Supporting Information

Profiling the Tuneable R-SMS-Phos Structure in the Rhodium(I)-Catalyzed Hydrogenation of Olefins: The Last Stand?

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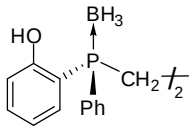
Experimental Procedures

General. All operations were conducted under N_2 or Ar atmosphere using anhydrous and degassed solvents. ^{1}H (300 MHz, internal Me_4Si), ^{13}C (75 MHz, internal $CDCl_3$), and ^{31}P NMR (120 MHz, external 85% H_3PO_4) were recorded for solutions in $CDCl_3$ if not stated otherwise.
The following compounds were prepared according to literature procedures: precursor **1a** (from oxazaPB)[1a], ligands (and their precursors **1**): **2d**,[1b] **2e–g,o**,[1c] **2h,j,k,m,n**[1d]; non-commercial olefins: methyl (*Z*)-3-acetamidobut-2-enoate (methyl *β*-acetamidocrotonate, **S3**) and methyl (*E*)-3-acetamidobut-2-enoate (**S4**),[2] *α*-acetamidostyrene (*N*-(1-phenylvinyl)acetamide, **S5**)[3].

(R_P,R_P)-1,2-Bis[(*o*-hydroxyphenyl)(phenyl)phosphino-*P*-borane]ethane (1a)[1a] from (R_P,R_P)-DiPAMP (2b) - Scheme 1, *step e*: To a cold (−20 °C) solution of (R_P,R_P)-DiPAMP (**2b**) (0.50 g, 1.1 mmol) in CH_2Cl_2 (20 mL) was added BBr_3 (750 μL, 7 equiv.). After stirring at r.t. for 1 h, MeOH (20 mL) was added at 0 °C and the mixture refluxed for 2 h monitoring the reaction by ^{31}P NMR. The mixture was concentrated and carefully neutralized with 0.1 M NaOH. (R_P,R_P)-SMS-Phos (**2a**) was extracted with CH_2Cl_2, dried and the residue was filtered through a pad of silica gel eluting with toluene/EtOAc 8:2 (R_f: 0.48) yielding a white powder (0.44 g, 93%): mp 130–132 °C; $[\alpha]_D^{25}$: +79.7 (c 1.0 in MeOH); ^{1}H NMR: δ = 2.15 (m, 4H; 2 CH_2), 6.45 (br s, 2H; 2 OH), 6.90 (m, 4H; Ar-H), 7.05 (m, 2H; Ar-H), 7.24–7.32 (m, 12H; Ar-H); ^{13}C NMR: δ = 22.4 (m), 115.5, 119.9 (m), 121.1 (m). 128.5 (m), 128.6, 131.6, 131.8 (d, *J*(C,P) = 9 Hz), 132.8 (m), 136.4 (m), 159.9 (m); ^{31}P NMR: δ = −39.5 (s); MS (EI): *m/z* (%): 430 (100) [M^+]; HR-MS (EI): *m/z* = 430.126, calcd. for $C_{26}H_{24}O_2P_2$ [M^+]: 430.125; anal. calcd. for $C_{26}H_{24}O_2P_2$ (430.42): C 72.55, H 5.62; found: C 72.45, H 5.71.



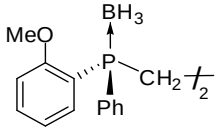
Scheme 1, *step c*: To (R_P,R_P)-SMS-Phos (**2a**) (0.40 g, 0.92 mmol) in THF (30 mL) was added $BH_3{\cdot}Me_2S$ (2 mmol) at 0 °C and the mixture left to warm up to r.t., then concentrated and washed with hexane/CH_2Cl_2 95:5 to yield (R_P,R_P)-**1a** (0.41 g, 97%): mp 194–196 °C; R_f: 0.33 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: +26.6 (c 1.0 in absolute MeOH); ^{1}H NMR (DMSO-d_6): δ = 0.15–1.40 (m, 6H; 2 BH_3), 2.50 (m, 4H; 2 CH_2), 6.80 (d, *J* = 8 Hz, 2H; Ar-H), 6.88 (t, *J* = 8 Hz, 2H; Ar-H), 7.32–7.72 (m, 14H; Ar-H), 10.45 (br s, 2H; 2 OH); ^{13}C NMR (DMSO-d_6): δ = 17.7 (m), 111.5 (d, *J*(C,P) = 54 Hz), 115.8, 119.3 (m), 128.5 (m), 129.0 (d, *J*(C,P) = 58 Hz), 130.8, 131.3 (m), 134.1, 135.2 (m), 160.0; ^{31}P NMR (DMSO-d_6): δ

