO}_2$ ) 60 (230–400 mesh). All reactions were carried out under an atmosphere of nitrogen in glassware, which had been flame-dried under a stream of nitrogen. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. THF,  $\text{Et}_2\text{O}$ , and  $\text{CH}_2\text{Cl}_2$  were dried by filtration through alumina according to the procedure of Grubbs.<sup>1</sup>

### I. Synthesis of the six-five ring system

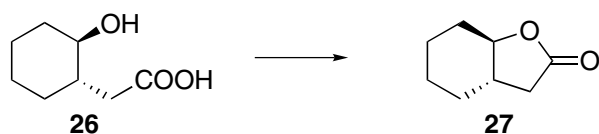


**2-Hydroxycyclohexylacetonitrile (11).<sup>2</sup>** To a cooled (0 °C) solution of acetonitrile (11.5 mL, 220 mmol) in 370 mL of THF was added *n*-BuLi (95.2 mL, 238 mmol, 2.50 M in hexanes). A solution of cyclohexene oxide (17.9 g, 183 mmol) in 555 mL of THF was added to the reaction mixture by cannula over 1 h. After 24 h at 22 °C, the reaction mixture was treated with 500 mL of saturated aqueous  $\text{NH}_4\text{Cl}$  and extracted

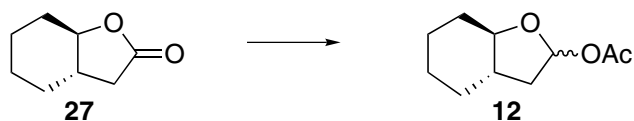
with 4 x 400 mL of Et<sub>2</sub>O. The combined organic layers were washed with 500 mL of aqueous 0.1 M H<sub>2</sub>SO<sub>4</sub>, 500 mL of brine, then dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. Purification of the resultant residue by flash chromatography (20:80 – 80:20 EtOAc/hexanes) provided the product as a yellow oil (15.3 g, 60%). The spectral data correlates with the previously reported data for **11**:<sup>3</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.34 (ddd, *J* = 15.0, 10.1, 4.9, 1H), 2.63 (dd, *J* = 16.8, 3.9, 1H), 2.49 (dd, *J* = 16.8, 7.4, 1H), 1.99 (m, 1H), 1.93 (m, 1H), 1.78 (m, 1H), 1.72 (m, 1H), 1.56 (m, 1H), 1.53 (d, *J* = 5.4, 1H), 1.21–1.31 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 119.1, 73.2, 42.1, 36.1, 30.5, 24.9, 25.0, 20.9; IR (thin film) 3421, 2938, 2859, 2246 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd for C<sub>8</sub>H<sub>12</sub>NO (M – H)<sup>+</sup> 138.0919, found 138.0923.



**2-Hydroxycyclohexylacetic acid (26).**<sup>4</sup> To a solution of NaOH (2.00 g, 50.0 mmol) in 50 mL of a 3:1 mixture of ethanol:water was added nitrile **11** (0.805 g, 5.79 mmol). The reaction mixture was heated to reflux for 20 h and then cooled to 0 °C. The reaction mixture was treated with dilute HCl and concentrated *in vacuo*. The remaining solution was extracted with 5 x 30 mL of Et<sub>2</sub>O. The combined organic layers were dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. Purification of the resultant residue by flash chromatography (10:90 EtOAc/hexanes) afforded **26** as a white solid (0.750 g, 82%). The spectral data correlates with the previously reported data for **26**:<sup>4</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.27 (td, *J* = 10.1, 4.4, 1H), 2.68 (dd, *J* = 15.5, 6.1, 1H), 2.23 (dd, *J* = 15.5, 6.4, 1H), 2.01 (m, 1H), 1.71–1.83 (m, 3H), 1.63 (m, 1H), 1.21–1.32 (m, 3H), 1.09 (m, 1H); <sup>13</sup>C NMR 179.1, 75.6, 42.7, 39.1, 36.3, 32.0, 25.8, 25.3; IR (KBr pellet) 3256, 2945, 2924, 2855, 1679 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub> (M – H<sub>2</sub>O)<sup>+</sup> 140.0837, found 140.0834.



**Six-five bicyclic lactone (27).**<sup>4</sup> To a solution of acid **26** (0.750 g, 4.75 mmol) in 30 mL of benzene was added one crystal of *para*-toluenesulfonic acid. The reaction mixture was heated to reflux with azeotropic removal of water, using a Dean Stark trap. After 3 h, the reaction mixture was cooled to 22 °C and concentrated *in vacuo*. The resultant residue was purified by flash chromatography (7:93 EtOAc/hexanes) to afford **27** (0.650 g, 98%). The spectral data correlates with the previously reported data for **27**:<sup>4</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.78 (td, *J* = 10.8, 3.8, 1H), 2.51 (dd, *J* = 16.3, 6.4, 1H), 2.22 (dd, *J* = 16.3, 13.3, 1H; m, 1H), 1.93 (m, 3H), 1.80 (m, 1H), 1.54 (qd, *J* = 11.9, 3.7, 1H), 1.27–1.42 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.8, 85.4, 45.0, 36.1, 30.4, 28.6, 25.5, 24.3; IR (thin film) 2930, 2865, 1772 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd for C<sub>8</sub>H<sub>11</sub>O<sub>2</sub> (M – H)<sup>+</sup> 139.0759, found 139.0764.

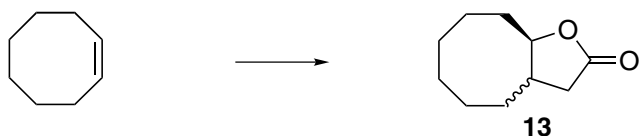


**General Procedure for Reduction and Acylation of  $\gamma$ -Lactones:**<sup>5</sup> To a cooled (–78 °C) solution of  $\gamma$ -lactone in CH<sub>2</sub>Cl<sub>2</sub> (0.10 – 0.20 M) was added DIBAL-H (1.2 equiv, 1.5 M in toluene). After the mixture was

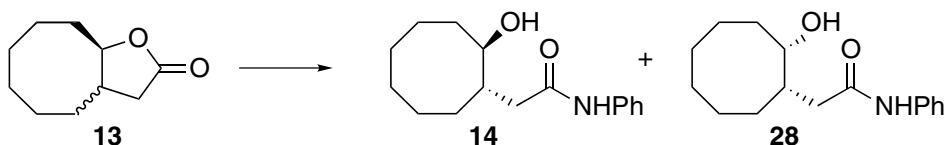
stirred at  $-78\text{ }^{\circ}\text{C}$  for 2 h, pyridine (4.0 equiv) and DMAP (1.2 equiv) were added, followed by the dropwise addition of  $\text{Ac}_2\text{O}$  (5.0 equiv). After the reaction mixture was allowed to warm to  $22\text{ }^{\circ}\text{C}$  over 12 h, 5 mL of saturated aqueous  $\text{NH}_4\text{Cl}$  was added and the reaction mixture was concentrated *in vacuo*. The remaining oil was dissolved in MTBE. The organic layer was washed with  $4 \times 10\text{ mL}$  of saturated aqueous  $\text{Na}_2\text{HPO}_4$ ,  $4 \times 10\text{ mL}$  of saturated aqueous  $\text{NaH}_2\text{PO}_4$ , and  $5 \times 10\text{ mL}$  of saturated aqueous  $\text{CuSO}_4$ . The organic phase was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo* to provide a dark orange residue.

**Six-five bicyclic acetate (12).** The standard reductive acylation procedure was followed with lactone **27** (0.741 g, 5.29 mmol) in 26 mL of  $\text{CH}_2\text{Cl}_2$  with DIBAL-H (4.23 mL, 6.35 mmol), pyridine (1.71 mL, 21.2 mmol), DMAP (0.779 g, 6.35 mmol), and  $\text{Ac}_2\text{O}$  (2.50 mL, 26.5 mmol). GC and  $^1\text{H}$  NMR spectroscopic analysis of the unpurified product showed a pair of diastereomers in a ratio of 64:36. Purification of the resultant residue by flash chromatography (1:3:96  $\text{Et}_3\text{N}/\text{EtOAc}/\text{hexanes}$ ) yielded **12** as a clear oil (0.514 g, 53%). The purified product was characterized as a mixture of diastereomers:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.31 (dd,  $J = 6.0, 4.7, 1\text{H}$ ), 6.27 (d,  $J = 5.3, 0.3\text{H}$ ), 3.45 (td,  $J = 10.5, 3.7, 1\text{H}$ ), 3.26 (td,  $J = 10.8, 3.8, 0.3\text{H}$ ), 2.49 (ddd,  $J = 13.0, 7.0, 6.0, 1\text{H}$ ), 2.20 (m, 1.3H), 2.13 (s, 3H), 2.10 (s, 0.9H), 2.07 (m, 0.3H), 1.93 (m, 1.3H), 1.83 (m, 1.3H), 1.73 (m, 1.3H), 1.58 (m, 1.3H), 1.16–1.45 (m, 6.5H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 168.2, 86.0, 95.4, 83.3, 80.7, 43.2, 39.9, 35.8, 35.6, 29.4, 28.4, 26.4, 26.3, 23.5, 23.4, 22.1, 22.0, 19.3, 19.2; IR (thin film) 2934, 2895, 1746  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_7\text{H}_{13}\text{O}_2$  ( $\text{M} - \text{C}_3\text{H}_3\text{O}$ ) $^+$  141.0915, found 141.0914. Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_3$ : C, 65.19; H, 8.75. Found: C, 65.23; H, 8.87.

