Supporting Information for

Enantiocontrolled Synthesis of Highly Functionalized Tropanes via [5 +2] Cycloaddition to η^3-Pyridinylmolybdenum π-Complexes

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General Methods. Unless otherwise indicated, all NMR data were collected at room temperature in $CDCl_3$ with internal $CHCl_3$ as the reference (δ 7.26 ppm for ^1H and 77.23 ppm for ^{13}C). Due to the restricted rotation about the C-N bond of the carbamate group, additional "satellite" peaks accompany the main signals. Signals for the "satellite" peaks are indicated in parentheses following the signal for the major peak. Measuring the ^{13}C NMR at 60 °C did not eliminate the peak broadening and did not remove the satellite peaks. IR spectra were measured in KBr pellets, unless stated otherwise. Melting points are uncorrected and were taken in open capillary tubes. MS were measured under fast atom bombardment (FAB) or electron impact (EI) conditions. Analytic thin-layer chromatography (TLC) was carried out on commercial Merck silica gel 60 plates, 0.25 thickness, with fluorescent indicator (F-254) or stained with 5% phosphomolybdic acid in ethanol. Column chromatography was performed with 32-63 μm silica gel (Woelm). THF was freshly distilled from sodium/benzophenone. Dichloromethane was distilled from CaH_2 and kept over molecular sieves under an atmosphere of dry argon. Triethylamine (TEA) was distilled from CaH_2 and kept under atmosphere of dry argon. Dry Et_2O was purchased from Mallinckrodt and used as received; other solvents were used as received. Unless otherwise specified, all reactions were carried out under an atmosphere of dry nitrogen or argon in oven dried (at least 6 h at 140 °C) glassware. Single crystals for X-ray analysis were obtained by slow diffusion of hexanes into methylene chloride solutions of the molybdenum complexes.

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1-Methoxycarbonyl-1,2,3,6-tetrahydropyridin-4-en-3-one (1a). To a solution of 1-benzyl-1,2,3,6-tetrahydropyridin-4-en-3-one[1] (2.231 g, 11.93 mmol) in methylene chloride (39 mL) under argon at room temperature was added methoxychloroformate (1.502 g, 15.89 mmol). The reaction mixture was stirred at room temperature for 16 hours. Solvents were removed under reduced pressure and the crude product was purified by flash chromatography over silica eluting with ether/hexane (2: 1) to afford the pyridone **1a** (1.484 g, 80 %) as a light yellow oil: R_f = 0.24 (ether/hexane, 2: 1); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 60 °C) δ 7.21 (dt, J = 10.0 Hz, 3.6 Hz, 1 H), 6.10 (dt, J = 10.8 Hz, 2.4 Hz, 1 H), 4.23 (br t, J = 2.4 Hz, 2 H), 4.05 (br s, 2 H), 3.65 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 155.7, 146.9 (145.9), 127.7, 53.2, 51.7 (51.4), 43.1; IR (neat, cm^{-1}): 1695 (s), 1455 (m), 1409 (w), 1380 (w), 1355 (w), 1227 (m), 1192 (m), 1109 (m), 974 (w), 768 (w); HRMS (EI) calcd for $C_7H_9NO_3$ (M^+) 155.0582, found 155.0580. Rapid decomposition of the sample precluded a successful elemental analysis.

1-[(R)-dihydro-4,4-dimethyl-2(3H)-furanone-3-yl]oxychloroformate. To a solution of phosgene (285 mL of 1.93M solution in toluene, 550 mmol) in MTBE (500 mL) at 0 °C under argon was added dropwise over 2 hours a solution of (R)-pantolactone (35.05 g, 269 mmol) and 2,6-lutidine (37.0 mL, 34.00 g, 317 mmol) in MTBE (630 mL). The resulting light yellow suspension was stirred at room temperature for 3 h. Ether (1 L) and 1.2 M aqueous HCl (1.5 L) were added and stirring was continued for an additional 25 minutes to destroy excess of phosgene. The organic layer was separated, washed with brine, dried ($MgSO_4$) and solvents were removed under reduced pressure to afford 1-[(R)-dihydro-4,4-dimethyl-2(3H)-furanone-3-yl]oxychloroformate (31.40 g, 60%) as a light yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.28 (s, 1 H), 4.10 (d, J = 9.3 Hz, 1 H), 4.04 (d, J = 9.3 Hz, 1 H), 1.28 (s, 3 H), 1.19 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 150.3, 81.2, 75.8, 40.1, 22.4, 19.4; IR (CH_2Cl_2, KCl, cm^{-1}): 2973 (m), 1797 (s), 1466 (w), 1144 (s); Anal. calcd for $C_7H_9ClO_4$: C, 43.66; H, 4.71. Found: C, 44.04; H, 4.84.

1-[(R)-Dihydro-4,4-dimethyl-2(3H)-furanone-3-yl]oxycarbonyl-1,2,3,6-tetrahydropyridin-4-en-3-one (1b). To a solution of 1-benzyl-1,2,3,6-tetrahydropyridin-4-en-3-one[1] (18.50 g, 99 mmol) in methylene chloride (800 mL) under argon at room temperature was added a solution of 1-[(R)-dihydro-4,4-dimethyl-2(3H)-furanone-3-yl]oxychloroformate (31.40 g, 163 mmol) in methylene chloride (100 mL). The reaction mixture was stirred at room temperature for 16 hours. Solvents were removed under reduced pressure and the crude product was purified by filtration through a short plug of silica eluting with ether/hexane (2: 1) to afford the pyridone **1b** (22.41 g, 89 %) as a light yellow oil: R_f = 0.38 (ether/hexane, 1: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dt, J = 10.4 Hz, 3.6 Hz, 0.5 H), 6.98 (dt, J = 10.4 Hz, 3.6 Hz, 0.5 H), 6.23 (d, J = 10.4 Hz, 1 H), 5.37 (s, 0.5 H), 5.34 (s, 0.5 H), 4.42-4.24 (m, 2 H), 4.22-4.19 (m, 2 H), 4.07-4.02 (m, 2 H), 1.24 (s, 1.5 H), 1.22 (s, 1.5 H), 1.13 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2 (191.9), 172.8 (172.6), 153.8, 146.4 (145.3), 127.6 (127.8), 76.4 (76.2), 51.7 (51.5), 43.4 (43.2), 40.4 (40.2), 23.1, 20.2 (two carbons); IR (KBr, cm^{-1}): 1794 (s), 1717 (s); Anal. calcd for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97; N, 5.53. Found: C, 56.67; H, 5.98; N, 5.44.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(3,4,5)-3-methoxy-1-methoxycarbonyl-1,2,3,6-tetrahydropyridin-3-yl]molybdenum [(±)-2a]. Molybdenum complex $Mo(CO)_3(DMF)_3$[2] (8.171 g, 20.47 mmol) was added to a Schlenk flask under a high stream of dry argon. Then, methylene chloride (75 mL), previously deoxygenated by sparging with dry argon for 15 minutes, was injected. A solution of pyridone **1a** (3.147 g, 20.31 mmol) in methylene chloride (20 mL) was added to the dark green solution that immediately turned dark red color. Then, a solution of TBDMSCl (3.136 g, 20.80 mmol) in methylene chloride (10 mL) was injected and the reaction mixture was stirred at room temperature under argon overnight. Solid KTp[3] (5.140 g, 20.38 mmol) was added to the reaction mixture and stirring was continued for 30 minutes. Then, TBAF•3 H_2O (16.36 g, 51.85 mmol) was added as solid and stirring was continued for an additional 30 minutes. Then, iodomethane (27.0 mL, 61.50 g, 433 mmol) was injected and the reaction mixture was stirred at room temperature for an additional 24 hours. The

crude reaction mixture was directly poured on a column of basic alumina (300 g) eluting with EtOAc/hexane (1: 3) to afford the molybdenum complex (±)-**2a** (6.53 g, 60%) as an orange solid: mp = 123-125 °C (EtOAc/hexane); R_f = 0.40 (EtOAc/hexane, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, 1 H), 7.87 (d, *J* = 8.4 Hz, 1 H), 7.64-7.62 (m, 3 H), 7.50 (d, *J* = 2.1 Hz, 1 H), 6.24-6.22 (m, 2 H), 6.18 (t, *J* = 2.4 Hz, 1 H), 4.62 (d, *J* = 16.2 Hz, 0.5 H), 4.53 (d, *J* = 15.9 Hz, 0.5 H), 4.30 (dd, *J* = 13.8 Hz, 2.1 Hz, 0.5 H), 4.15 (dd, *J* = 13.5 Hz, 3.0 Hz, 0.5 H), 3.99-3.90 (m, 1 H), 3.77-3.60 (m, 2H), 3.73 (s, 1 H), 3.72 (s, 2 H), 3.45 (d, *J* = 8.1 Hz, 0.5 H), 3.41 (d, *J* = 7.8 Hz, 0.5 H), 3.14 (s, 1.5 H), 3.09 (s, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 229.6 (229.0), 227.6 (227.3), 155.9 (155.7), 146.8, 144.8 (144.7), 144.3, 140.0 (139.9), 136.5 (136.3), 136.0, 134.6, 131.6 (131.4), 105.8, 105.6 (two carbons), 56.5, 55.4 (55.3), 53.6 (53.1, 52.9, 52.8), 45.1 (44.9), 41.9 (41.8); IR (KBr, cm^{-1}): 2957 (w), 1925 (s), 1832 (s), 1703 (m), 1504 (w), 1452 (m), 1408 (m), 1394 (w), 1305 (w), 1224 (m), 1238 (m), 1120 (m), 1049 (m), 767 (w), 721 (w); Anal. calcd for $C_{19}H_{22}N_7O_5BMo$: C, 42.64; H, 4.14; N,18.32. Found: C, 42.67; H, 4.27; N, 18.16.

Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(3,4,5)-(3S)-1-[(R)-dihydro-4,4-dimethyl-2(3H)-furanone-3-yl]oxycarbonyl-3-methoxy-1,2,3,6-tetrahydropyridin-3-yl]molybdenum [(-)-(S,R)-2b] and dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(3,4,5)-(3R)-1-[(R)-dihydro-4,4-dimethyl-2(3H)-furanone-3-yl]oxycarbonyl-3-methoxy-1,2,3,6-tetrahydropyridin-3-yl]molybdenum [(+)-(R,R)-2b]. Molybdenum complex $Mo(CO)_3(DMF)_3$ (25.30 g, 63.36 mmol) was added to a Schlenk flask under a high stream of dry argon. Then, methylene chloride (200 mL), previously deoxygenated by sparging with dry argon for 15 minutes, was injected to the Schlenk flask. A solution of pyridone **1b** (10.30 g, 40.71 mmol) in methylene chloride (25 mL) was added to the dark green solution that immediately turned bright red color. A solution of TBDMSCl (6.14 g, 40.72 mmol) in methylene chloride (25 mL) was injected and the reaction mixture was stirred at room temperature under argon overnight. Solid KTp (16.00 g, 63.46 mmol) was added, and stirring was continued for 30 minutes. Then, TBAF·3 H_2O (30.0 g, 95.00 mmol) was added as solid and stirring was continued for an

additional 30 minutes. Then, iodomethane (60 mL, 136.8 g, 963 mmol) was injected and the reaction mixture was stirred at room temperature for an additional 48 hours. The crude reaction mixture was directly poured on a column of basic alumina and eluted with EtOAc/hexane (1: 3) to afford a mixture of the diastereomeric molybdenum complexes **(-)-(S,R)-2b** and **(+)-(R,R)-2b** (18.45 g, 72 %) as an orange solid, inseparable by chromatography: $R_f = 0.40$ (EtOAc/hexane, 1:1); Anal. calcd for $C_{24}H_{28}N_7O_7$ BMo: C, 45.52; H, 4.46; N, 15.49. Found: C, 45.74; H, 4.52; N, 15.25.

Separation of the Diastereomers (-)-(S,R)-2b and (+)-(R,R)-2b.

Pure diastereomers **(-)-(S,R)-2b** and **(+)-(R,R)-2b** were obtained by crystallization from ethyl acetate. Since the diastereomers tend to crystallize selectively from the eluent solution after chromatography, the following fractions of the product were collected by a stepwise evaporation and filtration of the combined eluents from two preparations carried out as described above (total weight of products **(-)-(S,R)-2b** plus **(+)-(R,R)-2b** was 36.9 g):

Fraction I (26.2 g, molar ratio of diastereomers **(-)-2b/(+)-2b** 60/40);

Fraction II (6.2 g, molar ratio of diastereomers **(-)-2b/(+)-2b** 45/55);

Fraction III (1.5 g, molar ratio of diastereomers **(-)-2b/(+)-2b** 84/14);

Fraction IV (3.0 g, molar ratio of diastereomers **(-)-2b/(+)-2b** 19/81).

