Supporting Information

Molybdenum-mediated Cleavage Reactions of Isoxazoline Rings Fused in Bicyclic Frameworks Geoffrey K. Tranmer and William Tam*

Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry,

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

General Information: Standard column chromatography was performed on 230-400 mesh silica gel (obtained from Silicycle) using flash column chromatography techniques.²⁶ Analytical thin-layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} plates. All glassware was flame dried under an inert atmosphere of dry nitrogen. Infrared spectra were taken on a Bomem MB-100 FTIR spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Bruker-400 spectrometer. Chemical shifts for ¹H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ¹³C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0 ppm). High resolution mass spectra were done by McMaster Regional Centre for Mass Spectrometry at McMaster University, Hamilton, Ontario. Elemental analyses were performed by Canadian Microanalytical Service Ltd., British Columbia or by Quantitative Technologies Inc., New Jersey.

Reagents and Materials: Unless stated otherwise, commercial reagents were used without purification. Nitromethylbenzene $11a^{27}$ and cycloadducts $8a-8e^{2b}$ were prepared in accordance to our previously reported procedures.

²⁶ Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. **1978**, 43, 2923.

²⁷ (a) Kornblum, N.; Larson, H. O.; Blackwood, R. K.; Mooberry, D. D.; Oliveto, E. P.; Graham, G. E. *J. Am. Chem. Soc.* **1956**, 78, 1497. (b) Baruah, A.; Kalita, B.; Barua, N. C. *Synlett* **2000**, 1064.

Part I: Intermolecular 1,3-Dipolar Nitrile Oxide Cycloadditions of Bicyclic Alkenes 13 and 15a-c



1,3-Dipolar Nitrile Oxide Cycloaddition of Norbornadiene 13 with Nitrile Oxide 12a. A solution of **11a** (564.1 mg, 4.121 mmol) in toluene (15 mL) was added to a flame-dried flask containing norbornadiene **13** (4.3 mL, 39.85 mmol), (BOC)₂O (1.4178 g, 6.496 mmol), DMAP (49.0 mg, 0.4011 mmol) and toluene (20 mL) via a cannula over 30 minutes. The reaction mixture was stirred at room temperature for 18 h. The solvent was removed by rotary evaporation, and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 5:95, 1:9) to give a separable mixture of *exo-14a* (424.0 mg, 2.007 mmol, 49%) and *endo-14a* (96.1 mg, 0.455 mmol, 11%) as clear and colourless oils which solidified upon standing to viscous semi-solids.

Cycloadduct *exo*-14a. R_f 0.23 (EtOAc:Hexanes, 1:9); IR (neat, NaCl) 3063 (m), 2982 (s), 2954 (s), 2879 (m), 1591 (m), 1561 (m), 1497 (m), 1445 (s), 1356 (s), 1325 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.73 (m, 2H), 7.40 (m, 3H), 6.35 (dd, 1H, J = 5.7, 3.0 Hz), 6.10 (dd, 1H, J = 5.7, 3.2 Hz), 4.98 (d, 1H, J = 8.2 Hz), 3.79 (d, 1H, J = 8.2 Hz), 3.28 (s, 1H), 3.15 (s, 1H), 1.74 (d, 1H, J = 9.4 Hz), 1.62 (d, 1H, J = 9.4 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 155.7, 140.0, 135.5, 129.8, 129.3, 128.7, 126.7, 89.4, 57.6, 50.0, 45.1, 43.2. This is a known compound in the literature.²⁸

Cycloadduct *endo*-14a. R_f 0.15 (EtOAc:Hexanes, 1:9); IR (neat, NaCl) 2980 (s), 2954 (s), 2876 (m), 1655 (s), 1557 (m), 1449 (s), 1345 (m), 1253 (s), 1222 (m), 1078 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.70 (m, 2H), 7.39 (m, 3H), 6.18 (dd, 1H, J = 5.7, 2.9 Hz), 5.94 (dd, 1H, J = 5.7, 2.9 Hz), 5.40 (dd, 1H, J = 9.6, 4.1 Hz), 4.14 (dd, 1H, J = 9.6, 4.0 Hz), 3.37 (s, 2H), 1.63 (d, 1H, J = 8.9 Hz), 1.46 (d, 1H, J = 8.9 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 156.5, 135.0, 134.1, 129.7, 129.5, 128.7, 126.5, 87.5, 57.3, 48.9, 47.9, 46.9. This is a known compound in the literature.²⁸

²⁸ (a) Ambler, P. W.; Paton, R. M.; Tout, J. M. J. Chem. Soc., Chem. Commun. **1994**, 2661. (b) Sohar, P.; Bernath, G.; Frimpong-Manso, S.; Szabo, A. E.; Stajer, G. Magn. Reson. Chem. **1990**, 28, 1045.