## II. Synthesis of the eight-five ring system



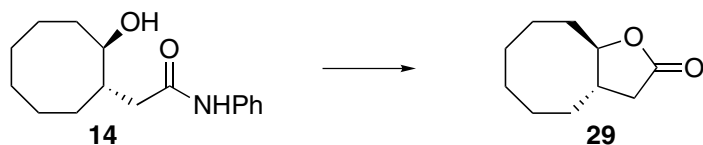
**Eight-five bicyclic lactone (13).**<sup>6</sup> To a solution of cyclooctene (5.64 mL, 43.0 mmol) in 430 mL of glacial acetic acid was added manganese (III) acetate (23 g, 86 mmol) and potassium acetate (127 g, 129 mmol). The reaction mixture was heated to reflux for 2 h and then cooled to  $22\text{ }^{\circ}\text{C}$ . The reaction mixture was treated with 1.6 mL of  $\text{H}_2\text{O}$  and extracted with  $5 \times 350\text{ mL}$  of  $\text{Et}_2\text{O}$ . The combined organic layers were washed with  $2 \times 350\text{ mL}$  of  $\text{H}_2\text{O}$ ,  $2 \times 350\text{ mL}$  of saturated aqueous  $\text{NaHCO}_3$ , dried ( $\text{MgSO}_4$ ), and concentrated *in vacuo* to provide a brown residue. GC and  $^1\text{H}$  NMR spectroscopic analysis of the unpurified residue showed a pair of diastereomers in a ratio of 72:28. Purification by flash chromatography (20:80  $\text{EtOAc}/\text{hexanes}$ ) provided the product as a clear oil (4.53 g, 62%). The spectral data correlates with the previously reported data for **13**.<sup>6</sup> The purified product was characterized as a mixture of diastereomers:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.67 (m, 1H), 4.43 (td,  $J = 9.4, 4.7, 2.6\text{H}$ ), 2.71 (dd,  $J = 16.1, 8.7, 2.6\text{H}$ ), 2.62 (dd,  $J = 16.5, 8.5, 1\text{H}$ ), 2.57 (m, 1H), 2.40 (m, 2.6H), 2.23 (m, 6.7H), 1.28–1.89 (m, 40H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  176.4, 176.2, 86.7, 85.4, 40.8, 39.3, 38.3, 36.8, 35.1, 34.7, 28.8, 28.7, 27.6, 27.4, 27.3, 26.9, 25.6, 25.2, 24.6, 22.2; IR (thin film) 2922, 2855, 1777  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_2$  ( $\text{M}$ ) $^+$  168.1150, found 168.1149.



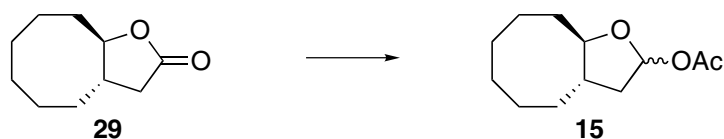
**2-(2-Hydroxycyclooctyl)-*N*-phenyl acetamide.** To a cooled (0 °C) solution of aniline (4.29 mL, 47.1 mmol) in 135 mL of THF was added *n*-BuLi (39.3 mL, 94.2 mmol, 2.40 M in hexanes).<sup>7</sup> The reaction mixture was stirred at 22 °C for 1 h, then cooled to –78 °C. A solution of lactone **13** (7.20 g, 42.8 mmol) in 215 mL of THF was slowly added to the reaction mixture over 30 min. After 1 h at 22 °C, the reaction mixture was treated with 50 mL of saturated aqueous NH<sub>4</sub>Cl and extracted with 4 x 200 mL of EtOAc. The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo* to provide an orange residue. Purification of the resultant residue by flash chromatography (1:4:95 – 1:19:80 Et<sub>3</sub>N/EtOAc/hexanes) afforded the mixture of diastereomers as an orange solid. Separation of the diastereomers was achieved by recrystallization methods. EtOAc was added dropwise to a hot (70 °C) solution of products **14** and **28** in hexanes until all crystals were dissolved. The mixture was allowed to cool slowly to 22 °C. The white crystals were collected by filtration and washed with cold (0 °C) hexanes, providing **14** (3.78 g, 36%).

**Trans-isomer 14.** mp 118 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.37 (s, 1H), 7.52 (d, *J* = 7.8, 2H), 7.29 (t, *J* = 7.9, 2H), 7.09 (t, *J* = 7.3, 1H), 3.62 (s, 1H), 3.50 (s, 1H), 2.73 (dd, *J* = 14.4, 5.3, 1H), 2.37 (dd, *J* = 14.4, 6.5, 1H), 2.14 (m, 1H), 1.40–1.95 (m, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.9, 138.3, 129.3, 124.6, 120.5, 76.2, 43.5, 41.8, 35.5, 30.6, 27.1, 26.5, 26.1, 24.2; IR (KBr pellet) 3283, 3080, 2921, 1667, 1602 cm<sup>–1</sup>; HRMS (EI) *m/z* calcd for C<sub>16</sub>H<sub>21</sub>ON (M – H<sub>2</sub>O)<sup>+</sup> 243.1623, found 243.1624. Anal. Calcd for C<sub>16</sub>H<sub>23</sub>O<sub>2</sub>N: C, 73.53; H, 8.87; N, 12.24. Found: C, 73.50; H, 8.96; N, 12.03.

**Cis-isomer 28.** mp 127 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 (s, 1H), 7.51 (d, *J* = 7.2, 2H), 7.29 (t, *J* = 7.6, 2H), 7.09 (t, *J* = 7.5, 1H), 3.90 (s, 1H), 2.59 (td, *J* = 10.4, 4.0, 1H), 2.35 (m, 2H), 2.00 (d, *J* = 3.8, 1H), 1.35–1.80 (m, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.6, 138.4, 129.2, 124.4, 120.0, 72.7, 43.0, 38.4, 33.2, 27.9, 27.6, 27.4, 25.9, 22.8; IR (KBr pellet) 3254, 3189, 2921, 2873, 1669 cm<sup>–1</sup>; HRMS (EI) *m/z* calcd for C<sub>16</sub>H<sub>21</sub>ON (M – H<sub>2</sub>O)<sup>+</sup> 243.1623, found 243.1622. Anal. Calcd for C<sub>16</sub>H<sub>23</sub>O<sub>2</sub>N: C, 73.53; H, 8.87; N, 12.24. Found: C, 73.45; H, 8.91; N, 5.29.



**Eight-five bicyclic lactone (29).** To a solution of amide **14** (1.52 g, 6.19 mmol) in 61 mL of dioxane was added 30 drops of concentrated HCl.<sup>8</sup> The reaction mixture was heated to reflux overnight. After cooling to 22 °C, the reaction mixture was treated with 20 mL of saturated aqueous NaHCO<sub>3</sub> and extracted with 6 x 100 mL of Et<sub>2</sub>O. The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. Purification of the resultant residue by flash chromatography (10:90 – 20:80 EtOAc/hexanes) yielded the product as an oil (0.748 g, 72%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.43 (td, *J* = 9.4, 4.7, 1H), 2.70 (dd, *J* = 17.3, 8.6, 1H), 2.43 (m, 1H), 2.17–2.29 (m, 2H), 1.96 (m, 1H), 1.27–1.80 (m, 10H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.1, 86.7, 40.8, 38.3, 35.1, 34.7, 27.6, 27.0, 24.7, 22.2; IR (thin film) 2923, 2853, 1777 cm<sup>–1</sup>; HRMS (EI) *m/z* calcd for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub> (M)<sup>+</sup> 168.1150, found 168.1150.

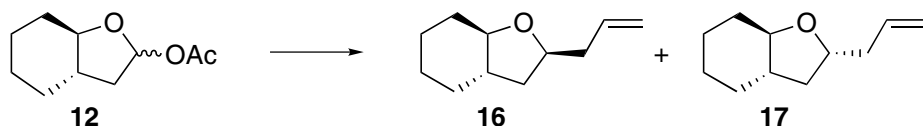


**Eight-five bicyclic acetate (15).** The standard reductive acylation procedure was followed with lactone **29** (0.298 g, 1.77 mmol) in 17 mL of CH<sub>2</sub>Cl<sub>2</sub> with DIBAL-H (1.4 mL, 2.1 mmol), pyridine (0.57 mL, 7.1

mmol), DMAP (0.260 g, 2.12 mmol), and  $\text{Ac}_2\text{O}$  (0.84 mL, 8.9 mmol). GC and  $^1\text{H}$  NMR spectroscopic analysis of the unpurified product showed a pair of diastereomers in a ratio of 68:32. Purification of the resultant residue by flash chromatography (1:2:97  $\text{Et}_3\text{N}/\text{EtOAc}/\text{hexanes}$ ) yielded **15** as a clear oil (0.254 g, 68%). Purification by flash chromatography and HPLC provided acetate **15** as variable mixtures of diastereomers. Fractions of pure isomers were not detected. The purified product was characterized as a mixture of diastereomers:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.19 (dd,  $J = 5.8, 2.3$ , 1H), 6.14 (d,  $J = 4.5$ , 1.2H), 4.01 (m, 2.2H), 2.56 (ddd,  $J = 13.8, 10.2, 5.8$ , 1H), 2.29 (m, 1.2H), 2.20 (dd,  $J = 12.9, 6.9, 1.2\text{H}$ ), 2.09 (m, 2.6H), 2.05 (s, 3H), 2.02 (s, 3.6H), 1.90 (m, 2H), 1.70 (m, 11H), 1.25–1.53 (m, 14H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 170.8, 98.1, 98.0, 86.9, 85.3, 42.8, 42.2, 42.1, 40.9, 37.3, 34.6, 34.3, 34.2, 28.0, 27.6, 27.2, 27.1, 25.7, 25.5, 23.5, 23.1, 21.8, 21.7; IR (thin film) 2925, 2855, 1742  $\text{cm}^{-1}$ ; HRMS (CI/isobutane)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{17}\text{O}_2$  ( $\text{M} - \text{C}_2\text{H}_3\text{O}$ ) $^+$  169.1228, found 169.1224.

