

*Supporting Information for*

**Enantiocontrolled Synthesis of Spirooxindoles Based on the  
[5 +2] Cycloaddition of a Tp(CO)<sub>2</sub>Mo(pyridinyl) Scaffold (Tp =  
Hydridotrispyrazolylborate)**

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**General Methods.** Unless otherwise indicated, all NMR data were collected at room temperature in CDCl<sub>3</sub> with CHCl<sub>3</sub> as the internal reference ( $\delta$  7.26 ppm for <sup>1</sup>H and 77.23 ppm for <sup>13</sup>C). Due to the restricted rotation about the C-N bond of the carbamate group, additional "satellite" peaks accompany the main signals in <sup>13</sup>C NMR. Signals for the "satellite" peaks are indicated in parentheses following the signal for the major peak. With the exception of compound ( $\pm$ )-8, measuring the <sup>13</sup>C NMR at 60 °C did not remove the satellite peaks. IR spectra were measured in KBr pellets or neat as thin films using a REACTIR™ with a silicon probe. 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  $\mu$ m silica gel (Woelm). THF was freshly distilled from sodium/benzophenone still. Dichloromethane was distilled from CaH<sub>2</sub> and kept over molecular sieves under atmosphere of dry argon. Triethylamine (TEA) was distilled from CaH<sub>2</sub> and kept

under atmosphere of dry argon. Dry ether was purchased from Mallinckrodt and used as received; other solvents were used as received. Unless otherwise specified, all reactions were carried out under atmosphere of dry nitrogen or argon in oven dried (at least 6 h at 140 °C) glassware. Racemic  $\pi$ -allyl molybdenum complex ( $\pm$ )-(1) and the complexes (+)-1 and (-)-1 of high enantiomeric purity (98% ee) were prepared according to the previously described procedure.<sup>1</sup> Methyleneoxindole 2 was obtained as described by Brush.<sup>2</sup>

( $\pm$ )-Dicarbonyl[hydridotris(1-pyrazolyl)borato][ $\eta$ -(2,3,4)-(1S,2R,5S,6S)-8-aza-2-methoxy-8-methoxycarbonyl-spiro[bicyclo[3.2.1]oct-3-ene-2-yl-6,3'-[3H]indole-2'(1'H)-one]molybdenum [( $\pm$ )-(3a)], dicarbonyl[hydridotris(1-pyrazolyl)borato][ $\eta$ -(2,3,4)-(1S,2R,5S,6S)-8-aza-2-methoxy-8-methoxycarbonyl-spiro[bicyclo[3.2.1]oct-3-ene-2-yl-6,3'-[3H]indole-2'(1'H)-one]molybdenum [(+)-3a], dicarbonyl[hydridotris(1-pyrazolyl)borato][ $\eta$ -(2,3,4)-(1R,2S,5R,6R)-8-aza-2-methoxy-8-methoxycarbonyl-spiro[bicyclo[3.2.1]oct-3-ene-2-yl-6,3'-[3H]indole-2'(1'H)-one]molybdenum [(-)-3a], ( $\pm$ )-dicarbonyl[hydridotris(1-pyrazolyl)borato][ $\eta$ -(2,3,4)-(1S,2R,5S,6R)-8-aza-2-methoxy-8-methoxycarbonyl-spiro[bicyclo[3.2.1]oct-3-ene-2-yl-6,3'-[3H]indole-2'(1'H)-one]molybdenum [( $\pm$ )-(3b)], dicarbonyl[hydridotris(1-pyrazolyl)borato][ $\eta$ -(2,3,4)-(1S,2R,5S,6R)-8-aza-2-methoxy-8-methoxycarbonyl-spiro[bicyclo[3.2.1]oct-3-ene-2-yl-6,3'-[3H]indole-2'(1'H)-one]molybdenum [(+)-3b] and dicarbonyl[hydridotris(1-pyrazolyl)borato][ $\eta$ -(2,3,4)-(1R,2S,5R,6S)-8-aza-2-methoxy-8-methoxycarbonyl-spiro[bicyclo[3.2.1]oct-3-ene-2-yl-6,3'-[3H]indole-2'(1'H)-one]molybdenum [(-)-3b]. To the

<sup>1</sup> Malinakova, H. C. Liebeskind, L. S. *Organic Letters*, in press.

<sup>2</sup> Petrounia, I. P.; Goldberg, J.; Brush, E. J. *Biochemistry* **1994**, 33(10), 2891-2899.

solid molybdenum complex ( $\pm$ )-**1** (4.52 g, 8.48 mmol), Sc(OTf)<sub>3</sub> (0.724 g, 1.47 mmol) and methyleneoxindole **2** (1.607 g, 11.08 mmol) was added methylene chloride (120 mL). The brown suspension was stirred at room temperature under argon for 10 minutes. Then a second portion of methyleneoxindole **2** (1.59 g, 10.96 mmol) was added as solid and stirring was continued for 30 minutes. The reaction mixture was filtered through a short layer of Celite<sup>®</sup> and silica eluting with EtOAc/hexanes (1:1) to afford the pure unreacted complex ( $\pm$ )-**1** (2.05 g, 45%) and later with EtOAc to elute a mixture of two products. The mixture was separated by flash chromatography over silica, eluting with EtOAc/hexane (1:1 and 2:1) and then with EtOAc to afford the molybdenum complex ( $\pm$ )-**3a** (1.909 g, 33%) and a minor cycloaddition product ( $\pm$ )-**3b** (0.407 g, 8%) as bright orange solids. An additional chromatographic separation of the complex ( $\pm$ )-**3a** over silica, eluting with EtOAc/hexane (1:1 and 2:1) allowed for the isolation of a fraction consisting of a single stable rotamer of ( $\pm$ )-**3a**. The recovered complex ( $\pm$ )-**1** (2.05 g, 3.84 mmol) was resubjected to the cycloaddition conditions to afford the adduct ( $\pm$ )-**3a** (0.77 g, 30%), adduct ( $\pm$ )-**3b** (0.23 g, 9%) and recovered complex ( $\pm$ )-**1** (0.39 g, 20%). The entire preparation was repeated once more from recycled complex ( $\pm$ )-**1** (0.30 g, 0.56 mmol) to yield the adduct ( $\pm$ )-**3a** (0.132 g, 26%), adduct ( $\pm$ )-**3b** (0.03 g, 7%) and recovered complex ( $\pm$ )-**1** (0.18 g, 45%).

Reactions with enantiopure complexes (+)-**1** (98% ee) and (-)-**1** (98% ee) were carried out according to the same procedure in a reaction vessel covered with aluminum foil. Thus complex (+)-**1** (98% ee,  $[\alpha]_D = +149^\circ$ , c 0.113 CHCl<sub>3</sub>) provided the recovered complex (+)-**1** in 98% ee, the molybdenum complex (+)-**3a** in 95% ee ( $[\alpha]_D = +272^\circ$ , c 0.114 CHCl<sub>3</sub>) and the complex (+)-**3b** in 95% ee ( $[\alpha]_D = +337^\circ$ , c 0.090 CHCl<sub>3</sub>). The complexes (+)-**3a** and (+)-**3b** prepared

from the recovered complex (+)-**1** (98% ee) retained the enantiomeric excess (95% ee) in both cases.

The complex (-)-**1** (98% ee,  $[\alpha]_D = -155^\circ$ ,  $c$  0.124  $\text{CHCl}_3$ ) provided the recovered complex (-)-**1** in 98% ee, the molybdenum complex (-)-**3a** in 95% ee and the complex (-)-**3b** in 95% ee ( $[\alpha]_D = -348^\circ$ ,  $c$  0.056  $\text{CHCl}_3$ ). The complexes (-)-**3a** and (-)-**3b**, prepared from the recovered complex (-)-**1** (98% ee), were obtained in 95% enantiomeric excess in both cases.

Enantiomeric purity of the combined major products (-)-**3a** (95% ee) was improved by dissolving the material (0.725 g) in EtOAc and concentrating the solution under reduced pressure to form a dense suspension. The complex (-)-**3a** (0.43 g, 97% ee,  $[\alpha]_D = -341^\circ$ ,  $c$  0.119  $\text{CHCl}_3$ ) of higher enantiomeric purity was isolated by vacuum filtration.

Analytical data for the molybdenum complex ( $\pm$ )-**3a** (a mixture of rotamers): mp = 187-190 °C decomp. (EtOAc/hexane);  $R_f = 0.24$  (EtOAc/hexane, 1 : 1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (t,  $J = 1.2$  Hz, 1 H), 8.05 (q,  $J = 2.0$  Hz, 1 H), 8.00 (d,  $J = 7.2$  Hz, 0.5 H), 7.97 (d,  $J = 7.2$  Hz, 0.5 H), 7.94 (s, 1 H), 7.64 (t,  $J = 2.0$  Hz, 1 H), 7.61 (t,  $J = 2.4$  Hz, 1 H), 7.49 (td,  $J = 2.0$  Hz, 0.4 Hz, 1 H), 7.41 (d,  $J = 2.0$  Hz, 1 H), 7.30 (tt,  $J = 7.6$  Hz, 1.2 Hz, 1 H), 7.06 (tdd,  $J = 7.6$  Hz, 2.8 Hz, 0.8 Hz, 1 H), 7.02 (d,  $J = 7.6$  Hz, 0.5 H), 6.97 (d,  $J = 7.6$  Hz, 0.5 H), 6.22 (t,  $J = 2.0$  Hz, 1 H), 6.20 (t,  $J = 2.4$  Hz, 1 H), 6.17 (t,  $J = 2.4$  Hz, 1 H), 4.96 (d,  $J = 6.0$  Hz, 0.6 H), 4.85 (d,  $J = 6.0$  Hz, 0.4 H), 4.64-4.62 (m, 0.4 H), 4.51 (d,  $J = 3.2$  Hz, 0.6 H), 3.82 (s, 1.2 H), 3.79 (d,  $J = 2.4$  Hz, 1 H), 3.76 (d,  $J = 4.0$  Hz, 0.6 H), 3.74 (d,  $J = 4.0$  Hz, 0.4 H), 3.72 (s, 1.8 H), 3.43 (s, 1.8 H), 3.38 (s, 1.2 H), 2.80-2.74 (m, 1 H), 2.34 (s, 0.5 H), 2.31 (s, 0.5 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  228.67 (228.44), 227.97 (227.72), 181.59 (181.54), 154.75 (154.03), 146.44, 144.92 (144.86), 142.02 (142.40), 140.84 (140.74), 139.97 (139.65), 136.58 (136.66), 136.00, 134.58, 129.26 (129.08), 128.92 (128.88), 126.23 (125.90), 121.90 (121.73), 110.16 (110.46), 105.90, 105.74,

