

Supporting Information for

Synthesis of Substituted Oxa- and Aza[3.2.1] and [4.3.1]bicyclics via an Unprecedented Molybdenum-Mediated 1,5-“Michael-Type” Reaction

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GENERAL METHODS

Unless otherwise indicated, all ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 MHz (400 MHz ^1H , 100 MHz ^{13}C) or Varian Inova 600 MHz (600 MHz ^1H , 150 MHz ^{13}C) at room temperature in CDCl_3 with internal CHCl_3 as the reference (7.27 ppm for ^1H and 77.23 ppm for ^{13}C). IR spectra were recorded on ASI ReactIR^R 1000 FT-IR spectrometer, equipped with a silicon probe. Peaks are reported (cm^{-1}) with the following relative intensities: s (strong, 67-100%), m (medium, 40-67%), w (weak, 20-40%) and br (broad). Melting points (mp) are uncorrected and were taken in open capillary tubes on a Thomas Hoover capillary melting point apparatus. *Since almost all of the Tp molybdenum complexes decompose at about 180-200 °C melting points are not significant and are not shown in the experimental section.* Optical rotations were measured with Perkin-Elmer 241MC or Perkin-Elmer Model 341 polarimeters. Analytical thin-layer chromatography (TLC) was carried out on commercial Baker-flex plastic-supported silica gel plates (thickness: 200 μm) with fluorescent indicator (F-254). Visualization was accomplished by UV light or stained with 5% phosphomolybdic acid (PMA) in ethanol. Flash column chromatography was performed with 32-63 μm silica gel. In some cases (as indicated) silica gel was first neutralized with Et_3N prior to chromatography. Dichloromethane (HPLC grade) and THF (99 %+) were purchased from EMD and Aldrich (respectively) and dried over 4Å molecular sieves before used. Dry diethyl ether was purchased from Mallinckrodt and used as received. Unless otherwise specified, all reactions were carried out under a nitrogen or argon atmosphere, and all reaction flasks were flamed or oven dried prior to use. The nomenclature for determining the chirality of the molybdenum complexes is straightward.¹

STARTING MATERIALS.

All enones, TiCl_4 (1.0 M in dichloromethane), and NaOCH_3 (powder) were purchased from Aldrich; *t*-BuOK, and KOSiMe_3 were purchased from Fluka. All chemicals were used as received. (\pm)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η^3 -2,3,4)-5-oxo-5,6-dihydro-2*H*-pyran-2-

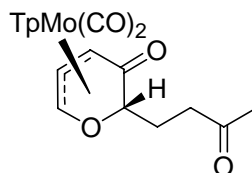
yl]molybdenum [(±)-**1**],² (-)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*)-(η³-2,3,4)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum [(-)-**1**],² (+)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*)-(η³-2,3,4)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum [(+)-**1**],² and (±)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(η³-2,3,4)-5-methoxy-1-benzoxycarbonyl-1,2-dihydropyridin-2-yl]molybdenum^{3,4} were prepared according to literature procedures. Both (-)-**1** and (+)-**1** were obtained in >99% ee by recrystallization from a mixture of CH₂Cl₂ and hexanes. The observed optical rotations were: [(-)-**1**, -550° (*c* 1.42, CH₂Cl₂); (-)-**1**, +555° (*c* 1.67, CH₂Cl₂)]. (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η³-2,3,4)-1-benzoxycarbonyl-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum [(±)-**2**] was synthesized in almost quantitative yield by the hydrolysis of a solution of (±)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(η³-2,3,4)-5-methoxy-1-benzoxycarbonyl-1,2-dihydropyridin-2-yl]molybdenum^{3,4} in methanol with 0.75N HCl (aqueous). (±)-**2**: TLC (*R_f* = 0.62, hexanes-EtOAc 1:1). IR (cm⁻¹): 3123 (w), 2957 (w), 2490 (m), 1965 (s), 1868 (s), 1706 (m), 1664 (m), 1505 (m), 1409 (s), 1305 (s), 1285 (s), 1220 (s), 1123 (s), 1054 (s). ¹H NMR (a mixture of two rotamers): δ 8.45 (d, *J* = 1.91 Hz, 0.4H), 8.42 (d, *J* = 1.91 Hz, 0.6H), 8.31 (d, *J* = 1.91 Hz, 0.6H), 7.76 (d, *J* = 1.91 Hz, 0.4H), 7.74 (d, *J* = 1.91 Hz, 0.6H), 7.70 (d, *J* = 1.91 Hz, 0.4H), 7.65 (d, *J* = 1.91 Hz, 0.6H), 7.62 (d, *J* = 1.91 Hz, 0.6H), 7.60 (d, *J* = 1.91 Hz, 0.4H), 7.58 (d, *J* = 1.91 Hz, 0.4H), 7.47-7.52 (m, 1.6H), 7.40-7.44 (m, 2.0H), 7.27-7.38 (m, 3.0H), 7.22 (dd, *J* = 6.35 Hz, *J* = 1.90 Hz, 0.4H), 6.28-6.30 (m, 1.6H), 6.22-6.24 (m, 1.0H), 5.97 (t, *J* = 2.22 Hz, 0.4H), 5.27 (AB quartet, *J* = 11.44 Hz, 0.4H), 5.24 (s, 0.6H), 4.74-4.77 (m, 1.0H), 4.09 (t, *J* = 6.35 Hz, 0.6H), 3.98 (t, *J* = 6.35 Hz, 0.4H), 3.41 (AB quartet, *J* = 20.01 Hz, 0.4H), 3.39 (AB quartet, *J* = 19.69 Hz, 0.6H). ¹³C NMR: δ 225.2, 224.7, 222.8, 222.1, 193.7, 193.0, 154.8, 154.0, 147.5, 147.4, 144.7, 143.6, 141.6, 141.5, 136.7, 136.62, 136.48, 136.44, 135.7, 135.5, 135.0, 129.1, 128.9, 128.8, 128.7, 128.4, 128.0, 106.36, 106.34, 106.1, 106.0, 94.0, 92.4, 69.1, 68.3, 64.7, 64.4, 64.1, 63.6, 48.1, 48.0.

GENERAL PROCEDURE FOR MUKAIYAMA-MICHAEL ADDITIONS.⁵

To a CH₂Cl₂ solution of the molybdenum complexes **1** and **2** (1.0 equiv) was successively added Et₃N (1.10-1.15 equiv) and *t*-BuMe₂SiOSO₂CF₃ (TBSOTf, 1.10 equiv). The reaction mixture was stirred at room temperature for about 10 min and was then cooled to -78 °C. To this cold solution was rapidly added a premixed CH₂Cl₂ solution of the indicated enones (1.4 equiv) and titanium tetrachloride (1.3 equiv) via syringe. The indicated enones were first dissolved in CH₂Cl₂ and then cooled to -78 °C. To this cold solution was then added titanium tetrachloride (1.0 M

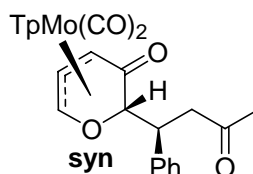
solution in CH₂Cl₂) via syringe. The reaction mixture was stirred at the indicated temperature for the indicated time, quenched with 1 mL of water or saturated sodium bicarbonate aqueous solution at -78 °C, and then partitioned between brine and dichloromethane. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The organic layers were combined, dried with Na₂SO₄ and the solvent was removed under vacuum to afford crude products. The crude products were purified by column chromatography to give solid organic products. The ratio of isomers was determined by ¹H NMR of the crude product. (Note: the reaction yields depended significantly on the quality of titanium tetrachloride.)

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][*(2S,6S)*-(*η*³-2,3,4)-5-oxo-6-(3-oxobutyl)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-3**.**



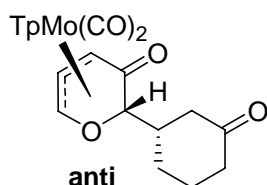
Following the general procedure, to a 10 mL CH₂Cl₂ solution of the molybdenum complex **1** (0.92 g, 2.0 mmol) was successively added Et₃N (307 μL, 2.2 mmol) and TBSOTf (506 μL, 2.2 mmol). The reaction mixture was stirred at room temperature for about 10 min and was then cooled to -78 °C. To this cold solution was rapidly added a premixed 10 mL CH₂Cl₂ solution of methyl vinyl ketone MVK (196 mg, 2.8 mmol) and titanium tetrachloride (2.6 mL, 2.6 mmol) via syringe. The reaction mixture was stirred at -78 °C for 5 min and quenched with 1 mL of saturated sodium bicarbonate aqueous solution at -78 °C. After work-up the crude product was purified by flash chromatography (1:1 hexanes-EtOAc) to give **3** as an orange solid (1.00 g, 94%). (±)-**3**: TLC (R_f = 0.43, 1:1 hexanes-EtOAc). IR (cm⁻¹): 3127 (w), 2934 (w), 2490 (m), 1957 (s), 1872 (s), 1714 (s), 1652 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1050 (s). ¹H NMR: δ 8.51 (d, *J* = 2.23 Hz, 1H), 7.93 (d, *J* = 1.91 Hz, 1H), 7.65 (d, *J* = 2.23 Hz, 1H), 7.61 (d, *J* = 2.22 Hz, 1H), 7.53 (d, *J* = 2.54 Hz, 1H), 7.36 (d, *J* = 2.23 Hz, 1H), 7.34 (dd, *J* = 4.76 Hz, *J* = 2.22 Hz, 1H), 6.31 (t, *J* = 2.22 Hz, 1H), 6.27 (t, *J* = 2.22 Hz, 1H), 6.22 (t, *J* = 2.22 Hz, 1H), 4.77 (dd, *J* = 6.03 Hz, *J* = 2.22 Hz, 1H), 4.17 (dd, *J* = 6.04 Hz, *J* = 4.76 Hz, 1H), 3.41 (dd, *J* = 6.99 Hz, *J* = 5.40 Hz, 1H), 2.54 (m, 2H), 2.18 (s, 3H), 1.97-2.04 (m, 2H). ¹³C NMR: δ 225.2, 223.8, 207.8, 195.4, 147.5, 143.7, 141.7, 136.5, 134.9, 107.9, 106.4, 106.2, 105.9, 75.7, 68.6, 65.0, 39.0, 30.0, 26.8. HRMS (FAB) calcd for C₂₀H₂₂BMoN₆O₅ ([M+H]⁺): 535.0799. Found: 535.0789.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η³-2,3,4)-5-oxo-6-(3-oxo-1-phenylbutyl)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-4.



Following the general procedure, to a 5 mL CH₂Cl₂ solution of the molybdenum complex **1** (500 mg, 1.09 mmol) was successively added Et₃N (174 μL, 1.25 mmol) and TBSOTf (275 μL, 1.20 mmol). The reaction mixture was stirred at room temperature for about 10 min and was then cooled to -78 °C. To this cold solution was rapidly added a premixed 5 mL CH₂Cl₂ solution of *trans*-4-phenyl-3-buten-2-one (204 mg, 1.53 mmol) and titanium tetrachloride (1.42 mL, 1.42 mmol) via syringe. The reaction mixture was stirred at -78 °C for 20 min and quenched with 1 mL of saturated sodium bicarbonate aqueous solution at -78 °C. After work-up the ¹H NMR spectrum of the crude product (582 mg) showed a mixture of the two diastereomers (*anti*:*syn* = 1:10) of **4** and the starting material **1** as well. Although **4** could not be separated from **1** the yield (71%) was estimated by the ¹H NMR spectrum of the crude product. The pure *syn* isomer was obtained by recrystallization of the crude product from a mixture of dichloromethane and hexanes. *Syn*-(±)-**4**: TLC (R_f = 0.54, 1:1 hexanes-EtOAc). IR (cm⁻¹): 3127 (w), 2490 (m), 1961 (s), 1872 (s), 1718 (s), 1652 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ¹H NMR: δ 8.48 (d, *J* = 2.22 Hz, 1H), 7.80 (d, *J* = 1.91 Hz, 1H), 7.58 (d, *J* = 2.54 Hz, 2H), 7.54 (d, *J* = 2.22 Hz, 1H), 7.49 (d, *J* = 2.22 Hz, 1H), 7.22-7.33 (m, 6H), 7.37 (dd, *J* = 4.63 Hz, *J* = 1.91 Hz, 1H), 6.29 (t, *J* = 2.22 Hz, 1H), 6.22 (t, *J* = 2.22 Hz, 1H), 6.15 (t, *J* = 2.22 Hz, 1H), 4.42 (dd, *J* = 6.03 Hz, *J* = 2.23 Hz, 1H), 3.80 (td, *J* = 7.31 Hz, *J* = 3.49 Hz, 1H), 3.64 (dd, *J* = 6.35 Hz, *J* = 4.76 Hz, 1H), 3.58 (d, *J* = 3.50 Hz, 1H), 2.98 (doublets of AB quartet, J_{AB} = 17.25 Hz, *J* = 7.31 Hz, 1H), 2.10 (s, 3H). ¹³C NMR: δ 225.4, 223.6, 206.5, 194.2, 147.5, 143.8, 141.7, 138.6, 136.5, 136.4, 134.9, 129.3, 128.5, 127.4, 108.2, 106.5, 106.1, 105.8, 79.0, 69.2, 64.5, 45.7, 43.4, 30.5. HRMS (FAB) calcd for C₂₅H₂₆BMoN₆O₅ ([M+H]⁺): 611.1112. Found: 611.1108.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η³-2,3,4)-5-oxo-6-(3'-oxocyclohexyl)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum [(±)-5], (+)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*R*,6*R*,1'*R*)-(η³-2,3,4)-5-oxo-6-(3'-oxocyclohexyl)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum [(+)-5] and (-)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*,1'*S*)-(η³-2,3,4)-5-oxo-6-(3'-oxocyclohexyl)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum [(-)-5].