1,3-Dipolar Nitrile Oxide Cycloaddition of Norbornadiene 13 with Nitrile Oxide 12b. A solution of **11b** (0.70 mL, 9.74 mmol) in toluene (10 mL) was added to a flame-dried flask containing norbornadiene **13** (10.5 mL, 97.32 mmol), (BOC)₂O (3.4316 g, 15.72 mmol), DMAP (0.1390 mg, 1.138 mmol) and toluene (20 mL) via a cannula over 10 minutes. The reaction mixture was stirred at room temperature for 45 h. The solvent was removed by rotary evaporation, and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 1:9, 15:85, 1:4) to give a separable mixture *exo*-**14b** (1.0387 g, 6.962 mmol, 71%) as a clear pale yellow oil and *endo*-**14b** (113.8 mg, 0.7628 mmol, 8%) as a clear pale yellow oil.

Cycloadduct *exo*-14b. R_f 0.22 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 3057 (m), 2980 (s), 2954 (s), 2923 (m), 2881 (w), 1625 (w), 1433 (m), 1388 (m), 1326 (s), 1264 (s), 919 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 6.24 (dd, 1H, J = 5.7, 3.0 Hz), 6.02 (dd, 1H, J = 5.7, 3.2 Hz), 4.75 (d, 1H, J = 8.0 Hz), 3.24 (d, 1H, J = 8.0 Hz), 3.17 (s, 1H), 2.98 (s, 1H), 1.90 (s, 3H), 1.62 (d, 1H, J = 9.3 Hz), 1.58 (d, 1H, J = 9.3 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 154.6, 139.7, 135.4, 87.7, 60.9, 49.7, 43.7, 42.9, 11.9. This is a known compound in the literature.²⁹

Cycloadduct *endo*-14b. R_f 0.15 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 3067 (m), 2979 (s), 2944 (s), 2872 (m), 1620 (m), 1455 (m), 1436 (s), 1386 (s), 1334 (m), 1252 (m), 1137 (w), 985 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 6.17 (dd, 1H, J = 5.7, 3.0 Hz), 6.07 (dd, 1H, J = 5.7, 2.9 Hz), 5.19 (dd, 1H, J = 9.4, 4.2 Hz), 3.66 (dd, 1H, J = 9.4, 4.2 Hz), 3.29 (s, 1H), 3.13 (s, 1H), 1.83 (s, 3H), 1.56 (dt, 1H, J = 8.9 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 155.2, 134.6, 134.3, 85.9, 60.5, 48.8, 47.9, 45.4, 12.2. This is a known compound in the literature.²⁹

²⁹ Krawczyk, H.; Gryff-Keller, A. J. Chem. Res. (S), **1996**, 452.



1,3-Dipolar Nitrile Oxide Cycloaddition of Norbornene 15a with Nitrile Oxide 12a. A solution of **11a** (0.5984 mg, 4.363 mmol) in toluene (15 mL) was added to a flame-dried flask containing norbornene **15a** (5.0 mL, 45.3 mmol), (BOC)₂O (1.6482 g, 7.552 mmol), DMAP (47.6 mg, 0.3896 mmol) and toluene (10 mL) via a cannula over 10 minutes. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 5:95, 1:9) to give **16a** (0.9150 g, 4.290 mmol, 98%) as a clear and colourless oil which solidified upon standing to a viscous semi-solid.

Cycloadduct 16a. R_f 0.63 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 2969 (s), 2944 (s), 2871 (s), 1563 (m), 1444 (s), 1357 (s), 1315 (m), 1264 (m), 1130 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.70 (m, 2H), 7.38 (m, 3H), 4.64 (d, 1H, J = 8.3 Hz), 3.48 (d, 1H, J = 8.3 Hz), 2.62 (s, 1H), 2.52 (s, 1H), 1.58 (m, 2H), 1.52 (d, 1H, J = 10 Hz), 1.35 (d, 1H, J = 10 Hz), 1.17 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 156.8, 129.6, 129.4, 128.6, 126.8, 87.8, 57.0, 42.9, 39.2, 32.3, 27.4, 22.7. This is a known compound in the literature.^{23,30}



1,3-Dipolar Nitrile Oxide Cycloaddition of Norbornene 15a with Nitrile Oxide 12b. A solution of **11b** (0.75 mL, 10.44 mmol) in toluene (10 mL) was added to a flame-dried flask containing norbornene **15a** (2.10 g, 22.30 mmol), (BOC)₂O (3.47 g, 15.90 mmol), DMAP (0.1311 g, 1.073 mmol) and toluene (10 mL) via a cannula over 10 minutes. The reaction mixture was stirred at room temperature for 18 h. The reaction was quenched with water (15 mL) and the aqueous layer extracted with dichloromethane (4×10 mL). The combined organic layers were washed with brine (10 mL) and dried over magnesium sulphate and filtered. The solvent was removed by rotary evaporation and the crude reaction mixture

³⁰ (a) Muri, D.; Bode, J. W.; Carreira, E. M. *Org. Lett.* **2000**, *2*, 539. (b) Chen, Y. J.; Li, C. N. *J. Chin. Chem. Soc.* **1993**, *40*, 203. (c) Fliege, W.; Huisgen, R. *Just. Lie. Ann. Chem.* **1973**, 2038.

was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **16b** (1.5112 g, 9.994 mmol, 96%) as a clear pale yellow oil.

