Supporting Information for

η^3 -Pyranyl and η^3 -Pyridinyl Molybdenum π -Complexes as Chiral Scaffolds for the Enantioselective Construction of Substituted Oxa- and Aza[3.3.1]bicyclics: First Enantio- and Regiocontrolled [5+3] Cycloaddition Reactions

by Ramón Gómez Arrayás and Lanny S. Liebeskind*

Sanford S. Atwood Chemistry Center, Emory University 1515 Pierce Drive, Atlanta, GA, 30322

GENERAL METHODS

All ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 MHz (400 MHz ^1H , 100 MHz ^{13}C) at room temperature in CDCl_3 with internal CHCl_3 as the reference (7.26 ppm for ^1H and 77.0 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). Optical rotations were measured at 25 °C with a Perkin-Elmer 241MC polarimeter. Melting points (mp) were taken in open capillary tubes on a Thomas Hoover capillary melting point apparatus. Analytical thin-layer chromatography (TLC) was carried out on commercial Aldrich aluminum-supported silica gel plates (thickness: 200 μm) with fluorescent indicator (F-254). Visualization was accomplished by UV light or staining with 5% phosphomolybdic acid in ethanol. Column chromatography was performed by the method of Still¹ with 32-63 μm silica gel (Woelm). HPLC was performed on a Millipore WatersTM 60C HPLC spectrometer with a CHIRALPAK AD column at room temperature using a WatersTM 486 UV detector (HPLC grade isopropanol and hexane were used). Dichloromethane (HPLC grade) and THF (99%+) were purchased from Merck and Aldrich, respectively, and dried over 4Å molecular sieves (2 weeks) before used. Dry diethyl ether was purchased from Mallinckrodt and used as received. CH_3CN was purchased from Aldrich and distilled from phosphorus pentoxide before use. TMSOTf and $\text{Sc}(\text{OTf})_3$ were purchased from Aldrich, Et_3N from Lancaster and PDC from Across; all were used as received.

¹ Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Preparation of Complex (±)-1a

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4,5)-2-ethoxypyr-3-en-2-

yl]molybdenum (II).² To a solution of compound **I** (4.0 g, 8.66 mmol) in dry CH₂Cl₂ (160 mL) was added Et₃OPF₆ (2.26 g, 9.1 mmol) as a solid in one portion. The mixture was stirred at room temperature for 14 h, the solvent was evaporated and the resulting orange solid was triturated with ether to afford the corresponding Mo-cation **II** (5.2 g, 95%) as an orange solid. Mp = 187-188 °C (decomp, CH₂Cl₂/Et₂O). IR (cm⁻¹): 2497 (w), 1988 (s), 1911 (s), 1529 (m), 1502 (m), 1409 (m), 1305 (m), 1220 (m), 1054 (m), 837 (s). ¹H NMR [(CD₃)₂CO, 300 MHz]: δ 8.75 (d, *J* = 1.8 Hz, 1H), 8.18 (d, *J* = 2.1 Hz, 1H), 8.02 (d, *J* = 2.1 Hz, 1H), 7.94 (t, *J* = 2.5 Hz, 2H), 7.90 (d, *J* = 2.1 Hz, 1H), 6.51 (t, *J* = 2.1 Hz, 1H), 6.41 (t, *J* = 2.1 Hz, 1H), 6.38 (t, *J* = 2.1 Hz, 1H), 5.48 (m, 1H), 5.22 (dd, *J* = 14.4, 1.8 Hz, 1H), 5.15 (dd, *J* = 7.2, 6.6 Hz, 1H), 4.89 (dd, *J* = 5.4, 1.8 Hz, 1H), 4.86-4.79 (m, 3H), 1.52 (t, *J* = 7.2 Hz, 3H). ¹³C NMR [(CD₃)₂CO, 75.5 MHz]: δ 222.9, 222.7, 185.8, 148.4, 145.9, 142.9, 138.6, 138.5, 137.0, 108.1, 107.6, 107.5, 74.6, 74.3, 71.9, 61.4, 56.2, 14.3. Anal. Calcd for C₁₈H₂₀N₆O₄BF₆MoP: C, 33.99; H, 3.17; N, 13.21. Found: C, 33.88; H, 3.14; N, 13.11.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(3,4,5)-2-ethoxypyr-3-en-2-

yl]molybdenum (III).² A suspension of **II** (1.47 g, 2.32 mmol) in MeOH (39 mL) was treated at 0 °C with NaBH₄ (122 mg, 3.2 mmol). The mixture was stirred at 0 °C for 45 min and it was immediately concentrated to dryness in an evaporator. The residue was stirred with CH₂Cl₂ (30 mL) for 15 min and the mixture was passed through a pad of silica gel (2.5:1 *n*-hexanes-EOAc as eluent). After concentration of the filtrate, **III** (1.09 g, 96%) was obtained as a yellow solid. TLC (5:1 *n*-hexanes-EtOAc, R_f = 0.30); mp = 186-188 °C. IR (cm⁻¹): 2976 (w), 2486 (w), 1953 (s), 1861 (s), 1505 (w), 1409 (m), 1305 (m), 1220 (m), 1123 (w), 1050 (s). ¹H NMR: δ 8.59 (d, *J* = 2.2 Hz, 1H), 7.91 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 2H),

7.51 (d, $J = 2.2$ Hz, 1H), 6.29 (t, $J = 2.2$ Hz, 1H), 6.17 (t, $J = 2.2$ Hz, 1H), 6.16 (t, $J = 2.2$ Hz, 1H), 4.71 (s, 1H), 4.19 (dd, $J = 7.3, 1.3$ Hz, 1H), 4.01 (m, 1H), 3.94 (m, 1H), 3.82 (dq, $J = 9.5, 7.0$ Hz, 1H), 3.68 (t, $J = 7.3$ Hz, 1H), 3.49 (dq, $J = 9.5, 7.0$ Hz, 1H), 1.22 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR: δ 227.5, 224.8, 146.8, 143.4, 140.6, 135.9, 135.8, 134.3, 105.9, 105.3, 105.2, 96.2, 73.4, 66.1, 65.1, 63.4, 62.3, 15.2. Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{N}_6\text{O}_4\text{BMo}$: C, 43.93; H, 4.30; N, 17.08. Found: C, 43.76; H, 4.32; N, 16.98.

($\pm$)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η -(2,3,4)-3,5-pyradien-2-yl]molybdenum

(1a). To a solution of **III** (1.0 g, 2.1 mmol) in dry CH_2Cl_2 (18 mL) at -30 °C was added Ph_3CPF_6 (945 mg, 2.52 mmol) as a solid in one portion. The mixture was stirred for 2 h at -30 °C and then it was slowly allowed to reach 0 °C. Addition of dry diethyl ether (30 mL) induced precipitation of an orange solid. The solvents were removed via cannula (covered with a piece of filter paper to prevent the removal of the solid). The remaining solid was washed with dry diethyl ether (2 x 20 mL), dried under vacuum for 1.5 h and re-dissolved in CH_2Cl_2 (22 mL). The solution was cooled to -30 °C, treated with Et_3N (439 μL , 3.15 mmol) and it was slowly allowed to reach room temperature. The reaction mixture was concentrated and the residue was purified by flash chromatography (3:1 *n*-hexanes- CH_2Cl_2) to afford **1a** (651 mg, 72%) as a yellow solid. TLC (9:1 *n*-hexanes-EtOAc, $R_f = 0.29$); mp = 186 – 188 °C with decomp (CH_2Cl_2 -*n*-hexanes). IR (cm^{-1}): 3150 (w), 3130 (w), 2482 (w), 1934 (s), 1849 (s), 1505 (w), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^1H NMR (CDCl_3): δ 8.24 (d, $J = 1.9$ Hz, 1H), 8.02 (d, $J = 1.9$ Hz, 1H), 7.76 (d, $J = 2.2$ Hz, 1H), 7.62 (d, $J = 2.2$ Hz, 1H), 7.60 (d, $J = 1.9$ Hz, 1H), 7.53 (dd, $J = 4.4, 2.5$ Hz, 1H), 7.50 (d, $J = 2.5$ Hz, 1H), 6.25 (t, $J = 2.2$ Hz, 1H), 6.21 (q, $J = 2.5$ Hz, 1H), 5.98 (td, $J = 5.6, 1.0$ Hz, 1H), 5.92 (d, $J = 5.6$ Hz, 1H), 4.73 (td, $J = 5.9, 2.5$ Hz, 1H), 2.45 (t, $J = 5.9$ Hz, 1H). ^{13}C NMR (CDCl_3): δ 229.6, 222.7, 145.9, 142.4, 140.5, 136.2, 135.9, 135.6, 134.4, 110.0, 109.4, 105.6, 105.5, 105.4, 60.0, 46.1.

Preparation of Complex ($\pm$)-1d

² This compound was described within the Supporting Information for: Alcudia, A.; Gómez Arrayás, R.; Liebeskind, L. S. *J. Org. Chem.* **2002**, 67, 5773-5778.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η -(3,4,5)-2-ethoxy-2-phenylpyr-3-en-2-yl]molybdenum (IV).² A suspension of **II**² (1.47 g, 2.32 mmol) in THF (24 mL) was treated at –78 °C with a 1.0 M solution of phenylmagnesium bromide in THF (2.88 mL, 2.88 mmol). The mixture was allowed to reach 0 °C over 2 h. The resulting yellow-orange solution was passed through a pad of silica gel with diethyl ether. After concentration, the residue was purified by flash chromatography (1:1 *n*-hexanes-CH₂Cl₂) to afford **IV** (996 mg, 76%) as a yellow solid. TLC (8:1 *n*-hexanes-EtOAc, *R_f* = 0.30); mp = 199–200 °C. IR (cm^{–1}): 2976 (w), 2930 (w), 2887 (w), 2482 (w), 1953 (s), 1861 (s), 1505 (w), 1409 (m), 1305 (m), 1220 (m), 1119 (m), 1050 (s). ¹H NMR (CDCl₃): δ 8.63 (d, *J* = 1.9 Hz, 1H), 8.10 (d, *J* = 1.9 Hz, 1H), 7.66–7.64 (m, 2H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.40 (m, 2H), 7.32 (m, 1H), 6.30 (t, *J* = 2.2 Hz, 1H), 6.24 (t, *J* = 2.2 Hz, 1H), 6.15 (t, *J* = 2.2 Hz, 1H), 4.87 (dd, *J* = 7.5, 2.2 Hz, 1H), 4.16 (m, 1H), 4.05–3.99 (m, 2H), 3.82 (t, *J* = 7.2 Hz, 1H), 3.50 (dq, *J* = 8.8, 7.2 Hz, 1H), 3.01 (dq, *J* = 8.8, 7.2 Hz, 1H), 1.04 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃): δ 229.1, 225.4, 146.8, 143.7, 143.1, 140.2, 135.9, 135.7, 134.3, 127.9, 127.6, 127.2, 105.8, 105.4, 97.0, 78.8, 68.1, 64.0, 62.3, 57.3, 14.8.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η -(2,3,4)-6-phenyl-3,5-pyradien-2-yl]molybdenum (1d). To a solution of **IV** (800 mg, 1.41 mmol) in dry CH₂Cl₂ (10 mL) at –30 °C was added Ph₃CPF₆ (656 mg, 1.69 mmol) as a solid in one portion. The mixture was stirred for 2 h at –30 °C and then it was slowly allowed to reach 0 °C. Addition of dry diethyl ether (24 mL) induced precipitation of an orange solid. The solvents were removed via cannula (covered with a piece of filter paper to prevent the removal of the solid). The remaining solid was washed with dry diethyl ether (2 x 15 mL), dried under vacuum for 1.5 h and re-dissolved in CH₂Cl₂ (18 mL). The solution was cooled to –30 °C, treated with Et₃N (295 μ L, 2.11 mmol) and it was slowly allowed to reach room temperature. The reaction mixture was concentrated and the residue was purified by flash chromatography (2:1 *n*-hexanes-CH₂Cl₂), to afford **1d** (556.5 mg, 76%) as an orange-red solid. TLC (2:1 *n*-hexanes-CH₂Cl₂, *R_f* = 0.18); mp = 206–207 °C with

decomp (CH₂Cl₂-*n*-hexanes). IR (cm⁻¹): 3146 (w), 3065 (w), 2482 (w), 1934 (s), 1853 (s), 1502 (w), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ¹H NMR (CDCl₃): δ 8.24 (d, *J* = 1.5 Hz, 1H), 8.11 (d, *J* = 1.5 Hz, 1H), 7.83 (d, *J* = 1.5 Hz, 1H), 7.77 (dd, *J* = 4.4, 2.5 Hz, 1H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.35-7.23 (m, 3H), 6.58 (d, *J* = 6.3 Hz, 1H), 6.28 (t, *J* = 1.9 Hz, 1H), 6.23 (t, *J* = 1.9 Hz, 1H), 6.19 (t, *J* = 1.9 Hz, 1H), 5.03 (m, 1H), 2.63 (t, *J* = 5.3 Hz, 1H). ¹³C NMR (CDCl₃): δ 229.8, 222.4, 145.8, 144.1, 142.4, 140.7, 136.2, 135.8, 134.4, 133.6, 128.1, 128.0, 124.4, 108.8, 106.3, 105.6, 105.5, 105.4, 63.1, 46.9. Anal. Calcd for C₂₂H₁₉N₆O₃BMo: C, 50.60; H, 3.67; N, 16.09. Found: C, 50.68; H, 3.69; N, 16.21.

