Supporting Information

Organometallic Enantiomeric Scaffolding: Sequential Semipinacol / 1,5-"Michael-like" Reactions as a Strategic Approach to Bridgehead-Quaternary Center Aza[3.3.1]: Application to the Total Synthesis of (-)-Adaline

Thomas C. Coombs, Yongqiang Zhang, Ethel C. Garnier-Amblard and Lanny S. Liebeskind*
lanny.liebeskind@emory.edu

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General Methods

Unless otherwise indicated, all reactions were carried out under a positive pressure of argon in oven- or flame-dried glassware using solvents dried over 4 Å molecular sieves or dispensed and used directly from a Seca Solvent System purchased from Glass Contour. Analytical thin-layer chromatography (TLC) was performed using commercial Merck KGaA aluminum-supported silica gel plates with fluorescent indicator (F-254). Visualization was accomplished using UV light, 5 % phosphomolybdic acid in ethanol, or aqueous $KMnO_4$. Flash column chromatography was carried out using 32-63 µm silica gel, with compressed air as a source of positive pressure. All reagents were used as received, with the exception of amines, which were distilled and stored over 4 Å molecular sieves prior to use.

^{1}H and ^{13}C NMR spectra were recorded on Mercury 300 (300 MHz ^{1}H, 75 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 $CHCl_3$ as internal reference (7.27 ppm for ^{1}H and 77.23 ppm for ^{13}C). Infrared spectra were recorded on an ASI ReactIR® 1000 FT-IR spectrometer equipped with a silicon probe. Peaks are reported with the following relative intensities: s (strong, 67-100 %), m (medium, 40-67 %), w (weak, 20-40 %), and br (broad). Melting points (mp) are uncorrected and were taken in open capillary tubes on a Thomas Hoover capillary melting point apparatus. *Since almost all of the Tp molybdenum complexes decompose over 180-200 °C, melting points are not significant and are not shown in the experimental section.* Optical rotations were measured with Perkin-Elmer Model 341 polarimeter. 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. The nomenclature for determining the chirality of the molybdenum complexes is straightforward.[1]

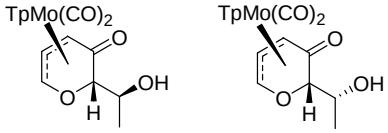
Syntheses of **1** and **2** were accomplished according to the literature.[2]

[1] Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1-36.
[2] Coombs, T. C.; Lee, M. D., IV; Wong, H.; Armstrong, M.; Cheng, B.; Chen, W.; Moretto, A. F.; Liebeskind, L. S. *J. Org. Chem.* **2008**, *73*, 882-888.

1. Preparation of Alkylidenes **3** and **4**

- *Mukaiyama – Aldol reaction on ketone **1** or **2***

Table 1, aldol product from acetaldehyde, X = O, R^1 = Me



anti *syn*

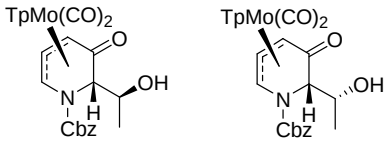
(-)- and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum. To a solution of (±)-**1** (3.00 g, 6.6 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL) were successively added Et_3N (1.06 mL, 7.6 mmol, 1.15 equiv) and TBSOTf (1.74 mL, 7.6 mmol, 1.15 equiv). The reaction mixture was stirred for 1 h at room temperature, and then cooled to –78 ºC. To this mixture was slowly added a low-temperature (–78 ºC) premixed solution of acetaldehyde (481 µL, 8.56 mmol, 1.3 equiv) and $TiCl_4$ (1.0 M in CH_2Cl_2, 8.56 mL, 8.56 mmol, 1.3 equiv) in CH_2Cl_2 (20 mL) *via* syringe. The mixture was stirred for 10 minutes at –78 ºC and then quenched with water (5 mL). The cold bath was removed, and the reaction mixture was allowed to warm to room temperature before it was transferred to a separatory funnel containing CH_2Cl_2 (60 mL) and water (100 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (40 mL). The combined organic phases were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated. The resulting solid product was washed with CH_2Cl_2 (2 x 20 mL) and a mixture of CH_2Cl_2 and hexanes (1:1 v/v, 3 x 20 mL) to afford pure (±)-*anti*-aldol product (2.12 g, 4.19 mmol, 65%) as a yellow solid. The filtrates were combined, concentrated, and subjected to flash chromatography over silica gel with hexanes-EtOAc (1:1) to give the corresponding *anti*-aldol product (2.07 g, 4.09 mmol, 62%) and the *syn*-aldol product (1.08 g, 2.13 mmol, 33%) as yellow solids.

Similar treatment of (-)-**1** (500 mg, 1.08 mmol, 1.0 equiv, 97.6 % ee) in CH_2Cl_2 (7 mL) with Et_3N (173 µL, 1.24 mmol, 1.15 equiv), and TBSOTf (286 µL, 1.24 mmol, 1.15 equiv), followed by addition of a premixed solution of $TiCl_4$ (1.0 M in CH_2Cl_2, 1.41 mL, 1.41 mmol, 1.3 equiv) and acetaldehyde (97 µL, 1.73 mmol, 1.6 equiv) in CH_2Cl_2 (2 mL), afforded (2*S*, 6*S*)-(-)-*anti* aldol product (345 mg, 0.68 mmol, 63 %, 97.6 %ee) {$[\alpha]_D^{25}$ -490 (*c* 0.22, CH_2Cl_2)}, and (2*S*, 6*S*)-(-)-*syn* aldol product (164 mg, 0.32 mmol, 30 %, 97.6 %ee) {$[\alpha]_D^{25}$ -514 (*c* 0.26, CH_2Cl_2)}.

(±)-*Anti*-aldol product: TLC: R_f = 0.39 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3401 (w), 3127 (w), 2980 (w), 2934 (w), 2899(w), 2486 (w), 1961 (s), 1872 (s), 1640 (m), 1505 (w), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 2.0 Hz, 1 H), 7.89 (d, *J* = 2.0 Hz, 1 H), 7.65 (d, *J* = 2.0 Hz, 1 H), 7.62 (d, *J* = 2.4 Hz, 1 H), 7.60 (d, *J* = 2.0 Hz, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 7.39 (dd, *J* = 4.8 Hz, 2.4 Hz, 1 H), 6.30 (t, *J* = 2.0 Hz, 1 H), 6.26 (t, *J* = 2.4 Hz, 1 H), 6.21 (t, *J* = 2.0 Hz, 1 H), 4.78 (dd, *J* = 6.4 Hz, 2.0 Hz, 1 H), 4.19 (dd, *J* = 6.4 Hz, 4.8 Hz, 1 H), 3.95 (app pent, *J* = 6.4 Hz, 1 H), 3.27 (d, *J* = 6.0 Hz, 1 H), 3.15 (br s, 1 H), 1.22 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 224.5, 223.6, 195.0, 147.6, 143.9, 141.7, 136.6 (2), 134.9, 107.4, 106.6, 106.3, 106.0, 78.9, 69.5, 68.8, 65.0, 18.6. Anal. Calcd for $C_{18}H_{19}BMoN_6O_5$: C, 42.72; H, 3.78; N, 16.60. Found: C, 42.32; H, 3.81; N, 16.17. HPLC: Daicel® Chiralpak AS-RH column, Isocratic solvent system: 65 % CH_3CN in H_2O, 1.0 mL/min, λ = 254 nm, (2*S*, 6*S*)-(-)-*anti*: $t_{(-)}$ = 22.29 min; (2*R*, 6*R*)-(+)-*anti*: $t_{(+)}$ = 15.30 min.

(±)-*Syn*-aldol product: TLC: R_f = 0.31 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3405 (w), 3127 (w), 2976 (w), 2934 (w), 2490 (w), 1961 (s), 1872 (s), 1644 (m), 1505 (m), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 1.9 Hz, 1 H), 7.90 (d, *J* = 1.6 Hz, 1 H), 7.66 (d, *J* = 1.6 Hz, 1 H), 7.62 (d, *J* = 2.0 Hz, 1 H), 7.59 (d, *J* = 2.0 Hz, 1 H), 7.51 (d, *J* = 1.6 Hz, 1 H), 7.43 (dd, *J* = 4.8 Hz, 2.0 Hz, 1 H), 6.33 (t, *J* = 2.2 Hz, 1 H), 6.28 (t, *J* = 2.2 Hz, 1 H), 6.23 (t, *J* = 2.2 Hz, 1 H), 4.84 (dd, *J* = 6.4 Hz, 2.0 Hz, 1 H), 4.20 (t, *J* = 6.0 Hz, 1 H), 4.10-4.15 (m, 1 H), 3.29 (d, *J* = 2.8 Hz, 1 H), 2.67 (br s, 1 H), 1.23 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.8, 223.8, 194.9, 147.4, 143.8, 141.7, 136.5(2), 134.9, 108.1, 106.4, 106.2, 105.9, 78.9, 70.3, 68.6, 65.0, 19.1. Anal. Calcd for $C_{18}H_{19}BMoN_6O_5$: C, 42.72; H, 3.78; N, 16.60. Found: C, 43.01; H, 3.94; N, 16.34. HPLC: Daicel® Chiralpak AS-RH column, isocratic solvent system: 60 % CH_3CN in H_2O (without TFA), 1.0 mL/min., λ = 254 nm, (2*S*, 6*S*)-(-)-*syn*: $t_{(-)}$ = 15.60 min; (2*R*, 6*R*)-(+)-*syn*: $t_{(+)}$ = 11.96 min.

Table 1, aldol product from acetaldehyde, X = NCbz, R^1 = Me



anti *syn*

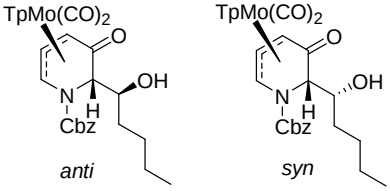
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-1-(benzyloxycarbonyl)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum. To a Schlenk flask charged with a solution of (±)-**2** (1.00 g, 1.68 mmol, 1.0 equiv) in CH_2Cl_2 (16 mL) were successively added Et_3N (269 µL, 1.93 mmol, 1.15 equiv) and TBSOTf (424 µL, 1.85 mmol, 1.1 equiv). The reaction mixture was stirred for 20 minutes at room temperature, and was cooled down to –78 ºC. To this mixture was slowly added a low temperature (–78 ºC) premixed solution of acetaldehyde (0.104 mg, 2.35 mmol, 1.4 equiv) and $TiCl_4$ (1.0 M in CH_2Cl_2, 2.18 mL, 2.18 mmol, 1.3 equiv) in CH_2Cl_2 (10 mL) *via* syringe. The mixture was stirred for 10 minutes at –78 ºC and then quenched with water (1 mL). The cold bath was removed, and the reaction mixture was warmed to room temperature. The solution was poured into a separatory funnel containing CH_2Cl_2 (30 mL) and water (30 mL), and the layers were separated. The organic layer was washed with water (2 x 20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (1:1). The first yellow band gave recovered starting material (0.075 g, 0.12 mmol, 8%), and the second yellow band afforded (±)-*syn* aldol product (0.105 g, 0.16 mmol, 10%) as a yellow solid after solvent removal. The third yellow band afforded (±)-*anti* aldol product (0.872 g, 1.36 mmol, 81%) as a yellow solid after solvent removal.

(±)-*Anti*-aldol product: TLC: R_f = 0.30 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3443 (w), 3123 (w), 2978 (w), 2490 (w), 1969 (s), 1864 (s), 1702 (m), 1664 (m), 1505 (m), 1409 (m), 1305 (s), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (a mixture of two rotamers) 8.59 (d, *J* = 2.1 Hz, 0.3 H), 8.42 (d, *J* = 3.0 Hz, 0.7 H), 8.38 (d, *J* = 1.8 Hz, 0.4 H), 7.68 (d, *J* = 2.1 Hz, 1 H), 7.65 (d, *J* = 2.1 Hz, 1.0 H), 7.65-7.60 (m, 2 H), 7.58 (d, *J* = 2.4 Hz, 0.8 H), 7.52-7.34 (m, 7.5 H), 7.15 (dd, *J* = 1.8, 6.3 Hz, 0.8 H), 6.27-6.31 (m, 1.5 H), 6.22-6.20 (m, 1.2 H), 5.76 (t, *J* = 2.4 Hz, 0.7 H), 5.27 (AB quartet, *J* = 11.1 Hz, 1.4 H), 5.20 (AB quartet, *J* = 11.8 Hz, 0.6 H), 4.81 (dd, *J* = 5.8 Hz, 1.5 Hz, 0.3 H), 4.76 (dd, *J* = 6.0 Hz, 1.8 Hz, 1 H), 4.30-4.27 (m, 1 H), 4.06 (t, *J* = 6.3 Hz, 0.6 H), 3.92 (t, *J* = 6.3 Hz, 0.8 H), 3.90 (d, *J* = 3.3 Hz, 0.8 H), 3.62 (d, *J* = 2.7 Hz, 0.6 H), 1.30 (t, *J* = 6.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 225.5, 224.9, 222.7, 221.6, 195.4, 195.3 156.2, 147.6, 147.5, 146.2, 144.7, 140.6, 136.7, 136.6, 136.5, 135.1, 134.9, 129.9, 129.1, 129.1, 128.9, 128.7, 128.5, 128.3, 99.6, 96.1, 71.7, 71.2, 70.1, 68.9, 66.1, 64.8, 63.3, 60.6, 60.5, 59.7, 19.7, 18.9, 14.4. Anal. Calcd for $C_{26}H_{26}BMoN_7O_6$: C, 48.85; H, 4.10; N, 15.34. Found: C, 48.21; H, 4.08; N, 15.12. HRMS (ESI) Calcd for $C_{26}H_{26}BMoN_7O_6$ ($[M]^+$): 641.1092. Found: 641.1091.

(±)-*Syn*-aldol product: TLC: R_f = 0.36 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3459 (w), 3123 (w), 2976 (w), 2486 (w), 1969 (s), 1864 (s), 1706 (m), 1664 (m), 1505 (w), 1409 (m), 1305 (s), 1220 (m), 1123 (m), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$) (a mixture of two rotamers): δ 8.54 (d, *J* = 1.9 Hz, 0.5 H), 8.43 (d, *J* = 2.4 Hz, 0.5 H), 8.38 (d, *J* = 2.4 Hz, 0.5 H), 7.71 (d, *J* = 1.9 Hz, 0.5 H), 7.68 (d, *J* = 1.9 Hz, 0.5 H), 7.64-7.65 (m, 1 H), 7.63 (d, *J* = 2.4 Hz, 0.5 H), 7.59 (d, *J* = 2.4 Hz, 0.5 H), 7.54 (d, *J* = 1.9 Hz, 0.5 H), 7.52 (d, *J* = 2.4 Hz, 0.5 H), 7.49-7.50 (m, 1.5 H), 7.42-7.43 (m, 2 H), 7.32-7.36 (m, 0.5 H), 7.18 (dd, *J* = 6.9 Hz, 1.5 Hz, 0.5 H), 6.29-6.30 (m, 1 H), 6.28 (t, *J* = 2.4 Hz, 0.5 H), 6.24 (t, *J* = 1.9 Hz, 0.5 H), 6.22 (t, *J* = 2.4 Hz, 0.5 H), 5.82 (t, *J* = 1.9 Hz, 0.5 H), 5.26 (AB quartet, *J* = 11.9 Hz, 1 H), 5.25 (AB quartet, *J* = 11.4 Hz, 1 H), 4.82 (dd, *J* = 6.2 Hz, 1.9 Hz, 0.5 H), 4.79 (dd, *J* = 6.2 Hz, 1.9 Hz, 0.5 H), 4.17-4.26 (m, 1 H), 4.07 (t, *J* = 6.2 Hz, 0.5 H), 3.95 (t, *J* = 6.2 Hz, 0.5 H), 3.76 (d, *J* = 4.8 Hz, 0.5 H), 3.68 (d, *J* = 4.3 Hz, 0.5 H), 3.27 (br s, 1 H), 1.26 (d, *J* = 6.6 Hz, 1 H), 1.21 (d, *J* = 6.2 Hz, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 225.5, 224.9, 222.8, 221.6, 198.0, 197.7, 155.2, 154.5, 147.6, 147.5, 146.1, 144.5, 140.9, 140.6, 136.8, 136.7, 136.54, 136.47, 135.5, 135.2, 135.1, 129.8, 129.0, 128.8, 128.6, 128.3, 106.53, 106.50, 106.12, 106.09, 106.06, 99.2, 95.8, 69.7, 69.0, 68.9, 68.6, 65.7, 64.9, 61.8, 61.6, 61.1, 60.2, 19.6, 19.0. HRMS (ESI) Calcd for $C_{26}H_{26}BMoN_7O_6$ ($[M]^+$): 641.1092. Found: 641.1096.

Relative stereochemistry was confirmed by X-ray analysis of a single crystal of the anti-aldol product, provided on Page 31.

Table 1, aldol product from acetaldehyde, X = NCbz, $R^1 = C_5H_{11}$



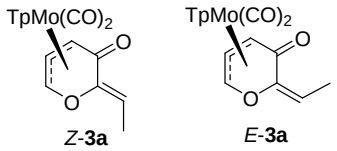
(-)- and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-1-(benzyloxycarbonyl)-6-(1-hydroxypentyl)-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum. Molybdenum complex (±)-**2** (10.0 g, 16.8 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (125 mL), and Et_3N (3.17 mL, 22.8 mmol, 1.4 equiv) and TBSOTf (5.02 mL, 21.8 mmol, 1.3 equiv) were added successively. The reaction mixture was stirred at room temperature for 30 minutes before it was cooled to –78 °C and a pre-mixed solution of $TiCl_4$ (1.0 M in CH_2Cl_2, 21.8 mL, 21.8 mmol, 1.3 equiv) and valeraldehyde (2.50 mL, 23.5 mmol, 1.4 equiv) in CH_2Cl_2 (10 mL) at –78 °C was added *via* cannula. The mixture was stirred for 15 minutes at –78 °C before it was quenched with a saturated aqueous solution of NH_4Cl (5 mL) and warmed to room temperature. The solution was transferred to a separatory funnel containing water (150 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (75 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). Overlapping fractions were subjected to a second chromatography under the same conditions, affording (±)-*anti* aldol product (6.47 g, 9.49 mmol, 57%), (±)-*syn* aldol product (0.808 g, 1.19 mmol, 7%), and recovered (±)-**2** (1.11 g, 1.87 mmol, 11%), all as orange solids.

Similar treatment of complex (-)-**2** (11.9 g, 20.0 mmol, 1.0 equiv, 97.5% ee) in CH_2Cl_2 (200 mL) with Et_3N (3.77 mL, 27.2 mmol, 1.4 equiv) and TBSOTf (5.98 mL, 26.0 mmol, 1.3 equiv), and then addition of a premixed solution of $TiCl_4$ (1.0 M in CH_2Cl_2, 26.0 mL, 26.0 mmol, 1.3 equiv) and valeraldehyde (2.98 mL, 28.0 mmol, 1.4 equiv) in CH_2Cl_2 (10 mL), afforded (2*S*, 6*S*)-(-)-*anti* aldol product (9.55 g, 14.0 mmol, 70 %, 97.3 %ee) {$[\alpha]_D^{25}$ -566 (*c* 0.12, CH_2Cl_2)}. Additionally, *syn* aldol product and (-)-**2** were collected together (1.98 g, HPLC ratio = 8:92).

<u>(±)-*Anti* aldol product:</u> TLC: R_f = 0.67 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3459 (br m), 3123 (w), 2957 (m), 2486 (m), 1969 (s), 1864 (s), 1702 (s), 1664 (s), 1505 (m), 1409 (s). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 2.0 Hz, 0.4 H), 8.40 (d, *J* = 1.6 Hz, 0.6 H), 8.36 (d, *J* = 1.6 Hz, 0.4 H), 7.68 (d, *J* = 2.0 Hz, 0.6 H), 7.64 (d, *J* = 1.6 Hz, 1.0 H), 7.63 (d, *J* = 2.0 Hz, 0.4 H), 7.60 (d, *J* = 2.0 Hz, 0.4 H), 7.57 (d, *J* = 2.0 Hz, 0.6 H), 7.48-7.51 (m, 2.8 H), 7.40-7.42 (m, 2.2 H), 7.31-7.37 (m, 2.0 H), 7.15 (dd, *J* = 6.4 Hz, 1.6 Hz, 0.6 H), 6.25-6.28 (m, 1.4 H), 6.18-6.21 (m, 1.0 H), 5.76 (t, *J* = 2.0 Hz, 0.6 H), 5.13-5.29 (m, 2.0 H), 4.81 (dd, *J* = 6.0 Hz, 2.0 Hz, 0.4 H), 4.77 (dd, *J* = 5.6 Hz, 1.6 Hz, 0.6 H), 4.04-4.10 (m, 1.0 H), 3.87-3.94 (m, 1.0 H), 3.85 (d, *J* = 2.4 Hz, 0.6 H), 3.60 (d, *J* = 2.4 Hz, 0.4 H), 2.97 (br s, 0.6 H), 1.98 (br s, 0.4 H), 1.48-1.72 (m, 2.0 H), 1.15-1.43 (m, 4.0 H), 0.91 (t, *J* = 7.2 Hz, 1.8 H), 0.81 (t, *J* = 7.2 Hz, 1.2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 226.0, 225.0, 222.7, 221.9, 195.4, 195.3, 155.7, 154.9, 147.6, 147.5, 146.1, 144.6, 140.6, 140.3, 136.7, 136.5, 136.4, 136.3, 129.8, 129.0, 128.8, 128.7, 128.6, 106.4, 106.3, 106.0, 99.5, 96.1, 75.5, 75.4, 69.8, 68.9, 66.0, 64.8, 62.8, 62.3, 60.9, 60.2, 33.4, 32.9, 28.3, 28.2, 22.8, 22.6, 14.2, 14.1. HRMS (ESI) Calcd for $C_{29}H_{33}BMoN_7O_6$ ($[M+H]^+$): 684.1634. Found: 684.1656. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (2*S*, 6*S*)-(-)-*anti*-**7b**: t_S = 9.16 min; (2*R*, 6*R*)-(+)-*anti*-**7b**: t_R = 8.44 min.

<u>(±)-*Syn* aldol product:</u> TLC: R_f = 0.75 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3459 (br), 2957 (m), 1969 (s), 1868 (s), 1710 (s), 1664 (m), 1505 (m), 1455 (w). ^{1}H NMR (a mixture of two rotamers) (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 1.6 Hz, 0.6 H), 8.41 (d, *J* = 2.0 Hz, 0.4 H), 8.36 (d, *J* = 1.6 Hz, 0.6 H), 7.70 (d, *J* = 1.6 Hz, 0.4 H), 7.67 (d, *J* = 1.6 Hz, 0.6 H), 7.63 (d, *J* = 2.0 Hz, 1.0 H), 7.61 (d, *J* = 2.4 Hz, 0.6 H), 7.58 (d, *J* = 2.4 Hz, 0.4 H), 7.48-7.52 (m, 2.2 H), 7.40-7.42 (m, 1.8 H), 7.29-7.36 (m, 3.0 H), 7.17 (d, *J* = 6.4 H, 0.4 H), 6.26-6.28 (m, 1.5 H), 6.22 (br s, 0.6 H), 6.20 (br s, 0.5 H), 5.79 (br s, 0.4 H), 5.19-5.31 (m, 2.0 H), 4.77 (t, *J* = 6.0 Hz, 1.0 H), 4.06 (t, *J* = 6.0 Hz, 0.6 H), 4.00 (br s, 0.4 H), 3.93 (t, *J* = 6.0 Hz, 1.0 H), 3.77 (d, *J* = 5.2 Hz, 0.4 H), 3.68 (d, *J* = 4.4 Hz, 0.6 H), 3.13 (d, *J* = 9.6 Hz, 0.6 H), 3.01 (d, *J* = 9.6 Hz, 0.4 H), 1.45-1.67 (m, 2.0 Hz), 1.23-1.37 (m, 4.0 H), 0.84-0.95 (m, 3.0 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.6, 225.0, 222.7, 221.5, 198.1, 197.6, 154.9, 154.2, 147.1, 147.0, 145.6, 144.2, 140.6, 140.3, 136.5, 136.4, 136.3, 136.2, 135.2, 134.9 (2), 134.7, 129.4, 128.7, 128.4, 128.2, 128.0, 106.1, 105.8, 105.7, 99.4, 96.2, 73.0, 72.6, 69.3, 68.4, 65.6, 64.8, 61.2, 61.1, 60.7, 59.8, 32.8, 32.5, 28.3, 28.2, 22.5, 22.4, 14.0, 13.9. HRMS (ESI) Calcd for $C_{29}H_{33}BMoN_7O_6$ ($[M+H]^+$): 684.1634. Found: 684.1663.

