Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z53415

© Wiley-VCH 2004

69451 Weinheim, Germany

Remarkable 4,4'-Substituent Effects on BINAP: Highly Enantioselective Ru-Catalysts for Asymmetric Hydrogenation of β-Aryl Ketoesters and Their Immobilization in Room-Temperature Ionic Liquids

Aiguo Hu,[#] Helen L. Ngo,[#] and Wenbin Lin*

Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, NC 27599

Experimental Section.

Materials and General Procedures. All of the chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were carried out under Argon with the use of standard inert atmosphere and Schlenk techniques. Solvents used in reactions were dried by standard procedures. NMR spectra were recorded on Bruker NMR 400 DRX spetrometer. ^{1}H-NMR spectra were recorded at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of the deuterated chloroform (δ 7.26). $^{13}C\{^{1}H\}$ NMR spectra were recorded at 100 MHz, and all of the chemical shifts are reported downfield in ppm relative to the carbon resonance of chloroform-d$_1$ (δ 77.0). $^{31}P\{^{1}H\}$ NMR spectra were recorded at 162 MHz, using 85% H_3PO_4 as external standard (δ 0.0) HR-FAB mass spectra and microanalysis results were obtained at UIUC mass spectrometry laboratory and microanalysis laboratory, respectively. MALDI-TOF mass spectra were obtained at Department of Chemistry at Duke University.

2,2'-bis(diphenylphosphino)-1,1'-binaphthyl-4,4'-bis(diethylphosphonate) (5) and **2,2'-bis(diphenylphosphino)-1,1'-binaphthyl-4,4'-bis(phosphonic acid) (6)** were synthesized according to literature procedure.[1]

1. Synthesis of 4,4'-substituted BINAPs.

Synthesis of (*R*)-4,4'-Dibromo-2,2'-bis(diphenylphosphinyl)-1,1'-binaphthyl (1a).[1] To a 1000 mL round bottom flask was added (*R*)-2,2'-bis(diphenylphosphinyl)-1,1'-binaphthyl[2] (30.0g, 46 mmol), anhydrous CH_2Cl_2 (700 mL) and pyridine (3.9 mL, 46 mmol). With vigorous stirring, Bromine (7.2 mL, 140 mmol) was carefully added *via* a syringe. After stirring at room temperature for 20hr, 1M aqueous sodium bisulfite was carefully added. This mixture was stirred for one hour until the organic layer turn from dark red to light yellow. The organic layer was separated and washed three times with brine, dried over anhydrous magnesium sulfate. After all volatile component were removed, the product was obtained as light brown solid. This bromination procedure was repeated twice and the crude products were used as starting materials, giving 38g light brown solid product. ^{31}P NMR showed that this crude product consisting of around 85% of dibromo- product together with around 10% monobromo- and some mutibromo- products. To get pure dibromo- product, this solid was extracted with 300 mL ethyl acetate with a Soxhlet extractor. The solid that precipitated out was further purified using the same procedure, giving 13.0 g (33%) pure product. The combined mother liquids was concentrated and dried in vacuum, gave 25g brown solid, consisting of mostly dibromo- product (based on ^{31}P NMR), but it can not be purified using Soxhlet extraction with ethyl acetate. $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.22 (d, $^3J_{H-H}$ = 8.3Hz, H_5), 7.72 (s, H_3), 7.66 (d, $^3J_{H-H}$ = 7.3Hz, Ph-*H*, 4H), 7.47 (m, $^3J_{H-H}$ = 7.8Hz, $^3J_{H-H}$ = 8.3Hz, $^4J_{H-H}$ = 1.0Hz, H_6), 7.40 (m, Ph-*H*, 8H), 7.28 (m, Ph-*H*, 8H), 6.86 (t, $^3J_{H-H}$ = 7.8Hz, H_7), 6.79 (d, $^3J_{H-H}$ = 8.3Hz, H_8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.2. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.9, 141.8, 134.4, 134.3, 134.0, 132.9, 132.6, 132.5, 132.3, 132.0, 131.9, 131.6, 131.5, 131.4, 131.2, 129.9, 128.6, 128.3, 128.1, 128.0, 127.4, 127.1, 126.7, 123.1, 122.9. FAB MS: 813.1 (Calc. 812.5 for M^+).