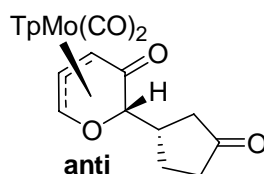


Following the general procedure, to a 12 mL CH_2Cl_2 solution of the molybdenum complex **1** (1.0 g, 2.17 mmol) was successively added Et_3N (353 μL , 2.50 mmol) and TBSOTf (556 μL , 2.39 mmol). The reaction mixture was stirred at room temperature for about 10 min and was then cooled to -78°C . To this cold solution was rapidly added a premixed 12 mL CH_2Cl_2 solution of cyclohexenone (276 mg, 3.04 mmol) and titanium tetrachloride (2.82 mL, 2.82 mmol) via syringe. The reaction mixture was stirred at -78°C for 30 min and quenched with 1 mL of saturated sodium bicarbonate aqueous solution at -78°C . After work-up the crude product was purified by flash chromatography (1:1 hexanes-EtOAc) to afford **5** as an orange solid (1.09 g, 91%). The ^1H NMR spectrum of the crude product showed a mixture of the two diastereomers (*anti:syn* = 40:1) of (\pm)-**5**. *Anti*-(\pm)-**5**: TLC (R_f = 0.59, 1:1 hexanes-EtOAc). IR (cm^{-1}): 3127 (w), 2945 (w), 2490 (w), 1961 (s), 1872 (s), 1710 (s), 1652 (s), 1505 (w), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ^1H NMR: δ 8.50 (d, J = 2.38 Hz, 1H), 7.90 (d, J = 1.91 Hz, 1H), 7.65 (d, J = 1.91 Hz, 1H), 7.63 (d, J = 2.38 Hz, 1H), 7.60 (d, J = 2.38 Hz, 1H), 7.52 (d, J = 2.38 Hz, 1H), 7.39 (dd, J = 4.28 Hz, J = 1.91 Hz, 1H), 6.30 (t, J = 2.38 Hz, 1H), 6.26 (t, J = 2.38 Hz, 1H), 6.22 (t, J = 2.38 Hz, 1H), 4.79 (dd, J = 6.19 Hz, J = 1.91 Hz, 1H), 4.13 (dd, J = 6.19 Hz, J = 4.76 Hz, 1H), 3.37 (d, J = 2.38 Hz, 1H), 2.22-2.47 (m, 5H), 2.06-2.10 (m, 1H), 1.63-1.82 (m, 3H). ^{13}C NMR: δ 224.9, 223.6, 210.8, 194.2, 147.6, 143.9, 141.7, 136.61, 136.57, 135.0, 108.0, 106.6, 106.3, 106.0, 79.4, 70.0, 64.7, 41.54, 41.46, 41.2, 28.1, 24.7. HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{23}\text{BMoN}_6\text{O}_5$ (M^+): 560.0877. Found: 560.0905.

Similar treatment of the chiral non-racemic (>99% ee) molybdenum complex (2*S*)-(-)-**1** (300 mg, 0.651 mmol) afforded (-)-**5** as an orange solid (288 mg, 80%) in 99.3% ee ($[\alpha]_D = -479^\circ$, c 1.27, CH_2Cl_2).

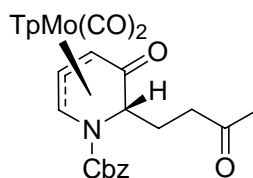
Similar treatment of the chiral non-racemic (>99% ee) molybdenum complex (2*R*)-(+)-**1** (530 mg, 1.17 mmol) afforded (+)-**5** as an orange solid (468 mg, 71%) in 99.3% ee ($[\alpha]_D = +481^\circ$, c 1.87, CH_2Cl_2).

(\pm)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η^3 -2,3,4)-5-oxo-6-(3-oxocyclopentyl)-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (\pm)-6**.**



Following the general procedure, to a 5 mL CH₂Cl₂ solution of the molybdenum complex **1** (500 mg, 1.09 mmol) was successively added Et₃N (174 μL, 1.25 mmol) and TBSOTf (275 μL, 1.20 mmol). The reaction mixture was stirred at room temperature for about 10 min and was then cooled to -78 °C. To this cold solution was rapidly added a premixed 5 mL CH₂Cl₂ solution of cyclopentenone (128 mg, 1.53 mmol) and titanium tetrachloride (1.42 mL, 1.42 mmol) via syringe. The reaction mixture was stirred at -78 °C for 30 min and quenched with 1 mL of saturated sodium bicarbonate aqueous solution at -78 °C. After work-up the crude product was purified by flash chromatography (1:1 hexanes-EtOAc) to afford **6** as an orange solid (350 mg, 70%). The ¹H NMR spectrum of the crude product showed a mixture of the two diastereomers (*anti:syn* = 7:1) of **6**. *Anti*-(±)-**6**: TLC (*R_f* = 0.53, 1:1 hexanes-EtOAc). IR (cm⁻¹): 3127 (w), 2961 (w), 2490 (m), 1961 (s), 1872 (s), 1737 (s), 1652 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ¹H NMR: δ 8.52 (d, *J* = 1.91 Hz, 1H), 7.92 (d, *J* = 1.43 Hz, 1H), 7.65 (d, *J* = 1.91 Hz, 1H), 7.63 (d, *J* = 1.91 Hz, 1H), 7.61 (d, *J* = 2.38 Hz, 1H), 7.53 (d, *J* = 2.38 Hz, 1H), 7.37 (dd, *J* = 4.63 Hz, *J* = 1.91 Hz, 1H), 6.32 (t, *J* = 2.38 Hz, 1H), 6.27 (t, *J* = 1.91 Hz, 1H), 6.23 (t, *J* = 2.38 Hz, 1H), 4.80 (dd, *J* = 6.19 Hz, *J* = 1.91 Hz, 1H), 4.15 (dd, *J* = 6.19 Hz, *J* = 4.76 Hz, 1H), 3.48 (d, *J* = 2.86 Hz, 1H), 2.81-2.84 (m, 1H), 2.08-2.41 (m, 5H), 1.93-1.98 (m, 1H). ¹³C NMR: δ 224.8, 223.6, 218.5, 194.3, 147.6, 143.9, 141.7, 136.6, 135.0, 107.7, 106.6, 106.3, 106.1, 78.1, 69.9, 64.7, 39.3, 39.0, 38.2, 25.9. HRMS (FAB) calcd for C₂₁H₂₁BMoN₆O₅ (M⁺): 546.0721. Found: 546.0734.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(7³-2,3,4)-1-benzyloxycarbonyl-5-oxo-6-(3-oxobutyl)-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-7.



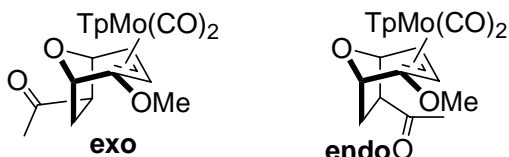
Following the general procedure, to a 10 mL CH₂Cl₂ solution of the molybdenum complex **2** (0.90 g, 1.51 mmol) was successively added Et₃N (231 μL, 1.66 mmol) and TBSOTf (382 μL, 1.66 mmol). The reaction mixture was stirred at room temperature for about 10 min and was then cooled to -78 °C. To this cold solution was rapidly added a premixed 10 mL CH₂Cl₂ solution of methyl vinyl ketone MVK (151 mg, 2.11 mmol) and titanium tetrachloride (1.97 mL, 1.97 mmol) via syringe. The reaction mixture was stirred at -78 °C for 10 min and quenched with 1 mL of

saturated sodium bicarbonate aqueous solution at $-78\text{ }^{\circ}\text{C}$. After work-up the crude product was purified by flash chromatography (1:1 hexanes-EtOAc) to afford **7** as an orange solid (908 mg, 90.3%). (\pm)-**7**: TLC ($R_f = 0.58$, 1:1 hexanes-EtOAc). IR (cm^{-1}): 3123 (w), 2957 (w), 2490 (m), 1969 (s), 1864 (s), 1706 (m), 1664 (m), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ^1H NMR (a mixture of two rotamers): δ 8.56 (d, $J = 1.91\text{ Hz}$, 0.5H), 8.42 (d, $J = 1.91\text{ Hz}$, 0.5H), 8.37 (d, $J = 1.91\text{ Hz}$, 0.5H), 7.70 (d, $J = 1.91\text{ Hz}$, 0.5H), 7.67 (s, 1H), 7.64 (d, $J = 2.22\text{ Hz}$, 0.5H), 7.62 (d, $J = 2.23\text{ Hz}$, 0.5H), 7.58 (d, $J = 2.44\text{ Hz}$, 0.5H), 7.53 (d, $J = 2.22\text{ Hz}$, 0.5H), 7.48-7.52 (m, 2H), 7.40-7.43 (m, 1H), 7.35-7.38 (m, 2H), 7.33 (dd, $J = 6.35\text{ Hz}$, $J = 1.50\text{ Hz}$, 0.5H), 7.08 (dd, $J = 6.35\text{ Hz}$, $J = 1.59\text{ Hz}$, 0.5H), 6.27-6.30 (m, 1.5H), 6.23 (t, $J = 2.22\text{ Hz}$, 0.5H), 6.21 (t, $J = 2.22\text{ Hz}$, 0.5H), 5.81 (t, $J = 2.22\text{ Hz}$, 0.5H), 5.24 (s, 0.5H), 5.23 (AB quartet, $J = 11.43\text{ Hz}$, 0.5H), 4.74 (dd, $J = 6.03\text{ Hz}$, $J = 1.90\text{ Hz}$, 0.5H), 4.71 (dd, $J = 6.04\text{ Hz}$, $J = 1.91\text{ Hz}$, 0.5H), 4.03 (t, $J = 6.19\text{ Hz}$, 0.5H), 3.91 (t, $J = 6.19\text{ Hz}$, 0.5H), 3.69 (t, $J = 6.67\text{ Hz}$, 0.5H), 3.61 (dd, $J = 6.99\text{ Hz}$, $J = 5.08\text{ Hz}$, 0.5H), 2.44-2.71 (m, 2H), 2.17 (s, 1.5H), 2.10 (s, 1.5H), 2.05-2.15 (m, 2H). ^{13}C NMR: δ 225.9, 225.2, 222.9, 221.7, 207.8, 207.4, 197.5, 196.9, 154.9, 153.9, 147.6, 147.5, 147.1, 144.6, 140.8, 140.5, 136.7, 136.6, 136.46, 136.39, 135.7, 135.4, 135.09, 135.04, 129.00, 128.96, 128.8, 128.6, 128.4, 106.5, 106.4, 106.05, 106.01, 98.4, 95.3, 69.4, 68.7, 65.2, 64.5, 59.6, 58.8, 57.5, 57.4, 39.6, 39.1, 30.1, 27.3, 26.7. HRMS (FAB) calcd for $\text{C}_{28}\text{H}_{28}\text{BMoN}_7\text{O}_6$ (M^+): 667.1248, found: 667.1245.

GENERAL PROCEDURE FOR METAL-MEDIATED 1,5-MICHAEL-TYPE ADDITIONS.

To a CH_2Cl_2 solution of the molybdenum complex **3-7** (1.0 equiv) was added the indicated amount of base (3.0-6.0 equiv). The reaction mixture was stirred at room temperature until TLC monitoring of the reaction mixture indicated the disappearance of the starting material. The indicated amount of Meerwein salt Me_3OBF_4 (2.5-5.0 equiv) was added as a solid, and the mixture was then stirred at room temperature for the indicated time. The reaction mixture was directly poured onto a short pad of silica gel. Elution with 50% ethyl acetate in hexanes, concentration and careful chromatographic purification afforded products **8-15** as yellow solids. Unless the isomers could be separated by flash column chromatography, the ratio of isomers was determined by ^1H NMR of the crude product.