- *Dehydration of β-hydroxy ketones*



Z-**3a** *E*-**3a**

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

There are two different methods to perform mesylation-elimination reactions:

To a solution of (±)-*syn*-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum (55 mg, 0.11 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added DMAP (6.7 mg, 0.055 mmol, 0.5 equiv), Et_3N (100 µL, 0.715 mmol, 6.5 equiv), and methanesulfonyl chloride (11.3 µL, 0.14 mmol, 1.3 equiv). The reaction mixture was stirred for 4 days at room temperature and then concentrated under reduced pressure. The crude reaction mixture was subjected to flash chromatography over silica gel with hexanes-EtOAc (7:3), affording the major isomer *Z*-(±)-**3a** (45 mg, 0.092 mmol, 85%) and the minor isomer *E*-(±)-**3a** (less than 1 mg) as yellow solids.

To a solution of (±)-*anti*-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum (205 mg, 0.41 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) was added DMAP (24.6 mg, 0.20 mmol, 0.5 equiv), Et_3N (85 µL, 0.61 mmol, 1.5 equiv), and methanesulfonyl chloride (42.6 µL, 0.53 mmol, 1.3 equiv). The reaction mixture was stirred for 10 minutes at room temperature and then passed through a short pad of silica gel (50% EtOAc in hexanes). The solvents were completely removed on a rotary evaporator, and the residue was dissolved in CH_2Cl_2 (15 mL). The solution was cooled to 0 ºC and DBU (91 µL, 0.61 mmol, 1.5 equiv) was slowly added *via* syringe. The reaction mixture was stirred for 1 hour at room temperature and then passed through a short pad of silica gel and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (7:3) afforded the major isomer *E*-(±)-**3a** (125 mg, 0.26 mmol, 63%) and the minor isomer *Z*-(±)-**3a** (61 mg, 0.12 mmol, 31%), both as yellow solids.

Similar treatment of (-)-*anti*-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum (600 mg, 1.18 mmol, 1.0 equiv, 97.6 %ee) in CH_2Cl_2 (7.6 mL) and DMAP (0.014 mg, 0.12 mmol, 0.1 equiv), Et_3N (246 µL, 1.77 mmol, 1.5 equiv), and methanesulfonyl chloride (149 µL, 1.53 mmol, 1.3 equiv) and then with DBU (352 µL, 2.35 mmol, 2.0 equiv) in CH_2Cl_2 (7.6 mL) afforded the major isomer *E*-(*S*)-(-)-**3a** (376 mg, 0.77 mmol, 65%, 97.6 %ee) {$[\alpha]_D^{25}$ -513 (*c* 0.13, CH_2Cl_2)} and the minor isomer *Z*-(*S*)-(-)-**3a** (168 mg, 0.34 mmol, 29 %, 97.6 %ee) {$[\alpha]_D^{25}$ -267 (*c* 0.19, CH_2Cl_2)}.

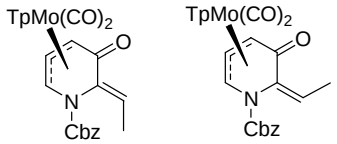
Similar treatment of (-)-*syn*-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum (200 mg, 0.40 mmol, 1.0 equiv, 97.6 %ee) in CH_2Cl_2 (2.5 mL) and DMAP (4 mg, 0.04 mmol, 0.1 equiv), Et_3N (83 µL, 0.60 mmol, 1.5 equiv), and methanesulfonyl chloride (50 µL, 0.51 mmol, 1.3 equiv) and then with DBU (0.12 mL, 0.79 mmol, 2.0 equiv) in CH_2Cl_2 (2.5 mL) afforded *Z*-(*S*)-(-)-**3a** (462 mg, 0.94 mmol, 80%, 97.6 %ee). No *E*-(*S*)-(-)-**3a** was detected by ^{1}H NMR.

*Procedure for converting mixtures of E-(-)-**3a** /Z-(-)-**3a** to Z-(-)-**3a**:*
To a 1:1 mixture of *E*-(-)-**3a** /*Z*-(-)-**3a** (0.285 g, 0.58 mmol, 1.0 equiv, 97.6 %ee) in dry dichloromethane (5.6 mL) was added Et_3N (94 µL, 0.67 mmol, 1.15 equiv) followed by TBSOTf (154 µL, 0.67 mmol, 1.15 equiv). After 10 minutes at 23 °C, the reaction mixture was quenched with water (2 mL). After extraction with dichloromethane, the organic layer was cooled to 0 °C and HCl (4.0 M in dioxane, 29 µL, 0.12 mmol, 0.2 equiv) was added. After 5 minutes, volatiles were removed under vacuum. The crude product was purified by silica gel chromatography using hexanes-EtOAc (1:1) to afford *Z*-**(-)-3a** (0.23 g, 82%, 97.1 %ee) as a yellow solid.

E-(±)-**3a**: TLC: R_f = 0.57 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3138 (w), 2926 (w), 2494 (w), 1965 (s), 1876 (s), 1660 (m), 1610 (s), 1505 (m), 1409 (m), 1351 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.48 (d, *J* = 1.8 Hz, 1 H), 7.93 (d, *J* = 2.4 Hz, 1 H), 7.65 (d, *J* = 2.4 Hz, 1 H), 7.61 (d, *J* = 2.4 Hz, 1 H), 7.59 (d, *J* = 2.4 Hz, 1 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 7.23 (dd, *J* = 4.8 Hz, 2.4 Hz, 1 H), 6.29 (t, *J* = 2.4 Hz, 1 H), 6.25

(t, J = 1.8 Hz, 1 H), 6.21 (t, J = 2.4 Hz, 1 H), 5.51 (q, J = 7.8 Hz, 1 H), 4.85 (dd, J = 6.0 Hz, 2.4 Hz, 1 H), 4.15 (dd, J = 6.0 Hz, 4.8 Hz, 1 H), 2.02 (d, J = 7.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): 224.7, 223.4, 184.0, 147.4, 143.8, 142.8, 141.7, 136.5, 136.4, 134.9, 117.5, 106.5, 106.2, 105.9, 104.9, 73.2, 65.2, 13.2. HRMS (ESI) Calcd for $C_{18}H_{17}BMoN_6O_4$ ([M]$^+$): 490.0458. Found: 490.0475. HPLC: Daicel® Chiralpak AS-RH column, isocratic solvent system: 55 % CH_3CN in H_2O (+ 0.1 % TFA), 1.0 mL/min, λ = 254 nm, *E*-(*S*)-(-)-**3a**: $t_{(-)}$ = 8.94 min; *E*-(*R*)-(+)-**3a**: $t_{(+)}$ = 7.43 min.

<u>*Z*-(±)-**3a**</u>: TLC: R_f = 0.49 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3127 (w), 2918 (w), 2490 (m), 1965 (s), 1880 (s), 1671 (m), 1617 (s), 1505 (m), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 1.6 Hz, 1 H), 7.90 (d, J = 2.0 Hz, 1 H), 7.71 (d, J = 2.0 Hz, 1 H), 7.62 (d, J = 2.0 Hz, 1 H), 7.59 (d, J = 2.4 Hz, 1 H), 7.51 (d, J = 2.0 Hz, 1 H), 7.29 (dd, J = 4.4 Hz, 2.0 Hz, 1 H), 6.28 (t, J = 2.0 Hz, 1 H), 6.26 (t, J = 2.0 Hz, 1 H), 6.19 (t, J = 2.0 Hz, 1 H), 6.03 (q, J = 7.6 Hz, 1 H), 4.90 (dd, J = 6.4 Hz, 2.4 Hz, 1 H), 4.28 (dd, J = 6.4 Hz, 4.8 Hz, 1 H), 1.61 (d, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.2, 223.2, 181.1, 147.3, 144.7, 143.4, 141.7, 136.5, 136.4, 134.9, 111.2, 106.4, 106.2, 105.8, 104.6, 71.3, 65.9, 10.2. HRMS (ESI) Calcd for $C_{18}H_{17}BMoN_6O_4$ ([M]$^+$): 490.0458. Found: 490.0480. HRMS (ESI) Calcd for $C_{16}H_{17}BMoN_6O_2$ ([M-2CO]$^+$): 434.0560. Found: 434.0565. HPLC: Daicel® Chiralpak AS-RH column, isocratic solvent system: 55 % CH_3CN in H_2O (+ 0.1 % TFA), 1.0 mL/min., λ = 254 nm, *Z*-(*S*)-(-)-**3a**: $t_{(-)}$ = 8.81 min; *Z*-(*R*)-(+)-**3a**: $t_{(+)}$ = 6.99 min.



Z-**4a** *E*-**4a**

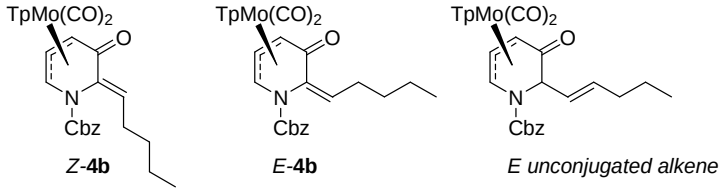
(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-2,3,4)-1-(benzyloxycarbonyl)-6-ethylene-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-4a. To a solution of (±)-*anti*-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-1-(benzyloxycarbonyl)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum (0.064 g, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added DMAP (0.006 g, 0.05 mmol, 0.5 equiv), Et_3N (21 μL, 0.15 mmol, 1.5 equiv), and methanesulfonyl chloride (10.5 μL, 0.13 mmol, 1.3 equiv). The reaction mixture was stirred 30 minutes at room temperature and then passed through a short pad of silica gel (50% EtOAc in hexanes). The solvents were completely removed on a rotary evaporator, and the residue was dissolved in CH_2Cl_2 (4 mL). DBU (22.5 μL, 0.15 mmol, 1.5 equiv) was slowly added *via* syringe. The reaction mixture was stirred overnight (16 h) at room temperature and then passed through a short pad of silica gel and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (1:1) afforded the major isomer *E*-(±)-**4a** (0.048 g, 0.08 mmol, 77%) and the minor isomer *Z*-(±)-**4a** (0.005 g, 0.01 mmol, 8%).

Similar treatment of (±)-*syn*-dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-1-(benzyloxycarbonyl)-6-(1-hydroxyethyl)-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum (162 mg, 0.254 mmol) over 1 h afforded a mixture of two isomers (0.139 g, 87%). HPLC analysis of the reaction mixture showed a ratio of *Z*/*E* = 96:4.

<u>*E*-(±)-**4a**</u>: TLC: R_f = 0.57 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3123 (w), 2490 (m), 1965 (s), 1880 (s), 1714 (s), 1671 (m), 1617 (s), 1505 (m), 1409 (m), 1305 (m), 1220 (m), 1123 (m), 1050 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.45 (d, J = 2.2 Hz, 1 H), 7.75 (d, J = 2.2 Hz, 1 H), 7.59 (d, J = 1.9 Hz, 1 H), 7.56 (d, J = 2.2 Hz, 1 H), 7.50 (d, J = 2.5 Hz, 1 H), 7.39-7.44 (m, 6 H), 7.24 (br s, 1 H), 6.63 (br s, 1 H), 6.29 (t, J = 2.2 Hz, 1 H), 6.22 (t, J = 2.2 Hz, 1 H), 5.99 (br s, 1 H), 5.26 (AB quartet, J = 12.1 Hz, 2 H), 4.82 (dd, J = 7.0 Hz, 2.2 Hz, 1 H), 4.00 (br s, 1 H), 2.11 (t, J = 7.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 225.1, 223.1, 188.0, 154.0, 147.5, 144.1, 141.1, 136.6, 136.4, 135.5, 135.0, 129.7, 129.2, 128.9 (3), 128.8, 106.4, 106.2, 106.1, 106.0, 91.9, 69.1, 66.0, 65.0, 14.9. HRMS (ESI) Calcd for $C_{26}H_{24}BMoN_7O_5$ ([M]$^+$): 623.0986. Found: 623.0980.

<u>*Z*-(±)-**4a**</u>: TLC: R_f = 0.51 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3123 (w), 2490 (m), 1969 (s), 1876 (s), 1722 (s), 1702 (m), 1671 (m), 1621 (m), 1505 (m), 1409 (m), 1305 (m), 1262 (m), 1220 (s), 1123 (m), 1050 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 1.6 Hz, 1 H), 8.02 (br s, 1 H), 7.76 (d, J = 1.9 Hz, 1 H), 7.57-7.59 (m, 2 H), 7.49 (dd, J = 2.2 Hz, 0.6 Hz, 1 H), 7.35-7.38 (m, 5 H), 7.19-7.21 (m, 1 H), 6.34 (q, J = 7.3 Hz, 1 H), 6.28 (t, J = 2.2 Hz, 1 H),

6.20 (t, J = 2.2 Hz, 1 H), 6.14 (br s, 1 H), 5.22 (s, 2 H), 4.81 (dd, J = 6.0 Hz, 2.5 Hz, 1 H), 4.24-4.26 (m, 1 H), 1.54-1.59 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.5, 223.7, 186.8, 147.6, 143.6, 142.1, 136.7, 136.5, 135.5, 135.0, 131.8, 129.0, 129.0 (2), 128.9 (2), 128.7, 127.3, 125.2, 106.5, 106.2, 106.0, 89.3, 69.1, 68.3, 16.0. HRMS (ESI) Calcd for $C_{26}H_{24}BMoN_7O_5$ ($[M]^+$): 623.0986. Found: 623.0988.



(-)- and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(*η*-2,3,4)-1-(benzyloxycarbonyl)-5-oxo-6-pentylene-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (-)-4b and (±)-4b. To a solution of (±)-*anti*-aldol product (0.133 g, 0.19 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added DMAP (0.012 g, 0.10 mmol, 0.5 equiv), Et_3N (40.8 μL, 0.29 mmol, 1.5 equiv), and methanesulfonyl chloride (20.7 μL, 0.25 mmol, 1.3 equiv). The reaction mixture was stirred for 1 h at room temperature and then passed through a short pad of silica gel with hexanes-EtOAc (1:1). The solvents were completely removed on a rotary evaporator, the residue was dissolved in CH_2Cl_2 (5 mL), and DBU (22.5 μL, 0.15 mmol, 0.8 equiv) was slowly added *via* syringe at 0 ^{o}C. The reaction mixture was stirred overnight at room temperature. HPLC analysis of the reaction mixture showed a ratio of *E*-(±)-**4a**/*Z*-(±)-**4b**/(±)-unconjugated alkene = 79:4:17 (HPLC "yield": 89%). Careful chromatography provided pure *Z*-(±)-**4b**, while *E*-(±)-**4b** and (±)-unconjugated alkene could not be separated.

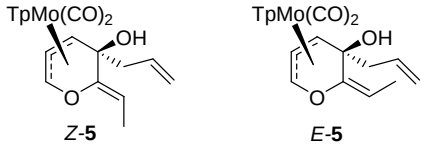
Similarly, (-)-*anti*-aldol product (5.01 g, 7.35 mmol, 1.0 equiv, 97.3 %ee) was dissolved in CH_2Cl_2 (100 mL) and DMAP (0.449 g, 3.68 mmol, 0.5 equiv), Et_3N (1.53 mL, 11.0 mmol, 1.5 equiv), and methanesulfonyl chloride (0.75 mL, 9.56 mmol, 1.3 equiv) were added sequentially. After 2 hours, the solution was passed through a short pad of silica gel (100 % ethyl acetate) and concentrated. The residue was dissolved in CH_2Cl_2 (100 mL), the solution was cooled to 0 ^{o}C, and DBU (1.10 mL, 7.35 mmol, 1.0 equiv) was added dropwise. The solution was warmed to room temperature and stirred 16 hours before it was poured into water (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *Z*-(*S*)-(-)-**4b** (0.259 g, 0.39 mmol, 5%) {$[\alpha]_D^{25}$ -370 (*c* 0.09, CH_2Cl_2)}, and an 83:17 mixture of *E*-(*S*)-(-)-**4b**/unconjugated alkene (3.36 g, 5.06 mmol, 69%, 97.8% ee).

<u>*E*-(±)-**4b**</u>: TLC: R_f = 0.57 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1969 (s), 1876 (s), 1710 (s), 1660 (s), 1602 (m), 1505 (m), 1467 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, J = 2.0 Hz, 1 H), 7.72 (d, J = 2.4 Hz, 1 H), 7.58 (d, J = 2.0 Hz, 1 H), 7.55 (br s, 1 H), 7.49 (d, J = 2.4 Hz, 1 H), 7.42 (br s, 2 H), 7.37-7.41 (m, 4 H), 7.24 (br s, 1 H), 6.48 (br s, 1 H), 6.27 (t, J = 2.4 Hz, 1 H), 6.20 (t, J = 2.0 Hz, 1 H), 5.97 (br s, 1 H), 5.24 (s, 2 H), 4.80 (dd, J = 6.0 Hz, 2.4 Hz, 1 H), 3.98 (br s, 1 H), 2.54-2.68 (m, 2 H), 1.25-1.44 (m, 4 H), 0.88 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.1, 223.0, 187.7, 153.9, 147.3, 144.1, 140.9, 136.5, 136.3, 135.3, 135.1, 134.8, 129.0, 128.8 (3), 128.7, 128.1, 106.3, 106.0, 105.8, 92.0, 69.0, 65.7, 65.0, 32.0, 28.3, 22.5, 14.1. HRMS (ESI) Calcd for $C_{29}H_{31}BMoN_7O_5$ ($[M+H]^+$): 666.1528. Found: 666.1550. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (*S*)-(-)-*E*-**4b**: t_S = 15.36 min; (*R*)-(+)-*E*-**4b**: t_R = 14.36 min; unconjugated alkene: t_C = 16.41 min.

<u>*Z*-(±)-**4b**</u>: TLC: R_f = 0.54 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1969 (s), 1880 (s), 1702 (s), 1668 (s), 1613 (m), 1505 (m), 1455 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 1.2 Hz, 1 H), 7.77 (d, J = 1.6 Hz, 1 H), 7.58-7.59 (m, 2 H), 7.50 (d, J = 2.0 Hz, 1 H), 7.34-7.43 (m, 6 H), 7.21 (br s, 1 H), 6.28 (br s, 1 H), 6.25 (t, J = 6.8 Hz, 1 H), 6.20 (br s, 1 H), 6.15 (br s, 1 H), 5.22 (br s, 2 H), 4.82 (dd, J = 6.4 Hz, 2.0 Hz, 1 H), 4.25 (br s, 1 H), 1.68-2.00 (m, 2 H), 1.18-1.38 (m, 4 H), 0.84 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.4, 223.7, 186.8, 147.4, 143.3, 142.0, 136.5, 136.4, 135.3, 134.9, 130.6, 130.1, 128.9 (2), 128.8, 128.7 (2), 128.6, 106.4, 106.1, 105.9, 88.8, 68.9, 68.2 (2), 30.8, 29.9, 22.6, 14.0. HRMS (ESI) Calcd for $C_{29}H_{31}BMoN_7O_5$ ($[M+H]^+$): 666.1528. Found: 666.1498.

*Note that Z and E isomers (above) are assigned by comparing the ^1H chemical shift differences ($\Delta\delta$) of the alkylidene proton, which are shifted downfield by 0.52, 0.15, and 0.23 ppm for **3a**, **4a**, and **4b** in the Z isomers, owing to the deshielding effect of the adjacent carbonyl group.*

2. Grignard Addition

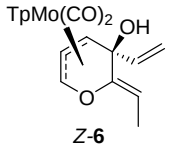


(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-5-allyl-6-ethylene-5-hydroxy-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-**5**. To a solution of *Z*-(±)-**3a** (120 mg, 0.25 mmol, 1.0 equiv) in THF (3 mL) was added allylmagnesium bromide (1.0 M in Et_2O, 0.37 mL, 0.37 mmol, 1.5 equiv) at –78 ºC. The reaction mixture was slowly warmed to –50 ºC over 1 hour, and then quenched with saturated $NaHCO_3$ solution (1 mL). The mixture was poured into a separatory funnel containing CH_2Cl_2 (10 mL) and H_2O (10 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (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 (4:1) afforded *Z*-(±)-**5** (114 mg, 0.22 mmol, 87%) as a bright yellow solid.

Similar treatment of *E*-(±)-**3a** (100 mg, 0.21 mmol, 1.0 equiv) with allylmagnesium bromide (0.31 mL, 0.31 mmol, 1.5 equiv) afforded *E*-(±)-**5** (88 mg, 0.17 mmol, 81%) as a bright yellow solid.

<u>*Z*-(±)-**5**</u>: TLC: R_f = 0.71 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3478 (br w), 3127 (w), 3146 (w), 3076 (w), 2918 (w), 2864 (w), 2482 (m), 1942 (s), 1845 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 1.9 Hz, 1 H), 7.94 (d, *J* = 1.9 Hz, 1 H), 7.69 (d, *J* = 1.9 Hz, 1 H), 7.58 (d, *J* = 2.2 Hz, 1 H), 7.57 (d, *J* = 2.5 Hz, 1 H), 7.50 (d, *J* = 2.5 Hz, 1 H), 7.04 (dd, *J* = 4.1 Hz, 2.5 Hz, 1 H), 6.28 (t, *J* = 2.2 Hz, 1 H), 6.22 (t, *J* = 2.2 Hz, 1 H), 6.21 (t, *J* = 2.2 Hz, 1 H), 5.93-6.03 (m, 1 H), 5.15-5.19 (m, 2 H), 4.94 (q, *J* = 7.0 Hz, 1 H), 4.64 (dd, *J* = 7.3 Hz, 2.5 Hz, 1 H), 3.60 (dd, *J* = 7.6 Hz, 4.4 Hz, 1 H), 3.18 (s, 1 H), 2.63 (doublets of AB quartet, *J* = 13.0 Hz, 8.3 Hz, 2 H), 1.58 (d, *J* = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 232.1, 225.3, 151.5, 147.0, 142.9, 141.8, 136.3, 136.2, 134.7, 133.9, 118.5, 107.2, 106.3, 105.9, 105.6, 102.6, 77.4, 75.7, 60.0, 52.1, 9.7. HRMS (ESI) Calcd for $C_{21}H_{23}BMoN_6O_4$ ($[M]^+$): 532.0928. Found: 532.0935.

<u>*E*-(±)-**5**</u>: TLC: R_f = 0.70 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3601 (m), 3474 (br w), 3127 (w), 3146 (w), 2922 (w), 2482 (m), 1938 (s), 1841 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1200 (s), 1123 (s), 1050 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 1.9 Hz, 1 H), 7.98 (d, *J* = 2.2 Hz, 1 H), 7.60 (d, *J* = 1.9 Hz, 1 H), 7.57 (d, *J* = 2.3 Hz, 2 H), 7.50 (d, *J* = 1.9 Hz, 1 H), 6.93 (dd, *J* = 4.4 Hz, 2.9 Hz, 1 H), 6.29 (t, *J* = 2.1 Hz, 1 H), 6.21 (t, *J* = 2.2 Hz, 2 H), 6.02 (dddd, *J* = 16.6 Hz, 10.2 Hz, 6.7 Hz, 3.5 Hz, 1 H), 5.16-5.22 (m, 2 H), 4.94 (q, *J* = 7.6 Hz, 1 H), 4.63 (dd, *J* = 7.6 Hz, 2.5 Hz, 1 H), 3.61 (dd, *J* = 7.3 Hz, 4.5 Hz, 1 H), 3.39 (s, 1 H), 2.68 (doublets of AB quartet, *J* = 13. 7 Hz, 5.6 Hz, 2 H), 1.75 (d, *J* = 7.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 232.1, 225.5, 149.5, 147.1, 143.5, 141.5, 136.3, 136.1, 134.7, 133.9, 118.7, 107.2, 106.2, 105.9, 105.7, 105.6, 81.2, 77.4, 60.8, 51.1, 11.6. HRMS (ESI) Calcd for $C_{21}H_{23}BMoN_6O_4$ ($[M]^+$): 532.0928. Found: 532.0937.