General Procedure for the [5+3] and [2+3] Cycloaddition Reactions. Method A: To a solution of Mo-complex (0.5 mmol) and allylic acetal **3** (432 mg, 2.0 mmol) in dry CH₂Cl₂ (5 mL) Sc(OTf)₃ (25 mg, 0.05 mmol, 10 mol%) was added at -78 °C under an Ar atmosphere. The mixture was stirred at -78 °C or it was slowly (over 2 h) allowed to reach higher temperature (as indicated). After the reaction was complete, the mixture was passed through a short pad of silica gel with 9:1 CH₂Cl₂-EtOAc. The filtrate was concentrated under vacuum and the residue was purified by flash chromatography. Method B: To a solution of Mo-complex (0.5 mmol) and allylic acetal **3** (432 mg, 2.0 mmol) in dry CH₂Cl₂ (5 mL) TMSOTf (13 μL, 0.065 mmol, 13 mol%) was added at -78 °C under Ar atmosphere. The isolation procedure is as described in method A.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]{η-(2,3,4)-(1*S*,2*R*,5*S*,6*S*)-6-ethoxy-7-methylen-9-oxabicyclo[3.3.1]non-3-en-2-yl}molybdenum (5a) and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]{η-(2,3,4)-(2*S*,4*aS*,7*S*,7*aS*)-7-ethoxy-6-methylencyclopenta[*b*]pyr-3-en-2-yl}molybdenum (6). Following the general procedure (method A), Sc(OTf)₃ (14.4 mg, 0.030 mmol) was added at -78 °C to a solution of **1a** (130 mg, 0.29 mmol) and **3** (251 mg, 1.16 mmol) in CH₂Cl₂ (3 mL). The mixture was slowly allowed to reach room temperature. After chromatographic purification (2:1 *n*-hexanes-CH₂Cl₂) **6** (6.1 mg,

4%) followed by **5a** (124.3 mg, 78%) were obtained as yellow solids. **5a**: TLC (9:1 *n*-hexanes-EtOAc, R_f = 0.24); mp > 200 °C. IR (cm^{-1}): 2976 (w), 2941 (w), 2895 (w), 2482 (w), 1942 (s), 1857 (s), 1505 (w), 1409 (m), 1305 (m), 1220 (m), 1119 (m), 1050 (s). ^1H NMR (CDCl_3): δ 8.64 (d, J = 1.9 Hz, 1H), 7.72 (d, J = 1.9 Hz, 1H), 7.67 (d, J = 1.9 Hz, 1H), 7.56 (d, J = 2.2 Hz, 1H), 7.55 (d, J = 2.2 Hz, 1H), 7.52 (d, J = 2.2 Hz, 1H), 6.30 (t, J = 2.2 Hz, 1H), 6.15 (t, J = 2.2 Hz, 1H), 6.14 (t, J = 2.2 Hz, 1H), 5.38 (d, J = 1.9 Hz, 1H), 5.12 (d, J = 1.9 Hz, 1H), 4.13 (m, 1H), 4.07 (m, 1H), 4.03 (dd, J = 5.3, 2.5 Hz, 1H), 3.97 (dd, J = 4.8, 1.6 Hz, 2H), 3.81-3.69 (m, 3H), 2.79 (dd, J = 14.0, 5.3 Hz, 1H), 2.50 (d, J = 14.0 Hz, 1H), 1.32 (t, J = 7.0 Hz, 3H). ^{13}C NMR (CDCl_3): δ 226.3, 147.2, 142.4, 142.2, 141.7, 135.9, 135.8, 134.3, 111.8, 105.9, 105.1, 105.0, 81.2, 69.8, 68.8, 68.2, 66.6, 66.3, 66.2, 40.4, 15.6. **6**: TLC (9:1 *n*-hexanes-EtOAc, R_f = 0.24); mp > 200 °C. IR (cm^{-1}): 2922 (m), 2853 (w), 2482 (w), 1934 (s), 1845 (s), 1505 (w), 1409 (m), 1305 (m), 1220 (m), 1200 (w), 1123 (m), 1050 (s). ^1H NMR: δ 8.55 (d, J = 1.9 Hz, 1H), 7.75 (s, 2H), 7.57 (d, J = 2.2 Hz, 1H), 7.55 (d, J = 2.2 Hz, 1H), 7.50 (d, J = 2.2 Hz, 1H), 7.00 (dd, J = 4.4, 2.2 Hz, 1H), 6.29 (t, J = 2.2 Hz, 1H), 6.20 (t, J = 2.2 Hz, 1H), 6.16 (t, J = 2.2 Hz, 1H), 5.14 (d, J = 8.9, 1H), 4.43 (m, 1H), 3.86 (s, 1H), 3.50 (q, J = 7.0 Hz, 2H), 3.32 (dd, J = 7.0, 4.4 Hz, 1H), 3.01 (d, J = 5.4 Hz, 1H), 2.91 (dd, J = 15.5, 8.2 Hz, 1H), 2.80 (m, 1H), 2.43 (m, 1H), 1.19 (t, J = 7.0 Hz, 3H). ^{13}C NMR: δ 226.7, 224.9, 150.0, 147.2, 142.1, 141.3, 135.9, 134.4, 111.1, 111.0, 106.0, 105.6, 105.2, 85.1, 79.3, 66.7, 64.5, 54.4, 41.6, 38.9, 29.7, 15.3. Anal. Calcd for $\text{C}_{22}\text{H}_{25}\text{BMoN}_6\text{O}_4$: C, 48.55; H, 4.63; N, 15.44. Found: C, 48.77; H, 4.34; N, 15.41.

(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]{ η -(2,3,4)-(1*S*,2*R*,5*S*,6*S*)-6-ethoxy-2-methyl-7-methylen-9-oxabicyclo[3.3.1]non-3-en-2-yl}molybdenum [(+)-5b**]. Method A: Following the general procedure, $\text{Sc}(\text{OTf})_3$ (24.7 mg, 0.05 mmol) was added at -78 °C to a solution of a 98% ee sample of (+)-**1b** (230 mg, 0.50 mmol) and **3** (432 mg, 2.0 mmol) in CH_2Cl_2 (5 mL). The mixture was slowly allowed to reach -10 °C. After chromatographic purification (2:1 to 1:1 *n*-hexanes- CH_2Cl_2) pure (+)-**5b** (226.7 mg, 81%) was obtained in 98% ee $\{[\alpha]_D +257.6$ (c 0.5,**

CH₂Cl₂)} as a yellow-orange solid. The racemic compound (±)-**5b** was obtained in the same manner. **Method B**: Following the general procedure, TMSOTf (7 µL, 0.034 mmol) was added at -78 °C to a solution of a 98% ee sample of (+)-**1b** (120 mg, 0.26 mmol) and **3** (225 mg, 1.04 mmol) in CH₂Cl₂ (2.5 mL). The mixture was slowly allowed to reach room temperature. After chromatography (2:1 to 1:1 *n*-hexanes-CH₂Cl₂) pure (+)-**5b** (120.6 mg, 83%) was obtained in 98% ee³ as a yellow solid. TLC (6:1 *n*-hexanes-EtOAc, R_f = 0.24); mp > 200 °C. IR (cm⁻¹): 2957 (m), 2930 (m), 2860 (w), 2478 (w), 1930 (s), 1845 (s), 1505 (w), 1409 (m), 1305 (m), 1212 (w), 1119 (m), 1050 (m). ¹H NMR (CDCl₃): δ 8.56 (s, 1H), 7.73 (s, 1H), 7.63 (s, 1H), 7.60 (s, 2H), 7.47 (s, 1H), 6.23 (s, 1H), 6.19 (s, 1H), 6.15 (s, 1H), 5.36 (s, 1H), 5.07 (s, 1H), 4.13 (m, 1H), 4.10 (dd, *J* = 5.7, 2.2 Hz, 1H), 4.03 (d, *J* = 7.3 Hz, 1H), 3.92 (m, 1H), 3.56-3.54 (m, 3H), 2.65-2.53 (m, 2H), 1.65 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃): δ 232.7, 227.3, 146.6, 145.9, 142.1, 140.2, 136.4, 135.7, 134.1, 110.7, 105.5, 105.3, 105.1, 88.7, 80.8, 74.0, 72.8, 70.5, 66.1, 56.6, 38.6, 22.6, 15.6. Anal. Calcd for C₂₃H₂₇N₆O₄BMo: C, 49.49; H, 4.87; N, 15.05. Found: C, 49.48; H, 4.90; N, 15.09.

(+)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1*S*,2*R*,5*S*,6*S*)-6-ethoxy-7-methylen-2-phenyl-9-oxabicyclo[3.3.1]non-3-en-2-yl]molybdenum [(+)-5c**]. **Method A**: Following the general procedure, Sc(OTf)₃ (17.0 mg, 0.034 mmol) was added at -78 °C to a solution of a 98% ee sample of (+)-**1c** (180 mg, 0.34 mmol) and **3** (298 mg, 1.38 mmol) in CH₂Cl₂ (3.4 mL). The mixture was stirred at -78 °C for 1 h. After chromatographic purification (1:1 *n*-hexanes-CH₂Cl₂) pure (+)-**5c** (170.8 mg, 80%) was obtained in 98% ee³ as a red crystalline solid. Recrystallization from *n*-hexanes-CH₂Cl₂ afford (+)-**5c** (116 mg, 55%) in > 99.5% ee³ {[α]_D +314.7 (*c* 0.5, CH₂Cl₂)}. The racemic compound (±)-**5c** was obtained in the same manner. **Method B**: Following the general procedure, TMSOTf (6 µL, 0.030 mmol) was added at -78 °C to a solution of (+)-**1c** (110 mg, 0.21 mmol) and **3** (182 mg, 0.84 mmol) in**

CH₂Cl₂ (2.2 mL). The mixture was stirred at -78 °C for 45 minutes. After chromatography (1:1 *n*-hexanes-CH₂Cl₂) pure (+)-**5c** (108.7 mg, 83%) was obtained as an orange-red solid. TLC (7:1 *n*-hexanes-EtOAc, *R_f* = 0.25); mp > 200 °C. IR (cm⁻¹): 2972 (w), 2953 (w), 2478 (w), 1934 (s), 1853 (s), 1505 (w), 1409 (m), 1305 (m), 1224 (w), 1119 (m), 1050 (m). ¹H NMR: δ 8.59 (d, *J* = 1.9 Hz, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.74 (bs, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 7.42 (bs, 1H), 7.36 (d, *J* = 2.2 Hz, 1H), 7.24 (m, 1H), 7.02 (bs, 1H), 6.93 (bs, 1H), 6.23 (t, *J* = 2.2 Hz, 2H), 5.73 (d, *J* = 1.9 Hz, 1H), 5.54 (t, *J* = 2.2 Hz, 1H), 5.37 (s, 1H), 4.85 (d, *J* = 1.9 Hz, 1H), 4.79 (d, *J* = 7.6 Hz, 1H), 4.67 (d, *J* = 4.8 Hz, 1H), 4.24 (dd, *J* = 5.1, 2.2 Hz, 1H), 4.18 (m, 1H), 4.02 (dd, *J* = 7.6, 2.5 Hz, 1H), 3.82-3.73 (m, 2H), 2.60-2.54 (m, 1H), 2.23 (d, *J* = 13.6 Hz, 1H), 1.35 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃): δ 232.1, 228.2, 146.9, 144.5, 141.9, 140.4, 139.4, 136.0, 135.8, 134.0, 128.9, 127.7, 126.3, 111.4, 105.6, 105.3, 104.0, 89.4, 80.7, 70.4, 70.0, 67.0, 66.3, 57.8, 38.9, 15.7.

(-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]{η-(2,3,4)-(1*S*,2*R*,5*S*,6*S*)-9-benzyloxycarbonyl-6-ethoxy-2-methyl-7-methylen-9-azabicyclo[3.3.1]non-3-en-2-yl}molybdenum [(-)-7a**].** Following the general procedure (method A), Sc(OTf)₃ (19 mg, 0.038 mmol) was added at -78 °C to a solution of a > 99.5% ee sample of (-)-**2a** (225 mg, 0.38 mmol) and **3** (328 mg, 1.50 mmol) in CH₂Cl₂ (3.8 mL). The mixture was slowly allowed to reach -10 °C. After chromatographic purification (1:4 *n*-hexanes-CH₂Cl₂) (-)-**7a** (220 mg, 84%) was obtained in > 99.5% ee³ {[α]_D -224.6 (*c* 0.5, CH₂Cl₂)} as a yellow-orange solid. The racemic compound (±)-**7a** was obtained in the same manner. TLC (4:1 *n*-hexanes-EtOAc, *R_f* = 0.24); mp > 200 °C. IR (cm⁻¹): 2976 (w), 2895 (w), 2478 (w), 1934 (s), 1849 (s), 1702 (m), 1409 (m), 1305 (m), 1212 (w), 1116 (m), 1050 (m). ¹H NMR (CDCl₃) (50:50 mixture of rotamers): δ 8.52 (s, 0.5H), 8.48 (s, 0.5H), 7.74 (s, 1H), 7.64 (s, 0.5H), 7.62 (s, 0.5H), 7.59 (s, 2H), 7.45 (s, 1H), 7.41-7.29 (m, 5H), 6.21 (m, 2H), 6.15 (d, *J* = 1.9 Hz, 1H), 5.43 (d, *J* = 1.6 Hz, 0.5H), 5.39 (d, *J* = 1.2 Hz, 0.5H), 5.25 (d, *J* = 12.4 Hz, 0.5H), 5.19 (d, *J* = 12.4 Hz, 0.5H), 5.12 (d, *J* = 12.7 Hz, 1H), 5.09 (s, 0.5H), 5.07 (d, *J* = 12.7 Hz, 0.5H), 4.63 (t, *J* = 4.1 Hz, 0.5H), 4.54 (t, *J* = 3.8 Hz,

0.5H), 4.27 (d, $J = 3.8$ Hz, 0.5H), 4.24 (d, $J = 3.9$ Hz, 0.5H), 4.01-3.80 (m, 3H), 3.76-3.57 (m, 2H), 2.59 (dd, $J = 13.0, 4.8$ Hz, 1H), 2.51-2.44 (m, 0.5H), 2.41-2.34 (m, 0.5H), 1.73 (s, 1.5H), 1.70 (s, 1.5H), 1.34 (t, $J = 7.0$ Hz, 1.5H), 1.27 (t, $J = 7.0$ Hz, 1.5H). ^{13}C NMR: δ 232.4, 231.8, 226.8, 226.1, 153.4, 153.1, 146.5, 146.1, 146.0, 142.3, 142.2, 140.2, 136.9, 136.7, 136.5, 135.8, 134.1, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 112.8, 112.7, 105.5, 105.4, 105.2, 105.1, 89.8, 89.3, 80.6, 80.0, 74.1, 67.3, 67.0, 65.9, 65.8, 56.8, 56.4, 54.7, 54.3, 52.8, 52.1, 38.9, 38.2, 23.5, 15.6, 15.5. Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{N}_7\text{O}_5\text{BMo}$: C, 53.85; H, 4.96; N, 14.18. Found: C, 53.81; H, 5.00; N, 14.19.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η -(2,3,4)-(1*S*,2*R*,5*S*,6*S*)-9-

benzyloxycarbonyl-6-ethoxy-2-methoxy-7-methylen-9-azabicyclo[3.3.1]non-3-en-2-

yl)molybdenum (7b). Method A: Following the general procedure, $\text{Sc}(\text{OTf})_3$ (23 mg, 0.045 mmol) was added at -78 °C to a solution of **2b** (275 mg, 0.45 mmol) and **3** (390 mg, 1.80 mmol) in CH_2Cl_2 (4.5 mL). The mixture was stirred at -78 °C for 1 h. After chromatographic purification (1:8 *n*-hexanes- CH_2Cl_2) pure **7b** (248 mg, 77%) was obtained as an orange solid.