Synthesis of (*R*)-4,4'-Dibromo-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (1).[3] To a mixture of **1a** (0.49g, 0.6mmole), $Ti(O^iPr)_4$ (0.12mL, 0.4mmole) and anhydrous benzene (10mL), triethoxysilane (0.7mL, 4.2mmole) was added. The pale brown slurry was heated to reflux for 1hr, and then cool to room temperature. The solvent was removed under vacuum, the residue was dissolved in CH_2Cl_2 (20mL) and then passed through a short silica-gel column, washed with CH_2Cl_2 (20mL). To the filtrate, Methanol (15mL) was added, and this mixture was concentrate to ca. 10mL, lots of white precipitate formed. After filtration and washing with methanol, the pure product was obtained as white crystals (0.42g, 90%). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.23 (d, $^3J_{H-H}$ = 8.3Hz, H_5), 7.71 (s, H_3), 7.44 (m, $^3J_{H-H}$ = 7.3Hz, $^3J_{H-H}$ = 7.8Hz, $^4J_{H-H}$ = 1.0Hz, H_6), 7.20 (m, Ph-*H*, 8H), 7.12 (m, Ph-*H*, 8H), 7.02 (m, Ph-*H*, 4H), 6.91 (m, $^3J_{H-H}$ = 7.3Hz, H_7), 6.74 (d, $^3J_{H-H}$ = 8.3Hz, H_8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -14.6. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.2, 144.0, 139.8, 137.2, 137.0, 136.8, 136.2, 136.0, 134.4, 134.3, 134.2, 134.1, 133.8, 132.9, 132.8, 132.7, 132.6, 131.7, 128.8, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.1, 126.7, 123.8. FAB HR-MS: 779.0267 (Calc. 779.0267 for $[M+H]^+$). $[\alpha]_D$ = +158.0° (CH_2Cl_2, *c* 0.05).

Synthesis of (*R*)-4,4'-Dichloro-2,2'-bis(diphenylphosphinyl)-1,1'-binaphthyl (2a). **1a** (0.49g, 0.6mmole), CuCl (0.6g, 6mmole) and anhydrous DMF (10mL) was heated at 130°C under Argon overnight. After cooled to room temperature, reaction mixture was filtered through Celite and washed with CH_2Cl_2 (20mL). The filtrate was washed 4 times with water and then dried on Magnesium sulfate. LC separation on silica-gel column (CH_2Cl_2/Acetone) giving pure product as white powder (0.34g, 80%). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.25 (d, $^3J_{H-H}$ = 8.3Hz, H_5), 7.67 (d, $^3J_{H-H}$ = 7.3Hz, Ph-*H*, 4H), 7.52 (s, H_3), 7.47 (m, $^3J_{H-H}$ = 6.7Hz, $^3J_{H-H}$ = 8.5Hz, $^4J_{H-H}$ = 1.3Hz, H_6), 7.39 (m, Ph-*H*, 8H), 7.26 (m, Ph-*H*, 8H), 6.86 (m, $^3J_{H-H}$ = 6.7Hz, $^3J_{H-H}$ = 8.5Hz, $^4J_{H-H}$ = 1.0Hz H_7), 6.79 (d, $^3J_{H-H}$ = 8.3Hz, H_8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.6. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.2, 141.1, 141.0, 134.5, 134.3, 134.1, 132.9, 132.7, 132.4, 132.3, 132.0, 131.8, 131.5, 131.4, 131.3, 131.2, 130.8, 129.5, 128.3, 128.1, 127.9, 127.8, 127.3, 126.6, 124.3. FAB MS: 723.2 (Calc. 723.6 for M^+).