105.78, 64.47 (63.65), 60.08 (59.69), 59.07, 58.46 (58.54), 56.89 (57.06), 54.79 (54.39), 52.76 (52.99), 43.67 (43.42); IR (KBr,  $\text{cm}^{-1}$ ): 3189 (m, br), 2951 (w), 1936 (s), 1844 (s), 1725 (m), 1713 (m), 1619 (w), 1503 (w), 1470 (m), 1448 (m), 1407 (m), 1327 (m), 1304 (m), 1264 (m), 1214 (m), 1118 (m), 1049 (m), 1007 (w), 754 (m), 720 (m), 669 (w); MS (FAB)  $m/z$  (relative intensity) 681 ( $\text{M}+\text{H}^+$ , 7), 652 (22), 624 (28), 549 (14), 307 (100); HRMS (FAB) calcd for  $\text{C}_{28}\text{H}_{28}\text{BMoN}_8\text{O}_6$  ( $\text{M}+\text{H}^+$ )<sup>+</sup> 681.1279, found 681.1260; Anal. calcd for  $\text{C}_{28}\text{H}_{27}\text{BMoN}_8\text{O}_6$ : C, 49.58; H, 4.01; N, 16.52. Found: C, 49.55; H, 3.93; N, 16.26.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for pure rotamer of ( $\pm$ )-**3a**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (d,  $J = 1.6$  Hz, 1 H), 8.18 (s, 1 H), 8.04 (d,  $J = 1.6$  Hz, 1 H), 7.99 (d,  $J = 7.2$  Hz, 1 H), 7.63 (d,  $J = 2.4$  Hz, 1 H), 7.61 (d,  $J = 2.0$  Hz, 1 H), 7.48 (d,  $J = 2.4$  Hz, 1 H), 7.40 (d,  $J = 2.0$  Hz, 1 H), 7.30 (td,  $J = 7.6$  Hz, 1.2 Hz, 1 H), 7.06 (td,  $J = 7.6$  Hz, 1.2 Hz, 1 H), 6.96 (d,  $J = 8.0$  Hz, 1 H), 6.21 (t,  $J = 2.0$  Hz, 1 H), 6.19 (t,  $J = 2.0$  Hz, 1 H), 6.16 (t,  $J = 2.0$  Hz, 1 H), 4.96 (d,  $J = 6.0$  Hz, 1 H), 4.50 (d,  $J = 3.6$  Hz, 1 H), 3.80 (d,  $J = 7.6$  Hz, 1 H), 3.74 (dd,  $J = 7.6$  Hz, 4.0 Hz, 1 H), 3.71 (s, 3 H), 3.42 (s, 3 H), 2.76 (dd,  $J = 12.8$  Hz, 6.4 Hz, 1 H), 2.32 (d,  $J = 13.2$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  228.68, 227.96, 181.76, 154.74, 146.43, 144.91, 142.06, 140.83, 140.03, 136.57, 136.04, 134.57, 129.27, 128.88, 126.22, 121.89, 110.17, 105.88, 105.77, 105.73, 64.47, 60.05, 59.09, 58.46, 56.88, 54.77, 52.74, 43.42.

Analytical data for the complex ( $\pm$ )-**3b**: mp = 218-219 °C decomp. (EtOAc/hexane);  $R_f = 0.62$  (EtOAc/hexane, 1:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (d,  $J = 2.0$  Hz, 0.3 H), 8.35 (d,  $J = 2.0$  Hz, 0.7 H), 7.96 (d,  $J = 2.0$  Hz, 0.5 H), 7.95 (d,  $J = 1.6$  Hz, 0.5 H), 7.67 (d,  $J = 4.4$  Hz, 1 H), 7.62 (t,  $J = 2.4$  Hz, 1 H), 7.59 (t,  $J = 2.0$  Hz, 1 H), 7.53 (d,  $J = 1.6$  Hz, 1 H), 7.47 (t,  $J = 2.4$  Hz, 1 H), 7.18 (qd,  $J = 7.6$  Hz, 1.2 Hz, 1 H), 7.00-6.94 (m, 1 H), 6.88 (d,  $J = 8.0$  Hz, 0.7 H), 6.85 (d,  $J = 7.6$  Hz, 0.3 H), 6.81 (d,  $J = 7.2$  Hz, 1 H), 6.20-6.17 (m, 3 H), 4.95 (d,  $J = 5.6$  Hz, 0.7 H), 4.87 (d,

$J = 5.2$  Hz, 0.3 H), 4.55 (d,  $J = 2.4$  Hz, 0.3 H), 4.52 (d,  $J = 2.8$  Hz, 0.7 H), 3.91 (d,  $J = 8.4$  Hz, 1 H), 3.82 (s, 1 H), 3.77-3.70 (m, 1 H), 3.68 (s, 2 H), 3.24 (s, 2 H), 3.21 (s, 1 H), 2.62 (s, 0.3 H), 2.59 (s, 0.7 H), 2.51 (d,  $J = 5.6$  Hz, 0.7 H), 2.48 (d,  $J = 6.0$  Hz, 0.3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  229.91, 227.85, 178.94, 153.85 (152.71), 146.19, 144.87 (144.72), 140.51 (140.42), 140.08, 139.65 (139.49), 136.46, 135.87, 135.41, 134.54, 128.30, 123.26, 123.20 (123.10), 122.53, 109.65 (109.49), 105.72 (two carbons), 67.79 (66.59), 59.79 (59.95), 59.41 (59.13), 56.92 (57.00), 56.23 (56.31), 56.13 (55.83), 52.50 (52.95), 43.71 (45.04); IR (neat,  $\text{cm}^{-1}$ ): 1934 (s), 1845 (s), 1710 (m), 1409 (m), 1305 (m), 1119 (m), 1050 (m), 756 (m), 721 (w); Anal. calcd for  $\text{C}_{28}\text{H}_{27}\text{BMoN}_8\text{O}_6$ : C, 49.58; H, 4.01; N, 16.52. Found: C, 49.74; H, 4.24; N, 16.23.

**$\text{CuCl}_2$ -mediated Demetallation (yields 60-70%):**

**( $\pm$ )(1S,5S,6S)-Spiro[8-aza-8-methoxycarbonylbicyclo[3.2.1]oct-3-ene-6,3'-[3H]indole-2,2'(1'H)-dione [( $\pm$ )-4] and (1R,5R,6R)-spiro[8-aza-8-methoxycarbonylbicyclo[3.2.1]oct-3-ene-6,3'-[3H]indole-2,2'(1'H)-dione [(+)-4].** To a solution of the molybdenum complex ( $\pm$ )-3a (0.306 g, 0.451 mmol) in THF (30.0 mL) at room temperature was added solid  $\text{Cu}^{\text{II}}\text{Cl}_2$  (1.009 g, 7.505 mmol). The resulting suspension was stirred at room temperature under argon for 30 minutes. During this time, the color slowly changed from orange-brown to brown-green. The reaction mixture was filtered through a layer of Celite<sup>®</sup>. Solvents were removed from the filtrate under reduced pressure and the resulting crude product was deposited on Celite<sup>®</sup> and purified by flash chromatography over silica eluting with EtOAc/hexane (1:1) to afford the enone ( $\pm$ )-4 (0.095 g, 71 %) as a clear oil which solidified upon storage at low temperature: mp = 189-191 °C (EtOAc/hexane);  $R_f = 0.15$  (EtOAc/hexane, 2:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (br s, 0.5 H), 8.08 (br s, 0.5 H), 7.26 (td,  $J = 7.5$  Hz; 1.5 Hz, 1 H), 7.25 (s, 1 H), 7.17 (dd,  $J = 9.3$  Hz, 5.4

Hz, 0.5 H), 7.11 (dd,  $J = 9.3$  Hz, 5.4 Hz, 0.5 H), 7.02 (t,  $J = 7.5$  Hz, 1 H), 6.95 (t,  $J = 7.8$  Hz, 1 H), 6.37 (dd,  $J = 9.6$  Hz, 1.2 Hz, 0.5 H), 6.35 (dd,  $J = 9.6$  Hz, 1.5 Hz, 0.5 H), 5.08 (d,  $J = 7.5$  Hz, 0.5 H), 4.98 (d,  $J = 5.7$  Hz, 0.5 H), 4.95 (d,  $J = 8.4$  Hz, 0.5 H), 4.87 (d,  $J = 5.7$  Hz, 0.5 H), 3.77 (s, 1.5 H), 3.70 (s, 1.5 H), 3.03-2.93 (m, 1 H), 2.00 (t,  $J = 14.8$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.72 (195.43), 180.33 (180.08), 154.38 (154.54), 151.66 (150.51), 141.81 (141.63), 129.57 (129.77), 129.45, 127.14 (127.24), 125.24 (125.38), 122.60 (122.71), 110.51 (110.44), 64.80 (64.68), 60.11 (60.43), 55.97 (55.07), 53.36 (53.17), 37.43 (37.17); IR (neat,  $\text{cm}^{-1}$ ): 3261 (s, br), 2965 (w), 1716 (s), 1617 (m), 1471 (m), 1404 (m), 1367 (w), 1327 (m), 1236 (m), 1102 (m), 1119 (w), 847 (w), 756 (m); MS (EI)  $m/z$  (relative intensity) 298 ( $\text{M}^+$ , 10), 262 (6), 212 (8), 154 (56), 145 (100), 117 (81), 109 (26), 95 (45), 90 (60), 63 (13), 51 (10); HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$  ( $\text{M}^+$ ) 298.0953, found 298.0953. Anal. calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$ : C, 64.42; H, 4.73; N, 9.39. Found: C, 63.72; H, 4.79; N, 9.18.

In the same way, the chiral non-racemic (97% ee) molybdenum complex (-)-**3a** (0.430 g, 0.634 mmol) afforded (+)-**4** as a white solid (0.118 g, 63 %) in >97%<sup>3</sup> ee ( $[\alpha]_{\text{D}} = +218^\circ$ ,  $c$  0.345 THF).

#### CAN-mediated Demetallation (yields 50%):

(1*S*,5*S*,6*S*)-spiro[8-aza-8-methoxycarbonylbicyclo[3.2.1]oct-3-ene-6,3'-[3*H*]indole-2,2'(1'*H*)-dione [(-)-**4**]. To an orange colored solution of the chiral non-racemic (95% ee) molybdenum complex (+)-**3a** (0.703 g, 1.037 mmol) and TEA (0.20 ml, 0.145 g, 1.437 mmol) in THF/water mixture (3:1, 60 mL) at 0 °C (ice bath) open to air was added a solution of CAN (4.555 g, 8.308

<sup>3</sup> The HPLC analyses were complicated by a partial separation of the two rotamers (arising from the hindered rotation about the C-N bond in the carbamate group) of the minor enantiomer resulting in a significant peak broadening. Thus the analysis apparently indicated enantiomeric excesses higher than 97% ee.

mmol) in water (55 mL) dropwise over 5 minutes. During the addition the solution turned dark and a gas evolved. After completing the addition, the dark color faded and a light yellow solution resulted. After an additional 10 minutes at room temperature, the reaction mixture was partitioned between methylene chloride and brine. The organic layer was washed with water, dried ( $\text{MgSO}_4$ ) and solvents were removed under reduced pressure to provide a crude product (0.294 g). The crude product was purified by flash chromatography over silica eluting with EtOAc/hexane (2:1) to afford the enone (-)-4 (0.156 g, 50 %) in  $>95\%^4$  ee ( $[\alpha]_D = -207^\circ$ ,  $c$  0.141  $\text{CHCl}_3$ ).

**(±)(1S,5S,6S)-Spiro[8-aza-8-methoxycarbonylbicyclo[3.2.1]octane-6,3'-[3H]indole-2,2'(1'H)-dione [(±)-5] and (1S,5S,6S)-spiro[8-aza-8-methoxycarbonylbicyclo[3.2.1]octane-6,3'-[3H]indole-2,2'(1'H)-dione [(-)-5].** To a solution of the spiroenone (±)-4 (0.104 g, 0.348 mmol) in a mixture of methanol and EtOAc (1:1, 10 mL) was added palladium black (10% on carbon, 0.048 g, 0.045 mmol of Pd) and hydrogen (from balloon) was bubbled through the suspension for 7 h at room temperature. The reaction mixture was then stirred for an additional 16 h at room temperature in the atmosphere of hydrogen. The suspension was filtered through Celite<sup>®</sup> and solvents removed under reduced pressure. The resulting crude product was purified by flash chromatography over silica, eluting with EtOAc/hexane (1:1) to yield the spiroketone (±)-5 (0.075 g, 72 %) as a white solid: mp = 209-210 °C (EtOAc/hexane);  $R_f = 0.24$  (EtOAc/hexane, 1:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (s, 1 H), 7.28 (t,  $J = 7.6$  Hz, 1 H), 7.21 (d,  $J = 7.6$  Hz, 0.5 H), 7.17 (d,  $J = 7.6$  Hz, 0.5 H), 7.06 (td,  $J = 7.6$  Hz, 1.2 Hz, 1 H), 6.96 (d,  $J =$

<sup>4</sup> The HPLC analyses were complicated by a partial separation of the two rotamers (arising from the hindered rotation about the C-N bond in the carbamate group) of the minor enantiomer resulting in a significant peak broadening. Thus the analysis apparently indicated enantiomeric excesses higher than 95% ee.



