Functionalized Oxepines via Fragmentation of Highly Strained Epoxides

Andrew J. Leyhane and Marc L. Snapper

*Department of Chemistry, Merkert Chemistry Center, Boston College, 2609 Beacon Street,
Chestnut Hill, MA 02467*

marc.snapper@BC.edu

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General Information

Starting materials and reagents were purchased from commercial suppliers and used without further purification except the following: dichloromethane, Et₂O, and benzene were used from a solvent purification system.¹ *m*-CPBA was washed with phosphate buffer (pH = 8.0) to remove acid and recrystallized from 25:1 CH₂Cl₂:Et₂O.² 3,5-Dinitrobenzoyl chloride was recrystallized from *t*-butyl methyl ether and hexanes. Hexanes and Et₂O used in chromatography were distilled before use.

All oxygen or moisture sensitive reactions were carried out under N₂ atm. in oven-dried (140 °C, ≥ 4 h) or flame-dried glassware. Air or moisture sensitive liquids were transferred by syringe and were introduced into the reaction flasks through rubber septa under positive N₂ pressure. Degassing refers to a flow of dry N₂ bubbling through reaction solvent for 15 min. Unless otherwise stated, reactions were stirred with a Teflon-covered stir bar. Concentration refers to the removal of solvent using a Büchi rotary evaporator, followed by use of a vacuum pump at approximately 1 torr. Silica gel chromatography refers to flash chromatography,³ and was performed using either Baxter brand silica gel 60 Å (230-400 Mesh ASTM) or EMD brand silica gel 60 Å (particle size 40-63 μm). Oxepine diastereomers were separated using a Horizon Biotage Flash System (MPLC) with 12-S, 12-M, or 40-M columns.

Proton nuclear magnetic resonance spectra (¹H-NMR) were measured on either a Varian Unity-300 instrument (300 MHz), a Varian Gemini-400 Instrument (400 MHz), or a Varian Gemini-500 instrument (500 MHz). Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent reference as the internal standard (CHCl₃: δ 7.26 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qi = quintet, sex = sextet, br = broad, m = multiplet), coupling constants (Hz), and integration. ¹³C-NMR spectra were recorded on either a Varian Unity-300 instrument (75 MHz), a Varian Gemini-400 Instrument (100 MHz), or a Varian Gemini-500 instrument (125 MHz) with complete proton decoupling. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent reference as the internal standard (CDCl₃: δ 77.23 ppm). Infrared spectra (IR) were measured on either a Mattson Galaxy Series FTIR 5000 spectrometer or a Nicolet Avatar 360 FT-IR spectrometer and are reported in wave numbers (cm⁻¹). Bands are characterized as broad (br), strong (s), medium (m), or weak (w). Elemental analyses (Anal.) were performed by Robertson Microlit Laboratories, Inc., Madison, NJ and are reported in percent atomic abundance. High resolution mass spectral analyses (HRMS) were performed by the Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign.

X-ray data was collected using a Bruker APEX CCD (charged coupled device) based diffractometer equipped with an LT-2 low temperature apparatus operating at 193 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data was measured using omega scans of 0.3° per frame for 45 seconds, such that a hemisphere was collected. A total of 1305 frames were collected with a maximum resolution of 0.90 Å. Cell parameters were retrieved

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

² (a) Schwartz, N. N.; Blumbergs, J. H. *J. Org. Chem.* **1964**, *29*, 1976. (b) Bortolini, O.; Campestrini, S.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1987**, *52*, 5093. (c) Traylor, T. G.; Mikstzal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770.

³ Stille, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

using SMART software⁴ and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software,⁵ which corrects for Lp and decay. Absorption corrections were applied using SADABS, supplied by George Sheldrick. The structures were solved by the direct method using the SHELXS-97 program⁶ and refined by least squares method on F^2 , SHELXL-97,⁷ incorporated in SHELXTL-PC V 6.10.⁸

All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawings are done at 30% ellipsoids.

NOE 1D experiments were measured on a Varian Gemini-500 instrument (500 MHz) with an indirect probe. Sample size was 5 mg and all samples were degassed to remove oxygen. The number of transients was 512 and the relaxation time was 800 ms. NOESY1D is the Varian implementation of the 1D NOE experiment using pulsed field gradients and selective pulses. The experiment involves a double-pulsed-field-gradient-spin-echo (DPFGSE) pulse sequence that achieves selective spin inversion effectively and cleanly. The NOE values obtained from the experiment were interpreted qualitatively and compared to the relative proton distances to assign the stereochemistry.⁹

Experimental Procedures

A round bottom flask (25 mL) was charged with cyclobutene **5** (348 mg, 1.90 mmol) in CH_2Cl_2 (5.1 mL) and *m*-CPBA (557 mg, 3.23 mmol). The flask was flushed with N_2 and the reaction was stirred at room temperature (rt). The consumption of starting material was monitored by TLC. Upon completion (3 h), the reaction was quenched with $Na_2S_2O_3$ (sat. aq.) (5 mL) and allowed to stir for 1 h. The mixture was diluted with CH_2Cl_2 (20 mL) and the organic layer was separated, washed with $NaHCO_3$ (sat. aq.), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting white solid was purified by silica gel chromatography (1:1 hexane:Et₂O). Epoxide **6** was obtained in 93% yield (346 mg, 1.76 mmol) and was recrystallized from *t*-butyl methyl ether to afford crystals suitable for X-ray analysis.

⁴ SMART V5.626 (NT) Software for the CCD Detector Systems; Bruker Analytical X-ray Systems, Madison, WI (2001).

⁵ SAINT V 5.01 (NT) Software for the CCD Detector Systems; Bruker Analytical X-ray Systems, Madison, WI (2001).

⁶ Sheldrick, G. M. SHELXS-90, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1990.

⁷ Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, 1997.

⁸ SHELXTL 6.0 (PC-Version), Program Library for Structure Solution and Molecular Graphics; Bruker Analytical X-ray Systems, Madison, WI (1998).

⁹ (a) Varian. (b) Stott, K.; Stonehouse, J.; Keeler, J.; Hwang, T. J.; Shaka, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4199.

Epoxide 6: mp = 78-79 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 4.06 (m, 2H), 3.97 (d, J = 9.6 Hz, 1H), 3.86 (d, J = 10.4 Hz, 1H), 3.73 (m, 1H), 3.73 (s, 3H), 3.45 (d, J = 10.4 Hz, 1H), 3.21, (dd, J = 8.0, 5.2 Hz, 1H), 3.06, (t, J = 5.2 Hz, 1H), 2.79, (dd, J = 8.0, 3.6 Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 172.8, 73.4, 69.7, 60.4, 54.4, 52.3, 51.8, 46.6, 42.1, 41.4. **IR** (KBr pellet) 3428 (br), 2987 (m), 2965 (m), 2920 (m), 2861 (m), 1725 (s), 1440 (m), 1341 (m), 1312 (m), 1264 (s), 1093 (s), 822 (m) cm^{-1} . **Anal.** Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$: C, 61.22; H, 6.16. Found: C, 61.40; H, 6.08.

A degassed solution of **6** (68.0 mg, 0.347 mmol) and BHT (115 mg, 0.521 mmol) in benzene (34.7 mL) in a heavy-wall sealed tube (150 mL) was placed in a silicone oil bath and heated to 200 °C. The reaction was monitored by TLC and stopped upon consumption of starting material (2 h). Concentration *in vacuo*, followed by filtration through basic alumina (1 cm plug) with hexanes (to separate BHT) followed by Et_2O afforded two diastereomers as a colorless oil. Medium pressure liquid chromatography (10-30% hexane: Et_2O) with a base-washed column (1% pyridine in EtOAc) was used to separate the diastereomers. Oxepine **7** was obtained as a colorless oil in 46% yield (31 mg, 0.16 mmol) and oxepine **8** was obtained as a colorless oil in 35% yield (24 mg, 0.12 mmol).

Oxepine 7: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.43 (s, 1H), 6.33 (d, J = 8.0 Hz, 1H), 4.77 (t, J = 8.0 Hz, 1H), 4.48 (d, J = 11.6 Hz, 1H), 4.34 (d, J = 11.6 Hz, 1H), 4.04 (t, J = 8.4 Hz, 1H), 3.74 (dd, J = 8.8, 6.8 Hz, 1H), 3.70 (s, 3H), 3.47 (dd, J = 8.0, 3.6 Hz, 1H), 3.34 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 171.9, 144.5, 134.1, 121.3, 102.2, 72.6, 70.7, 52.5, 45.9, 44.6. **IR** (NaCl thin film): 3055 (w), 2924 (w), 2853 (w), 2361(w), 2341(w), 1740 (m), 1651 (w), 1266 (s), 1196 (w), 1152 (m), 738 (s), 704 (w) cm^{-1} . **EI HRMS:** Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$ (^+M): 196.0736; Found: 196.0732.

