Supporting Information 1

A New Reaction Motif: "Homo S_N2'-Like" Direct Nucleophilic Addition to Neutral η^3-Allylmolybdenum Complexes. Total Synthesis of the Antimalarial (+)–Isofebrifugine

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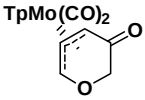
General Methods

All reactions were performed under an atmosphere of dry argon in oven-dried glasswares unless otherwise noted. Solvents (THF, DMSO, DMF, MeOH, CH_2Cl_2 and toluene) for reaction media were ACS reagent grade and purchased from Aldrich. Solvents were dried over 4 Å molecular sieves and titrated for water level with a Fisher Coulomatic K-F titrator before using. Hexanes, ethyl acetate (EtOAc), dichloromethane (DCM) and diethyl ether (Et_2O) used for extraction and chromatography were obtained from EM Science and used as purchased. Brine refers to a saturated aqueous solution of NaCl. Analytical thin-layer chromatography (TLC) was carried out using Merck Kieselgel 0.25 mm 60 F_{254} plates with visualization by UV or phosphomolybdic acid. ^{1}H NMR and ^{13}C NMR spectra were recorded on a VNMR 400 (400 MHz ^{1}H, 100 MHz ^{13}C), Varian INOVA 400 (400 MHz ^{1}H, 100 MHz ^{13}C), and Varian INOVA 600 (600 MHz ^{1}H, 150 MHz ^{13}C) instruments in $CDCl_3$, with the solvent residual peak as internal reference ($CDCl_3$: ^{1}H = 7.26 ppm, ^{13}C = 77.0 ppm) unless otherwise stated. Data are reported in the following order: chemical shifts (δ); multiplicities [br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)]; coupling constants, *J* (Hz); integration. Infrared (IR) spectroscopy was performed on an ASI ReactIR 1000 spectrometer. 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). Uncalibrated melting points were taken on a Thomas-Hoover melting point apparatus in open capillary tubes. *Since all of the Tp molybdenum complexes decompose over 180-200* °C*, melting points are not significant and are not provided in the experimental section.* High-resolution mass spectra were obtained on a JEOL JMS-SX102/SX102A/E instrument. Optical rotations were measured with a Perkin-Elmer Model 341polarimeter. HPLC was performed using an Agilent 1100 Series with UV detector (254 nm or 210 nm) and Daicel® Chiralpak AS-RH, Chiralpak AD-RH, Chiralcel OJ-RH, Chiralcel OD-RH, or Agilent Eclipse XDB-C8 columns. Samples for

HPLC analysis were prepared by dissolving 1-2 mg of of the pure material in approximately 0.5 mL of acetonitrile. One microliter (1 μL) of the solution was injected for analysis. Scaffolds **1** and **2** were prepared according to literature procedures.[1]



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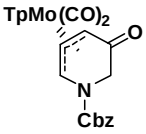
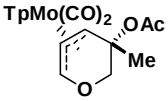


2

1. Prepartion of Substrates for the Homo S_N2'-like Reaction

(+) and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2R,5R)(*η*-2,3,4)-5-acetoxy-5-methyl-5,6-dihydro-2H-pyran-2-yl]molybdenum, (+)-3a and (±)-3a



3a

To a suspension of (±)-**1** (500 mg, 1.08 mmol, 1.0 equiv) in THF (25 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 0.54 mL, 1.62 mmol, 1.5 equiv) at -78 °C. The reaction mixture was slowly warmed to 0 °C over 30 minutes, stirred at 0 °C for 40 minutes, and then quenched with Ac_2O (176 mg, 1.73 mmol, 1.6 equiv). After stirring for 1 h at room temperature, the mixture was poured into a separatory funnel containing EtOAc (15 mL) and H_2O (15 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 10 mL), and the combined organic layer were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (3:1) afforded (±)–**3a** (406 mg, 0.78 mmol, 72%) as a yellow solid.

Similar treatment of (+)-**1** (53 mg, 0.11 mmol, 1.0 equiv, 96% ee) in THF (3 mL) with methylmagnesium bromide (3.0 M in Et_2O, 0.06 mL, 0.16 mmol, 1.5 equiv) afforded (2R,

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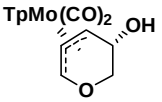
[1] Coombs, T. C.; Lee, M. D.; Wong, H.; Armstrong, M.; Cheng, B.; Chen, W.; Moretto, A. F.; Liebeskind, L. S., *J. Org. Chem.* **2008,** *73,* 882

5R)-(+)-**3a** (34 mg, 0.065 mmol, 60%) {$[\alpha]_D^{20}$ = +256.3, (c = 0.3, CH_2Cl_2)}, TLC (R_f =0.6, 2.5:1 hexanes: EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 1.6 Hz, 1 H), 7.91 (d, *J* = 2.0 Hz, 1 H), 7.66 (d, *J* = 2.0 Hz, 1 H), 7.58 (d, *J* = 2.0 Hz, 1 H), 7.55 (d, *J* = 1.6 Hz, 1 H), 7.49 (d, *J* = 2.4 Hz, 1 H), 7.01 (dd, *J* = 4.4 Hz, 2.4 Hz, 1 H), 6.28 (t, *J* = 2.0 Hz, 1 H), 6.20 (t, *J* = 2.0 Hz, 1 H), 6.18 (t, *J* = 2.0 Hz, 1 H), 5.25 (d, *J* = 8.0 Hz, 1 H), 3.49 (d, *J* = 11.2 Hz, 1 H), 3.34 (dd, *J* = 8.0 Hz, 3.6 Hz, 1 H), 2.56 (d, *J* = 10.8 Hz, 1 H), 2.02 (s, 3 H), 1.88 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.1 (Mo-CO), 224.7 (Mo-CO), 170.9 ($CH_3\underline{C}OO$), 146.7 (CH), 142.9 (CH), 141.5 (CH), 136.01 (CH), 135.96 (CH), 134.4 (CH), 109.7 (CH), 105.9 (CH), 105.6 (CH), 105.4 (CH), 79.1, 71.4, 70.8, 56.4, 29.1 (CH_3), 21.9 (CH_3). IR (cm^{-1}) 2968 (w), 2468 (m), 1945 (s), 1857 (s), 1729 (s). HRMS (FAB) Calcd. for $C_{19}H_{21}BMoN_6O_5$ ($[M+Na]^+$): 545.0618. Found: 545.0632.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-2,3,4)-5-hydroxy-5,6-dihydro-2H-pyran-2-yl]molybdenum, (±)-S1



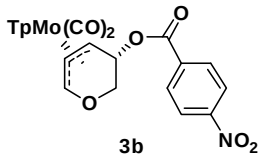
S1

To a solution of (±)-**1** (500 mg, 1.08 mmol, 1.0 equiv) in THF (30 mL) was added DIBAL (1.0 M in hexane, 1.62 mL, 1.62 mmol, 1.5 equiv) at 0 °C. The reaction mixture was stirred at 0 °C for 20 minutes, and then quenched with potassium sodium tartrate tetrahydrate (610 mg, 2.16 mmol, 2.0 equiv) and H_2O (10 mL). The mixture was poured into a separatory funnel containing EtOAc (15 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL), and the combined organic layer was dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**S1** (464 mg, 1.00 mmol, 93%) as an orange solid.

TLC (R_f = 0.27, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 2.0 Hz, 1 H), 7.88 (d, *J* = 2.0 Hz, 1 H), 7.72 (d, *J* = 2.0 Hz, 1 H), 7.57-7.60 (m, 1 H), 7.51 (d, *J* = 1.6 Hz, 1 H),

6.99 (dd, J = 4.4 Hz, 2.4 Hz, 1 H), 6.30 (t, J = 2.4 Hz, 1 H), 6.22 (t, J = 2.4 Hz, 1 H), 6.20 (t, J = 2.4 Hz, 1 H), 4.62-4.72 (m, 2 H), 3.68 (dd, J = 11.2 Hz, 6.4 Hz, 1 H), 3.45 (dd, J = 7.6 Hz, 4.4 Hz, 1 H), 2.50 (br s, 1 H), 2.37 (t, J = 10.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.4 (Mo-CO), 223.9 (Mo-CO), 146.8 (CH), 142.0 (CH), 141.9 (CH), 136.14 (CH), 136.09 (CH), 134.5 (CH), 110.3 (CH), 106.1 (CH), 105.7 (CH), 105.4 (CH), 71.7, 68.0, 67.2, 57.9. IR (cm^{-1}) 3127 (w), 2957 (w), 2490 (m), 1957 (s), 1872 (s), 1660 (s). HRMS (ESI) Calcd. for $C_{16}H_{17}BMoN_6O_4$ ([M-H]$^-$): 465.0375. Found: 465.0375.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-2,3,4)-5-*p*-nitrobenzoyloxy-5,6-dihydro-2Hpyran-2-yl]molybdenum, (±)-3b



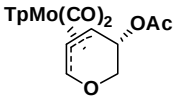
3b

To a solution of (±)-**S1** (464 mg, 1.00 mmol, 1.0 equiv) in DCM (40 mL) was added DMAP (366 mg, 3.00 mmol, 3.0 equiv), TEA (300 mg, 3.00 mmol, 3.0 equiv) and *p*-nitrobenzoyl chloride (558 mg, 3.00 mmol, 3.0 equiv). The reaction mixture was stirred at 40 °C overnight, and then concentrated to remove DCM and excess TEA. The residue was triturated with EtOAc (60 mL) and then filtered. The organic solution was concentrated for chromatography. Flash chromatography over silica gel with hexanes-EtOAc (2.7:1) afforded (±)–**3b** (594 mg, 0.97 mmol, 97%) as a yellow solid.

TLC (R_f = 0.71, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 2.0 Hz, 1 H), 8.24-8.31 (m, 4 H), 7.77 (d, J = 2.0 Hz, 1 H), 7.76 (d, J = 2.0 Hz, 1 H), 7.61 (d, J = 2.4 Hz, 1 H), 7.59 (d, J = 2.4 Hz, 1 H), 7.53 (d, J = 2.4 Hz, 1 H), 7.10 (dd, J = 4.4 Hz, 2.0 Hz, 1 H), 6.29 (t, J = 2.0 Hz, 1 H), 6.22 (t, J = 2.0 Hz, 1 H), 6.16 (t, J = 2.0 Hz, 1 H), 5.97 (ddd, J = 10.0 Hz, 6.8 Hz, 2.8 Hz, 1 H), 4.72 (d, J = 7.6 Hz, 1 H), 3.81 (dd, J = 11.2 Hz, 6.4 Hz, 1 H), 3.54 (dd, J = 7.6 Hz, 4.4

Hz, 1 H), 2.69 (t, J = 10.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.6 (Mo-CO), 224.2 (Mo-CO), 164.2 (Ar-COO), 150.5, 146.7, 141.8, 136.13, 136.11, 135.1, 134.5, 131.0, 123.4, 110.3, 106.0, 105.7, 105.3, 77.2, 69.9, 65.2, 64.4, 57.9. IR (cm^{-1}) 3123 (w), 2984 (w), 2486 (m), 1945 (s), 1857 (s), 1722 (s), 1606 (s). HRMS (ESI) Calcd. for $C_{23}H_{20}BMoN_7O_7$ ($[M+H]^+$): 616.0644. Found: 616.0657.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-2,3,4)-5-acetate-5,6-dihydro-2H-pyran-2-yl]molybdenum, (±)-S2



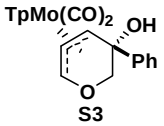
S2

To a solution of (±)-**S1** (200 mg, 0.43 mmol, 1.0 equiv) in DCM (20 mL) was added DMAP (157 mg, 1.29 mmol, 3.0 equiv), TEA (129 mg, 1.29 mmol, 3.0 equiv) and acetic anhydride (132 mg, 1.29 mmol, 3.0 equiv). The reaction mixture was stirred at 40 °C overnight, and then concentrated to remove DCM and excess TEA. The mixture was poured into a separatory funnel containing EtOAc (15 mL) and H_2O (15mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 10 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (3:1) afforded (±)–**S2** (190 mg, 0.40 mmol, 94%) as a yellow solid.

TLC (R_f = 0.57, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 2.0 Hz, 1 H), 7.76 (d, J = 2.0 Hz, 1 H), 7.73 (d, J = 2.0 Hz, 1 H), 7.58 (d, J = 2.4 Hz, 1 H), 7.57 (d, J = 2.0 Hz, 1 H), 7.51 (d, J = 2.0 Hz, 1 H), 7.04 (dd, J = 4.4 Hz, 2.4 Hz, 1 H), 6.29 (t, J = 2.4 Hz, 1 H), 6.20 (t, J = 2.0 Hz, 1 H), 6.18 (t, J = 2.0 Hz, 1 H), 5.60 (ddd, J = 8.8 Hz, 6.4 Hz, 2.8 Hz, 1 H), 4.67 (dt, J = 7.6 Hz, 2.4 Hz, 1 H), 3.67 (dd, J = 10.8 Hz, 6.8 Hz, 1 H), 3.45 (dd, J = 8.0 Hz, 4.0 Hz, 1 H), 2.56 (dd, J = 11.2 Hz, 9.6 Hz, 1 H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 227.8 (Mo-CO), 224.6 (Mo-CO), 170.9 ($CH_3\underline{C}OO$), 146.7 (CH), 141.91 (CH), 141.87 (CH), 136.1 (CH), 136.0

(CH), 134.5 (CH), 110.9 (CH), 106.0 (CH), 105.6 (CH), 105.3 (CH), 68.6, 65.1, 64.6, 57.8, 20.9 (CH_3). IR (cm^{-1}) 3146 (w), 2976 (w), 2482 (m), 1945 (s), 1857 (s), 1729 (s). HRMS (ESI) Calcd. for $C_{18}H_{19}BmoN_6O_5$ ($[M]^+$): 508.0559. Found: 508.0569.

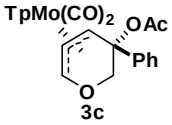
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-2,3,4)-5-hydroxy-5-phenyl-5,6-dihydro-2H-pyran-2-yl]molybdenum, (±)-S3



To a suspension of (±)-**1** (200 mg, 0.43 mmol, 1.0 equiv) in THF (25 mL) was added phenylmagnesium bromide (3.0 M in Et_2O, 0.22 mL, 0.65 mmol, 1.5 equiv) at 0 °C. The reaction mixture stirred at 0 °C for 30 minutes, and then quenched with saturated NH_4Cl. The mixture was poured into a separatory funnel containing EtOAc (15 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 10 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**S3** (174 mg, 0.32 mmol, 75%) as an orange solid.

TLC (R_f =0.37, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.0 Hz, 1 H), 7.86 (d, *J* = 2.0 Hz, 1 H), 7.81 (d, *J* = 1.2 Hz, 1 H), 7.79 (d, *J* = 1.2 Hz, 1 H), 7.74 (d, *J* = 1.6 Hz, 1 H), 7.58 (d, *J* = 2.0 Hz, 1 H), 7.56 (d, *J* = 2.0 Hz, 1 H), 7.51 (d, *J* = 2.0 Hz, 1 H), 7.38-7.42 (m, 2 H), 7.27-7.32 (m, 1 H), 7.13 (dd, *J* = 4.4 Hz, 2.0 Hz, 1 H), 6.31 (t, *J* = 2.0 Hz, 1 H), 6.21 (t, *J* = 2.0 Hz, 1 H), 6.16 (t, *J* = 2.4 Hz, 1 H), 4.63 (d, *J* = 7.6 Hz, 1 H), 3.83 (d, *J* = 11.6 Hz, 1 H), 3.51 (dd, *J* = 8.0 Hz, 4.8 Hz, 1 H), 2.85 (d, *J* = 11.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.2 (Mo-CO), 224.0 (Mo-CO), 148.7, 146.9, 142.3, 141.7, 136.1, 134.5, 128.5, 127.4, 124.5, 109.5, 106.1, 105.7, 105.3, 77.7, 77.2, 73.1, 72.8, 58.7. IR (cm^{-1}) 3451 (w), 3142 (w), 2482 (m), 1942 (s), 1849 (s), 1505 (s). HRMS (FAB) Calcd. for $C_{22}H_{21}BMoN_6O_4$ ($[M+H]^+$): 543.0844. Found: 543.0849. ($[M-OH]^+$): 525.0739. Found: 525.0739.