### III. Nucleophilic substitution of ring systems

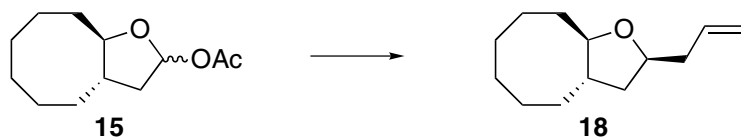
**General Procedure for Allylation of  $\gamma$ -Lactol Acetates:** A solution of acetate in  $\text{CH}_2\text{Cl}_2$  (0.10 M) was treated with allyltrimethylsilane (4 equiv) and then cooled to  $-78^\circ\text{C}$ . After treatment with Lewis acid (1.1 equiv), the reaction mixture was warmed to  $22^\circ\text{C}$  over 2 h. The reaction mixture was treated with saturated aqueous  $\text{Na}_2\text{HPO}_4$  (1 mL per mmol of acetate). The aqueous layer was then extracted three times with  $\text{CH}_2\text{Cl}_2$  (1 mL per mmol of acetate), and the organic phases were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated *in vacuo*.



**Six-five bicyclic alkene (16 and 17).** The standard allylation procedure was followed with acetate **12** (0.051 g, 0.28 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.4 mL, 0.3 mmol). GC and  $^1\text{H}$  NMR spectroscopic analysis of the unpurified product showed a pair of diastereomers in a 73:27 ratio of 1,3-*trans*:*cis* diastereomers. Purification by flash chromatography (2:98  $\text{Et}_2\text{O}/\text{pentane}$ ) provided the product as a clear oil (0.035 g, 76%). The major isomer **16** was isolated as a pure sample while the minor isomer **17** was isolated as a mixture of **16** and **17**. IR and mass spectrometry data were obtained for **16** and **17** as a mixture of diastereomers. IR (thin film) 2932, 2857, 1641, 1072  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_8\text{H}_{13}\text{O}$  ( $\text{M} - \text{C}_3\text{H}_5$ ) $^+$  125.0966, found 125.0969.

**Major Isomer 16.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.81 (ddt,  $J = 17.2, 10.3, 6.9$ , 1H), 5.09 (m, 1H), 5.06 (m, 1H), 4.12 (m, 1H), 3.08 (td,  $J = 10.1, 3.7$ , 1H), 2.40 (m, 1H), 2.29 (m, 1H), 2.16 (m, 1H), 1.90 (m, 1H), 1.81 (m, 1H), 1.71 (m, 2H), 1.60 (td,  $J = 11.7, 9.1$ , 1H), 1.15–1.35 (m, 4H), 1.07 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  135.5, 117.3, 84.2, 77.2, 44.7, 41.7, 35.9, 31.8, 29.6, 26.4, 24.8.

**Minor Isomer 17.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , distinctive peaks)  $\delta$  3.15 (td,  $J = 10.3, 3.7$ , 1H), 1.42 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , distinctive peaks)  $\delta$  82.9, 78.2, 46.7, 41.6, 40.0, 31.9, 29.5, 26.2, 24.8.



**Eight-five bicyclic alkene (18).** The standard allylation procedure was followed with acetate **15** (0.050 g, 0.24 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.04 mL, 0.3 mmol). GC and  $^1\text{H}$  NMR spectroscopic analysis of the unpurified

product showed a pair of diastereomers in a 93:7 ratio of 1,3-*trans*:*cis* diastereomers. Purification by flash chromatography (2:98 EtOAc/hexanes) provided the product as a colorless oil (0.038 g, 83%):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.81 (ddt,  $J = 17.2, 10.2, 7.0$ , 1H), 5.05 (m, 2H), 3.82 (quintet,  $J = 6.7$ , 1H), 3.66 (td,  $J = 8.5, 4.0$ , 1H), 2.33 (m, 1H), 2.17 (m, 1H), 2.04 (m, 2H), 1.83 (m, 2H), 1.69 (m, 4H), 1.60 (m, 1H), 1.33–1.46 (m, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  135.6, 117.0, 85.4, 76.5, 42.9, 41.3, 40.7, 35.5, 34.9, 28.2, 27.4, 25.5, 23.6; IR (thin film) 3075, 2922, 2853, 1641  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{23}\text{O}$  ( $\text{M} + \text{H}^+$ ) 195.1749, found 195.1748. Anal. Calcd for  $\text{C}_{13}\text{H}_{22}\text{O}$ : C, 80.36; H, 11.41. Found: C, 80.53; H, 11.55.

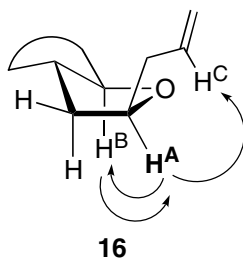
### Control Experiments for Allylation of $\gamma$ -Lactol Acetates **15**:

- (1) Lewis acid is required for substitution: Treatment of acetate **15** with allyltrimethylsilane in the absence of Lewis acid led only to recovered starting acetate **15**.
- (2) The diastereoselectivity of nucleophilic substitution is independent of the anomer ratio of the starting acetates: The standard allylation procedure was followed with a 78:22 anomer ratio of acetate **15** (0.015 g, 0.070 mmol) and  $\text{SnBr}_4$  (0.080 mL, 0.080 mmol, 1.0 M in  $\text{CH}_2\text{Cl}_2$ ). GC analysis of the unpurified product showed that allylated product **18** was formed as a 93:7 mixture of diastereomers. Reversing the nature of the major anomer of the acetate led to the same selectivity for formation of **18**. Allylation of a 14:86 anomer ratio of acetate **15** also led to allylated product **18** as a 93:7 mixture of diastereomers as determined using GC. Allylation reactions performed with anomeric acetate mixtures of 26:74 and 68:32 also afforded allylated product **18** as a 93:7 mixture of diastereomers.

## IV. Stereochemical proofs of allyl products

A. The stereochemistry of **16** and **17** was determined by analysis of nOe data:

Relevant DPGSE-nOe data (mixing time 2.0 s): (the peaks in the  $^1\text{H}$  NMR spectra were assigned using  $^1\text{H}/^1\text{H}$  COSY,  $^1\text{H}$  NMR chemical shifts, and  $^1\text{H}$  NMR coupling constants)

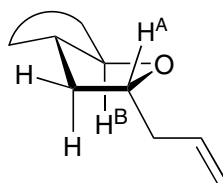


### Six-five bicyclic alkene (1,3-*trans*, major)

$\text{H}^{\text{A}}$  irradiated:  $\text{H}^{\text{B}}$  (1.53%),  $\text{H}^{\text{C}}$  (0.99%)

$\text{H}^{\text{B}}$  irradiated:  $\text{H}^{\text{A}}$  (1.81%)

Note: The absence of nOe between  $\text{H}^{\text{B}}$  and allyl protons indicates 1,3-*trans* isomer

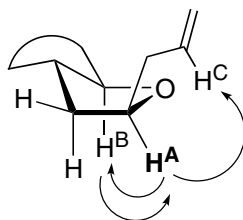
**17****Six-five bicyclic alkene (1,3-cis, minor)**

nOe experiments were performed for **17** using a 1:1 mixture of **16** and **17**.