A single crystallization of the Fraction I from boiling ethyl acetate (32 mL/1 g) afforded 11.8 g of pure **(-)-(S,R)-2b** (by ^{1}H NMR) as the first crystals and 2.9 g of pure **(+)-(R,R)-2b** (by ^{1}H NMR) as the second crystals. A single crystallization of the Fraction II from boiling ethyl acetate afforded 1.5 g of a mixture of diastereomers **(-)-2b** and **(+)-2b** in molar ratio 85/15. This material was combined with the Fraction III and a single crystallization from boiling ethyl acetate afforded 2.0 g of pure **(-)-(S,R)-2b** (by ^{1}H NMR). Crystallization of the Fraction IV from boiling

ethyl acetate afforded 1.0 g of pure (+)-**(R,R)-2b** (by ^{1}H NMR). Material contained in the combined filtrates from all the above described crystallizations was recrystallized twice from boiling ethyl acetate to afford 3.9 g of pure (+)-**(R,R)-2b** (by ^{1}H NMR). The material remaining in the filtrates (12.0 g, molar ratio of diastereomers (-)-**2b**/(+)-**2b** 35/65) could be further separated.

In summary, from 36.9 g of the mixture of diastereomers, 13.8 g (68%, based on 20.3 g theory) of the diasteromer (-)-**(S,R)-2b** and 7.8 g (48%, based on 16.5 g theory) of the diastereomer (+)-**(R,R)-2b** was obtained and 12.0 g of the mixture of diastereomers was recovered.

The precise diastereomeric excess (98% de) for both (-)-**(S,R)-2b** and (+)-**(R,R)** was determined by HPLC (Table S1, page 27). Additional recrystallization of the diastereomer (-)-**(S,R)-2b** (13.8 g, 98 % de) from ethyl acetate afforded (-)-**(S,R)-2b** (10.0 g, 99% de) with an improved de. The diastereomeric purity of the diastereomer (+)-**(R,R)-2b** (98% de) did not improve by an additional crystallization.

Analytical data for (-)-**(S,R)-2b:** mp = 188 – 192 °C decomp. (EtOAc/hexane); 99% de ($[\alpha]_D$ = -324 °, c 1.01 $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, J = 2.1 Hz, 1 H), 7.82 (d, J = 1.8 Hz, 1 H), 7.63 (br s, 2 H), 7.58 (d, J = 1.5 Hz, 1 H), 7.49 (d, J = 2.4 Hz, 1 H), 6.23 (t, J = 2.1 Hz, 1 H), 6.20 (t, J = 2.4 Hz, 1 H), 6.17 (t, J = 2.4 Hz, 1 H), 5.36 (s, 1 H), 4.57 (d, J = 16.2 Hz, 1 H), 4.21 (dd, J = 14.1 Hz, 2.4 Hz, 1 H), 4.03 (s, 1 H), 4.02 (s, 1 H), 3.95 (dt, J = 8.1 Hz, 1.2 Hz, 1 H), 3.71 (d, J = 15.9 Hz, 1 H), 3.67 (d, J = 7.5 Hz, 1 H), 3.60 (dd, J = 13.8 Hz, 1.8 Hz, 1 H), 3.07 (s, 0.3 H) 3.04 (s, 2.7 H), 1.25 (s, 3 H), 1.19 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 230.3, 226.8, 173.5, 153.6, 146.6, 144.9, 139.8, 136.5, 136.0, 134.7, 132.5, 105.8, 105.7 (two carbons), 76.5, 76.3, 56.9, 55.2, 52.6, 45.4, 42.3, 40.6, 22.8, 19.9; IR (neat, cm^{-1}): 1922 (s), 1830 (s), 1795 (m), 1710 (m), 1239 (s), 1119 (s), 760 (m), 721 (m). The absolute configuration of was assigned by X-ray crystallography of (-)-**2b**.

Analytical data for **(+)-(R,R)-2b:** mp = 215 °C decomp. (EtOAc/hexane); 98% de ($[\alpha]_D$ = +264 °, c 0.29 $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 1.8 Hz, 1 H), 7.86 (d, *J* = 1.8 Hz, 1 H), 7.62-7.61 (m, 3 H), 7.48 (d, *J* = 2.7 Hz, 1 H), 6.23 (t, *J* = 1.8 Hz, 1 H), 6.20 (t, *J* = 2.1 Hz, 1 H), 6.16 (t, *J* = 2.4 Hz, 1 H), 5.38 (s, 1H), 4.49 (d, *J* = 15.2 Hz, 1 H), 4.25 (dd, *J* = 14.1 Hz, 2.7 Hz, 1 H), 4.00 (d, *J* = 2.1 Hz, 2 H), 3.98-3.95 (m, 1 H), 3.84 (d, *J* = 15.9 Hz, 1 H), 3.72 (d, *J* = 8.4 Hz, 1 H), 3.52 (dd, *J* = 14.1 Hz, 1.5 Hz, 1 H), 3.12 (s, 0.3 H), 3.09 (s, 2.7 H), 1.20 (s, 3 H), 1.15 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 229.0, 227.8, 173.5, 153.9, 146.8, 144.8, 139.9, 136.6, 136.1, 134.7, 130.9, 105.8, 105.7, 105.6, 76.4, 76.2, 56.6, 55.6, 52.6, 45.1, 42.5, 40.4, 22.6, 19.9; IR (neat, cm^{-1}): 1926 (s), 1830 (s), 1791 (m), 1714 (s), 1224 (s), 1119 (s), 760 (s), 721 (s).

SmI_2-Mediated Removal of the Pantolactone Chiral Auxiliary.

Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(3,4,5)-(3S)-3-methoxy-1-methoxycarbonyl-1,2,3,6-tetrahydropyridin-3-yl]molybdenum [(-)-2a)] and dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(3,4,5)-(3R)-3-methoxy-1-methoxycarbonyl-1,2,3,6-tetrahydropyridin-3-yl]molybdenum [(+)-2a]. A solution of the molybdenum complex **(-)-(S,R)-2b** (5.07 g, 8.04 mmol) and HMPA (40.0 mL, 41.2 g, 230 mmol) in dry THF (175 mL) was thoroughly deoxygenated by sparging with dry argon for 15 minutes. Then, dry deoxygenated methanol (1.0 mL, 0.8 g, 25 mmol) was added. The commercially available 0.1 M solution of SmI_2 in THF (250 mL, 25.0 mmol) was added dropwise over 60 minutes. The resulting yellow suspension was stirred for an additional 60 minutes at room temperature under argon. The reaction mixture was partitioned between saturated aqueous $NaHCO_3$ and Et_2O; the organic layer was washed with saturated aqueous $NaHCO_3$ and concentrated under reduced pressure to approximately 100 mL. THF (250 mL) was added and the solution was concentrated under reduced pressure to approximately 250 mL. The resulting solution was placed in a 500 mL round-bottomed flask equipped with a magnetic stirrer and cooled to 0 °C. 3N aqueous NaOH (7.5 mL, 22.5 mmol) was added followed by neat methyl chloroformate (0.75 mL, 0.92 g, 9.78 mmol). The reaction

mixture was stirred for 5-10 minutes at 0 °C in air and then partitioned between water and ether. The organic layer was washed with water, dried ($MgSO_4$) and solvent removed under reduced pressure to afford a crude product as a brown oil. The crude product was purified by filtration through a short layer of basic alumina, eluting with EtOAc/hexane (1:3) and later (1:1) to yield the molybdenum complexes **(-)-2a** as a bright orange fluffy solid (3.14 g, 74%) in 98 % ee ($[\alpha]_D$ = -332 °, c 0.113 $CHCl_3$). In the same way, the molybdenum complex **(+)-(R,R)-2b** (5.26 g, 8.33 mmol) afforded **(+)-2a** as a bright orange fluffy solid (3.56 g, 80%) in 98 % ee ($[\alpha]_D$ = +333 °, c 0.116 $CHCl_3$).

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-5-methoxy-1-methoxycarbonyl-1,2-dihydropyridin-2-yl]molybdenum [(±)-3], dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(2R)-5-methoxy-1-methoxycarbonyl-1,2-dihydropyridin-2-yl]molybdenum [(-)-(R)-3] and dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(2S)-5-methoxy-1-methoxycarbonyl-1,2-dihydropyridin-2-yl]molybdenum [(+)-(S)-3]. To a solution of the molybdenum complex **(±)-2a** (7.09 g, 13.30 mmol) in methylene chloride (85 mL) in a Schlenk flask (500 mL) at (-70 °C - -60 °C) under argon was added solid $Ph_3C^+PF_6^-$ (6.10 g, 15.70 mmol). The temperature was allowed to slowly rise to 20 °C over 2 hours so that the increase of temperature from -70 °C to -40 °C occurred over 90 minutes. After stirring the reaction mixture at room temperature for 20 minutes, methylene chloride (100 mL) was added and the dark colored solution was cooled in an ice bath. TEA (12.0 mL, 8.71 g, 86.25 mmol) was added, and the reaction mixture was stirred for 10 minutes at 0 °C under argon. The entire reaction mixture was filtered through a short plug of basic alumina. The crude product was purified by flash chromatography over silica eluting with EtOAc/hexane (1:3) to yield the pure molybdenum complex **(±)-3** (5.45 g, 77%) as a bright orange solid: mp = 210-211 °C decomp. (EtOAc/hexane); R_f = 0.42 (EtOAc/hexane, 1: 3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, J = 2.1 Hz, 0.5 H), 8.23 (d, J = 1.5 Hz, 0.5 H), 8.21 (s, J = 1.8 Hz, 0.5 H), 8.13 (d, J = 1.8 Hz, 0.5 H), 7.77 (d, J = 2.1 Hz, 0.5 H), 7.70 (d, J = 2.1 Hz, 0.5 H), 7.65 (d, J = 2.1 Hz, 0.5 H), 7.63 (d, J =

2.4 Hz, 0.5 H), 7.61 (d, J = 2.1 Hz, 1 H), 7.49-7.48 (m, 1 H), 7.45 (dd, J = 5.7 Hz, 3.3 Hz, 0.5 H), 7.29 (dd, J = 5.7 Hz, 3.6 Hz, 0.5 H), 6.30 (t, J = 2.1 Hz, 0.5 H), 6.27 (t, J = 2.1 Hz, 0.5 H), 6.23-6.19 (m, 2 H), 5.88 (t, J = 1.5 Hz, 0.5 H), 5.71 (t, J = 1.2 Hz, 0.5 H), 4.69-4.65 (m, 1 H), 4.01 (s, 1.5 H), 3.90 (s, 1.5 H), 3.65 (s, 1 H), 3.63 (s, 2 H), 2.84 (t, J = 6.6 Hz, 0.5 H), 2.79 (t, J = 6.6 Hz, 0.5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 229.9 (228.8), 222.6 (223.4), 154.0 (153.8), 150.7 (151.4), 146.3 (146.4), 145.0, 143.3, 140.3 (140.8), 136.2 (136.4), 136.0 (136.1), 134.6, 106.0 (105.9), 105.6 (105.7), 92.7 (92.4), 92.0 (90.2), 60.3 (58.9), 55.5 (55.6), 54.2 (54.1), 51.9 (51.2); IR (KBr, cm^{-1}): 3129 (w), 2952 (w), 1935 (s), 1842 (s), 1713 (s), 1646 (w), 1407 (m), 1439 (m), 1306 (s), 1233 (m), 1123 (m), 1050 (m), 986 (w), 974 (w), 763 (m), 721 (m), 620 (w); Anal. calcd for $C_{19}H_{20}N_7O_5BMo$: C, 42.80; H, 3.78; N, 18.39. Found: C, 43.28; H, 3.92; N, 18.24. HRMS (FAB) calcd for $C_{19}H_{20}N_7O_5BMo$ (M^+) 535.0673, found 535.0699. In the same way, the chiral non-racemic molybdenum complex (-)-**2a** (2.51 g, 4.70 mmol) afforded (-)-**3** as a bright orange solid (1.85 g, 74%) in 98% ee ($[\alpha]_D$ = -140 °, c 0.118 $CHCl_3$). Also, the chiral non-racemic molybdenum complex (+)-**2a** (2.88 g, 5.40 mmol) afforded (+)-**3** as a bright orange solid (2.56 g, 89%) in 99% ee ($[\alpha]_D$ = +149 °, c 0.113 $CHCl_3$). However, care had to be taken to employ only a minimum amount of silica for the final chromatography and to carry out the purification as fast as possible in order to avoid partial racemization of the crude product.

