Cyclopentanone Ring Expansion Leading to Functionalized δ -Lactams: Short Synthesis of Simple Sedum Alkaloids[†]

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I. Compound Characterization:

Supplemental Material

Unless otherwise noted, all reactions were performed in oven dried glassware and were stirred under an atmosphere of ultra high purity Argon. The tetrahydrofuran used was distilled from sodium/benzophenone, and the dichloromethane was distilled from calcium hydride. All other reagents were used as received from commercial suppliers, unless otherwise noted. Analytical TLC analysis was conducted on precoated glass-backed silica gel plates (Merck Kieselgel 60 F₂₅₄, 250 μ thickness) and visualized with *p*-anisaldehyde or KMnO₄ stains. Column chromatography was performed using flash silica gel (particle size 230-400 mesh). Yields reported are for pure products (>95% based on their chromatographic and spectroscopic homogeneity), and are unoptimized. NMR spectra were obtained on a Varian XL-400 spectrometer, operating at 400 MHz for ¹H and 100 MHz for ¹³C, or a Bruker 400 spectrometer operating at the same frequencies. Chemical shifts are reported in ppm (δ) and are referenced to CDCl₃ (7.26 and 77.0 ppm).

Lactone **4a** (from epoxide **2a**): ¹H NMR (CDCl₃) δ 7.31-7.27 (m, 2H), 7.22-7.15 (m, 3H), 4.56-4.49 (m, 1H), 4.19-4.13 (m, 1H), 2.82-2.75 (m, 1H), 2.70-2.64 (m, 2H), 2.52-2.45 (m, 2H), 2.42-2.25 (m, 3H), 2.05-1.75 (m, 4H); ¹³C (CDCl₃) δ 175.6, 140.7, 128.5, 128.4, 126.1, 79.3, 51.2, 41.1, 36.6, 31.3, 28.2, 25.6; IR (neat) 2932, 1731, 1455, 1243, 1132, 750, 701 cm⁻¹; HRMS (FAB, M+H⁺) calcd. 359.0508 for C₁₅H₂₀IO₂, found 359.0510.

Lactone **4b** (from epoxide **2a**): ^1H NMR (CDCl_3) δ 7.35-7.16 (m, 5H), 4.44-4.33 (m, 2H), 2.86-2.79 (m, 1H), 2.73-2.65 (m, 1H), 2.47-2.29 (m, 4H), 2.18-1.83 (m, 6H); ^{13}C (CDCl_3) δ 175.0, 140.5, 128.6, 128.4, 126.3, 77.1, 49.1, 37.3, 36.3, 31.3, 31.2, 28.1, 27.0; IR (neat) 2932, 1731, 1455, 1243, 1132, 750, 701 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 359.0508 for $\text{C}_{15}\text{H}_{20}\text{IO}_2$, found 359.0502.

Lactone **5a** (from epoxide **2a**): ^1H NMR (CDCl_3) δ 7.35-7.15 (m, 5H), 4.45-4.40 (m, 1H), 3.53-3.51 (m, 1H), 2.86-2.80 (m, 1H), 2.73-2.65 (m, 1H), 2.47-2.41 (m, 1H), 2.35-2.29 (m, 1H), 2.14-1.74 (m, 8H); ^{13}C (CDCl_3) δ 174.9, 140.5, 128.6, 128.4, 126.3, 74.3, 58.7, 41.5, 36.6, 32.3, 32.0, 31.3, 24.5; IR (neat) 2864, 2103, 1727, 1456, 1252 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 274.1556 for $\text{C}_{15}\text{H}_{20}\text{N}_3\text{O}_2$, found 274.1530.

Lactone **5b** (from epoxide **2a**): ^1H NMR (CDCl_3) δ 7.32-7.17 (m, 5H), 4.70-4.64 (m, 1H), 3.46-3.43 (m, 1H), 2.84-2.65 (m, 2H), 2.43-2.33 (m, 2H), 2.15-1.79 (m, 8H); ^{13}C (CDCl_3) δ 175.8, 140.9, 128.6, 128.5, 126.2, 76.2, 60.8, 42.9, 37.0, 33.5, 32.5, 31.5, 25.9; IR (neat) 2949, 2103, 1733, 1445, 1290, 1138 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 274.1556 for $\text{C}_{15}\text{H}_{20}\text{N}_3\text{O}_2$, found 274.1548.

Lactam **6a** (from epoxide **2a**): ^1H NMR (CDCl_3) δ 7.72 (s, 1H), 7.31-7.14 (m, 5H), 4.38 (s, 1H), 3.87-3.81 (m, 1H), 3.55-3.47 (m, 1H), 2.80-2.58 (m, 2H), 2.39-2.20 (m, 2H), 1.89-1.51 (m, 6H), 1.43-1.19 (m, 2H); ^{13}C

(CDCl₃) δ 172.1, 142.0, 128.4, 128.3, 125.7, 71.8, 54.0, 42.9, 40.5, 31.6, 29.6, 20.0; IR (neat) 3313, 2941, 2858, 1634, 1460, 1344 cm⁻¹; HRMS (FAB, M+H⁺) calcd. 248.1651 for C₁₅H₂₁NO₂, found 248.1643.

Lactam **6b** (from epoxide **2a**): ¹H NMR (CDCl₃) δ 7.40 (s, 1H), 7.32-7.17 (m, 5H), 3.92-3.90 (m, 1H), 3.76-3.67 (m, 1H), 3.22 (s, 1H), 2.94-2.74 (m, 1H), 2.70-2.57 (m, 1H), 2.38-2.27 (m, 2H), 1.91-1.56 (m, 8H); ¹³C (CDCl₃) δ 172.7, 141.8, 128.45, 128.38, 125.9, 77.2, 67.7, 49.4, 42.9, 39.0, 32.3, 29.0, 19.5; IR (neat) 3433, 2942, 2859, 1654 cm⁻¹; HRMS (FAB, M+H⁺) calcd. 248.1651 for C₁₅H₂₁NO₂, found 248.1647.

Lactone **4a** (from epoxide **2b**): ¹H NMR (CDCl₃) δ 4.81-4.62 (m, 1H), 4.24-4.22 (m, 1H), 3.68-3.61 (m, 2H), 2.66-2.45 (m, 4H), 2.36-2.24 (m, 2H), 1.93-1.69 (m, 4H), 0.86 (s, 9H), 0.013 (s, 3H), 0.005 (s, 1H); ¹³C (CDCl₃) δ 175.0, 77.3, 58.3, 50.9, 40.6, 38.0, 30.5, 27.8, 25.8, 25.7, 18.2, -5.50, -5.52; IR (neat) 2958, 2863, 1723, 1476, 1362, 1238, 1096, 839, 773 cm⁻¹; HRMS (FAB, M+H⁺) calcd. 413.1009 for C₁₅H₂₉IO₃Si, found 413.0999.

Lactone **4b** (from epoxide **2b**): ¹H NMR (CDCl₃) δ 4.83-4.75 (m, 1H), 4.36-4.28 (m, 1H), 3.70-3.61 (m, 2H), 2.75-2.64 (m, 1H), 2.44-1.62 (m, 9H), 0.85 (s, 9H), 0.01 (s, 3H), 0.002 (s, 3H); ¹³C

(CDCl₃) δ 174.9, 74.7, 58.1, 49.2, 37.6, 37.4, 31.0, 28.2, 26.8, 25.8, 18.1, -5.5; IR (neat) 2945, 2860, 1726, 1458, 1360, 1251, 1190, 1092, 995, 824, 775 cm⁻¹; HRMS (FAB, M+H⁺) calcd. 413.1009 for C₁₅H₂₉IO₃Si, found 413.1025.

