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A Modular Design of Ruthenium Catalysts with Diamine and Binol-derived Phosphinite Ligands that are Enantiomerically-Matched for the Effective Asymmetric Transfer Hydrogenation of Simple Ketones

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Experimental section

All manipulations were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. $RuHCl(PPh_3)_3$ and the diphosphinite ligands were synthesized according literature. The other chemicals were purchased from Sigma-Aldrich. The ketones were washed with saturated K_2CO_3 solution and dried with anhydrous Na_2SO_4, and then distilled prior to use. The enantiomeric excess value of products was determined with a Perkin Elmer AutoSystem XL Gas Chromatograph system. Varian Gemini 300, Unity 400 and Unity 500 spectrometers were used to get the NMR spectra.

Trans-RuHCl[(*R*)-BINOP][(*R,R*)-DPEN] 1. (*R*)-2,2'-diphenylphosphinoyl-1,1'-Binapthyl [(*R)*-BINOP] (288 mg, 0.44 mmol) and $RuHCl(PPh_3)_3$ (370 mg, 0.4 mmol) were put into a 50 mL Schlenk flask and 10 mL of toluene were added. Stirring the mixture at 65 ^oC for 1 h resulted in a dark red solution. The solution was cooled to room temperature and then (*1R,2R*)-diphenyl ethylenediamine [(*R,R)*-DPEN] (85 mg, 0.4 mmol) was added. The color of the solution changed to yellow immediately. This was stirred at room temperature for 2 h, and then filtered through a Celite pad. The filtrate was concentrated under vacuum to about 1 mL and then 20 mL hexanes were

added to precipitate the product. The yellow solid was filtered and washed with hexanes (2 × 3 mL) (353 mg, Yield: 88 %; containing two isomers in the ratio 2:1). ^{1}H NMR (400 MHz, C_6D_6): Major isomer: δ -17.30 (dd, *J* = 24.0 Hz, *J* = 30.0 Hz), 2.16 (d, *J* = 7.2 Hz, 1H), 2.63 (m, 1H), 2.80-2.86 (m, 1H), 3.43-3.50 (m, 1H), 3.94-4.00 (m, 1H), 4.33-4.40 (m, 1H), 6.43-6.80 (m, 20H), 6.92-7.37 (m, 11H), 7.53-7.57 (m, 2H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.96-8.00 (m, 2H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.16-8.20 (m, 2H), 9.04-9.08 (m, 2H). Minor isomer: δ -13.37 (dd, *J* = 27.3 Hz, *J* = 33.9 Hz), 1.80 (m, 2H), 2.94 (m, 1H), 3.78 (m, 2H), 4.35 (m, 1H), 6.10-8.24 (m, 42H). ^{31}P NMR{^{1}H}(121.5 MHz, C_6D_6): Major isomer: δ 166.8 (AB, J_{pp} = 54.7 Hz), 167.3(AB, J_{pp} = 54.7 Hz). Minor isomer: δ 163.13 (d, J_{pp} = 53.0 Hz), 174.47 (d, J_{pp} = 53.6 Hz). Anal. Calcd for $C_{58}H_{49}ClN_2O_2P_2Ru$: C, 69.35; H, 4.92; N, 2.79. Found: C, 69.55; H, 5.07; N, 2.68.

Trans-RuHCl[(*R*)-BINOP][(*S*,*S*)-DPEN] 2. The procedure for the synthesis of complex **2** is similar to that for complex **1**. The yield of yellow powder is about 85 %. Two isomers are present in a molar ratio of 1/9. Yellow crystals of the major isomer suitable for the X-ray diffraction study were obtained from benzene/hexanes. ^{1}H NMR (300 MHz, C_6D_6): Major isomer: -17.33 (dd, *J* = 23.7 Hz, *J* = 29.7 Hz), 1.72-1.79 (m, 2H), 2.62 (d, *J* = 7.8 H, 1H), 3.11 (br, 1H), 3.52-3.67 (m, 2H), 4.20-4.30 (m, 1H), 5.99 (d, *J* = 7.5 Hz, 2H), 6.35-8.12 (m, 36H), 8.30 (t, *J* = 8.1 Hz, 2H), 9.15-9.24 (m, 2H). Minor isomer: δ -13.84 (dd, *J* = 27.0 Hz, *J* = 36.9 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): Major isomer: δ 164.0 (d, *J* = 53.7 Hz), 167.6 (d, *J* = 53.7 Hz). Minor isomer: δ 162.4 (d, *J* = 54.7 Hz), 174.5 (d, J = 54.7 Hz). Anal. Calcd for $C_{58}H_{49}ClN_2O_2P_2Ru$: C,