Oxepine 8: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.38 (s, 1H), 6.23 (d, J = 8.0 Hz, 1H), 4.82 (d, J = 8.0, 1H), 4.33 (m, 2H), 4.15 (m, 1H), 3.74 (s, 3H), 3.61 (m, 1H), 3.34 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 172.6, 142.5, 134.9, 120.5, 104.5, 73.8, 70.3, 52.5, 46.6, 45.0. **IR** (NaCl thin film): 2954 (m), 2849 (m), 1737 (s), 1695 (m), 1656 (m), 1435 (w), 1361 (w), 1302 (w), 1156 (m) cm^{-1} . **Anal.** Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$: C, 61.22; H, 6.16. Found: C, 61.35; H, 6.40.

A round bottom flask (5 mL) was charged with cyclobutene **I** (50 mg, 0.25 mmol) in CH_2Cl_2 (0.68 mL) and *m*-CPBA (65 mg, 0.38 mmol). The flask was flushed with N_2 and allowed to stir at rt. The consumption of starting material was monitored by TLC. Upon completion (1 h), the reaction was quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (sat. aq.) (1.5 mL), diluted with CH_2Cl_2 (1.5 mL) and allowed to

stir for 1 h. The mixture was diluted with CH_2Cl_2 (20 mL) and the organic layer was separated, washed with NaHCO_3 (sat. aq.), dried over MgSO_4 , filtered and concentrated *in vacuo*. The resulting oil was purified by silica gel chromatography (1:1 hexane:Et₂O). Epoxide **9** was obtained in 98% yield as a light yellow oil (53 mg, 0.25 mmol).

Epoxide 9: ¹H-NMR (400 MHz, CDCl_3): δ 7.35 (t, J = 8.0 Hz, 2H), 7.23 (m, 3H), 4.03 (m, 2H), 3.95 (d, J = 10.4 Hz, 1H), 3.82 (dd, J = 10.0, 6.8 Hz, 1H), 3.75 (s, 1H), 3.69 (t, J = 7.6 Hz, 1H), 3.53 (d, J = 10.4 Hz, 1H), 3.09 (t, J = 6.0 Hz, 1H), 2.99 (dd, J = 8.4, 4.0 Hz, 1H). ¹³C-NMR (100 MHz, CDCl_3): δ 140.6, 128.2, 126.3, 126.0, 73.4, 69.4, 59.2, 54.2, 51.4, 48.9, 43.7, 42.3. IR (NaCl thin film): 3056 (w), 2961 (w), 2851 (w), 2360 (w), 1266 (w), 736 (m), 701 (m) cm^{-1} . **Anal.** Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48; H, 6.59. Found C, 78.27; H, 6.87.

A degassed solution of epoxide **9** (178 mg, 0.831 mmol) and BHT (275 mg, 1.25 mmol) in benzene (83.1 mL) in a heavy-wall sealed tube (350 mL) was placed in a silicone oil bath and heated to 200 °C. The reaction was monitored by TLC and stopped upon consumption of starting material (2.5 h). Concentration *in vacuo*, followed by filtration through basic alumina (1 cm plug) with hexanes (to separate BHT) followed by Et₂O afforded two diastereomers as a colorless oil. Medium pressure liquid chromatography (5-10% Et₂O:hexane) with a base-washed column (1% pyridine in EtOAc) was used to separate the diastereomers. Oxepine **10** was obtained as a colorless oil (becomes solid at colder temperatures) in 53% yield (94.8 mg, 0.393 mmol) and oxepine **11** was obtained as a colorless oil (becomes solid at colder temperatures) in 15% yield (27.5 mg, 0.128 mmol).

Oxepine 10: mp = 46-48 °C. ¹H-NMR (400 MHz, CDCl_3): δ 7.26 (m, 5H), 6.49 (s, 1H), 6.34 (d, J = 8.0 Hz, 1H), 4.92 (t, J = 8.0 Hz, 1H), 4.19 (d, J = 11.6 Hz, 1H), 3.97 (t, J = 8.0 Hz, 1H), 3.90 (dt, J = 11.6, 2.0 Hz, 1H), 3.72 (dd, J = 8.0, 4.0 Hz, 1H), 3.64 (m, 1H), 3.41 (t, J = 8.0 Hz, 1H). ¹³C-NMR (100 MHz, CDCl_3): δ 142.4, 141.4, 134.3, 129.8, 128.2, 127.0, 121.6, 108.9, 71.9, 70.2, 46.9, 46.0. IR (KBr pellet): 3020 (m), 2960 (m), 2856 (m), 2813 (m), 2361 (w), 1696 (m), 1636 (s), 1304 (s), 1152 (s) cm^{-1} . **Anal.** Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48; H, 6.59. Found C, 78.32; H, 6.47.

Oxepine 11: mp = 60-62 °C. ¹H-NMR (400 MHz, CDCl_3): δ 7.33 (m, 2H), 7.24 (m, 1H), 7.18 (m, 2H), 6.45 (s, 1H), 6.23 (dd, J = 8.0, 2.8 Hz, 1H), 4.71 (dd, J = 8.0, 2.8 Hz, 1H), 4.39 (m, 2H), 3.64 (dd, J = 9.2, 7.6 Hz, 1H), 3.49 (m, 2H), 3.28 (m, 1H). ¹³C-NMR (100 MHz, CDCl_3): δ 144.0, 141.0, 135.0, 128.9, 127.6, 127.0, 122.0, 111.4, 73.8, 70.7, 49.8, 47.2. IR (KBr pellet): 3036 (w), 2998 (m), 2905 (m), 2845 (s), 1702 (s), 1653 (s), 1299 (s), 1162 (s). **EI HRMS:** Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$ (+M): 214.0994; Found: 214.0989.

A round bottom flask (5 mL) was charged with cyclobutene **II** (52.3 mg, 0.215 mmol) in CH_2Cl_2 (0.57 mL) and *m*-CPBA (72.5 mg, 0.430 mmol). The flask was flushed with N_2 and allowed to stir at rt. The consumption of starting material was monitored by TLC. Upon completion (4 h), the reaction was quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (sat. aq.) (1.5 mL), diluted with CH_2Cl_2 (1.5 mL) and allowed to stir for 1 h. The mixture was diluted with CH_2Cl_2 (20 mL) and the organic layer was separated, washed with NaHCO_3 (sat. aq.), dried over MgSO_4 , filtered and concentrated *in vacuo*. The resulting oil was purified by silica gel chromatography (1:1 hexane:Et₂O). Epoxide **12** was obtained in 97% yield as a light yellow solid (53 mg, 0.20 mmol).

Epoxide 12: mp = 146–148 °C. ¹H-NMR (400 MHz, CDCl_3): δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 4.06 (m, 2H), 3.97 (d, *J* = 10.4 Hz, 1H), 3.85 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.78 (t, *J* = 7.2 Hz, 1H), 3.68 (d, 1.6 Hz, 1H), 3.54 (d, 10.8 Hz, 1H), 3.13 (t, *J* = 6.4 Hz, 1H), 3.04 (dd, *J* = 8.0, 3.6 Hz, 1H). ¹³C-NMR (100 MHz, CDCl_3): δ 148.9, 146.8, 127.7, 124.1, 73.3, 69.9, 60.0, 54.7, 51.6, 49.3, 44.3, 42.7. IR (KBr pellet): 3440 (br), 3072 (w), 2969 (w), 2923 (w), 2863 (w), 1596 (m), 1513 (s), 1346 (s), 1316 (m) cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 65.05; H, 5.30; N, 5.12.

A degassed solution of **12** (23.7 mg, 0.0914 mmol) in benzene (9.1 mL, 10 mM) in a heavy-wall sealed tube (35 mL) was placed in a silicone oil bath and heated to 220 °C. The reaction was monitored by TLC and stopped upon consumption of starting material (4.5 h). Concentration *in vacuo*, followed by medium pressure liquid chromatography (10–20% Et₂O:hexane) with a base-washed column (1% pyridine in EtOAc) was used to separate the diastereomers. Oxepine **13** was obtained as a yellow solid in 52% yield (12.4 mg, 0.0478 mmol) and oxepine **14** was obtained as a yellow solid in 18% yield (4.3 mg, 0.018 mmol).

Oxepine 13: mp = 103–104 °C. ¹H-NMR (400 MHz, CDCl_3): δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 6.55 (s, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 4.90 (t, *J* = 8.0 Hz, 1H), 4.15 (d, *J* = 11.6 Hz, 1H), 3.95 (m, 2H), 3.87 (dd, *J* = 7.6, 4.0 Hz, 1H), 3.67 (m, 1H), 3.46 (dd, *J* = 9.2, 6.0 Hz, 1H). ¹³C-NMR (100 MHz, CDCl_3): δ 149.2, 143.2, 134.8, 130.4, 128.4, 123.3, 121.2, 107.4, 71.8, 70.9, 46.7, 46.5. IR (KBr pellet): 3440 (br), 3075 (m), 3053 (m), 3029 (s), 2942 (s), 2903 (s), 2849 (s), 1648 (w), 1449 (s), 1351 (m), 1153 (w), 1020 (m), 910 (m). EI HRMS: Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_4$ (⁺M): 259.0845; Found: 259.0840.