Method B: Following the general procedure, TMSOTf (5 μL , 0.021 mmol) was added at -78 °C to a solution of **2b** (100 mg, 0.16 mmol) and **3** (142 mg, 0.66 mmol) in CH_2Cl_2 (1.6 mL). The mixture was stirred at -78 °C for 1 h. After chromatography (1:8 *n*-hexanes- CH_2Cl_2), **7b** (95.6 mg, 82%) was obtained. TLC (5:1 *n*-hexanes-EtOAc, $R_f = 0.13$); mp > 200 °C. IR (cm^{-1}): 2976 (w), 2899 (w), 2482 (w), 1930 (s), 1845 (s), 1702 (m), 1424 (w), 1305 (m), 1212 (m), 1116 (m), 1050 (m). ^1H NMR (CDCl_3) (50:50 mixture of rotamers): δ 8.44 (d, $J = 1.6$ Hz, 0.5H), 8.41 (d, $J = 1.5$ Hz, 0.5H), 7.92 (d, $J = 1.6$ Hz, 0.5H), 7.89 (d, $J = 1.6$ Hz, 0.5H), 7.65 (d, $J = 1.9$ Hz, 0.5H), 7.63 (d, $J = 1.9$ Hz, 0.5H), 7.60 (m, 2H), 7.48 (s, 1H), 7.41-7.30 (m, 5H), 6.23-6.18 (m, 2H), 6.13 (t, $J = 1.9$ Hz, 1H), 5.45 (m, 0.5H), 5.42 (m, 0.5H), 5.26 (d, $J = 12.7$, 0.5H), 5.21 (d, $J = 12.1$ Hz, 0.5H), 5.13 (d, $J = 12.7$ Hz, 0.5H), 5.09 (d, $J = 12.1$ Hz, 0.5H), 5.07 (m, 1H), 4.62-4.56 (m, 1.5H), 4.51 (dd, $J = 5.1, 3.2$ Hz, 0.5H), 3.98-3.56 (m, 5H), 3.08 (s, 1.5 H), 3.02 (s, 1.5H), 2.67-2.47 (m, 2H), 1.35 (t, $J = 7.0$ Hz, 1.5H), 1.28 (t, $J = 7.0$ Hz, 1.5H). ^{13}C NMR:

δ 229.9, 229.5, 227.8, 227.5, 153.6, 153.4, 146.7, 145.0, 144.9, 143.3, 143.1, 140.8, 140.7, 137.0, 136.8, 136.5, 136.4, 136.0, 134.4, 128.6, 128.4, 128.1, 128.0, 127.7, 127.6, 113.7, 113.6, 105.8, 105.5, 80.5, 79.9, 67.7, 67.4, 66.2, 66.1, 58.1, 57.9, 55.3, 55.2, 53.8, 53.5, 53.2, 53.1, 53.0, 52.3, 39.2, 38.4, 15.9, 15.7. Anal. Calcd for $C_{31}H_{34}N_7O_6BMo$: C, 52.63; H, 4.84; N, 13.86. Found: C, 52.90; H, 5.03; N, 13.68.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]{ η -(2,3,4)-(2*S*,4*aS*,7*S*,7*aS*)-7-ethoxy-6-methylen-7*a*-phenylcyclopenta[*b*]pyr-3-en-2-yl}molybdenum (8). Following the general procedure (method A), $Sc(OTf)_3$ (20 mg, 0.040 mmol) was added at $-78^\circ C$ to a solution of **1d** (200 mg, 0.38 mmol) and **3** (331 mg, 1.51 mmol) in CH_2Cl_2 (3.8 mL). The mixture was stirred at $-78^\circ C$ for 2 h. After chromatographic purification (2:1 *n*-hexanes- CH_2Cl_2) **8** (240 mg, 85%) was obtained as a yellow solid. TLC (9:1 *n*-hexanes-EtOAc, R_f = 0.24); mp $> 200^\circ C$. IR (cm^{-1}): 3123 (w), 3057 (w), 2976 (w), 2868 (w), 2486 (w), 1938 (s), 1845 (s), 1505 (w), 1404 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (s). 1H NMR: δ 8.52 (d, J = 1.9 Hz, 1H), 7.86 (d, J = 1.9 Hz, 1H), 7.77 (d, J = 1.9 Hz, 1H), 7.60 (d, J = 1.9 Hz, 1H), 7.57 (d, J = 1.9 Hz, 1H), 7.50 (d, J = 1.9 Hz, 1H), 7.45-7.43 (m, 2H), 7.36 (dd, J = 4.1, 2.5 Hz, 1H), 7.28-7.16 (m, 3H), 6.28 (t, J = 1.9 Hz, 1H), 6.24 (t, J = 2.2 Hz, 1H), 6.18 (t, J = 2.2 Hz, 1H), 5.38 (m, 1H), 5.31 (d, J = 1.8 Hz, 1H), 5.15 (d, J = 1.9 Hz, 1H), 4.28 (dd, J = 6.7, 2.2 Hz, 1H), 4.03 (dd, J = 6.7, 4.1 Hz, 1H), 3.69 (dq, J = 9.3, 7.0 Hz, 3H), 3.59 (dq, J = 9.3, 7.0 Hz, 1H), 3.19-3.09 (m, 1H), 2.91 (dd, J = 9.2, 1.9 Hz, 1H), 2.74 (dd, J = 18.1, 1.9 Hz, 1H), 1.07 (t, J = 7.0 Hz, 3H). ^{13}C NMR: δ 227.8, 226.8, 147.4, 147.1, 141.9, 141.2, 140.9, 136.0, 134.4, 127.4, 126.7, 126.2, 108.8, 108.4, 106.0, 105.6, 105.2, 85.5, 82.0, 69.2, 66.0, 65.6, 43.6, 40.3, 15.4.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]{ η -(2,3,4)-(2*S*,4*aS*,7*R*,7*aS*)-6-oxo-7*a*-phenyl-7-(triisopropylsilyl)oxycyclopenta[*b*]pyr-3-en-2-yl}molybdenum (9). Following the general procedure (method A), $Sc(OTf)_3$ (23.5 mg, 0.047 mmol) was added at $-78^\circ C$ to a

solution of **1d** (246 mg, 0.47 mmol) and **4** (406 mg, 1.88 mmol) in CH₂Cl₂ (4.7 mL). The mixture was stirred at -78 °C for 1.5 h. After chromatographic purification (2:1 *n*-hexanes-CH₂Cl₂), **9** (253 mg, 87%) was obtained as a yellow solid. TLC (1:1 *n*-hexanes-CH₂Cl₂, *R_f* = 0.4); mp > 200 °C. IR (cm⁻¹): 2945 (m), 2868 (m), 2482 (w), 1945 (s), 1857 (s), 1756 (m), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (s). ¹H NMR (CDCl₃): δ 8.59 (d, *J* = 1.9 Hz, 1H), 7.83 (d, *J* = 1.9 Hz, 1H), 7.76 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.32-7.18 (m, 6H), 6.31 (t, *J* = 2.2 Hz, 1H), 6.28 (t, *J* = 2.2 Hz, 1H), 6.19 (t, *J* = 2.2 Hz, 1H), 5.81 (d, *J* = 2.2 Hz, 1H), 4.30 (dd, *J* = 7.0, 2.2 Hz, 1H), 4.19 (dd, *J* = 7.0, 2.5 Hz, 1H), 3.10 (d, *J* = 9.8 Hz, 1H), 2.84 (dd, *J* = 19.7, 9.8 Hz, 1H), 2.66 (bd, *J* = 19.7 Hz, 1H), 1.15 (m, 3H), 1.07-1.01 (m, 18H). ¹³C NMR: δ 227.9, 226.3, 211.9, 147.5, 141.8, 140.7, 140.1, 136.2, 136.1, 134.5, 127.7, 127.2, 126.8, 108.2, 106.1, 105.8, 105.4, 83.6, 76.0, 67.2, 66.2, 45.6, 40.8, 17.9, 17.7, 12.5.

(+)-(1S,5S,6S)-6-Ethoxy-7-methylen-2-phenyl-9-oxabicyclo[3.3.1]non-2-ene [(+)-10]. To a solution of a >99.5% ee sample of (+)-**5c** (125 mg, 0.20 mmol) in CH₂Cl₂ (3.2 mL) was added at room temperature 37% aqueous HCl (495 μL, 6.0 mmol) dropwise over 2 minutes. The mixture was stirred at room temperature for 20 minutes and EtOAc (30 mL) and water (30 mL) were then added. The organic layer was washed with saturated aqueous NaHCO₃ (30 mL), dried over Na₂SO₄ and evaporated. The residue was purified by flash chromatography (2:1 *n*-hexanes-CH₂Cl₂) to afford (+)-**10** (41.4 mg, 80%) in >99.5% ee³ {[α]_D +106.4 (*c* 0.94, CH₂Cl₂)} as a white solid. TLC (2:1 *n*-hexanes-CH₂Cl₂, *R_f* = 0.08); mp = 42-43 °C (white solid). IR (cm⁻¹): 3030 (w), 2976 (m), 2937 (m), 2899 (m), 1498 (w), 1432 (w), 1119 (s), 1065 (m). ¹H NMR (CDCl₃): δ 7.33-7.23 (m, 5H), 6.02 (t, *J* = 4.1 Hz, 1H), 5.12 (d, *J* = 1.6 Hz, 1H), 4.84 (d, *J* = 5.4 Hz, 1H), 4.67 (d, *J* = 1.9 Hz, 1H), 4.36 (t, *J* = 6.7 Hz, 1H), 4.02 (m, 1H), 3.68-3.57 (m, 2H), 2.63 (dd, *J* = 13.3, 4.8 Hz, 1H), 2.50-2.42 (m, 1H), 3.44 (dd, *J* = 19.0, 4.8 Hz, 1H), 2.18 (d, *J* = 13.3 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H). ¹³C NMR: δ 140.7, 138.8, 137.2, 128.5, 127.2, 125.7,

122.2, 109.1, 78.9, 70.3, 70.0, 65.5, 38.9, 23.4, 15.5. HRMS (FAB) $[M+Li]^+$ calcd for $C_{17}H_{20}O_2Li$: 263.1623. Found: 263.1629.

(-)-(1*R*,5*R*,6*R*)-9-Benzyloxycarbonyl-6-ethoxy-2-methyl-7-methylen-9-

azabicyclo[3.3.1]non-2-ene [(-)-11]. To a solution of a >99.5% ee sample of (-)-**7a** (90 mg, 0.13 mmol) in CH_2Cl_2 (2 mL) was added at room temperature 37% aqueous HCl (325 μ L, 3.9 mmol) dropwise over 2 minutes. The mixture was stirred at room temperature for 20 minutes and then EtOAc (20 mL) and water (20 mL) were added. The organic layer was washed with saturated aqueous $NaHCO_3$ (30 mL), dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (1:2 *n*-hexanes- CH_2Cl_2) to afford (-)-**11** (32.3 mg, 76%) as a colorless oil. $[\alpha]_D = -71.4$ (*c* 1.2, CH_2Cl_2). TLC (1:2 *n*-hexanes- CH_2Cl_2 , $R_f = 0.22$). IR (cm^{-1}): 2972 (w), 2937 (w), 2899 (w), 1702 (s), 1424 (m), 1324 (m), 1305 (m), 1116 (m). 1H NMR ($CDCl_3$): (mixture of rotamers 50:50) δ 7.40-7.31 (m, 5H), 5.40 (bs, 0.5H), 5.37 (bs, 0.5H), 5.21-5.12 (m, 3H), 4.75 (s, 1H), 4.64 (m, 0.5H), 4.54 (m, 0.5H), 4.48 (d, $J = 4.1$, 0.5H), 4.40 (d, $J = 4.0$ Hz, 0.5H), 3.80 (m, 0.5H), 3.74 (m, 0.5H), 3.67-3.53 (m, 2H), 2.48-2.37 (m, 1H), 2.30-2.14 (m, 3H), 1.62 (d, $J = 1.5$ Hz, 1.5H), 1.59 (d, $J = 1.6$ Hz, 1.5H), 1.22 (t, $J = 7.0$ Hz, 1.5H), 1.21 (t, $J = 7.0$ Hz, 1.5H). ^{13}C NMR: δ 154.5, 154.4, 141.6, 141.5, 136.8, 136.7, 132.4, 131.8, 128.5, 128.0, 127.8, 127.7, 121.0, 120.4, 110.2, 110.1, 78.9, 78.3, 67.1, 67.0, 65.3, 65.2, 52.3, 52.0, 49.6, 48.8, 37.8, 37.4, 23.4, 22.9, 20.5, 20.4, 15.5, 15.4. HRMS m/z $[M^+]$ calcd for $C_{20}H_{25}NO_3$: 327.1834. Found: 327.1822.