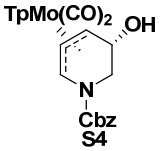
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-2,3,4)-5-acetoxy-5-phenyl-5,6-dihydro-2H-pyran-2-yl]molybdenum, (±)-3c



To a solution of (±)-**S3** (138 mg, 0.26 mmol, 1.0 equiv) in DCM (20 mL) was added DMAP (122 mg, 0.78 mmol, 3.0 equiv), TEA (78 mg, 0.77 mmol, 3.0 equiv) and Ac_2O (85 mg, 0.77 mmol, 3.0 equiv). The reaction mixture was stirred at 40 °C overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (15 mL) and H_2O (15mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (3:1) afforded (±)–**3c** (129 mg, 0.22 mmol, 85%) as a yellow solid.

TLC (R_f = 0.57, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.0 Hz, 1 H), 7.95 (d, *J* = 1.6 Hz, 1 H), 7.65-7.68 (m, 3 H), 7.58-7.60 (m, 2 H),7.52 (d, *J* = 2.4 Hz, 1 H), 7.41 (t, *J* = 7.2 Hz, 2 H), 7.30 (t, *J* = 7.2 Hz, 1 H), 7.13 (dd, *J* = 4.4, 2.0 Hz, 1 H), 6.31 (t, *J* = 2.0 Hz, 1 H), 6.20 (t, *J* = 2.0 Hz, 1 H), 6.19 (t, *J* = 2.0 Hz, 1 H), 4.90 (d, *J* = 7.2 Hz, 1 H), 4.38 (d, *J* = 11.6 Hz, 1 H), 3.50 (dd, *J* = 8.0 Hz, 4.8 Hz, 1 H), 2.96 (d, *J* = 11.6 Hz, 1 H), 2.12 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.8 (Mo-CO), 224.9 (Mo-CO), 169.8 ($CH_3\underline{C}OO$), 146.8, 146.1, 142.9, 141.4, 136.0, 134.5, 128.6, 127.4, 124.0, 108.8, 106.0, 105.6, 105.3, 80.3, 77.2, 72.8, 71.2, 57.4, 21.5 (CH_3). IR (cm^{-1}) 3427 (w), 2482 (m), 1945 (s), 1857 (s), 1737 (s), 1710 (s), 1505 (s). HRMS (FAB) Calcd. for $C_{24}H_{23}BMoN_6O_5$ ($[M\text{-}OAc]^+$): 525.0739. Found: 525.0745.

(+) and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2R,5R)-(η-2,3,4)-1-benzyloxycarbonyl5-hydroxy-5,6-dihydro-2H-pyridin-2-yl]molybdenum, (+)-S4 and (±)-S4



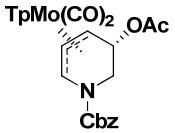
To a solution of (±)-**2** (500 mg, 0.84 mmol, 1.0 equiv) in THF (30 mL) was added DIBAL (1.0 M in hexane, 2.1 mL, 2.10 mmol, 2.5 equiv) at 0 °C. The reaction mixture was stirred at 0 °C for 20 minutes, and then quenched with potassium sodium tartrate tetrahydrate (740 mg, 2.52 mmol, 3.0 equiv) and H_2O (10 mL). The mixture was poured into a separatory funnel containing EtOAc (15 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 25 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**S4** (462 mg, 0.78 mmol, 93%) as an orange solid.

Similar treatment of (+)-**2** (500 mg, 0.84 mmol, 1.0 equiv, >99% ee) in THF (30 mL) with DIBAL (1.0 M in hexane, 2.1 mL, 2.10 mmol, 2.5 equiv) afforded (2R, 5R)-(+)-**S4** (458 mg, 0.77 mmol, 92%) {$[\alpha]_D^{20}$ = +467, (c = 0.1, CH_2Cl_2)}

TLC (R_f = 0.29, 2.5:1 hexanes:EtOAc). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.0 Hz, 0.4 H), 8.44 (d, *J* = 1.6 Hz, 0.6 H), 8.20 (d, *J* = 1.6 Hz, 0.6 H), 7.80 (d, *J* = 2.0 Hz, 0.4 H), 7.79 (d, *J* = 2.0 Hz, 0.6 H), 7.63 (d, *J* = 2.0 Hz, 0.6 H), 7.59-7.61 (m, 1.2 H), 7.57 (d, *J* = 2.4 Hz, 0.4 H), 7.56 (d, *J* = 2.0 Hz, 0.4 H), 7.47-7.51 (m, 2.0 H), 7.30-7.41 (m, 4.0 H), 7.14 (dd, *J* = 6.0 Hz, 1.6 Hz, 0.6 H), 6.91 (dd, *J* = 6.0 Hz, 1.2 Hz, 0.4 H), 6.23 (t, *J* = 2.0 Hz, 1.2 H), 6.20 (t, *J* = 2.0 Hz, 0.6 H), 6.16-6.18 (m, 0.8 H), 5.97 (t, *J* = 2.0 Hz, 0.4 H), 5.35 (d, *J* = 11.6 Hz, 0.4 H), 5.23 (d, *J* = 12.4 Hz, 1.2 H), 5.21 (d, *J* = 12.0 Hz, 0.4 H), 4.68-4.79 (m, 2 H), 3.80 (dd, *J* = 12.4 Hz, 6.8 Hz, 0.4 H), 3.74 (dd, *J* = 12.0 Hz, 6.4 Hz, 0.6 H), 3.42 (t, *J* = 6.8 Hz, 0.6 H), 3.31

(t, J = 6.4 Hz, 0.4 H), 2.81 (br s, 1 H), 1.91 (t, J = 12.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.5 (Mo-CO), 231.8 (Mo-CO), 223.8 (Mo-CO), 223.5 (Mo-CO), 155.7 (Cbz carbonyl), 155.2 (Cbz carbonyl), 146.75, 146.68, 143.9, 143.0, 140.8, 140.6, 135.98, 135.96, 135.9, 135.7, 134.4, 128.7, 128.6, 128.4, 128.0, 127.8, 105.9, 105.7, 105.5, 105.4, 92.5, 91.0, 69.0, 68.4, 68.3, 67.7, 67.6, 57.7, 57.4, 47.21 (N-CH_2), 47.20 (N-CH_2). IR (cm^{-1}) 3439 (w), 3127 (w), 2486 (m), 1942 (s), 1841 (s), 1695 (s), 1505 (s). HRMS (ESI) Calcd. for $C_{24}H_{24}BMoN_7O_5$ ($[M+NH_4]^+$): 617.1324. Found: 617.1325.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-2,3,4)-1-benzyloxycarbonyl-5-acetoxy-5, 6dihydro-2H-pyridin-2-yl]molybdenum, (±)-4a



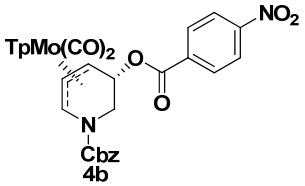
4a

To a solution of (±)-**S3** (200 mg, 0.34 mmol, 1.0 equiv) in DCM (20 mL) was added DMAP (157 mg, 1.01 mmol, 3.0 equiv), TEA (102 mg, 1.01 mmol, 3.0 equiv) and Ac_2O (111 mg, 1.01 mmol, 3.0 equiv). The reaction mixture was stirred at 40 °C overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (15 mL) and H_2O (15mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (3:1) afforded (±)–**4a** (204 mg, 0.32 mmol, 95%) as a yellow solid.

TLC (R_f = 0.53, 2.5:1 hexanes:EtOAc). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$) δ 8.47 (d, J = 1.2 Hz, 0.6 H), 8.46 (d, J = 2.0 Hz, 0.4 H), 8.24 (d, J = 1.2 Hz, 0.6 H), 7.68 (d, J = 2.0 Hz, 0.6 H), 7.67 (d, J = 2.0 Hz, 0.4 H), 7.64 (d, J = 2.0 Hz, 0.4 H), 7.59 (d, J = 2.4 Hz, 0.6 H), 7.58 (d, J = 2.4 Hz, 0.6 H), 7.55 (d, J = 2.0 Hz, 0.4 H), 7.52 (d, J = 2.0 Hz, 0.4 H),

7.45-7.50 (m, 2 H), 7.31-7.42 (m, 4 H), 7.15 (dd, J = 6.0 Hz, 1.6 Hz, 0.6 H), 6.89 (dd, J = 6.4 Hz, 1.6 Hz, 0.4 H), 6.26 (t, J = 2.4 Hz, 1 H), 6.22 (t, J = 2.4 Hz, 0.6 H), 6.16-6.19 (m, 1 H), 5.91 (t, J = 2.4 Hz, 0.4 H), 5.67-5.77 (m, 1 H), 5.31 (d, J = 11.6 Hz, 0.4 H), 5.21 (s, 1.2 H), 5.20 (d, J = 11.6 Hz, 0.4 H), 4.69-4.73 (m, 0.4 H), 4.66 (dt, J = 8.0 Hz, 2.0 Hz, 0.6 H), 3.64 (quintet, J = 6.4 Hz, 1 H), 3.45 (t, J = 7.2 Hz, 0.6 H), 3.37 (t, J = 6.8 Hz, 0.4 H), 2.18 (dd, J = 12.8 Hz, 9.2 Hz, 0.4 H), 2.12 (s, 1.2 H), 2.10 (s, 1.8 H), 2.07 (dd, J = 12.4 Hz, 9.6 Hz, 0.6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.8 (Mo-CO), 228.5 (Mo-CO), 224.1 (Mo-CO), 223.9 (Mo-CO), 170.8 ($CH_3\underline{C}OO$), 155.7 (Cbz carbonyl), 155.1 (Cbz carbonyl), 146.85, 146.78, 144.4, 143.4, 140.7, 140.6, 136.1, 136.00, 135.95, 135.7, 134.5, 128.9, 128.6, 128.5, 128.1, 128.0, 105.9, 105.8, 105.5, 105.4, 93.8, 92.4, 69.1, 68.9, 68.6, 67.9, 62.1, 61.8, 58.6, 58.1, 43.8 (N-CH_2), 43.7 (N-CH_2), 21.0 ($\underline{C}H_3COO$), 20.9 ($\underline{C}H_3COO$). IR (cm^{-1}) 3127 (w), 3034 (w), 2482 (m), 1942 (s), 1849 (s), 1729 (s), 1702 (s), 1505 (s). HRMS (ESI) Calcd. for $C_{26}H_{26}BMoN_8O_8$ ([M]$^+$): 641.1092. Found: 641.1101. ([M+NH_4]$^+$): 659.1435. Found: 659.1442.

(+) and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-2,3,4)-1-benzyloxycarbonyl-5-*p*-nitrobenzoyloxy5,6-dihydro-2H-pyridin-2-yl]molybdenum, (+)-4b and (±)-4b



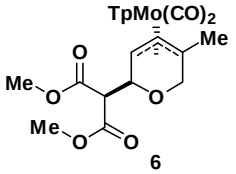
To a solution of (±)-**S4** (500 mg, 0.84 mmol, 1.0 equiv) in DCM (40 mL) was added DMAP (307 mg, 2.52 mmol, 3.0 equiv), TEA (252 mg, 2.52 mmol, 3.0 equiv) and *p*-nitrobenzoyl chloride (469 mg, 2.52 mmol, 3.0 equiv). The reaction mixture was stirred at 40 °C overnight, and then concentrated to remove DCM and excess TEA. The residue was triturated with EtOAc (60 mL) and then filtered. The organic solution was concentrated for chromatography. Flash chromatography over silica gel with hexanes-EtOAc (3:1) afforded (±)–**4b** (597 mg, 0.80 mmol,

95%) as a yellow solid. Similar treatment of (+)-**S3** (500 mg, 0.84 mmol, 1.0 equiv, >99% ee) in DCM (40 mL) with DMAP (307 mg, 2.52 mmol, 3.0 equiv), TEA (252 mg, 2.52 mmol, 3.0 equiv) and *p*-nitrobenzoyl chloride (469 mg, 2.52 mmol, 3.0 equiv) afforded (2R, 5R)-(+)-**4b** (574 mg, 0.77 mmol, 92%) {$[\alpha]_D^{20}$ = +242, (c = 0.1, CH_2Cl_2)}

TLC (R_f = 0.58, 2.5:1 hexanes: EtOAc). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.0 Hz, 1 H), 8.28-8.33 (m, 4 H), 8.25 (d, *J* = 2.0 Hz, 0.6 H), 7.70 (d, *J* = 2.0 Hz, 0.6 H), 7.69 (d, *J* = 2.0 Hz, 0.4 H), 7.66 (d, *J* = 2.0 Hz, 0.4 H), 7.62 (d, *J* = 2.4 Hz, 0.6 H), 7.59 (d, *J* = 2.0 Hz, 0.6 H), 7.57 (d, *J* = 2.4 Hz, 0.4 H), 7.55 (d, *J* = 2.0 Hz, 0.4 H), 7.51 (d, *J* = 2.0 Hz, 1 H), 7.49 (d, *J* = 2.0 Hz, 1 H), 7.29-7.45 (m, 4 H), 7.22 (dd, *J* = 6.4 Hz, 1.6 Hz, 0.6 H), 6.97 (dd, *J* = 6.4 Hz, 1.6 Hz, 0.4 H), 6.26-6.30 (m, 1 H), 6.25 (t, *J* = 2.0 Hz, 0.6 H), 6.16-6.19 (m, 1 H), 6.03-6.11 (m, 1 H), 5.95 (t, *J* = 2.0 Hz, 0.4 H), 5.34 (d, *J* = 12.0 Hz, 0.4 H), 5.23 (d, *J* = 11.6 Hz, 0.4 H), 5.22 (s, 1.2 H), 4.76 (d, *J* = 8.0 Hz, 0.4 H), 4.72 (d, *J* = 7.6 Hz, 0.6 H), 3.82 (t, *J* = 7.6 Hz, 0.4 H), 3.79 (t, *J* = 7.2 Hz, 0.6 H), 3.55 (t, *J* = 6.8 Hz, 0.6 H), 3.47 (t, *J* = 6.4 Hz, 0.4 H), 3.22 (dd, *J* = 12.4 Hz, 9.6 Hz, 0.4 H), 3.20 (dd, *J* = 12.8 Hz, 9.6 Hz, 0.6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 229.7 (Mo-CO), 229.2 (Mo-CO), 224.0 (Mo-CO), 223.7 (Mo-CO), 164.17 (Ar-COO), 164.22 (Ar-COO), 155.6 (Cbz carbonyl), 155.1 (Cbz carbonyl), 150.5, 146.81, 146.76, 144.2, 143.3, 140.7, 140.6, 136.2, 136.1, 135.8, 135.6, 135.14, 135.07, 134.6, 131.1, 128.9, 128.7, 128.51, 128.46, 128.2, 128.1, 123.4, 106.0, 105.8, 105.6, 105.4, 93.4, 92.1, 70.6, 70.5, 68.7, 68.0, 62.1, 62.0, 58.6, 58.1, 43.9 (N-CH_2), 43.8 (N-CH_2). IR (cm^{-1}) 3119 (w), 3061 (w), 2486 (m), 1942 (s), 1853 (s), 1710 (s), 1606 (m), 1529 (s). HRMS (ESI) Calcd. for $C_{31}H_{27}BMoN_8O_8$ ($[M]^+$): 748.1099. Found: 748.1103.