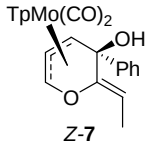


(-)- and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-5-hydroxy-6-propylene-5-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(-)-**6 and** *Z*-(±)-**6**. To a solution of *Z*-(±)-**3a** (488 mg, 1.0 mmol, 1.0 equiv) in THF (6 mL) was added vinylmagnesium bromide (0.87 M in THF, 0.23 mL, 2.0 mmol, 2.0 equiv) at –40 ºC. The mixture was stirred at –40 ºC for 1 hour, warmed to –10 ºC over 30 minutes, and then quenched with water (1 mL). The mixture was poured into a separatory funnel containing CH_2Cl_2 (10 mL) and water (10 mL). The layers

were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers dried over Na_2SO_4, filtered, and concentrated to give a yellow oil. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *Z*-(±)-**6** (506 mg, 0.98 mmol, 98%) as a bright yellow solid.

Similar treatment of *Z*-(-)-**3a** (25 mg, 0.050 mmol, 1.0 equiv, 97.1 %ee) in THF (2 mL) with vinylmagnesium bromide (1.0 M in THF, 0.21 mL, 0.20 mmol, 4.0 equiv) afforded *Z*-(2*S*, 5*S*)-(-)-**6** (21 mg, 0.041 mmol, 81%, 97.1 %ee) {$[\alpha]_D^{25}$ -214 (*c* 2.0, CH_2Cl_2)}.

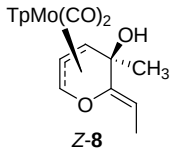
TLC: R_f = 0.66 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3474 (br w), 3146 (w), 3127 (w), 2918 (w), 2864 (w), 2482 (m), 1942 (s), 1845 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1197 (s), 1123 (s), 1050 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 2.0 Hz, 1 H), 7.94 (d, *J* = 2.0 Hz, 1 H), 7.69 (d, *J* = 2.0 Hz, 1 H), 7.59 (d, *J* = 2.4 Hz, 1 H), 7.57 (d, *J* = 2.4 Hz, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 7.07 (dd, *J* = 4.4 Hz, 2.4 Hz, 1 H), 6.28 (t, *J* = 2.4 Hz, 1 H), 6.22 (t, *J* = 2.0 Hz, 1 H), 6.19 (t, *J* = 2.0 Hz, 1 H), 6.11 (ddd, *J* = 17.2 Hz, 10.8 Hz, 0.8 Hz, 1 H), 5.46 (dd, *J* = 17.2 Hz, 1.2 Hz, 1 H), 5.08 (dd, *J* = 10.4 Hz, 0.8 Hz, 1 H), 5.04 (q, *J* = 6.8 Hz, 1 H), 4.59 (dd, *J* = 7.6 Hz, 2.4 Hz, 1 H), 3.67 (dd, *J* = 7.6 Hz, 4.4 Hz, 1 H), 3.34 (d, *J* = 0.8 Hz, 1 H), 1.58 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 232.5, 225.1, 150.9, 146.8, 145.0, 142.8, 141.6, 136.3, 136.1, 134.6, 111.4, 107.2, 106.1, 105.8, 105.5, 102.5, 76.4, 76.1, 60.2, 9.7. HRMS (ESI) Calcd for $C_{20}H_{21}BMoN_6O_4$ ($[M]^+$): 518.0771. Found: 518.0775. HPLC: Daicel® Chiralpak AS-RH column, isocratic solvent system: 50 % CH_3CN in H_2O (+ 0.1 % TFA), 0.9 mL/min, λ = 254 nm, *Z*-(2*S*, 5*S*)-(-)-**6**: $t_{(-)}$ = 14.39 min; *Z*-(2*R*, 5*R*)-(+)-**6**: $t_{(+)}$ = 16.46 min.



Z-**7**

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-6-ethylene-5-hydroxy-5-phenyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(±)-**7**. To a solution of *Z*-(±)-**3a** (300 mg, 0.62 mmol, 1.0 equiv) in THF (2 mL) was added phenylmagnesium bromide (1.0 M in THF, 1.23 mL, 1.23 mmol, 2.0 equiv) at –78 ºC. The mixture was stirred at –78 ºC for 2 hours, warmed to –15 ºC over 30 minutes, and then quenched with water (1 mL). The mixture was poured into a separatory funnel containing CH_2Cl_2 (10 mL) and H_2O (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *Z*-(±)-**7** (223 mg, 0.39 mmol, 64%) as a bright yellow solid.

TLC: R_f = 0.70 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3474 (br w), 3146 (w), 3127 (w), 2918 (w), 2864 (w), 2486 (m), 1942 (s), 1845 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, *J* = 1.8 Hz, 1 H), 7.95 (d, *J* = 2.1 Hz, 1 H), 7.74 (d, *J* = 1.5 Hz, 1 H), 7.72 (d, *J* = 7.2 Hz, 1 H), 7.67 (d, *J* = 1.8 Hz, 1 H), 7.57-7.54 (m, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 7.37 (app t, *J* = 7.5 Hz, 2 H), 7.26 (dd, *J* = 8.2 Hz, 5.1 Hz, 2 H), 7.14 (dd, *J* = 4.3 Hz, 1.8 Hz, 1 H), 6.30 (app t, *J* = 2.1 Hz, 1 H), 6.20 (app t, *J* = 2.1 Hz, 1 H), 6.17 (app t, *J* = 2.1 Hz, 1 H), 5.15 (q, *J* = 6.9 Hz, 2 H), 4.84 (dd, *J* = 7.6 Hz, 2.7 Hz, 1 H), 1.62 (d, *J* = 6.9 Hz, 3 H).^{13}C NMR (100 MHz, $CDCl_3$): δ 233.3, 225.5, 152.0, 149.3, 147.1, 143.2, 141.7, 136.4, 136.2, 134.8, 128.6 (2), 128.6, 127.5, 124.8, 106.6, 106.3, 105.9, 105.6, 103.8, 80.4, 61.1, 9.8. HRMS (ESI) Calcd for $C_{24}H_{23}BMoN_6O_4$ ($[M]^+$): 568.0928. Found: 568.0918.

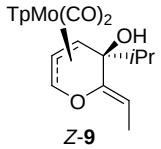


Z-**8**

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-6-ethylene-5-hydroxy-5-methyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(±)-**8**. To a solution of *Z*-(±)-**3a** (300 mg, 0.62 mmol, 1.0 equiv) in THF (4 mL) was added methylmagnesium bromide (3.0 M in Et_2O, 0.41 mL, 1.23 mmol, 2.0 equiv) at –78 ºC. The mixture was stirred at the same temperature for 1 hour, and then quenched with water (1 mL). The mixture was poured into a

separatory funnel containing CH_2Cl_2 (10 mL) and H_2O (10 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1), affording *Z*-(±)-**8** (220 mg, 0.44 mmol, 71%) as a bright yellow solid.

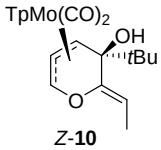
TLC: R_f = 0.72 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3462 (br w), 3146 (w), 3127 (w), 2926 (w), 2856 (w), 2482 (m), 1942 (s), 1841 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1200 (s), 1123 (s), 1050 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, *J* = 1.8 Hz, 1 H), 7.94 (d, *J* = 1.8 Hz, 1 H), 7.70 (d, *J* = 1.8 Hz, 1 H), 7.58-7.56 (m, 2 H), 7.49 (d, *J* = 1.8 Hz, 1 H), 7.04 (dd, *J* = 4.0 Hz, 2.7 Hz, 1 H), 6.28 (app t, *J* = 2.1 Hz, 1 H), 6.22-6.19 (m, 2 H), 4.99 (q, *J* = 6.9 Hz, 1 H), 4.66 (dd, *J* = 7.5 Hz, 2.4 Hz, 1 H), 3.54 (dd, *J* = 7.5 Hz, 4.5 Hz, 1 H), 3.26 (br s, 1 H), 1.67 (s, 3 H), 1.55 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 232.8, 225.0, 153.4, 147.0, 142.8, 141.9, 136.4, 136.2, 134.7, 107.6, 106.3, 105.9, 105.6, 101.0, 78.4, 74.1, 59.8, 35.8, 9.7. HRMS (ESI) Calcd for $C_{19}H_{21}BMoN_6O_4$ ($[M]^+$): 506.0771. Found: 506.0779.



Z-**9**

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(η-2,3,4)-6-ethylidene-5-hydroxy-5-isopropyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(±)-**9.** To a solution of *Z*-(±)-**3a** (25 mg, 0.050 mmol, 1.0 equiv) in dry THF (2 mL) at –40 °C was added isopropyl magnesium chloride (1.6 M in Et_2O, 128 µL, 0.20 mmol, 4 equiv). After one hour, the reaction mixture was quenched with water and extracted with dichloromethane (2 x 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The yellow oil was then purified by flash chromatography over silica gel with hexanes-EtOAc (4:1), affording *Z*-(±)-**9** (6.0 mg, 0.011 mmol, 21%) as a yellow solid.

TLC: R_f = 0.72 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 2956 (w), 2483 (w), 1956 (s), 1865 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.6 Hz, 1 H), 7.93 (d, *J* = 1.6 Hz, 1 H), 7.65 (d, *J* = 2.4 Hz, 1 H), 7.57-7.56 (m, 2 H), 7.48 (d, *J* = 2.4 Hz, 1 H), 6.98 (dd, *J* = 4.4, 2.4 Hz, 1 H), 6.27 (app t, *J* = 2.0 Hz, 1 H), 6.22-6.20 (m, 2 H), 4.93-4.89 (m, 1 H), 4.73 (dd, *J* = 7.6 Hz, 2.8 Hz, 1 H), 3.70 (dd, *J* = 7.6 Hz, 4.4 Hz, 1 H), 3.06 (br s, 1 H), 1.95-1.90 (m, 1 H), 1.56 (d, *J* = 7.2 Hz, 3 H), 1.19 (d, *J* = 6.4 Hz, 3 H), 1.03 (d, *J* = 6.8 Hz, 3 H).^{13}C NMR (100 MHz, $CDCl_3$): δ 232.8, 225.9, 151.4, 147.0, 143.1, 141.7, 136.4, 136.1, 134.7, 106.4, 106.2, 105.9, 105.7, 103.3, 77.8, 61.7, 42.6, 18.3, 16.9 (2), 9.7. HRMS (ESI) Calcd for $C_{21}H_{25}BMoN_6O_4$ ($[M]^+$): 534.1084. Found: 534.1080.

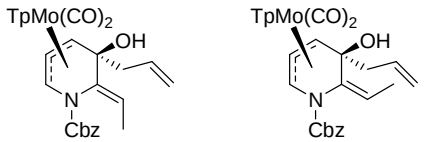


Z-**10**

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(η-2,3,4)-6-ethylidene-5-hydroxy-5-*tert*-butyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, *Z*-(±)-**10.** To a solution of *Z*-(±)-**3a** (0.100 g, 0.20 mmol, 1.0 equiv) in dry THF (2 mL) at –40 °C was added *tert*-butylmagnesium chloride (2.0 M in Et_2O, 205 µL, 0.41 mmol, 2 equiv). After one hour, the reaction mixture was quenched with water and extracted with dichloromethane (2 x 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The yellow oil was then purified by flash chromatography over silica gel with hexanes-EtOAc (4:1), affording *Z*-(±)-**10** as a yellow solid (28 mg, 0.051 mmol, 25%).

TLC: R_f = 0.68 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 2920 (w), 2469 (m), 1920 (s), 1829 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.8 Hz, 1 H), 7.95 (d, *J* = 1.8 Hz, 1 H), 7.61 (d, *J* = 1.5 Hz, 1 H), 7.58-7.56 (m, 2 H), 7.48 (d, *J* = 2.1 Hz, 1 H), 6.96 (dd, *J* = 4.0 Hz, 2.4 Hz, 1 H), 6.27 (app t, *J* = 2.1 Hz, 1 H), 6.22-6.20 (m, 2 H), 4.92 (q, *J* = 6.6 Hz, 1 H), 4.76 (dd, *J* = 7.6 Hz, 2.1 Hz, 1 H), 3.91 (dd, *J* = 7.6 Hz, 4.3 Hz, 1 H), 3.08 (br s, 1 H), 1.58 (d, *J* = 6.6 Hz, 3 H), 1.14 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 233.4, 226.7, 150.5, 147.0, 143.7, 141.4, 136.4, 136.1,

134.7, 106.2, 105.9, 105.7, 105.4, 104.6, 79.3, 78.8, 64.6, 41.8, 25.8 (3), 9.8. HRMS (ESI) Calcd for $C_{22}H_{27}BMoN_6O_4$ ($[M]^+$): 548.1241. Found: 548.1248.



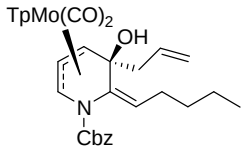
Z-**11** *E*-**11**

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-5-allyl-1-(benzyloxycarbonyl)-6-ethylene-5-hydroxy-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-11. To a solution of *Z*-(±)-**4a** (0.460 g, 0.74 mmol, 1.0 equiv) in THF (12 mL) was added allylmagnesium bromide (1.0 M in Et_2O, 0.89 mL, 0.89 mmol, 1.2 equiv) at –78 ºC. The reaction mixture was stirred at –78 ºC for 5 minutes and then quenched with water (1 mL). The mixture was poured into a separatory funnel containing CH_2Cl_2 (10 mL) and water (10 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *Z*-(±)-**11** (0.484 g, 0.73 mmol, 99%) as a bright yellow solid.

Similar treatment of *E*-(±)-**4a** (0.600 g, 0.97 mmol, 1.0 equiv) with allylmagnesium bromide (1.0 M in Et_2O, 1.1 mL, 1.16 mmol, 1.2 equiv) in THF (15 mL) afforded *E*-(±)-**11** (0.640 g, 0.96 mmol, 99%) as a bright yellow solid.

<u>*Z*-(±)-**11**</u>: TLC: R_f = 0.41 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3590 (w), 3470 (br w), 2941(w), 2918 (w), 2482 (m), 1949 (s), 1872 (s), 1849 (s), 1687 (s), 1505 (m), 1447 (s), 1409 (s), 1293 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (br s, 1 H), 7.90 (br s, 2 H), 7.60 (br s, 2 H), 7.49 (d, *J* = 1.4 Hz, 1 H), 7.30-7.44 (m, 5 H), 6.93 (br s, 1 H), 6.28 (br s, 1 H), 6.16-6.22 (m, 2 H), 5.82-5.90 (m, 1 H), 5.36-5.48 (m, 1 H), 5.28 (d, *J* = 12.0 Hz, 1 H), 5.05-5.13 (m, 2 H), 4.61-4.62 (m, 1 H), 3.74-3.76 (m, 1 H), 3.59-3.65 (m, 1 H), 3.03 (br s, 1 H), 2.56-2.60 (m, 1 H), 2.45-2.46 (m, 1 H), 1.49 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 231.3, 224.9, 155.6, 147.0, 143.2, 142.1, 136.5, 136.4, 136.2, 136.1, 134.7, 134.0, 128.7(2), 128.32, 128.30, 127.8, 118.5, 115.6, 106.2, 105.9, 105.7, 83.5, 83.1, 76.3, 68.3, 61.1, 49.7, 14.4. HRMS (ESI) Calcd for $C_{29}H_{30}BMoN_7O_5$ ($[M]^+$): 665.1456. Found: 665.1465.

<u>*E*-(±)-**11**</u>: TLC: R_f = 0.43 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3601 (m), 3478 (br w), 3123 (w), 2937 (w), 2482 (m), 1945 (s), 1845 (s), 1691 (s), 1505 (m), 1455 (w), 1409 (s), 1293 (s), 1220 (s), 1123 (s), 1073 (s), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.50 (d, *J* = 1.9 Hz, 1 H), 7.91 (d, *J* = 1.4 Hz, 1 H), 7.85 (br s, 1 H), 7.58 (d, *J* = 1.4 Hz, 2 H), 7.50 (d, *J* = 1.9 Hz, 1 H), 7.34-7.38 (m, 5 H), 7.00 (d, *J* = 4.8 Hz, 1 H), 6.28 (t, *J* = 2.4 Hz, 1 H), 6.20 (t, *J* = 2.4 Hz, 1 H), 6.17 (br s, 1 H), 5.80-5.97 (m, 1 H), 5.48 (br s, 1 H), 5.23-5.30 (m, 2 H), 5.12-5.16 (m, 2 H), 4.65 (dd, *J* = 7.2 Hz, 1.9 Hz, 1 H), 3.57 (br s, 1 H), 3.28 (br s, 1 H), 2.61 (doublets on the left side of AB quartet, *J* = 13. 8 Hz, 8.1 Hz, 1 H), 2.53-2.54 (m, 1 H), 1.93 (d, *J* = 7.1 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): 231.7, 224.6, 147.1, 143.1, 142.1, 136.6, 136.4, 136.2, 134.6, 134.3, 133.9(2), 128.7(3), 128.2, 127.7, 120.7, 118.7, 106.2, 105.8, 105.6, 83.1, 78.4, 68.1, 68.0, 60.3, 50.0, 13.2. HRMS (ESI) Calcd for $C_{29}H_{30}BMoN_7O_5$ ($[M]^+$): 665.1456. Found: 665.1435.



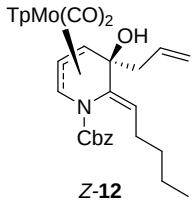
E-**12**

***E*-(-)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-5-allyl-1-(benzyloxycarbonyl)-5-hydroxy-6-pentylene-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum,** *E*-(-)-**12**. A mixture of compounds *E*-(-)-**4b**/unconjugated alkene (approx. 83:17) (0.194 g, 0.29 mmol, 1.0 equiv, 97.8% ee) was dissolved in THF (5 mL) and cooled to –78 °C. Allylmagnesium bromide (1.0 M in Et_2O, 0.32 mL, 0.32 mmol, 1.1 equiv) was added dropwise. After 15 minutes, additional allylmagnesium bromide (1.0 M in Et_2O, 0.32 mL, 0.32 mmol, 1.1 equiv) was added. After 15 minutes, water (1 mL) was added and the reaction mixture was warmed to room temperature.

The solution was poured into a separatory funnel containing water (10 mL) and CH_2Cl_2 (10 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL), dried over $MgSO_4$, filtered and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded *E*-(2*S*, 5*S*)-(-)-**12** (0.188 g, 0.27 mmol, 92%, 97.7% ee), containing 12% impurity by HPLC, as a yellow solid.

*Intermediate allylic alcohol E-(-)-**12**, containing an inseparable impurity, could be isolated and partially characterized as follows:*
TLC: R_f = 0.49 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3601 (m), 3474 (br w), 3123 (w), 2957 (w), 2930 (m), 2860 (w), 2482 (m), 1945 (s), 1845 (s), 1687 (s), 1505 (w), 1455 (w), 1409 (s), 1293 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.6 Hz, 1 H), 7.86 (d, *J* = 1.9 Hz, 1 H), 7.84 (br s, 1 H), 7.55 (d, *J* = 2.2 Hz, 2 H), 7.47 (d, *J* = 2.5 Hz, 1 H), 7.31-7.36 (m, 5 H), 6.97 (br s, 1 H), 6.26 (t, *J* = 2.2 Hz, 1 H), 6.17 (t, *J* = 2.2 Hz, 1 H), 6.16 (br s, 1 H), 5.85-5.95 (m, 1 H), 5.20-5.29 (m, 3 H), 5.07-5.11 (m, 2 H), 4.60 (dd, *J* = 7.3 Hz, *J* = 2.5 Hz, 1 H), 3.53-3.55 (m, 1 H), 3.20 (s, 1 H), 2.31-2.59 (m, 4 H), 1.10-1.30 (br s, 4 H), 0.81 (br s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 231.8, 224.4, 147.1 (2), 142.9, 142.1, 136.3, 136.1, 134.6, 133.9, 133.0, 128.6 (2), 128.3, 128.2 (2), 127.1, 118.6, 106.2, 105.8, 105.6, 83.3, 78.2, 68.1, 60.1, 49.9, 32.4, 26.9, 22.4, 14.2. HRMS (ESI) Calcd for $C_{32}H_{37}BMoN_7O_5$ ($[M+H]^+$): 708.1998. Found: 708.2029. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (2*S*, 5*S*)-(-)-*E*-**12**: t_S = 15.90 min; (2*S*, 5*S*)-(+)-*E*-**12**: t_R = 15.17 min.

*Note: The Grignard addition/semipinacol rearrangement sequence could be performed in one-pot, as described below for compound **20**.*

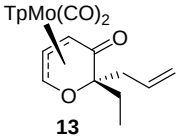


Z-**12**

***Z*-(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,5*S*)-(*η*-2,3,4)-5-allyl-1-(benzyloxycarbonyl)-5-hydroxy-6-pentylene-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum,** *Z*-(±)-**12**. Compound *Z*-(±)-**4b** (0.108 g, 0.16 mmol, 1.0 equiv) was dissolved in THF (10 mL) and cooled to –78 °C. Allylmagnesium bromide (1.0 M in Et_2O, 0.33 mL, 0.33 mmol, 2.0 equiv) was added. After 5 minutes, a saturated aqueous solution of NH_4Cl (1 mL) was added and the reaction mixture was warmed to room temperature. The solution was poured into water (20 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1 then 2:1) afforded *Z*-(±)-**12** (0.104 g, 0.15 mmol, 93%) as a yellow solid.

TLC: R_f = 0.48 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3466 (br w), 2930 (m), 1949 (s), 1872 (s), 1853 (s), 1691 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (br s, 1 H), 7.91 (d, *J* = 2.0 Hz, 1 H), 7.89 (br s, 1 H), 7.57 (t, *J* = 2.0 Hz, 2 H), 7.49 (d, *J* = 2.4 Hz, 1 H), 7.30-7.40 (m, 5 H), 6.89-6.93 (m, 1 H), 6.28 (t, *J* = 2.4 Hz, 1 H), 6.21 (br s, 1 H), 6.19 (t, *J* = 1.6 Hz, 1 H), 5.78-5.95 (m, 1 H), 5.24-5.34 (m, 2 H), 5.04-5.16 (m, 3 H), 4.60-4.68 (m, 1 H), 3.54-3.68 (m, 1 H), 3.05 (s, 1 H), 2.58 (dd, *J* = 13.6 Hz, 8.4 Hz, 1 H), 2.41-2.48 (m, 1 H), 1.82-1.98 (m, 1 H), 1.62-1.73 (m, 1 H), 1.23-1.43 (m, 4 H), 0.82-0.93 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 231.3, 224.8, 155.7, 147.0, 143.2, 141.9, 136.3, 136.1, 134.7, 134.6, 134.0, 128.6 (2), 128.4, 128.3, 127.7, 121.1, 118.4, 106.2, 105.8, 105.6, 83.4, 83.1, 76.2, 68.2, 61.1, 49.6, 31.3, 28.5, 22.8, 14.2. HRMS (ESI) Calcd for $C_{32}H_{37}BMoN_7O_5$ ($[M+H]^+$): 708.1997. Found: 708.1994.