Cycloadduct 16b. R_f 0.28 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 2959 (s), 2875 (s), 1754 (m), 1627 (m), 1455 (s), 1384 (s), 1331 (s), 1313 (m), 1256 (m), 1029 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 4.38 (d, 1H, J = 8.2 Hz), 2.91 (d, 1H, J = 8.2 Hz), 2.46 (s, 1H), 2.30 (s, 1H), 1.86 (s, 3H), 1.48 (m, 2H), 1.37 (d, 1H, J = 10.5 Hz), 1.17 (m, 1H), 1.11 (d, 1H, J = 10.5 Hz), 1.04 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ 155.3, 86.0, 60.4, 42.7, 37.8, 31.9, 27.0, 22.5, 11.8. This is a known compound in the literature.³¹



1,3-Dipolar Nitrile Oxide Cycloaddition of Norbornene 15b with Nitrile Oxide 12a. A solution of 11a (514.6 mg, 3.752 mmol) in toluene (15 mL) was added to a flame-dried flask containing 2hexvlbicvclo[2.2.1]hept-2-ene 15b³² (606.2 mg, 3.400 mmol), (BOC)₂O (1.2219 g, 5.599 mmol), DMAP (49.3 mg, 0.4035 mmol) and toluene (2 mL) via a cannula over 10 minutes. The reaction mixture was stirred at room temperature for 23 h. The reaction was quenched with water (15 mL) and the aqueous layer extracted with dichloromethane (4×10 mL). The combined organic layers were washed with brine (10 mL) and dried over magnesium sulfate and filtered. The solvent was removed by rotary evaporation, and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 5:95) to give **16c** (867.0 mg, 2.915 mmol, 86%) as a clear and colourless oil. **Cycloadduct 16c.** $R_f 0.16$ (EtOAc:hexanes = 1:49); IR (neat) 3060 (w), 2961 (s), 2930 (s), 2872 (s), 2858 (s), 1705 (w), 1592 (m), 1563 (m), 1464 (s), 1445 (s), 1327 (s), 1326 (m), 1310 (m), 1266 (m), 1235 (w), 1073 (w), 1025 (w) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.69 (m, 2H), 7.37 (m, 3H), 2.90 (d, 1H, J = 1.6 Hz), 2.55 (d, 1H, J = 4.0 Hz), 2.49 (d, 1H, J = 4.3 Hz), 1.24-1.74 (m, 15H), 1.19 (dd, 1H, J) = 10.4, 1.5 Hz), 0.87 (t, 3H, J = 6.9 Hz); ¹³C NMR (APT, CDCl₃, 100 MHz) δ 157.0, 129.8, 129.4, 128.6, 126.6, 96.7, 61.1, 45.6, 40.8, 35.0, 34.5, 31.7, 29.7, 27.4, 24.1, 23.1, 22.6, 14.1. Anal. Calcd. for C₂₀H₂₇NO: C, 80.76; H, 9.15. Found C, 80.88; H, 9.01.

³¹ Cunico, R. F.; Bedell, L. J. Org. Chem. 1983, 48, 2780.

³² Mayo, P.; Hecnar, T.; Tam, W. *Tetrahedron* **2001**, *57*, 5931.



1,3-Dipolar Nitrile Oxide Cycloaddition of Norbornene 15b with Nitrile Oxide 12b. A solution of **11b** (333.6 mg, 4.444 mmol) in toluene (8 mL) was added to a flame-dried flask containing 2-hexylbicyclo[2.2.1]hept-2-ene **15b** (292.7 mg, 1.641 mmol), (BOC)₂O (598.7 mg, 2.743 mmol), DMAP (25.0 mg, 0.2046 mmol) and toluene (8 mL) via a cannula over 15 minutes. The reaction mixture was stirred at room temperature for 42 h. The reaction was quenched with water (15 mL) and the aqueous layer extracted with dichloromethane (4×10 mL). The combined organic layers were washed with brine (10 mL) and dried over magnesium sulfate and filtered. The solvent was removed by rotary evaporation, and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **16d** (271.8 mg, 1.155 mmol, 70%) as a clear and colourless oil. **Cycloadduct 16d.** *R*_f 0.45 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 2958 (s), 2930 (s), 2872 (s), 2858 (s), 1794 (s), 1758 (s), 1460 (m), 1385 (m), 1331 (m), 1160 (m), 907 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.43 (d, 1H, *J* = 4.0 Hz), 2.35 (s, 1H), 2.30 (d, 1H, *J* = 4.4 Hz), 1.89 (s, 3H), 1.64 - 1.18 (m, 15H), 1.14 (dd, 1H, *J* = 10.3, 1.4 Hz), 0.87 (t, 3H, *J* = 6.8 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 155.6, 94.7, 64.7, 45.5, 39.5, 34.9, 34.3, 31.7, 29.7, 27.2, 24.8, 22.9, 22.6, 14.1, 12.2. HRMS calcd. for C₁₅H₂₅NO: m/z 235.1936, found m/z 235.1927.