(±)-(1*S*,5*S*,6*S*)-9-Benzyloxycarbonyl-6-ethoxy-7-methylen-9-azabicyclo[3.3.1]non-3-en-2-

one [(±)-12]. To the orange coloured solution of cycloadduct **7b** (100 mg, 0.14 mmol) and Et_3N (30 mL, 0.21 mmol) in a 3:1 mixture of THF-water (7 mL) at 0 °C and open to the air was added a solution of ceric ammonium nitrate (620 mg, 1.13 mmol) in water (3.5 mL) dropwise over 5

minutes. During the addition the solution turned a dark color and a gas was evolved. After completing the addition, the colour faded and a light yellow solution resulted. The reaction mixture was stirred at room temperature for an additional 5-7 minutes and then partitioned between CH₂Cl₂ (10 mL) and water (10 mL). The combined organic layers were washed with saturated aqueous NaHCO₃ (30 mL), dried (MgSO₄) and evaporated. The residue was purified by flash chromatography (1:2.5 *n*-hexanes-CH₂Cl₂) to afford (±)-**12** (34.6 mg, 75%) as a colorless oil. TLC (7:1 *n*-hexanes-EtOAc, *R_f* = 0.18). IR (cm⁻¹): 2976 (w), 2899 (w), 1702 (s), 1428 (m), 1336 (w), 1301 (m), 1119 (m), 1096 (m). ¹H NMR (CDCl₃): (64:36 mixture of rotamers) δ 7.39-7.31 (m, 5H), 7.04 (dd, *J* = 10.1, 5.4 Hz, 0.64H), 6.94 (dd, *J* = 10.1, 5.7 Hz, 0.36H), 6.23 (d, *J* = 10.1 Hz, 1H), 5.24-5.07 (m, 4H), 4.98 (s, 1H), 4.74 (m, 0.36H), 4.66 (m, 0.64H), 4.06 (d, *J* = 5.1 Hz, 0.64H), 3.98 (d, *J* = 5.0 Hz, 0.36H). ¹³C NMR (CDCl₃): δ 195.2, 195.0, 153.9, 153.6, 148.0, 146.7, 138.5, 136.0, 135.8, 130.8, 130.5, 128.6, 128.3, 128.0, 113.3, 113.2, 79.0, 78.5, 67.8, 66.2, 58.9, 58.3, 52.5, 51.8, 37.1, 36.7, 15.4, 15.3. HRMS *m/z* [M⁺] calcd for C₁₉H₂₁NO₄: 327.1471. Found: 327.1481.

(±)-(1*S*,5*S*,6*S*)-6-Ethoxy-2,7-dimethylen-9-oxabicyclo[3.3.1]non-3-ene [(±)-**13**]. To a solution of **5b** (85 mg, 0.15 mmol) in a 3:1 mixture of THF-water (12 mL) at room temperature and open to the air was treated with Et₃N (31 μL, 0.22 mmol). To the resulting mixture was added a solution of ceric ammonium nitrate (658 mg, 1.2 mmol) in water (4.5 mL) dropwise, over 1 minute. One minute later, the reaction mixture was diluted with CH₂Cl₂ (20 mL) and water (10 mL). The aqueous layer was extracted with CH₂Cl₂ (2 x 6 mL). The combined organic layers were washed with saturated aqueous NaHCO₃ (20 mL), dried over MgSO₄ and evaporated. The residue was purified by flash chromatography (3:1 *n*-hexanes-CH₂Cl₂) to afford **13** (21 mg, 72%) as a colorless oil with a strong banana-like odor. TLC (2:1 *n*-hexanes-CH₂Cl₂, *R_f* = 0.35). IR (cm⁻¹): 2976 (w), 2934 (m), 2895 (w), 1386 (w), 1116 (s), 1077 (m), 1058 (m), 884 (m). ¹H NMR (CDCl₃): δ 6.37 (d, *J* = 10.1 Hz, 1H), 5.90 (dd, *J* = 10.1, 4.1 Hz, 1H), 5.03 (m, 1H), 4.88 (s, 1H), 4.87 (m, 1H), 4.76 (s, 1H), 4.58 (d, *J* = 6.0 Hz, 1H), 4.52 (t, *J* = 5.1 Hz, 1H), 4.08 (m, 1H), 3.66 (q, *J* = 7.0 Hz, 2H), 2.79-2.73 (m, 1H), 2.24 (d, *J* = 13.3 Hz, 1H), 1.24

(t, $J = 7.0$ Hz, 3H). ^{13}C NMR: δ 141.9, 141.0, 128.6, 127.9, 110.7, 109.7, 79.0, 73.9, 70.6, 66.0, 42.4, 15.5. HRMS m/z [M^+] calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: 192.1150. Found: 192.1155.

(+)-(1R,5R,6R)-9-Benzyloxycarbonyl-6-ethoxy-2,7-dimethylen-9-azabicyclo[3.3.1]non-3-ene [(+)-14]. A solution of a >99.5% sample of (-)-**7a** (125 mg, 0.18 mmol) in a 3:1 mixture of THF-water (14 mL) at room temperature and open to the air was treated with Et_3N (37 μL , 0.27 mmol). To the resulting mixture was added a solution of ceric ammonium nitrate (790 mg, 1.4 mmol) in water (5.4 mL) dropwise, over 1 minute. One minute later, the reaction mixture was diluted with CH_2Cl_2 (25 mL) and water (15 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were washed with saturated aqueous NaHCO_3 (30 mL), dried over MgSO_4 and evaporated. The residue was purified by flash chromatography (1:1.5 *n*-hexanes- CH_2Cl_2) to afford (+)-**14** (45.3 mg, 77%) as a colorless oil. $[\alpha]_{\text{D}} +224.1$ (c 1.0, CH_2Cl_2). TLC (1:2 *n*-hexanes- CH_2Cl_2 , $R_f = 0.16$). IR (cm^{-1}): 2976 (w), 2945 (w), 2895 (w), 1702 (s), 1424 (m), 1297 (s), 1116 (m), 1096 (m). ^1H NMR (CDCl_3): (50:50 mixture of rotamers) δ 7.39-7.31 (m, 5H), 6.33 (dd, $J = 9.8, 4.4$ Hz, 1H), 5.88 (dd, $J = 9.8, 5.7$ Hz, 0.5H), 5.81 (dd, $J = 9.8, 5.4$ Hz, 0.5H), 5.23-4.86 (m, 9H), 3.95 (m, 0.5H), 3.88 (m, 0.5H), 3.80-3.57 (m, 2H), 2.65-2.53 (m, 1H), 2.23 (m, 1H), 1.25 (t, $J = 7.0$ Hz, 1.5H), 1.22 (t, $J = 7.0$ Hz, 1.5H). ^{13}C NMR: δ 154.2, 154.0, 141.9, 141.8, 141.2, 136.6, 130.3, 130.0, 128.5, 128.0, 127.8, 127.2, 126.2, 112.8, 112.2, 111.4, 111.3, 79.1, 78.6, 67.3, 65.7, 54.0, 53.4, 51.7, 51.1, 42.3, 41.8, 29.7, 15.5, 15.4. HRMS (FAB) [$\text{M}+\text{Li}$] $^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_3\text{Li}$: 332.1838. Found: 332.1836.

(+)-(1S,5R,6S)-6-Ethoxy-7-methylen-2-phenyl-9-oxabicyclo[3.3.1]non-2-en-4-one [(+)-15]. A solution of a >99.5% ee sample of (+)-**5c** (185 mg, 0.30 mmol) in CH_2Cl_2 (4 mL) was treated at room temperature with a mixture of pyridinium dichromate (450 mg, 1.20 mmol) and silica gel (500 mg). The resulting suspension was stirred under argon in the dark for 30 h. The mixture

was passed through a pad of Celite® (with a thin layer of silica gel on the top) with a 1:1 mixture of CH₂Cl₂-EtOAc. After concentration, the residue was purified by flash chromatography (1:1 *n*-hexanes-CH₂Cl₂) to afford (+)-**15** (61 mg, 76%) in > 99.5% ee³ {[α]_D +288.7 (*c* 0.97, CH₂Cl₂)} as a white solid. TLC (6:1 *n*-hexanes-EtOAc, R_f = 0.25); mp = 82-83 °C. IR (cm⁻¹): 2976 (w), 2907 (w), 1942 (w), 1675 (s), 1447 (w), 1266 (m), 1119 (m), 1092 (m). ¹H NMR (CDCl₃): δ 7.44 (m, 5H), 6.43 (s, 1H), 5.24 (m, 1H), 5.17 (dd, *J* = 6.3, 1.3 Hz, 1H), 4.75 (m, 1H), 4.51 (d, *J* = 6.3 Hz, 1H), 4.17-4.14 (m, 1H), 3.89 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.62 (dq, *J* = 9.2, 7.0 Hz, 1H), 2.88-2.82 (m, 1H), 2.26 (d, *J* = 13.6 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H). ¹³C NMR: δ 193.7, 157.7, 138.1, 134.8, 130.7, 129.2, 126.6, 123.4, 111.9, 76.9, 76.6, 71.0, 65.6, 37.7, 15.2. HRMS *m/z* [M⁺] calcd for C₁₇H₁₈O₃: 270.1256. Found: 270.1246.

(±)-(4a*S*,7*S*,7a*R*)-7-ethoxy-6-methylen-7a-phenylcyclopenta[b]pyr-3-en-2-one [(±)-**16**]. A solution of **8** (160 mg, 0.26 mmol) in CH₂Cl₂ (3.5 mL) was treated at room temperature with a mixture of pyridinium dichromate (388 mg, 1.03 mmol) and silica gel (450 mg). The resulting suspension was stirred under argon in the dark for 16 h. The mixture was passed through a pad of Celite® with a thin layer of silica gel on the top with a 1:1 mixture of CH₂Cl₂-EtOAc. After concentration, the residue was purified by flash chromatography (1:2 *n*-hexanes-CH₂Cl₂) to afford (±)-**16** (57.7 mg, 83%) as a white solid. TLC (1:2 *n*-hexanes-CH₂Cl₂, R_f = 0.18); mp = 58-59 °C. IR (cm⁻¹): 2976 (w), 2930 (w), 2899 (w), 1725 (s), 1447 (w), 1382 (w), 1243 (m), 1123 (m), 1096 (m), 1054 (m). ¹H NMR: δ 7.46-7.43 (m, 2H), 7.36-7.28 (m, 3H), 6.92 (dd, *J* = 9.8, 6.7 Hz, 1H), 5.88 (d, *J* = 9.8 Hz, 1H), 5.27 (s, 1H), 5.21 (s, 1H), 4.09 (s, 1H), 3.48 (td, *J* = 9.5, 6.7 Hz, 1H), 3.35 (dq, *J* = 9.5, 7.0 Hz, 1H), 3.04 (m, 1H), 2.94 (dq, *J* = 9.5, 7.0 Hz, 1H), 2.41 (ddt, *J* = 16.5, 9.5, 2.5 Hz, 1H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C NMR: δ 162.8, 147.8, 147.4, 137.8, 128.0, 127.8, 126.9, 120.3, 112.2, 93.5, 88.3, 65.1, 40.0, 36.3, 14.7.

DETERMINATION OF ENANTIOMERIC EXCESSES^a

Entry	Compound	hexane/ <i>i</i> -PrOH	mL/min	λ (nm)	(+)- (min)	(-)- (min)
1	(+)- 5b	90:10	0.9	223	7.6	9.2

2	(+)-5c	90:10	0.7	223	10.0	14.3
3	(-)-7a	90:10	0.3	223	36.7	30.0
4	(+)-15	98:2	0.7	294	31.5	39.2
5	(+)-10	60:40	0.7	254	7.3	8.5

a) CHIRALPAK AD chiral column was used.

Crystal Structure Analysis for 5b

A suitable crystal of **5b** was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 100 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 second frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART¹ software. Frame integration and final cell refinements were done using SAINT² software. The final cell parameters were determined from least-squares refinement on 7500 reflections. The SADABS³ program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V5.10).⁴ 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*⁵. Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V5.10 software. Additional details of data collection and structure refinement are given in Table 1.

References

1. SMART Version 5.624, **2000**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
2. SAINT Version 6.02, **2000**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
3. SADABS Version 2.03, **2001**, George Sheldrick, University of Göttingen,
4. SHELXTL V5.10, **2000**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
5. 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).

Details

The lattice also contained two disordered dichloromethane solvent molecules for every four Tp molybdenum complexes. Each dichloromethane molecule also was disordered about a center of symmetry.

Table S1. Crystal data and structure refinement for 5b.

Identification code	5b	
Empirical formula	$C_{28.50}H_{29}BClMoN_6O_4$	
Formula weight	661.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.9184(9) Å	$\alpha = 90^\circ$.
	b = 19.4040(14) Å	$\beta = 105.165(1)^\circ$.
	c = 12.6340(9) Å	$\gamma = 90^\circ$.
Volume	2820.0(4) Å ³	
Z	4	
Density (calculated)	1.559 Mg/m ³	
Absorption coefficient	0.607 mm ⁻¹	
F(000)	1352	
Crystal size	0.32 x 0.22 x 0.11 mm ³	
Theta range for data collection	1.97 to 33.05°.	
Index ranges	-17<=h<=18, -28<=k<=29, -19<=l<=19	
Reflections collected	49705	
Independent reflections	10289 [R(int) = 0.0467]	
Completeness to theta = 33.05°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0 and 0.913982	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10289 / 0 / 387	
Goodness-of-fit on F ²	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.1045	
R indices (all data)	R1 = 0.0502, wR2 = 0.1100	
Largest diff. peak and hole	1.296 and -0.872 e.Å ⁻³	

Table S2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 5b. U(eq) is Defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mo(1)	1525(1)	4548(1)	7399(1)	11(1)
B(1)	-146(2)	3137(1)	6646(2)	16(1)
C(1)	-1323(2)	4797(1)	7118(1)	17(1)
C(2)	-2367(2)	4431(1)	6864(2)	19(1)
C(3)	-2058(2)	3769(1)	6651(1)	19(1)
C(4)	1649(2)	3905(1)	5053(1)	18(1)
C(5)	1175(2)	3387(1)	4310(2)	21(1)
C(6)	437(2)	3031(1)	4795(1)	19(1)
C(7)	2436(2)	3171(1)	8926(1)	16(1)
C(8)	2150(2)	2481(1)	9015(2)	20(1)
C(9)	1112(2)	2397(1)	8227(2)	20(1)
C(10)	1130(1)	5686(1)	7777(1)	14(1)
C(11)	1163(1)	5236(1)	8682(1)	12(1)
C(12)	2277(1)	5028(1)	9286(1)	12(1)
C(13)	3260(1)	5559(1)	9374(1)	14(1)
C(14)	3209(2)	6109(1)	10237(1)	16(1)
C(15)	2139(2)	6551(1)	9842(1)	16(1)
C(16)	1972(1)	6810(1)	8684(1)	15(1)
C(17)	2102(1)	6212(1)	7921(1)	15(1)
C(18)	2416(2)	4546(1)	10222(1)	13(1)
C(19)	1479(2)	4169(1)	10400(1)	15(1)
C(20)	1623(2)	3705(1)	11261(2)	18(1)
C(21)	2711(2)	3601(1)	11973(2)	22(1)
C(22)	3654(2)	3975(1)	11820(2)	23(1)
C(23)	3507(2)	4442(1)	10962(2)	18(1)
C(24)	3211(2)	4549(1)	7673(2)	17(1)
C(25)	1611(2)	5232(1)	6297(1)	18(1)
C(26)	1400(2)	6683(1)	10440(2)	22(1)
C(27)	873(2)	7847(1)	8306(2)	22(1)

C(28)	-368(2)	8084(1)	7946(2)	28(1)
N(1)	-435(1)	4385(1)	7075(1)	14(1)
N(2)	-903(1)	3751(1)	6788(1)	15(1)
N(3)	1229(1)	3869(1)	5935(1)	15(1)
N(4)	482(1)	3327(1)	5766(1)	16(1)
N(5)	1621(1)	3491(1)	8148(1)	14(1)
N(6)	798(1)	3002(1)	7718(1)	16(1)
O(1)	3215(1)	5900(1)	8363(1)	15(1)
O(2)	867(1)	7114(1)	8236(1)	17(1)
O(3)	4215(1)	4533(1)	7847(1)	25(1)
O(4)	1712(2)	5613(1)	5620(1)	26(1)
C(1S)	9497(4)	9756(3)	573(4)	32(1)
Cl(1S)	10285(1)	9049(1)	297(1)	40(1)
Cl(2S)	10325(1)	9503(1)	150(1)	49(1)

Table S3. Bond Lengths [$\text{\AA}$] and Angles [$^\circ$] for 5b.