3. Semipinacol Rearrangement

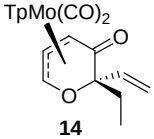


13

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-6-allyl-6-ethyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-13. To a solution of *Z*-(±)-**5** (61 mg, 0.11 mmol, 1.0 equiv) in CH_2Cl_2 (4 mL) was added HCl (4.0 M in dioxane, 32 µL, 0.13 mmol, 1.2 equiv) at 0 ºC. The reaction mixture was stirred at 0 ºC for 5 minutes and then passed through a short pad of silica gel. The solvents were completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (4:1) to afford (±)-**13** (58 mg, 0.11 mmol, 95 %) as an orange solid.

Similar treatment of *E*-(±)-**5** (27 mg, 0.051 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) with HCl (14 µL, 0.056 mmol, 4.0 M in dioxane, 1.1 equiv) at 0 ºC afforded (±)-**13** (25.5 mg, 0.048 mmol, 94 %) as an orange solid.

TLC: R_f = 0.49 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3594 (w), 3478 (br w), 3127 (w), 3146 (w), 3076 (w), 2918 (w), 2864 (w), 2482 (m), 1942 (s), 1845 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.53 (d, *J* = 1.9 Hz, 1 H), 7.96 (d, *J* = 1.4 Hz, 1 H), 7.68 (d, *J* = 1.4 Hz, 1 H), 7.62 (d, *J* = 2.4 Hz, 1 H), 7.57 (d, *J* = 2.4 Hz, 1 H), 7.53 (dd, *J* = 4.3 Hz, 1.9 Hz, 1 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 6.30 (t, *J* = 1.9 Hz, 1 H), 6.25 (t, *J* = 1.9 Hz, 1 H), 6.21 (t, *J* = 1.9 Hz, 1 H), 5.80-5.87 (m, 1 H), 5.14 (s, 1 H), 5.12 (d, *J* = 5.2 Hz, 1 H), 4.74 (dd, *J* = 5.7 Hz, 1.9 Hz, 1 H), 4.13 (t, *J* = 5.2 Hz, 1 H), 2.47 (doublet of AB quartet, *J* = 15.3 Hz, 7.2 Hz, 2 H), 1.6 (doublet of AB quartet, *J* = 14.3 Hz, 7.2 Hz, 2 H), 0.84 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 219.9, 217.5, 195.3, 144.5, 140.3, 138.7, 133.94, 133.87, 132.3, 130.4, 116.9, 108.3, 105.2, 104.9, 104.6, 82.9, 65.4, 65.2, 43.0, 30.1, 10.5. HRMS (ESI) Calcd for $C_{21}H_{23}BMoN_6O_4$ ($[M]^+$): 532.0928. Found: 532.0948.

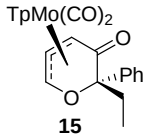


14

(-)- and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-6-ethyl-5-oxo-6-vinyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (-)- and (±)-14. To a solution of *Z*-(±)-**6** (16 mg, 0.031 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added HCl (4.0 M in dioxane, 8.0 µL, 0.031 mmol, 1.0 equiv) at 0 ºC. The reaction mixture was stirred at 0 ºC for 5 minutes and then passed through a short pad of silica gel. The solvents were completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (5:1) to afford (±)-**14** (16 mg, 0.031 mmol, 100%) as an orange solid.

Similar treatment of *Z*-(-)-**6** (23 mg, 0.040 mmol, 1.0 equiv, 97.1 %ee) in CH_2Cl_2 (2.5 mL) with HCl (4.0 M in dioxane, 12 µL, 0.050 mmol, 1.1 equiv) afforded (-)-(2*S*, 6*S*)-**14** (23 mg, 0.045 mmol, 99 %, 97.1 %ee) {$[\alpha]_D^{25}$ -225 (*c* 1.8, CH_2Cl_2)}.

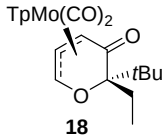
(±)-**14**: TLC: R_f = 0.49 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3146 (m), 3127 (m), 2980 (m), 2941 (m), 2880 (w), 2486 (m), 1961 (s), 1872 (s), 1660 (s), 1505 (s), 1409 (s), 1305 (s), 1262 (s), 1220 (s), 1123 (s), 1050 (s), 1015 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 1.6 Hz, 1 H), 7.94 (d, *J* = 2.4 Hz, 1 H), 7.69 (d, *J* = 2.0 Hz, 1 H), 7.58-7.61 (m, 3 H), 7.51 (d, *J* = 1.6 Hz, 1 H), 6.30 (t, *J* = 2.4 Hz, 1 H), 6.25 (t, *J* = 2.0 Hz, 1 H), 6.20 (t, *J* = 2.4 Hz, 1 H), 5.63 (dd, *J* = 17.2 Hz, 10.8 Hz, 1 H), 5.37 (dd, *J* = 17.2 Hz, *J* = 1.2 Hz, 1 H), 5.23 (dd, *J* = 10.4 Hz, 0.8 Hz, 1 H), 4.72 (dd, *J* = 5.6 Hz, 2.0 Hz, 1 H), 4.11 (dd, *J* = 5.6 Hz, 4.4 Hz, 1 H), 1.76 (doublets of AB quartet, *J* = 14.3 Hz, *J*= 7.3 Hz, 1 H), 1.55 (doublets of AB quartet, *J* = 14.3 Hz, *J* = 7.3 Hz, 1 H), 0.77 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 226.4, 224.0, 198.4, 147.7, 143.3, 141.6, 136.9, 136.5, 134.8, 115.4, 109.0, 106.5, 106.1, 105.8, 84.5, 70.1, 65.2, 64.7, 28.7, 7.2. HRMS (ESI) Calcd for $C_{20}H_{21}BMoN_6O_4$ ($[M]^+$): 518.0771. Found: 518.0778. HPLC: Daicel® Chiralcel OJ-RH column, Isocratic solvent system: 50 % CH_3CN in H_2O (+ 0.1 % TFA), 1.0 mL/min, λ = 254 nm, (2*S*, 6*S*)-(-)-**14**: $t_{(-)}$ = 13.62 min; (2*S*, 6*S*)-(+)-**14**: $t_{(+)}$ = 17.32 min.



15

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-6-ethyl-5-oxo-6-phenyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-15. To a solution of *Z*-(±)-**7** (18 mg, 0.032 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added HCl (4.0 M in dioxane, 8.0 µL, 0.035 mmol, 1.1 equiv) at 0 ºC. The reaction mixture was stirred at 0 ºC for 5 minutes and then passed through a short pad of silica gel. The solvents were completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (4:1) to afford (±)-**15** (17.7 mg, 0.031 mmol, 98 %) as an orange solid.

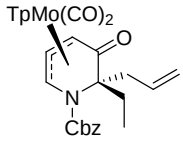
TLC: R_f = 0.47 (hexanes-EtOAc = 3:1). IR (cm^{-1}): 3146 (w), 3127 (w), 2980 (m), 2937 (w), 2490 (m), 1961 (s), 1876 (s), 1660 (m), 1505 (m), 1447 (m), 1409 (s), 1305 (s), 1258 (s), 1220 (s), 1123 (s), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.59 (d, *J* = 1.9 Hz, 1 H), 7.92 (d, *J* = 1.9 Hz, 1 H), 7.73 (d, *J* = 1.9 Hz, 1 H), 7.69 (dd, *J* = 4.4 Hz, 2.2 Hz, 1 H), 7.61 (d, *J* = 2.3 Hz, 1 H), 7.57 (d, *J* = 2.2 Hz, 1 H), 7.52 (d, *J* = 2.2 Hz, 1 H), 7.47-7.49 (m, 2 H), 7.36-7.40 (m, 2 H), 7.27-7.32 (m, 1 H), 6.33 (t, *J* = 2.2 Hz, 1 H), 6.26 (t, *J* = 2.2 Hz, 1 H), 6.18 (t, *J* = 2.2 Hz, 1 H), 4.70 (dd, *J* = 5.5 Hz, 2.2 Hz, 1 H), 4.04 (dd, *J* = 5.7 Hz, 4.5 Hz, 1 H), 1.88 (doublet of AB quartets, *J* = 14.3 Hz, 7.3 Hz, 2 H), 0.69 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 226.6, 223.9, 198.5, 147.7, 143.1, 141.7, 139.1, 136.54, 136.51, 134.8, 128.6 (2), 127.7, 125.5 (2), 108.5, 106.5, 106.1, 105.8, 85.1, 65.8, 65.1, 31.9, 7.7. HRMS (ESI) Calcd for $C_{24}H_{23}BMoN_6O_4$ ($[M]^+$): 568.0928. Found: 568.0949.



18

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(η-2,3,4)-6-ethyl-5-oxo-6-*tert*-butyl-5,6-dihydro-2*H*-pyran-2-yl]molybdenum, (±)-18. To a solution of *Z*-(±)-**10** (28 mg, 0.050 mmol, 1.0 equiv) in CH_2Cl_2 (3.1 mL) was added a solution of HCl (4.0 M in dioxane, 14 µL, 0.060 mmol, 1.1 equiv). The reaction mixture was refluxed for 10 minutes and then cooled to room temperature. The crude reaction mixture was purified by flash chromatography over silica gel with hexanes-EtOAc (4:1), affording (±)-**18** (27 mg, 0.049 mmol, 98%) as a yellow solid.

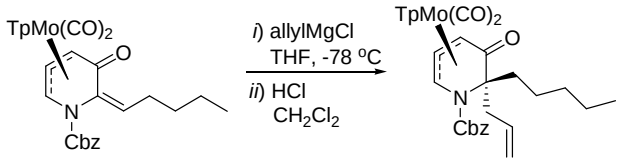
TLC: R_f =0.40 (hexanes-EtOAc = 4:1). IR (cm^{-1}): 3120 (w), 2485 (w), 1954 (s), 1859 (s), 1656 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 1.6 Hz, 1 H), 7.95 (d, *J* = 1.6 Hz, 1 H), 7.70 (d, *J* = 1.6 Hz, 1 H), 7.65 (dd, *J* = 4.3 Hz, 2.6 Hz, 1 H), 7.61 (d, *J* = 2.5 Hz, 1 H), 7.58 (d, *J* = 2.4 Hz, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 6.28 (app t, *J* = 2.4 Hz, 1 H), 6.25 (app t, *J* = 2.0 Hz, 1 H), 6.20 (app t, *J* = 2.4 Hz, 1 H), 4.69 (dd, *J* = 6.2 Hz, 2.2 Hz, 1 H), 4.10 (dd, *J* = 6.2 Hz, 4.6 Hz, 1 H), 1.79-1.61 (m, 2 H), 1.10 (s, 9 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 226.7, 224.4, 201.7, 147.6, 143.1, 141.5, 136.5, 136.5, 134.8, 112.1, 106.5, 106.1, 105.8, 87.5, 65.8, 64.2, 40.0, 27.9 (3), 27.3, 9.3. HRMS (ESI) Calcd for $C_{22}H_{27}BMoN_6O_4$ ($[M]^+$): 548.1241. Found: 548.1236.



19

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-6-allyl-1-(benzyloxycarbonyl)-6-ethyl-5-oxo-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (±)-19. To a solution of *E*-(±)-**11** (0.566 g, 0.85 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) was added HCl (4.0 M in dioxane, 235 µL, 0.94 mmol, 1.1 equiv) at 0 ºC. The reaction mixture was stirred at room temperature for 1 hour and then passed through a short pad of silica gel. The solvents were completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (4:1) to afford (±)-**19** (0.543 g, 0.82 mmol, 96%) as an orange solid.

TLC: R_f = 0.49 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3127 (w), 2980 (w), 2954 (w), 2486 (m), 1965 (s), 1884 (s), 1710 (s), 1664 (s), 1505 (w), 1459 (w), 1440 (w), 1301 (s), 1251 (m), 1220 (s), 1127 (m), 1054 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (br s, 1 H), 7.80 (br s, 1 H), 7.52-7.58 (m, 3 H), 7.47 (br s, 3 H), 7.38 (br s, 3 H), 7.17 (br s, 1 H), 6.27 (t, *J* = 1.9 Hz, 1 H), 6.19 (br s, 1 H), 5.85 (br s, 1 H), 5.23-5.25 (m, 2 H), 5.15-5.16 (m, 1 H), 5.02-5.10 (m, 2 H), 4.67 (dd, *J* = 5.7 Hz, 1.9 Hz, 1 H), 3.79 (br s, 1 H), 2.75 (br s, 1 H), 2.55 (br s, 1 H), 2.29 (br s, 2 H), 0.93 (br s 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): 224.8, 223.9, 199.7, 153.5, 147.3, 143.2, 141.5, 136.6 (2), 135.8, 134.9, 133.6, 129.3, 128.9 (2), 128.7 (2), 118.5, 106.4, 106.0, 105.8, 91.8, 69.6, 68.8, 62.5, 42.8, 27.2, 9.4. HRMS (ESI) Calcd for $C_{29}H_{30}BMoN_7O_5$ ($[M]^+$): 665.1456. Found: 665.1481.



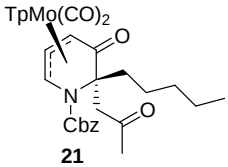
E-**4b** **20**

(-)- and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-6-allyl-1-(benzyloxycarbonyl)-5-oxo-6-pentyl-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (-)-20 and (±)-20. Compounds *E*-(±)-**4b**/unconjugated alkene (approx. 83:17) (7.97 g, 12.0 mmol, 1.0 equiv) were dissolved in THF (100 mL) and cooled to –78 °C. Allylmagnesium chloride (2.0 M in THF, 12.0 mL, 24.0 mmol, 2.0 equiv) was added dropwise. After 15 minutes, and then again after 25 minutes, additional allylmagnesium chloride (2.4 mmol, 1.2 mL, 0.2 equiv) was added, consuming the remainder of *E*-(±)-**4b**. After 10 minutes, aqueous saturated NH_4Cl (5 mL) was added, and the solution warmed to room temperature and was poured into water (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product *E*-**12** was dissolved in CH_2Cl_2 (100 mL) and HCl (4.0 M in dioxane, 3.3 mL, 13.2 mmol, 1.1 equiv) was added dropwise at room temperature. After 55 minutes, the solution was poured into water (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1), affording (±)-**20** (6.63g, 9.40 mmol, 78%) as an orange solid.

Similar treatment of *E*-(-)-**4b**/unconjugated alkene (approx. 83:17) (6.46 g, 9.74 mmol, 1.0 equiv, 97.8% ee) in THF (100 mL) with allylmagnesium bromide (1.0 M in Et_2O, 21.4 mL, 21.4 mmol, 2.2 equiv) and then HCl (4.0 M in dioxane, 2.68 mL, 10.7 mmol, 1.1 equiv) in CH_2Cl_2 (100 mL) afforded (2*S*, 6*S*)-(-)-**20** (5.31 g, 7.53 mmol, 77%, 97.7% ee) {$[\alpha]_D^{25}$ -437 (*c* 0.15, CH_2Cl_2)}.

TLC: R_f = 0.52 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2957 (m), 2486 (m), 1969 (s), 1884 (s), 1710 (s), 1664 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 2.0 Hz, 1 H), 7.80 (d, *J* = 2.4 Hz, 1 H), 7.48-7.59 (m, 5 H), 7.38 (br s, 5 H), 7.17 (br s, 1 H), 6.27 (t, *J* = 2.4 Hz, 1 H), 6.20 (t, *J* = 2.4 Hz, 1 H), 5.85 (br s, 1 H), 5.14-5.25 (m, 2 H), 5.02-5.10 (m, 2 H), 4.66 (dd, *J* = 6.0 Hz, 2.0 Hz, 1 H), 3.79 (br s, 1 H), 2.77 (br s, 1 H), 2.56 (br s, 1 H), 2.26 (br s, 2 H), 1.18-1.32 (m, 6 H), 0.88 (br s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 224.8, 223.7, 199.8, (156.2), 153.3, 147.1, (143.5), 143.0, 141.3, 136.5 (2), 135.7, 134.8, 133.5, 129.2, 128.8 (2), 128.6 (2), 118.4, 106.2, 105.9, 105.7, (92.5), 91.7, 69.0, 68.6, (63.2), 62.4 (2), (43.7), 42.7, (35.4), 33.9, 32.1, 23.9, 22.5, 14.1. HRMS (ESI) Calcd for $C_{32}H_{37}BMoN_7O_5$ ($[M+H]^+$): 708.1998. Found: 708.1993. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (50% to 75%), 1.5 mL/min, λ = 254 nm, (2*S*, 6*S*)-(-)-**20**: t_S = 14.26 min; (2*R*, 5*R*)-(+)-**20**: t_R = 14.91 min.

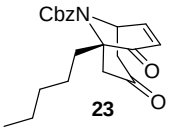
4. Total Synthesis of (-)-Adaline



(-)- and (±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-1-(benzyloxycarbonyl)-5-oxo-6-(2-oxopropyl)-6-pentyl-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum, (-)-21 and (±)-21. Terminal alkene complex (±)-**20** (1.00 g, 1.42 mmol, 1.0 equiv) was dissolved in DMF (40 mL) and water (2 mL), $PdCl_2$ (0.101 g, 0.57 mmol, 0.4 equiv), and CuCl (0.070 mg, 0.71 mmol, 0.5 equiv) were added sequentially. The reaction was stirred open to air for 38 hours and then poured into CH_2Cl_2 (100 mL). The layers were separated and the organic layer was washed with brine (3 x 100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was subjected to flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford (±)-**21** (0.710 g, 0.98 mmol, 69%) as an orange solid. *Some starting material (±)-**20** was recovered but not quantified.*

Similar treatment of (-)-**20** (1.50 g, 2.13 mmol, 1.0 equiv) with $PdCl_2$ (0.151 g, 0.85 mmol, 0.4 equiv) and CuCl (0.106 g, 1.07 mmol, 0.5 equiv) in DMF (50 mL)/water (2.5 mL) was carried out in triplicate. After 74 hours, the three reactions were combined and purified as described for the racemate above. Compound (-)-**21** was obtained (4.30 g, 5.96 mmol, 93%) {$[\alpha]_D^{25}$ -434 (*c* 0.095, CH_2Cl_2)} along with recovered (-)-**20** (98 mg, 0.14 mmol, 6 %).

TLC: R_f = 0.49 (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2926 (s), 1965 (s), 1880 (s), 1710 (s), 1668 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (br s, 0.9 H), 8.29 (br s, 0.1 H), 7.79 (d, *J* = 1.8 Hz, 0.9 H), 7.77 (br s, 0.1 H), 7.57-7.64 (m, 1.2 H), 7.45-7.54 (m, 4.4 H), 7.35-7.42 (m, 3.4 H), 7.21 (d, *J* = 5.4 Hz, 1 H), 6.27 (t, *J* = 2.4 Hz, 1 H), 6.19 (br s, 1 H), 5.84 (br s, 1 H), 5.28-5.30 (m, 0.4 H), 5.18 (AB quartet, *J* = 11.4 Hz, 1.6 H), 4.63 (d, *J* = 4.8 Hz, 1 H), 4.03-4.07 (br s, 0.2 H), 3.96 (t, *J* = 6.0 Hz, 0.8 H), 3.65 (d, *J* = 16.2 Hz, 1 H), 3.11 (d, *J* = 16.2 Hz, 0.8 H), 2.92 (d, *J* = 14.4 Hz, 0.2 H), 2.30 (dt, *J* = 13.8 Hz, 4.2 Hz, 1 H), 2.13 (s, 2.4 H), 1.99 (s, 0.6 H), 1.65 (dt, *J* = 12.6 Hz, 4.2 Hz, 1.2 H), 1.44-1.60 (m, 0.8 H), 1.16-1.36 (m, 4.6 H), 0.96-1.06 (br s, 0.4 H), 0.80-0.90 (t + br s, *J* = 7.2 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 225.1, 224.1, 206.3, 201.4, 153.4, 146.9, 142.6, 141.2, 136.3, 136.2, 135.3, 134.5, 128.9, 128.6 (3), 128.4, 106.0, 105.6, 105.5, 90.5, 68.5, 65.1, 62.9, 62.0, 49.1, 35.8, 31.9, 31.0, 24.4, 22.4, 13.9. HRMS (ESI) Calcd for: $C_{32}H_{37}BMoN_7O_6$ ($[M+H]^+$): 724.1947. Found: 724.1939.

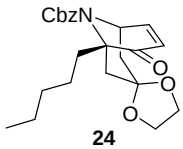


(-)- and (±)-(1*S*,5*R*)-9-Benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-one, (-)-23 and (±)-23. Molybdenum complex (±)-**21** (0.350 g, 0.50 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10 mL) and $KOSiMe_3$ (0.191 g, 1.49 mmol, 3.0 equiv) was added in one portion. The reaction mixture was stirred for 35 minutes, during which time it turned from dull orange to bright red. The mixture was passed through a pad of silica gel and concentrated. The red residue was dissolved in DME (10 mL) and cooled to 0 ^oC before $NOPF_6$ (91.1 mg, 0.50 mmol, 1.0 equiv) was added in one portion causing the solution to bubble and darken to black. After 25 minutes, the crude reaction mixture was passed through a pad of silica gel and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)-**23** (0.142 g, 0.40 mmol, 80%, 97.7% ee) as a clear, light yellow oil.

Similar treatment of (-)-**21** (4.14 g, 5.87 mmol, 1.0 equiv) with $KOSiMe_3$ (2.26 g, 17.6 mmol, 3.0 equiv) in CH_2Cl_2 (60 mL) and then $NOPF_6$ (1.07 g, 5.87 mmol, 1.0 equiv) in DMF (60 mL) afforded (-)-**23** (1.46 g, 4.12 mmol, 70%) {$[\alpha]_D^{25}$ -110 (*c* 0.67, CH_2Cl_2)}.

TLC: R_f = 0.30, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2957 (m), 1718 (s), 1687 (s), 1640 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.38 (m, 5 H), 7.01 (dd, *J* = 10.4 Hz, 6.0 Hz, 1 H), 6.12 (d, *J* = 10.0 Hz, 1 H), 5.44 (t, *J* = 6.0 Hz, 1 H), 5.19 (dd, *J* = 12.0 Hz, 9.2 Hz, 2 H), 2.68 (d, *J* = 15.6 Hz, 1 H), 2.62 (dd, *J* = 15.2 Hz, 6.8 Hz, 1 H), 2.26-2.50 (m, 4 H), 1.26-1.38 (m, 1 H), 1.12-1.25 (m, 4 H), 1.00-1.11 (m, 1 H), 0.83 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.3, 195.7, 155.2, 148.3, 135.7, 128.9 (2), 128.8, 128.6 (2), 128.0, 70.9, 68.3, 51.9, 51.3, 43.1, 35.4,

32.0, 24.1, 22.6, 14.1. HRMS (ESI) Calcd for $C_{21}H_{26}NO_4$ ([M+H]$^+$): 356.1856. Found: 356.1865. HPLC: Daicel® Chiralcel OJ-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1% TFA) 0-20 mins (20% to 50%), 20-30 mins (50%-85%), 1.5 mL/min, λ = 254 nm, (1*S*,5*R*)-(-)-**2**: $t_{(1S,5R)}$ = 23.50 min; (1*R*,5*S*)-(+)-**2**: $t_{(1R,5S)}$ = 25.27 min.

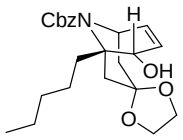


24

(-)- and (±)-(1*S*,5*R*)-9-Benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-one, (-)-24 and (±)-24. Ketone (±)-**23** (0.638 g, 1.80 mmol, 1.0 equiv, 97.7% ee) was dissolved in $CHCl_3$ (15 mL) before 2-ethyl-2-methyl-1,3-dioxolane (1.35 mL, 10.8 mmol, 6.0 equiv), ethylene glycol (20 µL, 0.36 mmol, 0.2 equiv), and BF_3•OEt_2 (0.25 mL, 1.98 mmol, 1.1 equiv) were added sequentially. The flask was sealed and the reaction stirred overnight at room temperature. After 12.5 hours, the solution was poured into a separatory funnel containing water (15 mL), and the flask was rinsed with CH_2Cl_2 (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded (±)-**24** (0.601 g, 1.50 mmol, 84%) as a white solid (mp 104-106 ^oC).