2. Homo S_N2'-like Reactions

(-) and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-3,4,5)-2-(1´-methoxycarbonyl)-methoxycarbonylmethyl-5-methyl-5,6-dihydro-2H-pyran-2-yl]molybdenum, (-)-6 and (±)-6

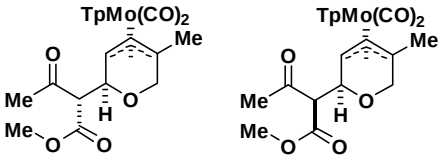


To a solution of (±)-**3a** (50 mg, 0.096 mmol, 1.0 equiv) in THF (5 mL) was added dimethyl malonate (39.6 mg, 0.30 mmol, 3.1 equiv), 60% NaH dispension (11.6 mg, 0.29 mmol, 3.0 equiv) and 15-crown-5-ether (4.23 mg, 0.019 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature for 8 hours, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**6** (56 mg, 0.095 mmol, 99%) as a yellow solid. Similar treatment of (+)-**3a** (34 mg, 0.065 mmol, 1.0 equiv, 96% ee) in THF (3 mL) with malonate (26.6 mg, 0.20 mmol, 3.1 equiv), 60% NaH dispension (7.8 mg, 0.20 mmol, 3.0 equiv) and 15-crown-5-ether (2.86 mg, 0.013 mmol, 0.2 equiv) afforded (2S, 3R)-(-)-**6** (38 mg, 0.065 mmol, 99%, 96% ee) $\{[\alpha]_D^{20} = -375.0, (c = 1.25, CH_2Cl_2)\}$

TLC (R_f = 0.41, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 1.2 Hz, 1 H), 7.73 (s, 1 H), 7.61 (m, 3 H), 7.48 (d, *J* = 1.6 Hz, 1 H), 6.24 (br s, 1 H), 6.22 (br s, 1 H), 6.15 (br s, 1 H), 4.52 (dd, *J* = 10.0 Hz, 2.0 Hz, 1 H), 4.16 (t, *J* = 7.2 Hz, 1 H), 3.92 (d, *J* = 7.2 Hz, 1 H), 3.90 (d, *J* = 13.6 Hz, 1 H), 3.84 (s, 3 H), 3.82 (d, *J* = 10.0 Hz, 1 H), 3.75 (s, 3 H), 3.68 (d, *J* = 14.0 Hz, 1 H), 1.87 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 229.8 (Mo-CO), 227.1 (Mo-CO), 167.8 (<u>C</u>OOMe), 167.5 (<u>C</u>OOMe), 146.9 (CH), 145.3 (CH), 140.2 (CH), 136.6 (CH), 136.0 (CH),

134.3 (CH), 105.7 (CH), 105.6 (CH), 105.1 (CH), 88.5, 70.0, 69.7, 63.4, 59.7, 58.7, 52.8, 52.7, 21.6 (CH_3). IR (cm^{-1}) 3164 (w), 3127 (w), 2957 (m), 2482 (m), 1934 (s), 1841 (s), 1733 (s), 1505 (s). HRMS (FAB) Calcd. for $C_{22}H_{25}BMoN_6O_7$ ($[M+NH_4]^+$): 612.1270. Found: 612.1267. HPLC: Daicel® Chiralcel OJ-RH column, isocratic solvent system: 45 % CH_3CN in H_2O (without TFA), 1.0 mL/min., λ = 254 nm, (2S, 3R)-(-)-**6**: $t_{(-)}$ = 15.9 min; (2R, 3S)-(+)-**6**: $t_{(+)}$ = 18.1 min.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-3,4,5)-2-(1´-methoxycarbonyl)acetonyl-5-methyl5,6-dihydro-2H-pyran-2-yl]molybdenum, (±)-7



7

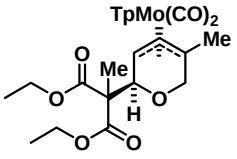
To a solution of (±)-**3a** (50 mg, 0.096 mmol, 1.0 equiv) in ACN (5 mL) was added methyl acetoacetate (34.8 mg, 0.30 mmol, 3.1 equiv), 60% NaH dispension (11.6 mg, 0.29 mmol, 3.0 equiv) and 15-crown-5-ether (4.23 mg, 0.019 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**7** (38 mg, 0.066 mmol, 69%) as two diastereomers and the recovered (±)-**1** (15mg, 0.029mmol, 30%). The two diastereomers were further purified over silica gel with hexanes-EtOAc (2:1) to provide samples for characterization.

Less porlar diastereomer: TLC (R_f = 0.37, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 1.6 Hz, 1 H), 7.72 (d, *J* = 1.6 Hz, 1 H), 7.56-7.62 (m, 3 H), 7.48 (d, *J* = 2.4 Hz, 1 H), 6.26 (t, *J* = 2.0 Hz, 1 H), 6.23 (t, *J* = 2.0 Hz, 1 H), 6.16 (t, *J* = 2.0 Hz, 1 H), 4.54 (dd, *J* = 10.4 Hz,

2.0 Hz, 1 H), 4.07 (dd, J = 7.2 Hz, 2.4 Hz, 1 H), 3.93 (d, J = 7.2 Hz, 1 H), 3.84 (d, J = 10.4 Hz, 1 H), 3.84 (s, 3 H), 3.78 (d, J = 14.0 Hz, 1 H), 3.64 (d, J = 14.0 Hz, 1 H), 2.27 (s, 3 H), 1.86 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 230.0 (Mo-CO), 227.0 (Mo-CO), 201.0 ($CH_3\underline{C}O$), 168.3 ($\underline{C}$OOMe), 146.9 (CH), 145.3 (CH), 140.0 (CH), 136.6 (CH), 136.0 (CH), 134.3 (CH), 105.7 (CH), 105.6 (CH), 105.2 (CH), 88.6, 69.9, 69.7, 67.2, 63.2, 59.6, 52.1, 27.4 ($\underline{C}H_3CO$), 21.6 (CH_3). IR (cm^{-1}) 3146 (w), 3127 (w), 2957 (m), 2482 (m), 1930 (s), 1841 (s), 1741 (s), 1714 (s), 1505 (s). HRMS (FAB) Calcd. for $C_{22}H_{25}BMoN_6O_6$ ([M+NH$_4$]$^+$): 596.1321. Found: 596.1318.

More polar diastereomer: TLC (R_f = 0.35, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 1.6 Hz, 1 H), 7.72 (d, J = 1.6 Hz, 1 H), 7.56-7.62 (m, 3 H), 7.48 (d, J = 2.0 Hz, 1 H), 6.25 (t, J = 2.0 Hz, 1 H), 6.21 (t, J = 2.0 Hz, 1 H), 6.15 (t, J = 2.0 Hz, 1 H), 4.51 (dd, J = 10.4 Hz, 2.0 Hz, 1 H), 3.99 (dd, J = 7.6 Hz, 1.6 Hz, 1 H), 3.92 (d, J = 10.4 Hz, 1 H), 3.87 (d, J = 8.0 Hz, 1 H), 3.76 (s, 3 H), 3.75 (d, J = 14.0 Hz, 1 H), 3.68 (d, J = 14.0 Hz, 1 H), 2.36 (s, 3 H), 1.87 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 229.9 (Mo-CO), 226.9 (Mo-CO), 201.2 (CH_3-$\underline{C}O$), 167.9 ($\underline{C}$OOMe), 146.9 (CH), 145.3 (CH), 140.2 (CH), 136.6 (CH), 136.0 (CH), 134.3 (CH), 105.7 (CH), 105.6 (CH), 105.1 (CH), 88.5, 69.9, 69.5, 67.2, 63.5, 59.7, 52.8, 25.6 ($\underline{C}H_3CO$), 21.7 (CH_3). IR (cm^{-1}) 3146 (w), 3019 (w), 2953 (m), 2482 (m), 1934 (s), 1841 (s), 1741 (s), 1714 (s), 1505 (s). HRMS (FAB) Calcd. for $C_{22}H_{25}BMoN_6O_6$ ([M+NH$_4$]$^+$): 596.1321. Found: 596.1318.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-3,4,5)-2-(1´-ethoxycarbonyl-1´-methyl) ethoxycarbonylmethyl -5-methyl-5,6-dihydro-2H-pyran-2-yl]molybdenum, (±)-8



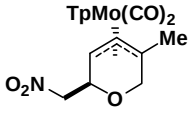
8

To a solution of (±)-**3a** (50 mg, 0.096 mmol, 1.0 equiv) in THF (5 mL) was added methyl diethylmalonate (52.2 mg, 0.30 mmol, 3.1 equiv), 60% NaH dispension (11.6 mg, 0.29 mmol,

3.0 equiv) and 15-crown-5-ether (4.23 mg, 0.019 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layer were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**8** (39 mg, 0.063 mmol, 66%) and the recovered (±)-**3a** (14mg, 0.027mmol, 28%).

TLC (R_f = 0.48, 3:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 1.2 Hz, 1 H), 7.84 (d, *J* = 2.0 Hz, 1 H), 7.74 (d, *J* = 1.6 Hz, 1 H), 7.60 (br s, 1 H), 7.49 (d, *J* = 2.0 Hz, 1 H), 6.26 (t, *J* = 2.0 Hz, 1 H), 6.23 (t, *J* = 2.0 Hz, 1 H), 6.15 (t, *J* = 2.0 Hz, 1 H), 4.72 (d, *J* = 1.6 Hz, 1 H), 4.16-4.30 (m, 6 H), 3.98 (d_{AB}, *J* = 14.0 Hz, 1 H), 3.63 (d_{AB}, *J* = 14.0 Hz, 1 H), 1.88 (s, 3 H), 1.67 (s, 3 H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 229.36 (Mo-CO), 229.32 (Mo-CO), 171.7 (<u>C</u>OOEt), 170.6 (<u>C</u>OOEt), 147.0 (CH), 144.8 (CH), 141.4 (CH), 136.4 (CH), 135.8 (CH), 134.3 (CH), 105.7 (CH), 105.5 (CH), 105.1 (CH), 84.8, 73.5, 73.0, 65.6, 61.6, 61.39, 61.36, 60.2, 21.4 (CH_3), 18.5 (CH_3), 14.1 (CH_3), 14.0 (CH_3). IR (cm^{-1}) 2988 (w), 2945 (w), 2482 (w), 1934 (s), 1849 (s), 1725 (s). HRMS (FAB) Calcd. for $C_{25}H_{31}BMoN_6O_7$ ($[M+H]^+$): 637.1480. Found: 637.1507. ($[M+NH_4]^+$): 654.1745. Found: 654.1776.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-3,4,5)-2-nitromethyl-5-methyl-5,6-dihydro-2Hpyran-2-yl]molybdenum, (±)-9

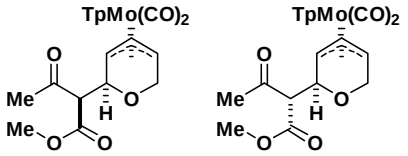


9

To a solution of (±)-**3a** (50 mg, 0.096 mmol, 1.0 equiv) in DMSO (5 mL) was added nitromethane (18.3 mg, 0.30 mmol, 3.1 equiv), 60% NaH dispension (11.6 mg, 0.29 mmol, 3.0 equiv). The reaction mixture was stirred at room temperature for 5 hours, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**9** (40 mg, 0.077 mmol, 80%)

TLC (R_f = 0.33, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.0 Hz, 1 H), 7.72 (d, *J* = 1.6 Hz, 1 H), 7.63 (d, *J* = 2.4 Hz, 1 H), 7.62 (d, *J* = 2.0 Hz, 1 H), 7.57 (d, *J* = 2.0 Hz, 1 H), 7.49 (d, *J* = 2.4 Hz, 1 H), 6.26 (t, *J* = 2.0 Hz, 1 H), 6.24 (t, *J* = 2.4 Hz, 1 H), 6.17 (t, *J* = 2.0 Hz, 1 H), 4.69-4.74 (m, 2 H), 4.59 (ddd, *J* = 8.0 Hz, 4.4 Hz, 2.0 Hz, 1 H), 3.96 (d, *J* = 14.4 Hz, 1 H), 3.92 (d, *J* = 7.6 Hz, 1 H), 3.79 (d, *J* = 14.0 Hz, 1 H), 3.72 (dd, *J* = 7.2 Hz, 2.0 Hz, 1 H), 1.86 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 230.5 (Mo-CO), 225.6 (Mo-CO), 146.9 (CH), 145.6 (CH), 139.5 (CH), 136.8 (CH), 136.1 (CH), 134.4 (CH), 105.8 (CH), 105.7 (CH), 105.3 (CH), 89.2, 78.9, 69.5, 69.1, 62.7, 55.6, 21.8 (CH_3). IR (cm^{-1}) 3146 (w), 2957 (w), 2486 (m), 1934 (s), 1845 (s), 1552 (s). HRMS (FAB) Calcd. for $C_{18}H_{20}BMoN_7O_5$. ([M+H]$^+$): 524.0746. Found: 524.0746.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-3,4,5)-2-(1´-methoxycarbonyl)acetonyl-5,6dihydro-2H-pyran-2-yl]molybdenum, (±)-10



10

To a solution of (±)-**3b** (50 mg, 0.081 mmol, 1.0 equiv) in ACN (5 mL) was added methyl acetoacetate (29 mg, 0.25 mmol, 3.1 equiv), 60% NaH dispension (9.7 mg, 0.24 mmol, 3.0 equiv)

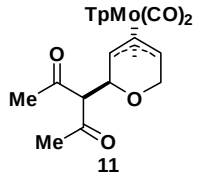
and 15-crown-5-ether (3.6 mg, 0.016 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layer were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**10** (43 mg, 0.076 mmol, 94%) as two diastereomers. The two diastereomers were further purified over silica gel with hexanes-EtOAc (2:1) to provide samples for characterization.

Less polar diastereomer: TLC (R_f = 0.29, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 2.0 Hz, 1 H), 7.70 (d, *J* = 2.0 Hz, 1 H), 7.65 (d, *J* = 1.6 Hz, 1 H), 7.58 (d, *J* = 2.0 Hz, 2 H), 7.52 (d, *J* = 1.6 Hz, 1 H), 6.31 (t, *J* = 2.0 Hz, 1 H), 6.17-6.19 (m, 2 H), 4.54 (dd, *J* = 10.4 Hz, 2.4 Hz, 1 H), 4.05-4.09 (m, 2 H), 3.87 (d, *J* = 10.4 Hz, 1 H), 3.82 (s, 3 H), 3.77 (t, *J* = 7.2 Hz, 1 H), 3.68 (dd, *J* = 12.8 Hz, 2.4 Hz, 1 H), 2.25 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 225.4 (Mo-CO), 224.6 (Mo-CO), 200.9 ($CH_3\underline{C}O$), 168.4 (<u>C</u>OOMe), 147.3 (CH), 142.2 (CH), 141.1 (CH), 136.1 (CH), 136.0 (CH), 134.4 (CH), 106.0 (CH), 105.43 (CH), 105.41 (CH), 69.8, 68.8, 67.0, 65.8, 63.2, 58.4, 52.6, 27.6 ($\underline{C}H_3CO$). IR (cm^{-1}) 3146 (w), 2957 (w), 2486 (m), 1942 (s), 1857 (s), 1741 (s), 1714 (s), 1505 (s). HRMS (FAB) Calcd. for $C_{21}H_{23}BMoN_6O_6$ ($[M+NH_4]^+$): 582.1188. Found:582.1164.

