**Enantioselective Hydrogenation of Aromatic Ketones Catalyzed by Ru Complexes of
Goodwin-Lions-type $\text{sp}^2\text{N}/\text{sp}^3\text{N}$ Hybrid Ligands R-BINAN-R'-Py**

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(1) Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 spectrometer. The chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane or in ppm relative to CHCl_3 (δ 7.26 in ^1H NMR and δ 77.0 in ^{13}C NMR). Signal patterns of ^1H NMR are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. Optical rotation measurements of chiral compounds were performed on a RUDOLPH AUTOPOL IV digital polarimeter using a 3 mm x 5 cm cell. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-700 system. Gas chromatography (GC) analyses were performed on Shimadzu GC-14B and GC-17A instruments. The signals of GC were detected by FID. High performance liquid chromatography (HPLC) analyses were performed on a Shimadzu LC-10AD instrument equipped with an SCL-10A system controller, a DGU-4A degasser, an SIL-10AXL autosampler, and a Shimadzu SPD-10A UV detector.

(2) Materials

Gases: H_2 gas of a 99.99999% purity grade was purchased from Nippon Sanso and used without purification. Argon gas obtained from Nippon Sanso was purified by being passed through a column of BASF R3-11 catalyst at 80 °C and then through a column of granular calcium sulfate.

Solvents: Solvents for hydrogenation were dried and degassed at reflux temperature in the presence of appropriate drying agents (2.5 g/1 L) under an argon stream for 6 h and distilled into Schlenk flasks: 2-Propanol from calcium oxide; ethanol and methanol from magnesium; dichloromethane from calcium hydride; toluene and THF from sodium benzophenone ketyl. These were degassed by three freeze–thaw cycles before hydrogenation.

Silica gels: Analytical thin-layer chromatography (TLC) was performed using Merck 5715 indicating plates precoated with silica gel 60F254 (layer thickness, 0.25 mm). The product spots

were visualized with a solution of phosphomolybdic acid. Flash column chromatography was performed using Daiko AP 300 or nacalai tesque Silica Gel 60 (spherical, neutral).

Ketone substrates: All of the compounds of interest were commercially available: Acetophenone (**2a**), 4-methoxyacetophenone (**2b**), 4-methylacetophenone (**2c**), 4-(trifluoromethyl)acetophenone (**2d**), 2-acetonaphthone (**2e**), propiophenone (**2f**), *n*-nonanophenone (**2g**), isobutyrophenone (**2h**), cyclohexylphenylketone (**2i**), 2,2-dimethylpropiophenone (**2j**), 1-benzosuberone (**2k**), 1-tetralone (**2l**), and 1-indanone (**2m**) were purchased from Aldrich. All of the ketone substrates were purified by distillation or recrystallization.

Authentic alcohol products: All of the racemic alcohol products were prepared by sodium borohydride reduction of the corresponding ketone substrates.

Ligands and catalyst precursors: The following compounds were commercially available: (*R*)- and (*S*)-1,1'-Binaphthyl-2,2'-diamine (Wako Chemicals), phenylboronic acid (Aldrich), pyridine-2-carboxaldehyde (Aldrich), 6-methylpyridine-2-carboxaldehyde (Aldrich), tetrakis(triphenylphosphine)palladium (Tokyo Kasei), Ru(π -CH₂C(CH₃)CH₂)₂(cod) (Acros), [RuCl₂(C₆H₆)]₂ (Aldrich), [RuCl₂(cod)]_n (Aldrich). Ru(cod)(cot) was prepared by the reaction of RuCl₃ and cyclooctadiene in the presence of zinc.¹ All other chemicals were obtained commercially and used without further purification unless otherwise stated.