Similar treatment of (-)-**23** (1.44 g, 4.07 mmol, 1.0 equiv) with 2-ethyl-2-methyl-1,3-dioxolane (3.05 mL, 24.4 mmol, 6.0 equiv), ethylene glycol (46 µL, 0.81 mmol, 0.2 equiv), and BF_3•OEt_2 (0.57 mL, 4.48 mmol, 1.1 equiv) in $CHCl_3$ (30 mL) afforded (-)-**24** (1.38 g, 3.46 mmol, 85%) {$[\alpha]_D^{25}$ -116 (*c* 1.33, CH_2Cl_2)}.

TLC: R_f = 0.25, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1718 (s), 1687 (s), 1455 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26-7.39 (m, 5 H), 7.01 (dd, *J* = 9.6 Hz, 6.6 Hz, 1 H), 6.18 (d, *J* = 10.2 Hz, 1 H), 5.22 (t, *J* = 6.6 Hz, 1 H), 5.13 (AB quart, *J* = 12.6 Hz, 2 H), 3.86-3.88 (m, 1 H), 3.76-3.83 (m, 3 H), 2.43 (dt, *J* = 12.6 Hz, 3.6 Hz, 1 H), 2.19 (dt, *J* = 12.0 Hz, 4.2 Hz, 1 H), 2.03 (dd, *J* = 14.4 Hz, 7.2 Hz, 1 H), 1.90-1.95 (m, 2 H), 1.78 (d, *J* = 13.8 Hz, 1 H), 1.25-1.32 (m, 1 H), 1.08-1.23 (m, 4 H), 0.96-1.03 (m, 1 H), 0.81 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 154.7, 147.8, 136.0, 129.4, 128.6 (2), 128.3 (3), 106.3, 69.6, 67.6, 64.9, 63.3, 50.2, 45.0, 36.3, 36.1, 32.0, 23.8, 22.5, 14.0. HRMS (ESI) Calcd for $C_{23}H_{30}NO_5$ ([M+H]$^+$): 400.2119. Found: 400.2116.

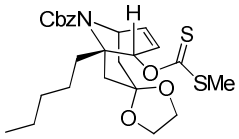


(-)- and (±)-(1*S*,2*S*,5*R*)-9-Benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-ol. Enone (±)-**24** (0.521 g, 1.30 mmol, 1.0 equiv) was dissolved in THF (10 mL) and MeOH (20 mL), and $CeCl_3$•$7H_2O$ (1.02 g, 2.74 mmol, 2.1 equiv) was added. The solution was stirred at room temperature for 30 minutes before it was cooled to 0 ^oC and $NaBH_4$ (0.098 g, 2.60 mmol, 2.0 equiv) was added in one portion. After 45 minutes at 0 ^oC, the solution was transferred to a separatory funnel containing water (20 mL) and CH_2Cl_2 (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded a single diastereomer of the equatorial allylic alcohol (0.493 g, 1.23 mmol, 94%) as a clear, colorless oil.

Similar treatment of (-)-**24** (1.30 g, 3.26 mmol, 1.0 equiv) with $CeCl_3$•$7H_2O$ (2.55 g, 6.85 mmol, 2.1 equiv) and $NaBH_4$ (0.247 g, 6.52 mmol, 2.0 equiv) in THF (20 mL)/MeOH (40 mL) afforded the expected equatorial allylic alcohol (1.28 g, 3.19 mmol, 98%) {$[\alpha]_D^{25}$ -8.8 (*c* 1.05, CH_2Cl_2)}.

TLC: R_f = 0.19, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3489 (br), 2957 (m), 1710 (s), 1455 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.37 (m, 5 H), 5.87 (dd, *J* = 9.6 Hz, 5.2 Hz, 1 H), 5.71 (dd, *J* = 9.6, 2.8 Hz, 1 H), 5.08 (s, 2 H), 4.88 (t, *J* = 4.8 Hz, 1 H), 4.29 (d, *J* = 11.2, 1 H), 3.97-4.02 (m, 1 H), 3.85-3.93 (m, 3 H), 2.63 (d, *J* = 11.2 Hz, 1 H), 2.20-

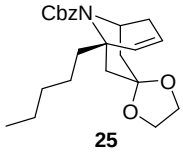
2.27 (m, 1 H), 2.07 (dd, *J* = 14.4 Hz, 2.4 Hz, 1 H), 1.91-2.00 (m, 3 H), 1.78 (d, *J* = 14.0 Hz, 1 H), 1.28-1.37 (m, 2 H), 1.16-1.28 (m, 4 H), 0.84 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 136.6, 130.3, 129.9, 128.7 (2), 128.3 (3), 107.8, 72.4, 67.4, 65.1, 63.5, 62.1, 50.8, 40.8, 40.0, 38.3, 32.4, 23.9, 22.9, 14.3. HRMS (ESI) Calcd for $C_{23}H_{32}NO_5$ ([M+H]$^+$): 402.2275. Found: 402.2272.



(+)- and (±)-(1*S*,2*S*,5*R*)-9-benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-2-methylthiocarbonothioyloxy-1-pentyl-9-azabicyclo[3.3.1]non-3-ene. A solution of equatorial allylic alcohol (0.454 g, 1.13 mmol, 1.0 equiv) in THF (2 mL) was added dropwise to a suspension of NaH (60 wt % dispersion in mineral oil, 0.453 g, 11.3 mmol, 10.0 equiv) in THF (15 mL) at –78 °C. The solution was warmed to 0 °C over 30 minutes, CS_2 (1.36 mL, 22.6 mmol, 20.0 equiv) and imidazole (0.038 g, 0.57 mmol, 0.5 equiv) were added, and the solution was warmed to room temperature. After 15 minutes, the solution was heated to reflux. After 45 minutes, MeI (1.41 mL, 22.6 mmol, 20.0 equiv) was added. The solution was refluxed for an additional 30 minutes, cooled to room temperature, and then poured into a separatory funnel containing CH_2Cl_2 (20 mL) and water (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash chromatography over silica gel with hexanes-EtOAc (4:1) afforded the corresponding xanthate (0.490 g, 0.99 mmol, 88%) as a clear, yellow oil.

Similar treatment of chiral, non-racemic equatorial allylic alcohol (0.754 g, 1.88 mmol, 1.0 equiv) with NaH (0.752 g, 18.8 mmol, 10.0 equiv), CS_2 (2.27 mL, 37.6 mmol, 20.0 equiv), imidazole (0.064 g, 0.94 mmol, 0.5 equiv), and MeI (2.34 mL, 37.6 mmol, 20.0 equiv) afforded the expected xanthate (0.835 g, 1.70 mmol, 90%) {$[\alpha]_D^{25}$ +40.5 (*c* 1.07, CH_2Cl_2)}.

TLC: R_f = 0.55, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2957 (m), 1710 (s), 1455 (m), 1393 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.39 (m, 5 H), 6.45 (d, *J* = 1.2 Hz, 1 H), 5.91 (ddd, *J* = 10.0 Hz, 4.8 Hz, 1.6 Hz, 1 H), 5.75 (dd, *J* = 10.0 Hz, 1.2 Hz, 1 H), 5.07-5.14 (m, 2 H), 4.97 (br s, 1 H), 3.95-4.04 (m, 2 H), 3.87-3.92 (m, 1 H), 3.80-3.85 (m, 1 H), 2.57 (s, 3 H), 2.14-2.28 (m, 3 H), 1.95 (d, *J* = 16.0 Hz, 1 H), 1.86 (d, *J* = 14.0 Hz, 1 H), 1.62-1.69 (m, 1 H), 1.29-1.37 (m, 2 H), 1.19-1.25 (m, 2 H), 1.08-1.17 (m, 2 H), 0.82 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.4, 155.8, 136.4, 132.8, 128.7 (2), 128.3 (3), 124.5, 107.2, 81.8, 67.6, 64.6, 63.4, 59.9, 51.4, 39.7, 39.2, 38.4, 32.3, 23.5, 22.9, 19.2, 14.2. HRMS (ESI) Calcd for $C_{25}H_{34}NO_5S_2$ ([M+H]$^+$): 492.1872. Found: 492.1867.



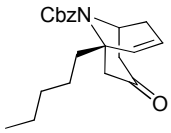
25

(+)- and (±)-(1*S*,5*R*)-9-benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-2-ene, (+)-25 and (±)-25. The xanthate (0.471 g, 0.96 mmol, 1.0 equiv) was dissolved in benzene (10 mL). AIBN (0.016 g, 0.10 mmol, 0.1 equiv) and Bu_3SnH (760 µL, 2.88 mmol, 3.0 equiv) were added sequentially and the solution was refluxed for 6 hours. The solution was concentrated and subjected to flash chromatography over silica gel with hexanes-EtOAc (4:1). Product fractions were collected and concentrated. The residue was passed through a short pad of silica gel impregnated with 10 % of powdered KF using hexanes-EtOAc (4:1), affording (±)-**25** (0.309 g, 0.80 mmol, 83%) as a clear, colorless oil.

Similar treatment of chiral, non-racemic xanthate (0.835 g, 1.70 mmol, 1.0 equiv) with AIBN (0.028 g, 0.17 mmol, 0.10 mmol) and Bu_3SnH (1.35 mL, 5.10 mmol, 3.0 equiv) in benzene (11 mL) afforded (+)-**25** (0.528 g, 1.37 mmol, 81%) {$[\alpha]_D^{25}$ +17.8 (*c* 0.98, CH_2Cl_2)}.

TLC: R_f = 0.52, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2953 (m), 1710 (s), 1455 (m), 1397 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.37 (m, 5 H), 5.75 (ddd, *J* = 10.0 Hz, 5.2 Hz, 1.6 Hz, 1 H), 5.32 (dt, *J* = 10.0 Hz, 1.6 Hz, 1 H), 5.14 (d, *J* = 12.4 Hz, 1 H), 5.07 (d, *J* = 12.4 Hz, 1 H), 4.80-4.83 (m, 1 H), 3.86-3.95 (m, 2 H), 3.76-3.84 (m, 2 H), 2.51-

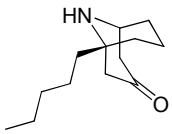
2.67 (m, 2 H), 2.05 (d, *J* = 13.6 Hz, 1 H), 1.91-1.99 (m, 2 H), 1.66-1.73 (m, 2 H), 1.12-1.33 (m, 7 H), 0.84 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 137.0, 134.8, 128.6 (2), 128.3 (2), 128.1, 124.1, 108.3, 67.1, 64.8, 63.3, 58.2, 48.1, 44.4, 41.2, 39.1, 32.3, 30.9, 23.5, 22.8, 14.3. HRMS (ESI) Calcd for $C_{23}H_{32}NO_4$ ($[M+H]^+$): 386.2325. Found: 386.2321.



(+)- and (±)-(1*S*,5*R*)-9-benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]non-2-ene. Ketal (±)-**25** (0.291 g, 0.75 mmol, 1.0 equiv) was dissolved in acetone (20 mL) and $Pd(MeCN)_2Cl_2$ (0.016 g, 0.06 mmol, 8 mol %) was added. The solution was stirred for 14 hours and then concentrated. Flash chromatography over silica gel with hexanes-EtOAc afforded the expected ketone (0.244 g, 0.71 mmol, 95%) as a clear, colorless oil.

Similar treatment of (+)-**25** (0.500 g, 1.30 mmol, 1.0 equiv) with $Pd(MeCN)_2Cl_2$ (0.027 g, 0.10 mmol, 8 mol %) in acetone (30 mL) afforded the expected ketone (0.394 g, 1.15 mmol, 89%, 97.6% ee) {$[\alpha]_D^{25}$ +8.3 (*c* 0.84, CH_2Cl_2)}.

TLC: R_f = 0.55, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1710 (s), 1455 (w), 1390 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.37 (m, 5 H), 5.76-5.80 (m, 1 H), 5.11-5.26 (m, 3 H), 5.06 (t, *J* = 6.8 Hz, 1 H), 2.78-2.86 (m, 1 H), 2.70 (d, *J* = 14.8 Hz, 1 H), 2.57-2.63 (m, 1 H), 2.47 (dd, *J* = 16.4 Hz, 8.4 Hz, 1 H), 2.14-2.24 (m, 2 H), 1.93 (dd, *J* = 18.4 Hz, 6.0 Hz, 1 H), 1.13-1.32 (m, 7 H), 0.84 (t, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 155.7, 136.4, 134.3, 128.8 (2), 128.5, 128.4 (2), 124.0, 67.6, 60.0, 50.5, 49.4, 46.4, 39.8, 32.1, 31.0, 23.5, 22.8, 14.2. HRMS (ESI) Calcd for $C_{21}H_{28}NO_3$ ($[M+H]^+$): 342.2063. Found: 342.2063. HPLC: Daicel® Chiralpak AS-RH column, Gradient solvent system was used (% CH_3CN in H_2O with 0.1 % TFA) 0-20 mins (20% to 50%), 20-30 mins (50%-85%), 1.5 mL/min, λ = 254 nm, (+)-(1*S*,5*R*): $t_{(1S,5R)}$ = 27.11 min; (-)-(1*R*,5*S*): $t_{(1R,5S)}$ = 25.96 min.



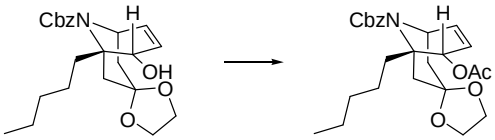
(-)- and (±)-(1*S*,5*R*)-1-pentyl-9-azabicyclo[3.3.1]nonan-3-one, (-)-Adaline and (±)-Adaline. The above described ketone (0.025 g, 0.07 mmol, 1.0 equiv) was dissolved in MeOH (2 mL) and $Pd(OH)_2/C$ (0.008 mg, 0.01 mmol, 0.15 equiv) was added. The mixture was stirred under an atmosphere of hydrogen for 11 hours before it was filtered on cotton and concentrated. The residue was dissolved in Et_2O (10 mL) and washed successively with water (2 x 10 mL), a 20 % aqueous solution of NaOH and brine (2 x 5 mL). The solution was dried over $MgSO_4$, filtered and concentrated to afford (±)-adaline (0.012 g, 0.06 mmol, 77%) as a clear, colorless oil.

Similar treatment of chiral, non-racemic ketone (0.332 g, 0.97 mmol, 1.0 equiv) with $Pd(OH)_2/C$ (0.102 g, 0.15 mmol, 0.15 equiv) in MeOH (20 mL) was carried out. In this case, the mixture was stirred under an atmosphere of hydrogen for 13 hours before it was passed through a plug of Celite with Et_2O (30 mL). The solution was washed successively with 20 % aqueous NaOH saturated with NaCl (2 x 50 mL) and H_2O (4 x 50 mL), dried over $MgSO_4$, filtered and concentrated to afford (-)-adaline (0.183 g, 0.87 mmol, 90%) {$[\alpha]_D^{25}$ -13.0 (*c* 0.73, $CHCl_3$)}, [Lit.[3] $[\alpha]_D$ = -13 ($CHCl_3$)].

<u>(±)-Adaline</u>: TLC: R_f = 0.17, ($CHCl_3$-MeOH = 15:1). IR (cm^{-1}): 3304 (br w), 2930 (s), 1706 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.68-3.69 (m, 1 H), 2.53 (dd, *J* = 16.8 Hz, 6.8 Hz, 1 H), 2.39 (d, *J* = 16.4 Hz, 2 H), 2.19 (d, *J* = 16.8 Hz, 1 H), 1.25-1.75 (m, 15 H), 0.89 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 54.7, 51.8, 49.8, 46.8, 44.9, 36.8, 32.5, 31.8, 22.7, 22.4, 18.0, 14.2. HRMS (ESI) Calcd for $C_{13}H_{24}NO$ ($[M+H]^+$): 210.1852. Found: 210.1850.

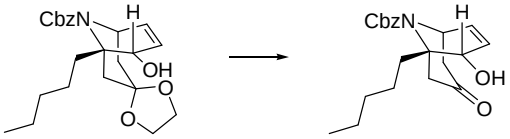
[3] Tursch, B.; Braekman, J. C.; Daloze, D.; Hootele, C.; Losman, D.; Karlsson, R.; Pasteels, J. M. *Tetrahedron Lett.* **1973**, *3*, 201-202. *Neither concentration nor temperature was provided for the optical rotation value.*

- *Stereochemical outcome of the reduction (footnote 14)*



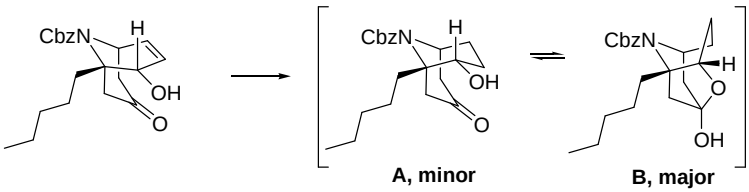
(±)-(1*S*,2*S*,5*R*)-2-Acetoxy-9-benzyloxycarbonyl-7-(1,1-dioxacyclopentyl)-1-pentyl-9-azabicyclo[3.3.1]non-3-ene. Under argon, allylic alcohol (0.034 g, 0.09 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (4 mL) and Et_3N (24 µL, 0.17 mmol, 2.0 equiv), Ac_2O (16 µL, 0.17 mmol, 2.0 equiv), and a crystal of DMAP were added sequentially. After 12.5 hours at room temperature, the solution was concentrated and subjected to flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford the expected allylic acetate (0.028 g, 0.06 mmol, 74%) as a clear, colorless oil.

TLC: R_f = 0.29, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 2930 (m), 1741 (s), 1710 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.36 (m, 5 H), 5.82-5.87 (m, 1 H), 5.59-5.61 (m, 2 H), 5.09 (dd, *J* = 19.6 Hz, 12.0 Hz, 2 H), 4.93 (br s, 1 H), 3.96 (t, *J* = 6.4 Hz, 2 H), 3.79-3.91 (m, 2 H), 2.10-2.27 (m, 3 H), 2.08 (s, 3 H), 1.89 (d, *J* = 14.8 Hz, 1 H), 1.84 (dt, *J* = 14.0, 2.4 Hz, 1 H), 1.53-1.61 (m, 1 H), 1.25-1.38 (m, 2 H), 1.17-1.24 (m, 2 H), 1.12 (hex, *J* = 7.6 Hz, 2 H), 0.83 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 155.8, 136.4, 132.0, 128.7 (2), 128.3 (3), 125.8, 107.3, 73.3, 67.5, 64.5, 63.4, 59.5, 51.2, 39.1, 39.0, 38.5, 32.4, 23.4, 22.9, 21.4, 14.3. HRMS (ESI) Calcd for $C_{25}H_{34}NO_6$ ($[M+H]^+$): 444.2381. Found: 444.2384.



(±)-(1*S*,2*S*,5*R*)-9-Benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]non-3-en-2-ol. Ketal (0.493 g, 1.23 mmol, 1.0 equiv) was dissolved in acetone (50 mL) and $Pd(MeCN)_2Cl_2$ (0.025 mg, 0.10 mmol, 8 mol %) was added. The flask was sealed and the solution stirred at room temperature. After 20.5 hours, the solution was concentrated and subjected to flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford the expected ketone (0.422 g, 1.18 mmol, 96%) as a clear, colorless oil.

TLC: R_f = 0.27, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3443 (br), 2930 (m), 1706 (s), 1455 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34-7.38 (m, 5 H), 5.73 (ddd, *J* = 10.2 Hz, 4.2 Hz, 1.8 Hz, 1 H), 5.67 (dd, *J* = 11.4 Hz, 1.2 Hz, 1 H), 5.17 (br s, 1 H), 5.14 (dd, *J* = 18.6 Hz, 12.6 Hz, 2 H), 4.50 (d, *J* = 4.8 Hz, 1 H), 2.71-2.75 (m, 2 H), 2.33-2.41 (m, 3 H), 1.88 (d, *J* = 6.0 Hz, 1 H), 1.70-1.75 (m, 1 H), 1.18-1.41 (m, 6 H), 0.86 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.5, 155.7, 136.2, 130.4, 129.7, 128.8 (2), 128.5, 128.3 (2), 70.8, 67.8, 63.1, 52.4, 44.8, 44.2, 37.4, 32.2, 23.4, 22.8, 14.3. HRMS (ESI) Calcd for $C_{21}H_{28}NO_4$ ($[M+H]^+$): 358.2013. Found: 358.2015.



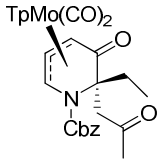
(±)-(1*S*,2*S*,5*R*)-9-Benzyloxycarbonyl-7-oxo-1-pentyl-9-azabicyclo[3.3.1]nonan-2-ol, (±)-A and (±)-B. Allylic alcohol (0.097 g, 0.27 mmol, 1.0 equiv) was dissolved in MeOH (5 mL) and PtO_2 (0.006 g, 0.03 mmol, 10 mol %) was added to the solution. The reaction mixture was stirred for 9.5 hours under an atmosphere of hydrogen before it was concentrated under reduced pressure. Flash chromatography over silica gel with hexanes-EtOAc (2:1) afforded (±)-**A**/(±)-**B** (0.085 g, 0.24 mmol, 88%), a 1.0:4.0-4.5 equilibrium mixture of isomers at room temperature (20 °C) in $CDCl_3$, as a clear, colorless oil. *A similar equilibrium involving intramolecular hemiketal formation from a bicyclic keto-alcohol has been reported by Speckamp and co-workers.*[4]

[4] Bok, T. R.; Kruk, C.; Speckamp, W. N. *Tetrahedron Lett.* **1978**, *7*, 657-660.

(±)-**A/B**: TLC: R_f = 0.20, (hexanes-EtOAc = 2:1). IR (cm^{-1}): 3374 (br), 2934 (m), 1702 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.37 (m, 5 H), 5.14 (d, *J* = 12.0 Hz, 1 H), 5.05 (d, *J* = 12.4 Hz, 1 H), 4.87 (br s, 0.2 H), 4.72 (t, *J* = 6.8 Hz, 0.8 H), 4.27 (br s, 0.8 H), 4.13 (d, *J* = 4.0 Hz, 0.8 H), 3.74 (br d, *J* = 9.2 Hz, 0.2 H), 2.51-2.70 (m, 1.6 H), 2.27-2.38 (m, 0.6 H), 2.09-2.19 (m, 1 H), 1.81-2.00 (m, 4 H), 1.54-1.73 (m, 3 H), 1.04-1.44 (m, 6 H), 0.81-0.86 (m, 3 H). *Note: Carbon peaks from the minor compound (±)-**A** are shown in parentheses* ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 155.8, 136.6, (136.3), (128.7), 128.6 (3), (128.4), (128.3), 128.2, 128.1, 104.5, 81.5, (71.3), (67.6), 67.4, 67.2, (64.3), (51.3), 48.9, 47.7, (44.9), (44.7), 44.3, (37.3), (36.0), 32.3, (32.2), (29.5), (27.2), 24.8, 24.2, (23.5), 23.1, (22.9), 22.7, 14.2. HRMS (ESI) Calcd for $C_{21}H_{30}NO_4$ ($[M+H]^+$): 360.2169. Found: 360.2166.

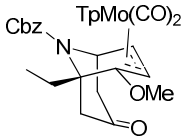
5. Characterization of the 1,5-"Michael-like" Intermediate (X = NCbz, R^1 = Me)

- *Model study*



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2*S*,6*S*)-(*η*-2,3,4)-1-(benzyloxycarbonyl)-6-ethyl-5-oxo-6-(2-oxopropyl)-5,6-dihydro-2*H*-pyridin-2-yl]molybdenum. Terminal alkene (±)-**19** (0.194 g, 0.29 mmol, 1.0 equiv) was completely dissolved in DMF (5 mL), and to this solution was added $PdCl_2$ (0.021 g, 0.12 mmol, 0.4 equiv), CuCl (0.014 g, 0.15 mmol, 0.5 equiv) and water (0.5 mL). The mixture was stirred open to air for 24 hours and then poured into a separatory funnel containing CH_2Cl_2 (10 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were washed with water (3 x 10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford the expected methyl ketone (0.168 g, 0.25 mmol, 85%) and the recovered starting material (±)-**19** (0.015 g, 8%).