More polar diastereomer: TLC (R_f = 0.27, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.6 Hz, 1 H), 7.71 (d, *J* = 2.0 Hz, 1 H), 7.65 (d, *J* = 1.6 Hz, 1 H), 7.56-7.58 (m, 2 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 6.31 (t, *J* = 2.4 Hz, 1 H), 6.16-6.18 (m, 2 H), 4.52 (dd, *J* = 10.0 Hz, 2.0 Hz, 1 H), 4.19 (dt, *J* = 7.2 Hz, 2.4 Hz, 1 H), 4.16 (d, *J* = 13.2 Hz, 1 H), 4.06-4.09 (m, 1 H), 3.98 (d, *J* = 10.0 Hz, 1 H), 3.75 (s, 3 H), 3.69-3.75 (m, 2 H), 2.34 (s, 3 H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 225.5 (Mo-CO), 224.4 (Mo-CO), 201.2 ($CH_3\underline{C}O$), 167.8 (<u>C</u>OOMe), 147.3 (CH), 142.3 (CH), 141.0 (CH), 136.02 (CH), 135.96 (CH), 134.4 (CH), 106.0 (CH), 105.44 (CH), 105.36 (CH), 69.7, 68.9, 67.1, 66.0, 63.0, 58.6, 52.8, 30.1 ($\underline{C}H_3CO$). IR (cm^{-1}) 3130 (w), 2957 (w), 2486 (m), 1942 (s), 1857 (s), 1733 (s), 1505 (s). HRMS (FAB) Calcd. for $C_{21}H_{23}BMoN_6O_6$ ($[M+NH_4]^+$): 582.1188. Found: 582.1164.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-3,4,5)-2-(1´-acetyl)acetonyl-5,6-dihydro-2Hpyran-2-yl]molybdenum, (±)-11

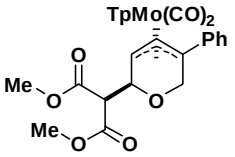


To a solution of (±)-**3b** (50 mg, 0.081 mmol, 1.0 equiv) in ACN (5 mL) was added 2,4-pentadione (25 mg, 0.25 mmol, 3.1 equiv), 60% NaH dispension (9.7 mg, 0.24 mmol, 3.0 equiv) and 15-crown-5-ether (3.6 mg, 0.016 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**11** (30 mg, 0.055 mmol, 68%) as a yellow solid.

TLC (R_f = 0.33, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.6 Hz, 1 H), 7.67 (d, *J* = 2.0 Hz, 1 H), 7.64 (d, *J* = 2.0 Hz, 1 H), 7.57-7.58 (m, 2 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 6.31 (t, *J* = 2.0 Hz, 1 H), 6.16-6.18 (m, 2 H), 4.61 (dd, *J* = 10.8 Hz, 2.0 Hz, 1 H), 4.17 (d, *J* = 10.8 Hz, 1 H), 4.02-4.07 (m, 3 H), 3.73 (t, *J* = 7.2 Hz, 1 H), 3.67 (dd, *J* = 12.8 Hz, 1.6 Hz, 1 H), 2.32 (s, 3 H), 2.20 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 225.5 (Mo-CO), 224.4 (Mo-CO), 202.5

($CH_3\underline{C}O$), 201.8 ($CH_3\underline{C}O$), 147.3 (CH), 142.3 (CH), 141.0 (CH), 136.1 (CH), 136.0 (CH), 134.4 (CH), 106.0 (CH), 105.45 (CH), 105.41 (CH), 76.6, 69.9, 68.9, 65.6, 63.0, 58.4, 31.4 ($\underline{C}H_3CO$), 27.1 ($\underline{C}H_3CO$). IR (cm^{-1}) 3146 (w), 2486 (m), 1942 (s), 1857 (s), 1722 (s), 1698 (s). HRMS (ESI) Calcd. for $C_{21}H_{23}BMoN_6O_5$. ($[M-C_5H_7O_2]^+$): 449.0431 Found: 449.0444.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-3,4,5)-2-(1´-methoxycarbonyl)methoxy-carbonylmethyl-5-phenyl-5,6-dihydro-2H-pyran-2-yl]molybdenum, (±)-12



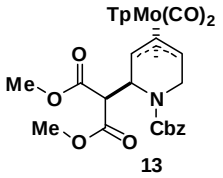
12

To a solution of (±)-**3c** (50 mg, 0.084 mmol, 1.0 equiv) in THF (5 mL) was added dimethyl malonate (34 mg, 0.26 mmol, 3.1 equiv), 60% NaH dispension (10 mg, 0.25 mmol, 3.0 equiv) and 15-crown-5-ether (3.7 mg, 0.017 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature for 8 hours, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**12** (49 mg, 0.076 mmol, 90%) as a yellow solid.

TLC (R_f = 0.34, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.0 Hz, 1 H), 7.71 (d, *J* = 2.0 Hz, 1 H), 7.63 (d, *J* = 2.4 Hz, 1 H), 7.44 (d, *J* = 2.0 Hz, 1 H), 7.40 (d, *J* = 2.0 Hz, 1 H), 7.15-7.27 (m, 5 H), 6.27 (t, *J* = 2.0 Hz, 1 H), 6.18 (t, *J* = 2.0 Hz, 1 H), 5.82 (d, *J* = 2.0 Hz, 1 H), 5.58 (t, *J* = 2.0 Hz, 1 H), 4.58-4.64 (m, 2 H), 4.44 (dd, *J* = 8.0 Hz, 2.4 Hz, 1 H), 4.41 (d, *J* = 14.0 Hz, 1 H), 4.14 (d, *J* = 14.0 Hz, 1 H), 3.87 (d, *J* = 7.2 Hz, 1 H), 3.86 (s, 3 H), 3.76 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 230.5 (Mo-CO), 227.2 (Mo-CO), 167.9 ($\underline{C}$OOMe), 167.5 ($\underline{C}$OOMe),

147.0, 145.0, 139.9, 137.9, 136.1, 136.0, 134.2, 128.7, 128.1, 126.0, 105.8, 105.6, 104.3, 89.2, 69.9, 65.7, 60.9, 58.9, 58.5, 52.82, 52.78. IR (cm^{-1}) 2957 (w), 2486 (m), 1934 (s), 1853 (s), 1733 (s), 1505 (s). HRMS (FAB) Calcd. for $C_{27}H_{27}BMoN_6O_7$ ($[M+NH_4]^+$): 674.1427. Found: 674.1427.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-3,4,5)-1-benzyloxycarbonyl-2-(1´-methoxycarbonyl)methoxycarbonylmethyl-5,6-dihydro-2H-pyridin-2-yl]molybdenum, (±)-13

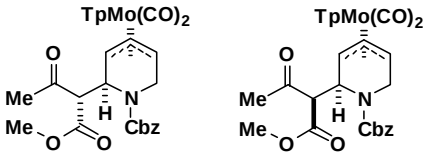


To a solution of (±)-**4a** (50 mg, 0.078 mmol, 1.0 equiv) in ACN (5 mL) was added dimethyl malonate (32.0 mg, 0.24 mmol, 3.1 equiv), 60% NaH dispension (9.36 mg, 0.23 mmol, 3.0 equiv) and 15-crown-5-ether (3.47 mg, 0.016 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature for 8 hours, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**13** (52 mg, 0.073 mmol, 94%) as a yellow solid.

TLC (R_f = 0.28, 2.5:1 hexanes:EtOAc). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$) δ 8.52-8.54 (m, 1 H), 7.84 (d, *J* = 2.0 Hz, 0.6 H), 7.81 (d, *J* = 2.0 Hz, 0.4 H), 7.67 (d, *J* = 2.0 Hz, 0.4 H), 7.65 (d, *J* = 2.0 Hz, 0.6 H), 7.57 (br s, 2 H), 7.50 (d, *J* = 2.0 Hz, 1 H), 7.28-7.37 (m, 5 H), 6.29 (br s, 1 H), 6.16-6.21 (m, 2 H), 5.05-5.15 (m, 2 H), 4.99-5.04 (m, 1 H), 4.65 (dt, *J* = 7.6 Hz, 2.4 Hz, 0.6 H), 4.52 (dt, *J* = 6.8 Hz, 2.4 Hz, 0.4 H), 4.15-4.31 (m, 2 H), 3.85 (d, *J* = 6.0 Hz, 0.6 H), 3.82 (s, 1.8 H), 3.81 (s, 1.2 H), 3.71-3.76 (m, 2.4 H), 3.67 (s, 1.8 H), 3.49 (s, 1.2 H). ^{13}C NMR (100 MHz, $CDCl_3$): 226.1 (Mo-CO), 225.5 (Mo-CO), 224.4 (Mo-CO), 223.9 (Mo-CO),

168.6 (COOMe), 168.4 (COOMe), 168.1 (COOMe), 167.8 (COOMe), 154.6 (Cbz carbonyl), 154.3 (Cbz carbonyl), 147.2, 142.84, 142.77, 140.99, 140.95, 136.6, 136.3, 136.03, 136.00, 134.39, 128.30, 128.0, 127.8, 127.7, 106.0, 105.6, 105.5, 105.43, 105.41, 69.2, 69.0, 67.4, 67.2, 65.5, 65.0, 64.3, 64.1, 58.0, 57.2, 52.6, 52.5, 52.4, 51.5. 51.3, 39.9 (N-CH_2), 39.4 (N-CH_2). IR (cm^{-1}): 2957 (w), 2486 (w), 1945 (s), 1857 (s), 1733 (s), 1702 (s). HRMS (ESI) Calcd. for $C_{19}H_{30}BMoN_7O_8$ ($[M+Na]^+$): 736.1195. Found: 736.1193.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-3,4,5)-1-benzyloxycarbonyl-2(1´-methoxycarbonyl)acetonyl-5,6-dihydro-2H-pyridin-2-yl]molybdenum, (±)-14



14

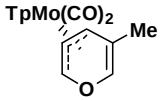
To a solution of (±)-**4b** (50 mg, 0.067 mmol, 1.0 equiv) in ACN (5 mL) was added methyl acetoacetate (24 mg, 0.21 mmol, 3.1 equiv), 60% NaH dispension (8 mg, 0.20 mmol, 3.0 equiv) and 15-crown-5-ether (2.9 mg, 0.013 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**14** (42 mg, 0.061 mmol, 91%) as two diastereomers. The two diastereomers were further purified over silica gel with hexanes-EtOAc (2:1) to provide samples for characterization.

TLC (R_f = 0.27, 2.5:1 hexanes:EtOAc). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$) δ 8.52-8.54 (m, 1 H), 7.84 (d, *J* = 1.6 Hz, 0.6 H), 7.82 (d, *J* = 2.0 Hz, 0.4 H), 7.66 (d, *J* = 2.0 Hz, 0.4 H), 7.64 (d, *J* = 2.0 Hz, 0.6 H), 7.57 (d, *J* = 2.4 Hz, 1.5 H), 7.50 (d, *J* = 2.4 Hz, 0.5 H),

7.27-7.36 (m, 5 H), 6.29 (t, J = 2.4 Hz, 1 H), 6.16-6.21 (m, 2 H), 5.15 (d_{AB}, J = 12.4 Hz, 0.4 H), 5.12 (d_{AB}, J = 13.2 Hz, 0.6 H), 5.06 (d_{AB}, J = 12.8 Hz, 0.6 H), 5.02 (d_{AB}, J = 12.4 Hz, 0.4 H), 5.02 (dd, J = 6.8 Hz, 2.8 Hz, 0.6 H), 4.97 (dd, J = 6.4 Hz, 2.8 Hz, 0.4 H), 4.53 (dt, J = 6.8 Hz, 2.8 Hz, 0.6 H), 4.43 (dt, J = 7.6 Hz, 2.8 Hz, 0.4 H), 4.11-4.29 (m, 3 H), 3.84 (s, 1.8 H), 3.80 (s, 1.2 H), 3.62-3.75 (m, 2 H), 2.27 (s, 1.8 H), 1.95 (s, 1.2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 226.1 (Mo-CO), 223.9 (Mo-CO), 201.6 (CH_3CO), 201.2 (CH_3CO), 169.6 (<u>C</u>OOMe), 169.4 (<u>C</u>OOMe), 154.7 (Cbz carbonyl), 154.1 (Cbz carbonyl), 147.2, 142.9, 140.9, 136.5, 136.1, 136.0, 134.4, 128.4, 128.31, 128.26, 128.0, 127.8, 127.7, 106.0, 105.6, 105.5, 105.4, 69.6, 69.5, 67.4, 67.2, 65.64, 65.56, 65.0. 64.9, 64.1, 52.6, 51.3, 51.0, 39.8 (N-CH_2), 39.5 (N-CH_2), 29.7, 28.93 (<u>C</u>H_3CO), 28.85 (<u>C</u>H_3CO). IR (cm^{-1}) 3127 (w), 2953 (w), 2486 (m), 1945 (s), 1857 (s), 1702 (s), 1505 (s). HRMS (ESI) Calcd. for $C_{29}H_{30}BMoN_7O_7$ ($[M+Na]^+$): 720.1246. Found: 720.1249.

TLC (R_f = 0.25, 2.5:1 hexanes:EtOAc). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$) δ 8.51-8.54 (m, 1 H), 7.78 (d, J = 2.0 Hz, 0.6 H), 7.75 (d, J = 2.0 Hz, 0.4 H), 7.67 (d, J = 2.0 Hz, 0.4 H), 7.65 (d, J = 2.0 Hz, 0.6 H), 7.56 (d, J = 2.0 Hz, 2 H), 7.50 (d, J = 2.4 Hz, 1 H), 7.26-7.37 (m, 5 H), 6.28-6.30 (m, 1 H), 6.16-6.20 (m, 2 H), 5.01-5.12 (m, 3 H), 4.48 (dt, J = 7.2 Hz, 2.4 Hz, 0.6 H), 4.38 (dt, J = 7.2 Hz, 2.8 Hz, 0.4 H), 4.26-4.32 (m, 1 H), 4.17-4.42 (m, 1 H), 3.78-3.84 (m, 1.4 H), 3.61-3.73 (m, 1.6 H), 3.59 (s, 1.8 H), 3.38 (s, 1.2 H), 2.35 (s, 1.8 H), 2.30 (s, 1.2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 225.3 (Mo-CO), 223.2 (Mo-CO), 221.9 (Mo-CO), 206.0 (CH_3<u>C</u>O), 202.1 (CH_3<u>C</u>O), 168.2 (<u>C</u>OOMe), 167.7 (<u>C</u>OOMe), 154.5 (Cbz carbonyl), 154.3 (Cbz carbonyl), 147.2, 142.6, 141.1, 136.0, 134.4, 128.3, 128.2, 127.9, 127.83, 127.77, 117.4, 116.2, 112.3, 106.0, 105.5, 105.4, 70.1, 69.6, 67.5, 66.3, 65.8, 65.5, 65.0, 63.7, 63.4, 52.5, 52.3, 51.2, 51.1, 39.0 (N-CH_2),30.8 (<u>C</u>H_3CO). IR (cm^{-1}) 2957 (w), 2490 (m), 1945 (s), 1861 (s), 1737 (s), 1706 (s). HRMS (ESI) Calcd. for $C_{29}H_{30}BMoN_7O_7$ ($[M+Na]^+$): 720.1246. Found: 720.1249.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(η-2,3,4)-5-methyl-2H-pyran-2-yl]-molybdenum, (±)-16[2]



16

To a solution of (±)-**3a** (50 mg, 0.096 mmol, 1.0 equiv) in DCM (5 mL) was added $TrPF_6$ (41 mg, 0.11 mmol, 1.1 equiv). The mixture was stirred at 0 °C for 3 hrs, and dry ether (20 mL) was added to complete the precipitation. The solvents were removed via cannula and the remaining solid was washed with dry ether (3 x 10 mL) then briefly dried under vacuum. The solid was then dissolved in THF (3 mL) and treated with 3.0 equiv sodium malonate solution in 3 mL THF (prepared from 11 mg NaH and 37 mg malonate) and 15-C-5 (4.3 mg, 0.019 mmol, 0.2 equiv). After 1 hr, the reaction was quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**16** (24 mg, 0.053 mmol, 55%) as a yellow solid and (±)–**6** (10 mg, 0.017 mmol, 18%) as a side product.

