Experimental

General. Diethyl ether, tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl under argon prior to use. 1-Adamantyl(dimethyl)phosphine–borane, *tert*-butyl(dimethyl)phosphine–borane, cyclohexyl(dimethyl)phosphine–borane, and dimethyl(phenyl) phosphine–borane were prepared according to the procedure described in the literature.

[(*S*)-1-boranato(1-adamantyl)methylphosphino-(*S*)-2-boranato(tert-butyl)methylphosphino]ethane (Ad^{t}Bu-BisP*–BH_3) (3a). To a stirred, cooled (0 °C) solution of (*S*)-1-adamantylmethylphosphine–borane (430 mg, 2.2 mmol) in THF (4 mL) was added *n*-BuLi (1.5 mL of 1.6 M hexane solution, 2.4 mmol) under Ar atmosphere. After 20 minutes, (*R*)-1-Boranato[1-adamantyl(methyl)phosphino]ethanol 2-tosylate was added mixture, and solution was heated at 55 °C during 1 h. The mixture was gradually warm to room temperature. The reaction mixture was quenched by 1 N HCl. The organic layer was separated and aqueous layer was extracted three times with EtOAc (40 mL). The combined extracts were washed $NaHCO_3$ aq, brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was recrystallized from toluene to give pure **3a** as colorless needles (748 mg, quant). : mp 198–200 □C; $[\alpha]_D$ 5.7□ (*c* 0.93, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.0–0.9 (brq, 6H), 1.1–1.2 (m, 15H), 1.5–1.6 (m, 3H), 1.7–2.0 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.1 (d, J_{CP} = 35 Hz), 5.6 (d, J_{CP} = 34 Hz), 14.4 (d, J_{CP} = 31 Hz), 15.9 (d, J_{CP} = 31 Hz), 25.2, 27.5 (d, J_{CP} = 9 Hz), 27.8, 30.6 (d, J_{CP} = 35 Hz), 35.9, 36.4; ^{31}P NMR (202 MHz, $CDCl_3$) δ 24.2 (J_{PB} = 33 Hz), 28.6–28.9 (J_{PB} = 105 Hz); IR (KBr) 2900, 2380, 1060, 890 cm^{-1}; FAB MS (rel intensity) 339 (M^+–H). Anal. Calcd for $C_{18}H_{40}P_2B_2$: C, 63.57; H, 11.86. Found: C, 63.38; H, 11.84.

[(*S*)-1-boranato(1-adamantyl)methylphosphino-(*S*)-2-boranato(cyclohexyl)methylphosphino]ethane (AdCy-BisP*–BH_3) (3b). Method A : This compound prepared from (*S*)-1-adamantylmethylphosphine–borane (300 mg, 1.5 mmol) and (*R*)-1-Boranato[*t*-butyl(methyl)phosphino]ethanol 2-tosylate (500 mg, 1.5 mmol) according to the procedure described for the preparation of **3a**. The crude product was recrystallized from toluene to give pure **3b** as colorless needles (549 mg, quant). : mp 197–199 □C; $[\alpha]_D$ 2.9□ (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz,

$CDCl_3$) δ 0.0–0.9 (brq, 6H), 1.1–1.2 (m, 15H), 1.5–1.6 (m, 3H), 1.7–2.0 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.1 (d, J_{CP} = 35 Hz), 5.6 (d, J_{CP} = 34 Hz), 14.4 (d, J_{CP} = 31 Hz), 15.9 (d, J_{CP} = 31 Hz), 25.2, 27.5 (d, J_{CP} = 9 Hz), 27.8, 30.6 (d, J_{CP} = 35 Hz), 35.9, 36.4; ^{31}P NMR (161 MHz, $CDCl_3$) δ 19.2 (J_{PB} = 49 Hz), 25.2 (J_{PB} = 52 Hz); IR (KBr) 2930, 2360, 1450, 1060, 900 cm^{-1}; FAB MS (rel intensity) 365 (M^+–H). Anal. Calcd for $C_{20}H_{42}P_2B_2$: C, 65.61; H, 11.56. Found: C, 65.57; H, 11.75.

[(*S*)-1-boranato(tert-butyl)methylphosphino-(*S*)-2-boranato(cyclohexyl)methyl phosphino]ethane (^{t}BuCy-BisP*–BH_3) (3c). This compound prepared from (*S*)-*tert*-butylmethylphosphine–borane (0.7 g, 5.9 mmol) and (*R*)-1-Boranato[cyclohexyl(methyl)phosphino]ethanol 2-tosylate (1.6 g, 1.5 mmol) according to the procedure described for the preparation of **3a**. The crude product was recrystallized from toluene to give pure **3c** as colorless needles (116 mg, 10 % yield) : mp 136–138 □C; $[\alpha]_D$ –12□ (*c* 0.29, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.0–0.9 (brq, 6H), 1.1–1.2 (m, 20H), 1.4–2.0 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.2 (d, J_{CP} = 34 Hz), 6.3 (d, J_{CP} = 36 Hz), 15.0 (d, J_{CP} = 30 Hz), 17.1 (d, J_{CP} = 34 Hz), 25.1 (d, J_{CP} = 2 Hz), 25.7 (d, J_{CP} = 2 Hz), 26.0 (d, J_{CP} = 2 Hz), 26.2, 26.4 (d, J_{CP} = 2 Hz), 26.5 (d, J_{CP} = 4 Hz), 27.6 (d, J_{CP} = 34 Hz), 32.9 (d, J_{CP} = 34 Hz),; ^{31}P NMR (202 MHz, $CDCl_3$) δ 18.2 (J_{PB} = 100 Hz), 28.9 (J_{PB} = 104 Hz); IR (KBr) 2930, 2370, 1065, 910, 760 cm^{-1}; FAB MS (rel intensity) 287 (M^+–H). Anal. Calcd for $C_{14}H_{36}P_2B_2$: C, 58.38; H, 12.60. Found: C, 58.42; H, 12.70.