(3) Preparation of (*R*)-3,3'-Diphenyl-1,1'-binaphthyl-2,2'-diamine (**7**) and the Characterization

(i) A dry, 500-mL Schlenk tube connected to a supply of argon was equipped with a Teflon-coated magnetic stirring bar and a glass stopper. The flask was charged with (*R*)-1,1'-binaphthyl-2,2'-diamine (**4**) (7.58 g, 26.7 mmol) and THF (120 mL). To the solution was added 1 M NaHMDS solution in THF (120 mL, 120 mmol) at rt and the reaction mixture was stirred at rt for 1 h to give an orange solution. After cooling the reaction mixture at 0 °C, a solution of (*t*-C₄H₉OOC)₂O (12.8 g, 58.7 mmol) in THF (50 mL) was added slowly. The resulting mixture was stirred at rt for another 3 h. After removal of the solvent under reduced pressure, the orange residue was dissolved in dichloromethane (200 mL), and then poured into water (100 mL). The organic layer was separated, and the aqueous layer was extracted three times with dichloromethane (100 mL). The combined organic layer (dichloromethane, total: 500 mL) was washed with brine (100 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give an orange residue, which contained the product. The orange residue was washed with boiling ethyl acetate (50 mL), and the unresolved yellowish solid was collected to afford the product **5** in 85% isolated yield (11.0 g), which was pure enough for the following reactions. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, *J* = 12.0 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.40 (t, *J* = 6.9 Hz, 2H), 7.24 (t, *J* = 6.9 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.14 (br, 2H), 1.38 (s, 18H). ¹³C NMR (150 MHz, CDCl₃) δ 153.07, 135.80, 132.72, 130.61, 130.04, 128.29, 127.22, 125.03, 124.94, 119.87, 117.85, 81.00, 28.26. (ii) To a solution of (*R*)-*N*2,*N*2'-bis(*tert*-butoxycarbonyl)-1,1'-binaphthyl-2,2'-diamine (**5**) (3.0 g, 6.2 mmol) in ether (60 mL) was added 1.42 M *t*-C₄H₉Li solution in pentane (22 mL, 31 mmol) at -20 °C and the resulting mixture was stirred at -10 °C for 4 h to give a reddish brown solution. After the mixture was cooled at -78 °C, a solution of I₂ (5.5 g, 21.7 mmol) in ether (30 mL) was slowly added dropwise. After the addition, the reddish brown solution was warmed to rt and stirred for 12 h. The reaction mixture was poured into brine (100 mL). The organic layer was separated, and the aqueous layer was extracted two times with ethyl acetate (100 mL). The combined organic layers (ether and

ethyl acetate, total: ca. 290 mL) were washed with saturated Na₂SO₃ aq (100 mL), brine (100 mL) and dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure afforded the product in 89% yield (3.63 g), which contained 37% of the 3,3'-diiodo compound. When three mol amounts of *t*-C₄H₉Li was added to **5**, an 86:14 mixture of mono and diiodo compounds was obtained in 78% total yield. The mixture can be used directly for the next step. (iii) A solution of (*R*)-3-iodo-*N*2,*N*2'-bis(*tert*-butoxycarbonyl)-1,1'-binaphthyl-2,2'-diamine, which contained 37% of 3,3'-diiodo compound, and Pd(P(C₆H₅)₃)₄ (215 mg, 0.186 mmol) in dimethoxyethane (50 mL) was stirred at rt for 30 min. After addition of C₆H₅B(OH)₂ (1.13 g, 9.3 mmol), NaHCO₃ (2.8 g, 33.3 mmol) and water (25 mL), the reddish brown suspension was refluxed for 20 h. After cooling to rt, ethyl acetate (100 mL) was added. The organic layers (dimethoxyethane and ethyl acetate, total: ca. 150 mL) were separated, and the aqueous layer was extracted three times with ethyl acetate (30 mL). The combined organic layers (dimethoxyethane and ethyl acetate, total: ca. 240 mL) were washed with brine (50 mL) and dried over anhydrous Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography (silica gel, 120 g; 25:1 to 5:1 hexane:ethyl acetate as eluent) to give the product (*R*)-3-phenyl-*N*2,*N*2'-bis(*tert*-butoxycarbonyl)-1,1'-binaphthyl-2,2'-diamine as a white solid in quantitative yield (3.2 g), which contained 37% of 3,3'-diphenyl compound. The mixture can be used directly for the next step. (iv) Repetition of the above procedure (ii) (conditions: substrate (3.2 g, 5.54 mmol), 1.42 M *t*-C₄H₉Li solution in pentane (19.7 mL, 28 mmol), I₂ (4.92 g, 19.4 mmol), ether (90 mL)) afforded (*R*)-3-iodo-3'-phenyl-*N*2,*N*2'-bis(*tert*-butoxycarbonyl)-1,1'-binaphthyl-2,2'-diamine as a white solid in 82% yield (2.98 g), which contained 37% of 3,3'-diphenyl compound. The mixture can be used directly for the next step. (v) Repetition of the above procedure (iii) (conditions: substrate (2.98 g, 4.52 mmol), Pd(P(C₆H₅)₃)₄ (215 mg, 0.186 mmol), C₆H₅B(OH)₂ (1.13 g, 9.3 mmol), NaHCO₃ (2.8 g, 33.3 mmol), dimethoxyethane (50 mL), water (25 mL)) afforded