General Procedure for [5+2] Cycloadditions. To a solution of the molybdenum complexes (±)-**3**, (-)-**3** or (+)-**3** (1 mmol) and the appropriate alkene (1.2-1.8 mmol) in methylene chloride (15.0 mL) at 0 °C (ice bath) under argon was injected the indicated volume of 1M solution of $EtAlCl_2$ in hexanes (0.2 - 1.8 mL, 0.2 - 1.8 mmol). The ice bath was removed and the dark orange solutions were stirred at room temperature under argon for the indicated time (10 min - 16 h). The reaction mixtures were then cooled to 0 °C in an ice bath and quenched by the addition of water (1-2 mL). Resulting emulsions were filtered through a short layer of silica, eluting with EtOAc/hexane mixtures. Solvents were removed from the eluent under reduced pressure to yield the crude product or mixture of products as orange solids (95%-100%). The crude products were

purified by flash chromatography over silica, eluting with EtOAc/hexane mixtures to afford the molybdenum complexes **4 - 13** as bright orange moisture and air stable solids.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(8,9,10)-(1S,2R,6S,7S,8R)-4,11-diaza-8-methoxy-11-methoxycarbonyl-4-methyltricyclo[5.3.1.$0^{2,6}$]undec-9-ene-3,5-dione-8-yl]molybdenum [(±)-4]. A solution of the molybdenum complex (±)-**3** (0.100 g, 0.188 mmol) and N-methylmaleimide (0.023 g, 0.208 mmol) in methylene chloride (3.0 mL) was treated with 1M solution of $EtAlCl_2$ in hexanes (0.225 mL, 0.225 mmol) for 10 minutes at room temperature. Eluting the silica with EtOAc/hexane (2:1) afforded 0.120 g (97%) of the crude product as an orange solid. Flash chromatography over silica, eluting with EtOAc/hexane (1:1) and later EtOAc/hexane (2:1), provided the molybdenum complex (±)-**4** (0.082 g, 68%) as an orange solid: mp = 250 °C decomp. (EtOAc/hexane); R_f = 0.12 (EtOAc/hexane, 2: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.02 (dd, *J* = 13.2 Hz, 1.6 Hz, 1 H), 7.63-7.61 (m, 3 H), 7.50 (t, *J* = 2.8 Hz, 1 H), 6.25 (q, *J* = 2.8 Hz, 1 H), 6.22 (t, *J* = 2.4 Hz, 1 H), 6.19- 6.17 (m, 1 H), 5.05 (s, 0.5 H), 4.93 (s, 0.5 H), 4.90 (d, *J* = 4.0 Hz, 0.5 H), 4.83 (d, *J* = 4.0 Hz, 0.5 H), 4.14 (dd, *J* = 7.8 Hz, 4.0 Hz, 0.5 H) 4.09 (dd, *J* = 7.6 Hz, 4.0 Hz, 0.5 H), 3.61 (s, 3 H), 3.52-3.48 (m, 3 H), 3.44 (s, 1.5 H), 3.35 (s, 1.5 H), 2.90 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 227.4 (227.1), 227.0 (226.6), 176.2 (175.8), 175.4 (174.9), 154.1 (154.0), 146.4, 144.8 (144.8), 141.1 (140.9), 136.7 (136.6), 136.2, 134.6, 129.4, 128.8, 106.0, 105.7 (two carbons), 62.3 (61.9), 61.5 (61.2), 60.1 (59.6), 56.8 (56.7), 53.6, 53.4, (53.3), 53.2, (53.1), 52.9; IR (KBr, cm^{-1}): 3120 (w), 2952 (w), 1928 (s), 1848 (s), 1774 (w), 1711 (s), 1503 (w), 1430 (m), 1408 (m), 1308 (m), 1283 (m), 1126 (m), 1126 (m), 997 (w), 770 (w), 721 (w), 662 (w); MS (FAB) m/z (relative intensity) 644 ($M+H^+$, 11), 618 (15), 590 (100), 577 (16); Anal. calcd for $C_{24}H_{25}N_8O_7BMo$: C, 44.74; H, 3.91; N, 17.39. Found: C, 44.78; H, 4.03; N, 17.20.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6R)-8-aza-2-methoxy-8-methoxycarbonyl-6-methylcarbonylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [exo-(±)-5a] and (±)-dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6S)-8-aza-2-

methoxy-8-methoxycarbonyl-6-methylcarbonylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [endo-(±)-5b]. A solution of the molybdenum complex (±)-**3** (0.403 g, 0.756 mmol) and methyl vinyl ketone (0.072 mL, 0.062 g, 0.887 mmol) which was previously distilled from K_2CO_3, in methylene chloride (11.0 mL) was treated with a 1M solution of $EtAlCl_2$ in hexanes (0.380 mL, 0.380 mmol) for 20 minutes at room temperature. Eluting silica with EtOAc/hexane (2:1) and later with EtOAc afforded the crude product 0.48 g (100%) as an orange solid. Flash chromatography over silica (130 g), eluting with EtOAc/hexane (1:1), provided molybdenum complex *exo*-(±)-**5a** (0.294 g, 65%) and molybdenum complex *endo*-(±)-**5b** (0.056 g, 14%). Analytical data for the complex *exo*-(±)-**5a**: mp = 233-235 °C decomp. (EtOAc/hexane); R_f = 0.42 (EtOAc/hexane, 2: 1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 1.5 Hz, 1 H), 7.97 (s, 1 H), 7.64-7.61 (m, 3 H), 7.49 (d, *J* = 1.8 Hz, 1 H), 6.24 - 6.21 (m, 2 H), 6.16 (t, *J* = 2.1 Hz, 1 H), 4.76 (d, *J* = 5.1 Hz, 0.5 H), 4.67 (d, *J* = 3.3 Hz, 0.5 H), 4.63 (d, *J* = 5.4 Hz, 0.5 H), 4.55 (d, *J* = 3.6 Hz, 0.5 H), 4.13-4.04 (m, 1 H), 3.68 (s, 1.5 H), 3.63 (s, 1.5 H), 3.42 (d, *J* = 7.8 Hz, 1 H), 3.43-3.35 (m, 1 H), 3.30 (s, 1.5 H), 3.26 (s, 1.5 H), 2.70-2.60 (m, 0.5 H), 2.56-2.49 (m, 0.5 H), 2.34 (s, 1.5 H), 2.28 (s, 1.5 H), 2.11-1.97 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.7 (228.1), 227.3 (227.8), 206.1 (206.0), 154.3 (154.2), 146.3, 144.7 (144.6), 140.6, 136.5, 136.0, 135.9, 135.7, 134.5, 105.8, 105.6 (two carbons), 62.8 (62.5), 59.5 (59.2, 59.1), 58.9 (59.0, 58.6), 56.7 (56.5), 52.9 (52.7), 52.6 (52.5), 33.9 (33.8), 29.3 (29.2); IR (KBr, cm^{-1}): 2947 (w), 1926 (s), 1837 (s), 1706 (s), 1503 (w), 1407 (m), 1305 (m), 1214 (m), 1170 (w), 1050 (m), 1013 (w), 785 (m), 761 (m), 723 (m); MS (FAB) m/z (relative intensity) 604 ($M+H^+$, 10), 574 (40), 549 (100); Anal. calcd for $C_{23}H_{26}N_7O_6BMo$: C, 45.79; H, 4.34; N, 16.25. Found: C, 45.53; H, 4.42; N, 16.07. Analytical data for the complex *endo*-(±)-**5b**: mp = 240-243 °C decomp. (EtOAc/hexane); R_f = 0.57 (EtOAc/hexane, 2: 1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (d, *J* = 1.5 Hz, 1 H), 7.99-7.93 (m, 1 H), 7.59-7.58 (m, 2 H), 7.48 (d, *J* = 2.1 Hz, 1 H), 7.46-7.42 (m, 1 H), 6.22 (t, *J* = 2.1 Hz, 1 H), 6.18 (t, *J* = 2.1 Hz, 1 H), 6.15 (t, *J* = 2.4 Hz, 1 H), 4.96-4.86 (m, 0.5 H), 4.84-4.76 (m, 0.5 H), 4.65-4.56 (m, 0.5 H), 4.53-4.50 (m, 0.5 H), 3.72 (s, 3 H), 3.66 (dd, *J* = 7.8 Hz, 3.9 Hz, 1 H), 3.50-3.41 (m, 1 H), 3.35 (d, *J* = 6.9 Hz, 1 H), 3.27 (s, 1.5 H), 3.25 (s, 1.5 H), 2.68-2.54 (m, 1

H), 2.41 (s, 3 H), 2.16-1.92 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 229.0, 227.9, 205.3, 174.2, 146.3, 144.7, 140.3 (two carbons), 136.4, 136.0, 135.8, 134.5, 105.8, 105.6 (two carbons), 59.1 (58.5), 57.8 (57.2), 57.0, 56.2, 53.6, 53.0, 33.0 (32.6), 30.8; IR (KBr, cm^{-1}): 3124 (w), 2951 (w), 1934 (s), 1848 (s), 1707 (s), 1503 (w), 1447 (m), 1407 (m), 1447 (m), 1395 (m), 1305 (m), 1215 (m), 1125 (m), 1050 (m), 764 (w), 722 (w); MS (FAB) m/z (relative intensity) 604 ($M+H^+$, 15), 577 (18), 549 (37); Anal. calcd for $C_{23}H_{26}BMoN_7O_6BMo$: C, 45.79; H, 4.34; N, 16.25. Found: C, 45.78; H, 4.39; N, 16.16.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(9,10,11)-(1S,2R,7S,8S,9R)-12-aza-9-methoxy-12-methoxycarbonyltricyclo[6.3.1.0^{2,7}]dodec-10-en-3-on-9-yl]molybdenum [(±)-6] and dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(9,10,11)-(1R,2S,7R,8R,9S)-12-aza-9-methoxy-12-methoxycarbonyltricyclo[6.3.1.0^{2,7}]dodec-10-en-3-on-9-yl]molybdenum [(-)-6]. A solution of the molybdenum complex (±)-**3** (0.513 g, 0.963 mmol) and cyclohexenone (0.125 mL, 0.124 g, 1.291 mmol) in methylene chloride (15.0 mL) was treated with a 1M solution of $EtAlCl_2$ in hexanes (0.500 mL, 0.500 mmol) for 30 minutes at room temperature. Eluting silica with EtOAc/hexane (1:1) and later with EtOAc afforded the crude product 0.693 g (100%) as an orange solid. Flash chromatography over silica (130 g), eluting with EtOAc/hexane (1:2) and gradually increasing the percentage of EtOAc to 100%, provided the recovered molybdenum complex (±)-**3** (0.044 g, 8%) and the molybdenum complex (±)-**6** (0.527 g, 87%) as a bright orange solid: mp = 180-185 °C (EtOAc/hexane); R_f = 0.38 (EtOAc/hexane, 2: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.0 Hz, 1 H), 7.97 (d, *J* = 1.6 Hz, 0.7 H), 7.94 (d, *J* = 1.6 Hz, 0.3 H), 7.62 (d, *J* = 2.0 Hz, 0.5 H), 7.60 (d, *J* = 0.4 Hz, 2.5 H), 7.48 (d, *J* = 2.4 Hz, 1 H), 6.22 (t, *J* = 2.4 Hz, 1 H), 6.21 (t, *J* = 2.4 Hz, 1 H), 6.16 (t, *J* = 2.0 Hz, 1 H), 4.97 (d, *J* = 4.4 Hz, 0.3 H), 4.95 (d, *J* = 4.4 Hz, 0.7 H), 4.56 (s, 0.7 H), 4.43 (s, 0.3 H), 4.09 (d, *J* = 4.4 Hz, 0.5 H), 4.07 (d, *J* = 4.0 Hz, 0.5 H), 3.69 (s, 0.9 H), 3.68 (s, 2.1 H), 3.41 (d, *J* = 7.6 Hz, 1 H), 3.32 (s, 2.1 H), 3.23 (s, 0.9 H), 3.11 (d, *J* = 8.8 Hz, 0.3 H), 3.09 (d, *J* = 8.8 Hz, 0.7 H), 2.99-2.90 (m, 1 H), 2.47-2.42 (m, 1 H), 2.21-2.04 (m, 2 H), 1.91-1.84 (m, 1 H), 1.74-1.54 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

227.9, 227.5, 211.1 (210.5), 154.3 (153.5), 146.3, 144.7 (144.6), 140.8 (140.5), 136.4, 136.0, 135.6, 134.4 (134.6), 105.8, 105.6, 64.4, 63.4 (63.1), 62.5, 59.1 (58.9), 58.7 (58.6), 56.6 (56.8), 53.1 (52.9), 52.7 (52.6), 49.6 (49.4), 38.7 (38.7), 28.4 (28.6), 21.1 (21.2); IR (KBr, cm^{-1}): 2947 (w), 1843 (s), 1932 (s), 1704 (s), 1503 (m), 1448 (m), 1407 (m), 1305 (m), 1212 (m), 1117 (m), 1049 (m), 1012 (w), 983 (w), 763 9m), 721 (m); MS (FAB) m/z (relative intensity) 630 ($M+H^+$, 18), 603 (21), 575 (100); Anal. calcd for $C_{25}H_{28}N_7O_6BMo$: C, 47.71; H, 4.48; N, 15.58. Found: C, 47.85; H, 4.59; N, 15.58. In the same way, the chiral non-racemic (98% ee) molybdenum complex **(-)-3a** (0.451 g, 0.846 mmol) afforded **(-)-6** as a bright orange solid (0.472 g, 88%) in 97% ee ($[\alpha]_D$ = -369 °, c 0.110 $CHCl_3$).