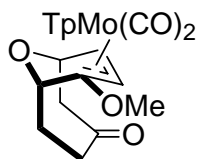
(\pm)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][$(1S,2S,5R,6R)$ -(η^3 -2,3,4)-6-acetyl-2-methoxy-8-oxabicyclo[3.2.1]oct-3-en-2-yl]molybdenum [(\pm)-**8-exo**] and (\pm)-dicarbonyl[hydridotris(1-pyrazolyl)borato][$(1S,2S,5R,6S)$ -(η^3 -2,3,4)-6-acetyl-2-methoxy-8-oxabicyclo[3.2.1]oct-3-en-2-yl]molybdenum [(\pm)-**8-endo**].



Following the general procedure, to a solution of the molybdenum complex **3** (210 mg, 0.395 mmol) in CH₂Cl₂ (20 mL) was added solid sodium methoxide (64 mg, 1.18 mmol). The reaction mixture was stirred at room temperature for 5 h. Me₃OBF₄ (172 mg, 1.18 mmol) was added as a solid and the mixture was then stirred at room temperature for 4 h. Purification by flash chromatography afforded the molybdenum complexes (±)-**8-exo** (151 mg, 74%) and (±)-**8-endo** (20 mg, 9%). (±)-**8-exo**: TLC (R_f = 0.57, 1:1 hexanes-EtOAc). IR (cm⁻¹): 3127 (w), 2922 (m), 2853(w), 2482 (m), 1926 (s), 1837 (s), 1710 (s), 1505 (m), 1409 (s), 1305 (s), 1212 (s), 1050(s). ¹H NMR: δ 8.46 (d, *J* = 1.91 Hz, 1H), 7.95 (d, *J* = 1.43 Hz, 1H), 7.62 (t, *J* = 2.28 Hz, 2H), 7.59 (d, *J* = 1.43 Hz, 1H), 7.51 (d, *J* = 2.38 Hz, 1H), 6.24 (t, *J* = 1.91 Hz, 1H), 6.22 (t, *J* = 1.91 Hz, 1H), 6.16 (t, *J* = 1.91 Hz, 1H), 4.45 (d, *J* = 5.71 Hz, 1H), 4.38 (d, *J* = 2.38 Hz, 1H), 3.83 (dd, *J* = 7.62 Hz, *J* = 2.86 Hz, 1H), 3.49 (d, *J* = 7.62 Hz, 1H), 3.37 (dd, *J* = 8.57 Hz, *J* = 4.76 Hz, 1H), 3.24 (s, 3H), 2.43 (dt, *J* = 12.38 Hz, *J* = 5.24 Hz, 1H), 2.29 (dd, *J* = 12.39 Hz, *J* = 9.05 Hz, 1H), 2.22 (s, 3H). ¹³C NMR: δ 229.2, 227.8, 207.6, 146.4, 144.8, 140.3, 136.5, 136.1, 134.5, 133.3, 105.8, 105.61, 105.57, 76.9, 75.7, 60.6, 58.9, 56.4, 52.7, 35.1, 27.7. HRMS (FAB) calcd for C₂₁H₂₃BMoN₆O₅ (M⁺): 548.0877. Found: 548.0853. (±)-**8-endo**: TLC (R_f = 0.69, hexanes-EtOAc 1:1). IR (cm⁻¹): 3127 (w), 2976 (w), 2945(w), 2482 (w), 1926 (s), 1841 (s), 1710 (s), 1505 (m), 1409 (s), 1305 (s), 1216 (s), 1050 (s). ¹H NMR: δ 8.46 (d, *J* = 1.90 Hz, 1H), 7.94 (d, *J* = 1.91 Hz, 1H), 7.60 (t, *J* = 1.91 Hz, 2H), 7.50 (d, *J* = 1.91 Hz, 1H), 7.42 (d, *J* = 1.91 Hz, 1H), 6.25 (t, *J* = 2.23 Hz, 1H), 6.18 (t, *J* = 2.23 Hz, 1H), 6.15 (t, *J* = 2.23 Hz, 1H), 4.62 (dd, *J* = 6.35 Hz, *J* = 1.90 Hz, 1H), 4.31 (d, *J* = 6.03 Hz, 1H), 3.59 (ddd, *J* = 10.35 Hz, *J* = 6.67 Hz, *J* = 4.45 Hz, 1H), 3.46 (AB quartet, *J* = 7.67 Hz, doublets of the AB left part, *J* = 4.76 Hz, 2H), 3.24 (s, 3H), 2.63 (dd, *J* = 12.71 Hz, *J* = 4.45 Hz, 1H), 2.40 (s, 3H), 2.14 (ddd, *J* = 12.38 Hz, *J* = 10.48 Hz, *J* = 6.36 Hz, 1H). ¹³C NMR: δ 230.0, 228.0, 205.6, 146.4, 144.8, 140.1, 136.5, 136.1, 134.5, 133.8, 105.8, 105.5, 75.8, 75.7, 58.0, 56.6, 55.6, 53.9, 32.7, 31.2. HRMS (FAB) calcd for C₂₁H₂₃BMoN₆O₅ (M⁺): 548.0877. Found: 548.0887.

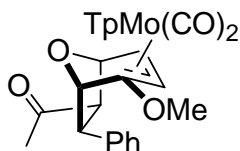
Following the general procedure, to a solution of the molybdenum complex **3** (154 mg, 0.289 mmol) in CH₂Cl₂ (20 mL) was added solid potassium trimethylsilylanolate (111 mg, 0.87 mmol). The reaction mixture was stirred at room temperature for 1 h. Me₃OBF₄ (107 mg, 0.723 mmol) was added as a solid and the mixture was then stirred at room temperature for 40 min. Purification by flash chromatography afforded the molybdenum complexes (±)-**8-exo** (150 mg, 95%) and (±)-**8-endo** (5 mg, 3%).

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*R*,6*S*,7*S*)-(η³-7,8,9)-7-methoxy-3-oxo-10-oxabicyclo[4.3.1]dec-8-en-7-yl]molybdenum [(±)-**13**].



Following the general procedure, to a solution of the molybdenum complex **3** (266 mg, 0.5 mmol) in CH₂Cl₂ (13 mL) was added solid potassium *t*-butoxide (140 mg, 1.25 mmol). The reaction mixture was stirred at room temperature for 1 h. Me₃OBF₄ (185 mg, 1.25 mmol) was added as a solid and the mixture was then stirred at room temperature for 1 h. Purification by flash chromatography afforded the molybdenum complex (±)-**8-endo** (6 mg, 2.2%) and an inseparable isomeric mixture of (±)-**8-exo** and (±)-**13** (198 mg, 73%). The ¹H NMR spectrum of the inseparable mixture showed a 2:3 ratio of **8-exo**:**13**. The pure isomer **13** was obtained by recrystallization from dichloromethane and hexanes. (±)-**13**: TLC (R_f = 0.57, 1:1 hexanes-EtOAc). IR (cm⁻¹): 3127 (w), 2941(w), 2482 (w), 1926 (s), 1837 (s), 1698 (s), 1505 (m), 1409 (m), 1305 (m), 1229 (s), 1050 (s). ¹H NMR: δ 8.44 (d, *J* = 2.38 Hz, 1H), 7.83 (d, *J* = 1.91 Hz, 1H), 7.63 (d, *J* = 2.39 Hz, 1H), 7.62 (d, *J* = 1.90 Hz, 1H), 7.56 (d, *J* = 1.91 Hz, 1H), 7.50 (d, *J* = 2.38 Hz, 1H), 6.24 (t, *J* = 2.38 Hz, 1H), 6.22 (t, *J* = 1.90 Hz, 1H), 6.17 (t, *J* = 1.90 Hz, 1H), 5.39 (dd, *J* = 5.24 Hz, *J* = 2.36 Hz, 1H), 4.07 (t, *J* = 3.81 Hz, 1H), 3.77 (s, 2H), 3.32 (dd, *J* = 13.34 Hz, *J* = 3.81 Hz, 1H), 2.98 (s, 3H), 2.90 (dd, *J* = 13.34 Hz, *J* = 4.28 Hz, 1H), 2.55-2.59 (m, 2H), 2.39-2.41 (m, 1H), 2.28-2.32 (m, 1H). ¹³C NMR: δ 230.4, 227.9, 212.4, 146.8, 144.9, 140.1, 136.7, 136.0, 134.7, 130.0, 105.9, 105.72, 105.71, 71.1, 67.8, 57.5, 56.3, 54.9, 54.8, 39.4, 28.9. HRMS (FAB) calcd for C₂₁H₂₃BMoN₆O₅ (M⁺): 548.0877. Found: 548.0867.

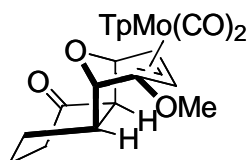
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*S*,2*S*,5*R*,6*R*,7*S*)-(η³-2,3,4)-6-acetyl-2-methoxy-7-phenyl-8-oxabicyclo[3.2.1]oct-3-en-2-yl]molybdenum [(±)-**9-exo**]



Following the general procedure, to a solution of the molybdenum complex **4** (126 mg, 0.207 mmol) in CH₂Cl₂ (10 mL) was added solid sodium methoxide (34 mg, 0.62 mmol). The reaction mixture was stirred at room temperature for 24 h. Me₃OBF₄ (77 mg, 0.518 mmol) was added as a solid and the mixture was then stirred at room temperature for 2 h. Purification by flash

chromatography afforded the molybdenum complex (\pm)-**9-*exo*** (92 mg, 71%). (\pm)-**9-*exo***: TLC (R_f = 0.66, 1:1 hexanes-EtOAc). IR (cm^{-1}): 3127 (w), 2949 (w), 2482 (w), 1992 (s), 1837 (s), 1710 (m), 1502 (m), 1409 (m), 1305 (m), 1212 (s), 1123 (m), 1050 (s). ^1H NMR: δ 8.42 (d, J = 1.91 Hz, 1H), 7.71 (d, J = 1.91 Hz, 1H), 7.63 (d, J = 1.91 Hz, 1H), 7.60 (d, J = 1.91 Hz, 1H), 7.58 (bs, 1H), 7.57 (bs, 2H), 7.47 (d, J = 1.91 Hz, 1H), 7.36 (t, J = 7.62 Hz, 2H), 7.27 (t, J = 7.30 Hz, 1H), 6.25 (t, J = 1.91 Hz, 1H), 6.22 (t, J = 1.91 Hz, 1H), 6.05 (t, J = 1.91 Hz, 1H), 4.70 (d, J = 5.72 Hz, 1H), 4.52 (d, J = 2.38 Hz, 1H), 4.23 (t, J = 6.19 Hz, 1H), 3.90 (dd, J = 7.63 Hz, J = 2.86 Hz, 1H), 3.82 (d, J = 6.67 Hz, 1H), 3.46 (d, J = 7.62 Hz, 1H), 2.23 (s, 3H), 2.07 (s, 3H). ^{13}C NMR: δ 230.5, 228.4, 206.7, 146.4, 145.1, 139.9, 136.6, 136.2, 136.1, 134.9, 134.5, 129.0, 128.5, 127.5, 105.7, 105.6, 105.5, 81.0, 61.3, 59.0, 53.6, 53.48, 53.46, 28.3. HRMS (FAB) calcd for $\text{C}_{27}\text{H}_{27}\text{BMoN}_6\text{O}_5$ (M^+): 624.1190. Found: 624.1205.

(\pm)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*1R,2R,7S,8S,9S*)-(η^3 -9,10,11)-9-methoxy-3-oxo-12-oxatricyclo[6.3.1.0^{2,7}]dodec-10-en-9-yl]molybdenum [(\pm)-10**], (+)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(*1R,2R,7S,8S,9S*)-(η^3 -9,10,11)-9-methoxy-3-oxo-12-oxatricyclo[6.3.1.0^{2,7}]dodec-10-en-9-yl]molybdenum [(+)-**10**] and (-)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(*1S,2S,7R,8R,9R*)-(η^3 -9,10,11)-9-methoxy-3-oxo-12-oxatricyclo[6.3.1.0^{2,7}]dodec-10-en-9-yl]molybdenum [(-)-**10**].**



Following the general procedure, to a solution of the molybdenum complex **5** (600 mg, 1.08 mmol) in CH_2Cl_2 (45 mL) was added solid sodium methoxide (291 mg, 5.39 mmol). The reaction mixture was stirred at room temperature for 20 h. Me_3OBF_4 (639 mg, 4.32 mmol) was added as a solid and the mixture was then stirred at room temperature for 1 h. Purification by flash chromatography afforded the molybdenum complex (\pm)-**10** (557 mg, 90%). (\pm)-**10**: TLC (R_f = 0.50, 1:1 hexanes-EtOAc). IR (cm^{-1}): 3127 (w), 3007 (m), 2482 (w), 1926 (s), 1837 (s), 1698 (m), 1409 (m), 1305 (m), 1278 (s), 1212 (s), 1123 (m), 1050 (s). ^1H NMR: δ 8.48 (d, J = 1.91 Hz, 1H), 7.95 (d, J = 1.91 Hz, 1H), 7.61 (d, J = 1.91 Hz, 2H), 7.59 (d, J = 1.91 Hz, 1H), 7.50 (d, J = 2.38 Hz, 1H), 6.25 (t, J = 1.91 Hz, 1H), 6.21 (t, J = 1.91 Hz, 1H), 6.16 (t, J = 1.91 Hz, 1H), 4.55 (d, J = 2.86 Hz, 1H), 4.13 (s, 1H), 3.91 (dd, J = 7.62 Hz, J = 3.33 Hz, 1H), 3.49 (d, J = 7.62 Hz, 1H), 3.27 (s, 3H), 3.14 (d, J = 9.05 Hz, 1H), 2.92 (ddd, J = 15.25 Hz, J = 9.53 Hz, J = 6.20 Hz, 1H), 2.41 (dt, J = 18.10 Hz, J = 5.24 Hz, 1H), 2.27 (ddd, J = 16.67 Hz, J = 9.53 Hz, J = 7.62 Hz, 1H), 2.03-2.06 (m,

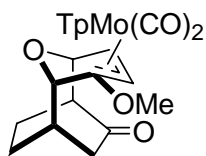
1H), 1.95-2.01 (m, 1H), 1.68-1.76 (m, 1H), 1.45-1.53 (m, 1H). ¹³C NMR: δ 228.8, 228.2, 212.2, 146.5, 144.7, 140.5, 136.5, 136.0, 134.5, 132.4, 105.8, 105.6, 105.5, 81.4, 79.2, 61.1, 58.1, 56.5, 52.7, 47.4, 38.9, 29.1, 20.9. HRMS (FAB) calcd for C₂₃H₂₅BMoN₆O₅ (M⁺): 574.1034. Found: 574.1011.