Note: There was nOe observed between H<sup>A</sup> and H<sup>B</sup>

B. The stereochemistry of **18** was determined by analysis of nOe data:

Relevant DPGSE-nOe data (mixing time 2.0 s): (the peaks in the <sup>1</sup>H NMR spectra were assigned using <sup>1</sup>H/<sup>1</sup>H COSY, <sup>1</sup>H NMR chemical shifts, and <sup>1</sup>H NMR coupling constants)

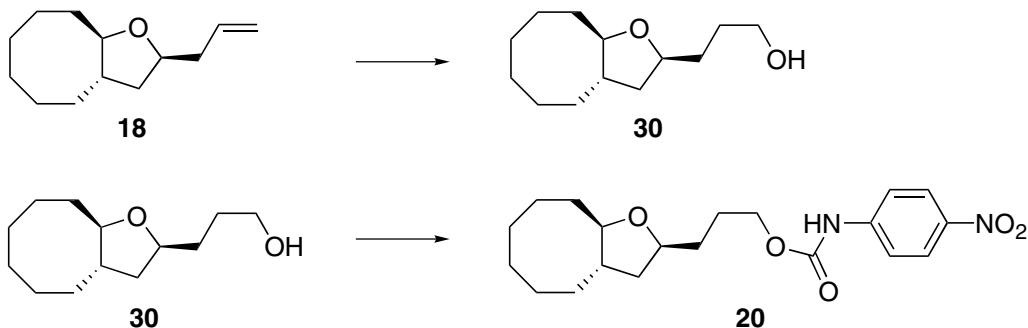
**18****Eight-five bicyclic alkene (1,3-trans, major)**

H<sup>A</sup> irradiated: H<sup>B</sup> (0.64 %), H<sup>C</sup> (0.55%)

H<sup>B</sup> irradiated: H<sup>A</sup> (0.82 %)

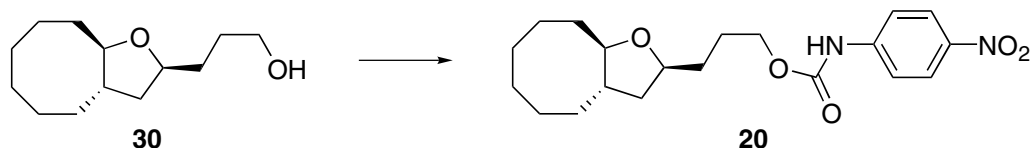
C. Configuration of **18**

The stereochemistry was assigned by conversion of **18** to **20**, whose structure was determined by X-ray crystallography.



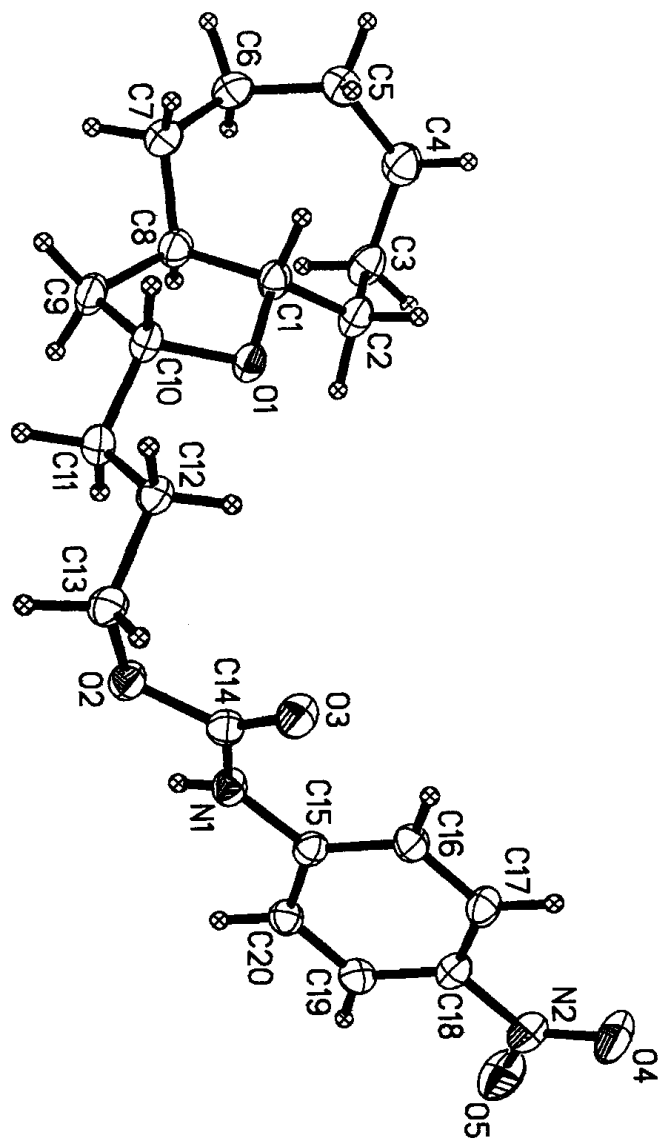
**Eight-five bicyclic alcohol (30).** To a cooled (0 °C) solution of alkene **18** (0.070 g, 0.40 mmol) in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 9-BBN (1.4 mL, 0.70 mmol, 0.50 M in THF) dropwise over 2 min. After 2 h at 22 °C, the reaction mixture was cooled to 0 °C and NaOH (1.7 mL, 1.0 M), EtOH (1.7 mL), and H<sub>2</sub>O<sub>2</sub> (0.9 mL, 30%) were

added. After 12 h at 22 °C, the reaction mixture was treated with 5 mL of brine solution. The aqueous layer was extracted with 4 x 10 mL of Et<sub>2</sub>O, and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The resultant residue was purified by flash chromatography (20:80 EtOAc/hexanes) to yield the product as a clear oil (0.070 g, 80%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.78 (m, 1H), 3.63 (m, 3H), 3.21 (s, 1H), 2.04 (m, 2H), 1.80 (m, 2H), 1.56–1.73 (m, 10H), 1.24–1.51 (m, 5H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 85.1, 76.8, 62.8, 42.5, 41.5, 34.9, 34.5, 32.9, 29.9, 27.6, 26.9, 24.9, 23.1; IR (thin film) 3406, 2922, 2852 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd for C<sub>13</sub>H<sub>24</sub>O<sub>2</sub> (M)<sup>+</sup> 212.1776, found 212.1771. Anal. Calcd for C<sub>13</sub>H<sub>24</sub>O<sub>2</sub>: C, 73.54; H, 11.39. Found: C, 73.28; H, 11.48.



**Eight-five bicyclic carbamate (20).** To a cooled (0 °C) solution of alcohol **30** (0.050 g, 0.24 mmol) in 0.67 mL of THF was added 4-nitrophenyl isocyanate (0.040 g, 0.25 mmol). After 15 h at 22 °C, the reaction mixture was treated with 1 mL of saturated aqueous NH<sub>4</sub>Cl and extracted with 4 x 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The residue was purified by flash chromatography (20:80 EtOAc/hexanes) to yield the product as a yellow solid (0.053 g, 60 %). A suitable crystal was grown for X-ray crystallography in a 1:1 mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexanes: mp 107.5 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 9.2, 2H), 7.57 (d, *J* = 9.2, 2H), 7.48 (s, 1H), 4.20 (td, *J* = 6.4, 1.6, 2H), 3.79 (quintet, *J* = 6.7, 1H), 3.67 (ddd, *J* = 12.6, 8.6, 4.1, 1H), 2.04 (m, 2H), 1.60–1.96 (m, 10H), 1.25–1.57 (m, 7H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 152.7, 143.9, 142.6, 124.9, 117.5, 84.9, 76.2, 65.9, 42.6, 41.5, 35.3, 34.6, 32.1, 27.8, 27.1, 25.8, 25.1, 23.3; IR (KBr pellet) 2923, 2868, 1737, 1505, 1333 cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>28</sub>O<sub>5</sub>N<sub>2</sub>: C, 63.81; H, 7.50. Found: C, 63.98; H, 7.51.



X-ray crystallography data for **20**

**X-ray Data Collection, Structure Solution and Refinement for 20.**

A colorless crystal of approximate dimensions 0.13 x 0.26 x 0.30 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART<sup>1</sup> program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT<sup>2</sup> and SADABS<sup>3</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>4</sup> program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $P\bar{1}$  was assigned and later determined to be correct.

The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. The analytical scattering factors<sup>5</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and  $U_{iso}$ ). At convergence,  $wR2 = 0.1268$  and  $GOF = 1.035$  for 357 variables refined against 4597 data. As a comparison for refinement on F,  $R1 = 0.0522$  for those 3102 data with  $I > 2.0\sigma(I)$ .

## References.

1. SMART Software Users Guide, Version 5.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
  2. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
  3. Sheldrick, G. M. SADABS, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
  4. Sheldrick, G. M. SHELXTL Version 5.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
  5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
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## Definitions:

$$wR2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w(F_o^2)^2)]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

$$Goof = S = [\Sigma(w(F_o^2 - F_c^2)^2) / (n-p)]^{1/2} \text{ where } n \text{ is the number of reflections and } p \text{ is the total number of parameters refined.}$$

The thermal ellipsoid plot is shown at the 50% probability level.

Table 1. Crystal data and structure refinement for **20**.