1,3-Dipolar Nitrile Oxide Cycloaddition of Norbornene 15c with Nitrile Oxide 12a. A solution of **11a** (0.4794 g, 3.496 mmol) in toluene (15 mL) was added to a flame-dried flask containing 2- (trimethylsilyl)bicyclo[2.2.1]hept-2-ene **15c**³² (512.9 mg, 3.084 mmol), (BOC)₂O (1.1475 g, 5.258 mmol), DMAP (39.9 mg, 0.3266 mmol) and toluene (10 mL) via a cannula over 10 minutes. The reaction mixture was stirred at room temperature for 23 h. The reaction was quenched with water (15 mL) and the aqueous layer extracted with dichloromethane (4×10 mL). The combined organic layers

were washed with brine (10 mL) and dried over magnesium sulfate and filtered. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 5:95) to give **16e** (0.7765 g, 2.720 mmol, 88%) as a clear and colourless oil. **Cycloadduct 16e.** $R_f 0.15$ (Et₂O:hexanes = 1:49); IR (CH₂Cl₂) 2965 (s), 2878 (w), 1594 (w), 1445 (w), 1351 (m), 1260 (s), 1005 (w) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.72 (m, 2H), 7.38 (m, 3H), 3.29 (s, 1H), 2.68 (d, 1H, *J* = 4.4 Hz), 2.52 (d, 1H, *J* = 4.3 Hz), 1.62 (m, 2H), 1.48 (tt, 1H, *J* = 12.8, 4.7 Hz), 1.37 (m, 1H), 1.26 (m, 1H), 1.19 (ddd, 1H, *J* = 10.4, 2.7, 1.3 Hz), 0.13 (s, 9H); ¹³C NMR (APT, CDCl₃, 100 MHz) δ 156.6, 129.8, 129.4, 128.0, 126.8, 91.3, 59.3, 46.3, 40.8, 34.4, 26.9, 22.6, -2.8. Anal. Calcd. for C₁₇H₂₃SiNO: C, 71.53; H, 8.12. Found C, 71.94; H, 7.84.



1,3-Dipolar Nitrile Oxide Cycloaddition of Norbornene 15c with Nitrile Oxide 12b. A solution of **11b** (280.3 mg, 2.044 mmol) in toluene (8 mL) was added to a flame-dried flask containing 2-(trimethylsilyl)bicyclo[2.2.1]hept-2-ene **15c**³² (270.0 mg, 1.623 mmol), (BOC)₂O (589.8 mg, 2.702 mmol), DMAP (23.5 mg, 0.1924 mmol) and toluene (8 mL) via a cannula over 15 minutes. The reaction mixture was stirred at room temperature for 19 h. The reaction was quenched with water (15 mL) and the aqueous layer extracted with dichloromethane (4×10 mL). The combined organic layers were washed with brine (10 mL) and dried over magnesium sulfate and filtered. The solvent was removed by rotary evaporation, and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **16f** (326.5 mg, 1.462 mmol, 90%) as a clear and colourless oil.

Cycloadduct 16f. R_f 0.43 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 2958 (s), 2899 (s), 2879 (s), 1794 (w), 1755 (m), 1456 (s), 1328 (s), 1322 (s), 1248 (s), 1166 (m), 919 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.74 (s, 1H), 2.56 (d, 1H, J = 4.4 Hz), 2.33 (d, 1H, J = 4.4 Hz), 1.90 (s, 3H), 1.58 - 1.51 (m, 2H), 1.41 (m, 1H), 1.28 (m, 1H), 1.14 (m, 1H), 1.09 (m, 1H), 0.08 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 154.9, 88.8, 63.1, 46.1, 39.6, 34.1, 26.7, 22.5, 12.1, -2.8. HRMS calcd. for C₁₂H₂₁SiNO: m/z 223.1392, found m/z 223.1386.

Part II: Mo-mediated Cleavage Reactions

General procedure for the Mo-mediated tandem N–O bond cleavage–retroaldol reaction. To a flame dried flask containing the isoxazoline (1 eq) and acetonitrile (0.08 M–0.06 M) was added molybdenum hexacarbonyl (1 eq) and distilled water (0.08–0.2 mL, 5–12.5 mmol, 20–60 eq. (usually 40 eq.), 1–4 M). A water condenser was then attached and the flask was heated to 80 °C for 3-16 hrs. The solvent was then removed using rotary evaporation and the crude reaction mixture purified by column chromatography.