Oxepine 14: mp = 130-132 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.21 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.48 (d, J = 2.0 Hz, 1H), 6.28 (dd, J = 8.0, 2.8 Hz, 1H), 4.61 (dd, J = 8.0, 2.4 Hz, 1H), 4.40 (t, J = 1.6 Hz, 2H), 3.64 (m, 2H), 3.43 (dd, J = 8.8, 6.8 Hz, 1H), 3.28 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 151.0, 141.9, 135.3, 128.6, 124.3, 121.9, 109.3, 73.4, 70.6, 49.5, 46.9. **IR** (KBr pellet): 3466 (br), 3061 (w), 3027 (s), 2919 (s), 2853 (w), 1693 (w), 1649 (m), 1598 (w), 1519 (s), 1349 (s), 1300 (m), 1154 (m), 936 (m), 753 (m). **EI HRMS**: Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_4$ (^+M): 259.0845; Found: 259.0849.

A round bottom flask (5 mL) was charged with cyclobutene **III** (106 mg, 0.464 mmol) in CH_2Cl_2 (1.2 mL) and *m*-CPBA (148 mg, 0.858 mmol). The flask was flushed with N_2 and allowed to stir at rt. The consumption of starting material was monitored by TLC. Upon completion (2 h), the reaction was quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (sat. aq.) (1.5 mL), diluted with CH_2Cl_2 (1.5 mL) and allowed to stir for 1 h. The mixture was diluted with CH_2Cl_2 (20 mL) and the organic layer was separated, washed with NaHCO_3 (sat. aq.), dried over MgSO_4 , filtered and concentrated *in vacuo*. The resulting oil was purified by silica gel chromatography (1:1 hexane:Et₂O). Epoxide **15** was obtained in 97% yield as a white solid (109 mg, 0.446 mmol).

Epoxide 15: mp = 82-84 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.13 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 4.04 (dd, J = 3.6, 2.0 Hz, 1H), 4.02 (d, J = 12.0, 1H), 3.93 (d, J = 10.0 Hz, 1H), 3.80 (m, 1H), 3.80 (s, 3H), 3.75 (d, J = 2.0 Hz, 1H), 3.62 (t, J = 6.8 Hz, 1H), 3.52 (d, J = 10.0 Hz, 1H), 3.04 (t, J = 6.0 Hz, 1H), 2.95 (dd, J = 8.0, 3.6 Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 157.8, 132.9, 127.5, 113.8, 73.6, 69.6, 59.2, 55.3, 54.5, 51.6, 49.2, 44.1, 41.9. **IR** (KBr pellet): 3047 (w), 3025 (w), 2954 (m), 2856 (m), 1609 (m), 1511 (s), 1250 (s) cm^{-1} . **Anal.** Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$: C, 73.75; H, 6.60. Found: C, 73.59; H, 6.42.

A degassed solution of **15** (18 mg, 0.074 mmol) and in benzene (7.4 mL, 10.0 mM) in a heavy-wall sealed tube (35 mL) was placed in a silicone oil bath and heated to 230 °C. The reaction was monitored by TLC and stopped upon consumption of starting material (3 h). Concentration *in vacuo*, followed by medium pressure liquid chromatography (10-20% Et₂O:hexane) with a base-washed column (1% pyridine in EtOAc) was used to separate the

diastereomers. Oxepine **16** was obtained as a colorless oil in 48% yield (8.6 mg, 0.035 mmol) and oxepine **17** was obtained as a colorless oil in 23% yield (4.2 mg, 0.017 mmol).

Oxepine 16: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.15 (d, $J = 6.8$ Hz, 2H), 6.83 (d, $J = 6.8$ Hz, 2H), 6.48 (d, $J = 2.0$ Hz, 1H), 6.32 (d, $J = 6.4$ Hz), 4.91 (t, $J = 6.4$ Hz, 1H), 4.18 (d, $J = 9.6$ Hz, 1H), 3.96 (t, $J = 6.4$ Hz, 1H), 3.92 (dt, $J = 9.2, 1.6$ Hz, 1H), 3.79 (s, 3H), 3.64 (dd, $J = 6.4, 3.2$ Hz, 1H), 3.62 (m, 1H), 3.42 (dd, $J = 6.8, 5.6$ Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 158.6, 142.3, 134.3, 133.6, 130.8, 121.8, 113.6, 109.3, 71.9, 70.1, 55.4, 46.8, 45.1. **IR** (NaCl thin film): 3080 (w), 3020 (w), 2949 (m), 2927 (s), 2840 (m), 1702 (m), 1653 (m), 1609 (m), 1511 (s), 1250 (m), 1146 (m) cm^{-1} . **EI HRMS:** Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$ (^+M): 244.1099; Found: 244.1103.

Oxepine 17: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.09 (d, $J = 6.8$ Hz, 2H), 6.86 (d, $J = 6.8$ Hz, 2H), 6.44 (s, 1H), 6.20 (dd, $J = 6.0, 2.0$ Hz, 1H), 4.68 (dd, $J = 6.4, 2.0$ Hz, 1H), 4.38 (s, 2H), 3.80 (s, 3H), 3.65 (t, $J = 6.4$ Hz, 1H), 3.46 (m, 1H), 3.23 (m, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 158.6, 141.0, 136.5, 135.1, 128.6, 122.2, 114.3, 111.8, 73.9, 70.7, 55.5, 49.9, 46.3. **IR** (NaCl thin film): 3031 (w), 2954 (m), 2829 (m), 1696 (m), 1642 (s), 1511 (s), 1304 (s), 1255 (s), 1146 (s), 814 (s) cm^{-1} . **EI HRMS:** Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$ (^+M): 244.1099; Found: 244.1102.

A round bottom flask (10 mL) was charged with cyclobutene **IV** (270 mg, 0.875 mmol) in CH_2Cl_2 (2.2 mL) and *m*-CPBA (206 mg, 1.19 mmol). The flask was flushed with N_2 and allowed to stir at rt. The consumption of starting material was monitored by TLC. Upon completion (3 h), the reaction was quenched with $\text{Na}_2\text{S}_2\text{O}_3(\text{sat. aq.})$ (3.0 mL), diluted with CH_2Cl_2 (3.0 mL) and allowed to stir for 1 h. The mixture was diluted with CH_2Cl_2 (30 mL) and the organic layer was separated, washed with $\text{NaHCO}_3(\text{sat. aq.})$, dried over MgSO_4 , filtered and concentrated *in vacuo*. The resulting oil was purified by silica gel chromatography (2:1 hexane: Et_2O). Epoxide **18** was obtained in 80% yield as a colorless oil (227 mg, 0.700 mmol).

Epoxide 18: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 4.05 (d, $J = 2.4$ Hz, 1H), 3.94 (m, 2H), 3.71 (s, 3H), 2.88 (m, 2H), 2.51 (dd, $J = 8.0, 4.0$ Hz, 1H), 2.10 (m, 1H), 1.68 (m, 3H), 0.88 (s, 9H), 0.08 (d, $J = 14.8, 6\text{H}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 173.2, 71.2, 63.9, 53.7, 52.0, 44.0, 41.0, 39.3, 34.7, 29.4, 26.0, 18.4, -4.6. **IR** (NaCl thin film): 3028 (w), 2954 (s), 2896 (m), 2858 (m), 1737 (s), 1472 (w), 1436 (w), 1256 (s), 1175 (m), 1076 (m), 1052 (m), 1002 (w), 836 (m) cm^{-1} . **HRMS:** Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_4\text{Si}$ ($\text{M}+1$): 325.1835; Found: 325.1838.

Oxepines 19 & 20: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.39 (m, 2H), 6.30 (d, $J = 7.6$ Hz, 1H), 6.22 (dd, $J = 8.0, 2.4$ Hz, 1H), 4.75 (t, $J = 8.0$ Hz, 1H), 4.69 (dd, $J = 7.6, 2.4$ Hz, 1H), 4.53 (m, 2H), 3.72 (s, 3H), 3.66 (s, 3H), 3.45 (dd, $J = 8.4, 4.4$ Hz, 1H), 3.20 (m, 1H), 3.12 (dt, $J = 9.2, 2.8$ Hz, 1H), 3.07 (m, 1H), 1.68 (m, 8H), 0.89 (d, $J = 1.6$ Hz, 18H), 0.07 (dd, $J = 4.0, 2.0$ Hz, 12H).