Identification code	kaw24 (Michelle Tran)	
Empirical formula	$C_{20}H_{28}N_2O_5$	
Formula weight	376.44	
Temperature	163(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 6.1314(3)$ Å	$\alpha = 98.3240(10)^\circ$ .
	$b = 12.8797(7)$ Å	$\beta = 103.4480(10)^\circ$ .
	$c = 13.1406(7)$ Å	$\gamma = 101.1760(10)^\circ$ .
Volume	$970.33(9)$ Å <sup>3</sup>	
Z	2	
Density (calculated)	1.288 Mg/m <sup>3</sup>	
Absorption coefficient	0.093 mm <sup>-1</sup>	
F(000)	404	
Crystal size	0.30 x 0.26 x 0.13 mm <sup>3</sup>	
Theta range for data collection	1.63 to 28.30°.	
Index ranges	$-8 \leq h \leq 8$ , $-17 \leq k \leq 17$ , $-17 \leq l \leq 17$	
Reflections collected	10529	
Independent reflections	4597 [R(int) = 0.0412]	
Completeness to theta = 28.30°	95.3 %	
Absorption correction	None	
Max. and min. transmission	0.9881 and 0.9728	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4597 / 0 / 357	
Goodness-of-fit on F <sup>2</sup>	1.035	
Final R indices [I > 2sigma(I)]	R1 = 0.0522, wR2 = 0.1072	
R indices (all data)	R1 = 0.0903, wR2 = 0.1268	
Extinction coefficient	0.0033(16)	
Largest diff. peak and hole	0.369 and -0.245 e.Å <sup>-3</sup>	

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **20**.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{\text{ij}}$  tensor.

	x	y	z	$U(\text{eq})$
O(1)	-4247(2)	2288(1)	2755(1)	23(1)
O(2)	2986(2)	4266(1)	3046(1)	25(1)
O(3)	1447(3)	4917(1)	1598(1)	28(1)
O(4)	3280(3)	3415(2)	-3366(1)	45(1)
O(5)	5749(3)	2467(1)	-2907(1)	44(1)
N(1)	3709(3)	3690(1)	1521(1)	24(1)
N(2)	4431(3)	3019(1)	-2698(1)	31(1)
C(1)	-6191(4)	1410(2)	2656(2)	24(1)
C(2)	-6772(4)	742(2)	1538(2)	29(1)
C(3)	-8158(4)	-416(2)	1346(2)	32(1)
C(4)	-10637(4)	-583(2)	1406(2)	37(1)
C(5)	-11060(4)	-161(2)	2472(2)	34(1)
C(6)	-9544(4)	-406(2)	3472(2)	34(1)
C(7)	-7481(4)	529(2)	4128(2)	32(1)
C(8)	-5542(4)	865(2)	3612(2)	26(1)
C(9)	-3454(4)	1705(2)	4390(2)	28(1)
C(10)	-3219(4)	2705(2)	3886(2)	24(1)
C(11)	-761(4)	3319(2)	4035(2)	24(1)
C(12)	-581(4)	4332(2)	3557(2)	23(1)
C(13)	1882(4)	4913(2)	3674(2)	25(1)
C(14)	2590(3)	4347(2)	2006(2)	23(1)
C(15)	3828(3)	3565(2)	461(2)	21(1)
C(16)	2339(4)	3897(2)	-340(2)	24(1)
C(17)	2550(4)	3720(2)	-1375(2)	26(1)
C(18)	4227(4)	3219(2)	-1602(2)	24(1)
C(19)	5736(4)	2897(2)	-815(2)	24(1)
C(20)	5529(3)	3071(2)	212(2)	23(1)

Table 3. Bond lengths [Å] and angles [°] for **20**.

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O(1)-C(1)	1.442(2)
O(1)-C(10)	1.448(2)
O(2)-C(14)	1.354(2)
O(2)-C(13)	1.453(2)
O(3)-C(14)	1.207(2)
O(4)-N(2)	1.229(2)
O(5)-N(2)	1.227(2)
N(1)-C(14)	1.366(3)
N(1)-C(15)	1.399(2)
N(2)-C(18)	1.464(3)
C(1)-C(2)	1.517(3)
C(1)-C(8)	1.536(3)
C(2)-C(3)	1.520(3)
C(3)-C(4)	1.515(3)
C(4)-C(5)	1.526(3)
C(5)-C(6)	1.534(3)
C(6)-C(7)	1.547(3)
C(7)-C(8)	1.524(3)
C(8)-C(9)	1.545(3)
C(9)-C(10)	1.530(3)
C(10)-C(11)	1.514(3)
C(11)-C(12)	1.523(3)
C(12)-C(13)	1.512(3)
C(15)-C(20)	1.398(3)
C(15)-C(16)	1.399(3)
C(16)-C(17)	1.387(3)
C(17)-C(18)	1.381(3)
C(18)-C(19)	1.388(3)
C(19)-C(20)	1.375(3)

C(1)-O(1)-C(10)	106.81(14)
C(14)-O(2)-C(13)	115.27(15)
C(14)-N(1)-C(15)	127.17(17)
O(5)-N(2)-O(4)	122.92(18)
O(5)-N(2)-C(18)	118.50(17)
O(4)-N(2)-C(18)	118.59(17)
O(1)-C(1)-C(2)	106.89(16)
O(1)-C(1)-C(8)	106.66(15)
C(2)-C(1)-C(8)	118.71(17)
C(1)-C(2)-C(3)	117.13(18)
C(4)-C(3)-C(2)	117.2(2)
C(3)-C(4)-C(5)	117.7(2)
C(4)-C(5)-C(6)	116.7(2)
C(5)-C(6)-C(7)	115.65(19)
C(8)-C(7)-C(6)	117.31(19)
C(7)-C(8)-C(1)	114.93(18)
C(7)-C(8)-C(9)	112.52(18)
C(1)-C(8)-C(9)	103.75(16)
C(10)-C(9)-C(8)	105.38(16)
O(1)-C(10)-C(11)	108.01(16)
O(1)-C(10)-C(9)	104.45(16)
C(11)-C(10)-C(9)	114.84(17)
C(10)-C(11)-C(12)	113.69(17)
C(13)-C(12)-C(11)	113.13(17)
O(2)-C(13)-C(12)	111.08(16)
O(3)-C(14)-O(2)	124.58(18)
O(3)-C(14)-N(1)	126.87(19)
O(2)-C(14)-N(1)	108.55(16)
C(20)-C(15)-N(1)	116.85(17)
C(20)-C(15)-C(16)	119.67(18)
N(1)-C(15)-C(16)	123.48(18)
C(17)-C(16)-C(15)	119.56(19)
C(18)-C(17)-C(16)	119.56(19)
C(17)-C(18)-C(19)	121.64(19)
C(17)-C(18)-N(2)	119.58(18)
C(19)-C(18)-N(2)	118.78(18)

C(20)-C(19)-C(18)	118.87(19)
C(19)-C(20)-C(15)	120.69(19)

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Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **20**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
O(1)	27(1)	23(1)	18(1)	6(1)	4(1)	2(1)
O(2)	26(1)	31(1)	21(1)	6(1)	8(1)	10(1)
O(3)	33(1)	32(1)	28(1)	10(1)	11(1)	18(1)
O(4)	59(1)	58(1)	26(1)	19(1)	13(1)	26(1)
O(5)	65(1)	49(1)	34(1)	11(1)	26(1)	31(1)
N(1)	26(1)	26(1)	23(1)	9(1)	6(1)	12(1)
N(2)	40(1)	31(1)	26(1)	8(1)	14(1)	11(1)
C(1)	27(1)	22(1)	21(1)	8(1)	3(1)	1(1)
C(2)	36(1)	27(1)	20(1)	6(1)	5(1)	1(1)
C(3)	42(1)	27(1)	24(1)	3(1)	9(1)	5(1)
C(4)	37(1)	36(1)	31(1)	4(1)	5(1)	-1(1)
C(5)	26(1)	41(1)	33(1)	9(1)	6(1)	4(1)
C(6)	32(1)	40(1)	33(1)	16(1)	14(1)	7(1)
C(7)	31(1)	42(1)	28(1)	14(1)	10(1)	9(1)
C(8)	28(1)	28(1)	22(1)	8(1)	5(1)	6(1)
C(9)	32(1)	31(1)	19(1)	9(1)	3(1)	3(1)
C(10)	29(1)	26(1)	16(1)	4(1)	4(1)	6(1)
C(11)	26(1)	25(1)	20(1)	4(1)	3(1)	5(1)
C(12)	26(1)	24(1)	19(1)	3(1)	6(1)	7(1)
C(13)	27(1)	26(1)	20(1)	1(1)	8(1)	6(1)
C(14)	22(1)	22(1)	23(1)	5(1)	6(1)	3(1)
C(15)	23(1)	19(1)	21(1)	5(1)	6(1)	2(1)
C(16)	23(1)	26(1)	25(1)	7(1)	7(1)	10(1)
C(17)	30(1)	27(1)	25(1)	11(1)	6(1)	11(1)
C(18)	30(1)	22(1)	21(1)	6(1)	8(1)	4(1)
C(19)	24(1)	23(1)	28(1)	6(1)	9(1)	9(1)
C(20)	23(1)	23(1)	25(1)	7(1)	5(1)	7(1)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **20**.

	x	y	z	U(eq)
H(1)	4360(40)	3322(18)	1900(18)	28(6)
H(1A)	-7590(50)	1780(20)	2750(20)	58(8)
H(2A)	-7560(40)	1132(19)	1029(19)	36(6)
H(2B)	-5180(50)	740(20)	1380(20)	48(7)
H(3A)	-8120(40)	-740(20)	630(20)	45(7)
H(3B)	-7310(40)	-820(20)	1890(20)	44(7)
H(4A)	-11240(50)	-1410(20)	1230(20)	52(8)
H(4B)	-11520(40)	-230(20)	850(20)	47(7)
H(5A)	-12710(50)	-510(20)	2420(20)	48(7)
H(5B)	-10840(40)	680(20)	2558(19)	41(7)
H(6A)	-8970(40)	-1053(19)	3211(18)	34(6)
H(6B)	-10510(40)	-535(19)	3980(19)	38(6)
H(7A)	-6760(40)	303(18)	4821(18)	30(6)
H(7B)	-8080(40)	1191(18)	4330(18)	32(6)
H(8A)	-5030(40)	171(19)	3344(18)	34(6)
H(9A)	-3740(40)	1882(19)	5070(20)	39(7)
H(9B)	-1960(40)	1449(18)	4440(17)	32(6)
H(10A)	-4180(30)	3194(16)	4165(15)	17(5)
H(11A)	0(30)	3528(16)	4815(17)	20(5)
H(11B)	60(40)	2822(17)	3719(17)	27(6)
H(12A)	-1360(40)	4133(16)	2802(18)	23(5)
H(12B)	-1310(40)	4828(17)	3915(17)	28(6)
H(13A)	2870(40)	5007(16)	4419(17)	22(5)
H(13B)	1970(40)	5623(18)	3457(17)	25(6)
H(16)	1230(40)	4191(18)	-193(18)	33(6)
H(17)	1540(40)	3934(17)	-1923(18)	29(6)
H(19)	6820(40)	2621(18)	-995(18)	31(6)
H(20)	6540(40)	2863(17)	764(17)	24(5)

Table 6. Torsion angles [°] for **20**.