Lactone **5a** (from epoxide **2b**): ¹H NMR (CDCl₃) δ 4.89-4.84 (m, 1H), 3.74-3.66 (m, 2H), 3.56-3.50 (m, 1H), 2.71-2.64 (m, 1H), 2.53-2.48 (m, 1H), 2.17-1.72 (m, 8H), 0.88 (s, 9H), 0.04 (s, 3H),

0.03 (s, 3H); ¹³C (CDCl₃) δ 174.9, 72.1, 58.9, 58.2, 41.4, 37.9, 32.5, 31.9, 25.9, 24.9, 18.2, -5.4, -5.9; IR (neat) 2948, 2929, 2854, 2096, 1726, 1461, 1253, 1092, 826, 769 cm⁻¹; HRMS (FAB, M+H⁺) calcd. 328.2057 for C₁₅H₂₉N₃O₃Si, found 328.2059.

Lactone **5b** (from epoxide **2b**): ¹H NMR (CDCl₃) δ 4.86-4.78 (m, 1H), 3.71-3.60 (m, 2H), 3.52-3.46 (m, 1H), 2.67-2.60 (m, 1H), 2.49-2.44 (m, 1H), 2.13-2.02 (m, 2H), 1.97-1.90 (m, 1H), 1.87-1.68

(m, 5H), 0.85 (s, 9H), 0.01 (s, 3H), -0.01 (s, 3H); ¹³C (CDCl₃) δ 174.8, 71.9, 58.8, 58.1, 41.3, 37.8, 32.4, 31.8, 25.8, 24.7, 18.0, -5.57, -5.60; IR (neat) 2967, 2939, 2854, 2086, 1736, 1461, 1253, 1186, 1092, 997, 931, 836, 779 cm⁻¹; HRMS (FAB, M+H⁺) calcd. 328.2057 for C₁₅H₂₉N₃O₃Si, found 328.2060.

Lactam **6a** (from epoxide **2b**): ¹H NMR (CDCl₃) δ 7.17 (s, 1H), 4.02-3.96 (m, 1H), 3.87-3.76 (m, 2H), 3.57-3.51 (m, 1H), 2.37-2.30 (m, 1H), 2.26-2.17 (m, 1H), 1.90-1.80 (m, 2H), 1.75-1.46 (m, 5H), 0.86 (m, 9H),

0.040 (s, 3H), 0.039 (s, 3H); ¹³C (CDCl₃) δ 171.5, 72.6, 62.5, 53.4, 43.6, 39.0, 30.9, 29.6,

25.7, 20.1, 18.0, 14.1, -5.64, -5.68; IR (neat) 3322, 3212, 2953, 2864, 1652, 1467, 1245, 1089, 830 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 302.2152 for $\text{C}_{15}\text{H}_{32}\text{NO}_3\text{Si}$, found 302.2148.

Lactam **6b** (from epoxide **2b**): ^1H NMR (CDCl_3) δ 6.71 (s, 1H), 4.08-4.02 (m, 1H), 3.93-3.78 (m, 3H), 3.73-3.67 (m, 1H), 2.41-2.23 (m, 2H), 1.91-1.50 (m, 7H), 1.44-1.37 (m, 1H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C (CDCl_3) δ 172.2, 69.4, 63.1, 49.3, 43.3, 38.0, 31.2, 29.2, 25.8, 19.6, 18.1, -5.59, -5.63; IR (neat) 3330, 2930, 2901, 2849, 1645, 1246, 1090, 832 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 302.2152 for $\text{C}_{15}\text{H}_{32}\text{NO}_3\text{Si}$, found 302.2148.

Lactone **4a** (from epoxide **2c**): ^1H NMR (CDCl_3) δ 7.37-7.27 (m, 5H), 4.83-4.76 (m, 1H), 4.47 (s, 2H), 4.25-4.19 (m, 1H), 3.60-3.49 (m, 2H), 2.68-2.42 (m, 4H), 2.36-2.22 (m, 2H), 1.94-1.78 (m, 4H); ^{13}C (CDCl_3) δ 175.2, 138.1, 128.4, 127.7, 73.2, 65.5, 50.9, 40.7, 35.4, 30.9, 27.9, 25.6; IR (neat) 2921, 2866, 1740, 1449, 1356, 1245, 1145, 1107 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 389.0614 for $\text{C}_{16}\text{H}_{22}\text{IO}_3$, found 389.0613.

Lactone **4b** (from epoxide **2c**): ^1H NMR (CDCl_3) δ 7.38-7.27 (m, 5H), 4.80-4.73 (m, 1H), 4.52-4.44 (m, 2H), 4.32-4.26 (m, 1H), 3.63-3.51 (m, 2H), 2.69-2.61 (m, 1H), 2.48-2.12 (m, 5H), 1.95-1.84 (m, 4H); ^{13}C (CDCl_3) δ 174.9, 138.0, 128.4, 127.8, 74.9, 73.2, 65.3, 49.3, 37.8, 35.0, 31.1, 28.1, 26.1; IR (neat) 2935, 2866, 1736, 1458, 1352, 1240, 1185, 1111, 1018 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 389.0614 for $\text{C}_{16}\text{H}_{22}\text{IO}_3$, found 389.0609.

Lactone **5a** (from epoxide **2c**): ^1H NMR (CDCl_3) δ 7.37-7.28 (m, 5H), 4.85-4.79 (m, 1H), 4.52-4.42 (m, 2H), 3.62-3.48 (m, 3H), 2.65-2.57 (m, 1H), 2.48-2.43 (m, 1H), 2.15-1.71 (m, 8H); ^{13}C (CDCl_3) δ 175.0, 138.0, 128.5, 127.8, 73.3, 72.3, 65.3, 58.8, 41.4, 35.4, 32.4, 31.9, 24.8; IR (neat) 2926, 2868, 2097, 1728, 1452, 1360, 1249, 1098 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 304.1661 for $\text{C}_{16}\text{H}_{22}\text{N}_3\text{O}_3$, found 304.1656.

Lactone **5b** (from epoxide **2c**): ^1H NMR (CDCl_3) δ 7.40-7.29 (m, 5H), 4.98-4.91 (m, 1H), 4.51 (s, 2H), 3.66-3.50 (m, 3H), 2.57-2.51 (m, 1H), 2.49-2.38 (m, 1H), 2.17-1.76 (m, 8H); ^{13}C (CDCl_3) δ 175.3, 138.1, 128.4, 127.8, 127.7, 74.2, 73.3, 65.7, 60.6, 42.5, 35.8, 33.0, 32.0, 25.4; IR (neat) 2944, 2868, 2092, 1733, 1459, 1365, 1243, 1142, 1093, 743 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 304.1661 for $\text{C}_{16}\text{H}_{22}\text{N}_3\text{O}_3$, found 304.1668.

Lactam **6a** (from epoxide **2c**): ^1H NMR (CDCl_3) δ 7.38-7.29 (m, 5H), 4.52 (s, 2H), 4.05-3.99 (m, 1H), 3.76-3.55 (m, 3H), 2.90 (s, 1H), 2.44-2.32 (m, 1H), 2.30-2.23 (m, 1H), 1.90-1.21 (m, 8H); ^{13}C (CDCl_3) δ 171.7, 137.6, 128.5, 127.9, 127.7, 73.4, 73.0, 68.9, 53.4, 43.4, 37.1, 30.9, 29.6, 20.1; IR (neat) 3324, 2968, 2896, 1641, 1476, 1451, 1409, 1351, 1310, 1094 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 278.1756 for $\text{C}_{16}\text{H}_{24}\text{NO}_3$, found 278.1746.

