Enantioselective Ring-opening of meso Aziridines Catalyzed by Tridentate Schiff-base Chromium(III) Complexes

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Supporting information

General. Solvents and reagents for all reactions were used as received from commercial suppliers unless noted otherwise. Tetrahydrofuran was distilled from the sodium ketyl of benzophenone; dichloromethane and acetonitrile were distilled from calcium hydride. Reagent grade acetone was distilled and stored over 4 Å sieves. 2,6-Lutidine was freshly distilled from calcium hydride under a positive nitrogen pressure. Azidotrimethylsilane , $CrCl_3$.3THF were purchased from Aldrich and handled under N_2 atmosphere.
Silica gel chromatographic purification was performed using EM Silica Gel 60 silica packed in glass columns. Analytical thin layer chromatography (TLC) was performed on EM Silica Gel 60 F_{245} glass plates coated with 0.25 mm silica gel, using UV light or acidic solution of Ce(IV) and Mo(VI) for visualization.
A Neslab CB-80 cryobath was used for temperature control of all reactions carried out below room temperature. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-400 (400 MHz or 100MHz) and Bruker AM-500 (500 MHz or 125 MHz). Chemical shifts are reported as δ in ppm relative to tetramethylsilane in ^{1}H spectra and relative to chloroform-*d* in ^{13}C spectra. Mass spectra were obtained on a JEOL AX-505 or SX-102 high resolution magnetic sector mass spectrometer. Melting points were obtained in open capillary tubes with Laboratory Device Mel-Temp-II melting point apparatus and are uncorrected. Infrared spectra were recorded on a Matteson Galaxy Series FTIR 3000 spectrometer in KBr pellets or as thing film in NaCl plates. High performance liquid chromatographic (HPLC) analyses were carried out using Hewlett Packard 1050 series using Chiracel OD or Chiralpak AS columns

Preparation of 3-(diphenylmethylsilyl)salicylaldehyde. To a solution of 2-(diphenylmethylsilyl)phenol[1] (7.260 g, 25.0 mmol) in 50 mL of dry toluene was added 2,6-lutidine (4.66 mL, 40 mmol) under nitrogen. A solution of tin (IV) chloride (1.17 mL, 10 mmol) in 10 mL of dry toluene was added to the reaction mixture slowly via an addition funnel and the reaction mixture was stirred for one hour under nitrogen. Solid paraformaldehyde (3.003 g, 100 mmol) was added, and the reaction mixture was heated to reflux for 17 h and then cooled to 0 ^{o}C and quenched with 2 *N* HCl at pH = 2. The mixture was filtered through Celite and the filter pad was rinsed with 150 mL of dichloromethane. The liquid phases were separated and the aqueous phase was extracted with dichloromethane (3 x 20 mL). The combined organic phases were washed with NH_4Cl (sat., 50 mL) and brine (50 mL), and then dried over Na_2SO_4. After filtration, solvent was removde under reduced pressure, and purification by flash chromatography on silica gel (3% EtOAc in hexanes) afforded 3-(diphenylmethylsilyl)-salicylaldehyde (5.69 g, 72% yield). Mp 60.7-62.7 ^{o}C; IR (thin film) 3068, 3049, 3022,

1657, 1604, 1574, 1486, 1427, 1383, 1295, 1266, 1251, 1218, 1191, 1111, 917, 829, 794, 780, 757, 726, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.37 (s, 1H), 9.90 (s, 1H), 7.61 (dd, 1H, J_1 = 1.7 Hz, J_2 = 7.6 Hz), 7.56-7.54 (m, 4H), 7.45-7.36 (m, 7H), 6.98 (t, 1H, J = 7.4 Hz), 0.94 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 196.7, 166.6, 145.1, 135.74, 135.68, 135.2, 129.5, 127.9, 125,0, 119.8, -3.43; HRMS (EI) calcd for $(C_{20}H_{18}O_2Si)^+$: 318.1076. Found: 318.1071.

Preparation of (1*S*, 2*R*)-*N*-(3-diphenylmethylsilylsalicylidene)-1-aminoindanol (10). To a solution of (1*S*,2*R*)-aminoindanol (1,52g, 10.2 mmol) in ethanol (100mL) was added 3-(diphenylmethylsilyl)salicylaldehyde (2.96 g, 9.29 mmol) at room temperature, the reaction mixture was stirred for 3h. Compound **10** (3.71g, 89% yield) crystallized from the reaction medium as a bright yellow solid. Mp.: 152.2-152.6 ^oC; IR (thin film) 3067,3047, 1624, 1294, 1248, 1107, 956, 831, 727 cm^{-1}; ^1H NMR ($CDCl_3$, 400MHz) δ 8.53 (s, 1H), 7.52-7.50 (m, 4H), 7.38-7.29 (m, 7H), 7.26-7.25 (m, 2H), 7.23-7.17 (m, 2H), 7.12 (d, 1H, *J*= 7.3 Hz), 6.84 (t, 1H, *J*= 7.4 Hz), 4.73 (d, 1H, *J*= 5.4 Hz), 4.69 (ddd, 1H, *J*= 5.4 Hz, *J*= 5.0 Hz, *J*= 5.9 Hz), 3.16 (dd, 1H, *J*= 5.9 Hz, *J*= 15.9 Hz), 3.03 (dd, 1H, *J*= 5.0 Hz, *J*= 15.9 Hz), 2.18 (s, br, 1H), 0.9 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 167.2, 166.3, 141.1, 140.9, 140.6, 136.4, 135.2, 134.2, 129.2, 128.6, 127.8, 127.0, 125.5, 124.9, 123.6, 118.7, 75.5, 75.1, 39.6, -3.2; HRMS (FAB) calcd for $(C_{29}H_{27}NO_2Si + Na)^+$: 472.1709. Found: 472.1709.