Following the general procedure, to a solution of the molybdenum complex **5** (112 mg, 0.20 mmol) in CH₂Cl₂ (10 mL) was added solid potassium trimethylsilylanonate (77 mg, 0.60 mmol). The reaction mixture was stirred at room temperature for 24 h. Me₃OBF₄ (74 mg, 0.50 mmol) was added as a solid and the mixture was then stirred at room temperature for 4 h. Purification by flash chromatography afforded the molybdenum complex (±)-**10** (111 mg, 96.5%), exclusively.

Similar treatment of the chiral non-racemic (99.3% ee) molybdenum complex (-)-**5** (100 mg, 0.65 mmol) afforded (+)-**10** as an orange solid (96 mg, 94%) in 99.3% ee. The ee could be increased to >99.9% by washing the product with acetonitrile ([α]_D = +372°, *c* 1.95, CH₂Cl₂)

Similar treatment of the chiral non-racemic (99.3% ee) molybdenum complex (+)-**5** (439 mg, 0.79 mmol) afforded (-)-**10** as an orange solid (431 mg, 97.6%) in 99.3% ee. The ee could be increased to >99.9% by washing the product with acetonitrile ([α]_D = -368°, *c* 2.44, CH₂Cl₂).

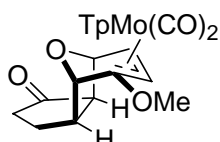
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1S,2S,3S,6R,7S)-(η³-3,4,5)-3-methoxy-8-oxo-12-oxatricyclo[5.2.2.1^{2,6}]dodec-4-en-3-yl]molybdenum [(±)-15**].**



Following the general procedure, to a solution of the molybdenum complex **5** (320 mg, 0.58 mmol) in CH₂Cl₂ (25 mL) was added solid potassium *tert*-butoxide (195 mg, 1.74 mmol). The reaction mixture was stirred at room temperature for 20 h. Me₃OBF₄ (215 mg, 1.45 mmol) was added as a solid and the mixture was then stirred at room temperature for 4 h. Purification by flash chromatography afforded an inseparable isomeric mixture of (±)-**10** and (±)-**15** (239 mg, 73%). The ¹H NMR spectrum of the inseparable mixture showed a 1:2 ratio of **10**:**15**. The pure isomer **15** was obtained by recrystallization from a mixture of dichloromethane and hexanes. (±)-**15**: TLC (R_f = 0.50, 1:1 hexanes-EtOAc). IR (cm⁻¹): 3127 (w), 2941 (w), 2482 (w), 1922 (s), 1833 (s), 1714 (s), 1505 (m), 1409 (s), 1305 (s), 1212 (s), 1123 (s), 1050 (s). ¹H NMR: δ 8.44 (s, 1H), 7.86 (s, 1H), 7.62 (d, *J* = 1.91 Hz, 1H), 7.58 (d, *J* = 1.43 Hz, 1H), 7.50 (d, *J* = 2.38 Hz, 1H), 7.10 (d, *J* = 2.38 Hz, 1H), 6.24 (t, *J* = 1.91 Hz, 1H), 6.20 (t, *J* = 1.91 Hz, 1H), 6.16 (t, *J* = 1.91 Hz, 1H), 4.42 (d, *J* = 7.15 Hz, 1H), 3.92 (d, *J* = 6.19 Hz, 1H), 3.75 (s, 2H), 3.03 (s, 3H), 2.83 (t, *J* = 5.14 Hz, 1H), 2.69 (m,

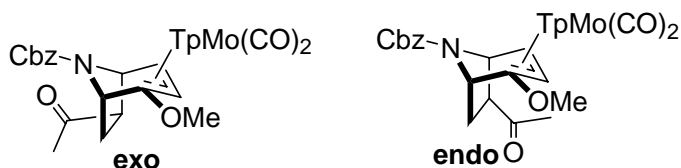
1H), 2.53 (bd, $J = 19.53\text{Hz}$, 1H), 2.29 (dd, $J = 19.53\text{ Hz}$, $J = 3.81\text{ Hz}$, 1H), 2.18-2.24 (m, 2H), 1.76-1.84 (m, 2H). ^{13}C NMR: δ 230.4, 228.9, 215.6, 146.7, 144.9, 140.5, 136.6, 136.0, 134.6, 131.6, 105.8, 105.7, 73.7, 73.1, 57.9, 57.3, 56.4, 54.6, 41.7, 34.8, 24.0, 22.0. HRMS (FAB) calcd for $\text{C}_{23}\text{H}_{25}\text{BMoN}_6\text{O}_5$ (M^+): 574.1034. Found: 574.1024.

(\pm)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][($1R,2R,6S,7S,8S$)-(η^3 -8,9,10)-8-methoxy-3-oxo-11-oxatricyclo[5.3.1.0^{2,6}]undec-9-en-8-yl]molybdenum [(\pm)-11].



Following the general procedure, to a solution of the molybdenum complex **6** (108 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was added solid sodium methoxide (54 mg, 1.0 mmol). The reaction mixture was stirred at room temperature for 45 h. Me_3OBF_4 (118 mg, 0.80 mmol) was added as a solid and the mixture was then stirred at room temperature for 1 h. Purification by flash chromatography afforded the molybdenum complex (\pm)-**11** (557 mg, 90%) exclusively. (\pm)-**11**: TLC ($R_f = 0.53$, 1:1 hexanes-EtOAc). IR (cm^{-1}): 3127 (w), 2968 (w), 2482 (w), 1926 (s), 1841 (s), 1733 (s), 1515 (m), 1409 (s), 1305 (s), 1212 (s), 1123 (s), 1050 (s). ^1H NMR: δ 8.46 (d, $J = 2.22\text{ Hz}$, 1H), 7.95 (d, $J = 1.91\text{ Hz}$, 1H), 7.62 (d, $J = 1.91\text{ Hz}$, 2H), 7.56 (d, $J = 1.91\text{ Hz}$, 1H), 7.50 (d, $J = 2.22\text{ Hz}$, 1H), 6.25 (t, $J = 2.22\text{ Hz}$, 1H), 6.22 (t, $J = 2.22\text{ Hz}$, 1H), 6.17 (t, $J = 2.22\text{ Hz}$, 1H), 4.38 (d, $J = 2.86\text{ Hz}$, 1H), 4.22 (d, $J = 1.59\text{ Hz}$, 1H), 3.84 (dd, $J = 7.62\text{ Hz}$, $J = 2.86\text{ Hz}$, 1H), 3.50 (d, $J = 5.94\text{ Hz}$, 1H), 3.26 (s, 3H), 3.19-3.23 (m, 1H), 3.06 (d, $J = 7.62\text{ Hz}$, 1H), 2.39-2.43 (m, 1H), 2.23-2.32 (m, 2H), 1.85-1.89 (m, 1H). ^{13}C NMR: δ 228.9, 228.1, 218.2, 146.5, 144.8, 140.4, 136.6, 136.1, 134.5, 132.2, 105.9, 105.65, 105.58, 83.1, 79.8, 60.0, 59.1, 56.5, 53.2, 48.1, 39.4, 26.8. HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{23}\text{BMoN}_6\text{O}_5$ (M^+): 560.0877. Found: 560.0874.

(\pm)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][($1S,2S,5R,6R$)-(η^3 -2,3,4)-6-acetyl-8-benzyloxycarbonyl-2-methoxy-8-azabicyclo[3.2.1]oct-3-en-2-yl]molybdenum [(\pm)-12-*exo*] and (\pm)-dicarbonyl[hydridotris(1-pyrazolyl)borato][($1S,2S,5R,6S$)-(η^3 -2,3,4)-6-acetyl-8-benzyloxycarbonyl-2-methoxy-8-azabicyclo[3.2.1]oct-3-en-2-yl]molybdenum [(\pm)-12-*endo*].

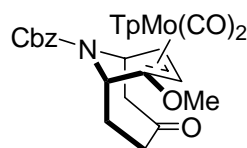


Following the general procedure, to a solution of the molybdenum complex **7** (840 mg, 1.24 mmol) in CH₂Cl₂ (85 mL) was added solid sodium methoxide (402 mg, 7.44 mmol). The reaction mixture was stirred at room temperature for 6 h. Me₃OBF₄ (918 mg, 6.20 mmol) was added as a solid and the mixture was then stirred at room temperature for 15 h. Purification by flash chromatography afforded the molybdenum complexes (±)-**12-exo** (760 mg, 79%) and (±)-**12-endo** (105 mg, 11%). (±)-**12-exo**: TLC (R_f = 0.49, 1:1 hexanes-EtOAc). IR (cm⁻¹): 3127 (w), 2945 (w), 2482 (m), 1930 (s), 1841 (s), 1710 (s), 1502 (m), 1409 (s), 1305 (s), 1212 (s), 1116 (s), 1050 (s). ¹H NMR (a mixture of two rotamers): δ 8.42 (d, *J* = 1.59 Hz, 0.4H), 8.39 (d, *J* = 1.59 Hz, 0.6H), 7.97 (d, *J* = 1.90 Hz, 0.6H), 7.95 (d, *J* = 1.59 Hz, 0.4H), 7.63 (d, *J* = 1.59 Hz, 0.4H), 7.60 (m, 2.6H), 7.47 (d, *J* = 2.22 Hz, 1H), 7.27-7.34 (m, 5H), 6.23 (t, *J* = 2.22 Hz, 1.2H), 6.18-6.21 (m, 0.8H), 6.14-6.15 (m, 1H), 5.08 (AB quartet, *J* = 12.39 Hz, 0.8H), 5.03 (AB quartet, *J* = 12.07 Hz, 1.2H), 4.77 (d, *J* = 6.03 Hz, 0.6H), 4.69 (d, *J* = 3.82 Hz, 0.4H), 4.65 (d, *J* = 5.82 Hz, 0.4H), 4.57 (d, *J* = 4.13 Hz, 0.6H), 4.11 (dd, *J* = 7.62 Hz, *J* = 4.13 Hz, 0.4H), 4.03 (dd, *J* = 7.62 Hz, *J* = 4.13 Hz, 0.6H), 3.39-3.41 (m, 1H), 3.33-3.36 (m, 1H), 3.30 (s, 1.8H), 3.22 (s, 1.2H), 2.55-2.61 (m, 1H), 2.31 (s, 1.2H), 2.12 (s, 1.8H), 2.05 (dd, *J* = 12.39 Hz, *J* = 7.94 Hz, 0.6H), 1.98 (dd, *J* = 12.86 Hz, *J* = 8.10 Hz, 0.4H). ¹³C NMR: δ 228.6, 228.3, 227.6, 227.5, 206.0, 205.9, 153.65, 153.56, 146.4, 144.8, 140.68, 140.60, 136.8, 136.6, 136.5, 136.1, 135.70, 135.66, 134.5, 128.5, 128.4, 128.3, 128.1, 127.9, 105.8, 105.6, 67.4, 62.8, 62.4, 59.5, 59.3, 59.14, 59.13, 58.5, 56.8, 56.6, 52.7, 52.4, 33.9, 33.7, 29.2, 29.1. HRMS (FAB) calcd for C₂₉H₃₀BMoN₇O₆ (M⁺): 681.1405. Found: 681.1415. (±)-**12-endo**: TLC (R_f = 0.69, 1:1 hexanes-EtOAc). IR (cm⁻¹): 3127 (w), 2918 (m), 2482 (m), 1930 (s), 1845 (s), 1702 (s), 1502 (m), 1409 (s), 1366 (m), 1212 (s), 1050 (s). ¹H NMR (a mixture of two rotamers): δ 8.42, 8.40 (s, s, 1H), 7.97 (s, 1H), 7.61, 7.60 (s, s, 2H), 7.49 (d, *J* = 1.91 Hz, 1H), 7.46 (d, *J* = 1.91 Hz, 1H), 7.32-7.44 (m, 6H), 6.22 (s, 1H), 6.19 (s, 1H), 6.15 (t, *J* = 1.90 Hz, 1H), 5.18 (AB quartet, *J* = 12.39 Hz, 0.8H), 5.15 (AB quartet, *J* = 12.38 Hz, 1.2H), 4.94 (s, 0.6H), 4.87 (s, 0.4H), 4.67 (d, *J* = 5.24 Hz, 0.4H), 4.58 (d, *J* = 5.24 Hz, 0.6H), 3.71 (dd, *J* = 7.63 Hz, *J* = 4.28 Hz, 1H), 3.44 (m, 0.6H), 3.37 (m, 1H), 3.31 (m, 0.4H), 3.27 (s, 1.2H), 3.23 (s, 1.8H), 2.60 (m, 1H), 2.38 (s, 1.8H), 2.36 (s, 1.2H), 2.10 (m, 0.4H), 1.94 (m, 0.6H). ¹³C NMR: δ 229.4, 229.0, 227.7, 227.4, 205.32, 205.31, 153.9, 153.4, 146.2, 144.8, 140.3, 140.2, 136.6, 136.5, 136.1, 135.6, 135.4, 134.5, 128.5, 128.1, 105.7, 105.6, 67.6, 59.3, 58.5, 58.2, 57.8, 57.1, 57.0, 56.9, 56.8, 56.0, 53.6, 53.4, 33.0, 32.6, 30.74, 30.67, 29.8. HRMS (FAB) calcd for C₂₉H₃₀BMoN₇O₆ (M⁺): 681.1405. Found: 681.1418.