Mo-mediated cleavage reaction of cycloadduct *exo*-14a (Table 1, entry 1). To a flame dried flask containing the cycloadduct *exo*-14a (41.1 mg, 0.1945 mmol) and acetonitrile (2.0 mL) was added molybdenum hexacarbonyl (57.4 mg, 0.2174 mmol) and distilled water (0.2 mL, 12.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 12 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give 17a (27.5 mg, 0.1283 mmol, 66%) as a clear pale yellow oil. **Cyclopentene 17a.** *R*_f 0.21 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 3063 (s), 2982 (s), 2952 (s), 2879 (m), 1591 (m), 1562 (m), 1497 (m), 1445 (m), 1356 (m), 1326 (m), 1019 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.77 (s, 1H), 7.94 (d, 2H, *J* = 7.2 Hz), 7.56 (t, 1H, *J* = 7.3 Hz), 7.46 (t, 2H, *J* = 7.4 Hz), 6.83 (m, 1H), 3.17 (dd, 1H, *J* = 16.5, 5.6 Hz), 3.08 (m, 1H), 2.98 (m, 2H), 2.86 (m, 1H), 2.29 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 199.0, 189.6, 151.4, 146.7, 137.0, 133.1, 128.6, 128.0, 44.7, 40.0, 34.8, 33.2. HRMS calcd. for C₁₄H₁₄O₂: m/z 214.0994, found m/z 214.0980.



Mo-mediated cleavage reaction of cycloadduct *endo*-14a (Table 1, entry 2). To a flame dried flask containing the cycloadduct *endo*-14a (30.8 mg, 0.1458 mmol) and acetonitrile (2.0 mL) was added

molybdenum hexacarbonyl (38.6 mg, 0.1462 mmol) and distilled water (0.2 mL, 12.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 12 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **17a** (21.9 mg, 0.1022 mmol, 70%) as a clear pale yellow oil. Spectral data as reported above.



Mo-mediated cleavage reaction of cycloadduct *exo*-14b (Table 1, entry 3). To a flame dried flask containing the cycloadduct *exo*-14b (84.6 mg, 0.5670 mmol) and acetonitrile (2.0 mL) was added molybdenum hexacarbonyl (156.6 mg, 0.5932 mmol) and distilled water (0.12 mL, 7.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 3 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give 17b (52.3 mg, 0.3438 mmol, 61%) as a clear pale yellow oil.

Cyclopentene 17b. R_f 0.29 (EtOAc:Hexanes, 1:3); IR (neat, NaCl) 3055 (m), 2940 (s), 2834 (s), 2717 (m), 1716 (s), 1683 (s), 1616 (s), 1434 (s), 1360 (m), 1262 (m), 1189 (m), 1074 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.74 (s, 1H), 6.79 (s, 1H), 2.83 (m, 3H), 2.62 (dd, 1H, J = 17.2, 5.7 Hz), 2.54 (dd, 1H, J = 17.2, 7.3 Hz), 2.21 (m, 2H), 2.14 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 207.7, 189.6, 151.4, 146.6, 49.7, 39.8, 34.6, 32.7, 30.2. HRMS calcd. for C₉H₁₂O₂: m/z 152.0837, found m/z 152.0825.



Mo-mediated cleavage reaction of cycloadduct *endo-***14b** (**Table 1, entry 4**). To a flame dried flask containing the cycloadduct *endo-***14b** (34.0 mg, 0.2279 mmol) and acetonitrile (3.5 mL) was added molybdenum hexacarbonyl (62.1 mg, 0.2352 mmol) and distilled water (0.2 mL, 12.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 12 h. The solvent was then removed

using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **17b** (21.6 mg, 0.1419 mmol, 62%) as a clear pale yellow oil. Spectral data as reported above.



Mo-mediated cleavage reaction of cycloadduct 16a (Table 1, entry 5). To a flame dried flask containing the cycloadduct **16a** (50.5 mg, 0.2368 mmol) and acetonitrile (2.0 mL) was added molybdenum hexacarbonyl (43.0 mg, 0.1629 mmol) and distilled water (~0.2 mL, 12.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 12 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **18a** (38.5 mg, 0.1780 mmol, 75%, as an inseparable 50:50 mixture of *cis/trans* isomers, measured by ¹H NMR) as a clear pale yellow oil.

Cyclopentane 18a. R_f 0.29 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 3062 (m), 2954 (s), 2871 (s), 1707 (s), 1650 (m), 1593 (m), 1444 (s), 1371 (m), 1279 (m), 1212 (m), 1001 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.64 (d, 0.5H, J = 2.2 Hz), 9.61 (d, 0.5H, J = 2.2 Hz), 7.94 (d, 2H, J = 7.4 Hz), 7.56 (t, 1H, J = 7.4 Hz), 7.46 (t, 2H, J = 7.4 Hz), 3.03 (dd, 2H, J = 9.7, 6.9 Hz), 2.84 (m, 1H), 2.49 (m, 1H), 2.23 (m, 1H), 1.99 (m, 2H), 1.90 (m, 1H), 1.49 (m, 1H), 1.23 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ 203.4, 199.5, 199.4, 136.94, 136.88, 133.0, 128.6, 128.0, 51.2, 50.6, 44.0, 43.9, 36.0, 35.4, 32.7, 32.6, 32.1, 25.65, 25.59. HRMS calcd. for C₁₄H₁₆O₂: m/z 216.1150, found m/z 261.1141.