C(10)-O(1)-C(1)-C(2)	-161.42(16)
C(10)-O(1)-C(1)-C(8)	-33.5(2)
O(1)-C(1)-C(2)-C(3)	159.36(19)
C(8)-C(1)-C(2)-C(3)	38.8(3)
C(1)-C(2)-C(3)-C(4)	67.8(3)
C(2)-C(3)-C(4)-C(5)	-62.7(3)
C(3)-C(4)-C(5)-C(6)	-45.5(3)
C(4)-C(5)-C(6)-C(7)	100.0(3)
C(5)-C(6)-C(7)-C(8)	-67.3(3)
C(6)-C(7)-C(8)-C(1)	68.5(3)
C(6)-C(7)-C(8)-C(9)	-173.02(18)
O(1)-C(1)-C(8)-C(7)	139.35(18)
C(2)-C(1)-C(8)-C(7)	-100.0(2)
O(1)-C(1)-C(8)-C(9)	16.1(2)
C(2)-C(1)-C(8)-C(9)	136.7(2)
C(7)-C(8)-C(9)-C(10)	-119.0(2)
C(1)-C(8)-C(9)-C(10)	5.8(2)
C(1)-O(1)-C(10)-C(11)	159.48(16)
C(1)-O(1)-C(10)-C(9)	36.8(2)
C(8)-C(9)-C(10)-O(1)	-25.5(2)
C(8)-C(9)-C(10)-C(11)	-143.64(18)
O(1)-C(10)-C(11)-C(12)	65.8(2)
C(9)-C(10)-C(11)-C(12)	-178.09(18)
C(10)-C(11)-C(12)-C(13)	-177.77(17)
C(14)-O(2)-C(13)-C(12)	84.2(2)
C(11)-C(12)-C(13)-O(2)	66.4(2)
C(13)-O(2)-C(14)-O(3)	1.2(3)
C(13)-O(2)-C(14)-N(1)	-179.36(16)
C(15)-N(1)-C(14)-O(3)	2.2(3)
C(15)-N(1)-C(14)-O(2)	-177.25(18)
C(14)-N(1)-C(15)-C(20)	164.00(19)
C(14)-N(1)-C(15)-C(16)	-16.5(3)
C(20)-C(15)-C(16)-C(17)	0.9(3)
N(1)-C(15)-C(16)-C(17)	-178.59(19)

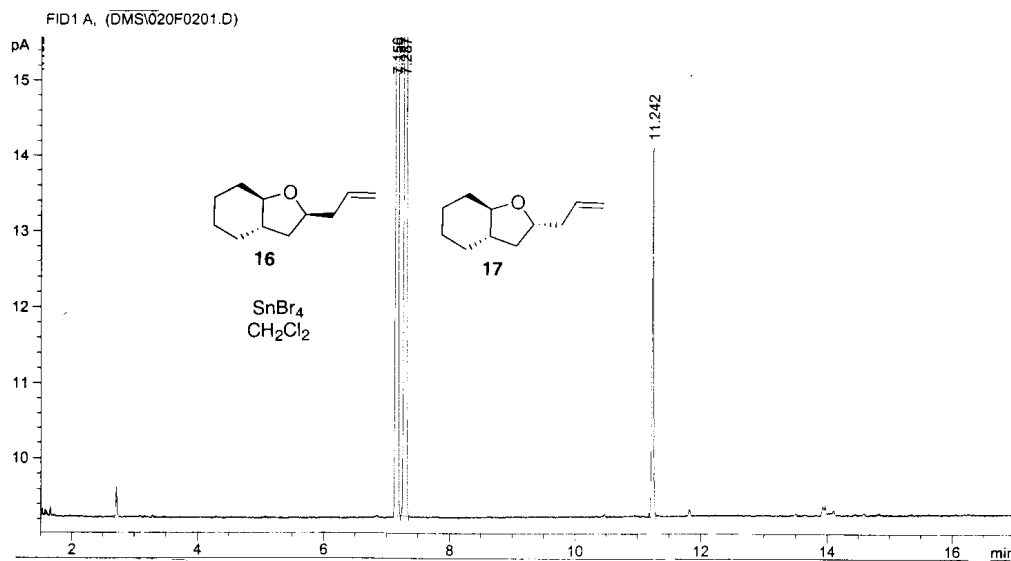
C(15)-C(16)-C(17)-C(18)	-0.1(3)
C(16)-C(17)-C(18)-C(19)	-0.7(3)
C(16)-C(17)-C(18)-N(2)	179.21(19)
O(5)-N(2)-C(18)-C(17)	-171.8(2)
O(4)-N(2)-C(18)-C(17)	8.4(3)
O(5)-N(2)-C(18)-C(19)	8.1(3)
O(4)-N(2)-C(18)-C(19)	-171.63(19)
C(17)-C(18)-C(19)-C(20)	0.8(3)
N(2)-C(18)-C(19)-C(20)	-179.17(18)
C(18)-C(19)-C(20)-C(15)	0.0(3)
N(1)-C(15)-C(20)-C(19)	178.66(18)
C(16)-C(15)-C(20)-C(19)	-0.8(3)

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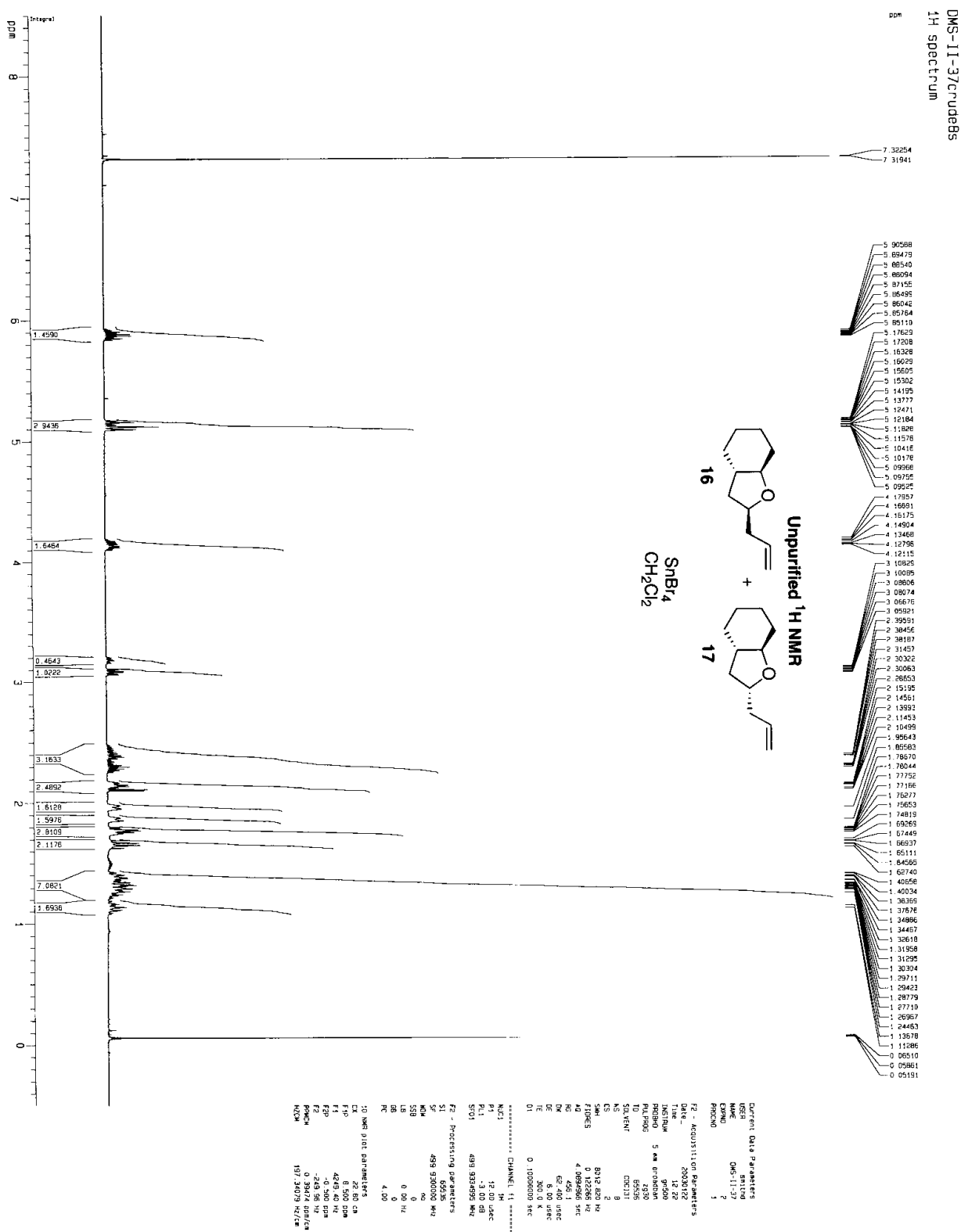
## V. Bibliography