Synthesis of (*R*)-4,4'-Dichloro-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (2). Starting from **2a** (0.22g, 0.3mmole), using the same procedure as for **1**, 0.19 g pure product was obtained as white crystals (91%). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.26 (d, $^3J_{H-H}$ = 8.3Hz, H_5), 7.52 (s, H_3), 7.44 (m, $^3J_{H-H}$ = 8.3Hz, $^3J_{H-H}$ = 7.3Hz, H_6), 7.21 (m, Ph-*H*, 8H), 7.12 (m, Ph-*H*, 8H), 7.02 (m, Ph-*H*, 4H), 6.92 (m, $^3J_{H-H}$ = 7.3Hz, $^3J_{H-H}$ = 7.8Hz, H_7), 6.74 (d, $^3J_{H-H}$ = 8.8Hz, H_8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -14.6. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.4, 143.2, 143.0, 137.0, 136.9, 136.8, 136.7, 136.3, 136.1, 134.5, 134.4, 134.3, 132.9, 132.8, 132.7, 132.6, 130.7, 130.1, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 126.6, 124.3. FAB HR-MS: 691.1277 (Calc. 691.1278 for $[M+H]^+$). $[\alpha]_D$ = +107.0° (CH_2Cl_2, *c* 0.05).

Synthesis of (*R*)-4,4'-Dimethyl-2,2'-bis(diphenylphosphinyl)-1,1'-binaphthyl (3a). A mixture of **1a** (1.0 g, 1.2 mmol), trimethylboroxine in 50% wt THF (0.73 mL), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), and 2M Na_2CO_3 (3 mL) was dissolved in DME (20 mL). The reaction mixture was heated to reflux for 48 hrs. The mixture was then allowed to cool to r.t. and extracted with EtOAc and washed with water 3 times. The organic layer was dried over $MgSO_4$ and solvent was removed under reduced pressure. The crude product was recrystallized in acetone to give pure product as white solid (0.70g, 83%). $^1H\ \{^{31}P\}$ NMR ($CDCl_3$): δ 7.89 (d, $^3J_{H-H}$ = 8.3 Hz, H_5, 2H), 7.58 (d, $^3J_{H-H}$ = 7.8Hz, Ph-*H*, 4H), 7.45 (d, $^3J_{H-H}$ = 7.3 Hz, Ph-*H*, 4H), 7.36 (m, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 2.0 Hz, H_6, Ph-*H*, 4H), 7.24 (m, Ph-*H*, 4H), 7.15 (m, Ph-*H,* 4H), 6.90 (m, H_7, 2H), 6.83 (m, H_8, 2H), 2.65 (s, 6H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.1.

Synthesis of (*R*)-4,4'-dimethyl-2,2'-bis(diphenylphosphino)-1,1'-binaphthal (3). Starting with **3a,** using the same procedure as for **1**, after recrystallization in methanol, pure product was obtained as white solid in quantitative yield. $^1H\ \{^{31}P\}$ NMR ($CDCl_3$): δ 7.95 (d, $^3J_{H-H}$ = 7.8 Hz, H_5, 2H), 7.37 (m, $^3J_{H-H}$ = 8.3Hz, $^4J_{H-H}$ = 4 Hz, H_6, 2H), 7.25 (s, 2H), 7.23 (s, 4H), 7.15 (m, 2H), 7.1 (m, Ph-*H*, 16H), 6.92 (m, 2H), 2.65 (s, CH_3, 6H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -13.4. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.5, 144.4, 144.0, 144.2, 143.9, 137.9, 134.8, 134.8, 134.2, 134.1, 133.9, 133.7, 133.6, 133.5, 132.9, 132.8, 132.4, 131.0, 128.4, 128.3, 127.9, 127.4, 126.4, 126.3, 125.4, 123.9, 19.9. MALDI MS: 651.3 (Calc. 650.7 for M^+). $[\alpha]_D$ = +120.8° (CH_2Cl_2, *c* 0.05).