Mo(1)-C(25)	1.9459(19)	C(3)-N(2)	1.342(2)
Mo(1)-C(24)	1.947(2)	C(3)-H(3)	0.9300
Mo(1)-N(3)	2.2221(14)	C(4)-N(3)	1.338(2)
Mo(1)-C(11)	2.2275(16)	C(4)-C(5)	1.391(3)
Mo(1)-N(5)	2.2487(15)	C(4)-H(4)	0.9300
Mo(1)-N(1)	2.2851(15)	C(5)-C(6)	1.382(3)
Mo(1)-C(10)	2.3330(17)	C(5)-H(5)	0.9300
Mo(1)-C(12)	2.4971(16)	C(6)-N(4)	1.342(2)
B(1)-N(2)	1.532(3)	C(6)-H(6)	0.9300
B(1)-N(4)	1.539(2)	C(7)-N(5)	1.340(2)
B(1)-N(6)	1.540(2)	C(7)-C(8)	1.393(2)
B(1)-H(1B)	1.07(2)	C(7)-H(7)	0.9300
C(1)-N(1)	1.339(2)	C(8)-C(9)	1.380(3)
C(1)-C(2)	1.395(3)	C(8)-H(8)	0.9300
C(1)-H(1)	0.9300	C(9)-N(6)	1.344(2)
C(2)-C(3)	1.382(3)	C(9)-H(9)	0.9300
C(2)-H(2)	0.9300	C(10)-C(11)	1.430(2)

C(10)-C(17)	1.519(2)	C(27)-H(27A)	0.9700
C(10)-H(10)	0.9800	C(27)-H(27B)	0.9700
C(11)-C(12)	1.407(2)	C(28)-H(28A)	0.9600
C(11)-H(11)	0.9800	C(28)-H(28B)	0.9600
C(12)-C(18)	1.483(2)	C(28)-H(28C)	0.9600
C(12)-C(13)	1.541(2)	N(1)-N(2)	1.361(2)
C(13)-O(1)	1.428(2)	N(3)-N(4)	1.359(2)
C(13)-C(14)	1.538(2)	N(5)-N(6)	1.3707(19)
C(13)-H(13)	0.9800	C(1S)-Cl(2S)	1.333(5)
C(14)-C(15)	1.509(2)	C(1S)-Cl(2S)#1	1.744(5)
C(14)-H(14A)	0.9700	C(1S)-Cl(1S)	1.749(5)
C(14)-H(14B)	0.9700	Cl(1S)-Cl(2S)	0.9052(18)
C(15)-C(26)	1.326(3)	Cl(2S)-C(1S)#1	1.744(5)
C(15)-C(16)	1.510(2)	Cl(2S)-Cl(2S)#1	2.075(3)
C(16)-O(2)	1.419(2)		
C(16)-C(17)	1.541(2)	C(25)-Mo(1)-C(24)	83.17(8)
C(16)-H(16)	0.9800	C(25)-Mo(1)-N(3)	80.53(7)
C(17)-O(1)	1.432(2)	C(24)-Mo(1)-N(3)	94.62(6)
C(17)-H(17)	0.9800	C(25)-Mo(1)-C(11)	99.65(7)
C(18)-C(19)	1.401(2)	C(24)-Mo(1)-C(11)	104.87(7)
C(18)-C(23)	1.404(2)	N(3)-Mo(1)-C(11)	160.42(6)
C(19)-C(20)	1.389(2)	C(25)-Mo(1)-N(5)	156.48(6)
C(19)-H(19)	0.9300	C(24)-Mo(1)-N(5)	89.43(6)
C(20)-C(21)	1.386(3)	N(3)-Mo(1)-N(5)	77.84(5)
C(20)-H(20)	0.9300	C(11)-Mo(1)-N(5)	103.82(6)
C(21)-C(22)	1.393(3)	C(25)-Mo(1)-N(1)	102.07(7)
C(21)-H(21)	0.9300	C(24)-Mo(1)-N(1)	172.13(6)
C(22)-C(23)	1.388(3)	N(3)-Mo(1)-N(1)	80.61(5)
C(22)-H(22)	0.9300	C(11)-Mo(1)-N(1)	80.22(6)
C(23)-H(23)	0.9300	N(5)-Mo(1)-N(1)	83.46(5)
C(24)-O(3)	1.160(2)	C(25)-Mo(1)-C(10)	63.38(7)
C(25)-O(4)	1.161(2)	C(24)-Mo(1)-C(10)	102.47(6)
C(26)-H(26A)	0.9300	N(3)-Mo(1)-C(10)	137.29(6)
C(26)-H(26B)	0.9300	C(11)-Mo(1)-C(10)	36.45(6)
C(27)-O(2)	1.425(2)	N(5)-Mo(1)-C(10)	140.14(6)
C(27)-C(28)	1.501(3)	N(1)-Mo(1)-C(10)	85.21(6)

C(25)-Mo(1)-C(12)	110.81(7)	C(7)-C(8)-H(8)	127.8
C(24)-Mo(1)-C(12)	74.54(6)	N(6)-C(9)-C(8)	109.03(16)
N(3)-Mo(1)-C(12)	162.70(5)	N(6)-C(9)-H(9)	125.5
C(11)-Mo(1)-C(12)	34.04(5)	C(8)-C(9)-H(9)	125.5
N(5)-Mo(1)-C(12)	88.43(5)	C(11)-C(10)-C(17)	117.02(14)
N(1)-Mo(1)-C(12)	108.52(5)	C(11)-C(10)-Mo(1)	67.76(9)
C(10)-Mo(1)-C(12)	59.50(5)	C(17)-C(10)-Mo(1)	118.22(11)
N(2)-B(1)-N(4)	108.11(14)	C(11)-C(10)-H(10)	115.2
N(2)-B(1)-N(6)	110.29(14)	C(17)-C(10)-H(10)	115.2
N(4)-B(1)-N(6)	107.13(14)	Mo(1)-C(10)-H(10)	115.2
N(2)-B(1)-H(1B)	110.1(12)	C(12)-C(11)-C(10)	115.68(14)
N(4)-B(1)-H(1B)	110.5(12)	C(12)-C(11)-Mo(1)	83.54(10)
N(6)-B(1)-H(1B)	110.7(12)	C(10)-C(11)-Mo(1)	75.80(9)
N(1)-C(1)-C(2)	110.72(17)	C(12)-C(11)-H(11)	121.4
N(1)-C(1)-H(1)	124.6	C(10)-C(11)-H(11)	121.4
C(2)-C(1)-H(1)	124.6	Mo(1)-C(11)-H(11)	121.4
C(3)-C(2)-C(1)	104.54(16)	C(11)-C(12)-C(18)	120.40(14)
C(3)-C(2)-H(2)	127.7	C(11)-C(12)-C(13)	116.03(14)
C(1)-C(2)-H(2)	127.7	C(18)-C(12)-C(13)	116.11(14)
N(2)-C(3)-C(2)	108.42(16)	C(11)-C(12)-Mo(1)	62.42(9)
N(2)-C(3)-H(3)	125.8	C(18)-C(12)-Mo(1)	117.57(11)
C(2)-C(3)-H(3)	125.8	C(13)-C(12)-Mo(1)	113.26(10)
N(3)-C(4)-C(5)	110.54(17)	O(1)-C(13)-C(14)	108.23(13)
N(3)-C(4)-H(4)	124.7	O(1)-C(13)-C(12)	113.31(13)
C(5)-C(4)-H(4)	124.7	C(14)-C(13)-C(12)	110.18(14)
C(6)-C(5)-C(4)	104.76(16)	O(1)-C(13)-H(13)	108.3
C(6)-C(5)-H(5)	127.6	C(14)-C(13)-H(13)	108.3
C(4)-C(5)-H(5)	127.6	C(12)-C(13)-H(13)	108.3
N(4)-C(6)-C(5)	108.27(16)	C(15)-C(14)-C(13)	110.27(14)
N(4)-C(6)-H(6)	125.9	C(15)-C(14)-H(14A)	109.6
C(5)-C(6)-H(6)	125.9	C(13)-C(14)-H(14A)	109.6
N(5)-C(7)-C(8)	111.06(16)	C(15)-C(14)-H(14B)	109.6
N(5)-C(7)-H(7)	124.5	C(13)-C(14)-H(14B)	109.6
C(8)-C(7)-H(7)	124.5	H(14A)-C(14)-H(14B)	108.1
C(9)-C(8)-C(7)	104.34(16)	C(26)-C(15)-C(16)	123.29(17)
C(9)-C(8)-H(8)	127.8	C(26)-C(15)-C(14)	123.44(17)

C(16)-C(15)-C(14)	113.24(15)	O(2)-C(27)-C(28)	107.35(16)
O(2)-C(16)-C(15)	113.47(14)	O(2)-C(27)-H(27A)	110.2
O(2)-C(16)-C(17)	107.29(13)	C(28)-C(27)-H(27A)	110.2
C(15)-C(16)-C(17)	110.29(14)	O(2)-C(27)-H(27B)	110.2
O(2)-C(16)-H(16)	108.6	C(28)-C(27)-H(27B)	110.2
C(15)-C(16)-H(16)	108.6	H(27A)-C(27)-H(27B)	108.5
C(17)-C(16)-H(16)	108.6	C(27)-C(28)-H(28A)	110.0
O(1)-C(17)-C(10)	111.22(13)	C(27)-C(28)-H(28B)	109.3
O(1)-C(17)-C(16)	107.94(13)	H(28A)-C(28)-H(28B)	109.5
C(10)-C(17)-C(16)	112.48(14)	C(27)-C(28)-H(28C)	109.1
O(1)-C(17)-H(17)	108.4	H(28A)-C(28)-H(28C)	109.5
C(10)-C(17)-H(17)	108.4	H(28B)-C(28)-H(28C)	109.5
C(16)-C(17)-H(17)	108.4	C(1)-N(1)-N(2)	106.09(14)
C(19)-C(18)-C(23)	117.17(16)	C(1)-N(1)-Mo(1)	133.80(12)
C(19)-C(18)-C(12)	122.02(15)	N(2)-N(1)-Mo(1)	120.10(11)
C(23)-C(18)-C(12)	120.81(15)	C(3)-N(2)-N(1)	110.22(15)
C(20)-C(19)-C(18)	121.60(16)	C(3)-N(2)-B(1)	128.36(15)
C(20)-C(19)-H(19)	119.2	N(1)-N(2)-B(1)	121.41(14)
C(18)-C(19)-H(19)	119.2	C(4)-N(3)-N(4)	106.34(14)
C(19)-C(20)-C(21)	120.39(17)	C(4)-N(3)-Mo(1)	130.58(12)
C(19)-C(20)-H(20)	119.8	N(4)-N(3)-Mo(1)	123.01(11)
C(21)-C(20)-H(20)	119.8	C(6)-N(4)-N(3)	110.09(15)
C(22)-C(21)-C(20)	119.07(17)	C(6)-N(4)-B(1)	130.29(15)
C(22)-C(21)-H(21)	120.5	N(3)-N(4)-B(1)	119.61(14)
C(20)-C(21)-H(21)	120.5	C(7)-N(5)-N(6)	105.98(14)
C(21)-C(22)-C(23)	120.45(17)	C(7)-N(5)-Mo(1)	132.76(12)
C(21)-C(22)-H(22)	119.8	N(6)-N(5)-Mo(1)	120.81(10)
C(23)-C(22)-H(22)	119.8	C(9)-N(6)-N(5)	109.58(14)
C(22)-C(23)-C(18)	121.31(17)	C(9)-N(6)-B(1)	128.10(15)
C(22)-C(23)-H(23)	119.3	N(5)-N(6)-B(1)	120.87(14)
C(18)-C(23)-H(23)	119.3	C(13)-O(1)-C(17)	111.01(12)
O(3)-C(24)-Mo(1)	178.24(16)	C(16)-O(2)-C(27)	113.67(14)
O(4)-C(25)-Mo(1)	175.68(16)	Cl(2S)-C(1S)-Cl(2S)#1	83.6(3)
C(15)-C(26)-H(26A)	120.0	Cl(2S)-C(1S)-Cl(1S)	30.54(13)
C(15)-C(26)-H(26B)	120.0	Cl(2S)#1-C(1S)-Cl(1S)	113.4(3)
H(26A)-C(26)-H(26B)	120.0	Cl(2S)-Cl(1S)-C(1S)	48.4(2)

Cl(1S)-Cl(2S)-C(1S)	101.0(3)
Cl(1S)-Cl(2S)-C(1S)#1	158.4(3)
C(1S)-Cl(2S)-C(1S)#1	96.4(3)
Cl(1S)-Cl(2S)-Cl(2S)#1	154.8(2)
C(1S)-Cl(2S)-Cl(2S)#1	56.7(2)
C(1S)#1-Cl(2S)-Cl(2S)#1	39.67(17)