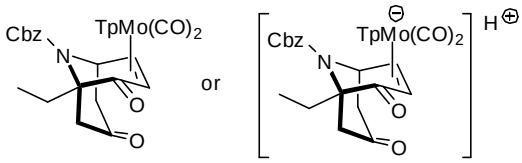
TLC: R_f = 0.49 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3127 (w), 2968 (w), 2486 (m), 1961 (s), 1876 (s), 1702 (s), 1664 (s), 1505 (m), 1409 (m), 1301 (s), 1254 (s), 1220 (s), 1127 (m), 1054 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.9 Hz, 1 H), 7.81 (d, *J* = 2.2 Hz, 1 H), 7.59 (d, *J* = 1.9 Hz, 1 H), 7.53 (br s, 2 H), 7.47-7.49 (m, 3 H), 7.39-7.41 (m, 3 H), 7.22-7.23 (m, 1 H), 6.29 (t, *J* = 2.2 Hz, 1 H), 6.21 (t, *J* = 1.9 Hz, 1 H), 5.87 (br s, 1 H), 5.18-5.19 (m, 2 H), 4.65 (d, *J* = 4.4 Hz, 1 H), 3.98 (d, *J* = 4.0 Hz, 1 H), 3.61 (d, *J* = 15.9 Hz, 1 H), 3.12 (d, *J* = 16.2 Hz, 1 H), 2.41 (qd, *J* = 14.0 Hz, 7.6 Hz, 1 H), 2.16 (s, 3 H), 1.79 (qd, *J* = 14.0 Hz, 7.3 Hz, 1 H), 1.26-1.31 (m, 2 H), 0.93 (t, *J* = 7.0 Hz, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 225.2, 224.4, 206.6, 201.4, 153.8, 147.2, 143.0, 141.6, 136.6, 136.5, 135.6, 134.8, 129.2, 128.9 (3), 128.7, 106.3, 105.9, 105.8, 90.8, 68.8, 65.7, 63.2, 62.4, 49.2, 31.4, 29.2, 9.97. HRMS (ESI) Calcd for $C_{29}H_{31}BMoN_7O_6$ ($[M+H]^+$): 682.1499. Found: 682.1499.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*S*,2*S*,5*R*)-(*η*^{3}-2,3,4)-9-benzyloxycarbonyl-1-ethyl-2-methoxy-7-oxo-9-azabicyclo[3.3.1]non-3-en-2-yl]molybdenum. To a solution of the methyl ketone (0.270 g, 0.40 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was added $KOSiMe_3$ (0.153 g, 1.19 mmol, 3.0 equiv). The reaction mixture was stirred at room temperature for 10 min and Me_3OBF_4 (0.158 g, 1.11 mmol, 2.8 equiv) was added. The reaction mixture was stirred at room temperature overnight and then passed through a short pad of silica gel. The solvents were completely removed on a rotary evaporator, and the residue was further purified by flash chromatography over silica gel with hexanes-EtOAc (4:1) to afford the expected compound (0.245 g, 0.35 mmol, 89%) as an orange solid.

TLC: R_f = 0.45 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3127 (w), 2926 (m), 2482 (w), 1930 (s), 1837 (s), 1710 (s), 1505 (m), 1409 (s), 1305 (s), 1220 (s), 1119 (s), 1073 (s), 1050 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35 (d, *J* = 1.9 Hz, 1

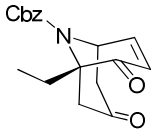
H), 7.81 (d, *J* = 1.4 Hz, 1 H), 7.64 (d, *J* = 2.4 Hz, 1 H), 7.60 (d, *J* = 21.9 Hz, 1 H), 7.50 (d, *J* = 2.4 Hz, 1 H), 7.46 (d, *J* = 1.4 Hz, 1 H), 7.43 (d, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 7.1 Hz, 1 H), 6.24 (t, *J* = 1.9 Hz, 1 H), 6.21 (t, *J* = 1.9 Hz, 1 H), 6.20 (t, *J* = 1.9 Hz, 1 H), 5.21 (AB quartet, *J* = 12.4 Hz, 2 H), 5.02-5.04 (m, 1 H), 3.95 (dd, *J* = 8.1 Hz, 2.8 Hz, 1 H), 3.55 (d, *J* = 8.1 Hz, 1 H), 2.95 (qd, *J* = 15.2 Hz, 7.6 Hz, 1 H), 2.89 (d, *J* = 14.8 Hz, 1 H), 2.82 (s, 3 H), 2.59-2.67 (m, 4 H), 1.11 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 230.0, 227.9, 208.9, 154.7, 146.3, 145.1, 142.8, 139.5, 136.54, 136.51, 135.9, 134.8, 128.6 (2), 128.27 (2), 128.22, 105.9, 105.78, 105.76, 67.7, 65.7, 57.8, 57.4, 55.5, 53.8, 50.5, 49.2, 25.4, 11.5. HRMS (ESI) Calcd for $C_{30}H_{32}BMoN_7O_6$ ([M]$^+$): 695.1561. Found: 695.1589.



(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(1*S*,3*S*,5*R*)-(η^2-3,4)-9-benzyloxycarbonyl-2,7-dioxo-1-ethyl-9-azabicyclo[3.3.1]non-3-ene]molybdenum. To a solution of the methoxy allyl molybdenum complex (0.050 g, 0.074 mmol) in CH_2Cl_2 (8 mL) was added $KOSiMe_3$ (0.028 g, 0.22 mmol, 3 equiv). The reaction mixture was stirred at room temperature for 10 min and then directly poured onto a short pad of silica gel and eluted with hexanes-EtOAc (1:1) to afford complex **26**.

*The ^{1}H NMR showed broad undefined peaks and is not reported here. Recrystallization from benzene produced single crystals suitable for X-ray diffraction analysis. The molecular structure of complex **26** was confirmed by X-ray diffraction analysis; details are provided on Page SI-23. The isolation of complex **26** strongly confirmed the possible formation of intermediate **22** via 1,5-"Michael-like" reaction. Insufficient evidence is available to differentiate between is a 17-electron Mo radical or an 18-electron Mo complex for **26** (the latter either a molybdenum hydride complex or a molybdenum allyl complex containing a hydroxyl group).*

TLC: R_f = 0.42 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 3123 (w), 2964 (m), 2941 (m), 2490 (m), 1976 (s), 1891 (s), 1714 (s), 1652 (s), 1505 (m), 1409 (s), 1305 (s), 1282 (s), 1212 (s), 1119 (s), 1073 (s), 1054 (s).



(±)-(1*S*,5*R*)-9-Benzyloxycarbonyl-1-ethyl-7-oxo-9-azabicyclo[3.3.1]non-3-en-2-one. To an orange solution of the above described molybdenum complex (0.259 g, 0.37 mmol, 1.0 equiv) and Et_3N (78.2 μL, 0.56 mmol, 1.5 equiv) in a 3:2 mixture of THF/water (25 mL) at 0 °C open to air was added dropwise over 5 min, a solution of cerium ammonium nitrate CAN (1.64 g, 2.99 mmol, 8.0 equiv) in water (5 mL). After complete addition, the solution had faded to a light yellow color. The reaction mixture was warmed to room temperature and stirred for an additional 10 min, before it was partitioned between CH_2Cl_2 (10 mL) and water (10 mL). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash chromatography over silica gel with hexanes-EtOAc (2:1) to afford the expected ketone (0.079 g, 0.25 mmol, 68%) as a colorless oil.

TLC: R_f = 0.50 (hexanes-EtOAc = 1:1). IR (cm^{-1}): 2968 (m), 2941 (m), 2482 (w), 1718 (s), 1687 (s), 1455 (s), 1397 (s), 1297 (s), 1224 (s), 1123 (m), 1069 (s), 1038 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37-7.47 (m, 5 H), 7.02 (dd, *J* = 10.0 Hz, 6.2 Hz, 1 H), 6.15 (d, *J* = 10.0 Hz, 1 H), 5.46 (dt, *J* = 6.2 Hz, 0.9 Hz, 1 H), 5.22 (AB quartet, *J* = 11.9 Hz, 2 H), 2.69 (the left side of AB quartet, *J* = 15.2 Hz, 1 H), 2.69 (doublets of the left side of AB quartet, *J* = 14.8 Hz, 6.7 Hz, 1 H), 2.56 (qd, *J* = 13.8 Hz, 7.1 Hz, 1 H), 2.40-2.44 (m, 2 H), 2.37 (doublets of the right side of AB quartet, *J* = 15.2 Hz, 1.9 Hz, 1 H), 0.87 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 204.3, 195.6, 155.1, 148.4, 135.8, 128.9 (2), 128.8, 128.6 (2), 128.1, 71.3, 68.3, 51.6, 51.4, 43.1, 28.4, 8.9. HRMS (ESI) Calcd for $C_{18}H_{19}NO_4$ ([M]$^+$): 313.1314. Found: 313.1316.

- *X-Ray diffraction study of compound **26** (a direct evidence to intermediate **22**)*

A suitable crystal of **26** was obtained by diffusion recrystallization from benzene. 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_{α} (0.71073Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART[5] software. Frame integration and final cell refinements were done using SAINT[6] software. The final cell parameters were determined from least-squares refinement on 5664 reflections. The SADABS[7] 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 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*[9]. Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V6.12 software.

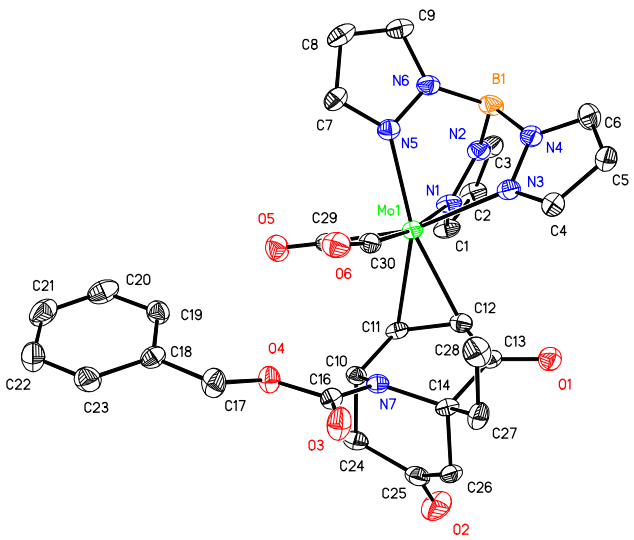


Figure 1. ORTEP View of Compound 26

Table 1. Crystal data and structure refinement for **26**

Identification code	**26**
Empirical formula	C_{29} H_{29} B Mo N_7 O_6
Formula weight	678.34
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal

[5] SMART Version 5.628, **2003**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[6] SAINT Version 6.36A, **2002**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[7] SADABS Version 2.10, **2003**, George Sheldrick, University of Göttingen.
[8] SHELXTL V6.12, **2002**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[9] 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).

Space group	I-4	
Unit cell dimensions	a = 21.1763(14) Å	α= 90°.
	b = 21.1763(14) Å	β= 90°.
	c = 12.8350(10) Å	γ = 90°.
Volume	5755.7(7) $Å^3$	
Z	8	
Density (calculated)	1.566 Mg/m^3	
Absorption coefficient	0.513 mm^{-1}	
F(000)	2776	
Crystal size	0.26 x 0.17 x 0.14 mm^3	
Theta range for data collection	1.86 to 28.36°.	
Index ranges	-28<=h<=28, -28<=k<=28, -17<=l<=17	
Reflections collected	29240	
Independent reflections	6173 [R(int) = 0.0590]	
Completeness to theta = 28.36°	86.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.828000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6173 / 0 / 398	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0801	
R indices (all data)	R1 = 0.0492, wR2 = 0.0814	
Absolute structure parameter	-0.01(3)	
Largest diff. peak and hole	0.555 and -0.542 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **26**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mo(1)	8744(1)	7133(1)	9046(1)	25(1)
B(1)	9394(2)	5901(2)	10239(4)	36(1)
C(1)	7784(2)	5924(2)	9324(4)	37(1)
C(2)	7791(2)	5318(2)	9719(4)	46(1)
C(3)	8376(2)	5227(2)	10085(4)	40(1)
C(4)	9329(2)	7448(2)	11393(3)	35(1)
C(5)	9644(2)	7147(2)	12201(4)	40(1)
C(6)	9699(2)	6538(2)	11910(4)	39(1)
C(7)	9981(2)	6625(2)	7852(4)	34(1)
C(8)	10413(2)	6148(2)	7905(4)	42(1)
C(9)	10275(2)	5820(2)	8785(4)	37(1)
C(10)	7715(2)	8176(2)	8174(3)	26(1)
C(11)	7762(2)	7553(2)	8739(3)	27(1)
C(12)	7885(2)	7553(2)	9830(3)	29(1)
C(13)	7949(2)	8141(2)	10405(3)	28(1)
C(14)	7909(2)	8777(2)	9793(3)	27(1)
C(16)	8338(2)	9137(2)	8103(3)	29(1)
C(17)	8735(2)	9374(2)	6418(4)	40(1)
C(18)	8772(2)	9092(2)	5365(4)	32(1)
C(19)	8763(2)	8453(2)	5199(4)	35(1)
C(20)	8807(2)	8216(2)	4203(4)	45(1)
C(21)	8870(2)	8607(3)	3392(4)	53(2)
C(22)	8886(3)	9244(3)	3533(4)	54(2)
C(23)	8851(2)	9491(2)	4511(4)	41(1)
C(24)	7016(2)	8401(2)	8103(3)	33(1)

C(25)	6761(2)	8621(2)	9151(4)	37(1)
C(26)	7211(2)	8989(2)	9816(3)	33(1)
C(27)	8300(2)	9269(2)	10381(3)	36(1)
C(28)	9010(2)	9173(2)	10403(4)	43(1)
C(29)	8534(2)	7089(2)	7565(3)	30(1)
C(30)	9207(2)	7904(2)	8574(3)	27(1)
N(1)	8343(2)	6194(2)	9464(3)	34(1)
N(2)	8713(2)	5753(2)	9955(3)	34(1)
N(3)	9184(2)	7036(2)	10646(3)	31(1)
N(4)	9415(2)	6467(2)	10965(3)	34(1)
N(5)	9582(2)	6584(2)	8658(3)	30(1)
N(6)	9763(2)	6072(2)	9245(3)	32(1)
N(7)	8089(2)	8667(2)	8688(3)	25(1)
O(1)	7979(2)	8150(2)	11347(2)	36(1)
O(2)	6221(2)	8531(2)	9395(3)	60(1)
O(3)	8531(2)	9646(1)	8377(3)	44(1)
O(4)	8384(1)	8952(1)	7080(2)	33(1)
O(5)	8438(2)	7074(2)	6681(3)	46(1)
O(6)	9502(1)	8296(2)	8182(3)	40(1)

Table 3. Bond lengths [Å] and angles [°] for **26**

Mo(1)-C(29)	1.955(4)	C(16)-O(3)	1.206(5)
Mo(1)-C(30)	1.998(4)	C(16)-N(7)	1.353(5)
Mo(1)-N(5)	2.178(4)	C(16)-O(4)	1.375(5)
Mo(1)-N(1)	2.229(4)	C(17)-O(4)	1.441(5)
Mo(1)-C(12)	2.261(4)	C(17)-C(18)	1.480(6)
Mo(1)-N(3)	2.264(4)	C(18)-C(19)	1.369(6)
Mo(1)-C(11)	2.296(4)	C(18)-C(23)	1.394(7)
B(1)-N(4)	1.519(6)	C(19)-C(20)	1.377(7)
B(1)-N(2)	1.521(7)	C(20)-C(21)	1.336(7)
B(1)-N(6)	1.540(6)	C(21)-C(22)	1.362(8)
C(1)-N(1)	1.327(5)	C(22)-C(23)	1.361(7)
C(1)-C(2)	1.379(6)	C(24)-C(25)	1.523(6)
C(2)-C(3)	1.339(7)	C(25)-O(2)	1.200(5)
C(3)-N(2)	1.332(6)	C(25)-C(26)	1.498(6)
C(4)-N(3)	1.331(5)	C(27)-C(28)	1.516(7)
C(4)-C(5)	1.389(6)	C(29)-O(5)	1.153(5)
C(5)-C(6)	1.349(7)	C(30)-O(6)	1.154(5)
C(6)-N(4)	1.361(6)	N(1)-N(2)	1.372(5)
C(7)-N(5)	1.339(5)	N(3)-N(4)	1.364(4)
C(7)-C(8)	1.364(7)	N(5)-N(6)	1.374(5)
C(8)-C(9)	1.359(6)	C(29)-Mo(1)-C(30)	81.72(17)
C(9)-N(6)	1.345(5)	C(29)-Mo(1)-N(5)	86.40(16)
C(10)-N(7)	1.463(5)	C(30)-Mo(1)-N(5)	88.18(16)
C(10)-C(11)	1.508(6)	C(29)-Mo(1)-N(1)	95.96(16)
C(10)-C(24)	1.558(5)	C(30)-Mo(1)-N(1)	171.63(16)
C(11)-C(12)	1.425(6)	N(5)-Mo(1)-N(1)	83.63(13)
C(12)-C(13)	1.454(6)	C(29)-Mo(1)-C(12)	105.59(16)
C(13)-O(1)	1.211(5)	C(30)-Mo(1)-C(12)	102.01(16)
C(13)-C(14)	1.563(6)	N(5)-Mo(1)-C(12)	165.14(14)
C(14)-N(7)	1.486(5)	N(1)-Mo(1)-C(12)	86.36(15)
C(14)-C(27)	1.529(6)	C(29)-Mo(1)-N(3)	166.26(15)
C(14)-C(26)	1.545(6)	C(30)-Mo(1)-N(3)	98.51(15)

N(5)-Mo(1)-N(3)	79.88(13)	N(7)-C(16)-O(4)	110.4(4)
N(1)-Mo(1)-N(3)	81.81(14)	O(4)-C(17)-C(18)	108.4(4)
C(12)-Mo(1)-N(3)	87.86(14)	C(19)-C(18)-C(23)	118.6(4)
C(29)-Mo(1)-C(11)	69.24(16)	C(19)-C(18)-C(17)	122.7(4)
C(30)-Mo(1)-C(11)	94.30(16)	C(23)-C(18)-C(17)	118.6(4)
N(5)-Mo(1)-C(11)	154.82(14)	C(18)-C(19)-C(20)	120.2(5)
N(1)-Mo(1)-C(11)	92.38(14)	C(21)-C(20)-C(19)	120.3(5)
C(12)-Mo(1)-C(11)	36.42(15)	C(20)-C(21)-C(22)	120.9(5)
N(3)-Mo(1)-C(11)	124.27(13)	C(23)-C(22)-C(21)	120.0(5)
N(4)-B(1)-N(2)	109.7(4)	C(22)-C(23)-C(18)	120.0(5)
N(4)-B(1)-N(6)	107.9(4)	C(25)-C(24)-C(10)	112.3(3)
N(2)-B(1)-N(6)	109.4(4)	O(2)-C(25)-C(26)	122.7(5)
N(1)-C(1)-C(2)	109.9(4)	O(2)-C(25)-C(24)	121.3(4)
C(3)-C(2)-C(1)	105.9(4)	C(26)-C(25)-C(24)	115.9(4)
N(2)-C(3)-C(2)	109.2(4)	C(25)-C(26)-C(14)	116.5(3)
N(3)-C(4)-C(5)	110.4(4)	C(28)-C(27)-C(14)	117.0(4)
C(6)-C(5)-C(4)	105.8(4)	O(5)-C(29)-Mo(1)	176.7(4)
C(5)-C(6)-N(4)	108.3(4)	O(6)-C(30)-Mo(1)	170.1(4)
N(5)-C(7)-C(8)	109.7(4)	C(1)-N(1)-N(2)	106.1(4)
C(9)-C(8)-C(7)	106.0(4)	C(1)-N(1)-Mo(1)	133.8(3)
N(6)-C(9)-C(8)	109.5(4)	N(2)-N(1)-Mo(1)	120.1(3)
N(7)-C(10)-C(11)	111.7(3)	C(3)-N(2)-N(1)	108.8(4)
N(7)-C(10)-C(24)	108.8(3)	C(3)-N(2)-B(1)	130.5(4)
C(11)-C(10)-C(24)	111.0(3)	N(1)-N(2)-B(1)	120.7(4)
C(12)-C(11)-C(10)	119.0(4)	C(4)-N(3)-N(4)	106.3(4)
C(12)-C(11)-Mo(1)	70.4(2)	C(4)-N(3)-Mo(1)	133.5(3)
C(10)-C(11)-Mo(1)	118.7(3)	N(4)-N(3)-Mo(1)	120.0(3)
C(11)-C(12)-C(13)	121.0(4)	C(6)-N(4)-N(3)	109.2(4)
C(11)-C(12)-Mo(1)	73.1(2)	C(6)-N(4)-B(1)	130.3(4)
C(13)-C(12)-Mo(1)	119.2(3)	N(3)-N(4)-B(1)	120.2(4)
O(1)-C(13)-C(12)	121.8(4)	C(7)-N(5)-N(6)	107.3(3)
O(1)-C(13)-C(14)	119.4(4)	C(7)-N(5)-Mo(1)	131.0(3)
C(12)-C(13)-C(14)	118.6(3)	N(6)-N(5)-Mo(1)	121.5(3)
N(7)-C(14)-C(27)	116.1(4)	C(9)-N(6)-N(5)	107.4(4)
N(7)-C(14)-C(26)	108.0(3)	C(9)-N(6)-B(1)	132.7(4)
C(27)-C(14)-C(26)	108.1(3)	N(5)-N(6)-B(1)	119.9(3)
N(7)-C(14)-C(13)	109.3(3)	C(16)-N(7)-C(10)	118.9(3)
C(27)-C(14)-C(13)	108.0(3)	C(16)-N(7)-C(14)	120.9(3)
C(26)-C(14)-C(13)	107.0(3)	C(10)-N(7)-C(14)	113.8(3)
O(3)-C(16)-N(7)	128.9(4)	C(16)-O(4)-C(17)	115.0(3)
O(3)-C(16)-O(4)	120.6(4)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **26**. 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}
Mo(1)	23(1)	23(1)	29(1)	-1(1)	1(1)	1(1)
B(1)	39(3)	25(3)	45(3)	8(2)	1(2)	6(2)
C(1)	26(2)	28(2)	57(3)	-3(2)	8(2)	-2(2)
C(2)	37(3)	36(3)	63(3)	1(2)	12(2)	-10(2)
C(3)	48(3)	27(2)	45(3)	4(2)	13(2)	2(2)
C(4)	37(3)	37(2)	31(2)	-2(2)	2(2)	3(2)