Synthesis of (*R*)-4,4'-diphenyl-2,2'-bis(diphenylphosphinyl)-1,1'-binaphthyl (4a). A mixture of **1a** (203 mg, 0.25 mmol), phenylboric acid (0.92 g, 0.75 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), 2M Na_2CO_3 (1 mL), ethanol (2 mL) and DME (12 mL) was heated to reflux under Argon for 48hr. After removal of all volatile components, CH_2Cl_2 (5 mL) was added, and this solution was washed with water for 3 times, dried on anhydrous magnesium sulfite. ^{31}P NMR showed that this crude product consisting of around 95% desired product and 5% of mono-phenyl product. It could not be purified at this stage, and was used directly to prepare **4**. $^{1}H\{^{31}P\}$ NMR ($CDCl_3$): δ 7.88 (d, $^{3}J_{H\text{-}H}$ = 8.5Hz, H_5), 7.67-7.12 (m, 34H), 7.01 (d, $^{3}J_{H\text{-}H}$ = 8.0Hz, H_7), 6.87 (m, H_8). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 29.1.

Synthesis of (*R*)-4,4'-Diphenyl-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (4). Starting from crude **4a**, using the same procedure as for **1**, after recrystallization in methanol, pure product was obtained as white powder (0.15 g, 77% for two steps). $^{1}H\{^{31}P\}$ NMR ($CDCl_3$): δ 7.95 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, H_5, 2H), 7.37 (m, $^{3}J_{H\text{-}H}$ = 8.3Hz, $^{4}J_{H\text{-}H}$ = 4 Hz, H_6, 2H), 7.25 (s, 2H), 7.23 (s, 4H), 7.15 (m, 2H), 7.1 (m, Ph-*H*, 16H), 6.92 (m, 2H), 2.65 (s, CH_3, 6H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -13.4. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 144.5, 144.4, 144, 144.2, 143.9, 137.9, 134.8, 134.8, 134.2, 134.1, 133.9, 133.7, 133.6, 133.5, 132.9, 132.8, 132.4, 131, 128.4, 128.3, 127.9, 127.4, 126.4, 126.37, 125.4, 123.9, 19.9. MALDI MS: 651.3 (Calc. 650.7 for M^+). $[\alpha]_D$ = +120.8° (CH_2Cl_2, *c* 0.05).

Synthesis of (*R*)-4,4'-Bis(trimethylsilyl)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (7). In a 25mL Schlenk flask, **1** (312mg, 0.4mmole) and anhydrous THF (10mL) was added under argon. This mixture was cooled down to -78°C using dry ice/acetone bath. After stirring at this temperature for 10min, n-BuLi (1.6M, 0.6mL, 0.96mmole) was slowly added *via* syringe. The solution turned from colorless to light yellow. It was stirred at this temperature for 3hr, and then TMSBr (0.16mL, 1.2mmole) was added. The reaction mixture was stirred at this temperature for 1hr and then warmed to room temperature and stirred overnight. After removal of solvent, and LC separation on silica-gel column (toluene/hexane), the final product was obtained as light yellow solid. This solid was recrystallized in methanol to give pure product as white crystals (167mg, 55%). $^{1}H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.03 (d, $^{3}J_{H\text{-}H}$ = 8.3Hz, H_5), 7.60 (s, H_3), 7.34 (m, H_6), 7.15 (m, Ph-*H*, 12H), 7.08 (m, Ph-*H*, 4H), 7.02 (m, Ph-*H*, 4H), 6.90 (m, H_7 & H_8), 0.34 (s, 18H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -14.2. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 138.0, 137.8, 136.6, 134.3, 134.2, 134.1, 133.1, 133.0. 132.9, 128.6, 128.3, 128.0, 127.9, 127.6, 126.0, 125.1, 0.3. FAB MS: 767.2845 (Calc. 767.2848 for $[M+H]^+$). $[\alpha]_D$ = +82.8° (CH_2Cl_2, *c* 0.05).

Other 4,4'-substituted BINAPs were synthesized in similar procedure.