7.6 Hz, 1 H), 4.89 (d,  $J = 8.4$  Hz, 0.5 H), 4.76 (d,  $J = 8.4$  Hz, 0.5 H), 4.58 (d,  $J = 5.6$  Hz, 0.5 H), 4.48 (d,  $J = 6.0$  Hz, 0.5 H), 3.78 (s, 2 H), 3.72 (s, 1 H), 2.87-2.78 (m, 1 H), 2.76-2.70 (m, 1 H), 2.65-2.56 (m, 1 H), 2.31-2.17 (m, 1 H), 2.07 (ap q,  $J = 14.4$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  205.39 (204.77), 182.32 (181.97), 155.46 (154.87), 142.05 (141.82), 129.44, 127.78 (127.97), 124.42 (124.59), 122.78 (122.91), 110.71 (110.65), 64.27 (64.21), 60.29 (59.85), 56.04 (55.25), 53.28 (53.16), 38.33 (38.22), 32.92 (32.78), 24.76 (24.57); IR (neat,  $\text{cm}^{-1}$ ): 1718 (s), 1621 (w), 1471 (s), 1332 (m), 1104 (m), 752 (m); HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$  ( $\text{M}^+$ ) 300.1110, found 300.1122.

In the same way, the chiral non-racemic (95% ee) molybdenum complex (-)-**4** (0.079 g, 0.265 mmol) afforded (-)-**5** as a white solid (0.061 g, 77%) ( $[\alpha]_{\text{D}} = -33^\circ$ ,  $c$  0.295  $\text{CHCl}_3$ ).<sup>5</sup>

(±) (1S,5S,6S)-Spiro[8-azabicyclo[3.2.1]octane-6,3'-[3H]indole-2,2'(1'H)-dione [(±)-**6**] and (1S,5S,6S)-spiro[8-azabicyclo[3.2.1]octane-6,3'-[3H]indole-2,2'(1'H)-dione [(-)-**6**]. To a solution of the spiroketone (±)-**5** (0.034 g, 0.114 mmol) in methylene chloride (7.0 mL) at room temperature under argon was injected neat TMSI (83  $\mu\text{l}$ , 0.116 g, 0.583 mmol). The resulting light yellow solution was heated to reflux for 2 h and then stirred at room temperature for 2 h under argon. The reaction mixture was then washed with 20% aqueous NaOH (3 mL). The aqueous layer was re-extracted with methylene chloride, the combined organic extracts were dried ( $\text{MgSO}_4$ ), and solvent was removed under reduced pressure to yield the crude amine (±)-**6** (0.018 g, 65%) as a white solid. Purification of the crude product by filtration through a short plug of silica yielded an analytically pure product. Analytical data for amine (±)-**6**: mp = 169-

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171 °C (EtOAc/hexane) Lit. 171-173 °C (EtOAc);<sup>6</sup>  $R_f = 0.17$  (EtOAc/hexane, 3:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (s br, 1 H), 7.27 (td,  $J = 7.6$  Hz, 1.2 Hz, 1 H), 7.22 (d,  $J = 6.8$  Hz, 1 H), 7.09 (td,  $J = 7.6$  Hz, 1.2 Hz, 1 H), 6.94 (d,  $J = 7.6$  Hz, 1 H), 3.93 (d,  $J = 8.0$  Hz, 1 H), 3.54 (d,  $J = 5.2$  Hz, 1 H), 2.65-2.58 (m, 3 H), 2.16-2.06 (m, 2 H), 2.04-1.96 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.40, 183.82, 141.36, 129.32, 128.72, 124.36, 123.04, 110.40, 66.90, 63.59, 58.30, 40.71, 32.66, 25.00; IR (neat, cm<sup>-1</sup>): 3269 (br, s), 1702 (s), 1621 (m), 1471 (m), 1235 (m), 980 (m), 810 (m), 729 (m); HRMS (EI) calcd for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> (M<sup>+</sup>) 242.1055, found 242.1057.

In the same way, the chiral non-racemic ketone (-)-**5** (0.055 g, 0.183 mmol) afforded (-)-**6** as a white solid (0.022 g, 50 %) in 95% ee ( $[\alpha]_D = -49^\circ$ , c 0.605 CHCl<sub>3</sub>).

(±) (1S,5S,6S)-Spiro[8-aza-2R-hydroxy-8-methoxycarbonylbicyclo[3.2.1]oct-3-ene-6,3'-[3H]indole-2'(1'H)-one [(±)-**7**]] and (1R,5R,6R)-spiro[8-aza-2S-hydroxy-8-methoxycarbonylbicyclo[3.2.1]oct-3-ene-6,3'-[3H]indole-2'(1'H)-one [(+)-**7**]]. To a solution of the enone (±)-**4** (0.095 g, 0.321 mmol) and CeCl<sub>3</sub>·7 H<sub>2</sub>O (0.128 g, 0.344 mmol) in chloroform (5.0 mL) and anhydrous ethanol (9.0 mL) at -75 °C under argon was added NaBH<sub>4</sub> (0.015 g, 0.396 mmol) as a solution in abs. ethanol (0.5 mL). The reaction mixture was stirred at -78 °C for 25 minutes. Celite<sup>®</sup> was added and solvents were removed under reduced pressure. The resulting solid was deposited on a short plug of silica and eluted with EtOAc/hexanes (4:1) to give the alcohol (±)-**7** (0.077 g, 80 %) as a colorless oil which forms a white foam on heating:  $R_f = 0.23$  (EtOAc/hexane, 4:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (br s, 0.4 H), 7.92 (br s, 0.6 H), 7.44 (d,  $J = 7.6$  Hz, 0.4 H), 7.40 (d,  $J = 7.6$  Hz, 0.6 H), 7.21 (td,  $J = 7.6$  Hz, 1.2 Hz, 1 H), 6.87 (td,  $J$

<sup>5</sup> Attempted chromatographic separation of the enantiomers of (±)-**5** on chiral phases Chiralpak AD and Chiracel OD was unsuccessful. Therefore enantiomeric excess (%ee) was not determined.

= 7.6 Hz, 1.2 Hz, 0.6 H), 6.96 (td,  $J = 7.6$  Hz, 1.2 Hz, 0.4 H), 6.88 (d,  $J = 5.6$  Hz, 0.6 H), 6.86 (d,  $J = 5.6$  Hz, 0.4 H), 5.95-5.86 (m, 1 H), 5.83 (dt,  $J = 16.4$  Hz, 1.6 Hz, 0.6 H), 5.80 (dt,  $J = 16.8$  Hz, 2.0 Hz, 0.4 H), 5.01 (d,  $J = 4.8$  Hz, 0.6 H), 4.97 (d,  $J = 4.8$  Hz, 0.4 H), 4.77 (t,  $J = 6.0$  Hz, 0.6 H), 4.65 (t,  $J = 6.0$  Hz, 0.4 H), 4.56 (d,  $J = 4.8$  Hz, 0.4 H), 4.44 (d,  $J = 4.4$  Hz, 0.6 H), 3.76 (s, 1 H), 3.70 (s, 2 H), 2.67 (ddd,  $J = 13.7$  Hz, 4.8 Hz, 1.6 Hz, 1 H), 2.55 (br s, 0.6 H), 2.42 (ap pent,  $J = 7.6$  Hz, 1 H), 2.13 (br s, 0.4 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.07 (180.97), 154.90 (154.46), 141.57 (141.33), 131.64, 130.84 (130.69), 130.10, 128.93 (128.89), 127.97 (127.86), 125.88 (125.61), 122.21 (122.08), 109.93 (109.80), 69.93 (69.72), 58.93 (58.71), 57.58 (57.37), 52.96 (52.87), 32.73 (32.87); IR (neat,  $\text{cm}^{-1}$ ): 3250 (s), 1706 (s), 1621 (w), 1471 (m), 1324 (m), 1231 (m), 1104 (m), 756 (m); HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$  ( $\text{M}^+$ ) 300.1110, found 300.1108. In the same way, the chiral non-racemic enone (+)-4 (0.084 g, 0.281 mmol) afforded (+)-7 as a white solid (0.061 g, 72 %) ( $[\alpha]_{\text{D}} = +93^\circ$ ,  $c$  0.215  $\text{CHCl}_3$ ).<sup>7</sup>

**(±)(2'R,3S,5'S)-5'-(1S,2-Dihydroxyethyl)-2'-(hydroxymethyl)-1'-methoxycarbonyl-spiro[3H-indole-3,3'-pyrrolidin]-2(1H)-one [(±)-8] and (2'S,3R,5'R)-5'-(1R,2-dihydroxyethyl)-2'-(hydroxymethyl)-1'-methoxycarbonyl-spiro[3H-indole-3,3'-pyrrolidin]-2(1H)-one [(-)-8].** A solution of the alcohol (±)-7 (0.052 g, 0.175 mmol) in methylene chloride (9.0 mL) and dry methanol (1.5 mL) was ozonized at  $-75^\circ\text{C}$  for 10 minutes. A blue color of excess ozone developed within the first two to three minutes. The reaction mixture was flushed with argon and inserted into an ice bath. A suspension of  $\text{NaBH}_4$  (0.022 g, 0.573 mmol) in dry methanol (5.0 mL) was added and the reaction mixture was stirred at  $0^\circ\text{C}$  under argon for 1 h. A

<sup>6</sup> Hollinshead, S. P.; Grubisha, D. S.; Bennett, D. W.; Cook J. M. *Heterocycles* **1989**, 29(3), 529-537.

<sup>7</sup> Attempted chromatographic separation of the enantiomers of (±)-7 on chiral phases Chiralpak AD and Chiracel OD was unsuccessful. Therefore enantiomeric excess (%ee) was not determined.

second portion of NaBH<sub>4</sub> (0.034 g, 0.898 mmol) was added as solid and the mixture was stirred at 0 °C for an additional 1 h. Then, a third portion of NaBH<sub>4</sub> (0.019 g, 0.512 mmol) was added as solid, the cooling bath was removed and the reaction mixture was stirred at room temperature under argon for 2.5 h. Solvents were removed under reduced pressure and the crude product was deposited on Celite.<sup>®</sup> Celite<sup>®</sup> was placed on top of a short plug of silica followed by eluting the column with a mixture of methanol/methylene chloride (1:9) to provide a crude product. The crude product was purified by flash chromatography over silica eluting with methanol/methylene chloride (1:9) to afford the spirotriol ( $\pm$ )-**8** (0.043 g, 73 %) as a colorless oil which forms a white foam on heating:  $R_f$  = 0.29 (methanol/methylene chloride, 1:9); <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, 60 °C)  $\delta$  10.24 (s, 1 H), 7.57 (d,  $J$  = 7.2 Hz, 1 H), 7.20 (td,  $J$  = 7.6 Hz, 1.2 Hz, 1 H), 6.97 (td,  $J$  = 7.6 Hz, 1.2 Hz, 1 H), 6.83 (d,  $J$  = 7.6 Hz, 1 H), 5.20 (br s, 1 H), 5.05 (br s, 1 H), 4.40 (br s, 1 H), 4.33-4.28 (m, 1 H), 3.90 (t,  $J$  = 3.6 Hz, 1 H), 3.79 (dd,  $J$  = 10.8 Hz, 4.8 Hz, 1 H), 3.72 (dd,  $J$  = 11.2 Hz, 4.4 Hz, 1 H), 3.63 (s, 3 H), 3.53 (dd,  $J$  = 11.6 Hz, 4.8 Hz, 1 H), 3.48 (dd,  $J$  = 11.6 Hz, 3.6 Hz, 1 H), 3.44-3.39 (m, 1 H), 2.48 (dd,  $J$  = 12.4 Hz, 10.0 Hz, 1 H), 2.11 (dd,  $J$  = 12.4 Hz, 7.8 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, 60 °C)  $\delta$  180.49, 157.58, 142.21, 128.04, 127.44, 125.45, 121.23, 109.08, 73.44, 64.45, 63.41, 61.54, 58.48, 53.72, 52.24, 37.05; IR (neat, cm<sup>-1</sup>): 3277 (s), 1702 (s), 1621 (w), 1455 (m), 1374 (m), 1243 (w), 1038 (w), 756 (w); HRMS (FAB) calcd for C<sub>16</sub>H<sub>21</sub>N<sub>2</sub>O<sub>6</sub> (M+H<sup>+</sup>) 337.1400, found 337.1417. In the same way, the chiral non-racemic allylic alcohol (+)-**7** (0.061 g, 0.203 mmol) afforded (-)-**8** as a white foamy solid (0.034 g, 51 %) in 97% ee ( $[\alpha]_D$  = - 1.8 °, c 1.15 CH<sub>3</sub>OH).