TLC (R_f = 0.70, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.0 Hz, 1 H), 7.96 (d, *J* = 2.0 Hz, 1 H), 7.83 (d, *J* = 2.0 Hz, 1 H), 7.59-7.61 (m, 2 H), 7.54 (dd, *J* = 4.0 Hz, 2.0 Hz, 1 H), 7.49 (d, *J* = 2.0 Hz, 1 H), 6.25 (t, *J* = 2.0 Hz, 1 H), 6.22 (t, *J* = 2.0 Hz, 1 H), 6.20 (t, *J* = 2.0 Hz, 1 H), 5.76 (br s, 1 H), 4.60 (dd, *J* = 5.2 Hz, 1.2 Hz, 1 H), 2.46 (dd, *J* = 6.0 Hz, 4.0 Hz, 1 H), 1.95 (d, *J* = 1.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.9 (Mo-CO), 223.4 (Mo-CO), 145.9,

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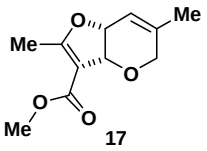
[2] Shu, C.; Alcudia, A.; Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 12477.

142.1, 141.1, 136.1, 135.9, 134.4, 130.2, 118.4, 108.7, 105.6, 105.5, 105.3, 65.1, 46.3, 18.1 (CH_3).

3. Annulative Demetalations

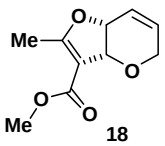
(±)-(3aR,7aR)-methyl 2,6-dimethyl-5,7a-dihydro-3aH-furo[3,2-b]pyran-3-carboxylate, (±)-17



To a solution of (±)-**7** (50 mg, 0.087 mmol, 1.0 equiv) in DMSO (5 mL) was added 60% NaH dispension (4.0 mg, 0.10 mmol, 1.2 equiv) and copper 2-ethylhexanoate (6.0 mg, 0.017 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature in dry air overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were washed with 3 M NH_3-H_2O, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**17** (15 mg, 0.071 mmol, 85%) as a colorless oil.

TLC (R_f = 0.34, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79-5.81 (m, 1 H), 4.69 (d, J =5.2 Hz, 1 H), 4.46 (br s, 1 H), 3.97 (s, 2 H), 3.76 (s, 3 H), 2.29 (s, 3 H), 1.78 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 165.9, 142.4, 114.2, 105.4, 77.2, 75.2, 66.1, 51.1, 19.6 (CH_3), 14.8 (CH_3). IR (cm^{-1}) 2949 (w), 1698 (s), 1629 (s). HRMS (ESI) Calcd. for $C_{11}H_{14}O_4$ ($[M+H]^+$): 211.0965. Found: 211.0961.

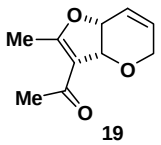
(±)-(3aR,7aR)-Methyl 2-methyl-5,7a-dihydro-3aH-furo[3,2-b]pyran-3-carboxylate, (±)-18



To a solution of (±)-**10** (50 mg, 0.089 mmol, 1.0 equiv) in DMSO (5 mL) was added 60% NaH dispension (4.3 mg, 0.11 mmol, 1.2 equiv) and copper 2-ethylhexanoate (6.3 mg, 0.018 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature in dry air overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were washed with 3 M NH_3-H_2O, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**18** (14.5 mg, 0.074 mmol, 83%) as a colorless oil.

TLC (R_f = 0.34, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (ddt, *J* = 10.4 Hz, 4.8 Hz, 1.6 Hz, 1 H), 6.10 (dt, *J* = 10.4 Hz, 2.0 Hz, 1 H), 4.78 (d, *J* = 5.6 Hz, 1 H), 4.42 (br s, 1 H), 4.18 (dd, *J* =16.4 Hz, 2.8 Hz, 1 H), 4.05 (dd, *J* = 16.4 Hz, 2.0 Hz, 1 H), 3.76 (s, 3 H), 2.31 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 165.8, 133.8, 119.8, 105.5, 76.0, 75.8, 62.5, 51.2, 14.8 (CH_3). IR (cm^{-1}) 2949 (w), 1698 (s), 1629 (s). HRMS (ESI) Calcd. for $C_{10}H_{12}O_4$ ($[M+H]^+$): 197.0808. Found: 197.0807.

(±)-1-((3aR,7aR)-2-Methyl-5,7a-dihydro-3aH-furo[3,2-b]pyran-3-yl)ethanone, (±)-19



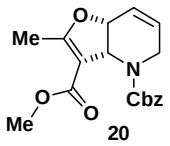
19

To a solution of (±)-**11** (50 mg, 0.090 mmol, 1.0 equiv) in DMSO (5 mL) was added 60% NaH dispension (4.3 mg, 0.11 mmol, 1.2 equiv) and copper 2-ethylhexanoate (6.4 mg, 0.018 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature in dry air overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were washed with 3 M NH_3-H_2O, dried over Na_2SO_4,

filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**19** (15 mg, 0.083 mmol, 92%) as a colorless oil.

TLC (R_f = 0.17, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29-6.33 (m, 1 H), 6.10-6.14 (m, 1 H), 4.80 (d, *J* = 5.6 Hz, 1 H), 4.45 (br s, 1 H), 4.18 (ddd, *J* = 18.2 Hz, 6.0 Hz, 1.6 Hz, 1 H), 4.04 (dq, *J* = 16.8 Hz, 2.0 Hz, 1 H),2.32 (s, 3 H), 2.30 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0 ($CH_3\underline{C}O$), 173.6, 133.7, 120.0, 114.5, 76.5, 75.8, 62.4, 28.9 ($\underline{C}H_3CO$), 15.4 (CH_3). IR (cm^{-1}) 2922 (w), 1668 (s), 1528 (s). HRMS (ESI) Calcd. for $C_{10}H_{12}O_3$ ($[M+H]^+$): 181.0859. Found: 189.0859.

(±)-4-Benzyl 3-methyl 2-methyl-5,7a-dihydrofuro[3,2-b]pyridine-3,4(3aH)-dicarboxylate, (±)-20



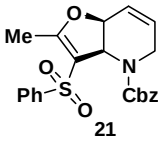
To a solution of (±)-**14** (50 mg, 0.072 mmol, 1.0 equiv) in DMSO (5 mL) was added 60% NaH dispension (3.5 mg, 0.086 mmol, 1.2 equiv) and copper 2-ethylhexanoate (5.0 mg, 0.014 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature in dry air overnight, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (5 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were washed with 3 M NH_3-H_2O, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**20** (20 mg, 0.060 mmol, 83%) as a colorless oil.

TLC (R_f = 0.33, 2.5:1 hexanes:EtOAc). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$) δ 7.28-7.41 (m, 5 H), 5.99-6.21 (m, 2 H), 5.63 (d, *J* = 8.0 Hz, 1 H), 5.17-5.23 (m, 2 H), 5.03 (d, *J* =8.8 Hz, 1 H), 4.27 (br s, 1 H), 3.53 (s, 3 H), 3.45-3.54 (m, 1 H), 2.18 (s, 3 H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 171.4, 165.6, 155.4, 136.6, 130.3, 129.7, 128.5, 128.1, 122.6, 100.8, 74.6, 67.4, 55.9, 50.8, 39.2 (N-CH_2), 15.1 (CH_3). IR (cm^{-1}) 2926 (w), 1698 (s), 1640 (s). HRMS (ESI) Calcd. for $C_{18}H_{19}NO_5$ ($[M+H]^+$): 330.1336. Found: 330.1335.

4. Total Synthesis of (+)–Isofebrifugine

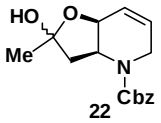
(+) and (±)- (3aS,7aR)-Benzyl 2-methyl-3-(phenylsulfonyl)-5,7a-dihydrofuro[3,2-b]-pyridine4(3aH)-carboxylate, (+) -21 and (±)-21



To a solution of (±)-**4b** (500 mg, 0.67 mmol, 1.0 equiv) in DMSO (40 mL) was added phenylsulfonyl acetone (416 mg, 2.1 mmol, 3.1 equiv), 60% NaH dispension (80 mg, 2.0 mmol, 3.0 equiv). The reaction mixture was stirred at room temperature under argon overnight, and then copper 2-ethylhexanoate (50 mg, 0.14 mmol, 0.2 equiv) and 60% NaH dispension (40 mg, 1.0 mmol, 1.5 equiv) were added. The mixture was stirred in dry air for 24 hours, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (50 mL) and H_2O (40 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 40 mL), and the combined organic layers were washed with 3 M NH_3-H_2O, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)–**21** (156 mg, 0.38 mmol, 57%) as light yellow oil. Similar treatment of (+)-**4b** (500 mg, 0.67 mmol, 1.0 equiv, >99% ee) in DMSO (40 mL) with phenylsulfonyl acetone (416 mg, 2.1 mmol, 3.1 equiv) and 60% NaH dispension (80 mg, 2.0 mmol, 3.0 equiv), and further demetalation with copper 2-ethylhexanoate (50 mg, 0.14 mmol, 0.2 equiv) and 60% NaH dispension (40 mg, 1.0 mmol, 1.5 equiv) afforded (3aS, 7aR)-(-)-**21** (150 mg, 0.37 mmol, 57%, >99% ee) $\{[\alpha]_D^{20} = -126.7, (c = 1.1, CH_2Cl_2)\}$

TLC (R_f = 0.28, 2.5:1 hexanes:EtOAc). ^{1}HNMR (a mixture of two rotamers) (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 1 H), 7.71 (d, *J* =7.6 Hz, 1 H), 7.30-7.58 (m, 8 H), 6.10 (d, *J* = 9.6 Hz, 1 H), 6.05 (dd, *J* = 10.4 Hz, 4.8 Hz, 1 H), 5.58-5.66 (m, 1 H), 5.23 (AB quartet, *J* = 12.0 Hz, 1.2 H), 5.17 (AB quartet, *J* = 12.0 Hz, 0.8 H), 4.99 (d, *J* = 9.2 Hz, 1 H), 4.22 (dd, *J* = 18.8 Hz, 4.8 Hz, 0.6 H), 4.18 (dd, *J* = 18.4 Hz, 4.4 Hz, 0.4 H), 3.68 (dd, *J* = 18.8 Hz, 2.0 Hz, 0.6 H), 3.05 (d, *J* = 18.4 Hz, 0.4 H), 2.26 (s, 1.2 H), 2.24 (s, 1.8 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.6, 155.5, 154.7, 142.3, 142.1, 136.4, 136.0, 132.8, 131.3, 130.3, 129.0, 128.5, 128.4, 128.2, 128.0, 127.9, 127.0, 126.7, 121.7, 121.5, 108.0, 74.4, 74.2, 67.9, 67.6, 56.4, 55.8, 39.3 (NCH_2), 38.8 (NCH_2), 14.6 (CH_3). IR (cm^{-1}) 3065 (w), 1702 (s), 1625 (s). HRMS (ESI) Calcd. for $C_{22}H_{21}NO_5S$ ($[M+H]^+$): 412.1213. Found: 412.1219. ($[M+NH_4]^+$): 429.1479. Found: 429.1484. HPLC: Daicel® Chiralcel OD-RH column, isocratic solvent system: 45 % CH_3CN in H_2O (without TFA), 1.0 mL/min., λ = 254 nm, (3aS, 7aR)-(-)-**21**: $t_{(-)}$ = 29.2 min; (3aR, 7aS)-(+)-**21**: $t_{(+)}$ = 32.5 min.

(+) and (±)-(3aS,7aS)-Benzyl-2-hydroxy-2-methyl-3,3a,5,7a-tetrahydrofuro[3,2-b]pyridine-4(2H)-carboxylate, (+) and (±)-22

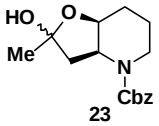


To a solution of (±)-**21** (130 mg, 0.32 mmol, 1.0 equiv) in THF/methanol (1/2 mL) was added Na_2HPO_4 (683 mg, 4.8 mmol, 15 equiv) and 10% sodium mercury amalgam (1.1 g, 4.8 mmol, 10 equiv) at -35 °C. The reaction mixture was warm to room temperature over 2 hours, and then quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (4 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 4 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in acetone/water (3/1 mL). The solution was

acidified by 1 M HCl to pH = 1, and then stirred for 20 minutes at room temperature. The mixture was neutralized to pH = 7 with saturated sodium carbonate solution, extracted with EtOAc (3 x 5 mL), dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (1:1) afforded (±)–**22** (81 mg, 0.28 mmol, 88%) as colorless oil. Similar treatment of (-)-**21** (130 mg, 0.32 mmol, 1.0 equiv, >99% ee) in THF/methanol (1/2 mL) with Na_2HPO_4 (683 mg, 4.8 mmol, 15 equiv) and 10% sodium mercury amalgam (1.1 g, 4.8 mmol, 10 equiv) at -35 °C afforded (3aS, 7aS)-(+)-**22** (80 mg, 0.28 mmol, 86%) {$[\alpha]_D^{20}$ = +24.1, (c = 0.5, CH_2Cl_2)}

TLC (R_f = 0.29, 1:1 hexanes:EtOAc). ^{1}HNMR (a mixture of hemiketal, hydroxylketone and corresponding rotamers) (400 MHz, $CDCl_3$) δ 7.27-7.48 (m, 5 H), 5.87 (dd, *J* =10.8 Hz, 2.0 Hz, 0.2 H), 5.62-5.80 (m, 1.8 H), 5.32 (br s, 0.4 H), 4.90-5.16 (m, 2.6 H), 4.60 (d, *J* = 8.0 Hz,0.4 H), 4.51 (br s, 0.6 H), 4.22-4.28 (m, 1 H), 3.65 (dq, *J* = 18.8 Hz, 2.4 Hz, 0.5 H), 3.48-3.59 (m, 0.5 H), 2.90 (dd, *J* = 16.4 Hz, 7.2 Hz, 0.4 H), 2.75 (s, 0.3 H), 3.38 (dd, *J* = 16.0 Hz, 6.0 Hz, 0.6 H), 2.28 (dd, *J* =13.2 Hz, 9.2 Hz, 0.2 H), 2.18 (br s, 1.7 H), 2.01 (dd, *J* =12.8 Hz, 9.6 Hz, 0.2 H), 1.84 (t, *J* =12.0 Hz, 0.4 H), 1.82 (s, 0.7 H), 1.50 (s, 1.5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 (Cbz carbonyl), 136.3, 128.5, 128.2, 128.0, 127.96, 127.92, 127.2, 125.9, 123.9, 105.0, 103.7, 71.7, 70.9, 67.4, 65.6, 52.0, 51.4, 49.3, 41.4, 40.2, 39.4, 39.1, 39.0, 38.5, 30.2, 29.0, 28.4. IR (cm^{-1}) 3424 (br s), 3038 (w), 2984 (w), 1698 (s). HRMS (ESI) Calcd. for $C_{16}H_{19}NO_4$ ($[M+Na]^+$): 312.1206. Found: 312.1209. ($[M+K]^+$): 328.0946. Found: 328.0948.