(*R*)-4,4'-Bis(triisoproylsilyl)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl(8). Yield: 21%. $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 7.97 (d, $^3J_{H-H}$ = 8.3Hz, H_5), 7.61 (s, H_3), 7.23 (m, H_6), 7.20 (m, Ph-*H*, 8H), 7.13 (m, Ph-*H*, 4H), 7.01 (m, Ph-*H*, 4H), 6.94 (m, Ph-*H*, 4H), 6.77 (m, H_7 & H_8), 1.44 (m, $^3J_{H-H}$ = 7.4Hz, 6H), 1.03 (d, $^3J_{H-H}$ = 7.4Hz, 36H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -13.7. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.3, 137.9, 134.8, 134.7, 134.6, 134.0, 133.5, 133.4, 133.3, 133.2, 133.1, 128.7, 128.5, 128.4, 128.2, 127.8, 125.7, 125.0, 19.4, 13.1. FAB MS: 935.7 (Calc. 935.4 for M^+). $[\alpha]_D$ = +69.0° (CH_2Cl_2, *c* 0.03).

(*R*)-4-triisoproylsilyl-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (8b). **8b** was obtained as a byproduct of **8**, Yield: 15%. $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.02 (d, $^3J_{H-H}$ = 8.5Hz, H_5), 7.96 (d, $^3J_{H-H}$ = 9.0Hz, $H_{5'}$), 7.64 (s, H_3), 7.36 (m, $^3J_{H-H}$ = 8.5Hz, $^3J_{H-H}$ = 8.0Hz, $^4J_{H-H}$ = 2.0Hz, H_6), 7.23-6.91 (m, Ph-*H*, 20H, H_7 & $H_{3', 4', 6', 7'}$), 6.74 (m, $H_{8, 8'}$), 1.40 (m, $^3J_{H-H}$ = 7.2Hz, 3H), 1.02 (d, $^3J_{H-H}$ = 7.2Hz, 18H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -13.9 (m), -14.7 (m).

(*R*)-4,4'-Diiodo-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (9). Yield: 74%. $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.08 (d, $^3J_{H-H}$ = 8.8Hz, H_5), 8.00 (s, H_3), 7.42 (m, $^3J_{H-H}$ = 7.8Hz, $^3J_{H-H}$ = 8.8Hz, H_6), 7.21-7.11 (m, Ph-*H*, 16H), 7.00 (m, Ph-*H*, 4H), 6.90 (m, $^3J_{H-H}$ = 7.8Hz, $^3J_{H-H}$ = 7.3Hz, H_7), 6.70 (d, $^3J_{H-H}$ = 7.3Hz, H_8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -14.4. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.4, 134.6, 134.5, 134.4, 134.3, 134.2, 134.1, 134.0, 133.2, 132.8, 132.7, 132.6, 132.2, 128.8, 128.3, 128.2, 128.1, 128.0, 127.9, 126.7. MALDI MS: 874.3 (Calc. 874.0 for M^+). $[\alpha]_D$ = +44.2° (CH_2Cl_2, *c* 0.05).

(*R*)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl-4,4'-Bis(diphenylmethanol) (10). Yield: 37%. $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.20 (m, H_5), 7.32-6.80 (m, Ar-*H*, 48H), 3.5 (br, 2H), $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -14.2. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.8, 146.7, 141.4, 141.3, 134.5, 134.4, 134.3, 134.2, 133.2, 132.5, 132.4, 132.3, 131.2, 131.1, 128.3, 128.0, 127.9, 127.8, 127.5, 127.4, 127.3, 127.0, 126.9, 125.9, 125.1, 83.6. FAB MS: 987.6 (Calc. 987.1 for M^+). $[\alpha]_D = +192.2°$ (MeOH, *c* 0.05).

(*R*)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl-4,4'-Bis(cyclopentanol) (11). Yield: 44%. $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.71 (d, $^3J_{H-H}$ = 8.8Hz, H_5), 7.50 (s, H_3), 7.37 (m, $^3J_{H-H}$ = 8.3Hz, $^3J_{H-H}$ = 8.8Hz, $^4J_{H-H}$ = 1.0Hz, H_6), 7.13 (m, Ph-*H*, 16H), 7.00 (m, Ph-*H*, 4H), 6.94 (m, H_7 & H_8), 4.12 (q, $^3J_{H-H}$ = 7.3Hz, 2H), 2.19 (m, 4H), 1.93 (m, 4H), 1.62(m, 4H), 1.26(t, $^3J_{H-H}$ = 7.3Hz, 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -14.1. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.1, 137.8, 137.7, 137.6, 134.7, 134.1, 134.0, 133.9, 133.8, 133.0, 132.9, 132.8, 131.6, 128.5, 128.4, 128.0, 127.9, 127.6, 127.5, 127.1, 125.9, 125.2, 84.5, 40.7, 40.6, 23.3, 23.2. FAB MS: 790.3 (Calc. 790.9 for M^+). $[\alpha]_D = +11.6°$ (CH_2Cl_2, *c* 0.15).