Epoxide 21: ¹H-NMR (400 MHz, CDCl₃): δ 7.34 (m, 5H), 4.53 (q, *J* = 12.4 Hz, 2H), 3.92 (m, 2H), 3.87 (d, *J* = 2.0 Hz, 1H), 3.57 (m, 2H), 2.34 (m, 3H), 2.02 (m, 1H), 1.71 (m, 2H), 1.52 (m, 1H), 0.88 (s, 9H), 0.07 (d, *J* = 14.4 Hz, 6H). ¹³C-NMR (100 MHz, CDCl₃): δ 138.4, 128.5, 127.7, 73.2, 71.6, 71.4, 63.7, 54.5, 52.0, 44.3, 38.3, 38.1, 34.9, 29.6, 26.1, 18.5, -4.5. **IR** (NaCl thin film): 3048 (w), 2954 (s), 2885 (w), 2859 (m), 1471 (w), 1362 (w), 1255 (m), 1059 (m) cm⁻¹. **EI HRMS:** Calcd for C₇₃H₃₄O₃Si(⁺M): 386.2277; Found: 386.2274.

Oxepine 22: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.31 (m, 5H), 6.35 (t, $J = 2.0$ Hz, 1H), 6.17 (dd, $J = 8.0, 2.4$ Hz, 1H), 4.73 (dd, $J = 8.0, 2.4$ Hz, 1H), 4.52 (m, 3H), 3.49 (dd, $J = 9.2, 3.6$ Hz, 1H), 3.31 (dd, $J = 9.2, 7.2$ Hz, 1H), 2.94 (m, 1H), 2.41 (m, 1H), 1.92 (m, 2H), 1.54 (m, 1H), 1.24 (m, 2H), 0.90 (s, 9H), 0.08 (d, $J = 3.2$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CD_3OD): δ 142.4, 140.0, 129.3, 128.8, 128.5, 110.3, 76.6, 74.2, 73.5, 44.7, 44.3, 36.5, 29.1, 26.5, 19.2, -4.0, -4.3. **IR** (NaCl thin film): 3087 (w), 3037 (w), 2955 (s), 2860 (s), 1684 (w), 1653 (m), 1471 (w), 1361 (m), 1254 (m), 1195 (m), 1115 (s), 866 (m), 837 (m), 426 (m) cm^{-1} . **EI HRMS:** Calcd for $\text{C}_{23}\text{H}_{34}\text{O}_3\text{Si} (^+\text{M})$: 386.2277; Found: 386.2277.

Oxepine 23: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.30 (m, 5H), 6.34 (d, $J = 2.4$ Hz, 1H), 6.15 (d, $J = 8.0$ Hz, 1H), 4.96 (t, $J = 8.0$ Hz, 1H), 4.94 (m, 3H), 3.74 (dd, $J = 8.8, 5.2$ Hz, 1H), 3.46 (t, $J = 8.0$ Hz, 1H), 3.10 (m, 1H), 2.77 (m, 1H), 1.90 (m, 1H), 1.70 (m, 2H), 1.55 (m, 1H), 0.89 (s, 9H), 0.07 (d, $J = 3.2$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 141.8, 138.7, 137.9, 128.4, 127.6, 127.5, 126.0, 110.1, 75.3, 74.5, 73.4, 43.7, 42.1, 36.4, 27.3, 26.2, 18.4, -4.1. **IR** (NaCl thin film): 3060 (m), 3028 (s), 2954 (s), 2921 (s), 2859 (s), 1682 (m), 1649 (m), 1462 (w), 1331 (w), 1255 (m), 1183 (m), 1129 (m), 1092 (m), 1037 (m), 835 (m) cm^{-1} . **EI HRMS:** Calcd for $\text{C}_{23}\text{H}_{34}\text{O}_3\text{Si} (^+\text{M})$: 386.2277; Found: 386.2280.

A round bottom flask (10 mL) was charged with epoxide **27** (110 mg, 0.523 mmol) in CH_2Cl_2 (1.0 mL). *t*-Butyldimethylsilylchloride (118 mg, 0.785 mmol) and imidazole (57.0 mg, 0.837 mmol) were added to the solution, which was then flushed with N_2 and allowed to stir at rt. The consumption of starting material was monitored by TLC. Upon completion (24 h), the reaction was quenched with $\text{NH}_4\text{Cl}_{(\text{sat. aq.})}$ (1.0 mL) and diluted with hexanes (4.0 mL). The organic layer was separated, washed with $\text{NaCl}_{(\text{sat. aq.})}$, dried over MgSO_4 , filtered and concentrated *in vacuo*. The resulting oil was purified by silica gel chromatography (4:1 hexane: Et_2O). Epoxide **24** was obtained in 66% yield (113 mg, 0.348 mmol) as a colorless oil.

Epoxide 24: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 4.07 (m, 1H), 3.99 (d, $J = 2.0$ Hz, 1H), 3.82 (dd, $J = 3.2, 2.0$ Hz, 1H), 3.71 (s, 3H), 3.01 (dd, $J = 8.0, 5.6$ Hz, 1H), 2.91 (dd, $J = 8.0, 3.2$ Hz, 1H), 2.73 (m, 1H), 1.89 (m, 1H), 1.69 (m, 3H), 0.88 (s, 9H), 0.08 (d, $J = 4.8$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 173.3, 73.6, 61.2, 54.8, 51.9, 51.7, 42.2, 41.9, 39.5, 35.2, 28.0, 26.2, 18.7, -4.7. **IR** (NaCl thin film): 2954 (s), 2886 (m), 2859 (m), 1737 (s), 1471 (w), 1437 (w), 1365 (w), 1255 (m), 1122 (m), 865 (m), 837 (m), 779 (w), 431 (m) cm^{-1} . **EI HRMS:** Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_4\text{Si} (\text{M}+1)$: 325.1835; Found: 325.1829.

A degassed solution of **24** (32.5 mg, 0.100 mmol) and BHT (44.0 mg, 0.200 mmol) in benzene (10.0 mL) in a heavy-wall sealed tube (35 mL) was placed in a silicone oil bath and heated to 220 °C. The reaction was monitored by TLC and stopped upon consumption of starting material (5 h). Concentration *in vacuo*, followed by filtration through basic alumina (1 cm plug) eluting with hexanes to remove the BHT afforded oxepines **25** and **26** as a slight yellow oil in 72% yield (23.4 mg, 0.0721 mmol, 1:3 ratio).

Oxepines 25 & 26: ¹H-NMR (400 MHz, CDCl₃): δ 6.40 (m, 2H), 6.28 (d, *J* = 8.0 Hz, 1H), 6.22 (dd, *J* = 7.6, 2.8 Hz, 1H), 4.77 (m, 1H), 4.74 (t, *J* = 8.0 Hz, 1H), 4.67 (dd, *J* = 8.0, 2.8 Hz, 1H), 4.51 (t, *J* = 4.4 Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 3.40 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.26 (dt, *J* = 9.2, 2.8 Hz, 1H), 3.21 (m, 1H), 3.02 (m, 1H), 1.68 (m, 8H), 0.90 (s, 9H), 0.88 (d, *J* = 2.0 Hz, 9H), 0.01 (d, *J* = 4.8 Hz, 6H), 0.07 (s, 6H).

A round bottom flask (50 mL) was charged with cyclobutene **VI** (610 mg, 3.14 mmol) in CH₂Cl₂ (7.8 mL) and *m*-CPBA (596 mg, 3.45 mmol). The flask was flushed with N₂ and allowed to stir at rt. The consumption of starting material was monitored by TLC. Upon completion (1.5 h), the reaction was quenched with Na₂S₂O₃(sat. aq.) (5.0 mL), diluted with CH₂Cl₂ (5.0 mL) and allowed to stir for 1 h. The mixture was diluted with CH₂Cl₂ (60 mL) and the organic layer was separated, washed with NaHCO₃(sat. aq.), dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting oil was purified by silica gel chromatography (1:2 hexane:Et₂O). Epoxide **27** was obtained in 89% yield as a white solid (577 mg, 2.74 mmol).

Epoxide 27: mp = 84-86 °C. ¹H-NMR (400 MHz, CDCl₃): δ 4.16 (dd, *J* = 9.6, 6.4 Hz, 1H), 4.09 (d, *J* = 2.0 Hz, 1H), 4.01 (t, *J* = 3.2 Hz, 1H), 3.73 (s, 3H), 3.02 (m, 2H), 2.80 (dd, *J* = 8.0, 4.4 Hz, 1H), 2.10 (m, 1H), 1.85 (m, 2H), 1.69 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 172.9, 73.3, 61.7, 55.4, 51.9, 51.8, 41.8, 41.7, 38.8, 33.6, 28.1. IR (KBr pellet): 3466 (br), 2987 (m), 2960 (m), 2867 (m), 2355 (w), 2333 (w), 1723 (s), 1435 (m), 1310 (m), 1217 (s), 1085 (s), 813 (s) cm⁻¹. HRMS (m/z): Calcd for (M+Na): 233.0790. Found: 233.0792.