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

Table S4. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 5b. 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}
Mo(1)	11(1)	12(1)	10(1)	0(1)	2(1)	0(1)
B(1)	16(1)	17(1)	14(1)	-1(1)	2(1)	-3(1)
C(1)	15(1)	19(1)	15(1)	0(1)	2(1)	2(1)
C(2)	11(1)	28(1)	18(1)	0(1)	1(1)	2(1)
C(3)	14(1)	25(1)	16(1)	0(1)	3(1)	-3(1)
C(4)	18(1)	21(1)	15(1)	0(1)	6(1)	3(1)
C(5)	26(1)	23(1)	15(1)	-2(1)	6(1)	6(1)
C(6)	20(1)	19(1)	14(1)	-5(1)	0(1)	3(1)
C(7)	18(1)	15(1)	14(1)	-1(1)	1(1)	2(1)
C(8)	26(1)	16(1)	17(1)	2(1)	3(1)	3(1)
C(9)	25(1)	14(1)	18(1)	1(1)	4(1)	-3(1)
C(10)	14(1)	14(1)	12(1)	-1(1)	2(1)	-1(1)
C(11)	11(1)	13(1)	12(1)	-2(1)	3(1)	0(1)
C(12)	12(1)	13(1)	11(1)	0(1)	3(1)	0(1)
C(13)	11(1)	14(1)	15(1)	0(1)	2(1)	-1(1)
C(14)	15(1)	15(1)	16(1)	-1(1)	0(1)	-1(1)
C(15)	18(1)	13(1)	16(1)	-2(1)	1(1)	-3(1)
C(16)	14(1)	13(1)	18(1)	1(1)	3(1)	-1(1)
C(17)	15(1)	14(1)	16(1)	1(1)	5(1)	-2(1)
C(18)	14(1)	14(1)	12(1)	-1(1)	4(1)	1(1)
C(19)	15(1)	15(1)	15(1)	1(1)	5(1)	0(1)
C(20)	21(1)	18(1)	19(1)	1(1)	10(1)	1(1)
C(21)	28(1)	20(1)	18(1)	7(1)	7(1)	5(1)
C(22)	20(1)	24(1)	21(1)	5(1)	-1(1)	5(1)
C(23)	15(1)	18(1)	18(1)	1(1)	2(1)	1(1)
C(24)	18(1)	17(1)	18(1)	-3(1)	5(1)	0(1)
C(25)	21(1)	18(1)	14(1)	-2(1)	5(1)	2(1)
C(26)	24(1)	24(1)	18(1)	-2(1)	4(1)	3(1)
C(27)	21(1)	12(1)	34(1)	1(1)	8(1)	1(1)
C(28)	23(1)	17(1)	41(1)	4(1)	5(1)	5(1)

N(1)	13(1)	16(1)	13(1)	-2(1)	1(1)	-1(1)
N(2)	14(1)	17(1)	13(1)	-2(1)	2(1)	-3(1)
N(3)	16(1)	17(1)	13(1)	-1(1)	4(1)	1(1)
N(4)	17(1)	14(1)	14(1)	-3(1)	1(1)	0(1)
N(5)	15(1)	14(1)	13(1)	-2(1)	2(1)	0(1)
N(6)	17(1)	14(1)	15(1)	-1(1)	3(1)	-3(1)
O(1)	13(1)	17(1)	17(1)	2(1)	5(1)	-1(1)
O(2)	16(1)	12(1)	21(1)	1(1)	2(1)	1(1)
O(3)	15(1)	26(1)	34(1)	-9(1)	6(1)	0(1)
O(4)	43(1)	21(1)	18(1)	3(1)	13(1)	0(1)
Cl(1S)	42(1)	51(1)	26(1)	-11(1)	7(1)	13(1)
Cl(2S)	45(1)	46(1)	44(1)	-1(1)	-9(1)	-5(1)

Table S5. Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 5b.

	x	y	z	U(eq)
H(1)	-1254	5263	7294	20
H(2)	-3105	4595	6843	23
H(3)	-2564	3399	6447	22
H(4)	2183	4231	4950	21
H(5)	1322	3299	3635	25
H(6)	-14	2651	4500	22
H(7)	3105	3381	9350	20
H(8)	2565	2152	9496	24
H(9)	696	1987	8072	23
H(10)	356	5853	7391	16
H(11)	479	5168	8963	14
H(13)	4006	5318	9612	16
H(14A)	3193	5886	10920	20
H(14B)	3898	6396	10372	20
H(16)	2573	7154	8683	18

H(17)	2085	6404	7199	18
H(19)	742	4232	9929	18
H(20)	985	3463	11361	22
H(21)	2811	3285	12544	26
H(22)	4387	3912	12297	27
H(23)	4145	4690	10875	21
H(26A)	741	6947	10149	27
H(26B)	1542	6511	11150	27
H(27A)	1315	8042	7834	26
H(27B)	1225	7993	9053	26
H(28A)	-735	7902	7233	42
H(28B)	-388	8578	7920	42
H(28C)	-774	7924	8463	42
H(1B)	-676(19)	2689(12)	6405(18)	21(6)

Crystal Structure Analysis of 7b

A suitable crystal of **7b** was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 100 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 second frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART¹ software. Frame integration and final cell refinements were done using SAINT² software. The final cell parameters were determined from least-squares refinement on 7173 reflections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V5.10).⁴ 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*⁵. Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V5.10 software. Additional details of data collection and structure refinement are given in Table 1.

References

- SMART Version 5.624, **2000**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
- SAINT Version 6.02, **2000**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
- SHELXTL V5.10, **2000**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
- 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).

Table S6. Crystal Data and Structure Refinement for 7b.

Identification code	7b	
Empirical formula	C ₃₁ H ₃₄ BMoN ₇ O ₆	
Formula weight	707.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.1564(8) Å	$\alpha = 90^\circ$.

	$b = 16.3391(12) \text{ \AA}$	$\beta = 101.298(2)^\circ$.
	$c = 19.2552(14) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$3133.4(4) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.500 Mg/m^3	
Absorption coefficient	0.474 mm^{-1}	
F(000)	1456	
Crystal size	$0.33 \times 0.17 \times 0.10 \text{ mm}^3$	
Theta range for data collection	$1.65 \text{ to } 33.14^\circ$.	
Index ranges	$-15 \leq h \leq 15, -25 \leq k \leq 24, -29 \leq l \leq 29$	
Reflections collected	54913	
Independent reflections	11377 [R(int) = 0.0612]	
Completeness to $\theta = 33.14^\circ$	95.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11377 / 0 / 421	
Goodness-of-fit on F^2	1.025	
Final R indices [I > 2 σ (I)]	$R1 = 0.0451, wR2 = 0.1017$	
R indices (all data)	$R1 = 0.0636, wR2 = 0.1067$	
Largest diff. peak and hole	$1.116 \text{ and } -1.098 \text{ e.\AA}^{-3}$	

Table S7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 7b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mo(1)	2673(1)	4160(1)	1910(1)	14(1)
B(1)	2738(3)	5942(2)	2806(1)	19(1)
C(1)	3865(2)	3976(1)	3603(1)	18(1)
C(2)	4015(2)	4423(1)	4231(1)	21(1)
C(3)	3640(2)	5213(1)	4016(1)	20(1)
C(4)	-380(2)	4967(1)	1981(1)	20(1)
C(5)	-935(2)	5656(1)	2241(1)	23(1)
C(6)	161(2)	6123(1)	2550(1)	22(1)
C(7)	4757(2)	5531(1)	1484(1)	22(1)
C(8)	5263(2)	6306(2)	1681(1)	26(1)
C(9)	4514(2)	6574(1)	2168(1)	24(1)
C(10)	947(2)	3480(1)	1192(1)	17(1)
C(11)	1435(2)	4141(1)	817(1)	17(1)
C(12)	2633(2)	3961(1)	597(1)	19(1)
C(13)	2918(2)	3094(1)	377(1)	19(1)
C(14)	2068(2)	2939(1)	-379(1)	21(1)
C(15)	582(2)	2951(1)	-354(1)	21(1)
C(16)	186(2)	2433(1)	225(1)	22(1)
C(17)	1122(2)	2611(1)	943(1)	17(1)
C(18)	-317(3)	3393(2)	-795(1)	28(1)
C(19)	-2103(3)	2015(2)	-82(2)	34(1)
C(20)	-3475(3)	2348(2)	-58(2)	40(1)
C(21)	2646(3)	5240(2)	-9(1)	31(1)
C(22)	3131(2)	1750(1)	908(1)	20(1)
C(23)	3089(2)	387(1)	1287(2)	29(1)
C(24)	2093(2)	-245(1)	1427(1)	23(1)
C(25)	744(3)	-216(2)	1107(1)	29(1)
C(26)	-139(2)	-831(2)	1244(1)	30(1)
C(27)	348(3)	-1463(2)	1689(2)	37(1)
C(28)	1678(3)	-1499(2)	2007(2)	34(1)

C(29)	2545(2)	-900(1)	1875(1)	26(1)
C(30)	2272(2)	3118(1)	2313(1)	17(1)
C(31)	4274(2)	3569(1)	1787(1)	19(1)
N(1)	970(2)	5002(1)	2121(1)	17(1)
N(2)	1287(2)	5724(1)	2470(1)	18(1)
N(3)	3415(2)	4462(1)	3043(1)	17(1)
N(4)	3288(2)	5228(1)	3308(1)	17(1)
N(5)	3752(2)	5344(1)	1815(1)	19(1)
N(6)	3615(2)	5999(1)	2240(1)	20(1)
N(7)	2508(2)	2493(1)	851(1)	18(1)
O(1)	-1156(2)	2572(1)	312(1)	27(1)
O(2)	3307(2)	4491(1)	236(1)	23(1)
O(3)	2451(2)	1181(1)	1203(1)	23(1)
O(4)	4186(2)	1614(1)	720(1)	25(1)
O(5)	2118(2)	2489(1)	2564(1)	24(1)
O(6)	5240(2)	3223(1)	1719(1)	25(1)

Table S8. Bond Lengths [Å] and Angles [°] for 7b.

Mo(1)-C(31)	1.945(2)	C(10)-C(17)	1.521(3)
Mo(1)-C(30)	1.946(2)	C(10)-H(10)	1.0000
Mo(1)-N(3)	2.2185(18)	C(11)-C(12)	1.396(3)
Mo(1)-C(11)	2.231(2)	C(11)-H(11)	1.0000
Mo(1)-N(5)	2.2479(18)	C(12)-O(2)	1.374(3)
Mo(1)-C(10)	2.295(2)	C(12)-C(13)	1.521(3)
Mo(1)-N(1)	2.3076(18)	C(13)-N(7)	1.456(3)
Mo(1)-C(12)	2.542(2)	C(13)-C(14)	1.561(3)
B(1)-N(2)	1.530(3)	C(13)-H(13)	1.0000
B(1)-N(6)	1.540(3)	C(14)-C(15)	1.520(3)
B(1)-N(4)	1.548(3)	C(14)-H(14A)	0.9900
B(1)-H(1B)	1.11(2)	C(14)-H(14B)	0.9900
C(1)-N(3)	1.344(3)	C(15)-C(18)	1.332(3)
C(1)-C(2)	1.395(3)	C(15)-C(16)	1.515(3)
C(1)-H(1)	0.9500	C(16)-O(1)	1.424(3)
C(2)-C(3)	1.386(3)	C(16)-C(17)	1.544(3)
C(2)-H(2)	0.9500	C(16)-H(16)	1.0000
C(3)-N(4)	1.340(3)	C(17)-N(7)	1.466(3)
C(3)-H(3)	0.9500	C(17)-H(17)	1.0000
C(4)-N(1)	1.345(3)	C(18)-H(18A)	0.9500
C(4)-C(5)	1.396(3)	C(18)-H(18B)	0.9500
C(4)-H(4)	0.9500	C(19)-O(1)	1.429(3)
C(5)-C(6)	1.383(3)	C(19)-C(20)	1.505(4)
C(5)-H(5)	0.9500	C(19)-H(19A)	0.9900
C(6)-N(2)	1.351(3)	C(19)-H(19B)	0.9900
C(6)-H(6)	0.9500	C(20)-H(20A)	0.9800
C(7)-N(5)	1.340(3)	C(20)-H(20B)	0.9800
C(7)-C(8)	1.392(3)	C(20)-H(20C)	0.9800
C(7)-H(7)	0.9500	C(21)-O(2)	1.430(3)
C(8)-C(9)	1.388(3)	C(21)-H(21A)	0.9800
C(8)-H(8)	0.9500	C(21)-H(21B)	0.9800
C(9)-N(6)	1.337(3)	C(21)-H(21C)	0.9800
C(9)-H(9)	0.9500	C(22)-O(4)	1.217(3)
C(10)-C(11)	1.440(3)	C(22)-O(3)	1.349(3)