(*R*)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl-4-cyclopentanol (11b). **11b** was obtained as a byproduct of **11**, Yield: 18%. $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 8.71 (d, $^3J_{H-H}$ = 8.8Hz, H_5), 7.88 (d, $^3J_{H-H}$ = 8.3Hz, $H_{5'}$), 7.82 (d, $^3J_{H-H}$ = 8.3Hz, $H_{6'}$), 7.50 (s, H_3), 7.45 (d, $^3J_{H-H}$ = 8.8Hz, H_6), 7.35 (m, $H_{3'}$, $H_{4'}$), 7.20-7.02 (m, Ph-*H*, 16H), 6.96-6.86 (m, Ph-*H*, 4H & H_7 & H_8), 4.12 (q, $^3J_{H-H}$ = 7.3Hz, 1H), 2.20 (m, 2H), 1.93 (m, 2H), 1.62 (m, 2H), 1.27(t, $^3J_{H-H}$ = 7.3Hz, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -14.4 (m), -14.8 (m).

2. Typical Procedure for the preparation of Ru(4,4'-BINAP)Cl_2 catalysts.

A mixture of $[Ru(benzene)Cl_2]_2$[4] (23 mg, 0.046 mmol) and 4,4'-dibromo-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (**1**) (78 mg, 0.1 mmol) in anhydrous DMF (2 mL) was heated at 100°C under Argon for 30min and then cooled to 25 °C. All the volatile components were removed under vacuum to give dark red solid. This solid was used for asymmetric hydrogenation without purification.

3. Typical procedure for asymmetric hydrogenation of β-aryl ketoester.

The catalyst (3.0 mg, 2.5 μmole, calculated on Ru) was weighted into a Teflon-capped vial (reaction flask) in dry box, and to this vial was added ethyl benzoylacetoacetate (47 μL, 0.25 mmol) and anhydrous methanol (1 mL) under Argon. The vial was quickly transferred inside a stainless steel autoclave, and sealed. After purging with Hydrogen for 6 times, final H_2 pressure was adjusted to 1400 psi. 20 hrs later, H_2 pressure was released and water (10 mL) was added. The hydrogenated product was extracted with diethyl ether and passed through a mini silica-gel column to remove metal complex. The conversions were assessed based on the integration of ^1H NMR peaks of the products and starting materials, while the e.e. values were determined using GC, SFC or HPLC.

Racemic samples were prepared using *rac*-BINAP as ligand, and were used to establish GC conditions. The absolute configurations of enantio-enriched products from the present experiments were assigned on GC, HPLC, and SFC to be same as those samples obtained from *(R)*-BINAP catalyzed reactions.

4. Typical procedure for the hydrogenation of ß-aryl ketoester in RTILs.

A mixture of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) (0.5 mL) and MeOH (0.5 mL) was syringed into a one-dram vial containing ethyl benzoylacetate (0.09 mL, 0.46 mmol) and Ru precatalyst (5.0 mg, 4.6 μmol). The vial was then placed into a 300 mL stainless steel autoclave and sealed. After purging with Hydrogen for 6 times, final H_2 pressure was adjusted to 1400 psi., and the reaction mixture was stirred at r.t. After 22 hrs, the reactor was depressurized and hexane was added to extract the product from $BMImBF_4$. The organic volatiles were then removed under reduced pressure to obtain the desired product.