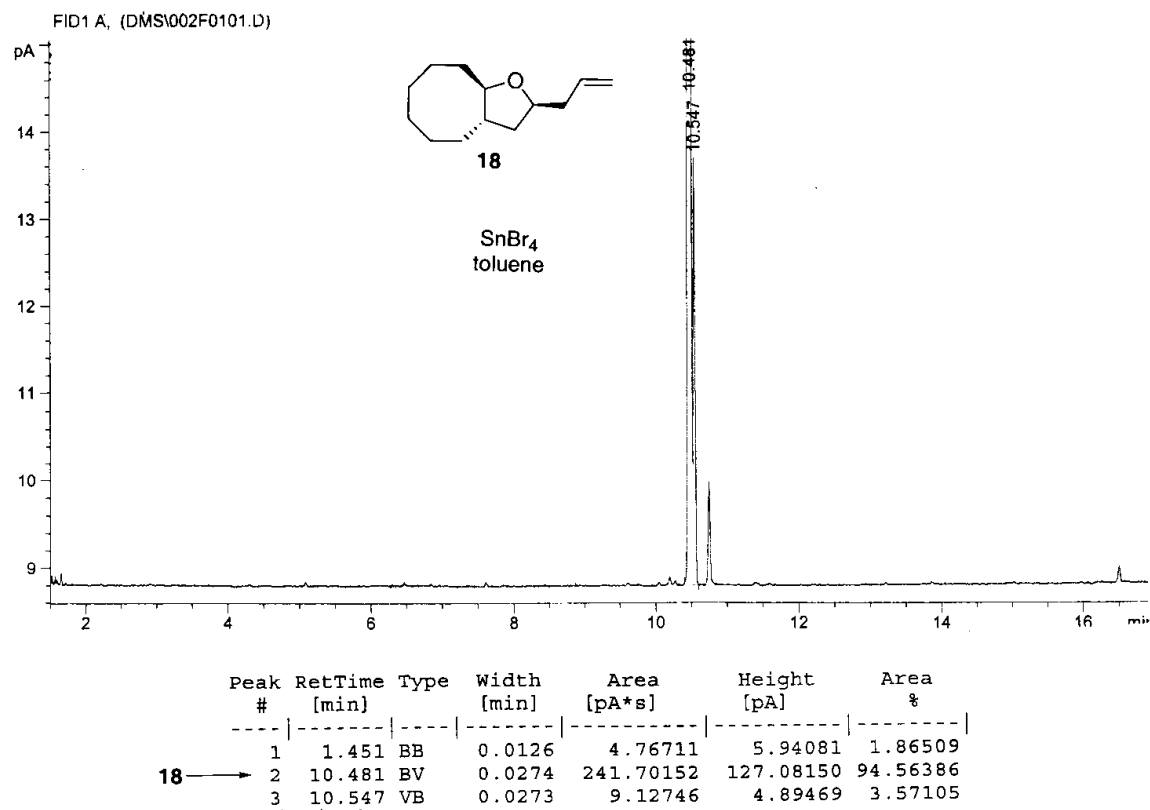
1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
2. Bartlett, P. A.; Ting, P. C. *J. Org. Chem.* **1986**, *51*, 2230–2240.
3. Mousseron, M.; Canet, M. *Bull. Soc. Chim. Fr.* **1952**, 190–197.
4. Pirkle, W. H.; Adam, P. E. *J. Org. Chem.* **1980**, *45*, 4111–4117.
5. Rychnovsky, S. D.; Powell, N. A. *J. Org. Chem.* **1997**, *62*, 6460–6461.
6. Fristad, W. E.; Peterson, J. R. *J. Org. Chem.* **1985**, *50*, 10–18.
7. Ooi, T.; Tayama, E.; Yamada, M.; Maruoka, K. *Synlett* **1999**, *6*, 729–730.
8. Askin, D.; Volante, R. P.; Ryan, K. M. *Tetrahedron Lett.* **1988**, *29*, 4245–4248.

## VI. Analytical Data

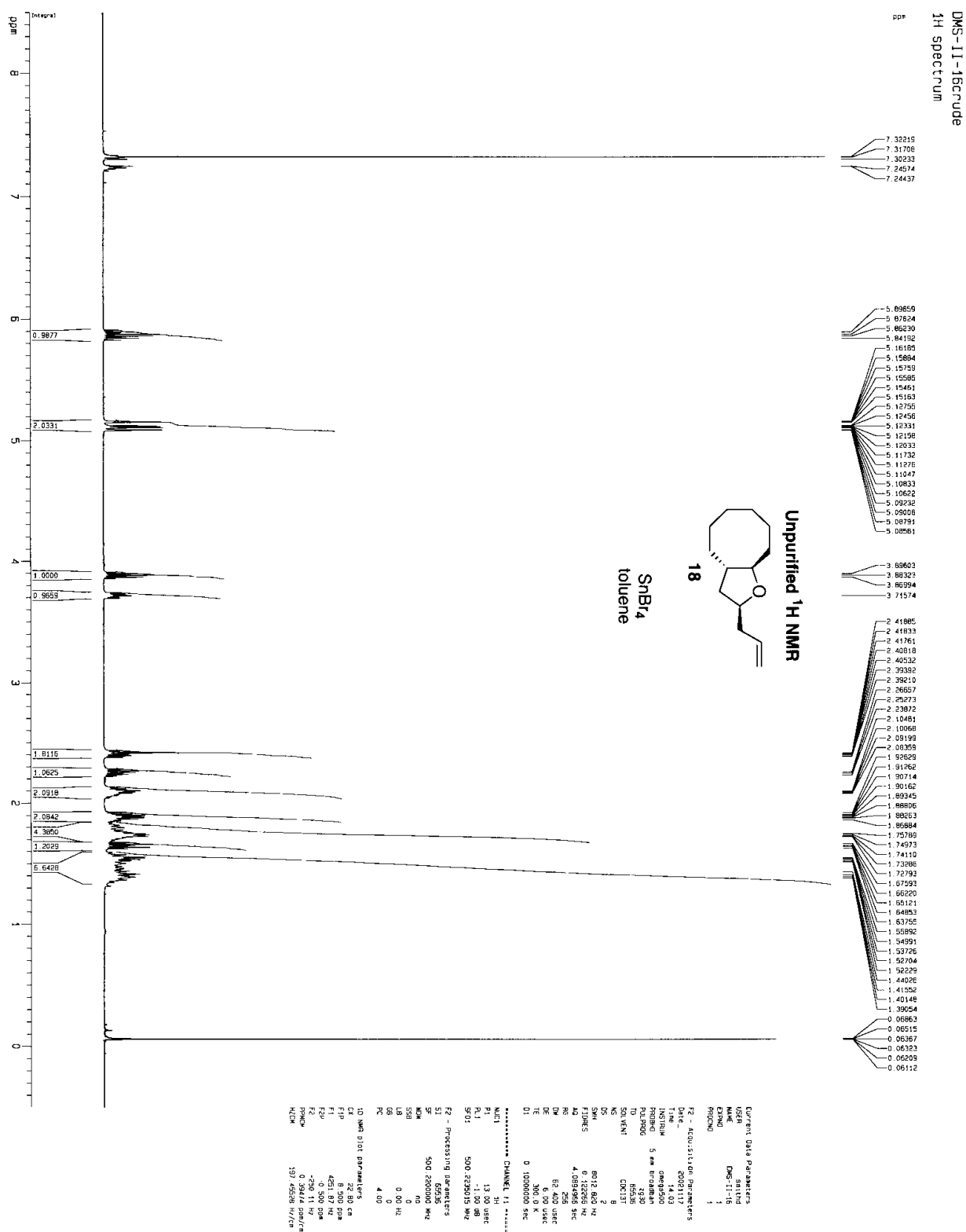
A. GC traces and  $^1\text{H}$  NMR spectra of Isomer Ratios:

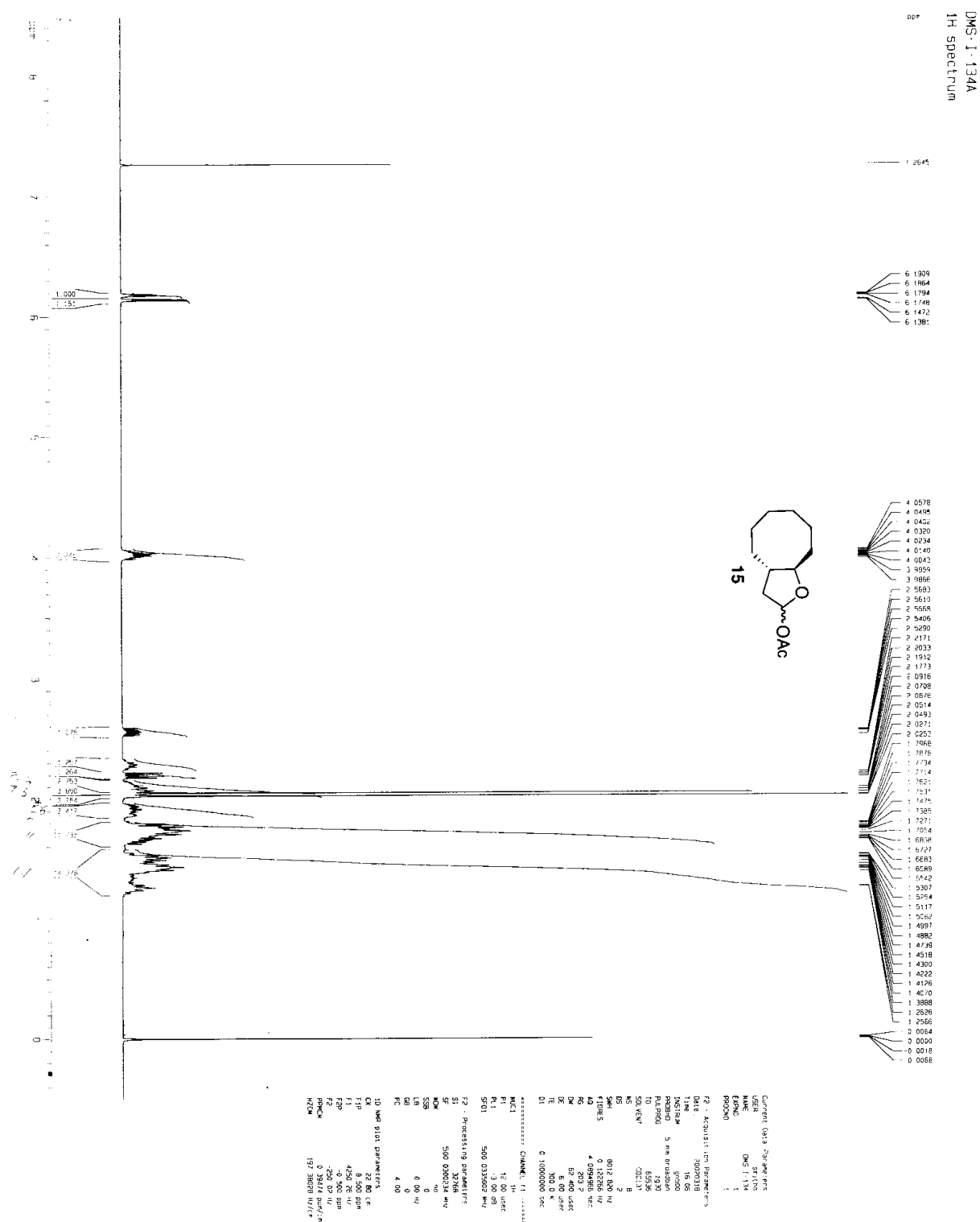
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Height %
1	1.452	BV	0.0122	4.77951	6.03930	4.80128
16 → 2	7.156	PB	0.0265	147.00282	79.63422	63.30971
17 → 3	7.287	BB	0.0273	65.72654	35.21637	27.99724
4	11.242	VB	0.0268	9.23741	4.89527	3.89177









B. Selected  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra:

DMS-*d*<sub>6</sub>-1-134B  
<sup>13</sup>C spectrum with <sup>1</sup>H decoupling

ppm

170.84  
170.79

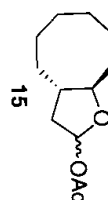
98.05  
98.01

86.95  
85.29

77.48  
77.23  
76.98

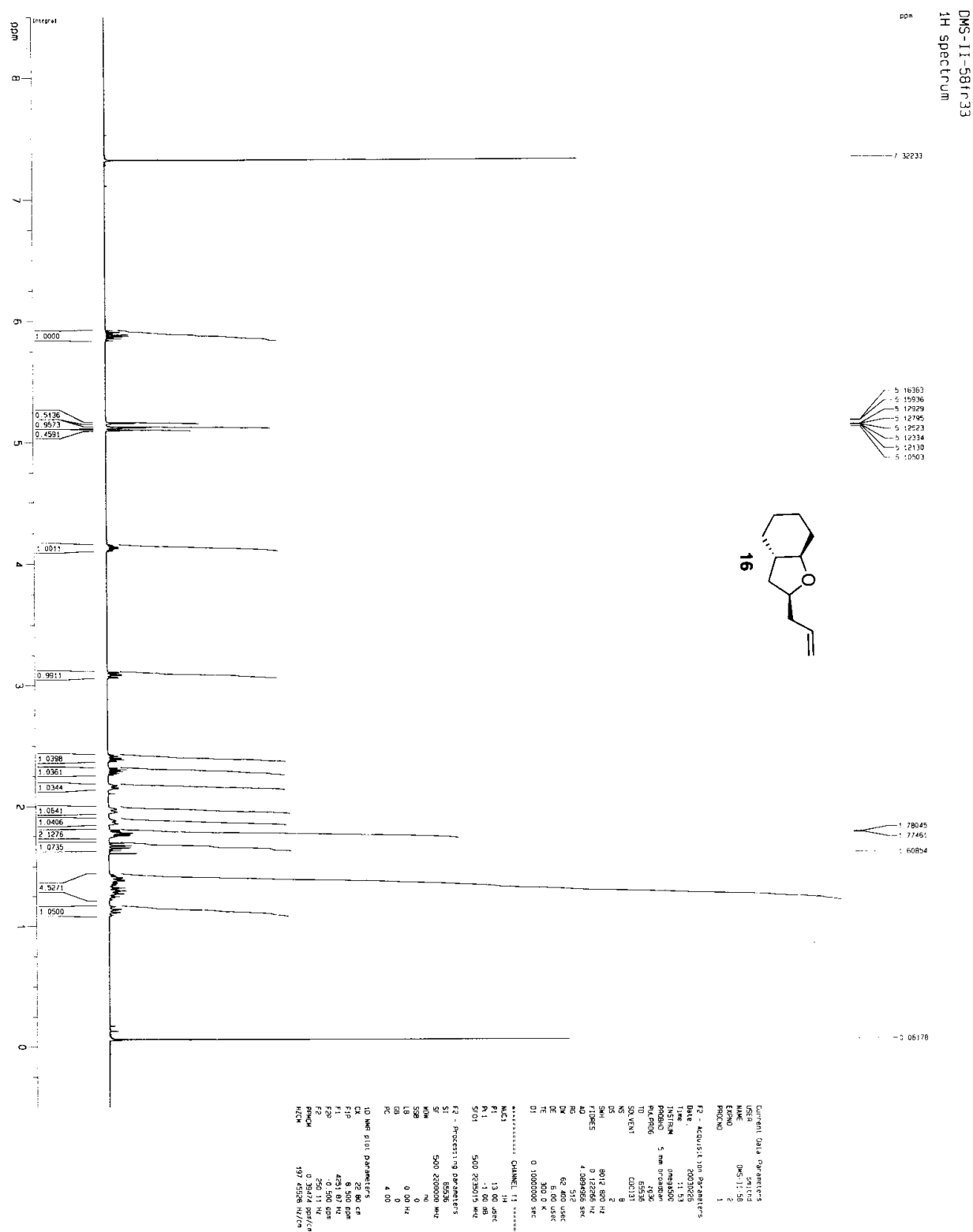
42.01  
42.23  
42.11  
40.84  
37.30  
34.58  
34.23  
34.23  
28.01  
27.62  
27.21  
27.15  
25.69  
25.50  
23.55  
23.13  
21.75  
21.64

0.21



ppm

Current Data Parameters  
 USER: galling  
 NAME: DMS-*d*<sub>6</sub>-1-134  
 EXPNO: 1  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 Date\_ : 20060601  
 Time : 16.30  
 INSTRUM : spect  
 PULPROG : zgpg30  
 PRGNAME : 13c-134B  
 F1 : 125.760153  
 SFO : 125.760153  
 DDC1 : 1  
 DDC2 : 1  
 DDC3 : 1  
 M0 : 2  
 M1 : 3000.000 Hz  
 FIDRES : 0.46388 Hz  
 AQ : 1.0819540 sec  
 RG : 9195.2  
 RW : 18.500 MHz  
 GB : 0.0000000  
 TE : 300.0 K  
 D1 : 0.2500000 sec  
 D11 : 0.0000000 sec  
 \*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 : <sup>13</sup>C  
 P1 : 6.50 MHz  
 PL1 : 0.00 dB  
 SFO1 : 125.760153 MHz  
 \*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 DDP002 : velt16  
 P002 : 125.760153  
 PCP002 : 80.00 MHz  
 PL002 : -3.00 dB  
 R12 : 13.50 dB  
 SFO2 : 500.1350002 MHz  
 F2 - Processing parameters  
 SI : 86536  
 SF : 125.760153 MHz  
 WDW : 0  
 SSB : 0  
 LB : 1.00 Hz  
 GB : 0  
 PC : 2.00  
 ID parameters  
 CX : 22.80 cm  
 FID : 200.000 GHz  
 F2 : 200.1350000 GHz  
 F2 : 10.000 GHz  
 F2 : -187.33 Hz  
 PWDW : 3.21623 GHz/cm  
 PWDW : 1158.05850 Hz/cm



DMS-II-58Bmajor  
13C spectrum with 1H decoupling