A degassed solution of **27** (100 mg, 0.476 mmol) and BHT (157 mg, 0.714 mmol) in benzene (47.6 mL) in a heavy-wall sealed tube (350 mL) was placed in a silicone oil bath and heated to 230 °C. The reaction was monitored by TLC and stopped upon consumption of starting material (3 h). Concentration *in vacuo*, followed by filtration through basic alumina (1 cm plug) with hexanes (to separate BHT) followed by Et₂O afforded two diastereomers as a colorless oil. Medium pressure liquid chromatography (1% MeOH:CH₂Cl₂) with a base-washed column (1% pyridine in EtOAc) was used to separate the diastereomers. Oxepine **28** was obtained as a light yellow oil in 30% yield (30 mg, 0.14 mmol) and oxepine **29** was obtained as a light yellow oil in 30% yield (30 mg, 0.14 mmol).

Oxepine 28: ¹H-NMR (400 MHz, CDCl₃): δ 6.58 (s, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.0 Hz, 1H), 4.76 (m, 1H), 3.73 (s, 1H), 3.66 (s, 3H), 3.45 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.23 (m, 1H), 2.10 (m, 1H), 1.94 (m, 1H), 1.58 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 172.3, 144.0, 138.1, 126.8, 103.2, 75.9, 52.1, 48.2, 42.5, 35.5, 28.5. IR (NaCl thin film): 3417 (br), 2925 (s), 2853 (m), 1733 (s), 1683 (s), 1652 (s), 1436 (m), 1313 (m), 1197 (s), 1093 (m), 1037 (w), 993 (w), 961 (w), 855 (w), 736 (m), 701 (w) cm⁻¹. EI HRMS: Calcd for C₁₁H₁₄O₄ (⁺M): 210.0892; Found: 210.0890.

Oxepine 29: ¹H-NMR (400 MHz, CDCl₃): δ 6.58 (d, *J* = 2.4 Hz, 1H), 6.22 (dd, *J* = 8.0, 2.8 Hz, 1H), 4.71 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.57 (m, 1H), 3.73 (s, 3H), 3.28 (dt, *J* = 8.8, 2.4 Hz, 1H), 3.07 (m, 1H), 1.85 (m, 5H). ¹³C-NMR (100 MHz, CDCl₃): δ 173.2, 142.3, 140.3, 127.8, 105.1, 75.1, 52.3, 49.6, 45.2, 35.5, 29.5. IR (NaCl thin film): 3430 (br), 2954 (m), 1736 (s), 1681 (m), 1654 (m), 1436 (m), 1352 (m), 1268 (m), 1196 (m), 1171 (m), 1024 (m), 737 (s), 703 (m). EI HRMS: Calcd for C₁₁H₁₄O₄ (⁺M): 210.0892; Found: 210.0897.

A round bottom flask (5 mL) was charged with cyclobutene **VII** (83 mg, 0.43 mmol) in CH₂Cl₂ (1.2 mL) and *m*-CPBA (81 mg, 0.47 mmol). The flask was flushed with N₂ and allowed to stir at rt. The consumption of starting material was monitored by TLC. Upon completion (1.5 h) the reaction was quenched with Na₂S₂O₃(sat. aq.) (1.0 mL), diluted with CH₂Cl₂ (1.0 mL) and allowed to stir for 1 h. The mixture was diluted with CH₂Cl₂ (30 mL) and the organic layer was separated, washed with NaHCO₃(sat. aq.), dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting oil was purified by silica gel chromatography (1:1 hexane:Et₂O). Epoxide **30** was obtained in 91% yield as a white solid (82 mg, 0.39 mmol).

Epoxide 30: mp = 53-56 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 4.10 (d, J = 2.0 Hz, 1H), 4.04 (m, 2H), 3.73 (s, 3H), 2.93 (m, 2H), 2.57 (dd, J = 8.0, 4.0 Hz, 1H), 2.14 (m, 1H), 1.91 (dd, J = 13.2, 6.8 Hz, 1H), 1.81 (m, 2H), 1.68 (dd, J = 13.2, 7.2 Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 173.2, 71.0, 63.6, 53.4, 52.2, 52.0, 44.3, 41.2, 39.4, 34.1, 29.5. **IR** (KBr pellet): 3455 (br), 2971 (m), 2905 (m), 1718 (s), 1440 (m), 1212 (s), 819 (m) cm^{-1} . **HRMS** (m/z): Calcd for ($M + \text{Na}$): 233.0790. Found: 233.0783.

A degassed solution of **30** (24 mg, 0.11 mmol) and BHT (38 mg, 0.17 mmol) in benzene (11.4 mL) in a heavy-wall sealed tube (35 mL) was placed in a silicone oil bath and heated to 230 °C. The reaction was monitored by TLC and stopped upon consumption of starting material (3 h). Concentration *in vacuo*, followed by filtration through basic alumina (1 cm plug) with hexanes (to separate BHT) followed by Et_2O afforded two diastereomers as a colorless oil. Medium pressure liquid chromatography (10-30% hexane: Et_2O) with a base-washed column (1% pyridine in EtOAc) was used to separate the diastereomers. Oxepine **31** was obtained as a colorless oil in 38% yield (9.0 mg, 0.043 mmol) and oxepine **32** was obtained as a colorless oil in 31% yield (7.5 mg, 0.036 mmol).

Oxepine 31: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.66 (d, J = 2.8 Hz, 1H), 6.27 (d, J = 8.0 Hz, 1H), 4.79 (t, J = 8.0 Hz, 1H), 4.50 (m, 1H), 3.79 (d, J = 8.0 Hz, 1H), 3.72 (s, 3H), 3.52 (dd, J = 8.0, 2.8 Hz, 1H), 3.02 (m, 1H), 1.80 (m, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 173.5, 144.0, 139.4, 128.2, 102.2, 75.1, 52.5, 47.0, 43.3, 37.4, 28.8. **IR** (NaCl thin film): 3497 (br), 2955 (s), 2878 (w), 1725 (s), 1649 (m), 1436 (w), 1309 (w), 1201 (s) cm^{-1} . **EI HRMS**: Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4$ (^+M): 210.0892; Found: 210.0897.

Oxepine 32: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.55 (s, 1H), 6.23 (dd, J = 8.0 Hz, 2.4 Hz, 1H), 4.77 (dd, J = 8.0, 2.4 Hz, 1H), 4.59 (t, J = 5.6 Hz, 1H), 3.73 (s, 3H), 3.22 (m, 1H), 3.14 (dt, J = 9.2, 2.8 Hz, 1H), 2.10 (m, 1H), 1.94 (m, 1H), 1.55 (m, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 173.2, 142.3, 139.8, 127.0, 106.0, 75.6, 52.3, 48.9, 44.0, 34.6, 29.3. **IR** (NaCl thin film): 3423 (br), 2954 (m), 1736 (s), 1681 (m), 1655 (m), 1437 (m), 1350 (m), 1274 (m), 1193 (m), 1167 (m), 1134 (m), 1059 (m), 1028 (m), 739 (m) cm^{-1} . **EI HRMS**: Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4$ (^+M): 210.0892; Found: 210.0888.

A round bottom flask (5 mL) was charged with oxepine **8** (30.8 mg, 0.157 mmol) in Et₂O (2.0 mL). The solution was then flushed with N₂ and cooled to 0 °C in an ice bath. An LAH solution (0.47 mL, 0.47 mmol, 1 M in Et₂O) was added dropwise by syringe to the reaction. The consumption of starting material was monitored by TLC. Upon completion (1 h), the reaction was treated with of H₂O (50 μ L), 15% aqueous NaOH (50 μ L), and then H₂O (150 μ L). After this treatment, a white precipitate formed and settled to the bottom of the flask. The reaction mixture was filtered and the salts were washed with Et₂O (3 x 5mL). The filtrate was concentrated *in vacuo* to afford a colorless oil. The resulting oil was purified by medium pressure liquid chromatography (1.5:1 hexane:EtOAc) using a base-washed column (1% pyridine in EtOAc). Oxepine **VIII** was obtained in 80% yield (21 mg, 0.12 mmol) as a colorless oil.

