Supporting Information

A widely applicable concept for predictable induction of preferred configuration in C_3-symmetric systems

Gebhard Haberhauer,* Thomas Oeser and Frank Rominger
Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg (Germany)

Experimental preparations for **2b**, **2c**, and **3a-d**:

General Methods. All chemicals were reagent grade and used as purchased. All moisture-sensitive reactions were performed under an inert atmosphere of argon using distilled dry solvents. Reactions were monitored by TLC analysis using silica gel 60 F_{254} thin layer plates. Flash chromatography was carried out on silica gel 60 (230-400 mesh). ^{1}H and ^{13}C NMR spectra were measured on a Bruker WH 300, Avance 300 and Avance 500. All chemical shifts (δ) are given in ppm relative to TMS. The spectra were referenced to deuterated solvents indicated in brackets in the analytical data. HRMS spectra were recorded on a JEOL JMS-700 instrument.

Preparation of Compound 2b. To a solution of **1** (140 mg, 0.20 mmol) in acetonitrile (45 mL) were added K_2CO_3 (276 mg, 2.00 mmol) and $C_{11}H_8NCH_2Br$ (265 mg, 1.07 mmol) at room temperature and the mixture was stirred at reflux for 8 h. The solvent was evaporated and the residue was dissolved in AcOEt, extracted with water and brine, dried over $MgSO_4$ and concentrated in vacuo. Purification was accomplished by chromatography on silica gel (DCM/AcOEt/MeOH/Et_3N : 75/25/4/0.1) to yield 209 mg (77%) of **2b** as a white solid.
Spectroscopic data for **2b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 4.7 Hz, 3 H), 8.54 (d, *J* = 9.1 Hz, 3 H), 7.93 (d, *J* = 8.2 Hz, 6 H), 7.76-7.64 (m, 6 H), 7.22 (m, 3 H), 7.10 (d, *J* = 8.3 Hz, 6 H), 5.29-5.10 (m, 9 H), 2.43 (s, 9 H), 2.04-1.95 (m, 3 H), 1.00 ppm (m, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ =

163.2, 156.7, 149.7, 147.3, 139.1, 136.8, 136.1, 132.4, 130.3, 127.6, 126.4, 122.3, 120.5, 49.6, 46.8, 34.6, 19.9, 17.3, 9.9 ppm; HRMS (FAB+) $[M+H]^+$: calculated: 1039.5459; observed: 1039.5436.

Preparation of Compound 2c. To a solution of **1** (188 mg, 0.35 mmol) in acetonitrile (75 mL) were added K_2CO_3 (511 mg, 3.70 mmol) and m-$BrH_2CC_6H_4CH_2Br$ (1.39 g, 5.25 mmol) at room temperature and the mixture was stirred at reflux for 9 h. The solvent was evaporated and the residue was dissolved in AcOEt, extracted with water and brine, dried over $MgSO_4$ and concentrated in vacuo. Purification was accomplished by chromatography on silica gel (DCM/AcOEt/MeOH/ : 75/25/1) to yield 210 mg (55%) of **2c** as a white solid.

Spectroscopic data for **2c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 9.3 Hz, 3 H), 7.28 (m, 6 H), 7.07 (m, 3 H), 6.93 (m, 3 H), 5.23-5.02 (m, 9 H), 4.41 (s, 6 H), 2.43 (s, 9 H), 2.05-1.93 (m, 3 H), 1.02 (d, *J* = 6.7 Hz, 9 H), 0.95 ppm (d, *J* = 6.74 Hz, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 155.8, 147.4, 138.8, 136.0, 132.2, 129.6, 128.8, 126.7, 126.2, 49.7, 46.7, 34.5, 32.7, 19.9, 17.4, 9.9 ppm; HRMS (FAB+) $[M+H]^+$: calculated: 1084.2448; observed: 1084.2441.

Preparation of Compound 3a. Ethanol (400 mL) containing **2a** (87 mg, 0.08 mmol) was heated to reflux under argon. A solution of $Ru(DMSO)_4Cl_2$ (39 mg, 0.08 mmol) in 50 mL of ethanol was added, and reflux was continued for 24 h. The solvent was removed by rotary evaporation and the residue was purified by column chromatography on a SP Sephadex C-25 support whereby only one mononuclear ruthenium species could be isolated. The hemicage species **3a** was eluted with 5:3 aqueous NaCl (0.1 M)/acetone. Acetone was removed from the fractions by evaporation, and the complex was precipitated by addition of saturated aqueous ammonium hexafluorophosphate. A typical yield of 65 mg (55%) of **3a**$(PF_6)_2$ as red crystals was obtained. Alternatively, if the chloride salt was needed, the complex was isolated by evaporation of the appropriate fraction to dryness, addition of acetonitrile to the residue, and filtration to remove NaCl.

Spectroscopic data for **3a**: ^{1}H NMR (300 MHz, CD_3CN): δ = 8.52 (d, *J* = 8.5 Hz, 3 H), 8.45 (d, *J* = 8.3 Hz, 3 H), 8.08 (m, 3 H), 7.85 (m, 3 H), 7.16 (d, *J* = 10.4 Hz, 3 H), 7.08 (s, 3 H), 6.34 (s, 3 H), 5.41 (d, *J* = 17.8 Hz, 3 H), 4.90-4.74 (m, 6 H), 2.11-2.03 (m, 3 H), 2.07 (s, 9 H), 1.06 (d, *J* = 6.6 Hz, 9 H), 0.74 ppm (d, *J* = 6.7 Hz, 9 H); ^{13}C NMR (75 MHz, CD_3CN): δ = 163.2, 157.6, 154.8, 152.0, 151.0, 147.5, 140.0, 139.7, 139.2, 137.8, 131.9, 131.8, 125.1, 124.8, 50.4, 44.4, 34.7, 19.6, 19.1, 18.4, 9.6 ppm; HRMS (ESI+) $[M - 2\ Cl^-]^{2+}$: calculated: 592.7376; observed: 592.7368.

Preparation of Compound 3b. Ethylene glycol (100 mL) containing **2a** (22 mg, 0.02 mmol) was heated to 140 °C under argon. $(NH_4)_2OsCl_6$ (9 mg, 0.02 mmol) was added, and the mixture was stirred

at reflux for 24 h. The solvent was removed and the dark-green residue was purified by column chromatography on a SP Sephadex C-25 support whereby only one mononuclear osmium species could be isolated. The hemicage species **3b** was eluted with 5:3 aqueous NaCl (0.1 M)/acetone. The green complex **3b**Cl_2 (13 mg, 50%) was isolated by evaporation of the appropriate fraction to dryness, addition of acetonitrile to the residue, and filtration to remove NaCl.

For **3b**: ^{1}H NMR (300 MHz, CD_3CN): δ = 8.48 (d, *J* = 8.5 Hz, 3 H), 8.40 (d, *J* = 8.4 Hz, 3 H), 7.89 (m, 3 H), 7.68 (m, 3 H), 7.16 (d, *J* = 10.3 Hz, 3 H), 6.91 (s, 3 H), 6.20 (s, 3 H), 5.39 (d, *J* = 17.7 Hz, 3 H), 4.86 (m, 3 H), 4.78 (d, *J* = 17.7 Hz, 3 H), 2.09-2.06 (m, 3 H), 2.08 (s , 9 H), 1.07 (d, *J* = 6.6 Hz, 9 H), 0.74 ppm (d, *J* = 6.7 Hz, 9 H); ^{13}C NMR (75 MHz, CD_3CN): δ = 163.2, 159.6, 156.6, 151.03, 150.97, 146.7, 140.2, 139.5, 138.7, 138.3, 131.8, 125.2, 124.8, 50.4, 44.3, 34.8, 19.6, 19.1, 18.3, 9.7 ppm; HRMS (ESI+) $[M - 2\ Cl^-]^{2+}$: calculated: 637.7661; observed: 637.7658.

Preparation of Compound 3c. Ethylene glycol (100 mL) containing **2b** (31 mg, 0.03 mmol) was heated to 140 °C under argon. $Ir(acac)_3$ (15 mg, 0.03 mmol) was added, and the mixture was stirred at reflux for 24 h. The solvent was removed and the yellow residue was dissolved in AcOEt, extracted with water and brine, dried over $MgSO_4$ and concentrated in vacuo. Purification was accomplished by chromatography on silica gel (DCM/AcOEt/MeOH/ : 75/25/3) to yield 18 mg (49%) of **3c** as a yellow solid.

For **3c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.2 Hz, 3 H), 7.56 (m, 6 H), 7.19 (m, 3 H), 7.00-6.85 (m, 6 H), 6.68 (m, 3 H), 5.61 (s, 3 H), 4.92-4.79 (m, 6 H), 4.57 (d, *J* = 16.6 Hz, 3 H), 2.23-2.09 (m, 3 H), 1.96 (s, 9 H), 1.12 (d, *J* = 6.6 Hz, 9 H), 0.75 ppm (d, *J* = 6.6 Hz, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0, 159.6, 149.3, 147.2, 143.1, 136.2, 136.1, 132.1, 131.2, 123.8, 121.4, 119.9, 118.4, 50.4, 46.4, 34.5, 19.5, 19.3, 9.0 ppm; HRMS (FAB+) $[M+H]^+$: calculated: 1229.4854; observed: 1229.4895.

Preparation of Compound 3d. To a solution of **2c** (200 mg, 0.18 mmol) and K_2CO_3 (372 mg, 2.70 mmol) in acetonitrile (250 mL) was added NH_3 (7M in MeOH, 0.3 mL, 2.10 mmol) in acetonitrile (20 mL) at reflux over a period of 9 h. The solvent was evaporated and the residue was dissolved in AcOEt, extracted with water and brine, dried over $MgSO_4$ and concentrated in vacuo. Purification was accomplished by chromatography on silica gel (DCM/AcOEt/MeOH/ : 75/25/3) to yield 140 mg (90%) of **3d** as a white solid.

For **3d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 9.8 Hz, 3 H), 7.14 (m, 6 H), 6.84 (m, 3 H), 5.70 (s, 3 H), 5.48 (d, *J* = 16.6 Hz, 3 H), 4.98 (m, 3 H), 4.86 (d, *J* = 16.7 Hz, 3 H), 3.19 (d, *J* = 13.1 Hz, 3 H), 3.67 (d, *J* = 13.1 Hz, 3 H), 2.37-2.23 (m, 3 H), 2.03 (s, 9 H), 1.19 (d, *J* = 6.7 Hz, 9 H), 0.91 ppm (d, *J* =

6.7 Hz, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5, 149.9, 139.4, 136.7, 131.44, 131.39, 128.9, 128.2, 125.6, 124.5, 60.4, 50.1, 47.1, 34.7, 19.5, 19.4, 9.7 ppm; HRMS (FAB+) $[M+H]^+$: calculated: 861.4928; observed: 861.4937.