Mo-mediated cleavage reaction of cycloadduct 16b (Table 1, entry 6). To a flame dried flask containing the cycloadduct 16b (77.1 mg, 0.5099 mmol) and acetonitrile (2.0 mL) was added molybdenum hexacarbonyl (140.0 mg, 0.5303 mmol) and distilled water (0.2 mL, 12.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 12 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column

chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **18b** (50.9 mg, 0.3301 mmol, 65%, as an inseparable 60:40 mixture of *cis/trans* isomers, measured by ¹H NMR) as a clear pale yellow oil.

Cyclopentane 18b. R_f 0.20 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 2959 (s), 2871 (s), 1738 (s), 1673 (s), 1455 (m), 1422 (m), 1360 (m), 1238 (m), 1184 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.62 (d, 0.4H, *J*= 2.0 Hz), 9.60 (d, 0.6H, *J* = 2.0 Hz), 2.80 (m, 1H), 2.47 (m, 3H), 2.26 (m, 2H), 2.13 (s, 3H), 1.89 (m, 4H), 1.37 (m, 1H), 1.18 (m, 1H) (integration to high). ¹³C NMR (CDCl₃, 100 MHz) δ 208.1, 203.4, 51.2, 50.6, 49.2, 49.0, 35.6, 35.0, 32.5, 32.4, 31.9, 30.3, 30.1, 25.6, 25.5. HRMS calcd. for C₉H₁₄O₂: m/z 154.0994, found m/z 154.0986.



Mo-mediated cleavage reaction of cycloadduct 16c (Table 1, entry 7). To a flame dried flask containing the cycloadduct **16c** (85.3 mg, 0.2868 mmol) and acetonitrile (3.5 mL) was added molybdenum hexacarbonyl (76.1 mg, 0.2883 mmol) and distilled water (0.2 mL, 12.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 12 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **18c** (64.9 mg, 0.2160 mmol, 75%) as a clear pale yellow oil. **Cyclopentane 18c.** R_f 0.49 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 3061 (w), 2954 (s), 2931 (s), 2870 (s), 1705 (s), 1682 (s), 1597 (m), 1448 (s), 1374 (s), 1275 (s), 1212 (s), 1001 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.94 (d, 2H, *J* = 8.7 Hz), 7.55 (t, 1H, *J* = 7.4 Hz), 7.45 (t, 1H, *J* = 7.4 Hz), 3.04 (d, 2H, *J* = 6.9 Hz), 2.97 (m, 1H), 2.49 (m, 1H), 2.42 (m, 2H), 2.14 (m, 1H), 1.87 (m, 3H), 1.55 (m, 2H), 1.38 (m, 1H), 1.27 (m, 7H), 0.86 (t, 3H, *J* = 6.7 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 213.2, 199.8, 137.0, 132.9, 128.5, 128.0, 50.8, 44.0, 42.0, 36.2, 35.6, 32.1, 31.6, 28.9, 27.7, 23.7, 22.5, 14.0. HRMS calcd. for C₂₀H₂₈O₂: m/z 300.2089, found m/z 300.2088.



Mo-mediated cleavage reaction of cycloadduct 16d (Table 1, entry 8). To a flame dried flask containing the cycloadduct 16d (40.0 mg, 0.1699 mmol) and acetonitrile (2.5 mL) was added molybdenum hexacarbonyl (46.9 mg, 0.1777 mmol) and distilled water (0.2 mL, 12.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 7 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give 18d (33.1 mg, 0.1389 mmol, 82%) as a clear pale yellow oil. Cyclopentane 18d. R_f 0.32 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 2954 (s), 2930 (s), 2860 (s), 1719 (s), 1467 (s), 1374 (s), 1179 (m), 1071 (m), 918 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.93 (q, 1H, J

= 8.2 Hz), 2.49 (d, 2H, *J* = 7.0 Hz), 2.41 (dt, 2H, *J* = 7.4, 1.9 Hz), 2.30 (m, 1H), 2.11 (s, 3H), 2.05 (m, 1H), 1.80 (m, 3H), 1.53 (m, 2H), 1.22 (m, 7H), 0.87 (t, 3H, *J* = 6.7 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 213.0, 208.3, 50.8, 49.2, 42.0, 35.8, 35.4, 31.9, 31.6, 30.3, 29.0, 27.8, 23.8, 22.5, 14.0. HRMS calcd. for C₁₅H₂₆O₂: m/z 238.1933, found m/z 238.1939.



Mo-mediated cleavage reaction of cycloadduct 16e (Table 1, entry 9). To a flame dried flask containing the cycloadduct 16e (100.2 mg, 0.3510 mmol) and acetonitrile (3.5 mL) was added molybdenum hexacarbonyl (95.5 mg, 0.3617 mmol) and distilled water (0.2 mL, 12.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 12 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give 18e (65.6 mg, 0.2274 mmol, 65%) as a clear pale yellow oil. Cyclopentane 18e. R_f 0.51 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 3061 (w), 2956 (s), 2867 (s), 1737 (w), 1687 (s), 1636 (s), 1597 (m), 1449 (s), 1373 (m), 1249 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.94 (m, 2H), 7.55 (m, 1H), 7.45 (m, 2H), 3.36 (m, 1H), 3.02 (dd, 2H, *J* = 6.8, 1.6 Hz), 2.49 (m, 1H), 2.01 (m, 1H), 1.86 (m, 2H), 1.70 (m, 1H), 1.40 (m, 1H), 1.16 (m, 1H), 0.20 (s, 9H). ¹³C NMR (CDCl₃,

100 MHz) δ 248.2, 199.9, 137.1, 132.9, 128.5, 128.0, 55.3, 43.9, 36.2, 33.0, 32.0, 25.9, -2.8. HRMS calcd. for C₁₇H₂₄O₂Si: m/z 288.1546, found m/z 288.1538.