(*R*)-3,3'-diphenyl-*N*2,*N*2'-bis(*tert*-butoxycarbonyl)-1,1'-binaphthyl-2,2'-diamine (**6**) as a white solid in quantitative yield (2.88 g). (vi) To a solution of the compound **6** dissolved in dichloromethane (40 mL), trifluoroacetic acid (10 mL, 135 mmol) was added at 0 °C and then stirred at 25 °C for 12 h. After the reaction mixture was quenched with 2 M NaOH (80 mL), the layers were separated, the organic layer was dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated. The residue was purified by flash column chromatography (silica gel, 60 g; 25:1 to 10:1 hexane:ethyl acetate as eluent) to obtain the product (*R*)-**7** (1.92 g) as a white solid in 60.4% total yield after 6 steps from (*R*)-**4**. ¹H NMR (600 MHz, CDCl₃) δ 7.79–7.81 (m, 2H), 7.76 (s, 2H), 7.61 (d, *J* = 7.6 Hz, 4H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.35 (s, 2H), 7.22–7.24 (m, 4H), 7.13–7.15 (m, 2H), 3.87 (s, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 140.90, 139.35, 133.21, 130.85, 129.90, 129.48, 128.97, 128.35, 128.28, 127.78, 126.92, 123.97, 122.74, 113.09. [α]_D²⁰ +101.40 (*c* 0.33, CHCl₃). HRMS *m/z* (M⁺) Calcd: 436.1939, Obsd: 436.1932. The ¹H and ¹³C NMR spectra are provided in Figure S1 and Figure S2. (*S*)-**7** was also prepared in the same way ([α]_D²⁰ –101.94 (*c* 0.29, CHCl₃)). The HPLC charts of (*R*)- and (*S*)-**7** are provided in Figure S3.

(4) Conversion of **7** and **4** to the Pyridylmethyl Derivatives

The ligands **1** were prepared by the imine formation of amines **7** and **4** with pyridine-2-carboxaldehydes followed by the successive NaBH₄ reduction.

(*R*)-3,3'-Diphenyl-*N*2,*N*2'-bis(pyridin-2-ylmethyl)-1,1'-binaphthyl-2,2'-diamine ((*R*)-**1a**):

To a solution of the amine (*R*)-**7** (1.31 g, 3.0 mmol) in toluene (40 mL) was added MS4A (10.0 g) and an excess of pyridine-2-carboxaldehyde (963 mg, 9.0 mmol) at rt. The reaction mixture was refluxed for 2 weeks. After cooling to 25 °C, the mixture was filtered, and carefully washed three times

with ethyl acetate (30 mL), the filtrate was collected and then the solvent was removed. The

residue was dissolved in methanol (40 mL), sodium borohydride (1.0 g, 26.3 mmol) was added in small portions and the reaction mixture was stirred at rt for 3 h. The solvent was removed and the residue was extracted three times with ethyl acetate (30 mL) and washed with brine (20 mL). The combined organic layers were dried and the solvent was removed in vacuo to obtain a yellowish solid. The residue was purified by flash column chromatography (silica gel, 60 g; 25:1 to 5:1 hexane:ethyl acetate as eluent) to afford 1.2 g of product (*R*)-**1a** in 64.7% yield after 2 steps. ¹H NMR (600 MHz, CDCl₃) δ 8.05 (d, *J* = 4.1 Hz, 2H), 7.79 (s, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 4H), 7.41 (t, *J* = 7.2 Hz, 4H), 7.32 (dd, *J*₁ = 7.6 Hz, *J*₂ = 15.2 Hz, 2H), 7.24 (d, *J* = 1.4 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.85 (t, *J* = 6.2 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 2H), 4.77 (br, 2H), 3.73 (d, *J* = 5.5 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 158.80, 148.59, 144.78, 141.20, 135.79, 133.94, 133.56, 131.22, 129.27, 129.23, 128.62, 127.93, 127.19, 126.56, 125.11, 123.27, 121.46, 121.29, 119.59, 52.87. [α]_D²⁵ -138.25 (c 0.5, CHCl₃). HRMS *m/z* (MH⁺) Calcd: 619.2815, Obsd: 619.2838. The ¹H and ¹³C NMR spectra are provided in Figure S4 and Figure S5.