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6R)-8-aza-2-methoxy-6,8-bis(methoxycarbonyl)bicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [(±)-7] and dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1R,2S,5R,6S)-8-aza-2-methoxy-6,8-bis(methoxycarbonyl)bicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [(-)-7]. A solution of the molybdenum complex **(±)-3** (0.498 g, 0.935 mmol) and methyl acrylate (0.100 mL, 0.095 g, 1.110 mmol) which was previously filtered through basic alumina, in methylene chloride (15.0 mL) was treated with a 1M solution of $EtAlCl_2$ in hexanes (1.825 mL, 1.825 mmol) for 55 minutes at room temperature. Eluting silica with EtOAc afforded the crude product 0.593 g (102%) as an orange solid. Flash chromatography ~~over silica (130 g)~~ eluting with EtOAc/hexane (1: 2) provided the recovered molybdenum complex **(±)-3** (0.026 g, 5%) and the molybdenum complex **(±)-7** (0.509 g, 88%) as a bright orange solid: mp = 177-179 °C (EtOAc/hexane); R_f = 0.45 (EtOAc/hexane, 1: 1); ^1H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, J = 1.8 Hz, 1 H), 7.97 (s, 1H), 7.62-7.60 (m, 3 H), 7.48 (d, J = 2.1 Hz, 1 H), 6.22 (t, J = 2.4 Hz, 1 H), 6.21 (t, J = 2.1 Hz, 1 H), 6.16 (t, J = 2.1 Hz, 1 H), 4.77 (d, J = 5.4 Hz, 0.5 H), 4.72 (d, J = 3.6 Hz, 0.5 H), 4.65 (d, J = 4.5 Hz, 0.5 H), 4.61 (d, J = 3.9 Hz, 0.5 H), 4.11-4.04 (m, 1 H), 3.71-3.67 (m, 6 H), 3.38 (dd, J = 7.5 Hz, 0.9 Hz, 1 H), 3.28-3.24 (m, 4 H), 2.55-2.44 (m, 1 H), 2.26-2.18 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.5, 227.8 (227.4), 173.9, 154.6, 146.4, 144.8 (144.7), 140.7, 136.5, 136.0,

135.8 (135.6), 134.5, 105.8, 105.6, 62.5 (62.3), 60.9, 60.4, 58.4 (58.9), 56.6 (56.7), 52.8, 52.5, 52.4, 50.9 (50.3), 35.7 (35.9); IR (KBr, cm^{-1}): 3120 (w), 2951 (w), 1933 (s), 1847 (s), 1732 (m), 1708 (m), 1504 (w), 1444 (m), 1407 (m), 1394 (m), 1306 (m), 1209 (m), 1116 (m), 1012 (w), 982 (w), 786 (w), 763 (w), 721 (w); Anal. calcd for $C_{23}H_{26}N_7O_7BMo$: C, 44.61; H, 4.23; N, 15.83. Found: C, 44.48; H, 4.27; N, 15.56. In the same way, the chiral non-racemic (98% ee) molybdenum complex **(-)-3a** (0.192 g, 0.361 mmol) afforded **(-)-7** as a bright orange solid (0.151 g, 70%) in 98% ee ($[\alpha]_D$ = -292 °, c 0.123 $CHCl_3$).

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6R)-8-aza-2-methoxy-6,8-bis(methoxycarbonyl)-6-methylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [(±)-8] and dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6R)-8-aza-2-methoxy-6,8-bis(methoxycarbonyl)-6-methylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [(+)-8]. A solution of the molybdenum complex **(±)-3** (0.509 g, 0.955 mmol) and methyl methacrylate (0.124 mL, 0.116 g, 1.159 mmol) that was previously filtered through basic alumina, in methylene chloride (20.0 mL) was treated with a 1M solution of $EtAlCl_2$ in hexanes (1.400 mL, 1.400 mmol) for 16 hours at room temperature. Eluting silica with EtOAc/hexane (1: 1) afforded the crude product 0.573 g (95 %) as an orange solid. Flash chromatography over silica (150 g), eluting with EtOAc/hexane (1:3) provided the recovered molybdenum complex **(±)-3** (0.111 g, 21%) and the molybdenum complex **(±)-8** (0.279 g, 47%) as an orange solid: mp = 246-247 °C decomp. (EtOAc/hexane); R_f = 0.28 (EtOAc/hexane, 1: 2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.0 Hz, 0.5 H); 8.43 (d, *J* = 2.0 Hz, 0.5 H), 8.01 (t, *J* = 2.0 Hz, 1 H), 7.65 (d, *J* = 1.6 Hz, 1 H); 7.61-7.60 (m, 2 H), 7.49 (t, *J* = 2.0 Hz, 1 H), 6.23 (q, *J* = 2.0 Hz, 1 H), 6.22 (t, *J* = 2.0 Hz, 1 H), 6.16 (t, *J* = 2.0, 1 H), 4.68 - 4.65 (m, 1 H), 4.56-4.53 (m, 1 H), 3.92-2.85 (m, 1 H), 3.69 (s, 1.5 H), 3.68 (s, 1.5 H), 3.66 (s, 1.5 H), 3.64 (s, 1.5 H), 3.59 (d, *J* = 7.6 Hz, 1 H), 3.37 (s, 1.5 H), 3.33 (s, 1.5 H), 3.12-3.05 (m, 1 H), 1.76 (s, 3 H), 1.70 (d, *J* = 10.0 Hz, 0.5 H), 1.67 (d, *J* = 10.4 Hz, 0.5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.4, 228.0, 176.9 (176.9), 154.0 (153.9), 146.4, 144.7 (144.6), 141.0 (141.0), 136.4 (136.5), 136.0, 135.5 (135.6), 134.5, 105.9, 105.6, 63.4, 62.9, 58.7

(58.3), 57.7 (57.3), 56.6 (56.5), 54.6 (54.9), 54.5 (54.4), 53.1 (52.8), 52.7 (52.6), 42.4 (42.8), 22.0 (21.8); IR (KBr, cm^{-1}): 2950 (w), 1936 (s), 1852 (s), 1731 (m), 1705 (m), 1504 (w), 1480 (w), 1442 (m), 1407 (m), 1395 (m), 1322 (m), 1305 (m), 1261 (m), 1216 (m), 1129 (m), 1051 (m), 1014 (m), 982 (m), 786 (m), 754 (m), 719 (m); Anal. calcd for $C_{24}H_{28}N_7O_7BMo$: C, 45.52; H, 4.45; N, 15.48. Found: C, 45.44; H, 4.55; N, 15.31. In the same way, the chiral non-racemic (96% ee) molybdenum complex (+)-**3a** (0.192 g, 0.0.361 mmol) afforded (+)-**8** as a bright orange solid (0.062 g, 51%) in 65% ee ($[\alpha]_D$ = +191 °, c 0.148, $CHCl_3$).

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6R)-8-aza-6-formyl-2-methoxy-8-methoxycarbonyl-6-methylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [exo-(±)-9a)], dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1R,2S,5R,6S)-8-aza-6-formyl-2-methoxy-8-methoxycarbonyl-6-methyl-bicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [exo-(-)-9a], (±)-dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6S)-8-aza-6-hydrocarbonyl-2-methoxy-8-methoxycarbonyl-6-methylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [endo-(±)-9b] and dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1R,2S,5R,6R)-8-aza-6-formyl-2-methoxy-8-methoxycarbonyl-6-methylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [endo-(-)-9b]. A solution of the molybdenum complex (±)-**3** (0.203 g, 0.382 mmol) and methacrolein (0.040 mL, 0.034 g, 0.483 mmol) in methylene chloride (6.0 mL) was treated with a 1M solution of $EtAlCl_2$ in hexanes (0.100 mL, 0.100 mmol) for 40 minutes at room temperature. Eluting silica with EtOAc afforded the crude product 0.257 g (110 %) as an orange solid. Flash chromatography over silica (100 g), eluting with EtOAc/hexane (1:3) and later with EtOAc/hexane (1:2), provided the recovered molybdenum complex (±)-**3** (0.050 g, 25%), molybdenum complex *exo*-(±)-**9a** (0.105 g, 45%) as an orange solid and molybdenum complex *endo*-(±)-**9b** (0.066 g, 29%) as a bright orange solid. Analytical data for the complex *exo*-(±)-**9a**: mp = 173-175 °C decomp. (EtOAc/hexane); R_f = 0.25 (EtOAc/hexane, 1: 1); ^1H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 0.5 H), 9.46 (s, 0.5 H), 8.42 (d, *J* = 2.0 Hz, 1 H), 7.98 (dd, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.62 (s, 3 H), 7.49 (s, 1 H), 6.24-6.21 (m, 2 H), 6.16 (t, *J* = 2.0 Hz, 1 H),

4.68 (d, J = 6.4 Hz, 0.5 H), 4.54-4.53 (m, 1 H), 4.42 (d, J = 3.6 Hz, 0.5 H), 3.87-3.81 (m, 1 H), 3.65 (s, 1.5 H), 3.63 (s, 1.5 H), 3.62-3.59 (m, 1 H), 3.34 (s, 1.5 H), 3.28 (s, 1.5 H), 2.84-2.75 (m, 1 H), 1.65 (s, 3 H), 1.64-1.60 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.5 (228.2), 227.8 (227.8), 201.5 (201.4), 153.8 (153.6), 146.3, 144.8 (144.7), 140.8 (140.7), 136.5 (136.5), 136.2 (135.8), 136.1, 134.5, 105.9, 105.6, 60.11, 59.7, 59.4, 58.3, 57.9 (57.8), 57.1, 56.8, 56.6, 39.1 (39.0), 18.2 (17.9); IR (KBr, cm^{-1}): 2952 (w), 1935 (s), 1847 (s), 1723 (m), 1700 (m), 1503 (w), 1446 (m), 1407 (m), 1395 (m), 1321 (w), 1305 (m), 1218 (m), 1124 (m), 1049 (m), 1017 9w), 763 (m), 721 (m); Anal. calcd for $C_{23}H_{26}N_7O_6BMo$: C, 45.79; H, 4.34; N, 16.25. Found: C, 46.01; H, 4.52; N, 16.04. Analytical data for the complex *endo*-(±)-**9b**: mp = 207-209 °C decomp. (EtOAc/hexane); R_f = 0.43 (EtOAc/hexane, 1: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (d, J = 2.4 Hz, 1 H), 8.39 (s, 1 H), 7.92 (dd, J = 10.4 Hz, 2.0 Hz, 1 H), 7.59-7.58 (m, 2 H), 7.50-7.46 (m, 2 H), 6.21 (q, J = 2.0 Hz, 1 H), 6.18 (q, J = 2.0 Hz, 1 H), 6.14 (t, J = 2.0 Hz, 1 H), 4.72 (d, J = 5.6 Hz, 0.5 H), 4.61 (d, J = 5.6 Hz, 0.5 H), 4.49 (d, J = 2.8 Hz, 0.5 H), 4.37 (dd, J = 3.6 Hz, 0.8 Hz, 0.5 H); 3.85-3.80 (m, 1 H), 3.74 (s, 1.5 H), 3.73 (s, 1.5 H), 3.34 (dd, J = 4.6 Hz, 1.2 Hz, 0.5 H), 3.32 (dd, J = 4.6 Hz, 1.2 Hz, 0.5 H), 3.24 (s, 1.5 H), 3.18 (s, 1.5 H), 2.75 (t, J = 12.4 Hz, 1 H), 1.78-1.67 (m, 1 H), 1.28 (s, 1.5 H), 1.22 (s, 1.5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.8 (228.1), 227.7 (227.3), 202.1 (201.8), 154.2, 146.3, 144.8 (144.7), 140.6 (140.4), 136.8 (136.6), 136.5 (136.4), 136.1, 134.5, 105.8, 105.6, 63.8, 62.9, 62.0 (61.8), 59.4 (58.8), 58.0 (57.3), 57.0 (56.8), 53.6 (53.5), 52.9 (52.9), 40.2 (39.7), 23.4 (23.4); IR (KBr, cm^{-1}): 2952 (w), 1936 (s), 1849 (s), 1706 (m), 1504 (w), 1448 (m), 1407 (m), 1320 (m), 1305 (m), 1213 (m), 1125 (m), 1049 (m), 1017 (w), 982 (w), 762 (m), 721 (m); Anal. calcd for $C_{23}H_{26}N_7O_6BMo$: C, 45.79; H, 4.34; N, 16.25. Found: C, 46.03; H, 4.44; N, 16.06. In the same way, the chiral non-racemic (98% ee) molybdenum complex (-)-**3a** (0.186 g, 0.348 mmol) afforded [*exo*-(-)-**9a**] as a bright orange solid (0.084 g, 40%) in 95.5 % ee ($[\alpha]_D$ = -205 °, c 0.200 $CHCl_3$) and [*endo*-(-)-**9b**] as a bright orange solid (0.045 g, 21%) in 95.5 % ee ($[\alpha]_D$ = -259 °, c 0.099 $CHCl_3$).