**[5+2] Cycloaddition of dimethyl ethylidenemalonate to the complex (±)-1:**

**(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-(1S,2R,5S,7S)-8-aza-2-methoxy-7-methyl-6,6,8-trimethoxycarbonylbicyclo[3.2.1]oct-3-ene-2-yl]molybdenum.** To the solution of the molybdenum complex (±)-1 (0.055 g, 0.104 mmol) in methylene chloride (2.5 mL) at room temperature under argon was injected dimethyl ethylidenemalonate (0.019 mL, 0.021 g, 0.133 mmol). Solid Sc(OTf)<sub>3</sub> (0.014 g, 0.028 mmol) was added and the reaction mixture was stirred at room temperature under argon for 90 minutes. Reaction mixture was directly filtered through a short layer of Celite<sup>®</sup> and silica eluting with EtOAc to afford the crude product. The crude product mixture was separated by flash chromatography over silica, eluting with EtOAc/hexane (1:2) and later with EtOAc/hexane (2:3) to afford the recovered molybdenum complex (±)-1 (0.016 g, 29%) as a bright orange solid and the [5+2] cycloadduct (0.027 g, 37%) as a bright orange solid: mp = 168-170 °C (EtOAc/hexane); R<sub>f</sub> = 0.34 (EtOAc/hexane, 1:1); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 2.1 Hz, 0.5 H), 8.38 (d, *J* = 1.8 Hz, 0.5 H), 7.91 (d, *J* = 1.8 Hz, 0.5 H), 7.89 (d, *J* = 1.8 Hz, 0.5 H), 7.60-7.59 (m, 2 H), 7.46 (td, *J* = 2.4 Hz, 0.4 Hz, 1 H), 7.39-7.37 (m, 1 H), 6.21 (t, *J* = 2.4 Hz, 1 H), 6.18 (q, *J* = 2.4 Hz, 1 H), 6.14 (t, *J* = 2.1 Hz, 1 H), 5.04 (dd, *J* = 4.0 Hz, 1.6 Hz, 0.5 H), 4.95 (d, *J* = 3.6 Hz, 1.6 Hz, 0.5 H), 4.36 (s, 0.5 H), 4.24 (s, 0.5 H), 3.92 (s, 1 H), 3.91 (s, 2 H), 3.86-3.74 (m, 1 H), 3.80 (s, 2 H), 3.71 (s, 1 H), 3.70 (s, 1 H), 3.69 (s, 2 H), 3.48-3.42 (m, 1 H), 3.35 (br s, 0.5 H), 3.32 (br s, 0.5 H), 3.18 (s, 1.5 H), 3.15 (s, 1.5 H), 1.11 (d, *J* = 7.6 Hz, 1.5 H), 1.07 (d, *J* = 8.0 Hz, 1.5 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 228.34 (227.43), 226.82, 170.62 (170.49), 170.02 (169.79), 154.56 (152.72), 146.33, 144.93 (144.79), 139.76 (139.60), 136.55, 136.44, 136.12, 134.55, 105.83, 105.67 (two carbons), 71.61 (71.13), 64.43 (65.39), 62.77 (61.83), 56.94 (56.78), 56.52, 54.33 (54.20), 52.95 (52.87), 52.60, 52.51, 48.16 (48.21), 16.94 (17.10); IR (KBr, cm<sup>-1</sup>): 2952 (w), 1940 (s), 1854 (s), 1736 (m), 1708

(w), 1504 (w), 1449 (m), 1407 (m), 1307 (m), 1254 (m), 1210 (m), 1118 (m), 1050 (m), 1015 (m), 984 (w), 1015 (w), 984 (w), 765 (m), 721 (m). HRMS (FAB) calcd for  $C_{26}H_{31}N_7O_9BMo$  ( $M+H^+$ ) 692.1322, found 692.1345; Anal. calcd for  $C_{26}H_{30}BMoN_7O_9$ : C, 45.23; H, 4.38; N, 14.20. Found: C, 45.95; H, 4.58; N, 13.78.

**(±)(1S,5S,6S)-Spiro[8-aza-2R-hydroxy-8-methoxycarbonylbicyclo[3.2.1]octane-6,3'-**

**[3H]indole-2'(1'H)-one [(±)-9].** To a solution of the allylic alcohol (±)-7 (0.012 g, 0.040 mmol) in abs. ethanol (3 mL) was added palladium black (10% on carbon, 0.012 g, 0.011 mmol of Pd) and hydrogen (from balloon) was bubbled through the suspension for 10 h at room temperature. Suspension was then filtered through Celite<sup>®</sup> and solvents removed under reduced pressure. The resulting crude product was purified by flash chromatography over silica, eluting with EtOAc/hexane (3:1) to yield the alcohol (±)-9 (0.092 g, 76%) as a colorless oil which forms a white foam on heating:  $R_f = 0.28$  (EtOAc);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.29 (s, 0.5 H), 8.17 (s, 0.5 H), 7.49 (ap t,  $J = 7.6$  Hz, 1 H), 7.24 (t,  $J = 8.0$  Hz, 1 H), 7.04 (td,  $J = 7.6$  Hz, 1.2 Hz, 0.5 H), 7.03 (td,  $J = 7.6$  Hz, 0.8 Hz, 0.5 H), 6.92 (d,  $J = 6.8$  Hz, 0.5 H), 6.91 (d,  $J = 7.2$  Hz, 0.5 H), 4.63-4.60 (m, 0.5 H), 4.50-4.47 (m, 0.5 H), 4.28 (s, 0.5 H), 4.14-4.06 (m, 1.5 H), 3.73 (s, 1.5 H), 3.68 (s, 1.5 H), 2.76 (br s, 1 H), 2.44-2.38 (m, 1 H), 2.31 (d,  $J = 14$  Hz, 1 H), 2.14-2.10 (m, 1 H), 1.99-1.90 (m, 1 H), 1.88-1.81 (2 H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  182.34 (182.27), 155.07 (154.54), 141.98 (141.73), 128.88, 128.57, 125.11 (124.93), 122.69 (122.52), 110.25 (110.13), 68.89 (68.48), 59.87 (59.58), 58.25 (58.15), 56.01 (55.49), 52.86 (52.79), 32.47 (32.31), 26.92, 26.52 (26.49); IR (neat,  $cm^{-1}$ ): 3393 (s), 3250 (s), 1710 (s), 1679 (m), 1621 (w), 1471 (m), 1405 (w), 1332 (w), 1123 (w), 1019 (w), 748 (m); HRMS (EI) calcd for  $C_{16}H_{18}N_2O_4$  ( $M^+$ ) 302.1266, found 302.1260.

**(±)(1S,5S,6S)-Spiro[8-aza-2S-hydroxy-8-methoxycarbonylbicyclo[3.2.1]octane-6,3'-**

**[3H]indole-2'(1'H)-one [(±)-10]**. To a solution of the ketone (±)-5 (0.016 g, 0.053 mmol) in THF at -78 °C was added a 1 M solution of L-Selectride® in THF (0.060 mL, 0.060 mmol). The reaction mixture was stirred at -78 °C for 50 minutes. The solution was then partitioned between chloroform and water. The organic layer was dried (MgSO<sub>4</sub>) and solvents were removed under reduced pressure to afford the crude product. The crude product was purified by flash chromatography over silica, eluting with EtOAc to yield the alcohol (±)-10 (0.0089 g, 56%) as a clear oil: *R<sub>f</sub>* = 0.19 (EtOAc); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (br s, 0.5 H), 8.00 (br s, 0.5 H), 7.39 (ap t, *J* = 8.0 Hz, 1 H), 7.26 (t, *J* = 8.0 Hz, 1 H), 7.05 (td, *J* = 7.6 Hz, 1.22 Hz, 1 H), 6.92 (d, *J* = 7.6 Hz, 0.5 H), 6.91 (d, *J* = 8.0 Hz, 0.5 H), 4.72 (br d, *J* = 7.2 Hz, 0.5 H), 4.64 (d, *J* = 7.2 Hz, 0.5 H), 4.40 (br s, 0.5 H), 4.24 (br s, 0.5 H), 4.03 (br s, 0.5 H), 3.95 (br s, 0.5 H), 3.81 (s, 1.5 H), 3.71 (s, 1.5 H), 2.75 (br s, 1 H), 2.62-2.55 (m, 1 H), 2.31-2.24 (m, 1 H), 2.13-2.02 (m, 1 H), 1.93-1.80 (m, 2 H), 1.74-1.69 (m, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 182.14, 156.69 (156.12), 141.98 (141.81), 128.99, 128.30 (128.24), 124.99 (124.86), 122.71 (122.26), 110.30 (110.20), 69.53 (69.21), 60.75 (60.41), 59.58 (58.94), 55.38 (54.95), 53.09 (52.91), 36.47 (36.31), 25.29 (25.17), 23.97 (23.72); IR (neat, cm<sup>-1</sup>): 3397 (s), 3250 (s), 1710 (s), 1621 (w), 1471 (m), 1409 (m), 1197 (m), 1123 (m), 992 (m), 748 (m); HRMS (EI) calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub> (M<sup>+</sup>) 302.1266, found 302.1257.

**Determination of Enantiomeric Excesses by HPLC.**

HPLC was performed on a Millipore Waters™ 600 HPLC spectrometer with a CHIRALPAK AD and CHIRACEL OD columns at room temperature using a Waters™ 486 UV detector (230

or 260 nm). Samples of products for HPLC analyses were prepared by dissolving 4 mg of the pure compounds in 4.0 - 8.0 mL of absolute ethanol. One microliter (1  $\mu$ L) 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 % ee by HPLC**

Entry	Compound	Column <sup>a</sup>	Eluent <sup>b</sup>	Retention time <sup>c</sup> of (-) isomer	Retention time <sup>c</sup> of (+) isomer
1	<b>3a</b>	A	4%	27.8 min	19.4 (24.2) <sup>d</sup> min
2	<b>3b</b>	A	10%	31.9 min	22.0 min
3	<b>4</b>	A	10%	19.8 (21.6) <sup>d</sup> min	24.1 min
4	<b>6</b>	A	10%	20.1 min	27.4 min
5	<b>8</b>	A	10% <sup>e</sup>	32.1 min	42.7 min

<sup>a</sup> A = CHIRALPAK AD. <sup>b</sup> % of isopropanol in hexane, flowrate 1 ml/min, detection at 230 nm. <sup>c</sup> in minutes. <sup>d</sup> Two rotamers (arising from the rotation about the C-N bond in the carbamate group) appear as two distinct peaks. <sup>e</sup> detection at 260 nm.