(*R*)-N2,N2'-Bis(pyridin-2-ylmethyl)-1,1'-binaphthyl-2,2'-diamine ((*R*)-1b**):** In a manner

similar to that described for (*R*)-**1a**, the ligand (*R*)-**1b** was

prepared as a white solid. Conditions:

(*R*)-1,1'-binaphthyl-2,2'-diamine (**4**) (1.42 g, 5.0 mmol),

anhydrous Na₂SO₄ (10.0 g), dichloromethane (40 mL),

pyridine-2-carboxaldehyde (1.18 g, 11 mmol), and then sodium borohydride (1.5 g, 39.4 mmol),

methanol (40 mL), 2.0 g of product (*R*)-**1b** was obtained in 85.8% yield after 2 steps. ¹H NMR

(600 MHz, CDCl₃) δ 8.46 (d, *J* = 4.8 Hz, 2H), 7.80 (d, *J* = 8.9 Hz, 2H), 7.76–7.77 (m, 2H),

7.44–7.46 (m, 2H), 7.19–7.21 (m 6H), 7.12 (d, *J* = 8.9 Hz, 2H), 7.07–7.08 (m, 4H), 4.65 (br, 2H),

4.53 (t, *J* = 2.7 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 159.80, 149.31, 143.96, 136.61, 133.99,

129.84, 128.26, 127.92, 126.84, 124.00, 122.19, 121.97, 120.90, 114.13, 112.25, 49.40. [α]_D²⁵

+31.7 (*c* 0.5, CHCl₃). HRMS *m/z* (MH⁺) Calcd: 467.2189, Obsd: 467.2153. The ¹H and ¹³C NMR spectra are provided in Figure S6 and Figure S7.

(*R*)-*N*2,*N*2'-Bis(6-methylpyridin-2-ylmethyl)-1,1'-binaphthyl-2,2'-diamine ((*R*)-1c): In

a manner similar to that described for (*R*)-1a, the ligand (*R*)-1c

was prepared as a white solid. Conditions:

(*R*)-1,1'-binaphthyl-2,2'-diamine (**4**) (1.0 g, 3.5 mmol), anhydrous Na₂SO₄ (10.0 g), dichloromethane (40 mL),

6-methylpyridine-2-carboxaldehyde (937 mg, 7.7 mmol), and then sodium borohydride (1.0 g, 26.3 mmol), methanol (30 mL), 1.13 g of product (*R*)-1c was obtained in 65.3% yield after 2 steps. ¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 8.9 Hz, 2H), 7.76–7.77 (m, 2H), 7.28–7.30 (m, 2H), 7.17–7.19 (m, 4H), 7.13–7.15 (m, 2H), 7.07–7.08 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 4.70 (br, 2H), 4.48 (br, 4H), 2.41 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 158.72, 157.88, 144.07, 136.75, 134.04, 129.76, 128.23, 127.87, 126.77, 124.00, 122.05, 121.43, 117.75, 114.22, 112.26, 49.21, 24.40. [α]_D²⁵ +16.4 (*c* 0.5, CHCl₃). HRMS *m/z* (MH⁺) Calcd: 495.2502, Obsd: 495.2505. The ¹H and ¹³C NMR spectra are provided in Figure S8 and Figure S9.

(*R*)-3,3'-Diphenyl-*N*2,*N*2',*N*2,*N*2'-bis(methyl)bis(pyridin-2-ylmethyl)-1,1'-

binaphthyl-2,2'-diamine: To a solution of (*R*)-1a (120 mg,

0.194 mmol) in ether (10 mL) was added 1.58 M *n*-C₄H₉Li solution in hexane (0.27 mL, 0.43 mmol) at –78 °C, the resulting mixture was stirred at 25 °C for 2 h to give a yellow solution.