Oxepine VIII: ¹H-NMR (400 MHz, CDCl₃): δ 6.36 (d, J = 2.4 Hz, 1H), 6.25 (dd, J = 7.6, 2.4 Hz, 1H), 4.64 (dd, J = 8.0, 2.8 Hz, 1H), 4.38 (d, J = 11.6 Hz, 1H), 4.28 (dt, J = 12.0, 2.0 Hz, 1H), 4.20 (t, J = 8.0 Hz, 1H), 3.59 (m, 4H), 3.09 (q, J = 8.0 Hz, 1H), 2.54 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 142.7, 134.5, 121.2, 107.5, 73.5, 70.1, 65.9, 44.8, 43.1. IR (NaCl thin film): 3421 (br), 2921 (s), 2856 (s), 1694 (s), 1654 (s), 1359 (m), 1308 (m), 1206 (m), 1160 (s), 1108 (m), 1071 (m), 1039 (s), 967 (m), 927 (m), 867 (m), 747 (m), 709 (m) cm⁻¹. EI HRMS: Calcd for C₉H₁₂O₃ (+M): 168.0787; Found: 168.0786.

A round bottom flask (10 mL) was charged with oxepine **VIII** (10.0 mg, 0.0595 mmol) in CH₂Cl₂ (2.0 mL). 3,5-Dinitrobenzoyl chloride (20.6 mg, 0.0892 mmol) was added to the reaction vessel as a solid. The reaction mixture was then flushed with N₂ and cooled to 0 °C in an ice bath. 4-Dimethylaminopyridine (10.9 mg, 0.0892 mmol) dissolved CH₂Cl₂ (1.0 mL) was added to the reaction by syringe. The consumption of starting material was monitored by TLC. Upon completion (1.5 h), the reaction was quenched with NH₄Cl_(sat. aq.) (2.0 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (4 x 4.0 mL). The organic layers were combined, dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting solid was purified by medium pressure liquid chromatography (3:1 hexane:EtOAc) using a base-washed column (1% pyridine in EtOAc). Oxepine **IX** was obtained in 84% yield (18.1 mg, 0.0500 mmol) as a thick yellow gum and was crystallized by slow evaporation of *t*-butyl methyl ether to afford yellow crystals suitable for X-ray analysis.

Oxepine IX: mp = 121-122 °C. ¹H-NMR (400 MHz, CDCl₃): δ 9.25 (t, J = 2.8 Hz, 1H), 9.14 (d, J = 2.8 Hz, 2H), 6.40 (d, J = 2.8 Hz, 1H), 6.27 (dd, J = 10.8, 3.6 Hz, 1H), 4.69 (dd, J = 10.8, 3.6 Hz, 1H), 4.38 (m, 4H), 4.23 (t, J = 10.8 Hz, 1H), 3.66 (t, J = 11.6 Hz, 1H), 3.12 (m, 1H), 2.91 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 162.5, 148.8, 142.9, 134.9, 133.5, 129.5, 122.7, 120.5, 106.1, 73.2, 70.2, 69.1, 45.1, 40.1. IR (NaCl thin film): 3099 (m), 2919 (m), 2850 (m), 2360 (w), 2342 (w), 1732 (s), 1695 (m), 1655 (m), 1629 (m), 1597 (w), 1544 (s), 1462 (m), 1345 (s),

1278 (s), 1207 (w), 1162 (s), 1120 (m), 1075 (m), 1027 (m), 974 (w), 923 (m), 867 (w), 831 (w), 773 (w), 730 (s), 721 (s) cm^{-1} . **EI HRMS:** Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_8$ (^+M): 362.0750; Found: 362.0746.

X-ray Crystal Structure of Compound 6

Table 1. Crystal data and structure refinement for **Compound 6**.

Identification code	ajl01t	
Empirical formula	$\text{C}_{10}\text{H}_{12}\text{O}_4$	
Formula weight	196.20	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2(1)/c$	
Unit cell dimensions	$a = 6.0680(6)$ Å	$a = 90^\circ$.
	$b = 10.6903(10)$ Å	$b = 92.640(2)^\circ$.
	$c = 14.2193(14)$ Å	$c = 90^\circ$.
Volume	$921.41(15)$ Å ³	
Z	4	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	0.110 mm^{-1}	
F(000)	416	
Crystal size	0.60 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.38 to 28.28° .	
Index ranges	$-6 \leq h \leq 8$, $-14 \leq k \leq 13$, $-18 \leq l \leq 15$	
Reflections collected	6682	
Independent reflections	2283 [$R(\text{int}) = 0.0504$]	

Completeness to theta = 28.28°	99.8%
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2283 / 0 / 127
Goodness-of-fit on F ²	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0472, wR2 = 0.1265
R indices (all data)	R1 = 0.0578, wR2 = 0.1318
Largest diff. peak and hole	0.415 and -0.315 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **Compound 6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(2)	2330(2)	4744(1)	4074(1)	35(1)
O(1)	5821(2)	8076(1)	3035(1)	39(1)
O(4)	-1515(2)	6142(1)	1082(1)	35(1)
C(7)	3525(2)	5889(1)	4229(1)	29(1)
C(3)	3964(2)	6327(1)	2361(1)	24(1)
C(6)	2993(2)	6633(1)	3351(1)	23(1)
C(9)	689(2)	6175(1)	2977(1)	27(1)
C(2)	1693(2)	5810(1)	2033(1)	23(1)
O(3)	1657(2)	6729(1)	495(1)	52(1)
C(1)	654(2)	6294(1)	1124(1)	26(1)
C(5)	3499(2)	7994(1)	3196(1)	32(1)
C(4)	4327(2)	7728(1)	2258(1)	30(1)
C(8)	236(3)	5102(2)	3647(1)	38(1)
C(10)	-2670(3)	6565(2)	225(1)	39(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **Compound 6**.

O(2)-C(7)	1.4344(17)
O(2)-C(8)	1.4347(18)
O(1)-C(5)	1.4400(19)
O(1)-C(4)	1.4442(16)
O(4)-C(1)	1.3248(16)
O(4)-C(10)	1.4494(15)
C(7)-C(6)	1.5024(17)
C(3)-C(4)	1.5219(18)
C(3)-C(2)	1.5372(17)
C(3)-C(6)	1.5849(18)
C(6)-C(5)	1.5055(18)
C(6)-C(9)	1.5519(17)
C(9)-C(8)	1.525(2)
C(9)-C(2)	1.5490(18)
C(2)-C(1)	1.5041(17)
O(3)-C(1)	1.1987(17)
C(5)-C(4)	1.474(2)
C(7)-O(2)-C(8)	105.61(10)
C(5)-O(1)-C(4)	61.47(9)
C(1)-O(4)-C(10)	116.13(11)
O(2)-C(7)-C(6)	103.69(10)

C(4)-C(3)-C(2)	117.17(10)
C(4)-C(3)-C(6)	86.78(10)
C(2)-C(3)-C(6)	88.82(9)
C(7)-C(6)-C(5)	126.60(11)
C(7)-C(6)-C(9)	105.87(10)
C(5)-C(6)-C(9)	116.18(11)
C(7)-C(6)-C(3)	123.63(11)
C(5)-C(6)-C(3)	89.00(10)
C(9)-C(6)-C(3)	89.76(9)
C(8)-C(9)-C(2)	116.16(12)
C(8)-C(9)-C(6)	102.04(10)
C(2)-C(9)-C(6)	89.60(10)
C(1)-C(2)-C(3)	118.15(11)
C(1)-C(2)-C(9)	119.48(11)
C(3)-C(2)-C(9)	91.66(9)
O(3)-C(1)-O(4)	123.46(12)
O(3)-C(1)-C(2)	124.61(12)
O(4)-C(1)-C(2)	111.88(11)
O(1)-C(5)-C(4)	59.41(9)
O(1)-C(5)-C(6)	106.82(11)
C(4)-C(5)-C(6)	91.52(11)
O(1)-C(4)-C(5)	59.13(9)
O(1)-C(4)-C(3)	105.54(10)
C(5)-C(4)-C(3)	92.63(10)
O(2)-C(8)-C(9)	106.46(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **Compound 6**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	45(1)	29(1)	30(1)	8(1)	-1(1)	-6(1)
O(1)	38(1)	35(1)	42(1)	3(1)	-6(1)	-12(1)
O(4)	27(1)	53(1)	25(1)	7(1)	-2(1)	-2(1)
C(7)	33(1)	29(1)	25(1)	4(1)	-2(1)	-1(1)
C(3)	23(1)	25(1)	24(1)	2(1)	2(1)	2(1)
C(6)	25(1)	23(1)	22(1)	1(1)	0(1)	2(1)
C(9)	24(1)	34(1)	22(1)	3(1)	3(1)	2(1)
C(2)	25(1)	23(1)	23(1)	2(1)	1(1)	0(1)
O(3)	35(1)	84(1)	35(1)	27(1)	1(1)	-6(1)
C(1)	28(1)	26(1)	23(1)	1(1)	2(1)	0(1)
C(5)	38(1)	25(1)	32(1)	1(1)	-1(1)	1(1)
C(4)	31(1)	29(1)	30(1)	6(1)	-1(1)	-4(1)
C(8)	36(1)	51(1)	28(1)	9(1)	2(1)	-14(1)
C(10)	36(1)	52(1)	29(1)	3(1)	-8(1)	5(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **Compound 6**.