For the catalyst re-use experiments, the reaction mixture was washed with degassed distilled hexane or ether three times (3 × 8 mL) under N_2 gas flow. The organic volatiles of the hexane extract were then removed under reduced pressure to obtain the desired product. New substrate and MeOH were added to the IL phase and another round of hydrogenation was performed.

Ethyl 3-hydroxy-3-phenylpropionate: ^1H NMR ($CDCl_3$): δ 7.29 (m, 5H), 5.08 (m, $^3J_{H\text{-}H} = 8.6Hz$, $^3J_{H\text{-}H} = 3.1Hz$, 1H), 4.12 (m, $^3J_{H\text{-}H} = 7.1Hz$, 2H), 3.61(br, 1H), 2.68 (m, $^2J_{H\text{-}H} = 16.2Hz$, $^3J_{H\text{-}H} = 9.0Hz$, $^3J_{H\text{-}H} = 3.9Hz$, 2H), 1.21 (t, $^3J_{H\text{-}H} = 7.1Hz$, 3H). GC (Supelco γ-Dex 225 30m × 0.25mm × 0.25μm, injector: 220°C, Column: from 70°C to 180°C programmed at 1°C/min, Detector: 250°C, carrier gas: He 1.0mL/min): $t_1 = 82.0$ min; $t_2 = 82.5$ min.

Ethyl 3-hydroxy-3-(4-methoxyphenyl)propionate: ^{1}H NMR ($CDCl_3$): δ 7.30 (d, $^3J_{H-H}$ = 8.6Hz, 2H), 6.88 (d, $^3J_{H-H}$ = 8.6Hz, 2H), 5.09 (m, $^3J_{H-H}$ = 9.0Hz, $^3J_{H-H}$ = 3.5Hz, 1H), 4.18 (q, $^3J_{H-H}$ = 7.0 Hz, 2H), 3.80 (s, 3H), 3.17(d, $^3J_{H-H}$ = 3.1Hz, 1H), 2.69 (m, $^2J_{H-H}$ = 16.0Hz, $^3J_{H-H}$ = 9.0Hz, $^3J_{H-H}$ = 3.5Hz, 2H), 1.26 (t, $^3J_{H-H}$ = 7.0Hz, 3H). SFC (Chiralpak AS, eluent: 1.5% MeOH in *sc*-CO_2, column temperature: 40°C, flow rate: 2mL/min): t_1 = 12.6 min; t_2 = 17.7 min.

Methyl 3-hydroxy-3-(4-chlorophenyl)propionate: ^{1}H NMR ($CDCl_3$): δ 7.31 (m, 4H), 5.08 (m, $^3J_{H-H}$ = 8.2Hz, $^3J_{H-H}$ = 3.9Hz, 1H), 3.72 (s, 3H), 3.37(d, $^3J_{H-H}$ = 3.1Hz, 1H), 2.70 (m, 2H). GC (Supelco β-Dex 120 30m × 0.25mm × 0.25μm, injector: 220°C, Column: from 70°C to 180°C programmed at 1°C/min, Detector: 250°C, carrier gas: He 1.0mL/min): t_1 = 108.3 min; t_2 = 108.7 min.

Methyl 3-hydroxy-3-(4-fluorophenyl)propionate: ^{1}H NMR ($CDCl_3$): δ 7.34 (m, 2H), 7.03 (m, 2H), 5.11 (m, $^3J_{H-H}$ = 8.6Hz, $^3J_{H-H}$ = 3.5Hz, 1H), 3.71 (s, 3H), 3.34(d, $^3J_{H-H}$ = 3.1Hz, 1H), 2.70 (m, $^2J_{H-H}$ = 16.4Hz, $^3J_{H-H}$ = 8.6Hz, $^3J_{H-H}$ = 3.9Hz, 2H). GC (Supelco β-Dex 120 30m × 0.25mm × 0.25μm, injector: 220°C, Column: from 70°C to 180°C programmed at 1°C/min, Detector: 250°C, carrier gas: He 1.0mL/min): t_1 = 86.8 min; t_2 = 87.3 min.