After the mixture was cooled at –78 °C, a solution of

methyl iodide (82.6 mg, 0.582 mmol) in ether (5 mL) was slowly added dropwise. After the addition, the yellow solution was warmed to rt and stirred overnight. The reaction mixture was poured into brine (30 mL). The organic layer was separated, and the aqueous layer was extracted

three times with ethyl acetate (30 mL). The combined organic layer was washed with saturated Na₂CO₃ aq (20 mL), and brine (30 mL) and dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure followed by flash column chromatography (silica gel, 60 g; 20:1 to 5:1 hexane:ethyl acetate as eluent) afforded the desired product in 55.8% yield (70 mg). ¹H NMR (600 MHz, CDCl₃) δ 8.19 (m, 2H), 7.72 (s, 4H), 7.14–7.44 (m, 18H), 6.86 (s, 2H), 5.86 (s, 2H), 4.10 (br, 4H), 2.01 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 158.80, 148.42, 147.85, 142.62, 141.41, 135.85, 135.80, 133.46, 131.21, 129.66, 128.42, 128.26, 127.46, 127.15, 126.47, 126.08, 125.44, 120.89, 120.52, 63.90, 41.62. [α]_D¹⁹ –27.83 (c 0.38, CHCl₃). HRMS *m/z* (MH⁺) Calcd: 647.3129, Obsd: 647.3140. The ¹H and ¹³C NMR spectra are provided in Figure S10 and Figure S11.

(5) Asymmetric Hydrogenation of Acetophenone

Acetophenone (600 μL, 5.00 mmol) and 2-propanol (2.0 mL) were placed into a dry, argon-filled 20-mL Schlenk tube with a Young's tap. The solution was degassed three times by the freeze-thaw method, and was transferred into a separate glass vessel located inside a stainless steel autoclave containing Ru(π-CH₂C(CH₃)CH₂)₂(cod) (1.6 mg, 5.0 μmol) and (*R*)-3,3'-diphenyl-*N*2,*N*2'-bis(pyridin-2-ylmethyl)-1,1'-binaphthyl-2,2'-diamine ((*R*)-**1a**) (3.10 mg, 5.0 μmol) in an inert atmosphere glovebox. A 10 mM 2-propanol solution of KOC(CH₃)₃ (0.5 mL, 5.0 μmol) which had been degassed by three freeze-thaw cycles was added to the mixture. The vessel was sealed within the stainless steel autoclave, removed from the glovebox, and connected to a hydrogen source. Hydrogen was initially introduced at 10 atm pressure with several quick release-fill cycles before being pressurized to 50 atm. The solution was vigorously stirred for 15 h at 25 °C. After carefully venting the hydrogen gas, the resulting reddish brown homogeneous solution was concentrated under reduced pressure to give the crude product. The chiral GC analysis relative to an internal standard (tetradecane, 198 mg, 1.0 mmol) showed that the

yield was 99% and the enantiomeric excess (ee) was 93.4% (*R*). GC (capillary column, Supelco β -DEX 120 (column length, 30 m; inside diameter, 0.25 mm; film thickness, 0.25 μ m); column temperature, 115 $^{\circ}$ C; detection temperature, 220 $^{\circ}$ C; carrier gas, helium; column pressure, 69.6 kPa; flow rate, 1.87 mL/min; split ratio, 100:1; t_R of acetophenone (**2a**), 16.5 min (factor 2.07); t_R of (*R*)-1-phenylethanol, 27.1 min (factor 2.13); t_R of (*S*)-1-phenylethanol, 28.5 min (factor 2.13); t_R of tetradecane, 33.4 min (factor 1.00). The product was purified by flash column chromatography (silica gel, 10 g; hexane, then diethyl ether as eluent) to give (*R*)-1-phenylethanol ((*R*)-**3a**) (606 mg, 99.3% isolated yield, 93.4% ee). ^1H NMR (600 MHz, CDCl_3) δ 7.33 (m, 4H), 7.27 (m, 1H), 4.87 (q, J = 6.2 Hz, 1H), 1.89 (br, 1H), 1.48 (d, J = 6.2 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 145.90, 128.60, 127.58, 125.48, 70.52, 25.27. Absolute configuration: *R*. $[\alpha]_{\text{D}}^{25}$ +47.38 (*c* 2.68, CH_2Cl_2), lit. $[\alpha]_{\text{D}}^{24}$ +48.6 (*c* 1.01, CH_2Cl_2) for 99% ee of (*R*)-**3a**.² Physical properties of (*R*)-**3a** were consistent with those previously reported.² The ^1H NMR spectrum and GC chart are provided in Figure S12 and Figure S13. When the reaction time is prolonged after 100% conversion of **2a**, 1-cyclohexylethanol is produced (24 h, 0.7% yield by GC^{2,3}).