	x	y	z	U(eq)
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H(7A)	5130	5730	4309	35
H(7B)	3024	6330	4793	35
H(3A)	5272	5760	2344	29
H(9A)	-479	6835	2929	32
H(2A)	1788	4877	1997	28
H(5A)	2527	8712	3355	38
H(4A)	4010	8231	1675	36
H(8A)	-776	5376	4133	46
H(8B)	-447	4389	3297	46
H(10A)	-4254	6413	268	59
H(10B)	-2124	6106	-314	59
H(10C)	-2411	7462	141	59

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

C(8)-O(2)-C(7)-C(6)	-40.78(14)
O(2)-C(7)-C(6)-C(5)	169.19(13)
O(2)-C(7)-C(6)-C(9)	27.69(14)
O(2)-C(7)-C(6)-C(3)	-72.91(15)
C(4)-C(3)-C(6)-C(7)	-136.79(12)
C(2)-C(3)-C(6)-C(7)	105.92(12)
C(4)-C(3)-C(6)-C(5)	-1.99(10)
C(2)-C(3)-C(6)-C(5)	-119.28(10)
C(4)-C(3)-C(6)-C(9)	114.20(9)
C(2)-C(3)-C(6)-C(9)	-3.09(9)
C(7)-C(6)-C(9)-C(8)	-5.30(14)
C(5)-C(6)-C(9)-C(8)	-151.46(13)
C(3)-C(6)-C(9)-C(8)	119.77(11)
C(7)-C(6)-C(9)-C(2)	-122.01(11)
C(5)-C(6)-C(9)-C(2)	91.83(13)
C(3)-C(6)-C(9)-C(2)	3.07(9)
C(4)-C(3)-C(2)-C(1)	42.35(16)
C(6)-C(3)-C(2)-C(1)	128.12(11)
C(4)-C(3)-C(2)-C(9)	-82.67(12)
C(6)-C(3)-C(2)-C(9)	3.10(9)
C(8)-C(9)-C(2)-C(1)	129.65(12)
C(6)-C(9)-C(2)-C(1)	-127.11(11)
C(8)-C(9)-C(2)-C(3)	-106.40(11)
C(6)-C(9)-C(2)-C(3)	-3.16(9)
C(10)-O(4)-C(1)-O(3)	-1.4(2)
C(10)-O(4)-C(1)-C(2)	-179.20(11)
C(3)-C(2)-C(1)-O(3)	24.6(2)
C(9)-C(2)-C(1)-O(3)	134.49(15)
C(3)-C(2)-C(1)-O(4)	-157.62(11)
C(9)-C(2)-C(1)-O(4)	-47.74(16)
C(4)-O(1)-C(5)-C(6)	81.57(11)
C(7)-C(6)-C(5)-O(1)	76.25(17)
C(9)-C(6)-C(5)-O(1)	-145.60(11)
C(3)-C(6)-C(5)-O(1)	-56.36(11)
C(7)-C(6)-C(5)-C(4)	134.66(13)
C(9)-C(6)-C(5)-C(4)	-87.19(13)
C(3)-C(6)-C(5)-C(4)	2.05(10)

C(5)-O(1)-C(4)-C(3)	-83.64(11)
C(6)-C(5)-C(4)-O(1)	-108.70(10)
O(1)-C(5)-C(4)-C(3)	106.56(10)
C(6)-C(5)-C(4)-C(3)	-2.14(10)
C(2)-C(3)-C(4)-O(1)	147.68(11)
C(6)-C(3)-C(4)-O(1)	60.67(11)
C(2)-C(3)-C(4)-C(5)	89.04(13)
C(6)-C(3)-C(4)-C(5)	2.03(10)
C(7)-O(2)-C(8)-C(9)	38.09(15)
C(2)-C(9)-C(8)-O(2)	76.46(14)
C(6)-C(9)-C(8)-O(2)	-19.09(15)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystal Structure of Compound IX

Table 1. Crystal data and structure refinement for **Compound IX**.

Identification code	ajl02t
Empirical formula	C ₁₄ H ₁₃ N ₂ O ₈
Formula weight	337.26
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n

Unit cell dimensions	a = 10.7652(15) Å	$\alpha = 90^\circ$.
	b = 5.7780(9) Å	$\beta = 96.903(4)^\circ$.
	c = 25.226(4) Å	$\gamma = 90^\circ$.
Volume	1557.7(4) Å ³	
Z	4	
Density (calculated)	1.438 Mg/m ³	
Absorption coefficient	0.120 mm ⁻¹	
F(000)	700	
Crystal size	0.3 x 0.2 x 0.2 mm ³	
Theta range for data collection	1.63 to 22.50°.	
Index ranges	-11<=h<=11, -6<=k<=6, -20<=l<=27	
Reflections collected	6771	
Independent reflections	2030 [R(int) = 0.0409]	
Completeness to theta = 22.50°	100.0%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2030 / 0 / 235	
Goodness-of-fit on F ²	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0956, wR2 = 0.2628	
R indices (all data)	R1 = 0.1077, wR2 = 0.2731	
Largest diff. peak and hole	1.307 and -0.355 e.Å ⁻³	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for **Compound IX**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(4)	6026(4)	10477(7)	446(2)	61(1)
O(8)	2831(4)	4448(8)	19(2)	65(1)
C(15)	4166(5)	4411(10)	804(2)	44(1)
C(11)	5775(5)	7211(9)	990(2)	38(1)
C(12)	6165(5)	6119(9)	1476(2)	41(1)
C(16)	4758(5)	6375(9)	653(2)	39(1)
C(14)	4517(5)	3274(10)	1281(2)	46(1)
N(17)	5925(5)	2994(9)	2116(2)	58(1)
O(1)	10939(4)	11600(8)	2403(2)	69(1)
C(10)	6446(5)	9251(10)	802(2)	42(1)
O(5)	6841(4)	3737(8)	2389(2)	65(1)
N(18)	3134(4)	3428(9)	443(2)	53(1)
O(3)	7545(4)	9569(8)	1083(2)	73(2)
C(13)	5513(5)	4182(10)	1603(2)	46(1)
O(2)	11649(4)	6292(8)	1059(2)	71(1)
O(7)	2646(4)	1669(9)	577(2)	75(2)
C(4)	11419(5)	9247(11)	1702(2)	52(2)
C(1)	10075(6)	9997(13)	1600(3)	75(2)
O(6)	5312(5)	1364(9)	2230(2)	93(2)
C(6)	10648(7)	6950(13)	730(3)	67(2)
C(2)	9985(7)	12174(11)	2011(3)	69(2)
C(5)	12114(6)	7739(12)	1472(2)	64(2)
C(8)	9644(5)	10705(10)	1049(2)	51(2)
C(7)	9833(8)	8554(16)	673(3)	89(3)
C(3)	11934(8)	10710(17)	2156(3)	93(3)

C(9)	8342(6)	11382(14)	899(4)	95(3)
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Table 3. Bond lengths [Å] and angles [°] for **Compound IX**

O(4)-C(10)	1.191(6)
O(8)-N(18)	1.230(6)
C(15)-C(16)	1.377(7)
C(15)-C(14)	1.384(8)
C(15)-N(18)	1.465(7)
C(11)-C(16)	1.390(7)
C(11)-C(12)	1.397(7)
C(11)-C(10)	1.489(8)
C(12)-C(13)	1.380(7)
C(14)-C(13)	1.370(8)
N(17)-O(6)	1.204(7)
N(17)-O(5)	1.211(6)
N(17)-C(13)	1.484(8)
O(1)-C(2)	1.379(8)
O(1)-C(3)	1.401(8)
C(10)-O(3)	1.316(6)
N(18)-O(7)	1.210(6)
O(3)-C(9)	1.464(7)
O(2)-C(6)	1.333(8)
O(2)-C(5)	1.382(8)
C(4)-C(5)	1.328(9)
C(4)-C(3)	1.476(10)
C(4)-C(1)	1.502(9)
C(1)-C(8)	1.471(9)
C(1)-C(2)	1.640(10)
C(6)-C(7)	1.273(11)
C(8)-C(9)	1.460(9)
C(8)-C(7)	1.591(11)
C(16)-C(15)-C(14)	123.0(5)
C(16)-C(15)-N(18)	119.3(5)
C(14)-C(15)-N(18)	117.6(5)
C(16)-C(11)-C(12)	120.7(5)
C(16)-C(11)-C(10)	117.2(5)
C(12)-C(11)-C(10)	122.0(5)
C(13)-C(12)-C(11)	117.6(5)
C(15)-C(16)-C(11)	118.3(5)
C(13)-C(14)-C(15)	116.5(5)
O(6)-N(17)-O(5)	125.0(5)
O(6)-N(17)-C(13)	117.0(6)
O(5)-N(17)-C(13)	118.0(5)
C(2)-O(1)-C(3)	108.2(5)
O(4)-C(10)-O(3)	123.9(5)
O(4)-C(10)-C(11)	123.8(5)
O(3)-C(10)-C(11)	112.3(5)
O(7)-N(18)-O(8)	124.5(5)
O(7)-N(18)-C(15)	118.3(5)
O(8)-N(18)-C(15)	117.2(5)
C(10)-O(3)-C(9)	117.0(5)