Mo-mediated cleavage reaction of cycloadduct 16f (Table 1, entry 10). To a flame dried flask containing the cycloadduct **16f** (70.6 mg, 0.3160 mmol) and acetonitrile (3.5 mL) was added molybdenum hexacarbonyl (89.2 mg, 0.3617 mmol) and distilled water (0.2 mL, 12.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 8 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **18f** (65.6 mg, 0.2274 mmol, 84%) as a clear pale yellow oil. **Cyclopentane 18f.** R_f 0.35 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 2956 (s), 2902 (s), 2867 (s), 1716 (s), 1636 (s), 1408 (m), 1372 (m), 1356 (s), 1249 (s), 1175 (m), 1154 (m), 843 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 3.29 (m, 1H), 2.45 (m, 2H), 2.26 (m, 1H), 2.09 (s, 3H), 1.89 (m, 1H), 1.77 (m, 2H), 1.66 (m, 1H), 1.28 (m, 1H), 1.03 (m, 1H), 0.17 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 247.9, 208.6, 55.2, 49.0, 35.7, 32.6, 31.8, 30.3, 25.8, -2.8. HRMS calcd. for C₁₂H₂₂O₂Si: m/z 266.1389, found m/z 266.1384.



Mo-mediated cleavage reaction of cycloadduct 8a (Table 2, entry 1). To a flame dried flask containing the cycloadduct 8a (20.9 mg, 0.1193 mmol) and acetonitrile (2.0 mL) was added molybdenum hexacarbonyl (33.3 mg, 0.1261 mmol) and distilled water (0.08 mL, 5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 3 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give 24a (13.2 mg, 0.07406 mmol, 62%, as an inseparable 67:33 mixture of *cis/trans* isomers, measured by ¹H NMR) as a clear pale yellow oil.

Attached-ring compound 24a. R_f 0.14 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 3058 (m), 2964 (s), 2881 (s), 1738 (s), 1716 (s), 1674 (m), 1455 (m), 1267 (m), 1155 (m), 1062 (m), 972 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.75 (s, 1H), 6.85 (0.67H, s), 6.80 (0.33H, s), 2.96–2.56 (m, 4H), 2.34–2.02 (m, 6H), 1.77 (m, 1H), 1.58 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ 220.1, 189.7, 152.3, 151.3, 146.4, 53.3, 52.9, 38.9, 38.7, 38.5, 37.7, 36.9, 36.8, 32.9, 32.6, 27.7, 26.8, 20.50, 20.47. HRMS calcd. for C₁₁H₁₄O₂: m/z 178.0994, found m/z 178.0990.



Mo-mediated cleavage reaction of cycloadduct 8b (Table 2, entry 2). To a flame dried flask containing the cycloadduct **8b** (30.9 mg, 0.1633 mmol) and acetonitrile (1.5 mL) was added molybdenum hexacarbonyl (46.2 mg, 0.1750 mmol) and distilled water (0.08 mL, 5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 3 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **24b** (18.9 mg, 0.09830 mmol, 60%, as an inseparable 60:40 mixture of *cis/trans* isomers, measured by ¹H NMR) as a clear pale yellow oil.

Attached-ring compound 24b. R_f 0.21 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 2936 (s), 2861 (s), 1705 (s), 1674 (m), 1447 (m), 1311 (w), 1263 (w), 1132 (m), 1068 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.73 (s, 1H), 6.83 (m, 0.6H), 6.80 (m, 0.4H), 6.17 (m, 0.5H), 3.60 (d, 0.25H, J = 5.2 Hz), 3.44 (d, 0.25H, J = 6.8 Hz), 3.01 (m, 0.75H), 2.91 (s, 0.25H), 2.85 (m, 0.5H), 2.77–2.52 (m, 3H), 2.42–2.28 (m, 4H), 2.23–2.05 (m, 4H), 2.00–1.86 (m, 2H), 1.75–1.64 (m, 3H), 1.43 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ 212.8, 212.3, 189.76, 189.72, 152.6, 151.6, 146.5, 137.1, 135.9, 81.2, 56.3, 55.5, 51.9, 48.9, 45.7, 42.4, 42.3, 39.1, 37.9, 37.7, 37.0, 36.9, 33.2, 32.4, 32.2, 31.1, 28.3, 28.0, 26.8, 25.0, 24.9, 22.4. HRMS calcd. for C₁₂H₁₆O₂: m/z 192.1150, found m/z 192.1161.