### Two-dimensional NMR Spectroscopy.

#### COSY and NOESY spectra of compound ( $\pm$ )-8.

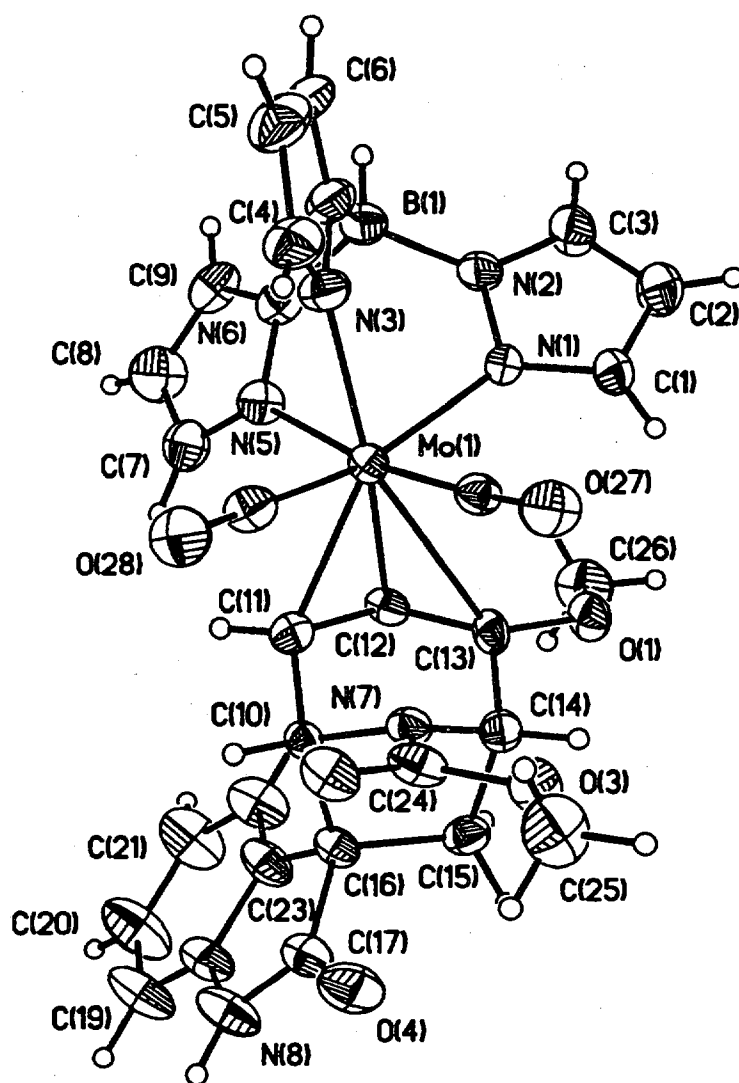
Two-dimensional spectra were acquired on an INOVA-600 (600 MHz <sup>1</sup>H) spectrometer using Varian standard micro-program at 25.0 °C for NOESY and 60.0 °C for COSY. A total of 512  $t_1$  increments and 2048  $t_2$  data points were employed. For COSY with tau (2 seconds) (pulse sequence: D1-90-D0-45-tau-FID), 32 scans were collected for each  $t_1$  FID and the spectrometer time was about 9 hours. For NOESY (pulse sequence: D1-90-D0-90-mix-90-FID), 48 scans were



accumulated for each  $t_1$  FID. Mixing time 0.2 seconds and relaxation delays 0.8 seconds were employed. Typical spectrometer time was about 16-20 hours. The spectra were measured in DMSO- $d_6$ .

**X-Ray Crystallographic Studies on Compound ( $\pm$ )-3a**

### Ortep Drawing of Complex ( $\pm$ )-3a



### Crystal Structure Analysis

A suitable crystal of **HMB265b2** was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 100 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated MoK $\alpha$  (0.071073Å) radiation. A hemisphere of data were measured using a series of combinations of phi and omega scans with 10 second frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all handled using SMART<sup>1</sup> software. Frame integration and final cell refinements were carried out using SAINT<sup>2</sup> software. The final cell parameters were determined from least-squares refinement on 8192 reflections. The SADABS<sup>3</sup> program was used to carry out absorption corrections.

The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V5.10).<sup>4</sup> 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<sub>ij</sub> 's related to the atom's ridden upon. The C-H distances were fixed at 0.93 Å, 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*<sup>5</sup>. Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V5.10 software. Additional details of data collection and structure refinement are given in Table 1.

### References

1. SMART Version 5.55, 2000, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
2. SAINT Version 6.02, 1999, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
3. SADABS, 1996, George Sheldrick, University of Göttingen,
4. SHELXTL V5.10, 1997, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
5. A. J. C. Wilson (ed), *International Tables for X-ray Crystallography, Volume C*. Kynoch, Academic Publishers, Dordrecht, 1992, Tables 6.1.1.4 (pp. 500-502) and 4.2.6.8 (pp. 219-222).

### **Details**

Overall, the crystal quality was somewhat poor and there was considerable, disordered solvent (dichloromethane, primarily) distributed throughout the crystal. Considerable effort was put forth trying to model this disorder, with only moderate success. The final results represent the molecular structure in the crystal lattice, with the contributions of the isolated, disordered solvent molecules subtracted out.

Table 1. Crystal data and structure refinement for 3a

Identification code	3a	
Empirical formula	C <sub>28</sub> H <sub>27</sub> B Mo N <sub>8</sub> O <sub>6</sub>	
Formula weight	678.33	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.6662(13) Å	α = 90°
	b = 30.647(4) Å	β = 91.996(2)°
	c = 12.9801(18) Å	γ = 90°
Volume	3842.9(9) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.172 Mg/m <sup>3</sup>	
Absorption coefficient	0.385 mm <sup>-1</sup>	
F(000)	1384	
Crystal size	0.10 x 0.04 x 0.04 mm <sup>3</sup>	
Theta range for data collection	1.33 to 28.79°	
Index ranges	-12 ≤ h ≤ 12, -33 ≤ k ≤ 41, -17 ≤ l ≤ 16	
Reflections collected	24776	
Independent reflections	9164 [R(int) = 0.0996]	
Completeness to theta = 28.79°	91.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	9164 / 0 / 397	
Goodness-of-fit on F <sup>2</sup>	1.087	
Final R indices [I > 2σ(I)]	R1 = 0.0894, wR2 = 0.1486	
R indices (all data)	R1 = 0.1769, wR2 = 0.1718	
Largest diff. peak and hole	0.641 and -0.702 e.Å <sup>-3</sup>	

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 3a.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{\text{ij}}$  tensor.

	x	y	z	$U(\text{eq})$
B(1)	9394(8)	2331(2)	1063(6)	52(2)
C(1)	10895(6)	2228(2)	3586(5)	54(2)
C(2)	11865(7)	2512(2)	3224(7)	76(2)
C(3)	11513(7)	2554(2)	2224(6)	62(2)
C(4)	6115(8)	2513(2)	2266(6)	69(2)
C(5)	6076(10)	2870(3)	1637(6)	84(3)
C(6)	7272(9)	2870(2)	1134(6)	74(2)
C(7)	8529(7)	1198(2)	565(5)	63(2)
C(8)	9031(9)	1301(3)	-384(6)	80(2)
C(9)	9393(7)	1719(3)	-343(5)	60(2)
C(10)	7106(6)	740(2)	3913(4)	36(1)
C(11)	7794(6)	950(2)	2982(4)	41(2)
C(12)	9236(6)	1063(2)	3121(5)	39(1)
C(13)	9586(6)	1197(2)	4115(5)	41(2)
C(14)	8821(6)	1008(2)	4998(5)	42(2)
C(15)	9123(6)	506(2)	4983(5)	47(2)
C(16)	7947(6)	314(2)	4300(5)	41(2)
C(17)	6947(6)	52(2)	4957(6)	51(2)
C(18)	7557(7)	-394(2)	3650(6)	63(2)
C(19)	7685(8)	-757(2)	3030(7)	81(3)
C(20)	8540(9)	-725(3)	2212(7)	101(3)
C(21)	9272(9)	-357(3)	2033(7)	88(3)
C(22)	9155(7)	6(2)	2663(6)	67(2)
C(23)	8286(6)	-10(2)	3467(6)	57(2)
C(24)	6359(7)	1099(2)	5498(5)	49(2)
C(25)	5934(8)	1306(3)	7186(6)	88(3)
C(26)	12025(7)	1238(2)	3755(6)	75(2)
C(27)	7835(6)	1889(2)	4237(5)	44(2)
C(28)	6143(7)	1531(2)	2905(5)	52(2)
Mo(1)	8109(1)	1685(1)	2867(1)	37(1)
N(1)	9999(5)	2101(2)	2858(4)	48(1)

N(2)	10382(6)	2322(2)	1993(4)	54(1)
N(3)	7279(5)	2278(2)	2114(4)	54(2)
N(4)	7986(6)	2500(2)	1399(4)	60(2)
N(5)	8594(5)	1546(2)	1178(4)	50(1)
N(6)	9174(5)	1865(2)	606(4)	49(1)
N(7)	7345(5)	1029(1)	4789(4)	39(1)
N(8)	6764(6)	-340(2)	4508(5)	66(2)
O(1)	10889(4)	1312(1)	4448(3)	52(1)
O(2)	5123(4)	1061(1)	5317(3)	54(1)
O(3)	6922(5)	1231(1)	6402(3)	59(1)
O(4)	6446(5)	169(2)	5761(4)	74(2)
O(27)	7673(5)	2037(2)	5063(4)	72(2)
O(28)	4986(5)	1449(2)	2959(4)	76(2)

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

B(1)-N(2)	1.513(9)	C(18)-C(23)	1.398(8)
B(1)-N(4)	1.534(9)	C(19)-C(20)	1.372(9)
B(1)-N(6)	1.557(9)	C(20)-C(21)	1.356(10)
C(1)-N(1)	1.318(7)	C(21)-C(22)	1.387(9)
C(1)-C(2)	1.374(8)	C(22)-C(23)	1.364(8)
C(2)-C(3)	1.337(9)	C(24)-O(2)	1.215(8)
C(3)-N(2)	1.331(8)	C(24)-O(3)	1.339(8)
C(4)-N(3)	1.357(8)	C(24)-N(7)	1.364(7)
C(4)-C(5)	1.366(10)	C(25)-O(3)	1.438(7)
C(5)-C(6)	1.347(10)	C(26)-O(1)	1.461(7)
C(6)-N(4)	1.366(8)	C(27)-O(27)	1.180(6)
C(7)-N(5)	1.332(8)	C(27)-Mo(1)	1.912(6)
C(7)-C(8)	1.376(9)	C(28)-O(28)	1.151(7)
C(8)-C(9)	1.329(9)	C(28)-Mo(1)	1.960(7)
C(9)-N(6)	1.335(7)	Mo(1)-N(3)	2.201(5)
C(10)-N(7)	1.453(7)	Mo(1)-N(1)	2.229(5)
C(10)-C(11)	1.541(7)	Mo(1)-N(5)	2.297(5)
C(10)-C(16)	1.609(8)	N(1)-N(2)	1.372(6)
C(11)-C(12)	1.441(7)	N(3)-N(4)	1.355(6)
C(11)-Mo(1)	2.276(5)	N(5)-N(6)	1.360(6)
C(12)-C(13)	1.384(8)		
C(12)-Mo(1)	2.215(5)	N(2)-B(1)-N(4)	108.7(6)
C(13)-O(1)	1.364(6)	N(2)-B(1)-N(6)	111.1(6)
C(13)-C(14)	1.501(8)	N(4)-B(1)-N(6)	107.9(5)
C(13)-Mo(1)	2.596(6)	N(1)-C(1)-C(2)	112.3(6)
C(14)-N(7)	1.444(7)	C(3)-C(2)-C(1)	103.9(6)
C(14)-C(15)	1.568(8)	N(2)-C(3)-C(2)	110.2(6)
C(15)-C(16)	1.533(8)	N(3)-C(4)-C(5)	110.2(7)
C(16)-C(23)	1.511(8)	C(6)-C(5)-C(4)	106.5(7)
C(16)-C(17)	1.539(8)	C(5)-C(6)-N(4)	108.1(7)
C(17)-O(4)	1.220(7)	N(5)-C(7)-C(8)	109.9(7)
C(17)-N(8)	1.344(8)	C(9)-C(8)-C(7)	106.6(7)
C(18)-C(19)	1.381(9)	C(8)-C(9)-N(6)	108.0(6)
C(18)-N(8)	1.384(8)	N(7)-C(10)-C(11)	107.3(4)