C(22)-N(7)	1.362(3)	N(5)-Mo(1)-C(10)	133.94(7)
C(23)-O(3)	1.444(3)	C(31)-Mo(1)-N(1)	172.22(8)
C(23)-C(24)	1.506(3)	C(30)-Mo(1)-N(1)	103.24(8)
C(23)-H(23A)	0.9900	N(3)-Mo(1)-N(1)	79.45(6)
C(23)-H(23B)	0.9900	C(11)-Mo(1)-N(1)	82.59(7)
C(24)-C(25)	1.388(3)	N(5)-Mo(1)-N(1)	84.01(6)
C(24)-C(29)	1.395(3)	C(10)-Mo(1)-N(1)	83.34(7)
C(25)-C(26)	1.405(4)	C(31)-Mo(1)-C(12)	70.51(8)
C(25)-H(25)	0.9500	C(30)-Mo(1)-C(12)	108.67(8)
C(26)-C(27)	1.371(4)	N(3)-Mo(1)-C(12)	160.46(7)
C(26)-H(26)	0.9500	C(11)-Mo(1)-C(12)	33.20(7)
C(27)-C(28)	1.371(4)	N(5)-Mo(1)-C(12)	86.67(7)
C(27)-H(27)	0.9500	C(10)-Mo(1)-C(12)	58.49(7)
C(28)-C(29)	1.372(3)	N(1)-Mo(1)-C(12)	112.63(7)
C(28)-H(28)	0.9500	N(2)-B(1)-N(6)	110.99(18)
C(29)-H(29)	0.9500	N(2)-B(1)-N(4)	106.80(18)
C(30)-O(5)	1.160(3)	N(6)-B(1)-N(4)	107.43(18)
C(31)-O(6)	1.162(3)	N(2)-B(1)-H(1B)	107.4(11)
N(1)-N(2)	1.365(2)	N(6)-B(1)-H(1B)	114.1(11)
N(3)-N(4)	1.368(2)	N(4)-B(1)-H(1B)	109.9(11)
N(5)-N(6)	1.372(2)	N(3)-C(1)-C(2)	110.46(19)
		N(3)-C(1)-H(1)	124.8
C(31)-Mo(1)-C(30)	81.89(9)	C(2)-C(1)-H(1)	124.8
C(31)-Mo(1)-N(3)	95.66(8)	C(3)-C(2)-C(1)	104.6(2)
C(30)-Mo(1)-N(3)	81.96(8)	C(3)-C(2)-H(2)	127.7
C(31)-Mo(1)-C(11)	102.02(8)	C(1)-C(2)-H(2)	127.7
C(30)-Mo(1)-C(11)	103.89(8)	N(4)-C(3)-C(2)	108.8(2)
N(3)-Mo(1)-C(11)	161.96(7)	N(4)-C(3)-H(3)	125.6
C(31)-Mo(1)-N(5)	89.15(8)	C(2)-C(3)-H(3)	125.6
C(30)-Mo(1)-N(5)	158.19(8)	N(1)-C(4)-C(5)	111.2(2)
N(3)-Mo(1)-N(5)	79.19(7)	N(1)-C(4)-H(4)	124.4
C(11)-Mo(1)-N(5)	97.39(7)	C(5)-C(4)-H(4)	124.4
C(31)-Mo(1)-C(10)	104.14(8)	C(6)-C(5)-C(4)	104.6(2)
C(30)-Mo(1)-C(10)	67.78(8)	C(6)-C(5)-H(5)	127.7
N(3)-Mo(1)-C(10)	140.51(7)	C(4)-C(5)-H(5)	127.7
C(11)-Mo(1)-C(10)	37.06(7)	N(2)-C(6)-C(5)	108.2(2)

N(2)-C(6)-H(6)	125.9	C(15)-C(14)-H(14A)	109.7
C(5)-C(6)-H(6)	125.9	C(13)-C(14)-H(14A)	109.7
N(5)-C(7)-C(8)	110.6(2)	C(15)-C(14)-H(14B)	109.7
N(5)-C(7)-H(7)	124.7	C(13)-C(14)-H(14B)	109.7
C(8)-C(7)-H(7)	124.7	H(14A)-C(14)-H(14B)	108.2
C(9)-C(8)-C(7)	104.5(2)	C(18)-C(15)-C(16)	121.7(2)
C(9)-C(8)-H(8)	127.7	C(18)-C(15)-C(14)	123.2(2)
C(7)-C(8)-H(8)	127.7	C(16)-C(15)-C(14)	115.13(19)
N(6)-C(9)-C(8)	108.9(2)	O(1)-C(16)-C(15)	113.27(19)
N(6)-C(9)-H(9)	125.6	O(1)-C(16)-C(17)	107.48(17)
C(8)-C(9)-H(9)	125.6	C(15)-C(16)-C(17)	110.37(18)
C(11)-C(10)-C(17)	117.96(18)	O(1)-C(16)-H(16)	108.5
C(11)-C(10)-Mo(1)	69.04(11)	C(15)-C(16)-H(16)	108.5
C(17)-C(10)-Mo(1)	121.28(14)	C(17)-C(16)-H(16)	108.5
C(11)-C(10)-H(10)	113.8	N(7)-C(17)-C(10)	109.61(17)
C(17)-C(10)-H(10)	113.8	N(7)-C(17)-C(16)	107.65(17)
Mo(1)-C(10)-H(10)	113.8	C(10)-C(17)-C(16)	111.63(17)
C(12)-C(11)-C(10)	113.63(19)	N(7)-C(17)-H(17)	109.3
C(12)-C(11)-Mo(1)	85.72(13)	C(10)-C(17)-H(17)	109.3
C(10)-C(11)-Mo(1)	73.90(12)	C(16)-C(17)-H(17)	109.3
C(12)-C(11)-H(11)	122.2	C(15)-C(18)-H(18A)	120.0
C(10)-C(11)-H(11)	122.2	C(15)-C(18)-H(18B)	120.0
Mo(1)-C(11)-H(11)	122.2	H(18A)-C(18)-H(18B)	120.0
O(2)-C(12)-C(11)	124.8(2)	O(1)-C(19)-C(20)	106.5(2)
O(2)-C(12)-C(13)	107.82(18)	O(1)-C(19)-H(19A)	110.4
C(11)-C(12)-C(13)	120.32(19)	C(20)-C(19)-H(19A)	110.4
O(2)-C(12)-Mo(1)	120.62(14)	O(1)-C(19)-H(19B)	110.4
C(11)-C(12)-Mo(1)	61.08(11)	C(20)-C(19)-H(19B)	110.4
C(13)-C(12)-Mo(1)	115.41(14)	H(19A)-C(19)-H(19B)	108.6
N(7)-C(13)-C(12)	111.16(17)	C(19)-C(20)-H(20A)	109.5
N(7)-C(13)-C(14)	107.50(17)	C(19)-C(20)-H(20B)	109.5
C(12)-C(13)-C(14)	108.04(18)	H(20A)-C(20)-H(20B)	109.5
N(7)-C(13)-H(13)	110.0	C(19)-C(20)-H(20C)	109.5
C(12)-C(13)-H(13)	110.0	H(20A)-C(20)-H(20C)	109.5
C(14)-C(13)-H(13)	110.0	H(20B)-C(20)-H(20C)	109.5
C(15)-C(14)-C(13)	109.87(18)	O(2)-C(21)-H(21A)	109.5

O(2)-C(21)-H(21B)	109.5	N(2)-N(1)-Mo(1)	119.30(13)
H(21A)-C(21)-H(21B)	109.5	C(6)-N(2)-N(1)	110.45(18)
O(2)-C(21)-H(21C)	109.5	C(6)-N(2)-B(1)	127.37(19)
H(21A)-C(21)-H(21C)	109.5	N(1)-N(2)-B(1)	121.56(17)
H(21B)-C(21)-H(21C)	109.5	C(1)-N(3)-N(4)	106.37(17)
O(4)-C(22)-O(3)	123.5(2)	C(1)-N(3)-Mo(1)	130.86(15)
O(4)-C(22)-N(7)	124.1(2)	N(4)-N(3)-Mo(1)	122.15(13)
O(3)-C(22)-N(7)	112.34(19)	C(3)-N(4)-N(3)	109.80(18)
O(3)-C(23)-C(24)	109.47(19)	C(3)-N(4)-B(1)	129.81(19)
O(3)-C(23)-H(23A)	109.8	N(3)-N(4)-B(1)	120.32(17)
C(24)-C(23)-H(23A)	109.8	C(7)-N(5)-N(6)	106.37(18)
O(3)-C(23)-H(23B)	109.8	C(7)-N(5)-Mo(1)	131.59(15)
C(24)-C(23)-H(23B)	109.8	N(6)-N(5)-Mo(1)	120.96(13)
H(23A)-C(23)-H(23B)	108.2	C(9)-N(6)-N(5)	109.60(18)
C(25)-C(24)-C(29)	118.5(2)	C(9)-N(6)-B(1)	128.21(19)
C(25)-C(24)-C(23)	122.4(2)	N(5)-N(6)-B(1)	121.05(17)
C(29)-C(24)-C(23)	119.1(2)	C(22)-N(7)-C(13)	117.82(18)
C(24)-C(25)-C(26)	120.2(2)	C(22)-N(7)-C(17)	123.29(18)
C(24)-C(25)-H(25)	119.9	C(13)-N(7)-C(17)	112.73(17)
C(26)-C(25)-H(25)	119.9	C(16)-O(1)-C(19)	113.37(19)
C(27)-C(26)-C(25)	119.4(2)	C(12)-O(2)-C(21)	117.29(19)
C(27)-C(26)-H(26)	120.3	C(22)-O(3)-C(23)	114.25(17)
C(25)-C(26)-H(26)	120.3		
C(26)-C(27)-C(28)	120.9(2)		
C(26)-C(27)-H(27)	119.5		
C(28)-C(27)-H(27)	119.5		
C(27)-C(28)-C(29)	120.0(3)		
C(27)-C(28)-H(28)	120.0		
C(29)-C(28)-H(28)	120.0		
C(28)-C(29)-C(24)	121.1(2)		
C(28)-C(29)-H(29)	119.5		
C(24)-C(29)-H(29)	119.5		
O(5)-C(30)-Mo(1)	175.77(18)		
O(6)-C(31)-Mo(1)	179.1(2)		
C(4)-N(1)-N(2)	105.57(17)		
C(4)-N(1)-Mo(1)	135.13(14)		

Table S9. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 7b. 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}
Mo(1)	14(1)	13(1)	15(1)	0(1)	2(1)	0(1)
B(1)	21(1)	16(1)	19(1)	-2(1)	3(1)	1(1)
C(1)	16(1)	17(1)	20(1)	4(1)	1(1)	1(1)
C(2)	19(1)	26(1)	17(1)	2(1)	-1(1)	-2(1)
C(3)	19(1)	25(1)	16(1)	-4(1)	0(1)	-1(1)
C(4)	18(1)	19(1)	22(1)	1(1)	3(1)	2(1)
C(5)	21(1)	23(1)	27(1)	4(1)	7(1)	7(1)
C(6)	26(1)	19(1)	21(1)	0(1)	5(1)	8(1)
C(7)	20(1)	25(1)	24(1)	0(1)	6(1)	-2(1)
C(8)	23(1)	25(1)	31(1)	0(1)	6(1)	-8(1)
C(9)	27(1)	17(1)	28(1)	0(1)	3(1)	-5(1)
C(10)	16(1)	17(1)	17(1)	-1(1)	2(1)	1(1)
C(11)	18(1)	18(1)	15(1)	-2(1)	-1(1)	1(1)
C(12)	23(1)	16(1)	17(1)	1(1)	2(1)	-2(1)
C(13)	20(1)	16(1)	21(1)	-1(1)	7(1)	-1(1)
C(14)	28(1)	21(1)	16(1)	-3(1)	7(1)	-3(1)
C(15)	25(1)	20(1)	19(1)	-7(1)	3(1)	-4(1)
C(16)	20(1)	22(1)	24(1)	-6(1)	4(1)	-2(1)
C(17)	16(1)	17(1)	19(1)	-2(1)	4(1)	-1(1)
C(18)	33(1)	26(1)	23(1)	0(1)	3(1)	-3(1)
C(19)	29(1)	38(2)	34(1)	3(1)	4(1)	-14(1)
C(20)	22(1)	41(2)	54(2)	8(1)	1(1)	-9(1)
C(21)	45(2)	21(1)	26(1)	8(1)	3(1)	-2(1)
C(22)	21(1)	17(1)	22(1)	-4(1)	4(1)	0(1)
C(23)	22(1)	17(1)	48(2)	6(1)	11(1)	6(1)
C(24)	21(1)	19(1)	28(1)	-3(1)	6(1)	1(1)
C(25)	26(1)	27(1)	33(1)	-3(1)	5(1)	4(1)
C(26)	20(1)	31(1)	40(1)	-18(1)	7(1)	-4(1)
C(27)	44(2)	26(1)	49(2)	-16(1)	28(1)	-13(1)
C(28)	46(2)	21(1)	40(2)	0(1)	19(1)	0(1)
C(29)	24(1)	23(1)	34(1)	2(1)	7(1)	5(1)
C(30)	15(1)	19(1)	17(1)	-3(1)	2(1)	0(1)
C(31)	21(1)	16(1)	18(1)	-1(1)	2(1)	-3(1)

N(1)	18(1)	15(1)	18(1)	-1(1)	2(1)	2(1)
N(2)	21(1)	16(1)	18(1)	0(1)	3(1)	4(1)
N(3)	17(1)	16(1)	17(1)	-1(1)	2(1)	1(1)
N(4)	18(1)	16(1)	17(1)	-3(1)	1(1)	1(1)
N(5)	21(1)	17(1)	19(1)	-1(1)	4(1)	-1(1)
N(6)	21(1)	15(1)	22(1)	0(1)	3(1)	-2(1)
N(7)	17(1)	16(1)	21(1)	-1(1)	6(1)	-1(1)
O(1)	17(1)	35(1)	29(1)	-9(1)	4(1)	-3(1)
O(2)	30(1)	19(1)	24(1)	2(1)	10(1)	-3(1)
O(3)	24(1)	14(1)	33(1)	1(1)	11(1)	3(1)
O(4)	24(1)	20(1)	33(1)	-2(1)	12(1)	2(1)
O(5)	27(1)	20(1)	24(1)	3(1)	3(1)	-2(1)
O(6)	18(1)	25(1)	31(1)	-3(1)	2(1)	4(1)

Table S10. Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 7b.

	x	y	z	U(eq)
H(1)	4053	3409	3574	22
H(2)	4309	4228	4700	26
H(3)	3633	5670	4321	24
H(4)	-888	4530	1737	24
H(5)	-1858	5778	2212	28
H(6)	127	6635	2779	26
H(7)	5080	5182	1159	27
H(8)	5964	6588	1520	32
H(9)	4623	7084	2410	29
H(10)	47	3587	1310	20
H(11)	852	4611	618	21
H(13)	3895	3031	372	23
H(14A)	2264	3368	-707	26
H(14B)	2310	2402	-557	26
H(16)	281	1843	105	26
H(17)	923	2216	1306	21
H(18A)	-1232	3388	-752	33
H(18B)	-42	3713	-1154	33
H(19A)	-1990	1462	132	41
H(19B)	-1976	1977	-578	41
H(20A)	-3527	2476	433	60
H(20B)	-4157	1938	-245	60
H(20C)	-3633	2846	-345	60
H(21A)	1802	5118	-336	47
H(21B)	3227	5564	-253	47
H(21C)	2456	5550	396	47
H(23A)	3867	401	1687	34
H(23B)	3419	243	852	34
H(25)	417	221	795	34
H(26)	-1064	-808	1031	36
H(27)	-245	-1883	1777	44
H(28)	2000	-1937	2318	41
H(29)	3467	-932	2094	32
H(1B)	2710(20)	6514(13)	3117(11)	5(5)

Table S11. Torsion Angles [°] for 7b.