Following the general procedure, to a solution of the molybdenum complex **7** (100 mg, 0.15 mmol) in CH₂Cl₂ (7.5 mL) was added solid potassium trimethylsilylanolate (57.9 mg, 0.45 mmol). The reaction mixture was stirred at room temperature for 1 h. Me₃OBF₄ (55.5 mg, 0.723 mmol)

was added as a solids and the mixture was then stirred at room temperature for 40 min. Purification by flash chromatography afforded the molybdenum complexes (\pm)-**12-*exo*** (97 mg, 95%) and (\pm)-**12-*endo*** (2 mg, 2%). The diastereoselectivity is strongly related to the trapping time with the Meerwein salt. HPLC analysis of the reaction mixture indicated an *exo* / *endo* ratio of 17:1 in 4 h after addition of Meerwein salts. Prolongation of the reaction time to 15 h resulted in an *exo* / *endo* ratio of 5:1.

(\pm)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*R*,6*S*,7*S*)-(η^3 -7,8,9)-8-benzyloxycarbonyl-7-methoxy-3-oxo-10-azabicyclo[4.3.1]dec-8-en-7-yl]molybdenum [(\pm)-**14**].

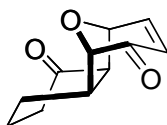


Following the general procedure, to a solution of the molybdenum complex **7** (100 mg, 0.15 mmol) in CH₂Cl₂ (10 mL) was added solid potassium *tert*-butoxide (50.4 mg, 0.45 mmol). The reaction mixture was stirred at room temperature for 1 h. Me₃OBF₄ (67 mg, 0.45 mmol) was added as a solids and the mixture was then stirred at room temperature for 4 h. Purification by flash chromatography afforded the molybdenum complexes (\pm)-**12-*exo*** (23 mg, 23%), (\pm)-**12-*endo*** (3 mg, 3%) and (\pm)-**14** (53 mg, 52%). **14** was often contaminated by small amount of the starting material **7**. However, the pure isomer **14** was obtained by recrystallization from a mixture of dichloromethane and hexanes. (\pm)-**14**: TLC (*R_f* = 0.58, 1:1 hexanes-EtOAc). IR (cm⁻¹): 3127 (w), 2957 (w), 2934 (w), 2482 (m), 1930 (s), 1841 (s), 1968 (s), 1505 (m), 1474 (s), 1305 (s), 1216 (s), 1119 (s), 1050 (s). ¹H NMR (a mixture of two rotamers): δ 8.40 (d, *J* = 2.22 Hz, 0.5H), 8.39 (d, *J* = 2.22 Hz, 0.5H), 7.87 (d, *J* = 2.22 Hz, 0.5H), 7.83 (d, *J* = 2.22 Hz, 0.5H), 7.62 (m, 2H), 7.59 (m, 1H), 7.49 (t, *J* = 2.22 Hz, 1H), 7.33-7.40 (m, 5H), 6.22-6.25 (m, 2H), 6.16-6.18 (m, 1H), 5.20 (s, 1H), 5.18 (AB quartet, *J* = 12.39 Hz, 1H), 5.00 (t, *J* = 3.81 Hz, 0.5H), 4.96 (t, *J* = 3.81 Hz, 0.5H), 4.67 (m, 0.5H), 4.58 (m, 0.5H), 3.89 (dd, *J* = 7.94 Hz, *J* = 2.54 Hz, 0.5H), 3.83 (dd, *J* = 8.26 Hz, *J* = 2.54 Hz, 0.5H), 3.77 (t, *J* = 8.10 Hz, 1H), 3.19 (dd, *J* = 13.65 Hz, *J* = 4.76 Hz, 0.5H), 3.05 (dd, *J* = 13.65 Hz, *J* = 4.45 Hz, 0.5H), 3.03 (s, 1.5H), 2.96 (s, 1.5H), 2.89 (dd, *J* = 11.12 Hz, *J* = 3.18 Hz, 0.5H), 2.86 (dd, *J* = 11.76 Hz, *J* = 3.50 Hz, 0.5H), 2.48-2.69 (m, 2H), 2.01-2.26 (m, 2H). ¹³C NMR: δ 230.1, 229.7, 227.5, 227.2, 211.2, 154.2, 153.7, 146.8, 145.03, 144.99, 140.4, 140.2, 136.7, 136.1, 134.7, 128.6, 128.4, 128.25, 128.19, 127.9, 105.9, 105.8, 105.7, 67.9, 67.8, 58.0, 57.8, 57.6, 56.9, 55.14, 55.09, 54.0, 53.6, 53.1, 47.6, 47.4, 39.9, 39.8, 27.8, 27.0. HRMS (FAB) calcd for C₂₉H₃₁BMoN₇O₆ ([M+H]⁺): 682.1483. Found: 682.1515.

DEMETALLATION OF 1,5-MICHAEL-TYPE ADDUCTS

To an orange solution of the adducts (\pm)-**10**, (+)-**10**, (-)-**10** and (\pm)-**12-exo** (1.0 mmol) and triethylamine (1.5 mmol) in a 3:1 mixture of THF / H₂O (50 mL) at 0 °C (ice bath) open to air was added a solution of ceric ammonium nitrate (8.0 mmol) in H₂O (25 mL) drop-wise over 5 min. After completion of the addition the color faded and a light yellow solution was formed. The ice bath was removed and the reaction mixtures were stirred for an additional 10 min at room temperature and then partitioned between dichloromethane (40 mL) and water (40 mL). The organic layers were washed with brine, dried with Na₂SO₄, and solvents were removed under vacuum to provide the crude products. The crude products were purified by flash chromatography to afford (\pm)-**16**, (+)-**16**, (-)-**16** and (\pm)-**17**, as colorless crystalline solids or oils.

(\pm)-**(1S,2R,7S,8S)-3-Oxo-12-oxatricyclo[6.3.1.0^{2,7}]dodec-10-en-9-one** [(\pm)-**16**], (+)-**(1R,2S,7R,8R)-3-oxo-12-oxatricyclo[6.3.1.0^{2,7}]dodec-10-en-9-one** [(+)-**16**] and (-)-**(1S,2R,7S,8S)-3-oxo-12-oxatricyclo[6.3.1.0^{2,7}]dodec-10-en-9-one** [(-)-**16**].



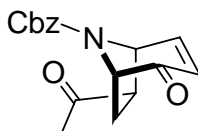
The molybdenum complex (\pm)-**10** (340 mg, 0.60 mmol) was treated with TEA (126 μ L, 0.90 mmol) and CAN (2.59 g, 4.8 mmol) according to the general procedure. Flash chromatography over silica gel eluting with a 1:1 EtOAc/hexanes mixture afforded the tricyclodione (\pm)-**16** (84 mg, 87%) as a colorless solid. (\pm)-**16**: TLC (R_f = 0.39, 1:1 hexanes-EtOAc); mp = 76-77 °C. IR (cm⁻¹): 2949 (m), 2872 (m), 1695(s), 1455 (m), 1378 (m), 1278 (s). ¹H NMR: δ 7.31 (dd, J = 9.85 Hz, J = 4.45 Hz, 1H), 6.04 (dd, J = 9.85 Hz, J = 1.28 Hz, 1H), 5.33 (d, J = 4.45Hz, 1H), 4.30 (s, 1H), 2.70-2.79 (m, 2H), 2.43 (t, J = 6.67Hz, 2H), 2.18-2.25 (m, 1H), 1.83-2.20 (m, 2H), 1.53-1.61 (m, 1H). ¹³C NMR: δ 209.2, 196.0, 151.9, 126.5, 88.0, 76.0, 53.2, 40.3, 38.8, 28.3, 20.4. HRMS (EI) calcd for C₁₁H₁₂O₃ (M⁺): 192.0786. Found: 192.0787.

Similar treatment of (-)-**10** (220 mg, 0.386 mmol) with TEA (80.6 μ L, 0.579 mmol) and CAN (1.67 g, 3.09 mmol) according to the general procedure and subsequent flash chromatography afforded the tricyclodione (+)-**16** (75.4 mg, 97%) as a colorless solid in >99.9 % ee ($[\alpha]_D$ = +274°, c 1.84, CH₂Cl₂). Mp = 83-84 °C.

Similar treatment of (+)-**10** (114 mg, 0.20 mmol) with TEA (41.7 μ L, 0.30 mmol) and CAN (864 mg, 1.6 mmol) according to the general procedure and subsequent flash chromatography afforded the tricyclodione (-)-**16** (35.6 mg, 93%) as a colorless solid in >99.9 % ee ($[\alpha]_D = -270^\circ$, c 1.07, CH_2Cl_2). Mp = 74-75 $^\circ\text{C}$.

The molybdenum complex (\pm)-**10** (57 mg, 0.10 mmol) was treated with CuCl_2 (94.1 mg, 0.70 mmol) in a 2 mL CH_2Cl_2 solution. The reaction mixture was stirred at room temperature for 2 h. The color of the solution changed from red-brown to green. Flash chromatography over silica gel eluting with a 1:1 EtOAc/hexanes mixture afforded the tricyclodione (\pm)-**16** (14 mg, 74%) as a colorless solid.

(\pm)-(1S,5S,6R)- 6-Acetyl-8-benzyloxycarbonyl-8-azabicyclo[3.2.1]oct-3-en-2-one (\pm)-[(\pm)-17**].**



The molybdenum complex (\pm)-**12-*exo*** (1.0 g, 1.47 mmol) was treated with TEA (310 μ L, 2.21 mmol) and CAN (6.45 g, 11.8 mmol) according to the general procedure. Flash chromatography over silica gel eluting with a 1:1 EtOAc/hexanes mixture afforded the tricyclodione (\pm)-**17** (0.38 g, 87%) as a colorless oil. (\pm)-**17**: TLC ($R_f = 0.27$, 1:1 hexanes-EtOAc). IR (cm^{-1}): 3034 (w), 2957 (w), 1702(s), 1409 (s), 1363 (s), 1312 (s), 1100(s). ^1H NMR: δ 7.28-7.38 (m, 6H), 6.03 (dd, $J = 9.84$ Hz, $J = 1.63$ Hz, 1H), 5.11 (AB quartet, $J = 12.38$ Hz, 2H), 5.06 (br s, 1H), 4.80 (br s, 0.4H), 4.73(br s, 0.6H), 3.04 (dd, $J = 9.21$ Hz, $J = 3.81$ Hz, 1H), 2.82 (br s, 0.6H), 2.66 (br s, 0.4H), 2.29, 2.24 (br s, br s, 3.4H), 1.91 (br s, 1.6H). ^{13}C NMR: δ 204.7, 204.5, 195.5, 195.1, 154.3, 154.1, 151.9, 150.9, 135.9, 128.7, 128.4, 128.15, 128.06, 67.9, 64.3, 56.5, 56.0, 54.8, 53.9, 29.9, 28.5, 27.5, 27.3. HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 300.1236. Found: 300.1230.