General Procedure for the Preparation of BisP* (1a–c) analogous. To a stirred, cooled (0 °C) solution of BisP*–BH_3 (**3a–c**) (1 mmol) in toluene (2 mL) was slowly added trifluoromethanesulfonic acid (444 μL, 5 mmol) under Ar atmosphere. The mixture was warmed to room temperature and stirred until BisP*–BH_3 disappeared by monitoring the reaction TLC. The solvent was removed *in vacuo* to leave a pasty oil, to which a solution of 3 N KOH / degassed EtOH (531 mg / 3 mL) was slowly added with vigorously stirred. The mixture was stirred at 55 °C until BisP*–boranetrifulate disappeared by monitoring the reaction TLC (ca. 2 h) and cooled to room temperature. The mixture was extracted degassed ether (70 mL) and dried Na_2SO_4. The solution was passed through a column (1 cm diameter) of basic alumina (20 g) using degassed ether.

The eluent was evaporated under reduced pressure to give pure unsymmetric BisP* (**1a–c**) as solid or oil.

General Procedure for the Preparation of Rhodium Complexes (2a–c). A solution of BisP* (1 mmol) in THF (4mL) was added to a stirred suspension of $[Rh(nbd)_2]BF_4$ (374 mg, 1 mmol) in THF (9 mL) under Ar atmosphere. The suspension gradually turned to an almost clear solution during 30 minuets, which was filtered under Ar to remove a small amount of precipitates. The filtrate was evaporated *in vacuo* and the residual was washed with hexane to give orange powder, Which was dried decreased pressure. Complexes 1a and 1d were recrystallized from THF / hexane to give dark red prisms and plates, respectively.

X-ray Crystallographic Analysis of [Rh(1a)(nbd)]BF_{Al} (2a). Crystallographic Data for $C_{25}H_{42}B_1F_4P_2Rh_1$; monoclinic, space group $P2_1$ (#4); $Z = 2$; $D = 1.475$ g cm^{-1}; cell constants $a = 11.045(6)$ Å, $b = 13.512(9)$ Å, $c = 17.94(2)$ Å; $\beta = 91.98(3)°$; $V = 2675(3)$ $Å^3$; temperature data collection 193 K; 4361 reflections measured, 4259 unique reflections ($I > 2.00\sigma(I)$); 596 variables; $R = 0.055$; $Rw = 0.075$; GOF = 1.75; bond lengths Rh1–P1 2.315(3) Å, Rh1–P2 2.316(3) Å, Rh1–nbd ca. 2.2 Å, bond angles P1–Rh1–P2 82.9(1)°, 1-Ad–P1–Me 106.3(6)°, t-Bu–P2–Me 104.8°, torsion angle P1–C–C–P2 –48.2(9)°.

General Procedure of Rh-Catalyzed Asymmetric Hydrogenation. A 50 mL Fisher-Porter tube was charged with 1 mmol of substrate and 2 μmol of the Rh-catalyst. The tube was connected to the hydrogen tank via stainless steel tubing. The vessel was evacuated and filled with hydrogen gas (Nippon Sanso, 99.9999%) to a pressure of about 2 atm. This operation was repeated and the bottle was immersed in a dry ice-ethanol bath. The upper cock of the bottle was opened and anhydrous methanol (2 mL) was added quickly using a syringe. After four vacuum / H_2 cycles, the tube was pressurized to an initial pressure of 2–6 atm. The tube was closed off and the cooling bath was removed. The solution was stirred at room temperature until no further hydrogen uptake was observed. The resulting solution was submitted to direct analysis for the enantiomeric excess values by HPLC or GC.

***N*-acetylphenylalanine methyl ester (4)** (HPLC, Daicel Chiralcel OJ, 1.0 mL/min, 10% 2-PrOH/hexane, (*R*) t_1 = 11 min; (*S*) t_2 = 17 min); ***N*-acetylalanine methyl ester (5)** (Capillary GC, Chrompack's Chiral-L-Val column (25 m), 120 °C,

isothermal, Carrier gas: N_2 (flow rate 10 cm/sec), (*R*) t_1 = 8.5 min; (*S*) t_2 = 9.1 min); ***N*-acetylvaline methyl ester (6a)** (Capillary GC, Chrompack's Chiral-L-Val column (25 m), 135 °C, isothermal, Carrier gas: N_2 (flow rate 8 cm/sec), (*R*) t_1 = 10 min; (*S*) t_2 = 11 min); ***N*-acetyl-α-cyclopentylglycine methyl ester (6b)** (Capillary GC, Chrompack's Chiral-L-Val column (25 m), 135 °C, isothermal, Carrier gas: N_2 (flow rate 53 cm/sec), (*R*) t_1 = 6.7 min; (*S*) t_2 = 7.4 min); ***N*-acetyl-α-cyclohexylglycine methyl ester (6c)** (Capillary GC, Chrompack's Chiral-L-Val column (25 m), 135 °C, isothermal, Carrier gas: N_2 (flow rate 53 cm/sec), (*R*) t_1 = 10 min; (*S*) t_2 = 11 min).