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6R,7R)-8-aza-7-ethyl-6-formyl-2-methoxy-8-methoxycarbonylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [exo-(±)-10a] and (±)-dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6S,7S)-8-aza-7-ethyl-6-formyl-2-methoxy-8-methoxycarbonylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [endo-(±)-10b]. A solution of the molybdenum complex (±)-**3** (0.494 g, 0.927 mmol) and *trans*-2-pentenal (0.116 mL, 0.099 g, 1.186 mmol) in methylene chloride (15.0 mL) was treated with a 1M solution of $EtAlCl_2$ in hexanes (0.450 mL, 0.450 mmol) for 60 minutes at room temperature. Eluting silica with EtOAc afforded the crude product 0.603 g (100%) as an orange solid. Flash chromatography over silica (150 g), eluting with EtOAc/hexane (1:4) and later with EtOAc/hexane (1:3), provided the recovered molybdenum complex (±)-**3** (0.071 g, 14%), molybdenum complex *exo*-(±)-**10a** (0.297 g, 42%) as a dark orange solid and molybdenum complex *endo*-(±)-**10b** (0.183 g, 32%) as a bright orange solid. Analytical data for the complex *exo*-(±)-**10a**: mp = 237-239 °C decomp. (EtOAc/hexane); R_f = 0.29 (EtOAc/hexane, 1: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 3.2 Hz, 0.5 H), 9.56 (d, *J* = 2.8 Hz, 0.5 H), 8.38 (d, *J* = 2.0 Hz, 1 H), 7.89 (s, 1 H), 7.63-7.62 (m, 2 H), 7.58 (d, *J* = 1.6 Hz, 1 H), 7.48 (d, *J* = 1.6 Hz, 1 H), 6.23 (t, *J* = 2.0 Hz, 1 H), 6.21 (t, *J* = 2.4 Hz, 1 H), 6.18 (t, *J* = 2.0 Hz, 1 H), 4.77 (d, *J* = 5.6 Hz, 0.5 H), 4.70-4.67 (m, 1 H), 4.58 (d, *J* = 4.0 Hz, 0.5 H), 4.08-4.02 (m, 1 H), 3.71 (s, 1.5 H), 3.69 (s, 1.5 H), 3.35 (d, *J* = 8.0 Hz, 1 H), 3.07 (s, 1.5 H), 3.05 (s, 1.5 H), 2.80-2.75 (m, 1 H), 2.67-2.56 (m, 1 H), 1.82-1.73 (m, 1 H), 1.63-1.57 (m, 1 H), 1.03 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 229.5 (228.8), 227.9 (228.5), 199.6, 154.0 (153.8), 146.3, 145.0 (144.9), 140.2, 138.1 (137.9), 136.6, 136.0, 134.5, 105.8, 105.7, 65.7 (65.6), 61.2 (61.7), 61.1 (60.7), 58.0, 57.3, 54.6, 53.9 (53.8), 53.0, 49.5 (49.2), 23.9, 13.3; IR (KBr, cm^{-1}): 2952 (w), 1931 (s), 1904 (s), 1844 (s), 1822 (s), 1718 (m), 1695 (m), 1522 (w), 1504 (w), 1447 (m), 1407 (m), 1395 (m), 1306 (m), 1219 (m), 1117 (m), 1050 (m), 1023 (w), 981 (w), 787 (w), 760 (m), 723 (m); Anal. calcd for $C_{24}H_{28}N_7O_6BMo$: C, 46.70; H, 4.57; N, 15.88. Found: C, 46.55; H, 4.60; N, 15.63. Analytical data for the complex *endo*-(±)-**10b**: mp = 210-212 °C decomp. (EtOAc/hexane); R_f = 0.40 (EtOAc/hexane, 1: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15-10.14

(m, 1 H), 8.40 (t, J = 2.4 Hz, 1 H), 7.99 (d, J = 2.0 Hz, 0.5 H), 7.95 (d, J = 1.6 Hz, 0.5 H), 7.61-7.59 (m, 2 H), 7.54 (d, J = 1.5 Hz, 0.5 H), 7.51 (d, J = 2.0 Hz, 0.5 H), 7.48 (t, J = 2.0 Hz, 1 H), 6.22 (q, J = 2.4 Hz, 1 H), 6.18 (q, J = 2.4 Hz, 1 H), 6.15 (t, J = 2.0 Hz, 1 H), 4.97 (t, J = 4.4 Hz, 0.5 H), 4.87 (t, J = 4.4 Hz, 0.5 H), 4.53 (s, 0.5 H), 4.37 (s, 0.5 H), 3.87-3.83 (m, 1 H), 3.74 (s, 0.9 H), 3.72 (s, 2.1 H), 3.38 (t, J = 6.4 Hz, 1 H), 3.32 (s, 0.9 H), 3.25 (s, 2.1 H), 2.87 (t, J = 4.9 Hz, 0.7 H), 2.80 (t, J = 4.8 Hz, 0.3 H), 2.77-2.72 (m, 1 H), 1.56-1.47 (m, 0.5 H), 1.46-1.38 (m, 0.5 H), 1.35-1.20 (m, 1 H), 0.99 (t, J = 7.2 Hz, 1.5 H), 0.96 (t, J = 7.2 Hz, 1.5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.1 (228.4), 228.0 (227.6), 200.4 (200.9), 154.6 (154.2), 146.3, 144.6 (144.7), 140.6 (140.8), 136.5 (136.4), 136.1, 135.6 (135.0), 134.5, 105.8, 105.6, 64.0 (64.7), 62.7 (61.9), 58.8, 57.9 (57.7), 57.0 (56.8), 57.0, 53.4 (53.6), 52.8 (53.0), 50.1 (50.7), 28.7 (28.8), 12.4 (12.7); IR (KBr, cm^{-1}): 2959 (w), 1941 (s), 1936 (s), 1708 (m), 1504 (w), 1448 (m), 1407 (m), 1394 (m), 1304 (m), 1253 (w), 1211 (m), 1116 (m), 1049 (m), 1071 (w), 1049 (m), 1021 (w), 763 (m), 720 (m); Anal. calcd for $C_{24}H_{28}N_7O_6BMo$: C, 46.70; H, 4.57; N, 15.88. Found: C, 46.88; H, 4.62; N, 15.60.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6S)-8-aza-2-methoxy-8-methoxycarbonyl-3'-oxaspiro[bicyclo[3.2.1]oct-3-ene-2-yl-6,1'-cyclopentane-2'-on]molybdenum [exo-(±)-11a] and (±)-dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6R)-8-aza-2-methoxy-8-methoxycarbonyl-3'-oxaspiro[bicyclo[3.2.1]oct-3-ene-2-yl-6,1'-cyclopentane-2'-on]molybdenum [endo-(±)-11b]. A solution of the molybdenum complex (±)-**3** (0.224 g, 0.420 mmol) and α-methylene-γ-butyrolactone (0.047 mL, 0.052 g, 0.536 mmol) in methylene chloride (7.0 mL) was treated with a 1M solution of $EtAlCl_2$ in hexanes (0.750 mL, 0.750 mmol) for 16 hours at room temperature. Eluting silica with EtOAc afforded the crude product as an orange solid. Due to a poor solubility, the crude product was deposited on celite and the solid was loaded on top of the chromatographic column. Flash chromatography over silica (100 g) eluting with EtOAc/hexane (2:1) and later with EtOAc/hexane (3:1), provided the molybdenum complex *endo*-(±)-**11b** (0.069 g, 26%) as an

orange solid and molybdenum complex *exo*-(±)-**11a** (0.159 g, 60%) as an orange solid. Analytical data for the complex *exo*-(±)-**11a**: mp = 256-257 °C decomp. (EtOAc/hexane); R_f = 0.27 (EtOAc/hexane, 2: 1); ^{1}H NMR (400 MHz, DMSO) δ 8.31 (d, *J* = 2.0 Hz, 0.7 H), 8.27 (d, *J* = 2.0 Hz, 0.3 H), 8.35-8.01 (m, 1 H), 7.90 (t, *J* = 4.0 Hz, 1 H), 7.86 (d, *J* = 2.4 Hz, 1 H), 7.82 (d, *J* = 2.0 Hz, 1 H), 7.81 (d, *J* = 2.0 Hz, 1 H), 6.35 (t, *J* = 2.4 Hz, 1 H), 6.32 (t, *J* = 2.4 Hz, 1 H), 6.29 (t, *J* = 2.0 Hz, 1 H), 4.50 (q, *J* = 8.8 Hz, 1 H), 4.42 (q, *J* = 6.4 Hz, 1 H), 4.38-4.27 (m, 3 H), 3.55 (d, *J* = 6.8 Hz, 1 H), 3.50 (s, 1 H), 3.45 (s, 2 H), 3.23 (s, 2 H), 3.18-3.12 (m, 1 H), 3.16 (s, 1 H), 2.60-2.51 (m, 1 H), 2.44-2.39 (m, 0.3 H), 2.35-2.30 (m, 0.7 H), 1.98 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO) δ 228.8, 227.9 (228.3), 180.0 (179.6), 153.6 (152.2), 145.6 (145.5), 144.0, 141.9 (142.8), 138.9, 137.2 (137.0), 136.4, 135.1, 106.2, 105.8, 65.8 (65.7), 60.9, 59.9 (59.8), 58.8 (58.3), 57.5 (57.7), 56.6, 53.7 (53.3), 53.0 (53.1), 51.9, 41.7 (42.1), 32.1 (31.9); IR (KBr, cm^{-1}): 2949 (w), 1940 (s), 1843 9s), 1756 (m), 1697 (m), 1503 (w), 1445 (m), 1393 (m), 1323 (m), 1304 (m), 1213 (m), 1169 (m), 1050 (m), 1022 (m), 771 (m), 760 (m); HRMS (FAB) calcd for $C_{24}H_{27}N_7O_7BMo$ (M^+) 633.1041, found 633.1068, calcd for $C_{23}H_{27}N_7O_6BMo$ (M-CO^+) 605.1092, found 605.1113; Anal. calcd for $C_{24}H_{26}N_7O_7BMo$: C, 45.66; H, 4.15; N, 15.53. Found: C, 45.75; H, 4.44; N, 15.08. Analytical data for the complex *endo*-(±)-**11b**: mp = 253-254 °C decomp. (EtOAc/hexane); R_f = 0.48 (EtOAc/hexane, 2: 1); ^{1}H NMR (400 MHz, DMSO) δ 8.31 (dd, *J* = 8.8 Hz, 2.0 Hz, 1 H), 7.89 (q, *J* = 2.0 Hz, 1 H), 7.85 (td, *J* = 5.6 Hz, 2.0 Hz, 2 H), 7.83 (s, 1.5 H), 7.77 (d, *J* = 2.0 Hz, 0.5 H), 6.35 (t, *J* = 2.0 Hz, 1 H), 6.31-6.29 (m, 2 H), 4.55 (d, *J* = 3.6 Hz, 0.5 H), 4.51-4.48 (m, 1.5 H), 4.43-4.37 (m, 2 H), 4.33 (t, *J* = 8.0 Hz, 1 H), 4.01-3.96 (m, 1 H), 3.59 (s, 1.5 H), 3.58 (s, 1.5 H), 3.51 (dd, *J* = 6.8 Hz, 4.8 Hz, 1 H), 3.29 (s, 1.5 H), 3.22 (s, 1.5 H), 2.44 (d, *J* = 2.8 Hz, 0.5 H), 2.41 (d, *J* = 3.2 Hz, 0.5 H), 2.27-2.15 (m, 1 H), 2.12-2.01 (m, 1 H); ^{13}C NMR (100 MHz, DMSO) δ 229.1 (228.8), 228.7 (228.5), 177.2 (177.1), 153.3 (153.3), 145.7 (145.6), 143.9, 141.5, 141.3, 137.0, 136.5 (136.4), 135.1 (135.0), 106.2, 105.8, 65.1 (65.0), 62.6 (61.9), 58.3, 57.7, 56.8, 56.5 (56.4), 55.6 (55.5), 54.3, 52.4 (52.4), 43.9 (43.1), 37.0 (36.8); IR (KBr, cm^{-1}): 1931 (s), 1844 (s), 1769 (m), 1707 (m), 1487 (w), 1504 (w), 1445 (m), 1407 (m), 1396 (m), 1325 (w), 1304 (m), 1251 (w), 1207 (m), 1171 (w), 1116 (m), 1049 (m), 1018 (m),