DETERMINATION OF ENANTIOMERIC EXCESSES BY HPLC

HPLC was performed on an Agilent 1100 Series HPLC chromatograph with ZORBAX Eclipse XDB-C8 (4.6 \times 150 mm, 5 μm), CHIRALPAK AS-RH, CHIRALPAK OD-RH and CHIRALPAK AD-RH columns at room temperature using a Diode Array Detector (DAD) with multiple wavelengths (210 nm, 230 nm, 254 nm, and 280 nm). Samples of products for HPLC analyses were prepared by dissolving several milligrams of pure compound in 2-3 mL of CH_3CN .

One microliter (1 μ L) of the solution was injected for the HPLC analysis. HPLC grade acetonitrile (or acetonitrile containing 0.1% of trifluoroacetic acid) and water were used. Racemic samples were run first to find both enantiomers. The results are listed in Table S1.

Table S1. Determination of % ee by HPLC^b

Entry	Compd	Column ^a	Retention time ^c of (-) isomer	Retention time ^c of (+) isomer
1	1	AS-RH	9.5	8.8
2	5	AS-RH	11.4	9.2
3	10	AS-RH	10.5	9.8
4	16	AD-RH	4.9	6.2

^a CHIRALPAK AS-RH, CHIRALPAK AD-RH. ^b Gradient eluent except for **16**: 40 % of CH₃CN in H₂O (3 min), 65 % of CH₃CN in H₂O (7.5 min), 99 % of CH₃CN in H₂O (9 min); for **16**, 30 % of CH₃CN, 70% of CH₃CN containing 0.1% of CF₃COOH. Flowrate 1 mL/min. DAD detector λ = 254 nm. ^c in minutes.

X-RAY CRYSTALLOGRAPHIC STUDIES.

Crystals of (\pm)-**13** were obtained by recrystallization from dichloromethane and hexanes. A suitable single crystal was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated MoK α (0.71073Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART⁶ software. Frame integration and final cell refinements were done using SAINT⁷ software. The final cell parameters were determined from least-squares refinement on 5054 reflections. The SADABS⁸ program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).⁹ Hydrogen atoms were placed their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij} 's related to the atom's ridden upon. The C-H distances were fixed at 0.93 Å (aromatic and amide), 0.98 Å (methine), 0.97 Å (methylene), or 0.96 Å (methyl). All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the

International Tables for X-ray Crystallography.¹⁰ Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Table S2.

Figure S1. ORTEP drawing of (\pm)-dicarbonyl[hydridotris(1-pyrazolyl)borato][(*1R,6S,7S*)-(η^3 -7,8,9)-7-methoxy-3-oxo-10-oxabicyclo[4.3.1]dec-8-en-7-yl]molybdenum [(\pm)-13**].**

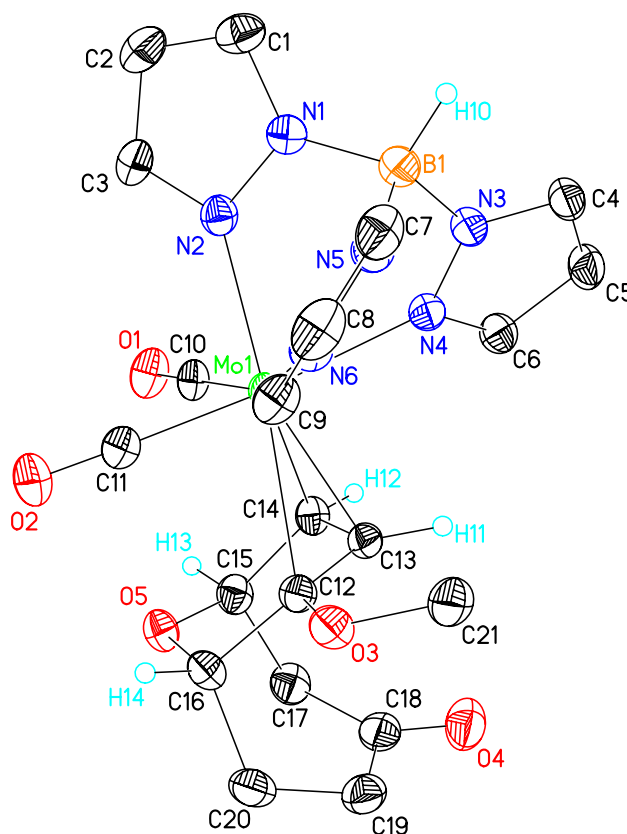


Table S2. Crystal data and structure refinement for (\pm)-**13**.

Identification code	zyq26s
Empirical formula	C ₂₂ H ₂₄ BC ₁₃ MoN ₆ O
Formula weight	665.57
Temperature	173(2) K
Wavelength	0.71073 Å

Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.7750(17) Å	$\alpha = 89.165(4)^\circ$.
	b = 10.558(2) Å	$\beta = 79.929(4)^\circ$.
	c = 15.442(3) Å	$\gamma = 67.509(3)^\circ$.
Volume	1299.3(4) Å ³	
Z	2	
Density (calculated)	1.701 Mg/m ³	
Absorption coefficient	0.860 mm ⁻¹	
F(000)	672	
Crystal size	0.29 x 0.20 x 0.12 mm ³	
Theta range for data collection	2.09 to 28.34°.	
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20	
Reflections collected	18179	
Independent reflections	6482 [R(int) = 0.0254]	
Completeness to theta = 28.34°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9038 and 0.7885	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6482 / 0 / 439	
Goodness-of-fit on F ²	1.121	
Final R indices [I > 2σ(I)]	R1 = 0.0306, wR2 = 0.0750	
R indices (all data)	R1 = 0.0326, wR2 = 0.0762	
Largest diff. peak and hole	1.333 and -0.970 e.Å ⁻³	

Table S3. Atomic coordinates (x 10⁴) and equivalent isotropic displacement

parameters ($\text{\AA}^2 \times 10^3$) for (\pm)-**13**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	13529(3)	5201(2)	3069(2)	26(1)
C(1)	14578(3)	6207(2)	4272(2)	29(1)
C(2)	13958(3)	7392(3)	4803(2)	33(1)
C(3)	12418(3)	8149(2)	4578(1)	27(1)
C(4)	14568(3)	5481(2)	1418(2)	30(1)
C(5)	14060(3)	6455(3)	820(2)	32(1)
C(6)	12590(3)	7458(2)	1275(1)	27(1)
C(7)	11898(3)	3672(2)	3676(2)	31(1)
C(8)	10255(3)	3919(2)	4021(2)	33(1)
C(9)	9378(3)	5294(2)	3903(1)	27(1)
C(10)	9985(3)	9870(2)	3398(1)	23(1)
C(11)	8236(3)	8614(2)	4279(1)	23(1)
C(12)	7333(2)	8123(2)	2741(1)	22(1)
C(13)	8589(2)	8289(2)	2124(1)	20(1)
C(14)	8775(3)	9568(2)	2240(1)	22(1)
C(15)	7171(3)	10814(2)	2542(1)	25(1)
C(16)	5759(2)	9352(2)	3129(1)	24(1)
C(17)	6265(3)	11392(2)	1760(2)	29(1)
C(18)	6104(3)	10329(2)	1182(2)	31(1)
C(19)	5052(3)	9529(2)	1549(2)	32(1)
C(20)	4426(3)	9621(2)	2544(2)	31(1)
C(21)	7949(3)	5888(2)	2114(2)	31(1)
C(1S)	1253(3)	2557(3)	781(2)	34(1)

Cl(1S)	607(1)	2117(1)	1839(1)	39(1)
Cl(2S)	-483(1)	3343(1)	260(1)	51(1)
Cl(3S)	2300(1)	3675(1)	867(1)	54(1)
Mo(1)	9993(1)	8047(1)	3230(1)	18(1)
N(1)	13464(2)	6260(2)	3765(1)	24(1)
N(2)	12101(2)	7473(2)	3952(1)	23(1)
N(3)	13455(2)	5880(2)	2179(1)	24(1)
N(4)	12213(2)	7113(2)	2095(1)	23(1)
N(5)	11988(2)	4844(2)	3353(1)	25(1)
N(6)	10416(2)	5859(2)	3492(1)	24(1)
O(1)	9958(2)	10952(2)	3542(1)	31(1)
O(2)	7222(2)	8918(2)	4913(1)	32(1)
O(3)	6967(2)	6982(2)	2766(1)	26(1)
O(4)	6809(2)	10125(2)	413(1)	41(1)
O(5)	6096(2)	10549(1)	3257(1)	25(1)

Table S4. Bond lengths [\AA] and angles [$^\circ$] for (\pm)-**13**.

B(1)-N(5)	1.530(3)
B(1)-N(1)	1.540(3)
B(1)-N(3)	1.541(3)
B(1)-H(10)	1.05(2)
C(1)-N(1)	1.341(3)
C(1)-C(2)	1.374(3)
C(1)-H(1)	0.88(3)
C(2)-C(3)	1.384(3)

C(2)-H(2)	0.90(3)
C(3)-N(2)	1.337(3)
C(3)-H(3)	0.90(3)
C(4)-N(3)	1.346(3)
C(4)-C(5)	1.368(3)
C(4)-H(4)	0.90(3)
C(5)-C(6)	1.392(3)
C(5)-H(5)	0.89(3)
C(6)-N(4)	1.333(3)
C(6)-H(6)	0.89(2)
C(7)-N(5)	1.353(3)
C(7)-C(8)	1.370(4)
C(7)-H(7)	0.89(3)
C(8)-C(9)	1.386(3)
C(8)-H(8)	0.85(3)
C(9)-N(6)	1.338(3)
C(9)-H(9)	0.93(2)
C(10)-O(1)	1.158(2)
C(10)-Mo(1)	1.943(2)
C(11)-O(2)	1.158(2)
C(11)-Mo(1)	1.951(2)
C(12)-O(3)	1.358(2)
C(12)-C(13)	1.389(3)
C(12)-C(16)	1.521(3)
C(12)-Mo(1)	2.549(2)
C(13)-C(14)	1.438(3)
C(13)-Mo(1)	2.2331(19)

C(13)-H(11)	0.97(2)
C(14)-C(15)	1.517(3)
C(14)-Mo(1)	2.291(2)
C(14)-H(12)	0.90(2)
C(15)-O(5)	1.420(2)
C(15)-C(17)	1.551(3)
C(15)-H(13)	0.94(2)
C(16)-O(5)	1.428(2)
C(16)-C(20)	1.541(3)
C(16)-H(14)	0.94(2)
C(17)-C(18)	1.507(3)
C(17)-H(15)	0.94(3)
C(17)-H(16)	0.93(3)
C(18)-O(4)	1.219(3)
C(18)-C(19)	1.512(3)
C(19)-C(20)	1.530(3)
C(19)-H(17)	0.92(3)
C(19)-H(18)	0.91(3)
C(20)-H(19)	0.96(3)
C(20)-H(20)	0.95(3)
C(21)-O(3)	1.435(3)
C(21)-H(21)	0.99(3)
C(21)-H(22)	0.96(3)
C(21)-H(23)	0.94(3)
C(1S)-Cl(1S)	1.750(2)
C(1S)-Cl(2S)	1.760(3)
C(1S)-Cl(3S)	1.770(3)

C(1S)-H(1S)	0.88(3)
Mo(1)-N(2)	2.2076(17)
Mo(1)-N(6)	2.2377(17)
Mo(1)-N(4)	2.2862(17)
N(1)-N(2)	1.368(2)
N(3)-N(4)	1.363(2)
N(5)-N(6)	1.367(2)
N(5)-B(1)-N(1)	107.32(17)
N(5)-B(1)-N(3)	110.20(17)
N(1)-B(1)-N(3)	107.76(17)
N(5)-B(1)-H(10)	110.9(13)
N(1)-B(1)-H(10)	112.2(13)
N(3)-B(1)-H(10)	108.3(13)
N(1)-C(1)-C(2)	109.0(2)
N(1)-C(1)-H(1)	119.7(17)
C(2)-C(1)-H(1)	131.2(17)
C(1)-C(2)-C(3)	104.6(2)
C(1)-C(2)-H(2)	128.9(19)
C(3)-C(2)-H(2)	126.5(19)
N(2)-C(3)-C(2)	111.0(2)
N(2)-C(3)-H(3)	118.0(16)
C(2)-C(3)-H(3)	131.0(16)
N(3)-C(4)-C(5)	108.81(19)
N(3)-C(4)-H(4)	118.9(17)
C(5)-C(4)-H(4)	132.3(17)
C(4)-C(5)-C(6)	104.5(2)