N(3)-C(1)-C(2)-C(3)	-0.5(3)
C(1)-C(2)-C(3)-N(4)	0.2(2)
N(1)-C(4)-C(5)-C(6)	0.1(3)
C(4)-C(5)-C(6)-N(2)	0.2(3)
N(5)-C(7)-C(8)-C(9)	1.2(3)
C(7)-C(8)-C(9)-N(6)	-1.0(3)
C(31)-Mo(1)-C(10)-C(11)	-91.30(13)
C(30)-Mo(1)-C(10)-C(11)	-166.22(14)
N(3)-Mo(1)-C(10)-C(11)	150.94(12)
N(5)-Mo(1)-C(10)-C(11)	11.51(16)
N(1)-Mo(1)-C(10)-C(11)	86.52(12)
C(12)-Mo(1)-C(10)-C(11)	-35.22(12)
C(31)-Mo(1)-C(10)-C(17)	19.48(18)
C(30)-Mo(1)-C(10)-C(17)	-55.44(16)
N(3)-Mo(1)-C(10)-C(17)	-98.28(18)
C(11)-Mo(1)-C(10)-C(17)	110.8(2)
N(5)-Mo(1)-C(10)-C(17)	122.28(16)
N(1)-Mo(1)-C(10)-C(17)	-162.71(17)
C(12)-Mo(1)-C(10)-C(17)	75.56(17)
C(17)-C(10)-C(11)-C(12)	-37.4(3)
Mo(1)-C(10)-C(11)-C(12)	77.82(16)
C(17)-C(10)-C(11)-Mo(1)	-115.23(17)
C(31)-Mo(1)-C(11)-C(12)	-18.48(14)
C(30)-Mo(1)-C(11)-C(12)	-102.97(14)
N(3)-Mo(1)-C(11)-C(12)	149.9(2)
N(5)-Mo(1)-C(11)-C(12)	72.23(13)
C(10)-Mo(1)-C(11)-C(12)	-116.10(18)
N(1)-Mo(1)-C(11)-C(12)	155.16(13)
C(31)-Mo(1)-C(11)-C(10)	97.62(13)
C(30)-Mo(1)-C(11)-C(10)	13.13(14)
N(3)-Mo(1)-C(11)-C(10)	-94.0(3)
N(5)-Mo(1)-C(11)-C(10)	-171.67(12)
N(1)-Mo(1)-C(11)-C(10)	-88.74(12)
C(12)-Mo(1)-C(11)-C(10)	116.10(18)
C(10)-C(11)-C(12)-O(2)	-179.32(19)
Mo(1)-C(11)-C(12)-O(2)	-109.0(2)
C(10)-C(11)-C(12)-C(13)	33.8(3)

Mo(1)-C(11)-C(12)-C(13)	104.17(19)
C(10)-C(11)-C(12)-Mo(1)	-70.35(15)
C(31)-Mo(1)-C(12)-O(2)	-83.74(17)
C(30)-Mo(1)-C(12)-O(2)	-157.62(16)
N(3)-Mo(1)-C(12)-O(2)	-36.9(3)
C(11)-Mo(1)-C(12)-O(2)	115.5(2)
N(5)-Mo(1)-C(12)-O(2)	6.53(17)
C(10)-Mo(1)-C(12)-O(2)	154.9(2)
N(1)-Mo(1)-C(12)-O(2)	88.63(17)
C(31)-Mo(1)-C(12)-C(11)	160.80(15)
C(30)-Mo(1)-C(12)-C(11)	86.92(14)
N(3)-Mo(1)-C(12)-C(11)	-152.38(19)
N(5)-Mo(1)-C(12)-C(11)	-108.92(13)
C(10)-Mo(1)-C(12)-C(11)	39.40(13)
N(1)-Mo(1)-C(12)-C(11)	-26.83(14)
C(31)-Mo(1)-C(12)-C(13)	48.71(16)
C(30)-Mo(1)-C(12)-C(13)	-25.17(17)
N(3)-Mo(1)-C(12)-C(13)	95.5(2)
C(11)-Mo(1)-C(12)-C(13)	-112.1(2)
N(5)-Mo(1)-C(12)-C(13)	138.99(16)
C(10)-Mo(1)-C(12)-C(13)	-72.69(16)
N(1)-Mo(1)-C(12)-C(13)	-138.92(15)
O(2)-C(12)-C(13)-N(7)	166.65(17)
C(11)-C(12)-C(13)-N(7)	-41.5(3)
Mo(1)-C(12)-C(13)-N(7)	28.5(2)
O(2)-C(12)-C(13)-C(14)	-75.6(2)
C(11)-C(12)-C(13)-C(14)	76.2(2)
Mo(1)-C(12)-C(13)-C(14)	146.20(14)
N(7)-C(13)-C(14)-C(15)	54.5(2)
C(12)-C(13)-C(14)-C(15)	-65.6(2)
C(13)-C(14)-C(15)-C(18)	130.0(2)
C(13)-C(14)-C(15)-C(16)	-48.7(2)
C(18)-C(15)-C(16)-O(1)	-9.3(3)
C(14)-C(15)-C(16)-O(1)	169.48(18)
C(18)-C(15)-C(16)-C(17)	-129.9(2)
C(14)-C(15)-C(16)-C(17)	48.9(2)
C(11)-C(10)-C(17)-N(7)	48.3(2)
Mo(1)-C(10)-C(17)-N(7)	-33.0(2)
C(11)-C(10)-C(17)-C(16)	-70.8(2)
Mo(1)-C(10)-C(17)-C(16)	-152.14(14)

O(1)-C(16)-C(17)-N(7)	-178.30(17)
C(15)-C(16)-C(17)-N(7)	-54.3(2)
O(1)-C(16)-C(17)-C(10)	-58.0(2)
C(15)-C(16)-C(17)-C(10)	66.0(2)
O(3)-C(23)-C(24)-C(25)	36.3(3)
O(3)-C(23)-C(24)-C(29)	-145.8(2)
C(29)-C(24)-C(25)-C(26)	0.8(4)
C(23)-C(24)-C(25)-C(26)	178.6(2)
C(24)-C(25)-C(26)-C(27)	-0.8(4)
C(25)-C(26)-C(27)-C(28)	0.7(4)
C(26)-C(27)-C(28)-C(29)	-0.7(4)
C(27)-C(28)-C(29)-C(24)	0.7(4)
C(25)-C(24)-C(29)-C(28)	-0.8(4)
C(23)-C(24)-C(29)-C(28)	-178.7(2)
C(31)-Mo(1)-C(30)-O(5)	28(3)
N(3)-Mo(1)-C(30)-O(5)	-69(3)
C(11)-Mo(1)-C(30)-O(5)	128(3)
N(5)-Mo(1)-C(30)-O(5)	-39(3)
C(10)-Mo(1)-C(30)-O(5)	136(3)
N(1)-Mo(1)-C(30)-O(5)	-146(3)
C(12)-Mo(1)-C(30)-O(5)	94(3)
C(30)-Mo(1)-C(31)-O(6)	-127(14)
N(3)-Mo(1)-C(31)-O(6)	-46(14)
C(11)-Mo(1)-C(31)-O(6)	131(14)
N(5)-Mo(1)-C(31)-O(6)	33(14)
C(10)-Mo(1)-C(31)-O(6)	169(100)
N(1)-Mo(1)-C(31)-O(6)	5(15)
C(12)-Mo(1)-C(31)-O(6)	120(14)
C(5)-C(4)-N(1)-N(2)	-0.4(2)
C(5)-C(4)-N(1)-Mo(1)	179.22(15)
C(31)-Mo(1)-N(1)-C(4)	175.5(5)
C(30)-Mo(1)-N(1)-C(4)	-53.9(2)
N(3)-Mo(1)-N(1)-C(4)	-132.9(2)
C(11)-Mo(1)-N(1)-C(4)	48.7(2)
N(5)-Mo(1)-N(1)-C(4)	147.0(2)
C(10)-Mo(1)-N(1)-C(4)	11.4(2)
C(12)-Mo(1)-N(1)-C(4)	63.2(2)
C(31)-Mo(1)-N(1)-N(2)	-4.9(6)
C(30)-Mo(1)-N(1)-N(2)	125.66(15)
N(3)-Mo(1)-N(1)-N(2)	46.62(14)

C(11)-Mo(1)-N(1)-N(2)	-131.74(15)
N(5)-Mo(1)-N(1)-N(2)	-33.46(15)
C(10)-Mo(1)-N(1)-N(2)	-169.08(15)
C(12)-Mo(1)-N(1)-N(2)	-117.31(15)
C(5)-C(6)-N(2)-N(1)	-0.4(3)
C(5)-C(6)-N(2)-B(1)	-171.4(2)
C(4)-N(1)-N(2)-C(6)	0.5(2)
Mo(1)-N(1)-N(2)-C(6)	-179.19(14)
C(4)-N(1)-N(2)-B(1)	172.03(19)
Mo(1)-N(1)-N(2)-B(1)	-7.6(2)
N(6)-B(1)-N(2)-C(6)	-127.7(2)
N(4)-B(1)-N(2)-C(6)	115.5(2)
N(6)-B(1)-N(2)-N(1)	62.2(2)
N(4)-B(1)-N(2)-N(1)	-54.6(2)
C(2)-C(1)-N(3)-N(4)	0.7(2)
C(2)-C(1)-N(3)-Mo(1)	-170.13(15)
C(31)-Mo(1)-N(3)-C(1)	-56.0(2)
C(30)-Mo(1)-N(3)-C(1)	24.96(19)
C(11)-Mo(1)-N(3)-C(1)	135.4(2)
N(5)-Mo(1)-N(3)-C(1)	-144.0(2)
C(10)-Mo(1)-N(3)-C(1)	64.4(2)
N(1)-Mo(1)-N(3)-C(1)	130.1(2)
C(12)-Mo(1)-N(3)-C(1)	-99.7(3)
C(31)-Mo(1)-N(3)-N(4)	134.42(16)
C(30)-Mo(1)-N(3)-N(4)	-144.62(17)
C(11)-Mo(1)-N(3)-N(4)	-34.2(3)
N(5)-Mo(1)-N(3)-N(4)	46.38(15)
C(10)-Mo(1)-N(3)-N(4)	-105.15(17)
N(1)-Mo(1)-N(3)-N(4)	-39.46(15)
C(12)-Mo(1)-N(3)-N(4)	90.7(2)
C(2)-C(3)-N(4)-N(3)	0.2(2)
C(2)-C(3)-N(4)-B(1)	177.1(2)
C(1)-N(3)-N(4)-C(3)	-0.6(2)
Mo(1)-N(3)-N(4)-C(3)	171.23(14)
C(1)-N(3)-N(4)-B(1)	-177.79(19)
Mo(1)-N(3)-N(4)-B(1)	-6.0(3)
N(2)-B(1)-N(4)-C(3)	-112.6(2)
N(6)-B(1)-N(4)-C(3)	128.2(2)
N(2)-B(1)-N(4)-N(3)	64.0(2)
N(6)-B(1)-N(4)-N(3)	-55.2(2)

C(8)-C(7)-N(5)-N(6)	-0.9(3)
C(8)-C(7)-N(5)-Mo(1)	-168.79(16)
C(31)-Mo(1)-N(5)-C(7)	26.8(2)
C(30)-Mo(1)-N(5)-C(7)	92.2(3)
N(3)-Mo(1)-N(5)-C(7)	122.7(2)
C(11)-Mo(1)-N(5)-C(7)	-75.2(2)
C(10)-Mo(1)-N(5)-C(7)	-82.2(2)
N(1)-Mo(1)-N(5)-C(7)	-156.9(2)
C(12)-Mo(1)-N(5)-C(7)	-43.7(2)
C(31)-Mo(1)-N(5)-N(6)	-139.59(16)
C(30)-Mo(1)-N(5)-N(6)	-74.2(3)
N(3)-Mo(1)-N(5)-N(6)	-43.66(15)
C(11)-Mo(1)-N(5)-N(6)	118.40(16)
C(10)-Mo(1)-N(5)-N(6)	111.44(16)
N(1)-Mo(1)-N(5)-N(6)	36.71(15)
C(12)-Mo(1)-N(5)-N(6)	149.89(16)
C(8)-C(9)-N(6)-N(5)	0.5(3)
C(8)-C(9)-N(6)-B(1)	168.1(2)
C(7)-N(5)-N(6)-C(9)	0.3(2)
Mo(1)-N(5)-N(6)-C(9)	169.73(15)
C(7)-N(5)-N(6)-B(1)	-168.41(19)
Mo(1)-N(5)-N(6)-B(1)	1.0(3)
N(2)-B(1)-N(6)-C(9)	135.0(2)
N(4)-B(1)-N(6)-C(9)	-108.6(2)
N(2)-B(1)-N(6)-N(5)	-58.6(3)
N(4)-B(1)-N(6)-N(5)	57.8(2)
O(4)-C(22)-N(7)-C(13)	16.9(3)
O(3)-C(22)-N(7)-C(13)	-163.68(18)
O(4)-C(22)-N(7)-C(17)	167.2(2)
O(3)-C(22)-N(7)-C(17)	-13.3(3)
C(12)-C(13)-N(7)-C(22)	-155.10(19)
C(14)-C(13)-N(7)-C(22)	86.8(2)
C(12)-C(13)-N(7)-C(17)	51.5(2)
C(14)-C(13)-N(7)-C(17)	-66.5(2)
C(10)-C(17)-N(7)-C(22)	153.3(2)
C(16)-C(17)-N(7)-C(22)	-85.1(2)
C(10)-C(17)-N(7)-C(13)	-55.0(2)
C(16)-C(17)-N(7)-C(13)	66.6(2)
C(15)-C(16)-O(1)-C(19)	93.9(2)
C(17)-C(16)-O(1)-C(19)	-143.9(2)

C(20)-C(19)-O(1)-C(16)	-168.4(2)
C(11)-C(12)-O(2)-C(21)	-8.3(3)
C(13)-C(12)-O(2)-C(21)	142.0(2)
Mo(1)-C(12)-O(2)-C(21)	-82.5(2)
O(4)-C(22)-O(3)-C(23)	0.6(3)
N(7)-C(22)-O(3)-C(23)	-178.82(19)
C(24)-C(23)-O(3)-C(22)	-164.5(2)