984 (w), 786 (w), 765 (m), 723 (m); HRMS (FAB) calcd for $C_{24}H_{26}N_7O_7BMo$ (M^+) 63.1041, found 633.1070; Anal. calcd for $C_{24}H_{26}N_7O_7BMo$: C, 45.66; H, 4.15; N, 15.53. Found: C, 45.99; H, 4.37; N, 14.95.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,6R)-8-aza-2-methoxy-6,8-bis(methoxycarbonyl)-7-(1'-methoxycarbonylmethylidene)bicyclo[3.2.1]oct-3-ene-2-yl]molybdenum [(±)-12]. A solution of the molybdenum complex (±)-3 (0.104 g, 0.195 mmol) and dimethyl 2,3-pentadienoate[4] (1.0 mL from a solution of 0.1590 g of neat allene in 4.0 mL of methylene chloride, 0.040 g, 0.256 mmol) in methylene chloride (3.0 mL) was treated with a 1M solution of $EtAlCl_2$ in hexanes (0.220 mL, 0.220 mmol) for 35 minutes at room temperature. Eluting silica with EtOAc/hexane mixtures 1: 2 and 1: 1 afforded the molybdenum complex (±)-**12** (0.077 g, 57%) as an orange solid: mp = 134 °C decomp. (EtOAc/hexane); R_f = 0.31 (EtOAc/hexane, 1: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 2.4 Hz, 0.2 H), 8.43 (ap t, J = 3.2 Hz, 0.8 H), 8.04 (d, J = 2.4 Hz, 0.2 H), 7.96 (dd, J = 6.0 Hz, 0.8 H), 7.60 (ap t, J = 2.4 Hz, 2 H), 7.55 (d, J = 1.6 Hz, 1 H), 7.48 (t, J = 1.6 Hz, 1 H), 6.24 (t, J = 2.0 Hz, 1 H), 6.21-6.18 (m, 2 H), 6.16 (t, J = 2.0 Hz, 1 H), 4.97 (s, 0.5 H), 4.86 (s, 0.5 H), 4.74 (d, J = 4.0 Hz, 0.5 H), 4.61 (d, J = 2.8 Hz, 0.5 H), 4.27 (d, J = 4.4 Hz, 1 H), 4.09-4.04 (m, 1 H), 3.81 (d, J = 2.4 Hz, 1 H), 3.71 (d, J = 1.2 Hz, 3 H), 3.69 (s, 1 H), 3.67 (s, 1 H), 3.65 (d, J = 2.0 Hz, 3 H), 3.44 (d, J = 7.6 Hz, 1 H), 3.22 (s, 0.5 H), 3.20 (s, 1.25 H), 3.17 (s, 1.25 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.3 (227.6), 226.9 (226.3), 170.7, 166.7, 159.3 (159.0), 154.5, 146.5 (two carbons), 145.0, 144.9, 140.4, 136.6, 136.2, 134.5, 130.5 (130.3), 113.2 (112.7), 106.0, 105.8 (two carbons), 63.7 (63.2), 61.2 (60.7), 60.5 (60.2), 57.5 (57.4), 56.9 (56.7), 53.5 (53.1, 53.0), 51.7 (52.6, 52.5); IR (neat, cm^{-1}): 1938 (s), 1857 (s), 1718 (s), 1444 (m), 1305 (m), 1208 (m), 1050 (m), 764 (m), 721 (m); Anal. calcd for $C_{26}H_{28}N_7O_9BMo$: C, 45.30; H, 4.09; N, 14.22. Found: C, 45.47; H, 4.27; N, 14.00.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S)-8-aza-6-ethoxycarbonyl-2-methoxy-8-methoxycarbonylbicyclo[3.2.1]oct-3,6-diene-2-

yl]molybdenum [(±)-13]. A solution of the molybdenum complex (±)-**3** (0.051 g, 0.096 mmol) and ethyl propiolate (0.013 mL, 0.0126 g, 0.128 mmol) in methylene chloride (2.0 mL) was treated with a 1M solution of $EtAlCl_2$ in hexanes (0.150 mL, 0.150 mmol) for 2.5 h at room temperature. Eluting silica with EtOAc/hexane (1: 3) and later with EtOAc/hexane (1: 2), provided the recovered molybdenum complex (±)-**3** (0.054 g, 11%) and molybdenum complex (±)-**13** (0.041g, 68%) as a dark orange solid: mp = 234-235 °C decomp. (EtOAc/hexane); R_f = 0.63 (EtOAc/hexane, 1: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 2.0 Hz, 0.5 H), 8.44 (d, *J* = 2.0 Hz, 0.5 H), 8.40 (d, *J* = 2.0 Hz, 0.5 H), 8.17 (d, *J* = 2.0 Hz, 0.5 H), 7.81 (d, *J* = 2.4 Hz, 0.5 H), 7.69 (d, *J* = 2.0 Hz, 0.5 H), 7.60 (d, *J* = 2.0 Hz, 0.5 H), 7.58 (d, *J* = 1.6 Hz, 0.5 H), 7.57-7.56 (m, 1 H), 7.47 (ap t, *J* = 1.6 Hz, 1 H), 6.86 (dd, *J* = 6.0 Hz, 1.6 Hz, 0.5 H), 6.75 (ap d, *J* = 0.8 Hz, 0.75 H), 6.74 (d, *J* = 1.6 Hz, 0.25 H), 6.72 (d, *J* = 1.2 Hz, 0.5 H), 6.24-6.22 (m, 2 H), 6.19-6.16 (m, 1 H), 5.15 (dt, *J* = 7.6 Hz, 1.6 Hz, 1 H), 4.41 (s, 0.25 H), 4.38-4.32 (m, 2 H), 4.19 (s, 0.75 H), 3.92 (s, 1.25 H), 3.81 (s, 1.75 H), 3.43 (d, *J* = 6.4 Hz, 0.25 H), 3.41 (d, *J* = 6.4 Hz, 0.25 H), 3.36 (s, 2 H), 3.35 (s, 1 H), 3.33 (d, *J* = 6.4 Hz, 0.25 H), 3.31 (d, *J* = 6.4 Hz, 0.25 H), 1.39 (td, *J* = 7.2 Hz, 2.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 231.2 (229.6), 225.8 (224.3), 161.6 (161.5), 155.5 (155.4), 148.3 (147.9), 147.2 (147.1), 146.1, 143.9, 143.3 (143.5), 140.6 (139.9), 136.3 (136.5), 135.8 (136.0), 134.7, 106.0 (105.9), 105.7 (105.8), 97.4, 93.7, 85.0 (84.9), 65.1 (63.5), 62.6 (62.4), 61.0 (61.0), 54.2 (53.7, 53.6), 52.3 (52.1), 14.5; IR (neat, cm^{-1}): 1961 (s), 1857 (s), 1714 (m), 1320 (m), 1123 (m), 1050 (m), 760 (m), 721 (m); Anal. calcd for $C_{24}H_{26}N_7O_7BMo$: C, 45.66; H, 4.15; N, 15.53. Found: C, 45.59; H, 4.23; N, 15.36.

Modifications of the Functional Group in the Cycloadduct (±)-6.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(9,10,11)-1S,2R,3R,7S,8S,9R)-12-aza-3-hydroxy-9-methoxy-12-methoxycarbonyltricyclo[6.3.1.0^{2,7}]dodec-10-en-9-yl]molybdenum [(±)-(14)]. To a stirred solution of the molybdenum complex (±)-**6** (0.207 g, 0.329 mmol) in a mixture of abs. ethanol (20 mL) and methylene chloride (5 0 mL) under argon at room temperature was added solid $NaBH_4$ (0.442 g, 11.683 mmol) in five (5) portions over 5.5 hours.

Water (0.5 mL) was added and the reaction mixture was filtered through a short layer of silica. Solvents were removed under reduced pressure to yield a crude product 0.223 g (107%) as an orange solid. The crude product was separated by flash chromatography over silica (30 g) eluting with EtOAc/hexane (1: 2) and later EtOAc/hexane (1:1) to provide a diastereomerically pure molybdenum complex (±)-**14** (0.113 g, 54%) as an orange solid along with a mixture of molybdenum complexes (±)-**14** (0.068 g, 33%) diastereomeric at C-3 (ratio of diastereomers 2:1). Thus, molybdenum complex (±)-**14** was obtained in 87% overall yield as a 7:1 mixture of diastereomers at C-3 . Analytical data for the major diastereomer (±)-**14**: mp = 228 °C decomp. (EtOAc/hexane); R_f = 0.37 (EtOAc/hexane, 1: 1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 1.8 Hz, 1 H), 7.95 (s, 1 H), 7.61-7.60 (m, 3 H), 7.48 (d, *J* = 1.8 Hz, 1 H), 6.22 (t, *J* = 2.1 Hz, 1 H), 6.19 (t, *J* = 1.8 Hz, 1 H), 6.16 (t, *J* = 2.1 Hz, 1 H), 4.45-4.42 (m, 1 H), 4.30 (s, 0.5 H), 4.31 (s, 0.5 H), 4.07-3.99 (m, 1 H), 3.75 (s, 0.75 H), 3.71 (s, 2.25 H), 3.40 (d, *J* = 7.5 Hz, 1 H), 3.27 (s, 0.75 H), 3.23 (s, 2.25 H), 2.52-2.40 (m, 2 H), 1.83-1.56 (m, 6 H), 1.50-1.37 (m, 2 H); MS (FAB) m/z (relative intensity) 632 ($M+H^+$, 14), 603 (31), 577 (65), 545 (60); IR (KBr, cm^{-1}): 3218 (m, br), 2930 (m), 1936 (s), 1843 (s), 1688 (m), 1503 (w), 1455 (m), 1407 (m), 1334 (w), 1305 (m), 1216 (m), 1117 (m), 1049 (m), 1017 (w), 982 (w), 762 (m), 721 (m); The minor diastereomer shows two sets of ^{1}H NMR signals distinct from the major isomer: at 3.73 ppm (s) and at 3.72 ppm (s) for COOMe; at 3.28 ppm (s) and at 3.21 ppm (s) for OMe. Complete characterization of the reduction product was carried out after converting the alcohol **14** to the acetate **15**.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(9,10,11)-(1S,2R,3R,7S,8S,9R)-3-acetoxy-12-aza-9-methoxy-12-methoxycarbonyltricyclo[6.3.1.$0^{2,7}$]dodec-10-en-9-yl]molybdenum [(±)-**15**]. To a solution of the diastereomerically pure molybdenum complex (±)-**14** (0.076 g, 0.119 mmol) in methylene chloride (3.0 mL) at room temperature under argon was added TEA (0.086 mL, 0.062 g, 0.618 mmol), acetic anhydride (0.125 mL, 0.125 g, 1.225 mmol) and solid DMAP (0.015 g, 0.123 mmol). The reaction mixture was stirred at room temperature for 16 hours. Then, the mixture was partitioned between water and methylene chloride. The organic

layer was dried ($MgSO_4$) and solvents removed under reduced pressure to yield a crude product. The crude product was purified by filtration through a short layer of silica (10 g) eluting with EtOAc/hexane (1:1) to afford a diastereomerically pure acetate (±)-**15** (0.072 g, 89%) as a bright orange solid: mp = 133-135 °C (EtOAc/hexane); R_f = 0.56 (EtOAc/hexane, 1: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 1.6 Hz, 1 H), 7.92 (d, *J* = 1.6 Hz, 1 H), 7.61 (d, *J* = 2.0 Hz, 1 H), 7.59 (d, *J* = 2.0 Hz, 1 H), 7.57 (d, *J* = 2.0 Hz, 1 H), 7.47 (d, *J* = 1.6 Hz, 1 H), 6.21-6.19 (m, 2 H), 6.15 (t, *J* = 2.0 Hz, 1 H), 5.32-5.40 (m, 1 H), 4.37 (d, *J* = 3.2 Hz, 1 H), 4.31 (s, 1 H), 4.01 (dd, *J* = 7.8 Hz, 3.8 Hz, 1 H), 3.74 (s, 0.2 H), 3.69 (s, 2.8 H), 3.38 (d, *J* = 7.2 Hz, 1 H), 3.21 (s, 0.2 H), 3.16 (s, 2.8 H), 2.65 (dd, *J* = 8.4 Hz, 5.2 Hz, 1 H), 2.46-2.40 (m, 1 H), 2.07 (s, 3 H), 1.86-1.79 (m, 1 H), 1.78-1.70 (m, 1 H), 1.68-1.60 (m, 1 H), 1.52-1.46 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.6 (228.2), 227.7 (227.4), 171.6, 152.8, 146.3, 144.6, 140.3, 138.9, 136.4, 135.9, 134.4, 105.8, 105.5, 69.9 (70.5), 63.8, 62.7 (63.1), 57.3 (two carbons), 56.7 (56.5), 53.0 (52.8), 52.2, 50.3, 46.4, 24.0, 23.9, 22.1, 17.1; IR (KBr, cm^{-1}): 2950 (m), 1936 (s), 1843 (s), 1731 (m), 1704 (m), 1503 (w), 1452 (m), 1407 (m), 1306 (m), 1270 (w), 1216 (m), 1116 (m), 1049 (m), 1021 (m), 760 (m), 721 (w); Anal. calcd for $C_{27}H_{32}N_7O_7BMo$: C, 48.16; H, 4.79; N, 14.56. Found: C, 48.09; H, 4.89; N, 14.38.