(6) Asymmetric Hydrogenation of Other Ketone Substrates

The procedure was the same as that for the asymmetric hydrogenation of acetophenone (**2a**). Listed below are the reaction conditions (amounts of substrate; $\text{Ru}(\pi\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)_2(\text{cod})$; ligand (*R*)-**1a**; $\text{KOC}(\text{CH}_3)_3$; amount of 2-propanol; H_2 , atm; temperature; time), conversion of substrate estimated by GC measurement or ^1H -NMR analysis of the crude reaction mixture, yield, enantiomeric excess, and the absolute configuration (abs). The enantiomeric excess of the products was determined by GC analysis or HPLC analysis. The structure of the products was determined by comparison of NMR, mass spectra, or optical rotation with reported values or those of the authentic samples. Table S1 lists the conditions for the ee analysis.

4-Methoxyacetophenone (2b): Conditions, 5.0 mmol (750 mg) of **2b**; 5 μ mol of

Ru(π -CH₂C(CH₃)CH₂)₂(cod); 5 μ mol of ligand (*R*)-**1a**; 5 μ mol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 15 h. Conversion, >99%; yield, 99.3%; ee, 97.6%; abs, *R*. $[\alpha]_D^{18} +49.5$ (*c* 4.42, CHCl₃), lit. $[\alpha]_D^{23} +53.2$ (*c* 1.30, CHCl₃) for 100% ee of (*R*)-**3b**.²

4-Methylacetophenone (2c): Conditions, 5.0 mmol (671 mg) of **2c**; 5 μ mol of Ru(π -CH₂C(CH₃)CH₂)₂(cod); 5 μ mol of ligand (*R*)-**1a**; 5 μ mol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 15 h. Conversion, >99%; yield, 99%; ee, 96.0%; abs, *R*. $[\alpha]_D^{18} +53.9$ (*c* 1.51, CHCl₃), lit. $[\alpha]_D^{23} -54.1$ (*c* 0.0532, CHCl₃) for 96% ee of (*S*)-**3c**.⁴

4-Trifluoromethylacetophenone (2d): Conditions, 5.0 mmol (941 mg) of **2d**; 5 μ mol of Ru(π -CH₂C(CH₃)CH₂)₂(cod); 5 μ mol of ligand (*R*)-**1a**; 5 μ mol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 80.0%; abs, *R*. $[\alpha]_D^{18} +21.7$ (*c* 2.24, CH₃OH), lit. $[\alpha]_D^{21} +29.8$ (*c* 1.08, CH₃OH) for 99% ee of (*R*)-**3d**.²

2-Acetonaphthone (2e): Conditions, 5.0 mmol (851 mg) of **2e**; 5 μ mol of Ru(π -CH₂C(CH₃)CH₂)₂(cod); 5 μ mol of ligand (*R*)-**1a**; 5 μ mol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 94.7%; abs, *R*. $[\alpha]_D^{18} +45.4$ (*c* 1.63, CHCl₃), lit. $[\alpha]_D^{25} +28.8$ (*c* 1.00, CHCl₃) for 58% ee of (*R*)-**3e**.⁴

Propiophenone (2f): Conditions, 5.0 mmol (671 mg) of **2f**; 5 μ mol of Ru(π -CH₂C(CH₃)CH₂)₂(cod); 5 μ mol of ligand (*R*)-**1a**; 5 μ mol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 97.7%; abs, *R*. $[\alpha]_D^{18} +46.9$ (*c* 2.39, CHCl₃), lit. $[\alpha]_D^{20} +47.0$ (*c* 1.4, CHCl₃) for 95% ee of (*R*)-**3f**.⁵