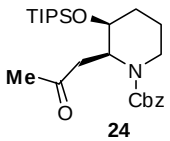
(+) and (±)-(3aS,7aS)-Benzyl-2-hydroxy-2-methylhexahydrofuro[3,2-b]pyridine4(2H)-carboxylate, (+) and (±)-23



To a solution of (±)-**22** (70 mg, 0.24 mmol, 1.0 equiv) in THF (3 mL) was added PtO_2 (5.5 mg, 0.024 mmol, 0.1 equiv). The reaction mixture was stirred at room temperature for 5 hours in hydrogen with a balloon attached to the flask. The mixture was filtered, and then the filtrate was concentrated. Flash chromatography over silica gel with hexanes-EtOAc (1:1) afforded (±)–**23** (67 mg, 0.23 mmol, 95%) as colorless oil. Similar treatment of (+)-**22** (80 mg, 0.24 mmol, 1.0 equiv, >99% ee) in THF (3 mL) with hydrogen in the presence of 10% PtO_2 afforded (3aS, 7aS)-(+)-**23** (77 mg, 0.23 mmol, 95%) {$[\alpha]_D^{20}$ = +19.8, (c = 0.85, CH_2Cl_2)}

TLC (R_f = 0.18, 1:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) (a mixture of hemiketal, hydroxylketone and corresponding rotamers) δ 7.26-7.38 (m, 5 H), 5.07-5.15 (m, 2 H), 4.98 (br s, 1 H), 4.65 (q, *J* = 6.8 Hz, 0.05 H), 4.34 (q, *J* = 6.8 Hz, 0.2 H), 3.98-4.01 (m, 0.75 H), 3.84 (br s, 1 H), 2.96 (dd, *J* = 16.0 Hz, 7.8 Hz, 1 H), 2.69 (br s, 1 H), 2.48 (dd, *J* = 15.6 Hz, 4.8 Hz, 1.3 H), 2.17 (br s, 2 H), 1.80-1.91 (m, 1 H), 1.65-1.75 (m, 1.7 H), 1.39-1.56 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3 ($CH_3\underline{C}O$), 155.9, 155.2, 136.6, 136.4, 128.5, 128.03, 127.96, 127.8, 103.6, 74.5, 73.4, 68.1, 67.3, 67.1, 53.4, 51.6, 40.9, 40.5, 39.8, 39.5, 38.9, 30.1, 28.0, 27.2, 23.7, 18.7 (CH_3). IR (cm^{-1}) 3443 (s), 2945 (w), 1695 (s). HRMS (ESI) Calcd. for $C_{16}H_{21}NO_4$ ($[M+H]^+$): 292.1543. Found: 292.1544.

(+) and (±)-(2S,3S)-Benzyl 2-(2-oxopropyl)-3-(triisopropylsilyloxy)piperidine-1-carboxylate, (+) and (±)-24



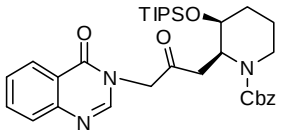
24

To a solution of (±)-**23** (60 mg, 0.21 mmol, 1.0 equiv) in DMF (1 mL) was added imidazole (43 mg, 0.63 mmol, 3 equiv) and TIPSCl (121 mg, 0.63 mmol, 3 equiv). The reaction mixture was stirred at room temperature overnight. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (4 mL), and the layers were separated. The aqueous layer was

extracted with EtOAc (2 x 3 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (6:1) afforded (±)–**24** (70 mg, 0.16 mmol, 75%) as colorless oil and (±)-**23** (12 mg, 0.042 mmol, 20%) was recovered. Similar treatment of (+)-**23** (60 mg, 0.21 mmol, 1.0 equiv, >99% ee) in DMF (1 mL) with imidazole (43 mg, 0.63 mmol, 3 equiv) and TIPSCl (121 mg, 0.63 mmol, 3 equiv) afforded (2S, 3S)-(+)-**24** (70 mg, 0.16 mmol, 75%) and (+)-**23** (12 mg, 0.042 mmol, 20%) was recovered. $\{[\alpha]_D^{20} = +34.8$, (c = 0.85, $CH_2Cl_2)\}$

TLC (R_f = 0.63, 2.5:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) (a mixture of rotamers) δ 7.27-7.37 (m, 5 H), 5.10 (AB quartet, *J* = 12.8 Hz, 1.2 H), 5.09 (s, 0.8 H), 4.99 (br s, 0.4 H), 4.90 (br s, 0.6 H), 4.03 (d, *J* = 12.4 Hz, 0.6 H), 3.78-3.92 (m, 1.4 H), 2.75-2.92 (m, 2 H), 2.56-2.65 (m, 1 H), 2.22 (s, 1.2 H), 2.06 (s, 1.8 H), 1.78-1.84 (m, 1.2 H), 1.61-1.67 (m, 0.8 H), 1.41-1.51 (m, 2 H), 1.08 (s, 8.4 H), 1.01 (s, 12.6). ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.2 ($CH_3\underline{C}O$), 206.9 ($CH_3\underline{C}O$), 165.3, 155.4, 155.1, 136.6, 128.4, 128.02, 127.96, 127.8, 69.4, 69.1, 67.4, 67.3, 53.3, 39.2, 38.8, 38.0, 37.8, 29.9, 29.4, 28.7, 24.3, 23.9, 18.0 ($CH(\underline{C}H_3)_2$), 17.9 ($CH(\underline{C}H_3)_2$), 12.2 ($\underline{C}H(CH_3)_2$), 12.1 ($\underline{C}H(CH_3)_2$). IR (cm^{-1}) 2945 (w), 2868 (w), 1702 (s). HRMS (ESI) Calcd. for $C_{25}H_{41}NO_4Si$ ($[M+H]^+$): 448.2878. Found: 448.2879. ($[M+NH_4]^+$): 465.3143. Found: 465.3145.

(+) and (±)-(2S,3S)-Benzyl 2-(2-oxo-3-(4-oxoquinazolin-3(4H)-yl)propyl)-3-(triisopropylsilyloxy)piperidine-1-carboxylate, (+) and (±)-25



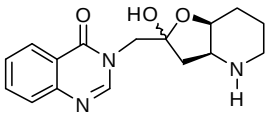
25

To a solution of (±)-**24** (60 mg, 0.13 mmol, 1.0 equiv) in DCM (2 mL) was added TEA (39 mg, 0.39 mmol, 3 equiv) and TMSOTf (87 mg, 0.39 mmol, 3 equiv) at room temperature. The reaction mixture was stirred 20 minutes. The mixture was loaded onto a plug of silica gel column,

and eluted with 20 mL hexanes-EtOAc (2:1) quickly. The solution was concentrated and dissolved again in THF (2 mL). To the solution was added NBS (28 mg, 0.16 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 30 minutes. To the reaction mixture was added 4-hydroxy-quinazoline (29 mg, 0.20 mmol, 1.5 equiv), 60% NaH dispension (8 mg, 0.20 mmol, 1.5 equiv) and 15-C-5 (5.8 mg, 0.026 mmol, 0.2 equiv). The reaction mixture was stirred for 2 hours at room temperature, and quenched with water. The mixture was poured into a separatory funnel containing EtOAc (5 mL) and H_2O (4 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 3 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (1:1) afforded (±)–**25** (51.5 mg, 0.087 mmol, 67%) as colorless oil. Similar treatment of (+)-**24** (60 mg, 0.13 mmol, 1.0 equiv, >99% ee) in the same sequence afforded (2S, 3S)-(+)-**25** (52 mg, 0.16 mmol, 67%). $\{[\alpha]_D^{20} = +48.8, (c = 0.48, CHCl_3)\}$

TLC (R_f = 0.33, 1:1 hexanes:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) (a mixture of rotamers) δ 8.27 (d, *J* = 8.0 Hz, 1 H), 8.03 (br s, 1 H), 7.70-7.80 (m, 2 H), 7.47-7.52 (m, 1 H), 7.26-7.33 (m, 5 H), 5.08-5.21 (m, 3 H), 4.90-4.95 (m, 2 H), 3.92-3.96 (m, 2 H), 3.11-3.16 (m, 1 H), 2.88-2.96 (m, 1 H), 2.70-2.80 (m, 1 H), 1.80-1.88 (m, 1 H), 1.66-1.71 (m, 1 H), 1.45-1.56 (m, 2 H), 1.09 (s, 18 H), 1.02 (br s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8 (CO), 161.0, 156.3, 147.1, 136.2, 134.3, 128.5, 128.1, 127.8, 127.4, 127.1, 126.8, 121.9, 69.2, 67.7, 53.8, 53.3, 38.2, 36.0, 29.7, 28.4, 23.8, 18.1 ($CH(\underline{C}H_3)_2$), 12.2 ($\underline{C}H(CH_3)_2$). IR (cm^{-1}) 2945 (w), 2868 (w), 1687 (s). HRMS (ESI) Calcd. for $C_{33}H_{45}N_3O_5Si$ ($[M+H]^+$): 592.3201. Found: 592.3208.

(+) and (±)-Isofebrifugine, (+) and (±)-26[3]



26

To (±)-**25** (40 mg, 0.068 mmol, 1.0 equiv) was added HCl (1.2 mL, 6 M), and the solution was refluxed for 90 minutes. The mixture was neutralized to pH=10 with solid Na_2CO_3, poured into a separatory funnel containing EtOAc (5 mL) and H_2O (4 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over deactivated alumina with $CHCl_3$-methanol (6:1) afforded (±)–**26** (13 mg, 0.043 mmol, 63%). Similar treatment of (+)-**25** (40 mg, 0.068 mmol, 1.0 equiv, >99% ee) with HCl (1.2 mL, 6 M) afforded (+)-**26** (13 mg, 0.043 mmol, 63%). {$[\alpha]_D^{20}$ = +129, (c = 0.30, $CHCl_3$)}

TLC (R_f = 0.27, 6:1 chloroform:methanol on alumina). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 8.30 (s, 1 H), 7.76 (dt, *J* = 6.8 Hz, 1.6 Hz, 2 H), 7.72 (t, *J* = 8.0 Hz, 1 H), 7.50 (dt, *J* = 8.0 Hz, 1.6 Hz, 1 H), 4.46 (d, *J* = 14.4 Hz, 1 H), 4.15 (d, *J* = 14.4 Hz, 1 H), 3.88 (q, *J* =2.8 Hz, 1 H), 3.29 (t, *J* = 3.2 Hz, 1 H), 3.00 (d, *J* = 11.2 Hz, 1 H), 2.53 (dt, *J* = 10.4 Hz, 1.6 Hz, 1 H), 2.05-2.15 (m, 2 H), 1.76-1.89 (m, 2 H), 1.50-1.58 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (C=O), 148.2, 148.0, 134.3, 127.5, 127.1, 126.9, 121.9, 105.4 (ketal carbon), 77.8 (CH), 55.7 (CH), 49.8 (CH_2), 44.5 (CH_2), 43.3 (CH_2), 26.8 (CH_2), 20.1 (CH_2). IR (cm^{-1}) 3304 (w), 2926 (w), 2853 (m), 1729 (w), 1675 (s), 1613 (s). HRMS (ESI) Calcd. for $C_{16}H_{19}N_3O_3$ ($[M+H]^+$): 302.1499. Found: 302.1501.

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[3] Wee, A. G. H.; Fan, G.-J., *Org. Lett.* **2008,** *10,* 3869

5. X-Ray Diffraction Study of (±)-8

A suitable crystal of **8** was obtained by diffusion recrystallization from EtOAc and methanol. The 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 (0.71073Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3o frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART5 software. Frame integration and final cell refinements were done using SAINT6 software. The final cell parameters were determined from least-squares refinement on 5664 reflections. The SADABS7 program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V6.12).8 Hydrogen atoms were placed their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic Uij ‘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 Crystallography9. Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V6.12 software.

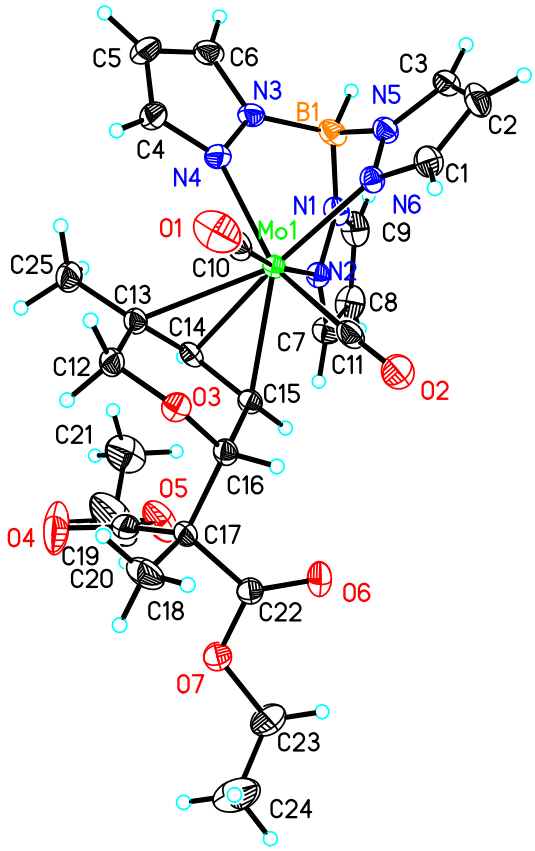

Figure 1. ORTEP View of Compound 8

Table 1. Crystal data and structure refinement for 8.