C(5)	40(3)	52(3)	29(2)	-5(2)	0(2)	7(2)
C(6)	44(3)	39(3)	34(3)	8(2)	0(2)	-2(2)
C(7)	29(2)	39(3)	35(2)	-6(2)	7(2)	-4(2)
C(8)	28(2)	48(3)	50(3)	-17(2)	11(2)	-1(2)
C(9)	29(2)	33(2)	51(3)	-9(2)	1(2)	4(2)
C(10)	21(2)	28(2)	28(2)	1(2)	-2(2)	2(2)
C(11)	21(2)	22(2)	37(3)	-3(2)	5(2)	2(2)
C(12)	22(2)	27(2)	38(3)	9(2)	6(2)	0(2)
C(13)	20(2)	32(2)	31(2)	0(2)	5(2)	5(2)
C(14)	23(2)	23(2)	33(2)	-4(2)	3(2)	5(2)
C(16)	28(2)	31(2)	28(2)	1(2)	2(2)	3(2)
C(17)	48(3)	32(3)	40(3)	7(2)	10(2)	-10(2)
C(18)	24(2)	36(3)	36(2)	-5(2)	3(2)	-1(2)
C(19)	32(2)	36(3)	36(3)	7(2)	0(2)	-1(2)
C(20)	30(2)	45(3)	61(4)	-15(3)	4(2)	-2(2)
C(21)	40(3)	83(5)	35(3)	-16(3)	-2(2)	12(3)
C(22)	51(3)	75(4)	37(3)	13(3)	6(2)	9(3)
C(23)	42(3)	31(2)	50(3)	8(2)	6(2)	1(2)
C(24)	25(2)	30(2)	44(3)	3(2)	-4(2)	3(2)
C(25)	28(2)	37(2)	44(3)	8(2)	-2(2)	8(2)
C(26)	37(3)	28(2)	34(2)	1(2)	10(2)	12(2)
C(27)	43(3)	39(3)	25(2)	-7(2)	2(2)	-1(2)
C(28)	47(3)	39(3)	42(3)	-1(2)	-5(2)	-6(2)
C(29)	27(2)	25(2)	36(2)	-4(2)	-1(2)	2(2)
C(30)	26(2)	26(2)	29(2)	2(2)	0(2)	2(2)
N(1)	30(2)	25(2)	48(2)	-2(2)	4(2)	4(2)
N(2)	38(2)	24(2)	40(2)	2(2)	5(2)	5(2)
N(3)	29(2)	30(2)	36(2)	1(2)	4(2)	4(2)
N(4)	39(2)	30(2)	34(2)	3(2)	3(2)	7(1)
N(5)	28(2)	28(2)	34(2)	-3(2)	-1(2)	0(2)
N(6)	30(2)	29(2)	36(2)	-6(2)	-3(2)	4(1)
N(7)	21(2)	23(2)	30(2)	-1(1)	0(1)	0(1)
O(1)	39(2)	35(2)	35(2)	2(1)	4(1)	2(1)
O(2)	26(2)	90(3)	63(3)	-12(2)	7(2)	0(2)
O(3)	69(2)	30(2)	32(2)	-5(1)	6(2)	-12(2)
O(4)	42(2)	30(2)	29(2)	0(1)	0(1)	-7(1)
O(5)	57(2)	47(2)	35(2)	-5(2)	-7(2)	3(2)
O(6)	32(2)	39(2)	50(2)	7(2)	4(2)	-3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **26**

	x	y	z	U(eq)
H(1)	9592	5527	10584	43
H(1A)	7431	6119	9001	44
H(2)	7451	5026	9728	55
H(3)	8528	4847	10390	48
H(4)	9230	7885	11375	42
H(5)	9791	7333	12830	48
H(6)	9901	6213	12297	47
H(7)	9966	6938	7323	41
H(8)	10743	6063	7425	51
H(9)	10504	5466	9038	45
H(10)	7881	8118	7451	31

H(11)	7440	7235	8515	32
H(12)	7630	7230	10213	35
H(17A)	9165	9438	6701	48
H(17B)	8521	9790	6383	48
H(19)	8725	8172	5773	42
H(20)	8793	7773	4091	54
H(21)	8903	8438	2709	63
H(22)	8923	9517	2948	65
H(23)	8880	9934	4611	49
H(24A)	6987	8752	7596	39
H(24B)	6752	8050	7841	39
H(26A)	7061	8968	10546	40
H(26B)	7192	9437	9599	40
H(27A)	8214	9687	10068	43
H(27B)	8147	9282	11110	43
H(28A)	9182	9240	9703	64
H(28B)	9104	8742	10633	64
H(28C)	9201	9475	10888	64

Table 6. Torsion angles [°] for **26**

N(1)-C(1)-C(2)-C(3)	-1.0(6)
C(1)-C(2)-C(3)-N(2)	1.6(6)
N(3)-C(4)-C(5)-C(6)	1.3(5)
C(4)-C(5)-C(6)-N(4)	-1.2(5)
N(5)-C(7)-C(8)-C(9)	-1.3(5)
C(7)-C(8)-C(9)-N(6)	1.8(5)
N(7)-C(10)-C(11)-C(12)	27.5(5)
C(24)-C(10)-C(11)-C(12)	-94.1(5)
N(7)-C(10)-C(11)-Mo(1)	-54.8(4)
C(24)-C(10)-C(11)-Mo(1)	-176.5(3)
C(29)-Mo(1)-C(11)-C(12)	176.1(3)
C(30)-Mo(1)-C(11)-C(12)	-104.4(3)
N(5)-Mo(1)-C(11)-C(12)	160.7(3)
N(1)-Mo(1)-C(11)-C(12)	80.6(3)
N(3)-Mo(1)-C(11)-C(12)	-1.1(3)
C(29)-Mo(1)-C(11)-C(10)	-70.8(3)
C(30)-Mo(1)-C(11)-C(10)	8.7(3)
N(5)-Mo(1)-C(11)-C(10)	-86.2(4)
N(1)-Mo(1)-C(11)-C(10)	-166.3(3)
C(12)-Mo(1)-C(11)-C(10)	113.1(4)
N(3)-Mo(1)-C(11)-C(10)	112.0(3)
C(10)-C(11)-C(12)-C(13)	1.6(6)
Mo(1)-C(11)-C(12)-C(13)	114.3(4)
C(10)-C(11)-C(12)-Mo(1)	-112.7(3)
C(29)-Mo(1)-C(12)-C(11)	-3.8(3)
C(30)-Mo(1)-C(12)-C(11)	80.8(3)
N(5)-Mo(1)-C(12)-C(11)	-146.7(5)
N(1)-Mo(1)-C(12)-C(11)	-99.0(3)
N(3)-Mo(1)-C(12)-C(11)	179.1(3)
C(29)-Mo(1)-C(12)-C(13)	-120.4(3)
C(30)-Mo(1)-C(12)-C(13)	-35.8(3)
N(5)-Mo(1)-C(12)-C(13)	96.7(6)
N(1)-Mo(1)-C(12)-C(13)	144.4(3)

N(3)-Mo(1)-C(12)-C(13)	62.5(3)
C(11)-Mo(1)-C(12)-C(13)	-116.6(4)
C(11)-C(12)-C(13)-O(1)	171.1(4)
Mo(1)-C(12)-C(13)-O(1)	-101.8(5)
C(11)-C(12)-C(13)-C(14)	-2.6(6)
Mo(1)-C(12)-C(13)-C(14)	84.5(4)
O(1)-C(13)-C(14)-N(7)	161.4(4)
C(12)-C(13)-C(14)-N(7)	-24.7(5)
O(1)-C(13)-C(14)-C(27)	34.3(5)
C(12)-C(13)-C(14)-C(27)	-151.8(4)
O(1)-C(13)-C(14)-C(26)	-81.9(5)
C(12)-C(13)-C(14)-C(26)	92.0(4)
O(4)-C(17)-C(18)-C(19)	-28.8(7)
O(4)-C(17)-C(18)-C(23)	154.4(4)
C(23)-C(18)-C(19)-C(20)	-2.4(7)
C(17)-C(18)-C(19)-C(20)	-179.2(4)
C(18)-C(19)-C(20)-C(21)	1.1(7)
C(19)-C(20)-C(21)-C(22)	-0.5(8)
C(20)-C(21)-C(22)-C(23)	1.2(9)
C(21)-C(22)-C(23)-C(18)	-2.6(8)
C(19)-C(18)-C(23)-C(22)	3.1(7)
C(17)-C(18)-C(23)-C(22)	-180.0(5)
N(7)-C(10)-C(24)-C(25)	-51.5(4)
C(11)-C(10)-C(24)-C(25)	71.8(4)
C(10)-C(24)-C(25)-O(2)	-144.5(4)
C(10)-C(24)-C(25)-C(26)	39.3(5)
O(2)-C(25)-C(26)-C(14)	146.6(4)
C(24)-C(25)-C(26)-C(14)	-37.2(5)
N(7)-C(14)-C(26)-C(25)	45.1(5)
C(27)-C(14)-C(26)-C(25)	171.4(4)
C(13)-C(14)-C(26)-C(25)	-72.4(4)
N(7)-C(14)-C(27)-C(28)	-55.2(5)
C(26)-C(14)-C(27)-C(28)	-176.7(4)
C(13)-C(14)-C(27)-C(28)	67.8(5)
C(30)-Mo(1)-C(29)-O(5)	34(7)
N(5)-Mo(1)-C(29)-O(5)	-55(7)
N(1)-Mo(1)-C(29)-O(5)	-138(7)
C(12)-Mo(1)-C(29)-O(5)	134(7)
N(3)-Mo(1)-C(29)-O(5)	-58(8)
C(11)-Mo(1)-C(29)-O(5)	132(7)
C(29)-Mo(1)-C(30)-O(6)	-44(2)
N(5)-Mo(1)-C(30)-O(6)	43(2)
N(1)-Mo(1)-C(30)-O(6)	31(3)
C(12)-Mo(1)-C(30)-O(6)	-148(2)
N(3)-Mo(1)-C(30)-O(6)	123(2)
C(11)-Mo(1)-C(30)-O(6)	-112(2)
C(2)-C(1)-N(1)-N(2)	0.0(5)
C(2)-C(1)-N(1)-Mo(1)	178.5(3)
C(29)-Mo(1)-N(1)-C(1)	-53.5(4)
C(30)-Mo(1)-N(1)-C(1)	-127.0(11)
N(5)-Mo(1)-N(1)-C(1)	-139.1(4)
C(12)-Mo(1)-N(1)-C(1)	51.8(4)
N(3)-Mo(1)-N(1)-C(1)	140.2(4)
C(11)-Mo(1)-N(1)-C(1)	15.9(4)
C(29)-Mo(1)-N(1)-N(2)	124.8(3)
C(30)-Mo(1)-N(1)-N(2)	51.3(13)

N(5)-Mo(1)-N(1)-N(2)	39.1(3)
C(12)-Mo(1)-N(1)-N(2)	-129.9(3)
N(3)-Mo(1)-N(1)-N(2)	-41.5(3)
C(11)-Mo(1)-N(1)-N(2)	-165.8(3)
C(2)-C(3)-N(2)-N(1)	-1.7(5)
C(2)-C(3)-N(2)-B(1)	179.6(5)
C(1)-N(1)-N(2)-C(3)	1.0(5)
Mo(1)-N(1)-N(2)-C(3)	-177.7(3)
C(1)-N(1)-N(2)-B(1)	179.9(4)
Mo(1)-N(1)-N(2)-B(1)	1.2(5)
N(4)-B(1)-N(2)-C(3)	-121.9(5)
N(6)-B(1)-N(2)-C(3)	119.9(5)
N(4)-B(1)-N(2)-N(1)	59.5(5)
N(6)-B(1)-N(2)-N(1)	-58.7(5)
C(5)-C(4)-N(3)-N(4)	-0.8(5)
C(5)-C(4)-N(3)-Mo(1)	-174.9(3)
C(29)-Mo(1)-N(3)-C(4)	132.2(7)
C(30)-Mo(1)-N(3)-C(4)	42.2(4)
N(5)-Mo(1)-N(3)-C(4)	128.8(4)
N(1)-Mo(1)-N(3)-C(4)	-146.2(4)
C(12)-Mo(1)-N(3)-C(4)	-59.6(4)
C(11)-Mo(1)-N(3)-C(4)	-59.0(4)
C(29)-Mo(1)-N(3)-N(4)	-41.2(8)
C(30)-Mo(1)-N(3)-N(4)	-131.2(3)
N(5)-Mo(1)-N(3)-N(4)	-44.6(3)
N(1)-Mo(1)-N(3)-N(4)	40.4(3)
C(12)-Mo(1)-N(3)-N(4)	127.0(3)
C(11)-Mo(1)-N(3)-N(4)	127.7(3)
C(5)-C(6)-N(4)-N(3)	0.7(5)
C(5)-C(6)-N(4)-B(1)	173.3(4)
C(4)-N(3)-N(4)-C(6)	0.1(5)
Mo(1)-N(3)-N(4)-C(6)	175.1(3)
C(4)-N(3)-N(4)-B(1)	-173.4(4)
Mo(1)-N(3)-N(4)-B(1)	1.6(5)
N(2)-B(1)-N(4)-C(6)	127.4(5)
N(6)-B(1)-N(4)-C(6)	-113.4(5)
N(2)-B(1)-N(4)-N(3)	-60.6(5)
N(6)-B(1)-N(4)-N(3)	58.5(5)
C(8)-C(7)-N(5)-N(6)	0.3(5)
C(8)-C(7)-N(5)-Mo(1)	-175.7(3)
C(29)-Mo(1)-N(5)-C(7)	41.6(4)
C(30)-Mo(1)-N(5)-C(7)	-40.3(4)
N(1)-Mo(1)-N(5)-C(7)	138.0(4)
C(12)-Mo(1)-N(5)-C(7)	-174.1(5)
N(3)-Mo(1)-N(5)-C(7)	-139.2(4)
C(11)-Mo(1)-N(5)-C(7)	56.0(6)
C(29)-Mo(1)-N(5)-N(6)	-134.0(3)
C(30)-Mo(1)-N(5)-N(6)	144.2(3)
N(1)-Mo(1)-N(5)-N(6)	-37.6(3)
C(12)-Mo(1)-N(5)-N(6)	10.3(7)
N(3)-Mo(1)-N(5)-N(6)	45.2(3)
C(11)-Mo(1)-N(5)-N(6)	-119.6(4)
C(8)-C(9)-N(6)-N(5)	-1.6(5)
C(8)-C(9)-N(6)-B(1)	179.6(4)
C(7)-N(5)-N(6)-C(9)	0.8(4)
Mo(1)-N(5)-N(6)-C(9)	177.3(3)

C(7)-N(5)-N(6)-B(1)	179.8(4)
Mo(1)-N(5)-N(6)-B(1)	-3.7(5)
N(4)-B(1)-N(6)-C(9)	120.1(5)
N(2)-B(1)-N(6)-C(9)	-120.5(5)
N(4)-B(1)-N(6)-N(5)	-58.5(5)
N(2)-B(1)-N(6)-N(5)	60.8(5)
O(3)-C(16)-N(7)-C(10)	161.7(4)
O(4)-C(16)-N(7)-C(10)	-21.5(5)
O(3)-C(16)-N(7)-C(14)	11.6(7)
O(4)-C(16)-N(7)-C(14)	-171.6(3)
C(11)-C(10)-N(7)-C(16)	150.1(3)
C(24)-C(10)-N(7)-C(16)	-87.0(4)
C(11)-C(10)-N(7)-C(14)	-57.8(4)
C(24)-C(10)-N(7)-C(14)	65.1(4)
C(27)-C(14)-N(7)-C(16)	-30.7(5)
C(26)-C(14)-N(7)-C(16)	90.9(4)
C(13)-C(14)-N(7)-C(16)	-153.1(4)
C(27)-C(14)-N(7)-C(10)	177.8(4)
C(26)-C(14)-N(7)-C(10)	-60.6(4)
C(13)-C(14)-N(7)-C(10)	55.4(4)
O(3)-C(16)-O(4)-C(17)	6.6(6)
N(7)-C(16)-O(4)-C(17)	-170.5(4)
C(18)-C(17)-O(4)-C(16)	176.7(4)

Symmetry transformations used to generate equivalent atoms:

6. X-Ray Diffraction Study of the *anti*-aldol product (X = NCbz, R^1 = Me)

Suitable crystal of *anti*-aldol product (X = NCbz, R^1 = Me) was obtained by diffusion recrystallization from CH_2Cl_2/hexanes. These crystals were 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 1000 CCD sealed tube diffractometer with graphite monochromated CuK_α (1.54178 Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3^o frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART[5] software. Frame integration and final cell refinements were done using SAINT[10] software. The final cell parameters were determined from least-squares refinement on 5420 reflections. The SADABS[11] program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V5.10).[12] All the hydrogen atoms were located in a difference Fourier map and were included in the final cycles of least squares with isotropic U_{ij} 's; all non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*.[9] Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V5.10 software.

[10] SAINT Version 6.02, **1999**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
[11] SADABS, **1996**, George Sheldrick, University of Göttingen.
[12] SHELXTL V5.10, **1997**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.

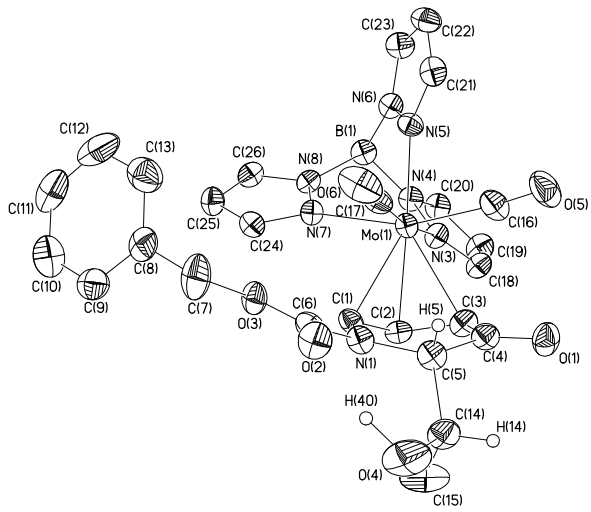


Figure 2. ORTEP View of *anti*-aldol product (X = NCbz, R^1 = Me)

Table 7. Crystal data and structure refinement for *anti*-aldol product (X = NCbz, R^1 = Me)

Identification code	*anti*-aldol product (X = NCbz, R^1 = Me)	
Empirical formula	C_{29} H_{33} B Mo N_7 O_6	
Formula weight	682.37	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4754(2) Å	α= 104.527(1)°.
	b = 12.8534(2) Å	β= 112.404(1)°.
	c = 13.4732(3) Å	γ = 103.191(1)°.
Volume	1513.55(5) $Å^3$	
Z	2	
Density (calculated)	1.497 Mg/m^3	
Absorption coefficient	4.005 mm^{-1}	
F(000)	702	
Crystal size	0.28 x 0.22 x 0.12 mm^3	
Theta range for data collection	3.81 to 66.04°.	
Index ranges	-12<=h<=12, -15<=k<=14, -13<=l<=15	
Reflections collected	6979	
Independent reflections	4400 [R(int) = 0.0169]	
Completeness to theta = 66.04°	83.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6451 and 0.4002	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4400 / 0 / 492	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.1112	
R indices (all data)	R1 = 0.0385, wR2 = 0.1118	
Largest diff. peak and hole	1.403 and -0.719 e.$Å^{-3}$	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for *anti*-aldol product (X = NCbz, R^1 = Me). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
B(1)	6844(5)	7750(4)	2832(4)	28(1)
C(1)	6402(4)	3586(3)	963(3)	25(1)
C(2)	6777(4)	4298(3)	400(3)	26(1)
C(3)	8264(5)	4637(3)	607(4)	30(1)
C(4)	9067(4)	3853(3)	837(3)	29(1)
C(5)	8343(4)	2744(3)	956(4)	28(1)
C(6)	6652(4)	2058(3)	1683(4)	31(1)
C(7)	5301(7)	1663(5)	2697(6)	50(1)
C(8)	4251(5)	2083(4)	3026(4)	37(1)
C(9)	2745(6)	1540(4)	2324(4)	40(1)
C(10)	1754(7)	1927(5)	2603(6)	56(1)
C(11)	2253(7)	2854(5)	3587(6)	57(2)
C(12)	3754(9)	3407(5)	4318(5)	62(2)
C(13)	4752(7)	3022(5)	4036(5)	52(1)
C(14)	8033(5)	1725(4)	-108(4)	36(1)
C(15)	6834(9)	1666(6)	-1196(5)	63(2)
C(16)	10161(5)	5908(4)	2692(4)	37(1)
C(17)	8401(4)	4637(3)	3167(3)	30(1)
C(18)	8011(5)	7171(4)	607(4)	30(1)
C(19)	7755(5)	8169(4)	532(4)	36(1)
C(20)	7242(5)	8493(4)	1319(4)	31(1)
C(21)	10088(5)	7444(4)	4838(4)	31(1)
C(22)	10229(5)	8465(4)	5575(4)	36(1)
C(23)	9072(5)	8732(4)	4938(4)	33(1)
C(24)	4814(4)	4796(3)	2285(3)	28(1)
C(25)	3849(5)	5280(4)	2500(4)	33(1)
C(26)	4439(4)	6421(4)	2672(3)	30(1)
C(1S)	1578(8)	8926(6)	3237(6)	78(2)
C(2S)	3026(7)	9201(6)	4388(6)	69(2)
C(3S)	4295(8)	9782(13)	4426(8)	179(7)
Mo(1)	8016(1)	5560(1)	2224(1)	22(1)
N(1)	7001(4)	2718(3)	1108(3)	27(1)
N(3)	7683(4)	6888(3)	1385(3)	26(1)
N(4)	7189(4)	7713(3)	1820(3)	26(1)
N(5)	8901(3)	7083(3)	3810(3)	26(1)
N(6)	8272(4)	7902(3)	3881(3)	26(1)
N(7)	5921(3)	5588(3)	2301(3)	24(1)
N(8)	5674(3)	6599(3)	2542(3)	25(1)
O(1)	10268(3)	4003(3)	859(3)	37(1)
O(2)	7172(3)	1319(2)	1865(3)	37(1)
O(3)	5663(3)	2293(2)	2009(2)	32(1)
O(4)	7706(5)	662(3)	29(3)	61(1)
O(5)	11407(3)	6114(3)	3036(3)	59(1)
O(6)	8662(4)	4090(3)	3724(3)	51(1)

Table 9. Bond lengths [Å] and angles [°] for *anti*-aldol product (X = NCbz, R^1 = Me)

B(1)-N(4)	1.531(6)	C(1)-C(2)	1.407(5)
B(1)-N(8)	1.536(6)	C(1)-N(1)	1.417(5)
B(1)-N(6)	1.547(6)	C(1)-Mo(1)	2.424(4)