Lactam **6b** (from epoxide **2c**): ^1H NMR (CDCl_3) δ 7.38-7.30 (m, 5H), 6.77 (s, 1H), 4.52 (s, 1H), 4.07-4.01 (m, 1H), 3.75-3.63 (m, 3H), 3.35 (s, 1H), 2.39-2.23 (m, 2H), 1.92-1.82 (m, 3H), 1.76-1.54 (m, 4H), 1.44-1.36 (m, 1H); ^{13}C (CDCl_3) δ 172.2, 137.6, 128.5, 127.9, 127.7, 77.2, 73.5, 69.3, 68.6, 49.4, 43.1, 36.2, 29.2, 19.6; IR (neat) 3337, 2948, 2865, 1648, 1095 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 278.1756 for $\text{C}_{16}\text{H}_{24}\text{NO}_3$, found 278.1777.

Lactone **4a** (from epoxide **2d**): ^1H NMR (CDCl_3) δ 4.62-4.59 (m, 1H), 4.24-4.13 (m, 1H), 2.75-2.62 (m, 1H), 2.56-2.25 (m, 5H), 2.01-1.85 (m, 2H), 1.71-1.32 (m, 4H), 1.18 (s, 3H), 1.16 (s, 3H), 0.91 (t, $J=10.4$ Hz, 9H), 0.53 (q, $J=10.8$ Hz, 6H); ^{13}C (CDCl_3) δ 175.9, 81.0, 72.7, 51.6, 41.6, 40.5, 31.9, 30.1, 29.9, 29.5, 28.6, 26.0, 7.1, 6.7; IR (neat) 2953, 2871, 1739, 1450, 1360, 1236, 1153, 1046, 715 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 455.1479 for $\text{C}_{18}\text{H}_{36}\text{IO}_3\text{Si}$, found 455.1461.

Lactone **4b** (from epoxide **2d**): ^1H NMR (CDCl_3) δ 4.94-4.37 (m, 2H), 2.70-2.62 (m, 1H), 2.48-2.35 (m, 3H), 2.18-2.13 (m, 2H), 1.98-1.39 (m, 6H), 1.21 (s, 3H), 1.19 (s, 3H), 0.93 (t, $J=10.4$ Hz, 9H), 0.56 (q, $J=9.6$ Hz, 6H); ^{13}C (CDCl_3) δ 175.1, 79.3, 72.7, 49.1, 40.7, 37.2, 31.3, 30.3, 29.9, 29.4, 28.1, 27.6, 7.1, 6.7; IR (neat) 2989, 2868, 1733, 1559, 1443, 621 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 455.1479 for $\text{C}_{18}\text{H}_{36}\text{IO}_3\text{Si}$, found 455.1464.

Lactone **5a** (from epoxide **2d**): ^1H NMR (CDCl_3) δ 4.55-4.49 (m, 1H), 3.60-3.56 (m, 1H), 2.68-2.59 (m, 1H), 2.54-2.48 (m, 1H), 2.09-2.05 (m, 2H), 1.96-1.78 (m, 5H), 1.72-1.64 (m, 1H), 1.61-1.57 (m, 1H), 1.45-1.34 (m, 1H), 1.21 (s, 3H), 1.20 (s, 3H), 0.93 (t, $J=8.0$ Hz, 9H), 0.56 (q, $J=7.6$ Hz, 6H); ^{13}C (CDCl_3) δ 175.0, 76.6, 72.8, 58.7, 41.5, 40.8, 32.3, 32.1, 30.29, 30.25, 29.4, 24.6, 7.1, 6.7; IR (neat) 2954, 2872, 2104, 1732, 1460, 1361, 1245, 1031, 725 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 370.2526 for $\text{C}_{18}\text{H}_{36}\text{N}_3\text{O}_3\text{Si}$, found 370.2516.

Lactone **5b** (from epoxide **2d**): ^1H NMR (CDCl_3) δ 4.78-4.69 (m, 1H), 2.48-3.45 (m, 1H), 2.47-2.37 (m, 2H), 2.16-2.13 (m, 1H), 2.01-1.43 (m, 10H), 1.21 (s, 3H), 1.20 (s, 3H), 0.94 (t, $J=8.0$ Hz, 9H), 0.56 (q, $J=8.0$ Hz, 6H); ^{13}C (CDCl_3) δ 176.0, 77.9, 72.8, 61.0, 43.2, 40.6, 33.9, 32.9, 30.3, 30.2, 29.5, 26.4, 7.1, 6.7; IR (neat) 2963, 2872, 2096, 1741, 1452, 1361, 1245, 1047, 737 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 370.2526 for $\text{C}_{18}\text{H}_{36}\text{N}_3\text{O}_3\text{Si}$, found 370.2508.

Lactam **6a** (from epoxide **2d**): ^1H NMR (CDCl_3) δ 7.33 (s, 1H), 3.79-3.76 (m, 1H), 3.58-3.45 (m, 1H), 2.40-2.17 (m, 2H), 1.86-1.25 (m, 10H), 1.21 (s, 6H), 0.93 (t, $J=8.1$ Hz, 9H), 0.57 (q, $J=10.8$, 6H); ^{13}C (CDCl_3) δ 171.8, 73.6, 72.5, 53.7, 43.3, 40.8, 33.5, 30.9, 29.80, 29.77, 29.6, 20.1, 7.0, 6.6; IR (neat) 3324, 3267, 2954, 2871, 1660, 1463, 1364, 1232, 1076, 1034, 1010, 960, 738, 713 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 344.2621 for $\text{C}_{18}\text{H}_{38}\text{NO}_3$, found 344.2603.

Lactam **6b** (from epoxide **2d**): ^1H NMR (CDCl_3) δ 6.99 (s, 1H), 3.78 (s, 1H), 3.69-3.67 (m, 1H), 2.37-2.26 (m, 2H), 1.92-1.84 (m, 2H) 1.70-1.37 (m, 8H), 1.22 (s, 6H), 0.93 (t, $J=6.0$ Hz, 9H), 0.57 (q, $J=7.6$ Hz, 6H); ^{13}C (CDCl_3) δ 172.5, 73.5, 68.6, 49.3, 43.1, 41.4, 32.2, 31.2, 29.8, 29.2, 19.5, 7.0, 6.6; IR (neat) 3349, 2954, 2871, 1652, 1459, 1405, 1364, 1240, 1158, 1051, 713 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 344.2621 for $\text{C}_{18}\text{H}_{38}\text{NO}_3$, found 344.2627.

Epoxide **2d**: A flame dried 25 mL three neck flask equipped with a reflux condenser was charged with magnesium turnings (1.07 g, 44.4 mmol) a small crystal of iodine and 7.0 mL of anhydrous ether. The flask was cooled to 0 $^\circ\text{C}$ and 4-bromobutene (1.0 g, 7.40 mmol) was added dropwise over the course of 5 min. The solution immediately turned from red to colorless. This contents of the flask were allowed to warm to room temp and stir for 4 hr before reagent grade acetone (0.363 mL, 14.8 mmol) was added neat. After an additional 2 hr of stirring, the reaction was quenched by the slow addition of 1N NaOH solution. The reaction mixture was passed over celite to remove excess magnesium turnings, and then extracted with ether (3x 50 mL). The combined organics were dried over MgSO_4 and concentrated *in vacuo*, and taken on to the next step without further purification.

The tertiary alcohol was then dissolved in 20 mL of anhydrous CH_2Cl_2 and cooled to -78 $^\circ\text{C}$. 2,6-Lutidine (2.15 mL, 18.5 mmol) was then added, followed by TESOTf (3.34 mL, 14.8 mmol) dropwise. After 2 hr, the reaction was quenched with water, and

then extracted with CH₂Cl₂ (3x 50 mL). The combined organics were dried over MgSO₄ and concentrated *in vacuo*, and taken on to the next step without further purification.