Oxidative Demetallation of the [5+2] Cycloaddition Products. To the orange colored solutions of cycloadducts (±)-**4**, (±)-**6**, (±)-**7**, (±)-**9a**, (-)-**6**, (-)-**7** and (-)-**9a** (1 mmol) and TEA (1.5 mmol) in THF/water mixture (3: 1, 50 mL) at 0 °C (ice bath) open to air was added a solution of CAN (8.0 mmol) in water (25 mL) dropwise over 5 minutes. During the addition, the solutions turned a dark color and a gas evolved. After completing the addition, the color faded and a light yellow solution resulted. The reaction mixtures were stirred for an additional 5-7 minutes at room temperature and then partitioned between methylene chloride (40 mL) and water (40 mL). The organic layers were washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$) and solvents were removed under reduced pressure to provide crude products. The crude products were separated by flash chromatography over silica eluting with EtOAc/hexane

mixtures to afford the tropanes (±)-**16,** (±)-**17,** (±)-**18** , (±)-**19,** (+)-**17,** (+)-**18** and (+)-**19,** as colorless oils which solidified on standing at low temperature (5 °C).

(±)- (1S,2R,6S,7S)-4,11-diaza-11-methoxycarbonyl-4-methyltricyclo[5.3.1.$0^{2,6}$]undec-9-ene-3,5,8-trione [(±)-16]. The molybdenum complex (±)-**4** (0.155 g, 0.2401 mmol) was treated with TEA (0.050 mL, 0.036 g, 0.360 mmol) and CAN (1.109 g, 1.995 mmol) according to the general procedure. Flash chromatography over silica eluting with EtOAc/hexane mixtures (1: 1) and (2: 1) afforded the tropane (±)-**16** (0.033 g, 52%): mp = 35-37 °C (EtOAc/hexane); R_f = 0.25 (EtOAc/hexane, 1:1); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 60 °C) δ 7.67 (dd, *J* = 10.0 Hz, 5.2 Hz, 1 H), 6.03 (d, *J* = 9.8 Hz, 1 H), 4.88 (d, *J* = 5.6 Hz, 1 H), 4.46 (s, 1 H), 3.59 (s, 3 H), 3.53 (d, *J* = 7.2 Hz, 1 H), 3.36 (d, *J* = 7.2 Hz, 1 H), 2.88 (s, 3 H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$, 60 °C)[6] δ 192.2, 175.0, 174.9, 152.2 (two carbons), 126.3, 66.8, 56.6 (56.7), 53.0 (52.9), 49.7, 45.5, 24.9; IR (neat, cm^{-1}): 1783 (w), 1699 (s, br), 1444 (m), 1385 (m), 1325 (m), 1125 (m), 993 (m), 735 (w); MS (EI) m/z (relative intensity) 264 (M^+, 57), 205 (100), 153 (48), 125 (75); HRMS (EI) calcd for $C_{12}H_{12}N_2O_5$ (M^+) 264.0746, found 264.0736; Anal. calcd for $C_{12}H_{12}N_2O_5$: C, 54.54; H, 4.58; N, 10.60. Found: C, 54.81; H, 4.85; N, 10.34.

(±)-(1S,2R,7S,8S)-12-aza-12-methoxycarbonyltricyclo[6.3.1.$0^{2,7}$]dodec-10-en-3,9-dione [(±)-17] and (1R,2S,7R,8R)-12-aza-12-methoxycarbonyltricyclo[6.3.1.$0^{2,7}$]dodec-10-en-3,9-dione [(+)-17]. The molybdenum complex (±)-**6** (0.151 g, 0.240 mmol) was treated with TEA (0.050 mL, 0.036 g, 0.360 mmol) and CAN (1.065 g, 1.944 mmol) according to the general procedure. Flash chromatography over silica eluting with EtOAc/hexane (1:1) afforded the tropane (±)-**17** (0.048 g, 81%): mp = 75-77 °C (EtOAc/hexane); R_f = 0.57 (EtOAc/hexane, 2:1); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 60 °C) δ 7.53 (dd, *J* = 10.0 Hz, 5.6 Hz, 1 H), 5.96 (d, *J* = 9.0 Hz, 1 H), 5.12 (d, *J* = 5.6 Hz, 1 H), 4.05 (s, 1 H), 3.58 (s, 3 H), 2.97 (d, *J* = 9.2 Hz, 1 H), 2.72-2.65 (m, 1 H), 2.48-2.42 (m, 1 H), 2.21 (pent, *J* = 8.4 Hz, 1 H), 2.16-2.12 (m, 1 H), 1.87-1.77 (m, 2 H), 1.24 (qd, *J* = 12.8 Hz, 3.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8 (208.2), 195.2 (194.7), 151.1, 152.9 (151.2), 127.8, 70.4, 56.3 (56.1), 53.7 (52.6), 53.2, 41.1 (40.3), 38.3, 28.5, 20.5; IR (neat, cm^{-1}):

2952 (w), 1708 (s), 1449 (m), 1386 (w), 1329 (m), 1298 (w), 1211 (m), 1124 (m), 976 (m), 800 (w), 781 (w); MS (EI) m/z (relative intensity) 249 (M^+, 100), 221 (77), 218 (46), 194 (95), 153 (42); HRMS (EI) calcd for $C_{13}H_{15}NO_4$ (M^+) 249.1001, found 249.1005; Anal. calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.06; N, 5.61. Found: C, 63.10; H, 6.42; N, 5.47. In the same way, the chiral non-racemic (97% ee) molybdenum complex (-)-**6** (0.103 g, 0.163 mmol) afforded (+)-**17** as a white solid (0.036 g, 87%) in 96 % ee ($[\alpha]_D$ = +82 °, c 0.920 $CHCl_3$).

(±)-(1S,5S,6R)-8-aza-6,8-bis(methoxycarbonyl)bicyclo[3.2.1]oct-3-en-2-one [(±)-18] and (1R,5R,6S)-8-aza-6,8-bis(methoxycarbonyl)bicyclo[3.2.1]oct-3-en-2-one [(+)-18]. The molybdenum complex (±)-**7** (0.149 g, 0.241 mmol) was treated with TEA (0.049 mL, 0.035 g, 0.352 mmol) and CAN (1.010 g, 1.842 mmol) according the general procedure. Flash chromatography over silica eluting with EtOAc/hexane (1: 2) afforded the tropane (±)-**18** (0.045 g, 77%): mp = 90-92 °C (EtOAc/hexane); R_f = 0.26 (EtOAc/hexane, 1: 1); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 60 °C) δ 7.54 (dd, *J* = 10.0 Hz, 5.6 Hz, 1 H), 5.96 (d, *J* = 10.0 Hz, 1 H), 4.94 (d, *J* = 5.6 Hz, 1 H), 4.48 (d, *J* = 8.4 Hz, 1 H), 3.67 (s, 3 H), 3.60 (s, 3 H), 3.13 (dd, *J* = 9.2 Hz, 3.6 Hz, 1 H), 2.70-2.60 (m, 1 H), 1.95 (dd, *J* = 14.0 Hz, 9.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 172.4, 154.8, 151.7 (150.5), 127.9, 64.1, 57.6, 53.2, 52.9, 46.0 (47.0), 28.8 (28.3); IR (neat, cm^{-1}): 2956 (w), 1731 (s), 1715 (s), 1448 (m), 1394 (w), 1320 (m), 1202 (m), 1104 (m), 1024 (w), (64 (w), 838 (w); MS (EI) m/z (relative intensity) 239 (M^+, 79), 208 (53), 207 (74), 180 (96), 179 (41), 154 (59), 153 (35), 152 (100), 137 (42), 126 (62), 125 (62), 120 (43), 105 (47), 101 (16), 59 (85), 55 (39); HRMS (EI) calcd for $C_{11}H_{13}NO_5$ (M^+) 239.0793, found 239.0798; Anal. calcd for $C_{11}H_{13}NO_5$: C, 55.22; H, 5.48; N, 5.85. Found: C, 55.67; H, 5.60; N, 5.80. In the same way, the chiral non-racemic (98% ee) molybdenum complex (-)-**7** (0.114 g, 0.184 mmol) afforded (+)-**18** as a white solid (0.025 g, 57%) in 98 % ee ($[\alpha]_D$ = +98 °, c 0.792 $CHCl_3$).

(±)-(1S,5S,6R)-8-aza-6-formyl-8-methoxycarbonyl-6-methylbicyclo[3.2.1]oct-3-en-2-one [(±)-19] and (1R,5R,6S)-8-aza-6-formyl-6,8-bis(methoxycarbonyl)-6-methyl-

bicyclo[3.2.1]oct-3-en-2-one [(+)-**19**]. The molybdenum complex (±)-**9a** (0.402 g, 0.667 mmol) was treated with TEA (0.138 mL, 0.100 g, 0.992 mml) and CAN (2.961 g, 5.401 mmol) according to the general procedure. Flash chromatography over silica eluting with EtOAc/hexane (1:2) afforded the tropane (±)-**19** (0.115 g, 77%): mp = 81-82 °C (EtOAc/hexane); R_f = 0.33 (EtOAc/hexane, 1: 1); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 60 °C) δ 9.59 (s, 1 H), 7.47 (dd, *J* = 10.0 Hz, 5.6 Hz, 1 H), 6.12 (dd, *J* = 10.0 Hz, 1.6 Hz, 1 H), 4.90 (d, *J* = 5.6 Hz, 1 H), 4.36 (d, *J* = 8.8 Hz, 1 H), 3.58 (s, 3 H), 2.95 (dd, *J* = 13.6 Hz, 8.8 Hz, 1 H), 1.38 (d, *J* = 14.8 Hz, 1 H), 1.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4, 194.8, 154.9, 150.1 (148.8), 129.7, 64.1, 58.1, 53.3, 33.5, 33.1, 17.5; IR (neat, cm^{-1}): 1702 (s), 1447 (m), 1320 (s), 1100 (m), 992 (w), 880 (w), 853 (m), 775 (w); HRMS (EI) calcd for $C_{11}H_{13}NO_4$ (M^+) 223.0844, found 223.0843; Anal. calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 58.97; H, 5.80; N, 6.38. In the same way, the chiral non-racemic (95% ee) molybdenum complex (-)-**9a** (0.055 g, 0.091 mmol) afforded (+)-**19** as a white solid (0.014 g, 70%) with $[\alpha]_D$ = +81 °, c 0.710, $CHCl_3$. Determination of the enantiomeric purity of the product by HPLC was not successful due to a poor separation of the optical antipodes under all conditions (stationary phases: Chiralpak AD and Chiracel OD) explored.

Determination of Enantiomeric Excesses by HPLC.

HPLC was performed on a Millipore Waters™ 600 HPLC chromatograph with a CHIRALPAK AD and CHIRACEL OD columns at room temperature using a Waters™ 486 UV detector (230 nm). Samples of products for HPLC analyses were prepared by dissolving 4 mg of the pure molybdenum complexes in 4.0 - 8.0 mL of absolute ethanol. One microliter (1 μL) of the solution was injected for the HPLC analysis. HPLC grade isopropanol and hexane were used. Racemic sample was run immediately prior to each analysis of an optically enriched material to verify efficiency of the separation. The results are listed in the following table.

Table S1. Determination of % de and % ee by HPLC

Entry	Compound	Column[a]	Eluent[b]	Retention time[c] of (-) isomer	Retention time[c] of (+) isomer
1	**2b**	A	40%	12.1 min	18.7 min
2	**2a**	B	15%	22.7 min	15.5 min
3	**3**	A	2%	36.7 min	31.9 min
4	**6**	B	30%	14.0 min	8.6 min
5	**7**	A	20%	9.7 min	15.4 min
6	**8**	A	10%	14.5 min	26.8 min
7	**9a**	A	20%	9.8 min	12.4 min
8	**9b**	A	20%	7.7 min	10.3 min
9	**17**	A	20%	12.0 min	14.2 min
10	**18**	A	5%	23.5 min	25.8 min

[a] A = CHIRALPAK AD, B = CHIRACEL OD.[b] % of isopropanol in hexane, flowrate 1 ml/min, detection at 230 nm. [c] in minutes