***n*-Nonanophenone (2g):** Conditions, 5.0 mmol (1.09 g) of **2g**; 5 μ mol of Ru(π -CH₂C(CH₃)CH₂)₂(cod); 5 μ mol of ligand (*R*)-**1a**; 5 μ mol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 94.2%; abs, *R*. $[\alpha]_D^{18} +26.6$ (*c* 1.65, CHCl₃), lit. $[\alpha]_D^{25} -23.8$ (*c* 2.5, CHCl₃) for 90% ee of (*S*)-**3g**.⁶

Isobutyrophenone (2h): Conditions, 5.0 mmol (741 mg) of **2h**; 5 μ mol of Ru(π -CH₂C(CH₃)CH₂)₂(cod); 5 μ mol of ligand (*R*)-**1a**; 5 μ mol of KOC(CH₃)₃; 2.5 mL of

2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 98.0%; abs, *R*.
[α]_D¹⁸ +45.9 (*c* 1.79, ether), lit. [α]_D²⁵ +39.3 (*c* 1.25, ether) for 86% ee of (*R*)-**3h**.⁵

Cyclohexylphenylketone (2i): Conditions, 5.0 mmol (941 mg) of **2i**; 5 μmol of Ru(π-CH₂C(CH₃)CH₂)₂(cod); 5 μmol of ligand (*R*)-**1a**; 5 μmol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 97.0%; abs, *R*.
[α]_D¹⁸ +26.6 (*c* 1.76, C₆H₆), lit. [α]_D²⁵ +26.8 (*c* 3.29, C₆H₆) for 92% ee of (*R*)-**3i**.⁷

2,2-Dimethylpropiophenone (2j): Conditions, 5.0 mmol (811 mg) of **2j**; 5 μmol of Ru(π-CH₂C(CH₃)CH₂)₂(cod); 5 μmol of ligand (*R*)-**1a**; 5 μmol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 85.9%; abs, *R*.
[α]_D¹⁸ +22.6 (*c* 2.55, C₆H₆), lit. [α]_D²⁵ +24.3 (*c* 2.2, C₆H₆) for 97% ee of (*R*)-**3j**.⁸

1-Benzosuberone (2k): Conditions, 5.0 mmol (801 mg) of **2k**; 5 μmol of Ru(π-CH₂C(CH₃)CH₂)₂(cod); 5 μmol of ligand (*R*)-**1a**; 5 μmol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 94.0%; abs, *R*.
[α]_D¹⁸ +28.1 (*c* 2.03, CH₃OH), lit. [α]_D²¹ +30.5 (*c* 1.07, CH₃OH) for 99% ee of (*R*)-**3k**.⁴

1-Tetralone (2l): Conditions, 5.0 mmol (731 mg) of **2l**; 5 μmol of Ru(π-CH₂C(CH₃)CH₂)₂(cod); 5 μmol of ligand (*R*)-**1a**; 5 μmol of KOC(CH₃)₃; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 99.0%; abs, *R*.
[α]_D¹⁸ -30.6 (*c* 4.42, CHCl₃), lit. [α]_D²⁷ -32.3 (*c* 1.0, CHCl₃) for 98% ee of (*R*)-**3l**.⁹

1-Indanone (2m): Conditions, 1.0 mmol (132 mg) of **2m**; 5 μmol of Ru(π-CH₂C(CH₃)CH₂)₂(cod); 5 μmol of ligand (*R*)-**1a**; 2.5 mL of 2-propanol; 50 atm of H₂; 25 °C; 18 h. Conversion, >99%; yield, 99%; ee, 93.0%; abs, *R*. [α]_D²⁰ -25.95 (*c* 1.05, CHCl₃), lit. [α]_D²³ +30.9 (*c* 1.99, CHCl₃) for 99% ee of (*S*)-**3m**.¹⁰

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Figure S1. ¹H NMR spectrum of (R)-3,3'-diphenyl-1,1'-binaphthyl-2,2'-diamine ((R)-7) (600 MHz, CDCl₃, 27 °C).

Figure S2. ¹³C NMR spectrum of (R)-3,3'-diphenyl-1,1'-binaphthyl-2,2'-diamine ((R)-7) (150 MHz, CDCl₃, 27 °C).

Figure S3. HPLC chart of (*R*)-7 (a), (*S*)-7 (b), and 1:1 mixture of (*R*)- and (*S*)-7 (c). (conditions: Column, CHIRALCEL OD; eluent, 1:99 2-propanol-hexane; flow rate, 0.5 mL/min).