C(4)-C(5)-H(5) 126.7(19)
C(6)-C(5)-H(5) 128.7(19)
N(4)-C(6)-C(5) 111.0(2)
N(4)-C(6)-H(6) 118.7(16)
C(5)-C(6)-H(6) 130.3(16)
N(5)-C(7)-C(8) 108.6(2)
N(5)-C(7)-H(7) 120.2(18)
C(8)-C(7)-H(7) 131.3(18)
C(7)-C(8)-C(9) 105.3(2)
C(7)-C(8)-H(8) 129.0(19)
C(9)-C(8)-H(8) 125.8(19)
N(6)-C(9)-C(8) 110.6(2)
N(6)-C(9)-H(9) 115.8(15)
C(8)-C(9)-H(9) 133.6(16)
O(1)-C(10)-Mo(1) 176.64(17)
O(2)-C(11)-Mo(1) 177.98(18)
O(3)-C(12)-C(13) 123.97(17)
O(3)-C(12)-C(16) 108.95(16)
C(13)-C(12)-C(16) 120.87(17)
O(3)-C(12)-Mo(1) 119.92(13)
C(13)-C(12)-Mo(1) 60.92(11)
C(16)-C(12)-Mo(1) 114.33(13)
C(12)-C(13)-C(14) 114.08(17)
C(12)-C(13)-Mo(1) 86.15(12)
C(14)-C(13)-Mo(1) 73.66(11)
C(12)-C(13)-H(11) 121.7(14)
C(14)-C(13)-H(11) 124.2(14)

Mo(1)-C(13)-H(11)110.3(14)
C(13)-C(14)-C(15)116.32(17)
C(13)-C(14)-Mo(1) 69.30(11)
C(15)-C(14)-Mo(1)120.65(13)
C(13)-C(14)-H(12)115.5(15)
C(15)-C(14)-H(12)112.3(15)
Mo(1)-C(14)-H(12)116.3(15)
O(5)-C(15)-C(14) 112.43(16)
O(5)-C(15)-C(17) 112.09(18)
C(14)-C(15)-C(17)111.02(17)
O(5)-C(15)-H(13) 102.2(15)
C(14)-C(15)-H(13)112.4(15)
C(17)-C(15)-H(13)106.2(15)
O(5)-C(16)-C(12) 112.39(16)
O(5)-C(16)-C(20) 111.34(17)
C(12)-C(16)-C(20)109.74(17)
O(5)-C(16)-H(14) 103.8(14)
C(12)-C(16)-H(14)110.4(14)
C(20)-C(16)-H(14)109.0(14)
C(18)-C(17)-C(15)114.76(17)
C(18)-C(17)-H(15)107.6(16)
C(15)-C(17)-H(15)108.7(16)
C(18)-C(17)-H(16)109.3(17)
C(15)-C(17)-H(16)108.8(16)
H(15)-C(17)-H(16)107(2)
O(4)-C(18)-C(17) 119.9(2)
O(4)-C(18)-C(19) 119.9(2)

C(17)-C(18)-C(19)120.2(2)
C(18)-C(19)-C(20)118.88(19)
C(18)-C(19)-H(17)106.4(16)
C(20)-C(19)-H(17)111.6(16)
C(18)-C(19)-H(18)104(2)
C(20)-C(19)-H(18)111.0(19)
H(17)-C(19)-H(18)104(2)
C(19)-C(20)-C(16)116.34(18)
C(19)-C(20)-H(19)111.7(15)
C(16)-C(20)-H(19)105.9(15)
C(19)-C(20)-H(20)106.8(16)
C(16)-C(20)-H(20)105.4(15)
H(19)-C(20)-H(20)111(2)
O(3)-C(21)-H(21) 110.3(16)
O(3)-C(21)-H(22) 111.9(15)
H(21)-C(21)-H(22)110(2)
O(3)-C(21)-H(23) 105.6(17)
H(21)-C(21)-H(23)110(2)
H(22)-C(21)-H(23)109(2)
Cl(1S)-C(1S)-Cl(2S)110.44(14)
Cl(1S)-C(1S)-Cl(3S)108.71(13)
Cl(2S)-C(1S)-Cl(3S)110.69(14)
Cl(1S)-C(1S)-H(1S)109.1(19)
Cl(2S)-C(1S)-H(1S)108.7(19)
Cl(3S)-C(1S)-H(1S)109.1(19)
C(10)-Mo(1)-C(11) 83.61(8)
C(10)-Mo(1)-N(2) 82.19(7)

C(11)-Mo(1)-N(2) 95.47(7)
C(10)-Mo(1)-C(13)102.65(8)
C(11)-Mo(1)-C(13)103.86(8)
N(2)-Mo(1)-C(13)160.45(7)
C(10)-Mo(1)-N(6)158.53(7)
C(11)-Mo(1)-N(6) 88.82(7)
N(2)-Mo(1)-N(6) 78.57(6)
C(13)-Mo(1)-N(6) 98.66(7)
C(10)-Mo(1)-N(4)101.57(7)
C(11)-Mo(1)-N(4)172.20(7)
N(2)-Mo(1)-N(4) 79.61(6)
C(13)-Mo(1)-N(4) 80.85(7)
N(6)-Mo(1)-N(4) 84.29(6)
C(10)-Mo(1)-C(14)65.75(8)
C(11)-Mo(1)-C(14)101.93(8)
N(2)-Mo(1)-C(14)141.07(7)
C(13)-Mo(1)-C(14)37.05(7)
N(6)-Mo(1)-C(14)135.66(7)
N(4)-Mo(1)-C(14) 85.59(7)
C(10)-Mo(1)-C(12)112.16(7)
C(11)-Mo(1)-C(12)73.90(7)
N(2)-Mo(1)-C(12)160.40(6)
C(13)-Mo(1)-C(12)32.92(7)
N(6)-Mo(1)-C(12) 84.69(6)
N(4)-Mo(1)-C(12)108.97(6)
C(14)-Mo(1)-C(12)58.40(7)
C(1)-N(1)-N(2) 109.40(17)

C(1)-N(1)-B(1)	130.13(19)
N(2)-N(1)-B(1)	120.46(16)
C(3)-N(2)-N(1)	105.97(17)
C(3)-N(2)-Mo(1)	131.88(15)
N(1)-N(2)-Mo(1)	122.07(12)
C(4)-N(3)-N(4)	109.70(17)
C(4)-N(3)-B(1)	128.95(18)
N(4)-N(3)-B(1)	121.14(16)
C(6)-N(4)-N(3)	105.95(17)
C(6)-N(4)-Mo(1)	134.25(15)
N(3)-N(4)-Mo(1)	119.63(12)
C(7)-N(5)-N(6)	109.22(18)
C(7)-N(5)-B(1)	129.23(19)
N(6)-N(5)-B(1)	120.09(16)
C(9)-N(6)-N(5)	106.39(17)
C(9)-N(6)-Mo(1)	131.07(15)
N(5)-N(6)-Mo(1)	121.86(13)
C(12)-O(3)-C(21)	117.46(16)
C(15)-O(5)-C(16)	115.07(15)

Table S5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (\pm)-**13**. 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}
B(1)	25(1)	24(1)	28(1)	-1(1)	-6(1)	-6(1)
C(1)	28(1)	36(1)	29(1)	10(1)	-10(1)	-16(1)
C(2)	39(1)	42(1)	26(1)	5(1)	-12(1)	-24(1)

C(3)	34(1)	31(1)	20(1)	0(1)	-4(1)	-17(1)
C(4)	23(1)	31(1)	31(1)	-9(1)	-1(1)	-8(1)
C(5)	28(1)	41(1)	24(1)	-6(1)	4(1)	-14(1)
C(6)	25(1)	32(1)	23(1)	1(1)	-1(1)	-12(1)
C(7)	44(1)	19(1)	30(1)	1(1)	-11(1)	-11(1)
C(8)	52(1)	28(1)	30(1)	6(1)	-12(1)	-25(1)
C(9)	34(1)	28(1)	26(1)	3(1)	-7(1)	-18(1)
C(10)	27(1)	24(1)	18(1)	-1(1)	-1(1)	-11(1)
C(11)	28(1)	20(1)	23(1)	2(1)	-5(1)	-12(1)
C(12)	22(1)	21(1)	24(1)	-1(1)	-5(1)	-8(1)
C(13)	21(1)	19(1)	20(1)	0(1)	-4(1)	-6(1)
C(14)	24(1)	22(1)	20(1)	1(1)	-2(1)	-9(1)
C(15)	28(1)	20(1)	26(1)	-1(1)	-4(1)	-8(1)
C(16)	20(1)	23(1)	26(1)	-1(1)	-1(1)	-7(1)
C(17)	31(1)	21(1)	31(1)	2(1)	-7(1)	-6(1)
C(18)	29(1)	25(1)	32(1)	2(1)	-13(1)	-1(1)
C(19)	29(1)	29(1)	36(1)	-2(1)	-13(1)	-6(1)
C(20)	21(1)	30(1)	40(1)	-1(1)	-6(1)	-8(1)
C(21)	34(1)	24(1)	37(1)	-5(1)	-8(1)	-13(1)
C(1S)	36(1)	33(1)	26(1)	2(1)	-1(1)	-8(1)
Cl(1S)	44(1)	40(1)	32(1)	12(1)	-5(1)	-17(1)
Cl(2S)	51(1)	63(1)	34(1)	6(1)	-17(1)	-13(1)
Cl(3S)	40(1)	53(1)	71(1)	15(1)	-1(1)	-25(1)
Mo(1)	19(1)	17(1)	18(1)	-1(1)	-1(1)	-8(1)
N(1)	24(1)	24(1)	24(1)	1(1)	-5(1)	-9(1)
N(2)	24(1)	22(1)	22(1)	-1(1)	-3(1)	-10(1)
N(3)	21(1)	25(1)	25(1)	-3(1)	-2(1)	-7(1)

N(4)	22(1)	25(1)	23(1)	-1(1)	-4(1)	-9(1)
N(5)	29(1)	19(1)	28(1)	1(1)	-7(1)	-8(1)
N(6)	25(1)	21(1)	27(1)	2(1)	-6(1)	-10(1)
O(1)	46(1)	26(1)	27(1)	1(1)	-5(1)	-20(1)
O(2)	34(1)	34(1)	25(1)	-2(1)	4(1)	-13(1)
O(3)	24(1)	23(1)	34(1)	-2(1)	-3(1)	-12(1)
O(4)	49(1)	42(1)	29(1)	-2(1)	-6(1)	-14(1)
O(5)25(1)	21(1)	25(1)	-3(1)	0(1)	-7(1)	

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (\pm)-**13**.

	x	y	z	U(eq)
H(1)	15510(30)	5470(30)	4237(16)	27(6)
H(2)	14420(40)	7630(30)	5210(20)	42(8)
H(3)	11650(30)	8980(30)	4778(16)	23(6)
H(4)	15460(30)	4680(30)	1384(18)	34(7)
H(5)	14550(40)	6420(30)	260(20)	41(8)
H(6)	11910(30)	8250(30)	1101(16)	23(6)
H(7)	12830(30)	2920(30)	3654(18)	35(7)
H(8)	9830(30)	3370(30)	4260(18)	36(7)
H(9)	8250(30)	5870(30)	4038(16)	25(6)
H(10)	14640(30)	4310(30)	2999(16)	26(6)
H(11)	9250(30)	7600(20)	1649(16)	24(6)

H(12)	9480(30)	9750(20)	1805(16)	23(6)
H(13)	7370(30)	11530(30)	2779(16)	23(6)
H(14)	5320(30)	9190(20)	3700(16)	22(6)
H(15)	6860(30)	11840(30)	1404(17)	32(7)
H(16)	5200(30)	12050(30)	1981(17)	31(7)
H(17)	5650(30)	8640(30)	1336(17)	28(6)
H(18)	4180(40)	9830(30)	1250(20)	49(8)
H(19)	3580(30)	10500(30)	2743(16)	25(6)
H(20)	4000(30)	8920(30)	2661(17)	29(6)
H(21)	7710(30)	6170(30)	1524(19)	34(7)
H(22)	9130(30)	5590(30)	2116(16)	26(6)
H(23)	7610(30)	5160(30)	2271(18)	38(7)
H(1S)	1950(40)	1810(30)	466(19)	41(8)

Table S7. Torsion angles [$^{\circ}$] for (\pm)-**13**.