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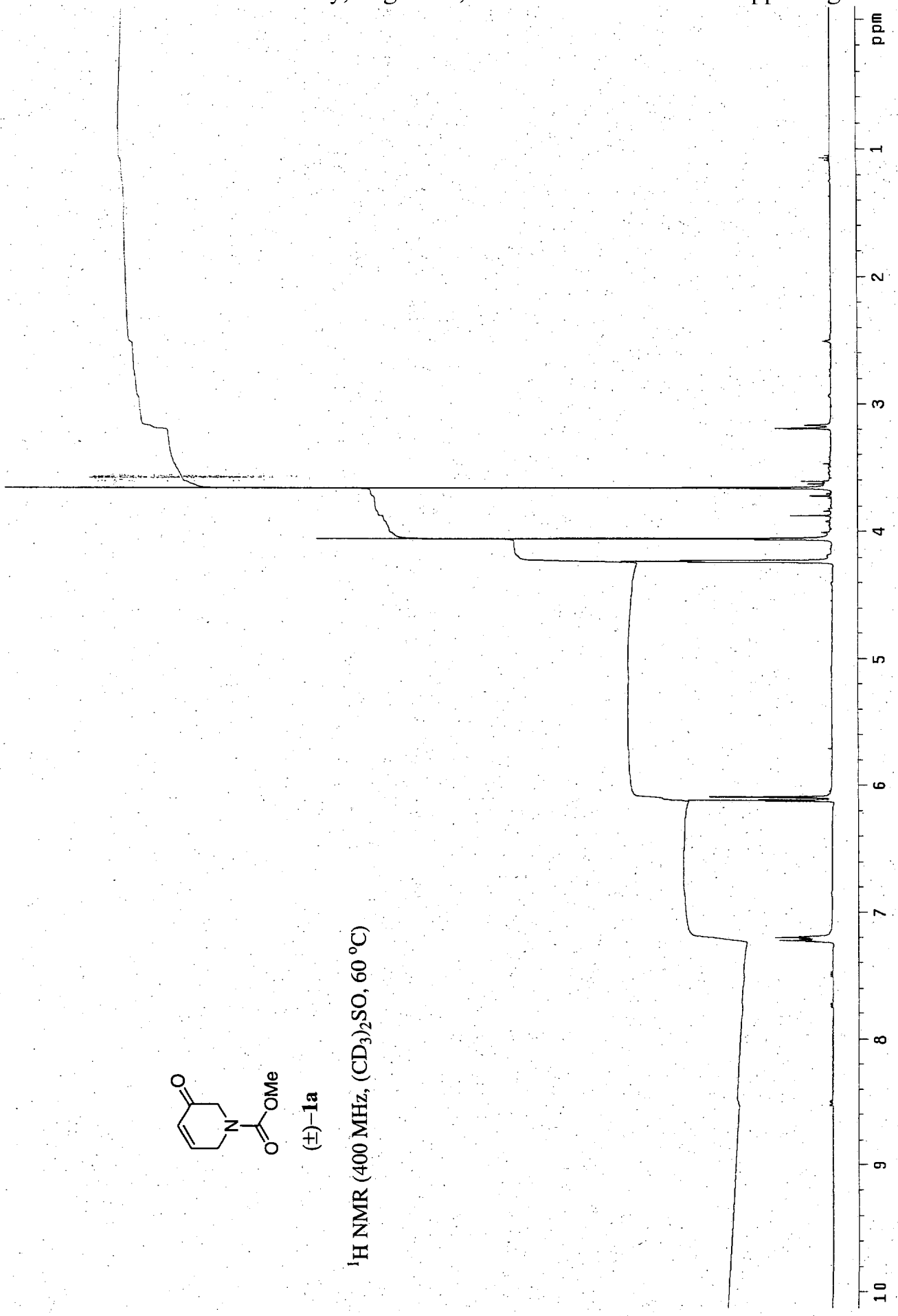
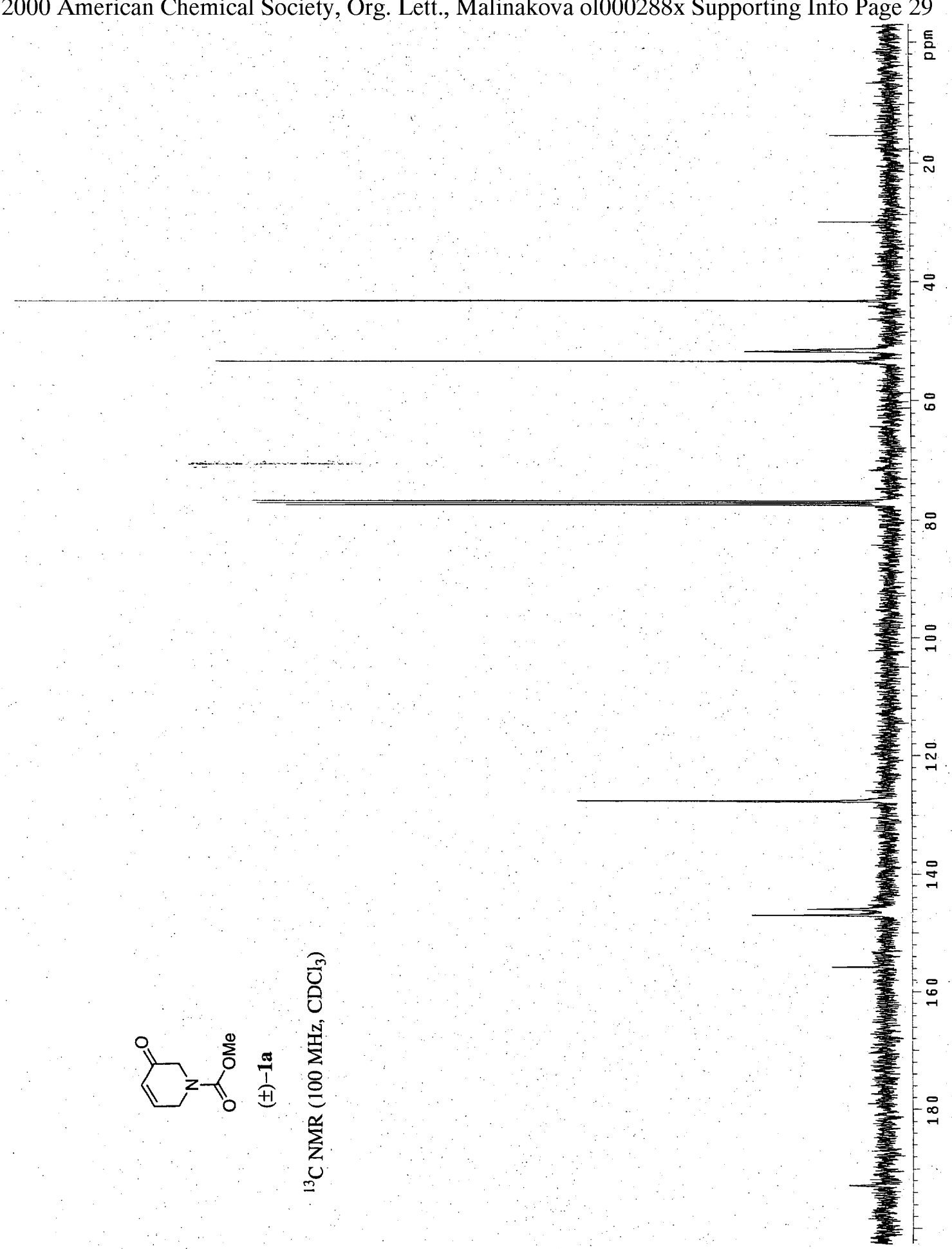


^{1}H NMR (400 MHz, $(CD_3)_2SO$, 60 °C)

(±)–**1a**



(±)-**1a**

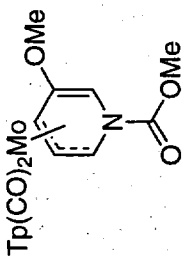
^{13}C NMR (100 MHz, $CDCl_3$)

(±)-**3**

^{1}H NMR (400 MHz, $CDCl_3$)

(±)-**3**

^{1}H NMR (400 MHz, $CDCl_3$)

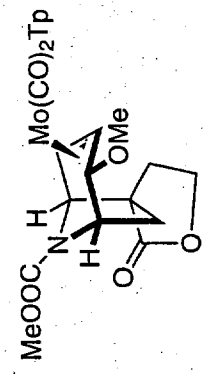


(±)–3

^{13}C NMR (100 MHz, $CDCl_3$)

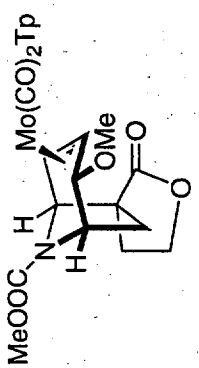
(±)-**11a**

^{1}H NMR (400 MHz, $(CD_3)_2SO$)



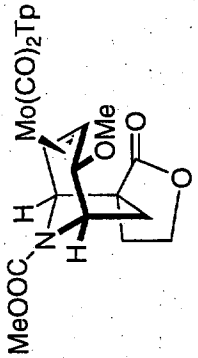
(±)-**11a**

^{13}C NMR (100 MHz, $(CD_3)_2SO$)



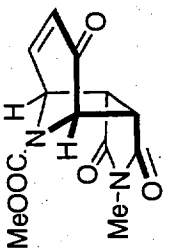
(±)–**11b**

^{1}H NMR (400 MHz, $(CD_3)_2SO$)



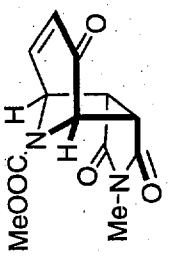
(±)–**11b**

^{13}C NMR (100 MHz, $(CD_3)_2SO$)



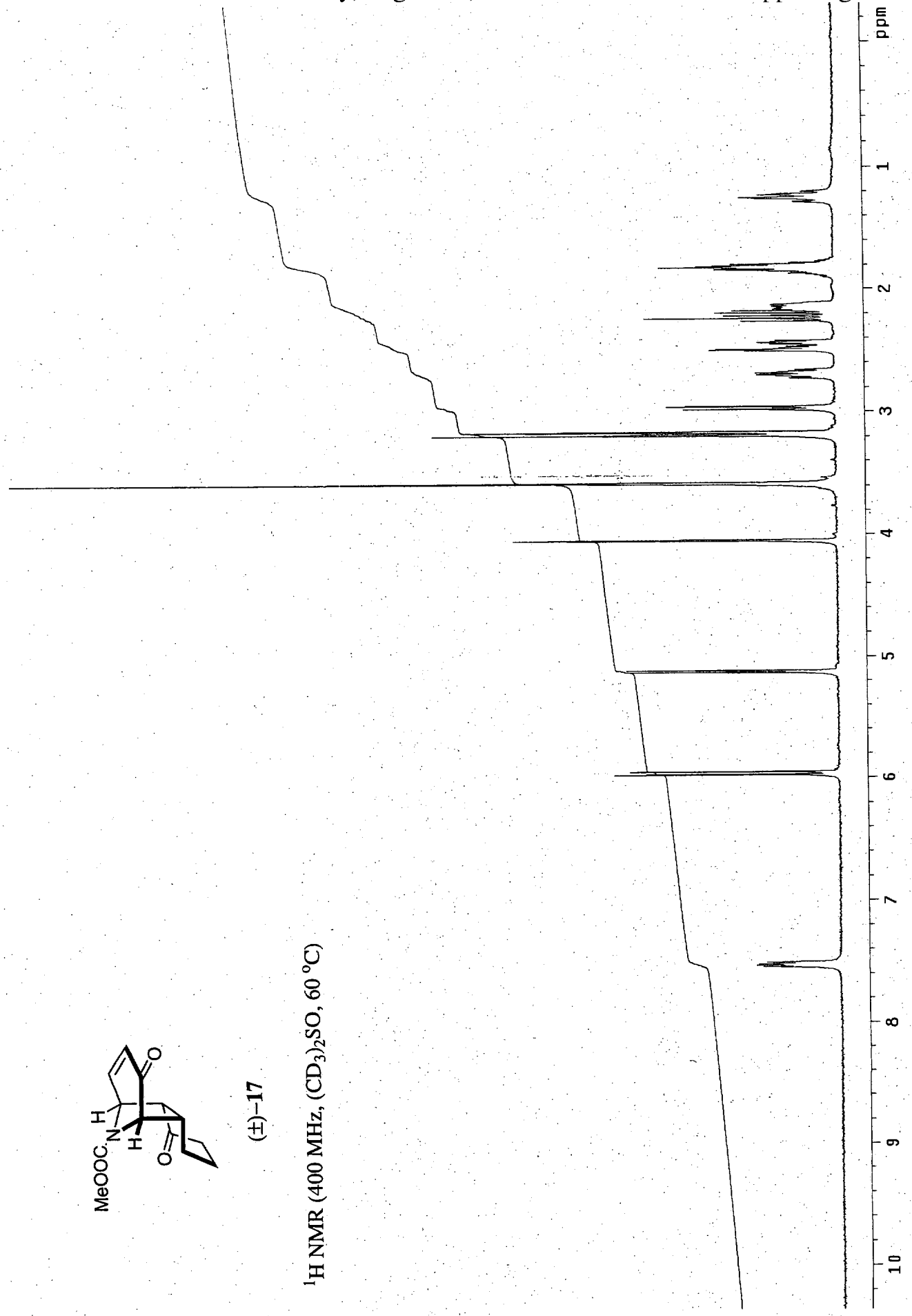
(±)–**16**

^{1}H NMR (400 MHz, $(CD_3)_2SO$, 60 °C)



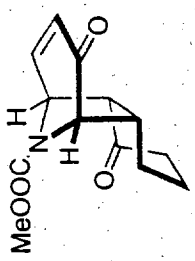
(±)–**16**

^{13}C NMR (100 MHz, $(CD_3)_2SO$, 60 °C)



(±)–**17**

^{1}H NMR (400 MHz, $(CD_3)_2SO$, 60 °C)



(±)–**17**

^{13}C NMR (100 MHz, $CDCl_3$)