C(2)-C(3)	1.411(6)	C(2)-C(3)-Mo(1)	67.6(2)
C(2)-Mo(1)	2.228(4)	C(4)-C(3)-Mo(1)	111.0(3)
C(3)-C(4)	1.472(6)	O(1)-C(4)-C(3)	122.5(4)
C(3)-Mo(1)	2.344(4)	O(1)-C(4)-C(5)	117.0(4)
C(4)-O(1)	1.216(5)	C(3)-C(4)-C(5)	120.3(4)
C(4)-C(5)	1.532(5)	N(1)-C(5)-C(4)	113.3(3)
C(5)-N(1)	1.490(5)	N(1)-C(5)-C(14)	113.1(3)
C(5)-C(14)	1.545(6)	C(4)-C(5)-C(14)	107.1(3)
C(6)-O(2)	1.228(5)	O(2)-C(6)-O(3)	123.9(4)
C(6)-O(3)	1.334(5)	O(2)-C(6)-N(1)	123.8(4)
C(6)-N(1)	1.364(5)	O(3)-C(6)-N(1)	112.2(3)
C(7)-O(3)	1.470(5)	O(3)-C(7)-C(8)	107.3(4)
C(7)-C(8)	1.490(7)	C(9)-C(8)-C(13)	118.4(5)
C(8)-C(9)	1.378(7)	C(9)-C(8)-C(7)	120.2(5)
C(8)-C(13)	1.387(7)	C(13)-C(8)-C(7)	121.4(5)
C(9)-C(10)	1.381(7)	C(8)-C(9)-C(10)	121.1(5)
C(10)-C(11)	1.358(9)	C(11)-C(10)-C(9)	120.2(6)
C(11)-C(12)	1.380(9)	C(10)-C(11)-C(12)	120.1(5)
C(12)-C(13)	1.389(9)	C(11)-C(12)-C(13)	119.7(5)
C(14)-O(4)	1.408(5)	C(8)-C(13)-C(12)	120.4(5)
C(14)-C(15)	1.493(8)	O(4)-C(14)-C(15)	110.5(5)
C(16)-O(5)	1.144(5)	O(4)-C(14)-C(5)	112.6(4)
C(16)-Mo(1)	1.991(4)	C(15)-C(14)-C(5)	111.7(4)
C(17)-O(6)	1.152(5)	O(5)-C(16)-Mo(1)	175.3(4)
C(17)-Mo(1)	1.942(4)	O(6)-C(17)-Mo(1)	178.2(4)
C(18)-N(3)	1.325(5)	N(3)-C(18)-C(19)	110.9(4)
C(18)-C(19)	1.390(6)	C(20)-C(19)-C(18)	105.4(4)
C(19)-C(20)	1.379(6)	N(4)-C(20)-C(19)	107.8(4)
C(20)-N(4)	1.345(5)	N(5)-C(21)-C(22)	111.1(4)
C(21)-N(5)	1.334(5)	C(23)-C(22)-C(21)	104.7(4)
C(21)-C(22)	1.370(6)	N(6)-C(23)-C(22)	109.2(4)
C(22)-C(23)	1.367(6)	N(7)-C(24)-C(25)	110.7(4)
C(23)-N(6)	1.337(5)	C(26)-C(25)-C(24)	104.8(4)
C(24)-N(7)	1.346(5)	N(8)-C(26)-C(25)	109.1(4)
C(24)-C(25)	1.383(6)	C(3S)-C(2S)-C(1S)	114.5(6)
C(25)-C(26)	1.376(6)	C(2S)-C(3S)-C(3S)#1	117.0(8)
C(26)-N(8)	1.348(5)	C(17)-Mo(1)-C(16)	81.04(18)
C(1S)-C(2S)	1.587(9)	C(17)-Mo(1)-N(5)	89.01(14)
C(2S)-C(3S)	1.343(9)	C(16)-Mo(1)-N(5)	82.05(15)
C(3S)-C(3S)#1	1.527(15)	C(17)-Mo(1)-C(2)	105.18(15)
Mo(1)-N(5)	2.196(3)	C(16)-Mo(1)-C(2)	106.78(16)
Mo(1)-N(7)	2.245(3)	N(5)-Mo(1)-C(2)	164.14(14)
Mo(1)-N(3)	2.292(3)	C(17)-Mo(1)-N(7)	94.26(15)
N(3)-N(4)	1.380(4)	C(16)-Mo(1)-N(7)	160.87(15)
N(5)-N(6)	1.366(5)	N(5)-Mo(1)-N(7)	79.32(12)
N(7)-N(8)	1.367(4)	C(2)-Mo(1)-N(7)	92.36(13)
N(4)-B(1)-N(8)	110.5(3)	C(17)-Mo(1)-N(3)	170.76(14)
N(4)-B(1)-N(6)	107.9(3)	C(16)-Mo(1)-N(3)	98.37(15)
N(8)-B(1)-N(6)	106.8(3)	N(5)-Mo(1)-N(3)	81.79(12)
C(2)-C(1)-N(1)	122.1(3)	C(2)-Mo(1)-N(3)	83.86(13)
C(2)-C(1)-Mo(1)	64.9(2)	N(7)-Mo(1)-N(3)	83.29(11)
N(1)-C(1)-Mo(1)	116.9(2)	C(17)-Mo(1)-C(3)	104.51(15)
C(1)-C(2)-C(3)	115.7(4)	C(16)-Mo(1)-C(3)	71.34(16)
C(1)-C(2)-Mo(1)	80.2(2)	N(5)-Mo(1)-C(3)	147.47(14)
C(3)-C(2)-Mo(1)	76.6(2)	C(2)-Mo(1)-C(3)	35.85(14)
C(2)-C(3)-C(4)	118.6(4)	N(7)-Mo(1)-C(3)	127.69(13)

N(3)-Mo(1)-C(3)	83.89(13)	C(20)-N(4)-B(1)	128.0(3)
C(17)-Mo(1)-C(1)	73.59(15)	N(3)-N(4)-B(1)	121.7(3)
C(16)-Mo(1)-C(1)	115.52(15)	C(21)-N(5)-N(6)	106.0(3)
N(5)-Mo(1)-C(1)	152.04(13)	C(21)-N(5)-Mo(1)	131.3(3)
C(2)-Mo(1)-C(1)	34.88(14)	N(6)-N(5)-Mo(1)	122.7(2)
N(7)-Mo(1)-C(1)	80.33(12)	C(23)-N(6)-N(5)	108.9(3)
N(3)-Mo(1)-C(1)	114.57(12)	C(23)-N(6)-B(1)	131.2(3)
C(3)-Mo(1)-C(1)	60.04(14)	N(5)-N(6)-B(1)	119.9(3)
C(6)-N(1)-C(1)	121.1(3)	C(24)-N(7)-N(8)	106.3(3)
C(6)-N(1)-C(5)	116.9(3)	C(24)-N(7)-Mo(1)	133.0(3)
C(1)-N(1)-C(5)	119.6(3)	N(8)-N(7)-Mo(1)	120.2(2)
C(18)-N(3)-N(4)	106.0(3)	C(26)-N(8)-N(7)	109.1(3)
C(18)-N(3)-Mo(1)	134.8(3)	C(26)-N(8)-B(1)	128.4(3)
N(4)-N(3)-Mo(1)	118.7(2)	N(7)-N(8)-B(1)	121.5(3)
C(20)-N(4)-N(3)	109.9(3)	C(6)-O(3)-C(7)	115.2(3)

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

Table 10. Anisotropic displacement parameters ($Å^2$x 10^3) for *anti*-aldol product (X = NCbz, R^1 = Me). 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)	35(2)	20(2)	34(2)	14(2)	15(2)	15(2)
C(1)	23(2)	18(2)	31(2)	7(2)	11(2)	7(2)
C(2)	31(2)	24(2)	23(2)	10(2)	12(2)	13(2)
C(3)	41(2)	22(2)	36(2)	15(2)	22(2)	16(2)
C(4)	31(2)	23(2)	32(2)	9(2)	14(2)	12(2)
C(5)	30(2)	23(2)	35(2)	13(2)	14(2)	15(2)
C(6)	32(2)	20(2)	34(2)	10(2)	11(2)	5(2)
C(7)	60(3)	46(3)	75(4)	45(3)	45(3)	25(3)
C(8)	50(3)	31(2)	43(2)	26(2)	27(2)	15(2)
C(9)	51(3)	36(3)	37(2)	19(2)	20(2)	14(2)
C(10)	49(3)	55(3)	72(4)	31(3)	31(3)	17(3)
C(11)	79(4)	60(4)	77(4)	42(3)	60(4)	41(3)
C(12)	111(5)	50(3)	48(3)	21(3)	52(4)	34(4)
C(13)	53(3)	45(3)	45(3)	21(2)	16(3)	7(3)
C(14)	46(3)	24(2)	43(2)	12(2)	25(2)	16(2)
C(15)	82(5)	50(3)	37(3)	4(2)	14(3)	30(4)
C(16)	29(2)	26(2)	46(3)	7(2)	12(2)	11(2)
C(17)	29(2)	22(2)	30(2)	8(2)	7(2)	8(2)
C(18)	40(2)	28(2)	33(2)	16(2)	21(2)	16(2)
C(19)	50(3)	32(2)	40(2)	25(2)	25(2)	18(2)
C(20)	38(2)	26(2)	37(2)	19(2)	18(2)	16(2)
C(21)	33(2)	30(2)	36(2)	21(2)	16(2)	14(2)
C(22)	37(2)	33(2)	28(2)	9(2)	9(2)	7(2)
C(23)	41(2)	21(2)	37(2)	10(2)	18(2)	14(2)
C(24)	28(2)	24(2)	30(2)	13(2)	12(2)	10(2)
C(25)	29(2)	34(2)	41(2)	17(2)	19(2)	13(2)
C(26)	32(2)	34(2)	31(2)	15(2)	16(2)	20(2)
C(3S)	41(4)	391(19)	121(7)	187(11)	24(5)	30(7)
Mo(1)	23(1)	17(1)	28(1)	12(1)	12(1)	9(1)
N(1)	29(2)	20(2)	34(2)	13(1)	14(2)	12(1)
N(3)	33(2)	23(2)	32(2)	16(1)	19(2)	15(2)
N(4)	33(2)	18(2)	34(2)	14(1)	16(2)	14(1)
N(5)	27(2)	25(2)	24(2)	10(1)	8(1)	9(1)
N(6)	32(2)	18(2)	33(2)	13(1)	17(2)	12(1)
N(7)	26(2)	23(2)	30(2)	13(1)	14(1)	13(1)
N(8)	31(2)	25(2)	26(2)	12(1)	15(2)	15(1)
O(1)	36(2)	33(2)	52(2)	16(1)	26(2)	17(1)
O(2)	47(2)	28(2)	51(2)	24(1)	27(2)	21(1)
O(3)	37(2)	27(2)	43(2)	21(1)	24(1)	11(1)
O(4)	108(3)	22(2)	65(2)	19(2)	50(2)	26(2)
O(5)	28(2)	47(2)	76(3)	-5(2)	18(2)	11(2)
O(6)	60(2)	32(2)	45(2)	26(2)	6(2)	11(2)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for *anti*-aldol product (X = NCbz, R^1 = Me)

	x	y	z	U(eq)
H(1S1)	1506	9650	3154	117
H(1S2)	704	8506	3278	117

H(1S3)	1629	8454	2569	117
H(2S1)	2945	9656	5058	83
H(2S2)	3072	8465	4472	83
H(3S1)	4179	10454	4220	215
H(3S2)	4436	9276	3820	215
H(1)	5480(40)	3390(30)	910(30)	17(9)
H(2)	6080(40)	4550(30)	-40(30)	21(10)
H(3)	8570(50)	5090(40)	280(40)	30(11)
H(5)	9020(50)	2700(40)	1650(40)	33(12)
H(9)	2310(70)	890(50)	1620(50)	69(18)
H(10)	780(70)	1540(50)	2160(50)	56(16)
H(11)	1620(60)	3130(40)	3860(40)	47(14)
H(12)	4020(70)	4040(60)	4980(60)	80(20)
H(13)	5780(70)	3330(50)	4500(50)	70(18)
H(14)	8960(50)	1790(40)	-140(40)	29(11)
H(18)	8370(40)	6710(30)	210(30)	20(10)
H(19)	7860(40)	8500(30)	70(40)	20(10)
H(20)	6890(50)	9140(40)	1510(40)	32(11)
H(21)	10590(40)	7020(30)	4960(30)	13(9)
H(22)	10900(50)	8890(40)	6260(40)	33(12)
H(23)	8770(40)	9250(40)	5100(30)	11(9)
H(24)	4760(50)	3990(40)	2180(40)	30(11)
H(25)	2970(50)	4920(40)	2510(40)	30(11)
H(26)	4110(50)	7020(40)	2880(40)	39(13)
H(15A)	7190(80)	2360(70)	-1300(60)	80(20)
H(1B)	6510(50)	8520(40)	3080(40)	44(13)
H(7B)	4810(70)	770(60)	2200(50)	70(18)
H(15B)	6740(60)	1110(50)	-1830(50)	57(16)
H(4O)	7430(100)	780(80)	720(80)	130(30)
H(7A)	5990(100)	1720(80)	3170(80)	110(30)
H(15C)	5980(90)	1620(70)	-1160(70)	90(30)

Table 12. Torsion angles [°] for *anti*-aldol product (X = NCbz, R^1 = Me)

N(1)-C(1)-C(2)-C(3)	-37.4(5)
Mo(1)-C(1)-C(2)-C(3)	69.8(3)
N(1)-C(1)-C(2)-Mo(1)	-107.2(3)
C(1)-C(2)-C(3)-C(4)	30.5(5)
Mo(1)-C(2)-C(3)-C(4)	102.5(3)
C(1)-C(2)-C(3)-Mo(1)	-72.0(3)
C(2)-C(3)-C(4)-O(1)	169.2(4)
Mo(1)-C(3)-C(4)-O(1)	-115.6(4)
C(2)-C(3)-C(4)-C(5)	-5.4(6)
Mo(1)-C(3)-C(4)-C(5)	69.8(4)
O(1)-C(4)-C(5)-N(1)	170.9(3)
C(3)-C(4)-C(5)-N(1)	-14.2(5)
O(1)-C(4)-C(5)-C(14)	-63.7(5)
C(3)-C(4)-C(5)-C(14)	111.2(4)
O(3)-C(7)-C(8)-C(9)	90.8(5)
O(3)-C(7)-C(8)-C(13)	-89.1(6)
C(13)-C(8)-C(9)-C(10)	1.0(7)
C(7)-C(8)-C(9)-C(10)	-178.9(4)
C(8)-C(9)-C(10)-C(11)	-0.3(8)
C(9)-C(10)-C(11)-C(12)	-0.6(8)
C(10)-C(11)-C(12)-C(13)	0.9(8)

C(9)-C(8)-C(13)-C(12)	-0.7(7)
C(7)-C(8)-C(13)-C(12)	179.2(4)
C(11)-C(12)-C(13)-C(8)	-0.2(8)
N(1)-C(5)-C(14)-O(4)	-69.0(5)
C(4)-C(5)-C(14)-O(4)	165.5(4)
N(1)-C(5)-C(14)-C(15)	56.0(6)
C(4)-C(5)-C(14)-C(15)	-69.5(6)
N(3)-C(18)-C(19)-C(20)	0.0(5)
C(18)-C(19)-C(20)-N(4)	-0.5(5)
N(5)-C(21)-C(22)-C(23)	-1.1(5)
C(21)-C(22)-C(23)-N(6)	0.9(5)
N(7)-C(24)-C(25)-C(26)	-1.1(5)
C(24)-C(25)-C(26)-N(8)	1.2(5)
C(1S)-C(2S)-C(3S)-C(3S)#1	171.8(15)
O(6)-C(17)-Mo(1)-C(16)	-19(11)
O(6)-C(17)-Mo(1)-N(5)	-101(11)
O(6)-C(17)-Mo(1)-C(2)	87(11)
O(6)-C(17)-Mo(1)-N(7)	-180(100)
O(6)-C(17)-Mo(1)-N(3)	-106(11)
O(6)-C(17)-Mo(1)-C(3)	49(11)
O(6)-C(17)-Mo(1)-C(1)	102(11)
O(5)-C(16)-Mo(1)-C(17)	-41(5)
O(5)-C(16)-Mo(1)-N(5)	49(5)
O(5)-C(16)-Mo(1)-C(2)	-144(5)
O(5)-C(16)-Mo(1)-N(7)	36(5)
O(5)-C(16)-Mo(1)-N(3)	130(5)
O(5)-C(16)-Mo(1)-C(3)	-150(5)
O(5)-C(16)-Mo(1)-C(1)	-108(5)
C(1)-C(2)-Mo(1)-C(17)	25.7(3)
C(3)-C(2)-Mo(1)-C(17)	-93.9(3)
C(1)-C(2)-Mo(1)-C(16)	110.8(3)
C(3)-C(2)-Mo(1)-C(16)	-8.9(3)
C(1)-C(2)-Mo(1)-N(5)	-127.1(5)
C(3)-C(2)-Mo(1)-N(5)	113.3(5)
C(1)-C(2)-Mo(1)-N(7)	-69.3(2)
C(3)-C(2)-Mo(1)-N(7)	171.1(2)
C(1)-C(2)-Mo(1)-N(3)	-152.3(2)
C(3)-C(2)-Mo(1)-N(3)	88.1(2)
C(1)-C(2)-Mo(1)-C(3)	119.6(3)
C(3)-C(2)-Mo(1)-C(1)	-119.6(3)
C(2)-C(3)-Mo(1)-C(17)	95.9(3)
C(4)-C(3)-Mo(1)-C(17)	-17.5(3)
C(2)-C(3)-Mo(1)-C(16)	171.0(3)
C(4)-C(3)-Mo(1)-C(16)	57.6(3)
C(2)-C(3)-Mo(1)-N(5)	-152.2(2)
C(4)-C(3)-Mo(1)-N(5)	94.4(3)
C(4)-C(3)-Mo(1)-C(2)	-113.4(4)
C(2)-C(3)-Mo(1)-N(7)	-11.3(3)
C(4)-C(3)-Mo(1)-N(7)	-124.7(3)
C(2)-C(3)-Mo(1)-N(3)	-88.0(2)
C(4)-C(3)-Mo(1)-N(3)	158.6(3)
C(2)-C(3)-Mo(1)-C(1)	35.0(2)
C(4)-C(3)-Mo(1)-C(1)	-78.4(3)
C(2)-C(1)-Mo(1)-C(17)	-154.1(3)
N(1)-C(1)-Mo(1)-C(17)	-39.2(3)
C(2)-C(1)-Mo(1)-C(16)	-82.8(3)

N(1)-C(1)-Mo(1)-C(16)	32.1(3)
C(2)-C(1)-Mo(1)-N(5)	152.3(3)
N(1)-C(1)-Mo(1)-N(5)	-92.8(4)
N(1)-C(1)-Mo(1)-C(2)	114.9(4)
C(2)-C(1)-Mo(1)-N(7)	108.5(2)
N(1)-C(1)-Mo(1)-N(7)	-136.6(3)
C(2)-C(1)-Mo(1)-N(3)	30.5(3)
N(1)-C(1)-Mo(1)-N(3)	145.4(3)
C(2)-C(1)-Mo(1)-C(3)	-36.0(2)
N(1)-C(1)-Mo(1)-C(3)	78.9(3)
O(2)-C(6)-N(1)-C(1)	-177.7(4)
O(3)-C(6)-N(1)-C(1)	3.3(5)
O(2)-C(6)-N(1)-C(5)	-15.5(6)
O(3)-C(6)-N(1)-C(5)	165.5(3)
C(2)-C(1)-N(1)-C(6)	178.3(4)
Mo(1)-C(1)-N(1)-C(6)	102.3(4)
C(2)-C(1)-N(1)-C(5)	16.6(5)
Mo(1)-C(1)-N(1)-C(5)	-59.3(4)
C(4)-C(5)-N(1)-C(6)	-153.4(3)
C(14)-C(5)-N(1)-C(6)	84.5(4)
C(4)-C(5)-N(1)-C(1)	9.0(5)
C(14)-C(5)-N(1)-C(1)	-113.1(4)
C(19)-C(18)-N(3)-N(4)	0.6(5)
C(19)-C(18)-N(3)-Mo(1)	-170.9(3)
C(17)-Mo(1)-N(3)-C(18)	135.4(8)
C(16)-Mo(1)-N(3)-C(18)	49.7(4)
N(5)-Mo(1)-N(3)-C(18)	130.4(4)
C(2)-Mo(1)-N(3)-C(18)	-56.4(4)
N(7)-Mo(1)-N(3)-C(18)	-149.5(4)
C(3)-Mo(1)-N(3)-C(18)	-20.3(4)
C(1)-Mo(1)-N(3)-C(18)	-73.4(4)
C(17)-Mo(1)-N(3)-N(4)	-35.3(10)
C(16)-Mo(1)-N(3)-N(4)	-120.9(3)
N(5)-Mo(1)-N(3)-N(4)	-40.3(3)
C(2)-Mo(1)-N(3)-N(4)	132.9(3)
N(7)-Mo(1)-N(3)-N(4)	39.8(3)
C(3)-Mo(1)-N(3)-N(4)	169.0(3)
C(1)-Mo(1)-N(3)-N(4)	116.0(3)
C(19)-C(20)-N(4)-N(3)	0.9(5)
C(19)-C(20)-N(4)-B(1)	173.4(4)
C(18)-N(3)-N(4)-C(20)	-0.9(4)
Mo(1)-N(3)-N(4)-C(20)	172.2(3)
C(18)-N(3)-N(4)-B(1)	-173.9(4)
Mo(1)-N(3)-N(4)-B(1)	-0.8(4)
N(8)-B(1)-N(4)-C(20)	131.1(4)
N(6)-B(1)-N(4)-C(20)	-112.4(4)
N(8)-B(1)-N(4)-N(3)	-57.2(5)
N(6)-B(1)-N(4)-N(3)	59.3(4)
C(22)-C(21)-N(5)-N(6)	0.9(5)
C(22)-C(21)-N(5)-Mo(1)	178.8(3)
C(17)-Mo(1)-N(5)-C(21)	43.0(4)
C(16)-Mo(1)-N(5)-C(21)	-38.1(4)
C(2)-Mo(1)-N(5)-C(21)	-163.2(4)
N(7)-Mo(1)-N(5)-C(21)	137.5(4)
N(3)-Mo(1)-N(5)-C(21)	-137.8(4)
C(3)-Mo(1)-N(5)-C(21)	-73.0(4)

C(1)-Mo(1)-N(5)-C(21)	93.5(4)
C(17)-Mo(1)-N(5)-N(6)	-139.4(3)
C(16)-Mo(1)-N(5)-N(6)	139.5(3)
C(2)-Mo(1)-N(5)-N(6)	14.4(6)
N(7)-Mo(1)-N(5)-N(6)	-44.9(3)
N(3)-Mo(1)-N(5)-N(6)	39.8(3)
C(3)-Mo(1)-N(5)-N(6)	104.5(3)
C(1)-Mo(1)-N(5)-N(6)	-88.9(4)
C(22)-C(23)-N(6)-N(5)	-0.3(5)
C(22)-C(23)-N(6)-B(1)	178.5(4)
C(21)-N(5)-N(6)-C(23)	-0.4(4)
Mo(1)-N(5)-N(6)-C(23)	-178.5(3)
C(21)-N(5)-N(6)-B(1)	-179.4(3)
Mo(1)-N(5)-N(6)-B(1)	2.5(4)
N(4)-B(1)-N(6)-C(23)	119.9(4)
N(8)-B(1)-N(6)-C(23)	-121.2(4)
N(4)-B(1)-N(6)-N(5)	-61.3(4)
N(8)-B(1)-N(6)-N(5)	57.6(4)
C(25)-C(24)-N(7)-N(8)	0.6(4)
C(25)-C(24)-N(7)-Mo(1)	172.5(3)
C(17)-Mo(1)-N(7)-C(24)	-37.7(4)
C(16)-Mo(1)-N(7)-C(24)	-112.5(5)
N(5)-Mo(1)-N(7)-C(24)	-125.9(4)
C(2)-Mo(1)-N(7)-C(24)	67.7(3)
N(3)-Mo(1)-N(7)-C(24)	151.3(3)
C(3)-Mo(1)-N(7)-C(24)	74.3(4)
C(1)-Mo(1)-N(7)-C(24)	34.9(3)
C(17)-Mo(1)-N(7)-N(8)	133.3(3)
C(16)-Mo(1)-N(7)-N(8)	58.5(5)
N(5)-Mo(1)-N(7)-N(8)	45.1(3)
C(2)-Mo(1)-N(7)-N(8)	-121.3(3)
N(3)-Mo(1)-N(7)-N(8)	-37.8(3)
C(3)-Mo(1)-N(7)-N(8)	-114.7(3)
C(1)-Mo(1)-N(7)-N(8)	-154.2(3)
C(25)-C(26)-N(8)-N(7)	-0.9(4)
C(25)-C(26)-N(8)-B(1)	-169.4(4)
C(24)-N(7)-N(8)-C(26)	0.2(4)
Mo(1)-N(7)-N(8)-C(26)	-173.0(2)
C(24)-N(7)-N(8)-B(1)	169.7(3)
Mo(1)-N(7)-N(8)-B(1)	-3.5(4)
N(4)-B(1)-N(8)-C(26)	-132.1(4)
N(6)-B(1)-N(8)-C(26)	110.7(4)
N(4)-B(1)-N(8)-N(7)	60.6(4)
N(6)-B(1)-N(8)-N(7)	-56.6(4)
O(2)-C(6)-O(3)-C(7)	4.6(6)
N(1)-C(6)-O(3)-C(7)	-176.4(4)
C(8)-C(7)-O(3)-C(6)	177.1(4)

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

Table 13. Hydrogen bonds for *anti*-aldol product (X = NCbz, R^1 = Me) [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4O)...O(2)	1.06(9)	1.68(9)	2.715(5)	166(8)

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

7. Copies of ^{1}H and ^{13}C-NMR spectra