N(1)-C(1)-C(2)-C(3)	-0.2(2)
C(1)-C(2)-C(3)-N(2)	0.3(3)
N(3)-C(4)-C(5)-C(6)	0.5(3)
C(4)-C(5)-C(6)-N(4)	-0.6(3)
N(5)-C(7)-C(8)-C(9)	-1.1(2)
C(7)-C(8)-C(9)-N(6)	1.2(3)
O(3)-C(12)-C(13)-C(14)	-178.47(17)
C(16)-C(12)-C(13)-C(14)	32.3(3)
Mo(1)-C(12)-C(13)-C(14)	-70.19(15)
O(3)-C(12)-C(13)-Mo(1)	-108.28(18)
C(16)-C(12)-C(13)-Mo(1)	102.53(17)

C(12)-C(13)-C(14)-C(15)	-36.9(2)
Mo(1)-C(13)-C(14)-C(15)	-114.90(16)
C(12)-C(13)-C(14)-Mo(1)	78.02(15)
C(13)-C(14)-C(15)-O(5)	46.7(2)
Mo(1)-C(14)-C(15)-O(5)	-33.8(2)
C(13)-C(14)-C(15)-C(17)	-79.8(2)
Mo(1)-C(14)-C(15)-C(17)	-160.28(14)
O(3)-C(12)-C(16)-O(5)	170.58(16)
C(13)-C(12)-C(16)-O(5)	-36.1(3)
Mo(1)-C(12)-C(16)-O(5)	33.3(2)
O(3)-C(12)-C(16)-C(20)	-65.0(2)
C(13)-C(12)-C(16)-C(20)	88.4(2)
Mo(1)-C(12)-C(16)-C(20)	157.81(14)
O(5)-C(15)-C(17)-C(18)	-79.6(2)
C(14)-C(15)-C(17)-C(18)	47.0(3)
C(15)-C(17)-C(18)-O(4)	-116.0(2)
C(15)-C(17)-C(18)-C(19)	64.9(3)
O(4)-C(18)-C(19)-C(20)	169.8(2)
C(17)-C(18)-C(19)-C(20)	-11.1(3)
C(18)-C(19)-C(20)-C(16)	-51.1(3)
O(5)-C(16)-C(20)-C(19)	82.0(2)
C(12)-C(16)-C(20)-C(19)	-43.1(3)
O(1)-C(10)-Mo(1)-C(11)	31(3)
O(1)-C(10)-Mo(1)-N(2)	-65(3)
O(1)-C(10)-Mo(1)-C(13)	134(3)
O(1)-C(10)-Mo(1)-N(6)	-39(3)
O(1)-C(10)-Mo(1)-N(4)	-143(3)

O(1)-C(10)-Mo(1)-C(14)	138(3)
O(1)-C(10)-Mo(1)-C(12)	101(3)
O(2)-C(11)-Mo(1)-C(10)	-122(5)
O(2)-C(11)-Mo(1)-N(2)	-40(5)
O(2)-C(11)-Mo(1)-C(13)	137(5)
O(2)-C(11)-Mo(1)-N(6)	38(5)
O(2)-C(11)-Mo(1)-N(4)	10(5)
O(2)-C(11)-Mo(1)-C(14)	175(5)
O(2)-C(11)-Mo(1)-C(12)	123(5)
C(12)-C(13)-Mo(1)-C(10)	-111.40(12)
C(14)-C(13)-Mo(1)-C(10)	5.08(13)
C(12)-C(13)-Mo(1)-C(11)	-24.96(13)
C(14)-C(13)-Mo(1)-C(11)	91.53(12)
C(12)-C(13)-Mo(1)-N(2)	146.16(18)
C(14)-C(13)-Mo(1)-N(2)	-97.4(2)
C(12)-C(13)-Mo(1)-N(6)	65.96(12)
C(14)-C(13)-Mo(1)-N(6)	-177.56(11)
C(12)-C(13)-Mo(1)-N(4)	148.70(12)
C(14)-C(13)-Mo(1)-N(4)	-94.82(12)
C(12)-C(13)-Mo(1)-C(14)	-116.48(16)
C(14)-C(13)-Mo(1)-C(12)	116.48(16)
C(13)-C(14)-Mo(1)-C(10)	-174.56(14)
C(15)-C(14)-Mo(1)-C(10)	-65.47(16)
C(13)-C(14)-Mo(1)-C(11)	-97.26(12)
C(15)-C(14)-Mo(1)-C(11)	11.83(17)
C(13)-C(14)-Mo(1)-N(2)	148.11(12)
C(15)-C(14)-Mo(1)-N(2)	-102.80(17)

C(15)-C(14)-Mo(1)-C(13)	109.1(2)
C(13)-C(14)-Mo(1)-N(6)	3.46(16)
C(15)-C(14)-Mo(1)-N(6)	112.54(16)
C(13)-C(14)-Mo(1)-N(4)	80.65(11)
C(15)-C(14)-Mo(1)-N(4)	-170.26(16)
C(13)-C(14)-Mo(1)-C(12)	-34.83(11)
C(15)-C(14)-Mo(1)-C(12)	74.26(16)
O(3)-C(12)-Mo(1)-C(10)	-166.51(14)
C(13)-C(12)-Mo(1)-C(10)	78.80(13)
C(16)-C(12)-Mo(1)-C(10)	-34.33(16)
O(3)-C(12)-Mo(1)-C(11)	-90.56(15)
C(13)-C(12)-Mo(1)-C(11)	154.76(13)
C(16)-C(12)-Mo(1)-C(11)	41.63(14)
O(3)-C(12)-Mo(1)-N(2)	-31.6(3)
C(13)-C(12)-Mo(1)-N(2)	-146.24(18)
C(16)-C(12)-Mo(1)-N(2)	100.6(2)
O(3)-C(12)-Mo(1)-C(13)	114.7(2)
C(16)-C(12)-Mo(1)-C(13)	-113.13(19)
O(3)-C(12)-Mo(1)-N(6)	-0.26(15)
C(13)-C(12)-Mo(1)-N(6)	-114.94(12)
C(16)-C(12)-Mo(1)-N(6)	131.93(14)
O(3)-C(12)-Mo(1)-N(4)	81.83(15)
C(13)-C(12)-Mo(1)-N(4)	-32.85(13)
C(16)-C(12)-Mo(1)-N(4)	-145.98(13)
O(3)-C(12)-Mo(1)-C(14)	153.96(17)
C(13)-C(12)-Mo(1)-C(14)	39.28(12)
C(16)-C(12)-Mo(1)-C(14)	-73.85(14)

C(2)-C(1)-N(1)-N(2)	-0.1(2)
C(2)-C(1)-N(1)-B(1)	-179.1(2)
N(5)-B(1)-N(1)-C(1)	121.9(2)
N(3)-B(1)-N(1)-C(1)	-119.5(2)
N(5)-B(1)-N(1)-N(2)	-57.1(2)
N(3)-B(1)-N(1)-N(2)	61.5(2)
C(2)-C(3)-N(2)-N(1)	-0.3(2)
C(2)-C(3)-N(2)-Mo(1)	-176.89(15)
C(1)-N(1)-N(2)-C(3)	0.2(2)
B(1)-N(1)-N(2)-C(3)	179.44(18)
C(1)-N(1)-N(2)-Mo(1)	177.20(13)
B(1)-N(1)-N(2)-Mo(1)	-3.6(2)
C(10)-Mo(1)-N(2)-C(3)	31.72(19)
C(11)-Mo(1)-N(2)-C(3)	-51.04(19)
C(13)-Mo(1)-N(2)-C(3)	137.6(2)
N(6)-Mo(1)-N(2)-C(3)	-138.72(19)
N(4)-Mo(1)-N(2)-C(3)	135.07(19)
C(14)-Mo(1)-N(2)-C(3)	65.6(2)
C(12)-Mo(1)-N(2)-C(3)	-106.9(2)
C(10)-Mo(1)-N(2)-N(1)	-144.35(15)
C(11)-Mo(1)-N(2)-N(1)	132.88(15)
C(13)-Mo(1)-N(2)-N(1)	-38.5(3)
N(6)-Mo(1)-N(2)-N(1)	45.21(14)
N(4)-Mo(1)-N(2)-N(1)	-41.00(14)
C(14)-Mo(1)-N(2)-N(1)	-110.43(16)
C(12)-Mo(1)-N(2)-N(1)	77.1(2)
C(5)-C(4)-N(3)-N(4)	-0.3(2)

C(5)-C(4)-N(3)-B(1)	-174.9(2)
N(5)-B(1)-N(3)-C(4)	-122.0(2)
N(1)-B(1)-N(3)-C(4)	121.1(2)
N(5)-B(1)-N(3)-N(4)	63.9(2)
N(1)-B(1)-N(3)-N(4)	-53.0(2)
C(5)-C(6)-N(4)-N(3)	0.5(2)
C(5)-C(6)-N(4)-Mo(1)	-174.65(15)
C(4)-N(3)-N(4)-C(6)	-0.1(2)
B(1)-N(3)-N(4)-C(6)	175.00(18)
C(4)-N(3)-N(4)-Mo(1)	175.85(13)
B(1)-N(3)-N(4)-Mo(1)	-9.0(2)
C(10)-Mo(1)-N(4)-C(6)	-58.2(2)
C(11)-Mo(1)-N(4)-C(6)	170.7(5)
N(2)-Mo(1)-N(4)-C(6)	-137.9(2)
C(13)-Mo(1)-N(4)-C(6)	43.0(2)
N(6)-Mo(1)-N(4)-C(6)	142.7(2)
C(14)-Mo(1)-N(4)-C(6)	5.9(2)
C(12)-Mo(1)-N(4)-C(6)	60.3(2)
C(10)-Mo(1)-N(4)-N(3)	127.22(14)
C(11)-Mo(1)-N(4)-N(3)	-3.9(6)
N(2)-Mo(1)-N(4)-N(3)	47.50(14)
C(13)-Mo(1)-N(4)-N(3)	-131.63(15)
N(6)-Mo(1)-N(4)-N(3)	-31.88(14)
C(14)-Mo(1)-N(4)-N(3)	-168.65(14)
C(12)-Mo(1)-N(4)-N(3)	-114.26(14)
C(8)-C(7)-N(5)-N(6)	0.6(2)
C(8)-C(7)-N(5)-B(1)	166.6(2)

N(1)-B(1)-N(5)-C(7)	-108.5(2)
N(3)-B(1)-N(5)-C(7)	134.5(2)
N(1)-B(1)-N(5)-N(6)	56.2(2)
N(3)-B(1)-N(5)-N(6)	-60.9(2)
C(8)-C(9)-N(6)-N(5)	-0.8(2)
C(8)-C(9)-N(6)-Mo(1)	-171.25(15)
C(7)-N(5)-N(6)-C(9)	0.1(2)
B(1)-N(5)-N(6)-C(9)	-167.35(18)
C(7)-N(5)-N(6)-Mo(1)	171.64(13)
B(1)-N(5)-N(6)-Mo(1)	4.2(2)
C(10)-Mo(1)-N(6)-C(9)	96.6(3)
C(11)-Mo(1)-N(6)-C(9)	27.53(19)
N(2)-Mo(1)-N(6)-C(9)	123.36(19)
C(13)-Mo(1)-N(6)-C(9)	-76.30(19)
N(4)-Mo(1)-N(6)-C(9)	-156.12(19)
C(14)-Mo(1)-N(6)-C(9)	-78.4(2)
C(12)-Mo(1)-N(6)-C(9)	-46.40(18)
C(10)-Mo(1)-N(6)-N(5)	-72.6(3)
C(11)-Mo(1)-N(6)-N(5)	-141.67(15)
N(2)-Mo(1)-N(6)-N(5)	-45.84(14)
C(13)-Mo(1)-N(6)-N(5)	114.49(15)
N(4)-Mo(1)-N(6)-N(5)	34.68(15)
C(14)-Mo(1)-N(6)-N(5)	112.39(15)
C(12)-Mo(1)-N(6)-N(5)	144.39(15)
C(13)-C(12)-O(3)-C(21)	0.1(3)
C(16)-C(12)-O(3)-C(21)	152.46(18)
Mo(1)-C(12)-O(3)-C(21)	-73.1(2)

C(14)-C(15)-O(5)-C(16)	-50.8(2)
C(17)-C(15)-O(5)-C(16)	75.1(2)
C(12)-C(16)-O(5)-C(15)	44.8(2)
C(20)-C(16)-O(5)-C(15)	-78.8(2)

REFERENCES

1. Sloan, T. E., *Top. Stereochem.* **1981**, 12, 1-36.
2. Yin, J.; Liebeskind, L. S., *J. Am. Chem. Soc.* **1999**, 121, 5811-5812.
3. Moretto, A. F.; Liebeskind, L. S., *J. Org. Chem.* **2000**, 65, (22), 7445-7455.
4. Malinakova, H. C.; Liebeskind, L. S., *Org. Lett.* **2000**, 2, (24), 3909-3911.
5. The full details of the Mukaiyama-Michael additions to η^3 -pyranyl and η^3 -pyridinylmolybdenum π -complexes will be published in a full paper together with Mukaiyama aldol reactions.
6. SMART Version 5.628, 2003, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
7. SAINT Version 6.36A, 2002, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
8. SADABS Version 2.08, 2003, George Sheldrick, University of Göttingen.
9. SHELXTL V6.12, 2002, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
10. A. J. C. Wilson (ed), *International Tables for X-ray Crystallography, Volume C*. Kynoch, Academic Publishers, Dordrecht, 1992, Tables 6.1.1.4 (pp. 500-502) and 4.2.6.8 (pp. 219-222).