Figure S4. ^1H NMR spectrum of (R)-Ph-BINAN-H-Py ((R)-1a) (600 MHz, CDCl_3 , 27 °C).

Figure S5. ^{13}C NMR spectrum of (R) -Ph-BINAN-H-Py ((R) -1a) (150 MHz, CDCl_3 , 27°C).

Figure S6. ^1H NMR spectrum of (R) -H-BINAN-H-Py ((R) -1b) (600 MHz, CDCl_3 , 27°C).

Figure S7. ¹³C NMR spectrum of (R)-H-BINAN-H-Py ((R)-1b) (150 MHz, CDCl₃, 27 °C).

Figure S8. ^1H NMR spectrum of (R)-H-BINAN-Me-Py ((R)-1c) (600 MHz, CDCl_3 , 27 °C).

Figure S9. ¹³C NMR spectrum of (R)-H-BINAN-CH₃-Py ((R)-1c) (150 MHz, CDCl₃, 27 °C).

Figure S10. ^1H NMR spectrum of *N*-methylated (*R*)-1a (600 MHz, CDCl_3 , 27 $^\circ\text{C}$).

Figure S11. ^{13}C NMR spectrum of *N*-methylated (*R*)-1a (150 MHz, CDCl_3 , 27 °C).

Figure S12. ^1H NMR spectrum of 1-phenylethanol obtained by the asymmetric hydrogenation of acetophenone (2a) with (R)-Ph-BINAN-H-Py ((R)-1a) (600 MHz, CDCl_3 , 27 °C).

Figure S13. GC analysis of 1-phenylethanol (conditions: SUPELCO β -DEX 120 (0.25 mm x 30 m); column temperature, 115 °C; detection temperature, 220 °C; carrier gas, helium; column pressure, 69.6 kPa; flow rate, 1.87 mL/min; split ratio, 100:1). **a:** Authentic racemic sample. **b:** The product (*R*)-**3a** with 93.4% ee obtained by the asymmetric hydrogenation of acetophenone (**2a**) using (*R*)-Ph-BINAN-H-Py ((*R*)-**1a**). **c:** The product (*S*)-**3a** with 93.5% ee obtained with (*S*)-**1a**. In both cases, the peak of 1-cyclohexylethanol (t_R = 18.7 min) is not detected.

Table S1. GC and HPLC Conditions for Determination of Ee and Conversion and Retention Times of **2** and (*R*)- and (*S*)-**3**

entry	substrate	<i>t</i> _R , min			condition (column temperature) ^a
		2	(<i>R</i>)- 3	(<i>S</i>)- 3	
1	2a	16.5	27.1	28.5	A (115 °C)
2	2b	16.8	49.4	51.4	A (130 °C to 145 °C, increase at 1 °C/min)
3	2c	25.7	30.9	33.8	A (130 °C)
4	2d	9.9	16.2	16.9	A (145 °C)
5	2e	58.2	74.3	77.3	A (140 °C to 160 °C, increase at 1 °C/min)
6	2f	18.2	42.4	45.9	A (115 °C)
7	2g	— ^b	10.8	15.2	B
8	2h	— ^b	18.0	22.0	B
9	2i	— ^b	13.4	15.8	B
10	2j	25.2	49.7	45.8	C (120 °C)
11	2k	— ^b	15.0	21.0	B
12	2l	— ^b	18.2	15.2	B
13	2m	— ^b	25.4	20.9	B

^aGC conditions (**A**): Supelco β-DEX 120 (column length, 30 m; inside diameter, 0.25 mm; film thickness, 0.25 μm); injector temperature = 220 °C; detector temperature = 220 °C; carrier gas, helium 1.87 mL/min. HPLC conditions (**B**): DAICEL CHIRALCEL OD (4.6 mm x 250 mm); eluent, 1:50 2-propanol–hexane; flow rate, 1 mL/min; detection, 254-nm light. GC conditions (**C**): CP-Chirasil-DEX CB (column length, 25 m; inside diameter, 0.25 mm; film thickness, 0.25 μm); injector temperature = 220 °C; detector temperature = 220 °C; carrier gas, helium 1.87 mL/min.

^bThe conversion of **2** was determined by ¹H-NMR analysis.