Identification code	**8**	
Empirical formula	C25 H31 B Mo N6 O7	
Formula weight	634.31	
Temperature	172(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.7954(8) Å	□= 90°.
	b = 19.950(2) Å	□= 93.417(2)°.

	c = 17.7491(19) Å □ = 90°.
Volume	2755.3(5) Å3
Z	4
Density (calculated)	1.529 Mg/m3
Absorption coefficient	0.531 mm-1
F(000)	1304
Crystal size	0.14 x 0.13 x 0.04 mm3
Theta range for data collection	1.54 to 30.44°.
Index ranges	-11<=h<=11, -27<=k<=27, -24<=l<=25
Reflections collected	52396
Independent reflections	8080 [R(int) = 0.0907]
Completeness to theta = 30.44°	96.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9806 and 0.9294
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	8080 / 0 / 365
Goodness-of-fit on F2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.1045
R indices (all data)	R1 = 0.0759, wR2 = 0.1178
Largest diff. peak and hole	0.891 and -0.920 e.Å-3

Table 2. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for 8. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	8779(5)	2509(2)	10820(2)	23(1)
C(1)	6893(4)	3596(2)	9350(2)	25(1)
C(2)	6667(4)	4019(2)	9953(2)	29(1)
C(3)	7317(4)	3674(2)	10576(2)	26(1)
C(4)	12390(4)	2414(2)	9642(2)	28(1)

C(5)	13317(4)	2550(2)	10315(2)	36(1)
C(6)	12125(4)	2551(2)	10851(2)	30(1)
C(7)	6409(4)	1058(2)	10114(2)	26(1)
C(8)	6171(4)	958(2)	10875(2)	32(1)
C(9)	7024(4)	1486(2)	11232(2)	30(1)
C(10)	9424(4)	2638(2)	8179(2)	26(1)
C(11)	6337(4)	2315(2)	8350(2)	24(1)
C(12)	10347(4)	1382(2)	7526(2)	21(1)
C(13)	10358(3)	1285(1)	8367(2)	19(1)
C(14)	8900(3)	1044(1)	8685(2)	18(1)
C(15)	7295(3)	1199(1)	8291(1)	17(1)
C(16)	7271(3)	1217(1)	7433(1)	19(1)
C(17)	7047(3)	514(2)	7041(2)	20(1)
C(18)	7438(5)	592(2)	6206(2)	35(1)
C(19)	8146(4)	-46(2)	7400(2)	27(1)
C(20)	8316(8)	-857(2)	8398(2)	75(2)
C(21)	8843(6)	-701(2)	9162(2)	49(1)
C(22)	5160(4)	303(2)	7049(2)	22(1)
C(23)	3226(4)	-565(2)	6633(2)	46(1)
C(24)	3064(6)	-861(2)	5878(2)	63(1)
C(25)	12107(4)	1092(2)	8714(2)	27(1)
Mo(1)	8431(1)	2117(1)	8971(1)	15(1)
N(1)	7710(3)	1872(1)	10709(1)	22(1)
N(2)	7344(3)	1609(1)	10005(1)	19(1)
N(3)	10565(3)	2412(1)	10515(1)	22(1)
N(4)	10722(3)	2320(1)	9754(1)	21(1)
N(5)	7881(3)	3077(1)	10354(1)	21(1)
N(6)	7628(3)	3021(1)	9589(1)	19(1)
O(1)	9964(4)	2957(1)	7707(1)	43(1)
O(2)	5147(3)	2479(1)	7973(1)	37(1)

O(3)	8722(2)	1566(1)	7177(1)	21(1)
O(4)	9433(3)	-253(1)	7152(2)	58(1)
O(5)	7468(3)	-289(1)	8014(1)	41(1)
O(6)	4026(3)	646(1)	7255(1)	35(1)
O(7)	4957(3)	-303(1)	6753(2)	47(1)

Table 3. Bond lengths [Å] and angles [°] for 8.

B(1)-N(1)	1.526(4)	C(8)-C(9)	1.379(5)
B(1)-N(3)	1.536(4)	C(8)-H(8A)	0.9500
B(1)-N(5)	1.545(4)	C(9)-N(1)	1.342(4)
B(1)-H(1B)	1.09(3)	C(9)-H(9A)	0.9500
C(1)-N(6)	1.340(4)	C(10)-O(1)	1.153(4)
C(1)-C(2)	1.381(4)	C(10)-Mo(1)	1.944(3)
C(1)-H(1A)	0.9500	C(11)-O(2)	1.158(3)
C(2)-C(3)	1.374(4)	C(11)-Mo(1)	1.955(3)
C(2)-H(2A)	0.9500	C(12)-O(3)	1.424(3)
C(3)-N(5)	1.337(4)	C(12)-C(13)	1.504(4)
C(3)-H(3A)	0.9500	C(12)-H(12A)	0.9900
C(4)-N(4)	1.340(4)	C(12)-H(12B)	0.9900
C(4)-C(5)	1.384(4)	C(13)-C(14)	1.385(4)
C(4)-H(4A)	0.9500	C(13)-C(25)	1.512(4)
C(5)-C(6)	1.369(5)	C(13)-Mo(1)	2.521(3)
C(5)-H(5A)	0.9500	C(14)-C(15)	1.429(4)
C(6)-N(3)	1.351(4)	C(14)-Mo(1)	2.235(3)
C(6)-H(6A)	0.9500	C(14)-H(14A)	1.0000
C(7)-N(2)	1.340(4)	C(15)-C(16)	1.522(3)
C(7)-C(8)	1.388(4)	C(15)-Mo(1)	2.339(3)
C(7)-H(7A)	0.9500	C(15)-H(15A)	1.0000

C(16)-O(3)	1.425(3)	Mo(1)-N(6)	2.219(2)
C(16)-C(17)	1.571(4)	Mo(1)-N(4)	2.233(2)
C(16)-H(16A)	1.0000	Mo(1)-N(2)	2.303(2)
C(17)-C(19)	1.524(4)	N(1)-N(2)	1.370(3)
C(17)-C(22)	1.531(4)	N(3)-N(4)	1.375(3)
C(17)-C(18)	1.540(4)	N(5)-N(6)	1.366(3)
C(18)-H(18A)	0.9800		
C(18)-H(18B)	0.9800	N(1)-B(1)-N(3)	110.4(2)
C(18)-H(18C)	0.9800	N(1)-B(1)-N(5)	108.4(2)
C(19)-O(4)	1.193(4)	N(3)-B(1)-N(5)	107.2(2)
C(19)-O(5)	1.331(4)	N(1)-B(1)-H(1B)	110.6(16)
C(20)-C(21)	1.427(5)	N(3)-B(1)-H(1B)	110.6(15)
C(20)-O(5)	1.460(4)	N(5)-B(1)-H(1B)	109.5(15)
C(20)-H(20A)	0.9900	N(6)-C(1)-C(2)	110.5(3)
C(20)-H(20B)	0.9900	N(6)-C(1)-H(1A)	124.7
C(21)-H(21A)	0.9800	C(2)-C(1)-H(1A)	124.7
C(21)-H(21B)	0.9800	C(3)-C(2)-C(1)	105.0(3)
C(21)-H(21C)	0.9800	C(3)-C(2)-H(2A)	127.5
C(22)-O(6)	1.193(3)	C(1)-C(2)-H(2A)	127.5
C(22)-O(7)	1.322(4)	N(5)-C(3)-C(2)	108.7(3)
C(23)-O(7)	1.450(4)	N(5)-C(3)-H(3A)	125.6
C(23)-C(24)	1.464(5)	C(2)-C(3)-H(3A)	125.6
C(23)-H(23A)	0.9900	N(4)-C(4)-C(5)	111.2(3)
C(23)-H(23B)	0.9900	N(4)-C(4)-H(4A)	124.4
C(24)-H(24A)	0.9800	C(5)-C(4)-H(4A)	124.4
C(24)-H(24B)	0.9800	C(6)-C(5)-C(4)	105.0(3)
C(24)-H(24C)	0.9800	C(6)-C(5)-H(5A)	127.5
C(25)-H(25A)	0.9800	C(4)-C(5)-H(5A)	127.5
C(25)-H(25B)	0.9800	N(3)-C(6)-C(5)	108.9(3)
C(25)-H(25C)	0.9800	N(3)-C(6)-H(6A)	125.6

C(5)-C(6)-H(6A)	125.6	C(14)-C(15)-C(16)	116.9(2)
N(2)-C(7)-C(8)	111.3(3)	C(14)-C(15)-Mo(1)	67.89(14)
N(2)-C(7)-H(7A)	124.4	C(16)-C(15)-Mo(1)	118.57(18)
C(8)-C(7)-H(7A)	124.4	C(14)-C(15)-H(15A)	115.1
C(9)-C(8)-C(7)	104.5(3)	C(16)-C(15)-H(15A)	115.1
C(9)-C(8)-H(8A)	127.8	Mo(1)-C(15)-H(15A)	115.1
C(7)-C(8)-H(8A)	127.8	O(3)-C(16)-C(15)	111.7(2)
N(1)-C(9)-C(8)	108.7(3)	O(3)-C(16)-C(17)	111.3(2)
N(1)-C(9)-H(9A)	125.6	C(15)-C(16)-C(17)	114.6(2)
C(8)-C(9)-H(9A)	125.6	O(3)-C(16)-H(16A)	106.2
O(1)-C(10)-Mo(1)	177.8(3)	C(15)-C(16)-H(16A)	106.2
O(2)-C(11)-Mo(1)	174.9(3)	C(17)-C(16)-H(16A)	106.2
O(3)-C(12)-C(13)	114.7(2)	C(19)-C(17)-C(22)	108.1(2)
O(3)-C(12)-H(12A)	108.6	C(19)-C(17)-C(18)	109.8(2)
C(13)-C(12)-H(12A)	108.6	C(22)-C(17)-C(18)	106.4(2)
O(3)-C(12)-H(12B)	108.6	C(19)-C(17)-C(16)	115.1(2)
C(13)-C(12)-H(12B)	108.6	C(22)-C(17)-C(16)	108.9(2)
H(12A)-C(12)-H(12B)	107.6	C(18)-C(17)-C(16)	108.3(2)
C(14)-C(13)-C(12)	119.5(2)	C(17)-C(18)-H(18A)	109.5
C(14)-C(13)-C(25)	119.2(2)	C(17)-C(18)-H(18B)	109.5
C(12)-C(13)-C(25)	112.9(2)	H(18A)-C(18)-H(18B)	109.5
C(14)-C(13)-Mo(1)	62.01(15)	C(17)-C(18)-H(18C)	109.5
C(12)-C(13)-Mo(1)	111.64(17)	H(18A)-C(18)-H(18C)	109.5
C(25)-C(13)-Mo(1)	122.64(18)	H(18B)-C(18)-H(18C)	109.5
C(13)-C(14)-C(15)	116.2(2)	O(4)-C(19)-O(5)	124.0(3)
C(13)-C(14)-Mo(1)	84.83(17)	O(4)-C(19)-C(17)	124.3(3)
C(15)-C(14)-Mo(1)	75.78(15)	O(5)-C(19)-C(17)	111.7(3)
C(13)-C(14)-H(14A)	121.0	C(21)-C(20)-O(5)	111.7(3)
C(15)-C(14)-H(14A)	121.0	C(21)-C(20)-H(20A)	109.3
Mo(1)-C(14)-H(14A)	121.0	O(5)-C(20)-H(20A)	109.3

C(21)-C(20)-H(20B)	109.3
O(5)-C(20)-H(20B)	109.3
H(20A)-C(20)-H(20B)	107.9
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(6)-C(22)-O(7)	124.9(3)
O(6)-C(22)-C(17)	125.1(3)
O(7)-C(22)-C(17)	109.9(2)
O(7)-C(23)-C(24)	108.0(3)
O(7)-C(23)-H(23A)	110.1
C(24)-C(23)-H(23A)	110.1
O(7)-C(23)-H(23B)	110.1
C(24)-C(23)-H(23B)	110.1
H(23A)-C(23)-H(23B)	108.4
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(13)-C(25)-H(25A)	109.5
C(13)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(13)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

C(10)-Mo(1)-C(11)	80.79(13)
C(10)-Mo(1)-N(6)	93.40(10)
C(11)-Mo(1)-N(6)	82.17(10)
C(10)-Mo(1)-N(4)	90.84(11)
C(11)-Mo(1)-N(4)	157.54(11)
N(6)-Mo(1)-N(4)	77.54(9)
C(10)-Mo(1)-C(14)	105.68(11)
C(11)-Mo(1)-C(14)	101.98(11)
N(6)-Mo(1)-C(14)	160.86(9)
N(4)-Mo(1)-C(14)	100.34(9)
C(10)-Mo(1)-N(2)	172.97(11)
C(11)-Mo(1)-N(2)	101.76(11)
N(6)-Mo(1)-N(2)	80.54(8)
N(4)-Mo(1)-N(2)	84.40(8)

C(14)-Mo(1)-N(2)	80.33(9)
C(10)-Mo(1)-C(15)	101.61(11)
C(11)-Mo(1)-C(15)	65.77(11)
N(6)-Mo(1)-C(15)	141.41(9)
N(4)-Mo(1)-C(15)	136.64(9)
C(14)-Mo(1)-C(15)	36.33(9)
N(2)-Mo(1)-C(15)	85.39(9)
C(10)-Mo(1)-C(13)	76.82(11)
C(11)-Mo(1)-C(13)	113.08(10)
N(6)-Mo(1)-C(13)	159.73(9)
N(4)-Mo(1)-C(13)	84.81(8)
C(14)-Mo(1)-C(13)	33.17(9)
N(2)-Mo(1)-C(13)	107.80(9)
C(15)-Mo(1)-C(13)	58.77(9)
C(9)-N(1)-N(2)	110.0(3)
C(9)-N(1)-B(1)	128.8(2)
N(2)-N(1)-B(1)	121.2(2)
C(7)-N(2)-N(1)	105.6(2)
C(7)-N(2)-Mo(1)	134.89(19)
N(1)-N(2)-Mo(1)	119.50(17)
C(6)-N(3)-N(4)	109.3(2)
C(6)-N(3)-B(1)	129.0(2)
N(4)-N(3)-B(1)	119.9(2)
C(4)-N(4)-N(3)	105.6(2)
C(4)-N(4)-Mo(1)	132.9(2)
N(3)-N(4)-Mo(1)	121.38(17)
C(3)-N(5)-N(6)	109.6(2)

C(3)-N(5)-B(1)	130.0(2)
N(6)-N(5)-B(1)	120.4(2)
C(1)-N(6)-N(5)	106.1(2)
C(1)-N(6)-Mo(1)	131.89(19)
N(5)-N(6)-Mo(1)	122.00(17)
C(12)-O(3)-C(16)	115.9(2)
C(19)-O(5)-C(20)	118.4(3)
C(22)-O(7)-C(23)	118.4(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for 8. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	31(2)	23(2)	15(1)	-3(1)	-2(1)	4(1)
C(1)	27(2)	22(2)	26(2)	2(1)	2(1)	2(1)
C(2)	31(2)	20(2)	36(2)	-1(1)	7(1)	7(1)
C(3)	24(2)	25(2)	28(2)	-10(1)	5(1)	-1(1)
C(4)	20(1)	23(2)	40(2)	-3(1)	3(1)	-2(1)
C(5)	19(2)	33(2)	53(2)	-8(2)	-8(2)	-2(1)
C(6)	29(2)	24(2)	33(2)	-9(1)	-13(1)	6(1)
C(7)	29(2)	24(2)	24(1)	1(1)	5(1)	-6(1)
C(8)	31(2)	35(2)	31(2)	12(1)	12(1)	-2(1)

C(9)	35(2)	36(2)	19(1)	6(1)	8(1)	6(1)
C(10)	30(2)	29(2)	19(1)	-6(1)	4(1)	5(1)
C(11)	29(2)	25(2)	17(1)	-6(1)	0(1)	6(1)
C(12)	19(1)	28(2)	18(1)	-3(1)	4(1)	1(1)
C(13)	18(1)	21(1)	17(1)	-2(1)	-1(1)	4(1)
C(14)	23(1)	16(1)	14(1)	-2(1)	2(1)	4(1)
C(15)	19(1)	21(1)	12(1)	-1(1)	2(1)	0(1)
C(16)	19(1)	23(2)	14(1)	-1(1)	1(1)	3(1)
C(17)	19(1)	24(2)	17(1)	-5(1)	1(1)	3(1)
C(18)	47(2)	38(2)	21(2)	-11(1)	9(1)	-4(2)
C(19)	23(2)	21(2)	38(2)	-10(1)	-4(1)	1(1)
C(20)	130(5)	50(3)	43(2)	5(2)	-8(3)	54(3)
C(21)	65(3)	34(2)	45(2)	5(2)	-12(2)	15(2)
C(22)	22(1)	30(2)	15(1)	-3(1)	-3(1)	5(1)
C(23)	24(2)	53(2)	62(3)	-17(2)	5(2)	-14(2)
C(24)	51(3)	71(3)	64(3)	-13(2)	-25(2)	-2(2)
C(25)	22(2)	32(2)	26(2)	-2(1)	-2(1)	6(1)
Mo(1)	16(1)	18(1)	11(1)	0(1)	1(1)	1(1)
N(1)	26(1)	28(1)	12(1)	0(1)	2(1)	5(1)
N(2)	19(1)	22(1)	15(1)	0(1)	2(1)	2(1)
N(3)	22(1)	23(1)	21(1)	-5(1)	-5(1)	1(1)
N(4)	20(1)	24(1)	20(1)	-4(1)	1(1)	-2(1)
N(5)	23(1)	21(1)	19(1)	-3(1)	1(1)	2(1)
N(6)	20(1)	20(1)	16(1)	-1(1)	2(1)	2(1)
O(1)	66(2)	36(1)	29(1)	4(1)	19(1)	-11(1)