TES ether was dissolved in 20 mL of anhydrous CH₂Cl₂ and cooled to 0 °C. To this was added *m*CPBA (4.15 g, 18.5 mmol) dissolved in 15 mL of ether. The reaction was allowed to warm to room temp and stir overnight. The mixture was diluted with CH₂Cl₂ (50 mL) and washed first with a saturated sodium bisulfite solution (1x 50 mL), and then a saturated sodium bicarbonate solution (1x 50 mL). The combined organics were dried over MgSO₄ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (80 % hexanes, 20% ethyl acetate) to give epoxide **2d** (1.21 g, 67 %) as a colorless oil. ¹H NMR (CDCl₃) δ 2.89-2.86 (m, 1H), 2.72-2.69 (m, 1H), 2.44-2.41 (m, 1H), 1.62-1.49 (m, 4H), 1.19 (s, 3H), 1.17 (s, 3H), 0.91 (t, *J*=10.0 Hz, 9H), 0.54 (q, *J*=10.4 Hz, 6H); ¹³C (CDCl₃) δ 72.7, 52.6, 47.1, 40.7, 29.9, 29.6, 27.5, 7.0, 6.7; IR (neat) 2955, 2919, 2861, 2884, 1467, 1249, 1102, 838, 773 cm⁻¹; HRMS (EI, M⁺) calcd. 244.1858 for C₁₃H₂₈O₂Si⁺, found 244.1832.

Lactone **4a** (from epoxide **2e**): ¹H NMR (CDCl₃) δ 4.60-4.54 (m, 1H), 4.17-4.11 (m, 1H), 2.66-2.60 (m, 1H), 2.49-2.20 (m, 5H), 1.92-1.79 (m, 2H), 1.62-1.53 (m, 1H), 1.47-1.17 (m, 9H), 0.80 (t, *J*=6.8 Hz, 3H); ¹³C (CDCl₃) δ 175.7, 80.2, 51.3, 41.4, 34.9, 31.6, 31.4, 28.7, 28.4, 26.0, 25.1, 22.3, 13.9; IR (neat) 2966, 2857, 2848, 1715, 1468, 1354, 1248, 1179, 1081, 973, 726 cm⁻¹; HRMS

(FAB, M+H⁺) calcd. 339.0821 for C₁₃H₂₄IO₂, found 339.0825.

Lactone **4b** (from epoxide **2e**): ¹H NMR (CDCl₃) δ 4.50-4.44 (m, 1H), 4.39-4.34 (m, 1H), 2.70-2.62 (m, 1H), 2.44-2.38 (m, 1H), 2.34-2.28 (m,

2H), 2.17-2.06 (m, 2H), 2.00-1.84 (m, 2H), 1.71-1.64 (m, 2H), 1.52-1.21 (m, 8H), 0.84 (t, $J=6.8$ Hz, 3H); ^{13}C (CDCl_3) δ 174.9, 78.5, 53.3, 48.8, 37.0, 35.0, 31.5, 31.1, 28.8, 28.0, 27.7, 25.3, 22.4, 13.9; IR (neat) 2956, 2929, 2857, 1716, 1558, 1458, 1240, 1092, 1010, 947 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 339.0821 for $\text{C}_{13}\text{H}_{24}\text{IO}_2$, found 339.0821.

Lactone **5a** (from epoxide **2e**): ^1H NMR (CDCl_3) δ 4.78-4.71 (m, 1H), 3.47-3.41 (m, 1H), 2.49-2.35 (m, 2H), 2.15-2.09 (m, 1H), 2.00-1.84 (m, 5H), 1.72-1.64 (m, 1H), 1.57-1.50 (m, 1H), 1.44-1.21 (m, 8H), 0.87 (t, $J=7.2$ Hz, 3H); ^{13}C (CDCl_3) δ 176.0, 77.3, 61.0, 43.0, 35.4, 33.8, 32.8, 31.6, 28.9, 26.3, 25.3, 22.5, 14.0; IR (neat) 2936, 2861, 2089, 1735, 1457, 1355, 1318, 1248, 1153, 1052, 1008 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 254.1869 for $\text{C}_{13}\text{H}_{24}\text{N}_3\text{O}_2$, found 254.1874.

Lactone **5b** (from epoxide **2e**): ^1H NMR (CDCl_3) δ 4.56-4.49 (m, 1H), 3.57-3.52 (m, 1H), 2.65-2.56 (m, 1H), 2.52-2.47 (m, 1H), 2.11-1.99 (m, 2H), 1.97-1.67 (m, 5H), 1.54-1.49 (m, 1H), 1.47-1.21 (m, 8H), 0.86 (t, $J=6.8$ Hz, 3H); ^{13}C (CDCl_3) δ 175.0, 75.8, 58.7, 41.4, 35.3, 32.2, 32.0, 31.6, 28.9, 25.4, 24.5, 22.4, 13.9; IR (neat) 2930, 2861, 2095, 1729, 1457, 1330, 1248, 1204, 1128, 1008 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 254.1869 for $\text{C}_{13}\text{H}_{24}\text{N}_3\text{O}_2$, found 254.1862.

Lactam **6a** (from epoxide **2e**): ^1H NMR (CDCl_3) δ 7.65 (s, 1H), 4.55 (s, 1H), 3.81-3.75 (m, 1H), 3.54-3.49 (m, 1H), 3.81-3.75 (m, 1H), 3.54-3.45 (m, 1H), 2.38-2.32 (m, 1H), 2.27-2.18 (m, 1H), 1.89-1.80 (m, 2H), 1.73-1.38 (m, 6H), 1.32-1.19 (m, 8H), 0.86 (t, $J=6.8$ Hz, 3H); ^{13}C (CDCl_3) δ 172.0, 72.5, 54.1, 42.6,

38.9, 31.7, 30.8, 29.7, 29.2, 25.2, 22.5, 20.1, 14.0; IR (neat) 3407, 3289, 3215, 2928, 2861, 1651, 1462, 1351, 1086 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 228.1964 for $\text{C}_{13}\text{H}_{26}\text{NO}_2$, found 228.1967.

Lactam **6a** (from epoxide **2e**): ^1H NMR (CDCl_3) δ 7.35 (s, 1H), 3.84-3.65 (m, 3H), 2.37-2.21 (m, 2H), 1.92-1.82 (m, 2H), 1.75-1.59 (m, 2H), 1.54-1.48 (m, 2H), 1.45-1.36 (m, 2H), 1.35-1.22 (m, 8H), 0.86 (t, $J=7.2$ Hz, 3H); ^{13}C (CDCl_3) δ 172.8, 68.0, 49.2, 42.7, 37.3, 31.8, 29.2, 29.0, 25.8, 22.6, 19.4, 14.0; IR (neat) 3327, 3233, 2929, 2854, 1651, 1470 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 228.1964 for $\text{C}_{13}\text{H}_{26}\text{NO}_2$, found 228.1959.