N(7)-C(10)-C(16)	100.7(4)	C(18)-C(23)-C(16)	108.0(6)
C(11)-C(10)-C(16)	110.9(4)	O(2)-C(24)-O(3)	124.3(5)
C(12)-C(11)-C(10)	116.3(5)	O(2)-C(24)-N(7)	124.1(7)
C(12)-C(11)-Mo(1)	69.0(3)	O(3)-C(24)-N(7)	111.5(6)
C(10)-C(11)-Mo(1)	121.8(4)	O(27)-C(27)-Mo(1)	176.6(5)
C(13)-C(12)-C(11)	113.1(5)	O(28)-C(28)-Mo(1)	177.5(6)
C(13)-C(12)-Mo(1)	89.2(4)	C(27)-Mo(1)-C(28)	83.7(3)
C(11)-C(12)-Mo(1)	73.6(3)	C(27)-Mo(1)-N(3)	94.7(2)
O(1)-C(13)-C(12)	124.4(5)	C(28)-Mo(1)-N(3)	82.6(2)
O(1)-C(13)-C(14)	109.4(5)	C(27)-Mo(1)-C(12)	103.1(2)
C(12)-C(13)-C(14)	119.1(5)	C(28)-Mo(1)-C(12)	105.2(2)
O(1)-C(13)-Mo(1)	122.0(4)	N(3)-Mo(1)-C(12)	161.1(2)
C(12)-C(13)-Mo(1)	58.6(3)	C(27)-Mo(1)-N(1)	87.5(2)
C(14)-C(13)-Mo(1)	115.0(4)	C(28)-Mo(1)-N(1)	159.0(2)
N(7)-C(14)-C(13)	110.4(5)	N(3)-Mo(1)-N(1)	79.09(19)
N(7)-C(14)-C(15)	103.0(4)	C(12)-Mo(1)-N(1)	95.44(19)
C(13)-C(14)-C(15)	105.8(5)	C(27)-Mo(1)-C(11)	103.9(2)
C(16)-C(15)-C(14)	104.4(5)	C(28)-Mo(1)-C(11)	68.2(2)
C(23)-C(16)-C(15)	119.3(5)	N(3)-Mo(1)-C(11)	142.9(2)
C(23)-C(16)-C(17)	102.1(5)	C(12)-Mo(1)-C(11)	37.39(19)
C(15)-C(16)-C(17)	110.3(5)	N(1)-Mo(1)-C(11)	132.69(19)
C(23)-C(16)-C(10)	115.4(5)	C(27)-Mo(1)-N(5)	170.8(2)
C(15)-C(16)-C(10)	103.1(4)	C(28)-Mo(1)-N(5)	102.1(2)
C(17)-C(16)-C(10)	106.1(4)	N(3)-Mo(1)-N(5)	79.18(19)
O(4)-C(17)-N(8)	125.8(6)	C(12)-Mo(1)-N(5)	82.4(2)
O(4)-C(17)-C(16)	126.5(6)	N(1)-Mo(1)-N(5)	84.61(19)
N(8)-C(17)-C(16)	107.6(6)	C(11)-Mo(1)-N(5)	84.94(19)
C(19)-C(18)-N(8)	129.0(6)	C(27)-Mo(1)-C(13)	72.5(2)
C(19)-C(18)-C(23)	121.6(7)	C(28)-Mo(1)-C(13)	111.0(2)
N(8)-C(18)-C(23)	109.4(6)	N(3)-Mo(1)-C(13)	159.49(19)
C(20)-C(19)-C(18)	117.5(7)	C(12)-Mo(1)-C(13)	32.23(19)
C(21)-C(20)-C(19)	121.6(7)	N(1)-Mo(1)-C(13)	84.27(18)
C(20)-C(21)-C(22)	120.8(7)	C(11)-Mo(1)-C(13)	57.4(2)
C(23)-C(22)-C(21)	119.2(7)	N(5)-Mo(1)-C(13)	111.25(18)
C(22)-C(23)-C(18)	119.2(6)	C(1)-N(1)-N(2)	104.6(5)
C(22)-C(23)-C(16)	132.8(6)	C(1)-N(1)-Mo(1)	133.1(4)

N(2)-N(1)-Mo(1)	122.1(4)	C(7)-N(5)-Mo(1)	135.3(5)
C(3)-N(2)-N(1)	108.8(6)	N(6)-N(5)-Mo(1)	119.3(4)
C(3)-N(2)-B(1)	131.3(6)	C(9)-N(6)-N(5)	110.2(6)
N(1)-N(2)-B(1)	118.8(5)	C(9)-N(6)-B(1)	129.4(6)
N(4)-N(3)-C(4)	105.8(5)	N(5)-N(6)-B(1)	120.3(5)
N(4)-N(3)-Mo(1)	122.3(4)	C(24)-N(7)-C(14)	126.1(6)
C(4)-N(3)-Mo(1)	131.7(5)	C(24)-N(7)-C(10)	121.8(5)
N(3)-N(4)-C(6)	109.2(6)	C(14)-N(7)-C(10)	104.4(4)
N(3)-N(4)-B(1)	119.9(5)	C(17)-N(8)-C(18)	112.8(6)
C(6)-N(4)-B(1)	130.9(6)	C(13)-O(1)-C(26)	118.0(5)
C(7)-N(5)-N(6)	105.2(5)	C(24)-O(3)-C(25)	114.2(5)

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Symmetry transformations used to generate equivalent atoms:

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
B(1)	57(5)	51(5)	49(5)	9(4)	5(4)	-10(4)
C(1)	49(4)	58(4)	55(5)	3(3)	-11(3)	-18(3)
C(2)	52(5)	82(6)	92(7)	16(5)	-18(4)	-24(4)
C(3)	53(5)	81(5)	54(5)	7(4)	6(4)	-29(4)
C(4)	63(5)	59(5)	85(6)	6(4)	-3(4)	20(4)
C(5)	90(7)	79(6)	82(7)	0(5)	-16(5)	34(5)
C(6)	94(6)	68(6)	58(5)	19(4)	-23(5)	2(5)
C(7)	67(5)	68(5)	54(5)	-8(4)	3(4)	0(4)
C(8)	106(7)	79(6)	55(6)	-12(4)	18(5)	9(5)
C(9)	57(4)	87(6)	37(4)	5(4)	16(3)	13(4)
C(10)	33(3)	35(3)	39(4)	0(3)	-1(3)	-2(3)
C(11)	44(4)	40(4)	40(4)	0(3)	5(3)	4(3)
C(12)	29(3)	34(3)	53(4)	2(3)	5(3)	1(3)
C(13)	26(3)	42(4)	55(4)	-4(3)	-8(3)	1(3)
C(14)	43(4)	50(4)	35(4)	0(3)	5(3)	-4(3)
C(15)	41(4)	52(4)	49(4)	14(3)	0(3)	6(3)
C(16)	30(3)	37(4)	56(4)	0(3)	11(3)	-1(3)
C(17)	40(4)	40(4)	72(5)	8(3)	5(3)	0(3)
C(18)	52(4)	39(4)	100(6)	1(4)	11(4)	-1(3)
C(19)	81(6)	40(5)	126(8)	-13(4)	41(6)	-14(4)
C(20)	101(7)	58(6)	149(9)	-37(5)	66(7)	-18(5)
C(21)	84(6)	72(6)	111(7)	-20(5)	43(5)	1(5)
C(22)	61(5)	52(5)	91(6)	-8(4)	30(4)	9(4)
C(23)	37(4)	38(4)	97(6)	-5(4)	15(4)	-2(3)
C(24)	59(5)	40(4)	49(4)	-2(3)	30(4)	-4(3)
C(25)	106(7)	102(7)	59(5)	-24(4)	36(5)	-12(5)
C(26)	35(4)	90(6)	100(6)	10(5)	9(4)	0(4)
C(27)	52(4)	36(4)	43(4)	0(3)	4(3)	-2(3)
C(28)	45(4)	66(5)	47(4)	10(3)	13(3)	5(3)
Mo(1)	34(1)	38(1)	39(1)	0(1)	4(1)	0(1)
N(1)	51(3)	44(3)	49(3)	1(2)	-11(3)	-6(3)

N(2)	61(4)	57(4)	44(4)	14(3)	5(3)	-19(3)
N(3)	56(4)	48(3)	58(4)	13(3)	1(3)	5(3)
N(4)	74(4)	58(4)	47(4)	10(3)	-5(3)	6(3)
N(5)	51(3)	50(4)	49(3)	-1(3)	9(3)	2(3)
N(6)	41(3)	66(4)	42(3)	10(3)	9(3)	4(3)
N(7)	34(3)	39(3)	46(3)	6(2)	6(2)	-3(2)
N(8)	51(4)	39(3)	111(5)	3(3)	34(4)	-6(3)
O(1)	34(2)	62(3)	58(3)	-2(2)	4(2)	-9(2)
O(2)	41(3)	54(3)	69(3)	-3(2)	22(2)	-3(2)
O(3)	63(3)	68(3)	47(3)	-8(2)	20(3)	-11(2)
O(4)	85(4)	67(3)	73(4)	6(3)	34(3)	-11(3)
O(27)	95(4)	66(3)	-55(3)	-10(3)	19(3)	4(3)
O(28)	36(3)	92(4)	100(4)	19(3)	8(3)	1(3)

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Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^{-3}$ ) for 3a.

	x	y	z	U(eq)
H(1B)	9758	2524	535	63
H(1A)	10874	2136	4268	65
H(2A)	12595	2644	3589	91
H(3A)	11989	2722	1756	75
H(4)	5441	2441	2732	83
H(5A)	5364	3073	1570	101
H(6A)	7561	3086	684	89
H(7A)	8195	925	751	76
H(8B)	9103	1114	-944	96
H(9A)	9739	1881	-882	72
H(10A)	6120	680	3778	43
H(11A)	7560	809	2322	50
H(12A)	9934	960	2647	46
H(14A)	9095	1143	5658	51
H(15A)	10016	446	4694	57
H(15B)	9112	384	5673	57
H(19)	7208	-1013	3161	98
H(20A)	8620	-961	1769	121
H(21A)	9859	-347	1481	105
H(22)	9663	257	2538	81
H(25A)	6409	1402	7807	132
H(25B)	5445	1041	7318	132
H(25C)	5289	1527	6955	132
H(26A)	12879	1332	4084	112
H(26B)	11861	1401	3131	112
H(26C)	12081	933	3596	112
H(8A)	6213	-537	4730	80

Table 6. Torsion angles [°] for **3a**.

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N(1)-C(1)-C(2)-C(3)	0.1(9)
C(1)-C(2)-C(3)-N(2)	1.6(9)
N(3)-C(4)-C(5)-C(6)	-3.7(10)
C(4)-C(5)-C(6)-N(4)	4.3(9)
N(5)-C(7)-C(8)-C(9)	-0.5(9)
C(7)-C(8)-C(9)-N(6)	2.2(9)
N(7)-C(10)-C(11)-C(12)	54.0(6)
C(16)-C(10)-C(11)-C(12)	-55.1(6)
N(7)-C(10)-C(11)-Mo(1)	-26.5(6)
C(16)-C(10)-C(11)-Mo(1)	-135.6(4)
C(10)-C(11)-C(12)-C(13)	-34.2(7)
Mo(1)-C(11)-C(12)-C(13)	81.9(4)
C(10)-C(11)-C(12)-Mo(1)	-116.1(4)
C(11)-C(12)-C(13)-O(1)	178.7(5)
Mo(1)-C(12)-C(13)-O(1)	-109.5(5)
C(11)-C(12)-C(13)-C(14)	31.3(7)
Mo(1)-C(12)-C(13)-C(14)	103.1(5)
C(11)-C(12)-C(13)-Mo(1)	-71.8(4)
O(1)-C(13)-C(14)-N(7)	159.3(5)
C(12)-C(13)-C(14)-N(7)	-48.8(7)
Mo(1)-C(13)-C(14)-N(7)	17.6(6)
O(1)-C(13)-C(14)-C(15)	-89.9(5)
C(12)-C(13)-C(14)-C(15)	61.9(7)
Mo(1)-C(13)-C(14)-C(15)	128.4(4)
N(7)-C(14)-C(15)-C(16)	25.2(6)
C(13)-C(14)-C(15)-C(16)	-90.8(5)
C(14)-C(15)-C(16)-C(23)	133.1(6)
C(14)-C(15)-C(16)-C(17)	-109.3(5)
C(14)-C(15)-C(16)-C(10)	3.6(5)
N(7)-C(10)-C(16)-C(23)	-162.7(5)
C(11)-C(10)-C(16)-C(23)	-49.3(7)
N(7)-C(10)-C(16)-C(15)	-30.8(5)
C(11)-C(10)-C(16)-C(15)	82.5(6)
N(7)-C(10)-C(16)-C(17)	85.1(5)

C(11)-C(10)-C(16)-C(17)	-161.6(5)
C(23)-C(16)-C(17)-O(4)	175.7(7)
C(15)-C(16)-C(17)-O(4)	47.9(9)
C(10)-C(16)-C(17)-O(4)	-63.0(8)
C(23)-C(16)-C(17)-N(8)	-1.9(7)
C(15)-C(16)-C(17)-N(8)	-129.7(6)
C(10)-C(16)-C(17)-N(8)	119.3(6)
N(8)-C(18)-C(19)-C(20)	179.4(8)
C(23)-C(18)-C(19)-C(20)	-1.0(13)
C(18)-C(19)-C(20)-C(21)	2.1(14)
C(19)-C(20)-C(21)-C(22)	-1.5(15)
C(20)-C(21)-C(22)-C(23)	-0.3(13)
C(21)-C(22)-C(23)-C(18)	1.4(11)
C(21)-C(22)-C(23)-C(16)	178.2(8)
C(19)-C(18)-C(23)-C(22)	-0.8(11)
N(8)-C(18)-C(23)-C(22)	178.9(7)
C(19)-C(18)-C(23)-C(16)	-178.3(7)
N(8)-C(18)-C(23)-C(16)	-1.4(8)
C(15)-C(16)-C(23)-C(22)	-55.0(11)
C(17)-C(16)-C(23)-C(22)	-176.7(8)
C(10)-C(16)-C(23)-C(22)	68.7(10)
C(15)-C(16)-C(23)-C(18)	122.1(6)
C(17)-C(16)-C(23)-C(18)	0.3(7)
C(10)-C(16)-C(23)-C(18)	-114.3(6)
O(27)-C(27)-Mo(1)-C(28)	-110(10)
O(27)-C(27)-Mo(1)-N(3)	-28(10)
O(27)-C(27)-Mo(1)-C(12)	146(10)
O(27)-C(27)-Mo(1)-N(1)	51(10)
O(27)-C(27)-Mo(1)-C(11)	-175(10)
O(27)-C(27)-Mo(1)-N(5)	20(11)
O(27)-C(27)-Mo(1)-C(13)	136(10)
O(28)-C(28)-Mo(1)-C(27)	13(15)
O(28)-C(28)-Mo(1)-N(3)	-83(15)
O(28)-C(28)-Mo(1)-C(12)	115(15)
O(28)-C(28)-Mo(1)-N(1)	-53(15)
O(28)-C(28)-Mo(1)-C(11)	121(15)



O(28)-C(28)-Mo(1)-N(5)	-160(15)
O(28)-C(28)-Mo(1)-C(13)	81(15)
C(13)-C(12)-Mo(1)-C(27)	-18.6(4)
C(11)-C(12)-Mo(1)-C(27)	95.8(4)
C(13)-C(12)-Mo(1)-C(28)	-105.5(4)
C(11)-C(12)-Mo(1)-C(28)	8.9(4)
C(13)-C(12)-Mo(1)-N(3)	142.1(6)
C(11)-C(12)-Mo(1)-N(3)	-103.5(7)
C(13)-C(12)-Mo(1)-N(1)	70.2(4)
C(11)-C(12)-Mo(1)-N(1)	-175.5(3)
C(13)-C(12)-Mo(1)-C(11)	-114.4(5)
C(13)-C(12)-Mo(1)-N(5)	154.0(4)
C(11)-C(12)-Mo(1)-N(5)	-91.7(3)
C(11)-C(12)-Mo(1)-C(13)	114.4(5)
C(12)-C(11)-Mo(1)-C(27)	-93.5(4)
C(10)-C(11)-Mo(1)-C(27)	15.2(5)
C(12)-C(11)-Mo(1)-C(28)	-170.8(4)
C(10)-C(11)-Mo(1)-C(28)	-62.0(5)
C(12)-C(11)-Mo(1)-N(3)	148.6(4)
C(10)-C(11)-Mo(1)-N(3)	-102.7(5)
C(10)-C(11)-Mo(1)-C(12)	108.7(6)
C(12)-C(11)-Mo(1)-N(1)	6.1(5)
C(10)-C(11)-Mo(1)-N(1)	114.9(4)
C(12)-C(11)-Mo(1)-N(5)	84.0(3)
C(10)-C(11)-Mo(1)-N(5)	-167.3(5)
C(12)-C(11)-Mo(1)-C(13)	-35.2(3)
C(10)-C(11)-Mo(1)-C(13)	73.5(5)
O(1)-C(13)-Mo(1)-C(27)	-85.4(5)
C(12)-C(13)-Mo(1)-C(27)	161.0(4)
C(14)-C(13)-Mo(1)-C(27)	51.0(4)
O(1)-C(13)-Mo(1)-C(28)	-161.3(4)
C(12)-C(13)-Mo(1)-C(28)	85.2(4)
C(14)-C(13)-Mo(1)-C(28)	-24.9(5)
O(1)-C(13)-Mo(1)-N(3)	-31.9(8)
C(12)-C(13)-Mo(1)-N(3)	-145.5(5)
C(14)-C(13)-Mo(1)-N(3)	104.4(6)

O(1)-C(13)-Mo(1)-C(12)	113.6(6)
C(14)-C(13)-Mo(1)-C(12)	-110.1(6)
O(1)-C(13)-Mo(1)-N(1)	3.8(4)
C(12)-C(13)-Mo(1)-N(1)	-109.7(4)
C(14)-C(13)-Mo(1)-N(1)	140.2(4)
O(1)-C(13)-Mo(1)-C(11)	154.6(5)
C(12)-C(13)-Mo(1)-C(11)	41.0(3)
C(14)-C(13)-Mo(1)-C(11)	-69.0(4)
O(1)-C(13)-Mo(1)-N(5)	85.7(5)
C(12)-C(13)-Mo(1)-N(5)	-27.8(4)
C(14)-C(13)-Mo(1)-N(5)	-137.9(4)
C(2)-C(1)-N(1)-N(2)	-1.6(7)
C(2)-C(1)-N(1)-Mo(1)	-176.0(5)
C(27)-Mo(1)-N(1)-C(1)	31.0(6)
C(28)-Mo(1)-N(1)-C(1)	96.3(8)
N(3)-Mo(1)-N(1)-C(1)	126.3(6)
C(12)-Mo(1)-N(1)-C(1)	-71.9(6)
C(11)-Mo(1)-N(1)-C(1)	-75.7(6)
N(5)-Mo(1)-N(1)-C(1)	-153.7(6)
C(13)-Mo(1)-N(1)-C(1)	-41.6(6)
C(27)-Mo(1)-N(1)-N(2)	-142.6(5)
C(28)-Mo(1)-N(1)-N(2)	-77.3(8)
N(3)-Mo(1)-N(1)-N(2)	-47.3(4)
C(12)-Mo(1)-N(1)-N(2)	114.5(4)
C(11)-Mo(1)-N(1)-N(2)	110.7(4)
N(5)-Mo(1)-N(1)-N(2)	32.7(4)
C(13)-Mo(1)-N(1)-N(2)	144.7(4)
C(2)-C(3)-N(2)-N(1)	-2.6(8)
C(2)-C(3)-N(2)-B(1)	164.9(7)
C(1)-N(1)-N(2)-C(3)	2.5(7)
Mo(1)-N(1)-N(2)-C(3)	177.7(4)
C(1)-N(1)-N(2)-B(1)	-166.8(6)
Mo(1)-N(1)-N(2)-B(1)	8.4(7)
N(4)-B(1)-N(2)-C(3)	-112.5(8)
N(6)-B(1)-N(2)-C(3)	128.9(7)
N(4)-B(1)-N(2)-N(1)	54.0(7)

N(6)-B(1)-N(2)-N(1)	-64.6(7)
C(5)-C(4)-N(3)-N(4)	1.6(9)
C(5)-C(4)-N(3)-Mo(1)	177.2(5)
C(27)-Mo(1)-N(3)-N(4)	127.9(5)
C(28)-Mo(1)-N(3)-N(4)	-149.1(5)
C(12)-Mo(1)-N(3)-N(4)	-33.2(9)
N(1)-Mo(1)-N(3)-N(4)	41.3(5)
C(11)-Mo(1)-N(3)-N(4)	-111.5(5)
N(5)-Mo(1)-N(3)-N(4)	-45.2(5)
C(13)-Mo(1)-N(3)-N(4)	77.7(7)
C(27)-Mo(1)-N(3)-C(4)	-47.1(7)
C(28)-Mo(1)-N(3)-C(4)	35.9(6)
C(12)-Mo(1)-N(3)-C(4)	151.7(7)
N(1)-Mo(1)-N(3)-C(4)	-133.7(7)
C(11)-Mo(1)-N(3)-C(4)	73.5(7)
N(5)-Mo(1)-N(3)-C(4)	139.8(7)
C(13)-Mo(1)-N(3)-C(4)	-97.4(8)
C(4)-N(3)-N(4)-C(6)	1.1(8)
Mo(1)-N(3)-N(4)-C(6)	-175.0(5)
C(4)-N(3)-N(4)-B(1)	178.2(6)
Mo(1)-N(3)-N(4)-B(1)	2.1(8)
C(5)-C(6)-N(4)-N(3)	-3.4(9)
C(5)-C(6)-N(4)-B(1)	180.0(7)
N(2)-B(1)-N(4)-N(3)	-61.1(7)
N(6)-B(1)-N(4)-N(3)	59.5(8)
N(2)-B(1)-N(4)-C(6)	115.2(8)
N(6)-B(1)-N(4)-C(6)	-124.2(7)
C(8)-C(7)-N(5)-N(6)	-1.4(8)
C(8)-C(7)-N(5)-Mo(1)	-176.7(5)
C(27)-Mo(1)-N(5)-C(7)	172.3(13)
C(28)-Mo(1)-N(5)-C(7)	-59.1(7)
N(3)-Mo(1)-N(5)-C(7)	-139.0(7)
C(12)-Mo(1)-N(5)-C(7)	44.9(7)
N(1)-Mo(1)-N(5)-C(7)	141.1(7)
C(11)-Mo(1)-N(5)-C(7)	7.3(7)
C(13)-Mo(1)-N(5)-C(7)	59.4(7)

C(27)-Mo(1)-N(5)-N(6)	-2.5(17)
C(28)-Mo(1)-N(5)-N(6)	126.1(4)
N(3)-Mo(1)-N(5)-N(6)	46.1(4)
C(12)-Mo(1)-N(5)-N(6)	-130.0(4)
N(1)-Mo(1)-N(5)-N(6)	-33.8(4)
C(11)-Mo(1)-N(5)-N(6)	-167.5(4)
C(13)-Mo(1)-N(5)-N(6)	-115.5(4)
C(8)-C(9)-N(6)-N(5)	-3.2(8)
C(8)-C(9)-N(6)-B(1)	-178.7(7)
C(7)-N(5)-N(6)-C(9)	2.8(7)
Mo(1)-N(5)-N(6)-C(9)	179.0(4)
C(7)-N(5)-N(6)-B(1)	178.8(6)
Mo(1)-N(5)-N(6)-B(1)	-4.9(7)
N(2)-B(1)-N(6)-C(9)	-122.3(7)
N(4)-B(1)-N(6)-C(9)	118.6(7)
N(2)-B(1)-N(6)-N(5)	62.6(7)
N(4)-B(1)-N(6)-N(5)	-56.5(7)
O(2)-C(24)-N(7)-C(14)	-170.5(6)
O(3)-C(24)-N(7)-C(14)	12.1(8)
O(2)-C(24)-N(7)-C(10)	-26.1(9)
O(3)-C(24)-N(7)-C(10)	156.5(5)
C(13)-C(14)-N(7)-C(24)	-145.5(5)
C(15)-C(14)-N(7)-C(24)	101.9(6)
C(13)-C(14)-N(7)-C(10)	65.2(5)
C(15)-C(14)-N(7)-C(10)	-47.3(5)
C(11)-C(10)-N(7)-C(24)	141.9(5)
C(16)-C(10)-N(7)-C(24)	-102.1(6)
C(11)-C(10)-N(7)-C(14)	-67.2(5)
C(16)-C(10)-N(7)-C(14)	48.8(5)
O(4)-C(17)-N(8)-C(18)	-174.7(7)
C(16)-C(17)-N(8)-C(18)	3.0(8)
C(19)-C(18)-N(8)-C(17)	176.8(8)
C(23)-C(18)-N(8)-C(17)	-2.9(9)
C(12)-C(13)-O(1)-C(26)	-8.2(8)
C(14)-C(13)-O(1)-C(26)	141.9(5)
Mo(1)-C(13)-O(1)-C(26)	-79.7(6)

O(2)-C(24)-O(3)-C(25)

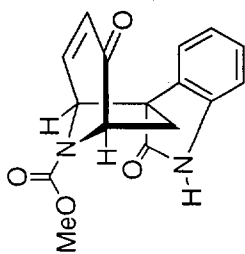
3.0(9)

N(7)-C(24)-O(3)-C(25)

-179.6(5)

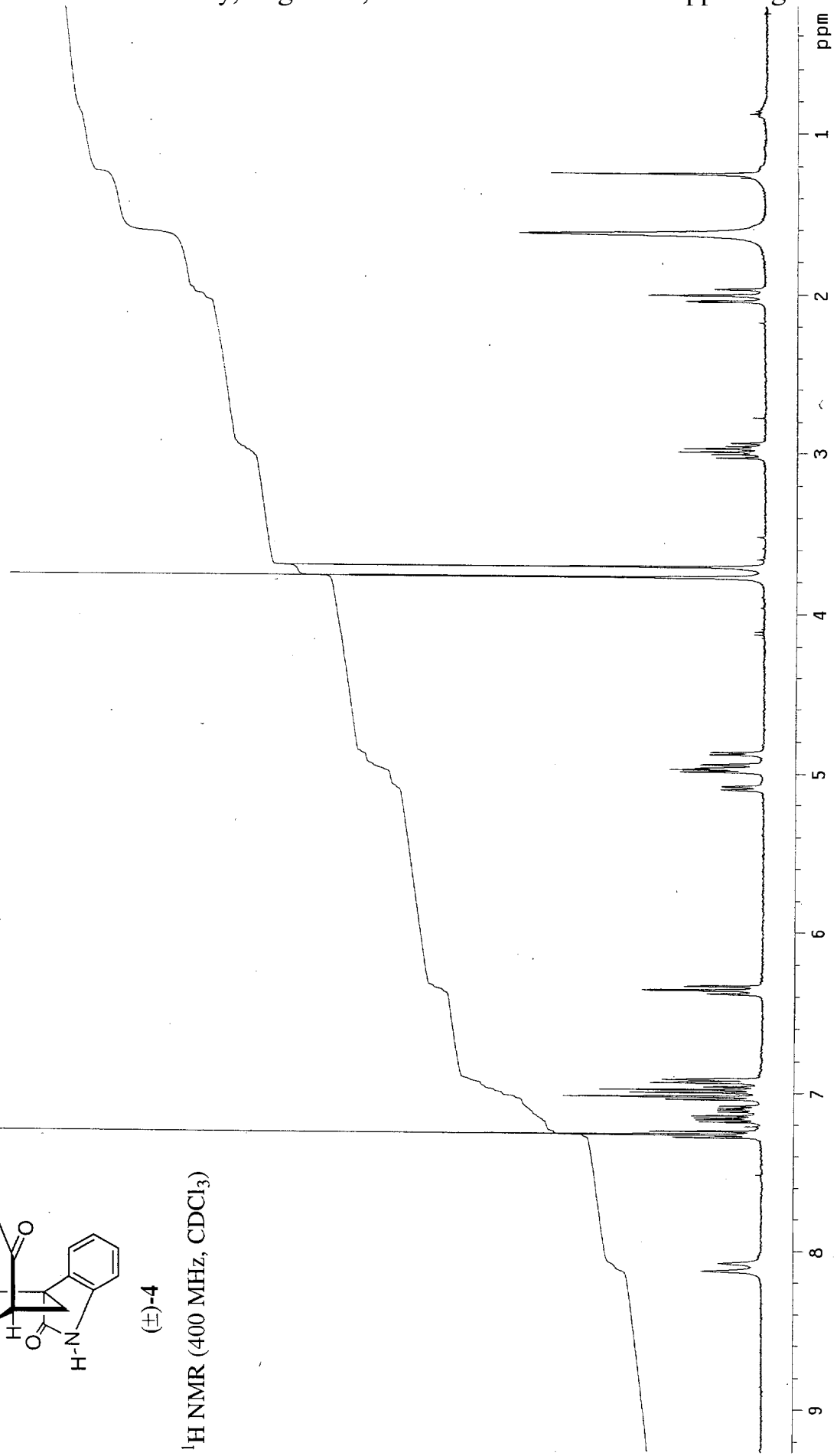
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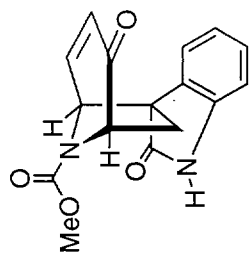
Symmetry transformations used to generate equivalent atoms:



(±)-4

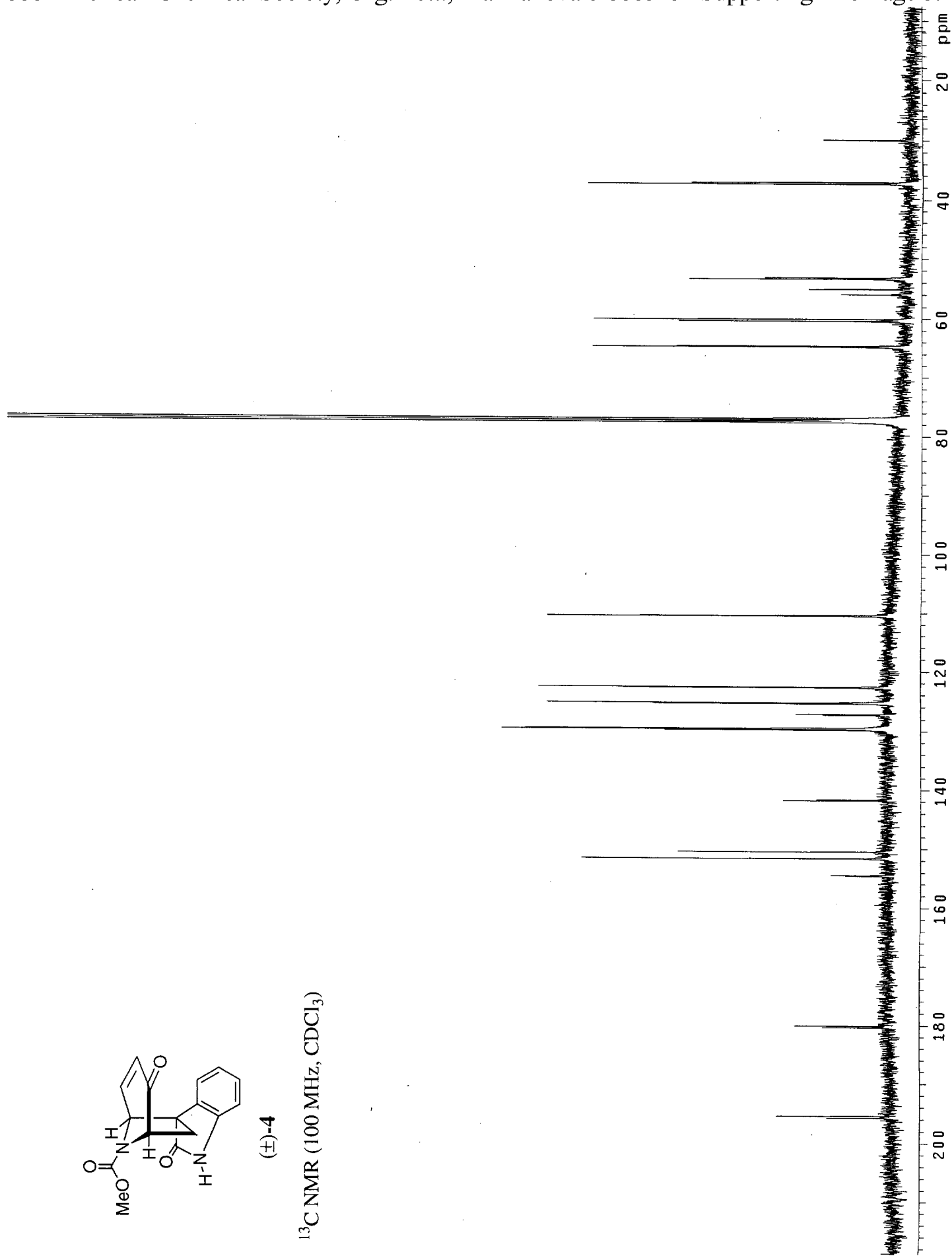
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

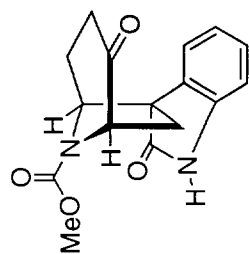




(±)-4

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)





(±)-5

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