Methyl 3-hydroxy-3-(2-chlorophenyl)propionate: ^{1}H NMR ($CDCl_3$): δ 7.61 (m, 1H), 7.30 (m, 2H), 7.20 (m, 1H), 5.11 (m, $^3J_{H-H}$ = 9.8Hz, $^3J_{H-H}$ = 3.1Hz, 1H), 3.72 (s, 3H), 3.51(d, $^3J_{H-H}$ = 3.5Hz, 1H), 2.85 (m, $^2J_{H-H}$ = 16.4Hz, $^3J_{H-H}$ = 2.3Hz, 1H), 2.57 (m, $^2J_{H-H}$ = 16.4Hz, $^3J_{H-H}$ = 9.8Hz, 1H). HPLC (Chiralpak AD, eluent: Isopropanol:Hexane = 3:97, flow rate: 1mL/min): t_1 = 14.8 min; t_2 = 16.4 min.

Methyl 3-hydroxy-3-(4-trifluoromethylphenyl)propionate: ^{1}H NMR ($CDCl_3$): δ 7.61 (d, $^3J_{H-H}$ = 8.6Hz, 2H), 7.49 (m, $^3J_{H-H}$ = 8.6Hz, 2H), 5.19 (m, 1H), 3.73 (s, 3H), 3.34(d, $^3J_{H-H}$ = 3.5Hz, 1H), 2.74 (s, 1H), 2.72 (s, 1H). GC (Supelco β-Dex 120 30m × 0.25mm × 0.25μm, injector: 220°C, Column: from 70°C to 180°C programmed at 1°C/min, Detector: 250°C, carrier gas: He 1.0mL/min): t_1 = 84.9 min; t_2 = 85.6 min.

Methyl 3-hydroxy-3-(3-trifluoromethylphenyl)propionate: ^{1}H NMR ($CDCl_3$): δ 7.65 (s, 1H), 7.54 (m, 2H), 7.47 (m, 1H), 5.19 (m, $^3J_{H-H}$ = 7.0Hz, $^3J_{H-H}$ = 1.3Hz, 1H), 3.72 (s, 3H), 3.60(d, $^3J_{H-H}$ = 3.1Hz, 1H), 2.72 (m, 1H), 2.72 (s, $^3J_{H-H}$ = 7.2Hz, $^3J_{H-H}$ =

1.5Hz, 1H). HPLC (Chiralpak AD, eluent: Isopropanol/Hexane = 5/95, flow rate: 1mL/min): t_1 = 9.6 min; t_2 = 10.2 min.

Methyl 3-hydroxy-3-(2-trifluoromethylphenyl)propionate: ^{1}H NMR ($CDCl_3$): δ 7.82 (d, $^3J_{H\text{-}H}$ = 7.8Hz, 1H), 7.61 (m, 2H), 7.39 (m, $^3J_{H\text{-}H}$ = 7.8Hz, 1H), 5.55 (m, 1H), 3.75 (s, 3H), 3.55(d, $^3J_{H\text{-}H}$ = 2.8Hz, 1H), 2.74 (m, $^2J_{H\text{-}H}$ = 22.5Hz, $^3J_{H\text{-}H}$ = 5.7Hz, $^3J_{H\text{-}H}$ = 1.0Hz,, 1H). GC (Supelco β-Dex 120 30m × 0.25mm × 0.25μm, injector: 220°C, Column: from 70°C to 180°C programmed at 1°C/min, Detector: 250°C, carrier gas: He 1.3mL/min): t_1 = 72.3 min; t_2 = 72.8 min.

References:

1. M. Kant, S. Bischoff, R. Siefken, E. Gruendemann, A. Koeckritz, *Eur. J. Org. Chem.* **2001**, 477.
2. T. Shimada, H. Kurushima, Y.-H. Cho, T. Hayashi, *J. Org. Chem.* **2001**, *66,* 8854.
3. A. Allen, Jr., L. Ma, W. Lin, *Tetrahedron Lett.* **2002**, *1*, 43.
4. R.A. Zelonka, M.C. Baird, *Can. J. Chem.*, 1972, *50*, 3063.