Lactone **4a** (from epoxide **2f**): ^1H NMR (CDCl_3) δ 4.67-4.61 (m, 1H), 4.21-4.15 (m, 1H), 2.72-2.66 (m, 1H), 2.54-2.26 (m, 5H), 1.96-1.86 (m, 2H), 1.67-1.58 (m, 1H), 1.50-1.29 (m, 3H), 0.09 (t, $J=7.2$ Hz, 3H). ^{13}C NMR (CDCl_3) δ 176.0, 80.1, 65.8, 51.5, 41.6, 37.1, 31.8, 28.6, 26.0, 18.5, 13.6; IR (neat) 2960, 2870, 1711, 1357, 1252, 1056, 1008 cm^{-1} ; HRMS (FAB, $\text{M}+\text{H}^+$) calcd. 297.0352 for $\text{C}_{10}\text{H}_{18}\text{IO}_2$, found 297.0349; $[\alpha]_{\text{D}}^{25} = 48.83^\circ$ ($c=0.06$, CHCl_3)

Lactone **4b** (from epoxide **2f**): ^1H NMR (CDCl_3) δ 4.55-4.49 (m, 1H), 4.34-4.38 (m, 1H), 2.74-2.66 (m, 1H), 2.48-2.42 (m, 1H), 2.37-2.33 (m, 2H), 2.17-2.12 (m, 2H), 2.00-1.90 (m, 2H), 1.74-1.67 (m, 1H), 1.53-1.20 (m, 3H), 0.92 (t, $J=8.0$ Hz, 3H). ^{13}C NMR (CDCl_3) δ 175.1, 78.3, 48.9, 37.1, 37.0, 31.2, 28.2, 27.8, 18.6, 13.7; IR (neat) 2958, 2871, 1727, 1459, 1242, 1120, 1023 cm^{-1} ; HRMS

(FAB, $M+H^+$) calcd. 297.0352 for $C_{10}H_{18}IO_2$, found 297.0348; $[\alpha]_D^{25} = -6.95^\circ$ ($c=0.03$, $CHCl_3$).

Lactone **5a** (from epoxide **2f**): 1H NMR ($CDCl_3$) δ 4.59-4.52 (m, 1H), 3.59-3.54 (m, 1H), 2.66-2.59 (m, 1H), 2.54-2.48 (m, 1H), 2.09-2.02 (m, 2H), 1.99-1.70 (m, 5H), 1.56-1.34 (m, 3H), 0.93 (t, $J=7.2$ Hz, 3H). ^{13}C

NMR ($CDCl_3$) δ 175.0, 75.6, 58.7, 41.4, 37.3, 32.3, 32.1, 24.5, 18.7, 13.7; IR (neat) 2960, 2935, 2873, 2101, 1728, 1460, 1253, 1200, 1144, 1030 cm^{-1} ; HRMS (FAB, $M+H^+$) calcd. 212.1399 for $C_{10}H_{18}N_3O_2$, found 212.1378; $[\alpha]_D^{25} = -18.42^\circ$ ($c=0.02$, $CHCl_3$).

Lactone **5b** (from epoxide **2f**): 1H NMR ($CDCl_3$) δ 4.81-4.75 (m, 1H), 3.50-3.43 (m, 1H), 2.49-2.38 (m, 2H), 2.16-2.11 (m, 1H), 1.99-1.87 (m, 5H), 1.71-1.67 (m, 1H), 1.56-1.37 (m, 3H), 0.93 (t, $J=7.2$ Hz, 3H). ^{13}C

NMR ($CDCl_3$) δ 176.1, 76.9, 61.0, 43.1, 37.4, 33.8, 32.8, 26.4, 18.6, 15.3, 13.7; IR (neat) 2959, 2874, 1738, 1456, 1249, 1153 cm^{-1} ; HRMS (FAB, $M+H^+$) calcd. 212.1399 for $C_{10}H_{18}N_3O_2$, found 212.1391; $[\alpha]_D^{25} = 29.49^\circ$ ($c=0.01$, $CHCl_3$).

Lactam **6a** (from epoxide **2f**): 1H NMR ($CDCl_3$) δ 7.72 (s, 1H), 4.06 (m, 1H), 3.81-3.75 (m, 1H), 3.55-3.45 (m, 1H), 2.40-2.18 (m, 2H),

1.89-1.81 (m, 2H), 1.75-1.20 (m, 8H), 0.89 (t, $J=9.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 172.2, 72.3, 54.2, 42.5, 41.1, 30.7, 29.6, 20.0, 18.5, 14.1; IR (neat) 3318, 2955, 2931, 2871, 1645, 1467 cm^{-1} ; HRMS (FAB, $M+H^+$) calcd. 186.1494 for $C_{10}H_{20}NO_2$, found 186.1495.

Lactam **6b** (from epoxide **2f**): ^1H NMR (CDCl_3) δ 7.44 (s, 1H), 3.96 (s, 1H), 3.88-3.82 (s, 1H), 3.73-3.68 (m, 1H), 2.39-2.22 (m, 2H), 1.89-1.80 (m, 2H), 1.76-1.61 (m, 2H), 1.55-1.32 (m, 6H), 0.92 (t, $J=3.6$, 3H); ^{13}C NMR (CDCl_3) δ 172.9, 67.8, 49.3, 42.6, 39.4, 31.0, 29.0, 19.4, 19.0, 14.0; IR (neat) 3302, 2953, 2871, 1655, 1467, 1411, 1351, 1308 cm^{-1} ; HRMS (FAB) m/z ($\text{M}+\text{H}^+$) calcd. 186.1494 for $\text{C}_{10}\text{H}_{20}\text{NO}_2^+$, found 186.1496.

(-)-epihalosaline (**8a**): A 10 mL flask was charged with lactam **6a** (from epoxide **2f**) (0.027 g, 0.15 mmol) and dissolved in 1 mL of anhydrous ether. To this solution, lithium aluminum hydride (0.028 g, 0.75 mmol) was added in one portion. After 2 hr the reaction mixture was quenched with 3 mL of a 10% NaOH solution, and then extracted with ethyl acetate (3x 25 mL). The combined organics were dried over MgSO_4 and concentrated *in vacuo*. The crude product was purified via column chromatography (91% CH_2Cl_2 , 7.6 % MeOH, 1.4% NH_4OH) to afford (-)-epihalosaline (**8a**) (0.019 g, 76%) as a colorless oil. ^1H NMR (CDCl_3) δ 3.85-3.79 (m, 1H), 3.66 (s, 1H), 3.08-3.03 (m, 1H), 2.77-2.70 (m, 1H), 2.64-2.56 (m, 1H), 1.84-1.79 (m, 1H), 1.66-1.08 (m, 9H), 0.91 (t, $J=6.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 72.7, 58.3, 45.9, 42.3, 40.4, 34.1, 27.0, 24.4, 18.6, 14.2; IR (neat) 3309, 2929, 2856, 1456, 1123 cm^{-1} ; HRMS (FAB) m/z ($\text{M}+\text{H}^+$) calcd. 172.1701 for $\text{C}_{10}\text{H}_{22}\text{NO}^+$, found 172.1690; $[\alpha]_{\text{D}}^{25} = 29.61^\circ$ ($c=0.01$, CHCl_3).

halosaline (**8b**): ^1H NMR (CDCl_3) δ 3.95-3.89 (m, 3H), 3.13-3.09 (m, 1H), 2.97-2.91 (m, 1H), 2.64-2.57 (m, 1H), 1.84-1.80 (m, 1H), 1.66-

1.25 (m, 11H), 0.91 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 68.7, 54.8, 46.8, 41.9, 40.1, 31.3, 25.9, 24.6, 19.0, 14.2; IR (neat) 3364, 2975, 2899, 1455, 1381, 1090, 1050, 881 cm^{-1} ; HRMS (FAB) m/z ($\text{M}+\text{H}^+$) calcd. 172.1701 for $\text{C}_{10}\text{H}_{22}\text{NO}^+$, found 172.1690; $[\alpha]_{\text{D}}^{25} = -18.20^\circ$ ($c=0.30$, CHCl_3).