C(14)-C(13)-C(12)	123.8(5)
C(14)-C(13)-N(17)	118.1(5)
C(12)-C(13)-N(17)	118.1(5)
C(6)-O(2)-C(5)	119.3(6)
C(5)-C(4)-C(3)	122.4(6)
C(5)-C(4)-C(1)	134.1(6)
C(3)-C(4)-C(1)	103.4(6)
C(8)-C(1)-C(4)	115.5(6)
C(8)-C(1)-C(2)	110.4(6)
C(4)-C(1)-C(2)	104.0(5)
C(7)-C(6)-O(2)	140.5(8)
O(1)-C(2)-C(1)	100.0(5)
C(4)-C(5)-O(2)	123.7(6)
C(9)-C(8)-C(1)	120.2(6)
C(9)-C(8)-C(7)	104.1(6)
C(1)-C(8)-C(7)	107.3(5)
C(6)-C(7)-C(8)	129.7(7)
O(1)-C(3)-C(4)	108.6(6)
O(3)-C(9)-C(8)	107.9(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **Compound IX**. 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(4)	57(3)	56(2)	64(3)	20(2)	-15(2)	-15(2)
O(8)	66(3)	75(3)	53(3)	-8(2)	0(2)	-20(2)
C(15)	40(3)	49(3)	44(3)	-6(3)	9(2)	-5(3)
C(11)	32(3)	38(3)	44(3)	3(2)	6(2)	4(2)
C(12)	37(3)	39(3)	47(3)	3(3)	8(2)	5(2)
C(16)	39(3)	44(3)	35(3)	-1(2)	8(2)	0(2)
C(14)	43(3)	43(3)	55(4)	1(3)	12(3)	-5(3)
N(17)	59(3)	56(3)	61(3)	15(3)	10(3)	7(3)
O(1)	55(3)	83(3)	67(3)	-24(3)	-6(2)	11(2)
C(10)	33(3)	48(3)	44(3)	5(3)	-1(2)	2(3)
O(5)	62(3)	69(3)	60(3)	13(2)	-9(2)	-1(2)
N(18)	51(3)	57(3)	53(3)	-10(3)	9(2)	-16(3)
O(3)	37(2)	92(3)	85(3)	50(3)	-19(2)	-21(2)
C(13)	49(3)	45(3)	47(3)	4(3)	13(3)	8(3)
O(2)	66(3)	84(3)	61(3)	-18(3)	4(2)	18(3)
O(7)	81(3)	72(3)	73(3)	-4(2)	7(2)	-42(3)
C(4)	38(3)	59(4)	60(4)	6(3)	8(3)	12(3)
C(1)	60(4)	71(5)	91(5)	19(4)	-1(4)	-7(4)
O(6)	95(4)	83(4)	95(4)	49(3)	-9(3)	-28(3)
C(6)	60(4)	62(4)	74(5)	5(4)	-8(4)	1(4)
C(2)	72(4)	41(3)	96(5)	-8(3)	15(4)	-9(3)
C(5)	64(4)	74(4)	50(4)	5(3)	-11(3)	-18(4)
C(8)	37(3)	50(3)	63(4)	18(3)	-7(3)	-10(3)
C(7)	91(6)	115(7)	58(4)	4(5)	-8(4)	-35(6)
C(3)	80(5)	122(7)	76(5)	-16(5)	2(4)	41(5)
C(9)	40(4)	99(6)	138(7)	73(6)	-13(4)	-20(4)

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

	x	y	z	U(eq)
H(12A)	6855	6689	1710	49
H(16A)	4479	7137	326	47
H(14A)	4089	1933	1380	55
H(1A)	9530	8711	1703	90
H(6A)	10494	5870	446	80
H(2A)	10142	13673	1841	83
H(2B)	9165	12226	2151	83
H(5A)	12980	7648	1598	77
H(8A)	10192	11995	951	61
H(7A)	9250	8452	360	107
H(3A)	12492	9781	2414	112
H(3B)	12428	11994	2027	112
H(9A)	8172	12878	1068	113
H(9B)	8170	11559	507	113

Table 6. Torsion angles [$^\circ$] for **Compound IX**.

C(16)-C(11)-C(12)-C(13)	0.6(7)
C(10)-C(11)-C(12)-C(13)	-177.3(5)
C(14)-C(15)-C(16)-C(11)	1.8(8)
N(18)-C(15)-C(16)-C(11)	-176.9(5)
C(12)-C(11)-C(16)-C(15)	-1.6(7)
C(10)-C(11)-C(16)-C(15)	176.4(4)
C(16)-C(15)-C(14)-C(13)	-0.9(8)
N(18)-C(15)-C(14)-C(13)	177.8(5)
C(16)-C(11)-C(10)-O(4)	16.2(8)
C(12)-C(11)-C(10)-O(4)	-165.8(5)
C(16)-C(11)-C(10)-O(3)	-165.1(5)
C(12)-C(11)-C(10)-O(3)	12.9(7)
C(16)-C(15)-N(18)-O(7)	178.2(5)
C(14)-C(15)-N(18)-O(7)	-0.5(8)
C(16)-C(15)-N(18)-O(8)	-1.1(7)
C(14)-C(15)-N(18)-O(8)	-179.8(5)
O(4)-C(10)-O(3)-C(9)	-7.4(9)
C(11)-C(10)-O(3)-C(9)	173.9(6)
C(15)-C(14)-C(13)-C(12)	-0.2(8)
C(15)-C(14)-C(13)-N(17)	-179.4(5)
C(11)-C(12)-C(13)-C(14)	0.3(8)
C(11)-C(12)-C(13)-N(17)	179.5(4)
O(6)-N(17)-C(13)-C(14)	-3.7(8)
O(5)-N(17)-C(13)-C(14)	176.7(5)
O(6)-N(17)-C(13)-C(12)	177.1(5)
O(5)-N(17)-C(13)-C(12)	-2.5(8)
C(5)-C(4)-C(1)-C(8)	-51.8(10)
C(3)-C(4)-C(1)-C(8)	126.3(7)

C(5)-C(4)-C(1)-C(2)	-172.9(7)
C(3)-C(4)-C(1)-C(2)	5.3(7)
C(5)-O(2)-C(6)-C(7)	-6.4(14)
C(3)-O(1)-C(2)-C(1)	39.4(7)
C(8)-C(1)-C(2)-O(1)	-151.2(5)
C(4)-C(1)-C(2)-O(1)	-26.8(6)
C(3)-C(4)-C(5)-O(2)	177.7(7)
C(1)-C(4)-C(5)-O(2)	-4.4(12)
C(6)-O(2)-C(5)-C(4)	27.8(9)
C(4)-C(1)-C(8)-C(9)	177.6(6)
C(2)-C(1)-C(8)-C(9)	-64.8(8)
C(4)-C(1)-C(8)-C(7)	59.2(7)
C(2)-C(1)-C(8)-C(7)	176.8(5)
O(2)-C(6)-C(7)-C(8)	-2.7(16)
C(9)-C(8)-C(7)-C(6)	-158.8(8)
C(1)-C(8)-C(7)-C(6)	-30.4(10)
C(2)-O(1)-C(3)-C(4)	-39.3(8)
C(5)-C(4)-C(3)-O(1)	-163.4(6)
C(1)-C(4)-C(3)-O(1)	18.2(8)
C(10)-O(3)-C(9)-C(8)	-150.0(6)
C(1)-C(8)-C(9)-O(3)	-50.5(10)
C(7)-C(8)-C(9)-O(3)	69.5(8)

Symmetry transformations used to generate equivalent atoms:

AJL-1-248-2-13C-ME00
Pulse Sequence: s2pu1

AJL-1-248-1
AOL-1-248-13C
Pulse Sequence: s2pul1

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AXL-1-22P-HMBC
Pulse Sequence: zgpg30
Solvent: CDCl3
Ambient temperature
Acquisition: 1000 MHz
Relax. delay: 1.000 sec
Acq. time: 1.195 sec
F2: 100.626100 MHz
1300 Hz
Observed: 100.626100 MHz
Power: 50 dB
WALTZ-16 modulated
Line broadening: 1.0 Hz
F2 size: 65536
Total time: 24 min, 20 sec

ADJ-5-143-13C

Pulse Sequence: zgpg30

AQ: 0.13160000

SI: 0.00000000

F2: 125.760