Mo-mediated cleavage reaction of cycloadduct 8c (Table 2, entry 3). To a flame dried flask containing the cycloadduct 8c (31.3 mg, 0.1766 mmol) and acetonitrile (2.0 mL) was added molybdenum hexacarbonyl (49.6 mg, 0.1879 mmol) and distilled water (0.12 mL, 7.5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 3 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give 24c (16.9 mg, 0.09378 mmol, 53%, as an inseparable 50:50 mixture of *cis/trans* isomers, measured by ¹H NMR) as a clear pale yellow oil.

Attached-ring compound 24c. R_f 0.26 (EtOAc:Hexanes, 1:3); IR (neat, NaCl) 3067 (w), 2940 (s), 2877 (s), 1748 (s), 1716 (s), 1674 (m), 1433 (m), 1371 (m), 1264 (m), 1174 (m), 1063 (m), 934 (m), 735 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.75 (s, 1H), 6.85 (m, 0.5H), 6.80 (m, 0.5H), 4.39 (t, 1H, J = 9.6 Hz), 4.02 (d, 1H, J = 17.2 Hz), 3.90 (m, 1H), 3.84 (dd, 1H, J = 17.2, 11.1 Hz), 2.91 (m, 1H), 2.69 (m, 3H), 2.43 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 215.7, 215.5, 189.34, 189.30, 151.3, 150.4, 146.8, 146.0, 71.6, 71.5, 70.9, 70.3, 50.9, 50.4, 37.9, 37.0, 36.4, 36.0, 32.84, 32.75. HRMS calcd. for C₁₀H₁₂O₃: m/z 180.0786, found m/z 180.0782.



Mo-mediated cleavage reaction of cycloadduct 8d (Table 2, entry 4). To a flame dried flask containing the cycloadduct 8d (22.8 mg, 0.0879 mmol) and acetonitrile (1.5 mL) was added molybdenum hexacarbonyl (23.1 mg, 0.0875 mmol) and distilled water (0.06 mL, 3.75 mmol). A water condenser was then attached and the flask was heated to 80 °C for 3 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give 24d (16.9 mg, 0.06441 mmol, 73%, as an inseparable 60:40 mixture of *cis/trans* isomers, measured by ¹H NMR) as a clear pale yellow oil.

Attached-ring compound 24d. R_f 0.24 (EtOAc:Hexanes, 1:4); IR (neat, NaCl) 3054 (w), 2957 (s), 2928 (s), 2861 (s), 1737 (s), 1715 (s), 1683 (m), 1470 (m), 1455 (m), 1155 (m), 1077 (m) cm⁻¹; ¹H

NMR (CDCl₃, 400 MHz) δ 5.99 (m, 0.4H), 5.79 (m, 1H), 5.60 (m, 0.6H), 3.61 (m, 1H), 3.07 (m, 1H), 2.48 (m, 2H), 2.34 (m, 2H), 2.20–1.87 (m, 4H), 1.77–1.52 (m, 5H), 1.27 (m, 6H), 0.88 (t, 3H, J = 6.7 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 136.2, 134.8, 130.0, 128.8, 58.3, 58.1, 53.2, 53.0, 45.2, 45.1, 41.4, 41.3, 38.72, 38.67. HRMS calcd. for C₁₇H₂₆O₂: m/z 262.1933, found m/z 262.1938.



Mo-mediated cleavage reaction of cycloadduct 8e (Table 2, entry 5). To a flame dried flask containing the cycloadduct **8e** (20.2 mg, 0.0921 mmol) and acetonitrile (1.5 mL) was added molybdenum hexacarbonyl (25.8 mg, 0.0977 mmol) and distilled water (0.08 mL, 5 mmol). A water condenser was then attached and the flask was heated to 80 °C for 3 h. The solvent was then removed using rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 1:4) to give **24e** (13.7 mg, 0.06163 mmol, 67%, as an inseparable mixture of 4 stereoisomers, ~ 42:39:14:5, measured by ¹³C NMR) as a clear pale yellow oil.

Attached-ring compound 24e. R_f 0.26 (EtOAc:Hexanes, 1:3); IR (neat, NaCl) 2964 (m), 2938 (m), 2876 (m), 2825 (w), 1727 (vs), 1444 (m), 1402 (m), 1357 (m), 1326 (m), 1274 (w), 1202 (m), 1156 (m), 1103 (s), 1042 (m) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 6.04 (m, 0.5H), 5.75 (m, 1H), 5.63 (m, 1H), 4.11 (s, 2H), 3.73 (m, 1H), 3.42 (s, 3H), 3.09 (m, 1H), 2.32 (m, 2H), 2.22–1.90 (m, 5H), 1.78–1.54 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 220.4, 220.3, 208.2, 208.1, 136.7, 135.4, 129.1, 127.9, 59.4, 54.8, 54.6, 53.2, 53.0, 45.2, 45.0, 38.7, 38.6, 30.2, 28.3, 26.7, 26.6, 20.6. HRMS calcd. for C₁₃H₁₈O₃: m/z 222.1256, found m/z 222.1247.