Lactams **11a** & **11b**: ^1H NMR (CDCl_3) δ 7.29-7.16 (m, 11H), 7.00 (s, 1H), 3.90-3.74 (m, 3H), 3.64-3.60 (m, 1H), 3.50-3.44 (m, 1H), 2.83-2.62 (m, 4H), 2.53-2.37 (m, 4H), 1.97-1.94 (m, 2H), 1.91-1.26 (m, 18H); ^{13}C NMR (CDCl_3) δ 178.3, 178.2, 141.9, 128.38, 128.36, 128.34, 125.78, 125.76, 69.9, 67.5, 53.5, 51.2, 43.0, 42.2, 40.2, 39.5, 36.6, 35.5, 32.0, 31.7, 29.7, 29.6, 23.1, 23.0; IR (neat) 3371, 3274, 3206, 3079, 3060, 3021, 2924, 2855, 1650, 1455, 1182, 1095, 696 cm^{-1} ; HRMS (FAB) m/z ($\text{M}+\text{H}^+$) calcd. 262.1807 for $\text{C}_{16}\text{H}_{24}\text{NO}_2^+$, found 262.1802.

lactone 4a (from epoxide 2a)

lactone **4b** (from epoxide **2a**)

lactone 5a (from epoxide 2a)

lactone 5a (from epoxide 2a)

lactone 5b (from epoxide 2a)

lactam **6b** (from epoxide **2a**)

lactone 4a (from epoxide 2b)

lactone **4a** (from epoxide **2b**)

lactone **4b** (from epoxide **2b**)

lactone **5a** (from epoxide **2b**)

77.32
77.00
76.69
72.57

— 62.51

———— 53.38

———— 43.58

_____ 39.00

30.91

29.55
25.74

20.74

_____ 20.10
 _____ 17.99

— 14.10

-5.64

-5.68

lactam **6b** (from epoxide **2b**)

lactam **6b** (from epoxide **2b**)

lactone 4a (from epoxide 2c)

lactone **4a** (from epoxide **2c**)

lactone 4b (from epoxide 2c)

lactone 4b (from epoxide 2c)

lactone 5a (from epoxide 2c)

lactone 5a (from epoxide 2c)

lactone **5b** (from epoxide **2c**)

lactone **5b** (from epoxide **2c**)

lactam **6a** (from epoxide **2c**)

lactam 6b (from epoxide 2c)

lactam **6b** (from epoxide **2c**)

lactam **6b** (from epoxide **2c**)

lactone **4a** (from epoxide **2d**)

175.92

80.99
77.43
77.01
76.58
72.66

51.59

41.59
40.48
31.86
30.10
29.94
29.48
28.59
25.99

7.05
6.65

lactone 5b (from epoxide 2d)

Lactam 6a (from epoxide 2d)

lactone **4a** (from epoxide **4e**)

175.69

80.22
77.32
77.00
76.68

51.32

41.36
34.94
31.63
31.42
28.67
28.39
25.96
25.05
22.31
13.86

78.45
77.31
76.99
76.67

53.34
48.83

36.97
34.95
31.49
31.14
28.79
28.03
27.71
25.25
22.38

13.90

Lactone 5a (from epoxide 2e)

lactone 5a (from epoxide 4e)

175.98

77.32
77.27
77.00
76.69

60.97

43.04
35.41
33.78
32.81
31.60
28.86
26.30
25.30
22.47
13.97

lactone 5b (from epoxide 4e)

172.78

77.31
76.99
76.67

68.00

49.16

42.71

37.30

31.76

29.23

29.02

25.75

22.55

19.40

14.01

lactone **4a** (from epoxide **4f**)

lactone 4b (from epoxide 4f)

lactone 4b (from epoxide 4f)

lactone **5a** (from epoxide **4f**)

lactone 5b (from epoxide 4f)

lactam **6a** (from epoxide **2f**)

lactam **6b** (from epoxide **2f**)

III. X-Ray Structures:

Table 1. Crystal data and structure refinement for x0353.

Identification code	x0353
Empirical formula	C ₉ H ₁₇ N O ₃
Formula weight	187.24
Temperature	110 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions deg. 109.300(6) deg. deg.	a = 5.1268(3)Å alpha = 90 b = 27.0317(12)Å beta = c = 7.1313(3)Å gamma = 90
Volume	932.76(9) Å ³
Z, Calculated density	4, 1.333 Mg/m ³
Absorption coefficient	0.099 mm ⁻¹
F(000)	408
Crystal size	0.8705 x 0.2090 x 0.0585 mm
Theta range for data collection	4.27 to 28.13 deg.
Limiting indices	-6<=h<=6, -35<=k<=35, -9<=l<=9
Reflections collected / unique	10423 / 2269 [R(int) = 0.0501]
Completeness to theta = 28.13	99.3 %
Absorption correction	Analytical
Max. and min. transmission	0.995 and 0.956
Refinement method F ²	Full-matrix least-squares on
Data / restraints / parameters	2269 / 0 / 130
Goodness-of-fit on F ²	1.108
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.0954
R indices (all data)	R1 = 0.0819, wR2 = 0.1055
Largest diff. peak and hole	0.350 and -0.244 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for x0353. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	2004(3)	315(1)	8352(2)	16(1)
O(2)	4145(3)	-2039(1)	9938(2)	20(1)
O(3)	1817(3)	-2094(1)	15951(2)	25(1)
N(1)	2501(3)	-503(1)	8953(2)	12(1)
C(1)	1026(3)	-111(1)	8060(2)	12(1)
C(2)	-1890(4)	-193(1)	6689(2)	14(1)
C(3)	-2506(4)	-726(1)	6014(3)	17(1)
C(4)	-1469(4)	-1071(1)	7799(3)	15(1)
C(5)	1641(4)	-1023(1)	8785(2)	12(1)
C(6)	2688(4)	-1250(1)	10868(2)	13(1)
C(7)	2367(4)	-1811(1)	10883(2)	14(1)
C(8)	3147(4)	-2027(1)	12967(3)	17(1)
C(9)	1418(4)	-1826(1)	14152(3)	19(1)

Table 3. Bond lengths [Å] and angles [deg] for x0353.

O(1)-C(1)	1.244(2)
O(2)-C(7)	1.439(2)
O(2)-H(2O)	0.82(3)
O(3)-C(9)	1.428(2)
O(3)-H(3O)	0.84(3)
N(1)-C(1)	1.336(2)
N(1)-C(5)	1.467(2)
N(1)-H(1N)	0.86(2)
C(1)-C(2)	1.508(2)
C(2)-C(3)	1.520(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.524(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.521(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.530(2)
C(5)-H(5A)	1.0000
C(6)-C(7)	1.526(2)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.522(2)
C(7)-H(7A)	1.0000
C(8)-C(9)	1.513(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(7)-O(2)-H(2O)	108.9(18)
C(9)-O(3)-H(3O)	109.1(17)
C(1)-N(1)-C(5)	127.93(15)
C(1)-N(1)-H(1N)	117.0(15)
C(5)-N(1)-H(1N)	115.1(15)
O(1)-C(1)-N(1)	121.36(16)
O(1)-C(1)-C(2)	120.20(15)
N(1)-C(1)-C(2)	118.43(15)
C(1)-C(2)-C(3)	113.74(14)
C(1)-C(2)-H(2A)	108.8
C(3)-C(2)-H(2A)	108.8
C(1)-C(2)-H(2B)	108.8
C(3)-C(2)-H(2B)	108.8
H(2A)-C(2)-H(2B)	107.7
C(2)-C(3)-C(4)	109.67(14)
C(2)-C(3)-H(3A)	109.7
C(4)-C(3)-H(3A)	109.7
C(2)-C(3)-H(3B)	109.7
C(4)-C(3)-H(3B)	109.7
H(3A)-C(3)-H(3B)	108.2
C(5)-C(4)-C(3)	110.93(15)

C(5)-C(4)-H(4A)	109.5
C(3)-C(4)-H(4A)	109.5
C(5)-C(4)-H(4B)	109.5
C(3)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	108.0
N(1)-C(5)-C(4)	111.10(14)
N(1)-C(5)-C(6)	107.73(13)
C(4)-C(5)-C(6)	113.11(14)
N(1)-C(5)-H(5A)	108.3
C(4)-C(5)-H(5A)	108.3
C(6)-C(5)-H(5A)	108.3
C(7)-C(6)-C(5)	113.61(14)
C(7)-C(6)-H(6A)	108.8
C(5)-C(6)-H(6A)	108.8
C(7)-C(6)-H(6B)	108.8
C(5)-C(6)-H(6B)	108.8
H(6A)-C(6)-H(6B)	107.7
O(2)-C(7)-C(8)	106.87(14)
O(2)-C(7)-C(6)	109.60(14)
C(8)-C(7)-C(6)	113.25(14)
O(2)-C(7)-H(7A)	109.0
C(8)-C(7)-H(7A)	109.0
C(6)-C(7)-H(7A)	109.0
C(9)-C(8)-C(7)	113.18(15)
C(9)-C(8)-H(8A)	108.9
C(7)-C(8)-H(8A)	108.9
C(9)-C(8)-H(8B)	108.9
C(7)-C(8)-H(8B)	108.9
H(8A)-C(8)-H(8B)	107.8
O(3)-C(9)-C(8)	112.54(15)
O(3)-C(9)-H(9A)	109.1
C(8)-C(9)-H(9A)	109.1
O(3)-C(9)-H(9B)	109.1
C(8)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.8

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for x0353.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	
U12						
O(1)	16(1)	12(1)	16(1)	1(1)	2(1)	-
2(1)						
O(2)	30(1)	19(1)	14(1)	2(1)	10(1)	
10(1)						
O(3)	44(1)	20(1)	13(1)	-2(1)	12(1)	-
13(1)						
N(1)	10(1)	13(1)	12(1)	0(1)	2(1)	-
2(1)						
C(1)	13(1)	14(1)	9(1)	-1(1)	5(1)	
1(1)						
C(2)	12(1)	15(1)	11(1)	2(1)	1(1)	
1(1)						
C(3)	16(1)	17(1)	13(1)	0(1)	-2(1)	-
1(1)						
C(4)	14(1)	12(1)	17(1)	0(1)	2(1)	-
3(1)						
C(5)	14(1)	9(1)	14(1)	-1(1)	4(1)	-
1(1)						
C(6)	15(1)	13(1)	12(1)	-1(1)	3(1)	-
1(1)						
C(7)	17(1)	13(1)	12(1)	-1(1)	5(1)	
1(1)						
C(8)	21(1)	15(1)	14(1)	2(1)	5(1)	
2(1)						
C(9)	27(1)	17(1)	15(1)	2(1)	9(1)	-
2(1)						

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for x0353.

	x	y	z	U(eq)
H(20)	3410(50)	-2019(9)	8730(40)	36(7)
H(30)	1030(50)	-2372(10)	15680(40)	40(7)

H(1N)	4150(50)	-448(8)	9730(30)	22(6)
H(2A)	-2225	21	5504	16
H(2B)	-3190	-89	7377	16
H(3A)	-1583	-808	5033	20
H(3B)	-4522	-770	5366	20
H(4A)	-2403	-989	8773	18
H(4B)	-1936	-1417	7362	18
H(5A)	2563	-1198	7938	15
H(6A)	4665	-1165	11493	16
H(6B)	1664	-1100	11684	16
H(7A)	406	-1899	10130	17
H(8A)	2931	-2391	12867	20
H(8B)	5118	-1954	13688	20
H(9A)	1902	-1474	14475	23
H(9B)	-558	-1841	13327	23

Table 6. Torsion angles [deg] for x0353.

C(5)-N(1)-C(1)-O(1)	
179.19(16)	
C(5)-N(1)-C(1)-C(2)	-0.3(3)
O(1)-C(1)-C(2)-C(3)	
163.18(16)	
N(1)-C(1)-C(2)-C(3)	-17.4(2)
C(1)-C(2)-C(3)-C(4)	47.3(2)
C(2)-C(3)-C(4)-C(5)	-61.2(2)
C(1)-N(1)-C(5)-C(4)	-13.2(2)
C(1)-N(1)-C(5)-C(6)	-
137.60(17)	
C(3)-C(4)-C(5)-N(1)	
43.35(19)	
C(3)-C(4)-C(5)-C(6)	
164.64(14)	
N(1)-C(5)-C(6)-C(7)	-
170.40(14)	
C(4)-C(5)-C(6)-C(7)	66.4(2)
C(5)-C(6)-C(7)-O(2)	
66.46(19)	
C(5)-C(6)-C(7)-C(8)	-
174.32(15)	
O(2)-C(7)-C(8)-C(9)	-
179.33(15)	
C(6)-C(7)-C(8)-C(9)	59.9(2)
C(7)-C(8)-C(9)-O(3)	
169.35(15)	

Table 7. Hydrogen bonds for x0353 [Å and deg.].

D-H...A <(DHA)	d(D-H)	d(H...A)	d(D...A)
O(2)-H(2O)...O(3)#1 170(2)	0.82(3)	1.89(3)	2.6995(18)
O(3)-H(3O)...O(2)#2 176(3)	0.84(3)	1.85(3)	2.6916(19)
N(1)-H(1N)...O(1)#3 178(2)	0.86(2)	2.03(2)	2.8823(19)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z-1 #2 x-1/2,-y-1/2,z+1/2 #3 -x+1,-y,-z+2

Table 1. Crystal data and structure refinement for x0354.

Identification code	x0354
Empirical formula	C ₉ H ₁₇ N O ₃
Formula weight	187.24
Temperature	110 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions 65.30(3) deg. 88.44(2) deg. 77.37(3) deg.	a = 6.1600(14) Å alpha = b = 8.885(3) Å beta = c = 9.942(3) Å gamma =
Volume	481.1(3) Å ³
Z, Calculated density	2, 1.292 Mg/m ³
Absorption coefficient	0.096 mm ⁻¹
F(000)	204
Crystal size	0.6400 x 0.2898 x 0.1346 mm
Theta range for data collection	3.94 to 27.48 deg.
Limiting indices 11<=l<=12	-7<=h<=7, -11<=k<=11, -
Reflections collected / unique	5205 / 2198 [R(int) = 0.0313]
Completeness to theta = 27.48	99.8 %
Absorption correction	Analytical
Max. and min. transmission	0.991 and 0.974
Refinement method F ²	Full-matrix least-squares on
Data / restraints / parameters	2198 / 0 / 130
Goodness-of-fit on F ²	0.896
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0812
R indices (all data)	R1 = 0.0749, wR2 = 0.0899
Largest diff. peak and hole	0.246 and -0.217 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for x0354. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	12302(2)	-1582(1)	6066(1)	23(1)
O(2)	5570(2)	2948(1)	7839(1)	26(1)
O(3)	3710(2)	3777(1)	3426(1)	24(1)
N(1)	9393(2)	-460(2)	7022(2)	19(1)
C(1)	11224(2)	-1639(2)	7168(2)	18(1)
C(2)	11987(2)	-3088(2)	8664(2)	22(1)
C(3)	10590(2)	-3004(2)	9925(2)	23(1)
C(4)	8152(2)	-2244(2)	9374(2)	21(1)
C(5)	7915(2)	-439(2)	8209(2)	18(1)
C(6)	5540(2)	455(2)	7545(2)	20(1)
C(7)	5180(2)	2380(2)	6734(2)	20(1)
C(8)	2841(2)	3249(2)	5976(2)	23(1)
C(9)	2382(2)	2998(2)	4603(2)	25(1)

Table 3. Bond lengths [Å] and angles [deg] for x0354.

O(1)-C(1)	1.2550(17)
O(2)-C(7)	1.4316(18)
O(2)-H(2O)	0.83(2)
O(3)-C(9)	1.4274(18)
O(3)-H(3O)	0.86(2)
N(1)-C(1)	1.3248(18)
N(1)-C(5)	1.4747(18)
N(1)-H(1N)	0.895(15)
C(1)-C(2)	1.504(2)
C(2)-C(3)	1.519(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.517(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.513(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.521(2)
C(5)-H(5A)	1.0000
C(6)-C(7)	1.522(2)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.526(2)
C(7)-H(7A)	1.0000
C(8)-C(9)	1.515(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(7)-O(2)-H(2O)	107.0(13)
C(9)-O(3)-H(3O)	107.1(13)
C(1)-N(1)-C(5)	125.86(13)
C(1)-N(1)-H(1N)	114.5(9)
C(5)-N(1)-H(1N)	119.0(9)
O(1)-C(1)-N(1)	120.72(14)
O(1)-C(1)-C(2)	119.56(13)
N(1)-C(1)-C(2)	119.70(14)
C(1)-C(2)-C(3)	115.03(13)
C(1)-C(2)-H(2A)	108.5
C(3)-C(2)-H(2A)	108.5
C(1)-C(2)-H(2B)	108.5
C(3)-C(2)-H(2B)	108.5
H(2A)-C(2)-H(2B)	107.5
C(4)-C(3)-C(2)	110.37(13)
C(4)-C(3)-H(3A)	109.6
C(2)-C(3)-H(3A)	109.6
C(4)-C(3)-H(3B)	109.6
C(2)-C(3)-H(3B)	109.6
H(3A)-C(3)-H(3B)	108.1
C(5)-C(4)-C(3)	108.92(12)

C(5)-C(4)-H(4A)	109.9
C(3)-C(4)-H(4A)	109.9
C(5)-C(4)-H(4B)	109.9
C(3)-C(4)-H(4B)	109.9
H(4A)-C(4)-H(4B)	108.3
N(1)-C(5)-C(4)	108.78(12)
N(1)-C(5)-C(6)	109.77(12)
C(4)-C(5)-C(6)	114.01(12)
N(1)-C(5)-H(5A)	108.0
C(4)-C(5)-H(5A)	108.0
C(6)-C(5)-H(5A)	108.0
C(5)-C(6)-C(7)	113.59(12)
C(5)-C(6)-H(6A)	108.8
C(7)-C(6)-H(6A)	108.8
C(5)-C(6)-H(6B)	108.8
C(7)-C(6)-H(6B)	108.8
H(6A)-C(6)-H(6B)	107.7
O(2)-C(7)-C(6)	105.81(12)
O(2)-C(7)-C(8)	110.24(11)
C(6)-C(7)-C(8)	113.03(12)
O(2)-C(7)-H(7A)	109.2
C(6)-C(7)-H(7A)	109.2
C(8)-C(7)-H(7A)	109.2
C(9)-C(8)-C(7)	114.98(12)
C(9)-C(8)-H(8A)	108.5
C(7)-C(8)-H(8A)	108.5
C(9)-C(8)-H(8B)	108.5
C(7)-C(8)-H(8B)	108.5
H(8A)-C(8)-H(8B)	107.5
O(3)-C(9)-C(8)	112.37(12)
O(3)-C(9)-H(9A)	109.1
C(8)-C(9)-H(9A)	109.1
O(3)-C(9)-H(9B)	109.1
C(8)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.9

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for x0354.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	
U12						
O(1)	16(1)	23(1)	23(1)	-7(1)	4(1)	-
2(1)						
O(2)	37(1)	19(1)	24(1)	-12(1)	3(1)	-
7(1)						
O(3)	23(1)	20(1)	24(1)	-8(1)	-1(1)	
1(1)						
N(1)	17(1)	16(1)	16(1)	-2(1)	1(1)	-
2(1)						
C(1)	14(1)	16(1)	23(1)	-7(1)	-1(1)	-
6(1)						
C(2)	17(1)	18(1)	26(1)	-4(1)	-2(1)	-
3(1)						
C(3)	30(1)	18(1)	20(1)	-6(1)	-3(1)	-
5(1)						
C(4)	26(1)	19(1)	18(1)	-8(1)	5(1)	-
5(1)						
C(5)	20(1)	19(1)	19(1)	-11(1)	2(1)	-
5(1)						
C(6)	20(1)	19(1)	23(1)	-10(1)	5(1)	-
6(1)						
C(7)	21(1)	19(1)	23(1)	-12(1)	4(1)	-
5(1)						
C(8)	21(1)	20(1)	29(1)	-12(1)	5(1)	-
2(1)						
C(9)	17(1)	24(1)	34(1)	-13(1)	-1(1)	-
3(1)						

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for x0354.

	x	y	z	U(eq)
H(20)	5850(30)	3910(30)	7400(20)	49(6)
H(30)	4990(30)	3080(30)	3590(20)	62(7)

H(1N)	8950(20)	280(18)	6084(17)	13(4)
H(2A)	13546	-3119	8913	26
H(2B)	11982	-4167	8595	26
H(3A)	10752	-4163	10728	28
H(3B)	11126	-2299	10336	28
H(4A)	7616	-2931	8943	25
H(4B)	7243	-2248	10211	25
H(5A)	8431	228	8684	22
H(6A)	4509	178	8349	24
H(6B)	5159	10	6842	24
H(7A)	6302	2667	5975	24
H(8A)	1744	2813	6701	27
H(8B)	2597	4484	5697	27
H(9A)	2686	1765	4861	30
H(9B)	785	3488	4259	30

Table 6. Torsion angles [deg] for x0354.

C(5)-N(1)-C(1)-O(1)	
176.27(13)	
C(5)-N(1)-C(1)-C(2)	-2.2(2)
O(1)-C(1)-C(2)-C(3)	
178.55(13)	
N(1)-C(1)-C(2)-C(3)	-3.0(2)
C(1)-C(2)-C(3)-C(4)	
35.06(17)	
C(2)-C(3)-C(4)-C(5)	-
62.41(15)	
C(1)-N(1)-C(5)-C(4)	-
24.98(19)	
C(1)-N(1)-C(5)-C(6)	-
150.36(14)	
C(3)-C(4)-C(5)-N(1)	
56.01(15)	
C(3)-C(4)-C(5)-C(6)	
178.87(12)	
N(1)-C(5)-C(6)-C(7)	-
74.64(15)	
C(4)-C(5)-C(6)-C(7)	
163.04(12)	
C(5)-C(6)-C(7)-O(2)	-
63.53(15)	
C(5)-C(6)-C(7)-C(8)	
175.74(12)	
O(2)-C(7)-C(8)-C(9)	
169.38(13)	
C(6)-C(7)-C(8)-C(9)	-
72.44(17)	
C(7)-C(8)-C(9)-O(3)	-
65.42(17)	

Table 7. Hydrogen bonds for x0354 [Å and deg.].

D-H...A <(DHA)	d(D-H)	d(H...A)	d(D...A)
O(2)-H(2O)...O(3)#1 171.9(18)	0.83(2)	1.95(2)	2.7785(19)
O(3)-H(3O)...O(1)#2 178.9(19)	0.86(2)	1.83(2)	2.6906(17)
N(1)-H(1N)...O(1)#2 168.6(12)	0.895(15)	2.033(16)	2.915(2)

Symmetry transformations used to generate equivalent atoms:
#1 $-x+1, -y+1, -z+1$ #2 $-x+2, -y, -z+1$