Preparation of catalyst (1*S*,2*R*)-10·CrN_3. In a flame dried Schlenk flask under nitrogen atmosphere, (*1S*,2*R*)-ligand **10** (763 mg, 1.70 mmol) was disolved in dry THF (30 mL). 2,6-lutidine (0.79 mL, 6.81 mmol, freshly distilled from CaH_2) was added to the flask, followed by chromium (III) chloride tetrahydrofuran complex (1:3, 97%) (636 mg, 1.70 mmol). The resulting dark brown solution was stirred under nitrogen for 12 hours and then diluted with *t*-butylmethylether (200 mL) and washed with NH_4Cl and brine. The organic portion was dried over Na_2SO_4, and then concentrated under reduced pressure. The dark brown air stable solid thus obtained was treated with $TMSN_3$ (2.25 mL, 17mmol) and was stirred under a nitrogen atmosphere overnight at room temperature. Volatile materials were removed *in vacuo*. Flash column chromatography (13-20% acetone in hexane) afforded 459 mg (50% yield) of the complex as an air-stable brown solid. IR (KBr pellet) 3553, 3381, 3045, 2903, 2063, 1620, 1583, 1531, 1427, 1390, 1307, 1228, 1105, 1053, 952, 893, 858; HRMS (FAB) calcd for $(C_{29}H_{25}CrNO_2Si)^+$: 499.1060. Found: 499.1047.

Procedure for the ARO reaction of *N*-(2,4-dinitro)benzyl-7-azabicyclo-[4,1,0]-heptane. To a solution of complex (1*S*, 2*R*)-**10.**CrN_3 (10.8 mg, 0.02 mmol) in acetone (1mL) was added the aziridine (55.5 mg, 0.20 mmol) under nitrogen at room temperature. After stirring for 15 minutes, the reaction mixture was cooled to -30 ^oC. Azidotrimethylsilane (29 μL, 0.22 mmol) was added via syringe. The reaction mixture was stirred at -30 ^oC for 48 hours. After TLC analysis revealed complete consumption of starting aziridine, the mixture was concentrated in vacuo at low temperature, and the residue was purified by flash chromatography (10% acetone/hexane) to afford 2-azido-*N*-(2,4-dinitrobenzyl)cyclohexylamine as an oil (61mg, 95%yield). HPLC analysis on a Chiralpak AS column (5% EtOH/hexane, 1mL/min.) indicated 94% enantiomeric excess. IR (thin film) 3111, 3101, 2927, 2856, 2099, 1603, 1535, 1531, 1503, 1461, 1450, 1346, 1261, 1148, 1131, 1108, 1062, 909, 847, 835, 731 cm^{-1}; ^1H NMR ($CDCl_3$, 400MHz) δ 8.78 (d, 1H, *J*=2.3 Hz), 8.43 (dd, 1H, *J*=2.3 Hz, *J*=8.5 Hz), 8.08 (d, 1H,

J=8.5 Hz), 4.27 (d, 1H, *J*=16.1 Hz), 4.17 (d, 1H, *J*=16.1 Hz), 3.17 (ddd, 1H, *J*=4.3 Hz, *J*=10.0 Hz, *J*=11.0 Hz), 2.38 (ddd, 1H, *J*=4.1 Hz, *J*=10.2 Hz, *J*=10.2 Hz), 2.12-1.98 (m, 2H), 1.84 (s, br, 1H), 1.82-1.69 (m, 2H), 1.44-1.16 (m, 3H), 1.13-0.99 (m, 1H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 148.6, 146.7, 143.7, 132.1, 127.1, 120.0, 65.5, 60.8, 47.6, 31.3, 30.4, 24.3, 24.1; Exact mass (CI) calcd for ($C_{13}H_{16}N_6O_4$+H): 321.1311. Found: 321.1299.

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(1) Prepared in 64% yield from 2-bromophenol by the method of Yamamoto. Maruoka, K.; Itoh, T.; Araki, Y.; Shirasaka, T.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2975.