69.35; H, 4.92; N, 2.79. Found: C, 69.67; H, 4.78, N, 2.60.

Trans-RuHCl[(*R*)-xylBINOP][(*R,R*)-DPEN] 3. The procedure for the synthesis of complex **3** as a mixture of two isomers (2:1 ratio) is similar to that for complex **1**. Yield: 84 %. The minor isomer changed to major isomer upon recrystallization. Pale yellow single crystals of the major isomer suitable for X-ray formed in benzene/hexanes. ^{1}H NMR (300 MHz, C_6D_6): Major isomer: δ -17.47 (dd, J = 23.4 Hz, J = 30.6 Hz). Minor isomer: δ -13.25 (dd, J = 25.5 Hz, J = 29.7 Hz). ^{31}P NMR{^{1}H}(121.5 MHz, C_6D_6): Major isomer: δ 177.1 (J_{pp} = 55.03 Hz), 164.6 (J_{pp} = 55.0 Hz). Minor isomer: δ 169.5 (d, J_{pp} = 55.6 Hz), 165.7 (d, J_{pp} = 55.6 Hz). Anal. Calcd for $C_{66}H_{65}ClN_2O_2P_2Ru$: C, 70.99; H, 5.87; N, 2.51. Found: C, 71.25; H, 5.47; N, 2.31.

Trans-RuHCl[Xyl-(*R*)-BINOP][(*S,S*)-DPEN] 4. The procedure for the synthesis of complex **4** is similar to that for complex **1**. The yield is about 80 % of a yellow powder as one isomer. ^{1}H NMR (300 MHz, C_6D_6): -17.49 (dd, J = 24.3 Hz, J = 30.6 Hz), 1.69 (s, 6H), 1.91 (s, 6H), 2.01 (s, 6H), 2.10 (m, 1H), 2.42 (s, 6H), 2.70 (d, J = 7.5 Hz, 1H), 3.39 (br, 1H), 3.45-3.56 (m, 1H), 3.68-3.72 (m, 1H), 4.33-4.41 (m, 1H), 6.06 (d, J = 7.5 Hz, 2H), 6.33 (d, J = 9.3 Hz, 2H), 6.42-8.19 (m, 30H), 9.22 (br, 2H). ^{31}P{^{1}H} NMR: 167.7 (d, J_{pp} = 55.6 Hz), 165.6 (d, J_{pp} = 55.6 Hz). Anal. Calcd for $C_{66}H_{65}ClN_2O_2P_2Ru$: C, 70.99; H, 5.87; N, 2.51. Found: C, 70.82; H, 6.08; N, 2.73.

Typical procedure for the ruthenium catalyzed asymmetric transfer hydrogenation of ketones. In a glovebox, the ruthenium complex (4.0×10^{-3} mmol) and the base $KOCMe_3$ (4.5 mg, 0.04 mmol) were added in a 4 ml vial. Then 2-propanol (2 mL) was added. The mixture was stirred for 2 min. The substrate was added and the

solution was diluted with 2-propanol to the desired concentration. The base dissolved completely at this stage. This mixture was stirred at room temperature. The conversion and enantiomeric excess of the products were determined by NMR and chiral GC analysis, respectively.

X-ray Structure Analysis. Data were collected on a Nonius Kappa-CCD diffractometer using MoK_{α} radiation. The CCD data were integrated and scaled using the DENZO-SMN software package and the structures were solved and refined using SHELXTL V6.0. The hydrides were located and refined with isotropic thermal parameters.