O(2)	37(1)	42(2)	30(1)	-7(1)	-14(1)	16(1)
O(3)	23(1)	26(1)	15(1)	3(1)	0(1)	1(1)
O(4)	32(1)	42(2)	101(2)	5(2)	24(2)	15(1)
O(5)	63(2)	31(1)	28(1)	5(1)	2(1)	23(1)
O(6)	22(1)	37(1)	47(1)	-10(1)	7(1)	6(1)
O(7)	21(1)	43(2)	77(2)	-35(1)	6(1)	-6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 8.

	x	y	z	U(eq)
H(1A)	6573	3699	8838	30
H(2A)	6171	4454	9939	34
H(3A)	7358	3833	11081	31
H(4A)	12874	2391	9164	33
H(5A)	14518	2626	10388	43
H(6A)	12357	2635	11374	35
H(7A)	5966	772	9721	31
H(8A)	5559	606	11099	38
H(9A)	7111	1563	11761	36
H(12A)	11194	1733	7417	26
H(12B)	10726	960	7294	26
H(14A)	8980	692	9086	21

H(15A)	6265	987	8503	21
H(16A)	6240	1487	7262	22
H(18A)	7308	157	5951	53
H(18B)	8619	753	6172	53
H(18C)	6637	915	5962	53
H(20A)	7518	-1244	8390	90
H(20B)	9334	-989	8125	90
H(21A)	9404	-1092	9402	73
H(21B)	7835	-578	9437	73
H(21C)	9651	-324	9172	73
H(23A)	2377	-200	6675	55
H(23B)	3010	-909	7018	55
H(24A)	1900	-1040	5783	95
H(24B)	3902	-1225	5844	95
H(24C)	3280	-517	5501	95
H(25A)	12640	765	8390	40
H(25B)	11979	895	9214	40
H(25C)	12835	1492	8765	40
H(1B)	8890(40)	2651(14)	11415(16)	16(7)

Table 6. Torsion angles [°] for 8.

N(6)-C(1)-C(2)-C(3)	0.5(4)
C(1)-C(2)-C(3)-N(5)	-0.5(4)
N(4)-C(4)-C(5)-C(6)	-1.4(4)

C(4)-C(5)-C(6)-N(3)	0.9(4)
N(2)-C(7)-C(8)-C(9)	0.0(4)
C(7)-C(8)-C(9)-N(1)	0.3(4)
O(3)-C(12)-C(13)-C(14)	32.3(4)
O(3)-C(12)-C(13)-C(25)	-179.8(2)
O(3)-C(12)-C(13)-Mo(1)	-36.9(3)
C(12)-C(13)-C(14)-C(15)	-29.0(4)
C(25)-C(13)-C(14)-C(15)	-174.9(2)
Mo(1)-C(13)-C(14)-C(15)	71.4(2)
C(12)-C(13)-C(14)-Mo(1)	-100.3(2)
C(25)-C(13)-C(14)-Mo(1)	113.7(2)
C(13)-C(14)-C(15)-C(16)	35.1(4)
Mo(1)-C(14)-C(15)-C(16)	111.9(2)
C(13)-C(14)-C(15)-Mo(1)	-76.8(2)
C(14)-C(15)-C(16)-O(3)	-44.3(3)
Mo(1)-C(15)-C(16)-O(3)	33.9(3)
C(14)-C(15)-C(16)-C(17)	83.4(3)
Mo(1)-C(15)-C(16)-C(17)	161.63(18)
O(3)-C(16)-C(17)-C(19)	83.2(3)
C(15)-C(16)-C(17)-C(19)	-44.7(3)
O(3)-C(16)-C(17)-C(22)	-155.3(2)
C(15)-C(16)-C(17)-C(22)	76.8(3)
O(3)-C(16)-C(17)-C(18)	-40.0(3)
C(15)-C(16)-C(17)-C(18)	-167.9(2)
C(22)-C(17)-C(19)-O(4)	135.7(3)

C(18)-C(17)-C(19)-O(4)	20.1(4)
C(16)-C(17)-C(19)-O(4)	-102.3(4)
C(22)-C(17)-C(19)-O(5)	-42.5(3)
C(18)-C(17)-C(19)-O(5)	-158.2(3)
C(16)-C(17)-C(19)-O(5)	79.5(3)
C(19)-C(17)-C(22)-O(6)	132.2(3)
C(18)-C(17)-C(22)-O(6)	-110.0(3)
C(16)-C(17)-C(22)-O(6)	6.5(4)
C(19)-C(17)-C(22)-O(7)	-51.4(3)
C(18)-C(17)-C(22)-O(7)	66.4(3)
C(16)-C(17)-C(22)-O(7)	-177.1(2)
O(1)-C(10)-Mo(1)-C(11)	27(7)
O(1)-C(10)-Mo(1)-N(6)	-54(7)
O(1)-C(10)-Mo(1)-N(4)	-132(7)
O(1)-C(10)-Mo(1)-C(14)	127(7)
O(1)-C(10)-Mo(1)-N(2)	-85(8)
O(1)-C(10)-Mo(1)-C(15)	90(7)
O(1)-C(10)-Mo(1)-C(13)	143(7)
O(2)-C(11)-Mo(1)-C(10)	-38(3)
O(2)-C(11)-Mo(1)-N(6)	57(3)
O(2)-C(11)-Mo(1)-N(4)	31(3)
O(2)-C(11)-Mo(1)-C(14)	-142(3)
O(2)-C(11)-Mo(1)-N(2)	135(3)
O(2)-C(11)-Mo(1)-C(15)	-145(3)
O(2)-C(11)-Mo(1)-C(13)	-109(3)

C(13)-C(14)-Mo(1)-C(10)	30.40(18)
C(15)-C(14)-Mo(1)-C(10)	-88.34(18)
C(13)-C(14)-Mo(1)-C(11)	114.06(17)
C(15)-C(14)-Mo(1)-C(11)	-4.68(18)
C(13)-C(14)-Mo(1)-N(6)	-145.2(2)
C(15)-C(14)-Mo(1)-N(6)	96.1(3)
C(13)-C(14)-Mo(1)-N(4)	-63.43(16)
C(15)-C(14)-Mo(1)-N(4)	177.83(15)
C(13)-C(14)-Mo(1)-N(2)	-145.85(16)
C(15)-C(14)-Mo(1)-N(2)	95.40(16)
C(13)-C(14)-Mo(1)-C(15)	118.7(2)
C(15)-C(14)-Mo(1)-C(13)	-118.7(2)
C(14)-C(15)-Mo(1)-C(10)	100.74(18)
C(16)-C(15)-Mo(1)-C(10)	-8.8(2)
C(14)-C(15)-Mo(1)-C(11)	175.0(2)
C(16)-C(15)-Mo(1)-C(11)	65.5(2)
C(14)-C(15)-Mo(1)-N(6)	-148.49(16)
C(16)-C(15)-Mo(1)-N(6)	102.0(2)
C(14)-C(15)-Mo(1)-N(4)	-3.1(2)
C(16)-C(15)-Mo(1)-N(4)	-112.6(2)
C(16)-C(15)-Mo(1)-C(14)	-109.5(3)
C(14)-C(15)-Mo(1)-N(2)	-79.93(16)
C(16)-C(15)-Mo(1)-N(2)	170.6(2)
C(14)-C(15)-Mo(1)-C(13)	34.12(15)
C(16)-C(15)-Mo(1)-C(13)	-75.4(2)

C(14)-C(13)-Mo(1)-C(10)	-149.97(18)
C(12)-C(13)-Mo(1)-C(10)	-37.1(2)
C(25)-C(13)-Mo(1)-C(10)	101.6(2)
C(14)-C(13)-Mo(1)-C(11)	-76.15(19)
C(12)-C(13)-Mo(1)-C(11)	36.7(2)
C(25)-C(13)-Mo(1)-C(11)	175.5(2)
C(14)-C(13)-Mo(1)-N(6)	147.3(2)
C(12)-C(13)-Mo(1)-N(6)	-99.8(3)
C(25)-C(13)-Mo(1)-N(6)	38.9(4)
C(14)-C(13)-Mo(1)-N(4)	117.94(16)
C(12)-C(13)-Mo(1)-N(4)	-129.2(2)
C(25)-C(13)-Mo(1)-N(4)	9.6(2)
C(12)-C(13)-Mo(1)-C(14)	112.9(3)
C(25)-C(13)-Mo(1)-C(14)	-108.4(3)
C(14)-C(13)-Mo(1)-N(2)	35.53(17)
C(12)-C(13)-Mo(1)-N(2)	148.42(18)
C(25)-C(13)-Mo(1)-N(2)	-72.8(2)
C(14)-C(13)-Mo(1)-C(15)	-37.41(15)
C(12)-C(13)-Mo(1)-C(15)	75.48(19)
C(25)-C(13)-Mo(1)-C(15)	-145.8(3)
C(8)-C(9)-N(1)-N(2)	-0.5(3)
C(8)-C(9)-N(1)-B(1)	-179.6(3)
N(3)-B(1)-N(1)-C(9)	119.5(3)
N(5)-B(1)-N(1)-C(9)	-123.3(3)
N(3)-B(1)-N(1)-N(2)	-59.5(3)

N(5)-B(1)-N(1)-N(2)	57.7(3)
C(8)-C(7)-N(2)-N(1)	-0.2(3)
C(8)-C(7)-N(2)-Mo(1)	176.9(2)
C(9)-N(1)-N(2)-C(7)	0.5(3)
B(1)-N(1)-N(2)-C(7)	179.6(3)
C(9)-N(1)-N(2)-Mo(1)	-177.19(19)
B(1)-N(1)-N(2)-Mo(1)	2.0(3)
C(10)-Mo(1)-N(2)-C(7)	171.2(8)
C(11)-Mo(1)-N(2)-C(7)	60.7(3)
N(6)-Mo(1)-N(2)-C(7)	140.5(3)
N(4)-Mo(1)-N(2)-C(7)	-141.2(3)
C(14)-Mo(1)-N(2)-C(7)	-39.7(3)
C(15)-Mo(1)-N(2)-C(7)	-3.4(3)
C(13)-Mo(1)-N(2)-C(7)	-58.5(3)
C(10)-Mo(1)-N(2)-N(1)	-12.0(9)
C(11)-Mo(1)-N(2)-N(1)	-122.6(2)
N(6)-Mo(1)-N(2)-N(1)	-42.68(19)
N(4)-Mo(1)-N(2)-N(1)	35.58(19)
C(14)-Mo(1)-N(2)-N(1)	137.1(2)
C(15)-Mo(1)-N(2)-N(1)	173.4(2)
C(13)-Mo(1)-N(2)-N(1)	118.28(19)
C(5)-C(6)-N(3)-N(4)	-0.2(3)
C(5)-C(6)-N(3)-B(1)	-164.6(3)
N(1)-B(1)-N(3)-C(6)	-131.0(3)
N(5)-B(1)-N(3)-C(6)	111.1(3)

N(1)-B(1)-N(3)-N(4)	66.0(3)
N(5)-B(1)-N(3)-N(4)	-51.9(3)
C(5)-C(4)-N(4)-N(3)	1.3(3)
C(5)-C(4)-N(4)-Mo(1)	177.8(2)
C(6)-N(3)-N(4)-C(4)	-0.7(3)
B(1)-N(3)-N(4)-C(4)	165.4(3)
C(6)-N(3)-N(4)-Mo(1)	-177.69(19)
B(1)-N(3)-N(4)-Mo(1)	-11.6(3)
C(10)-Mo(1)-N(4)-C(4)	-31.8(3)
C(11)-Mo(1)-N(4)-C(4)	-99.2(4)
N(6)-Mo(1)-N(4)-C(4)	-125.1(3)
C(14)-Mo(1)-N(4)-C(4)	74.3(3)
N(2)-Mo(1)-N(4)-C(4)	153.4(3)
C(15)-Mo(1)-N(4)-C(4)	76.2(3)
C(13)-Mo(1)-N(4)-C(4)	44.9(3)
C(10)-Mo(1)-N(4)-N(3)	144.3(2)
C(11)-Mo(1)-N(4)-N(3)	76.8(4)
N(6)-Mo(1)-N(4)-N(3)	51.0(2)
C(14)-Mo(1)-N(4)-N(3)	-109.6(2)
N(2)-Mo(1)-N(4)-N(3)	-30.5(2)
C(15)-Mo(1)-N(4)-N(3)	-107.7(2)
C(13)-Mo(1)-N(4)-N(3)	-139.0(2)
C(2)-C(3)-N(5)-N(6)	0.4(3)
C(2)-C(3)-N(5)-B(1)	177.6(3)
N(1)-B(1)-N(5)-C(3)	122.5(3)

N(3)-B(1)-N(5)-C(3)	-118.3(3)
N(1)-B(1)-N(5)-N(6)	-60.7(3)
N(3)-B(1)-N(5)-N(6)	58.5(3)
C(2)-C(1)-N(6)-N(5)	-0.2(3)
C(2)-C(1)-N(6)-Mo(1)	-178.7(2)
C(3)-N(5)-N(6)-C(1)	-0.1(3)
B(1)-N(5)-N(6)-C(1)	-177.6(3)
C(3)-N(5)-N(6)-Mo(1)	178.57(19)
B(1)-N(5)-N(6)-Mo(1)	1.1(3)
C(10)-Mo(1)-N(6)-C(1)	42.9(3)
C(11)-Mo(1)-N(6)-C(1)	-37.3(3)
N(4)-Mo(1)-N(6)-C(1)	133.0(3)
C(14)-Mo(1)-N(6)-C(1)	-141.3(3)
N(2)-Mo(1)-N(6)-C(1)	-140.7(3)
C(15)-Mo(1)-N(6)-C(1)	-70.5(3)
C(13)-Mo(1)-N(6)-C(1)	103.0(3)
C(10)-Mo(1)-N(6)-N(5)	-135.4(2)
C(11)-Mo(1)-N(6)-N(5)	144.4(2)
N(4)-Mo(1)-N(6)-N(5)	-45.3(2)
C(14)-Mo(1)-N(6)-N(5)	40.3(4)
N(2)-Mo(1)-N(6)-N(5)	41.0(2)
C(15)-Mo(1)-N(6)-N(5)	111.1(2)
C(13)-Mo(1)-N(6)-N(5)	-75.3(3)
C(13)-C(12)-O(3)-C(16)	-42.4(3)
C(15)-C(16)-O(3)-C(12)	48.0(3)

C(17)-C(16)-O(3)-C(12)	-81.5(3)
O(4)-C(19)-O(5)-C(20)	-1.9(5)
C(17)-C(19)-O(5)-C(20)	176.4(3)
C(21)-C(20)-O(5)-C(19)	120.6(4)
O(6)-C(22)-O(7)-C(23)	3.0(5)
C(17)-C(22)-O(7)-C(23)	-173.4(3)
C(24)-C(23)-O(7)-C(22)	134.6(4)

Symmetry transformations used to generate equivalent atoms: