Supporting Information For

A Novel Chiral Ferrocenyl Phosphine Ligand from Sugar: Applications in Rh-Catalyzed Asymmetric Hydrogenation Reactions

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Ligand synthesis

1. Synthesis of (3a*S*,3'a*S*,4*S*,4'*S*,6*S*,6'*S*,6a*S*,6'a*S*)-5,5'-[1,1'-ferrocenyl]-bis-[tetrahydro-2,2,4,6-tetramethyl-4*H*-phospholo[3,4-*d*]-1,3-dioxole] (**3**)

n-BuLi (2.5 M solution in *n*-hexane, 50.6 mL, 126.4 mmol) was added dropwise to a solution of **8** (15.8 g, 63.2 mmol) in THF (200 mL) at -78 °C. The resulting dark red solution was stirred at room temperature for 1.5 h. The above solution was slowly added to a solution of cyclic sulfate **7** (31.9 g, 126.4 mmol) in THF (700 mL) at -78 °C, and then warmed up to room temperature for 4 h. The mixture was cooled to -78 °C again, *n*-BuLi (2.5 M solution in *n*-hexane, 53.1 mL, 132.7 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 20 h, and then heated at reflux for 2 h. The solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of dichloromethane, and was passed through a short silica-gel plug (eluent: ethyl ether: hexane = 3:7). Recrystallization from ethyl ether and hexane gave pure **3** as orange crystalline (17.4 g, 49 %). ¹H NMR (360 MHz, C₆D₆) = 4.52 (dd, *J* = 7.7, 9.9 Hz, 2H), 4.31 (dd, *J* = 7.1, 10.4 Hz, 2H), 4.14-4.12 (m, 4H), 4.05 (s, 2H), 3.72 (m, 2H), 2.38-2.30 (m, 4H), 1.51-1.44 (m, 18H), 0.78 (t, *J* = 6.9 Hz, 6H); ¹³C NMR (100 MHz, C₆D₆) = 117.6, 82.3 (m), 77.4 (d, *J* = 37.3 Hz), 75.2 (d, *J* = 25.3 Hz), 72.5, 72.1, 70.4, 27.7 (d, *J* = 14.5 Hz), 26.5 (m), 14.2 (d, *J* = 31.7 Hz), 11.2; ³¹P NMR (145 MHz, C₆D₆) = 39.3; mp 152-154 °C; [α]_D²⁰ = -4.938 (c = 1.0, CHCl₃); HRMS calcd for C₂₈H₄₀O₄P₂Fe (MH⁺): 559.1829, found: 559.1846.

2. Synthesis of [Rh(COD)(**3**)]PF₆ (**11**)

A solution of **3** (91 mg, 0.16 mmol) in CH₂Cl₂ (2 mL) was added dropwise to a solution of [Rh(COD)₂]PF₆ (71 mg, 0.15 mmol) in CH₂Cl₂ (2 mL) at -10 °C. The resulting mixture was stirred at ambient temperature for 15 min. Degassed hexane (10 mL) was added into the solution under vigorous stirring. The resulting yellow precipitate was filtered, washed with hexane (3 x 10 mL), and dried under vacuum. Yield: 89 mg, 64 %. ¹H NMR (360 MHz, CD₂Cl₂) = 5.68 (t, *J* = 6.7 Hz, 2H), 4.76 (s, 2H), 4.60 (s, 2H), 4.38-4.25 (m, 8H), 4.11 (s, 2H), 3.13-3.08 (m, 2H), 2.79-2.67 (m, 2H), 2.52 (dd, *J* = 7.1, 15.8 Hz, 2H), 2.38-2.25 (m, 4H), 2.14 (m, 2H), 1.88 (dd, *J* = 7.6, 19.9 Hz, 6H), 1.51 (s, 6H), 1.45 (s, 6H), 0.67 (dd, *J* = 7.3, 14.3 Hz, 6H); ¹³C NMR (100 MHz, CD₂Cl₂) = 119.0, 102.6, 90.0 (d, *J* = 7.3 Hz), 83.2 (m), 80.6, 78.9 (m), 76.6, 74.3, 72.5, 70.3 (m),

35.7, 34.3 (m), 27.9 (m), 27.4 (d, $J = 1.8$ Hz), 27.3, 14.2, 11.5; ^{31}P NMR (145 MHz, CD_2Cl_2) = 68.35 (d, $J = 147$ Hz), -143.98 (hept, $J = 711$ Hz); HRMS calcd for $\text{C}_{36}\text{H}_{52}\text{O}_4\text{P}_2\text{FeRh}$ (M PF_6^-): 769.1745, found: 769.1769.

General procedure of hydrogenation with *in situ* made catalyst

A solution of $[\text{Rh}(\text{COD})_2]\text{PF}_6$ (2.3 mg, 0.0050 mmol) and ligand **3** (3.1 mg, 0.0055 mmol) in THF (3 mL) was stirred in a glove-box for 10 min to allow the corresponding catalyst precursor to form. After substrate (0.5 mmol) was added, the mixture was hydrogenated in an autoclave for the time mentioned in the tables. After carefully releasing the hydrogen, the reaction mixture was passed through a short silica-gel plug to remove the catalyst. After removing the solvent, the desired product was obtained and was used for chiral GC or HPLC to measure the enantiomeric excess. For hydrogenation of dehydroamino acids, the enantiomeric excesses were measured after conversion to their corresponding methyl esters by treatment with TMSCHN_2 (TMS = trimethylsilyl).