1 (*a*) M. Stephan, B. Modec and B. Mohar, *Tetrahedron Lett*., 2011, **52**, 1086–1089; (*b*) M. Stephan, D. Šterk and B. Mohar, *Adv. Synth. Catal.*, 2009, **351**, 2779–2786; (*c*) B. Zupančič, B. Mohar and M. Stephan, *Org. Lett.*, 2010, **12**, 1296–1299; (*d*) B. Zupančič, B. Mohar and M. Stephan, *Org. Lett.*, 2010, **12**, 3022–3025 (therein, **1i** was prepared using 3-bromocyclohexene (= 2-cyclohexenyl bromide)).
2 G. Zhu, Z. Chen and X. Zhang, *J. Org. Chem.*, 1999, **64**, 6907–6910.
3 M. J. Burk, G. Casy and N. B. Johnson, *J. Org. Chem.*, 1998, **63**, 6084–6085.

= +18.5 (br m); MS (FAB): *m/z* (%): 457 (7) [M^+−H]; anal. calcd. for $C_{26}H_{30}B_2O_2P_2$ (458.08): C 68.17, H 6.60; found: C 68.04, H 6.77.

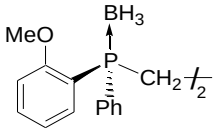
General Procedures for the Preparation of 1b,c,l,p–z by Derivatization of 1a (Scheme 1, *step a*):
(A) A mixture of **1a** (458 mg, 1 mmol), K_2CO_3 (553 mg, 4 mmol), and the appropriate (substituted)alkyl halide or tosylate (2.5–3 mmol) in acetone (10 mL) was stirred at r.t. or refluxed until TLC showed complete conversion. The mixture was concentrated, filtered trough a pad of silica gel eluting with CH_2Cl_2. The product was recrystallized from hexane/CH_2Cl_2.
(B) A mixture of **1a** (458 mg, 1 mmol), K_2CO_3 (553 mg, 4 mmol), and the appropriate (substituted)alkyl halide or tosylate (2.5–3 mmol) in DMF (5 mL) was stirred at 40 °C until TLC showed complete conversion. The mixture was concentrated, filtered trough a pad of silica gel eluting with CH_2Cl_2. The product was recrystallized from hexane/CH_2Cl_2.
(C) To a stirred solution of **1a** (458 mg, 1 mmol) in THF (10 mL) was added NaH (60 mg, 2.5 mmol) at 0 °C. After 15 min the appropriate acid chloride (2.5 mmol) was added and left to stir for 1 h. The mixture was quenched with H_2O (0.1 mL), concentrated, and the residue was filtered trough a pad of silica gel eluting with CH_2Cl_2. The product was recrystallized from hexane/CH_2Cl_2.

(R_P,R_P)-1,2-Bis[(*o*-anisyl)(phenyl)phosphino-*P*-borane]ethane ((R_P,R_P)-1b).



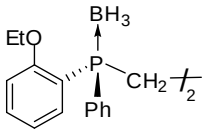
Prepared according to the general procedure (A) from (R_P,R_P)-**1a** using iodomethane (0.85 g, 0.37 mL, 6.0 mmol). Colorless crystals (465 mg, 96%): ^{1}H NMR: δ = 0.25–1.70 (br m, 6H; 2 BH_3), 2.59 (m, 4H; 2 CH_2), 3.61 (s, 6H; 2 Me), 6.80 (m, 2H; Ar-H), 7.03 (m, 2H; Ar-H), 7.32–7.50 (m, 8H; Ar-H), 7.66 (m, 4H; Ar-H), 7.86 (m, 2H; Ar-H).

(S_P,S_P)-1,2-Bis[(*o*-anisyl)(phenyl)phosphino-*P*-borane]ethane ((S_P,S_P)-1b).



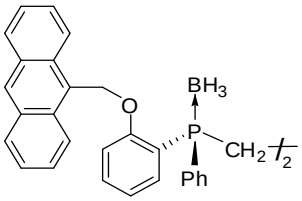
Prepared according to the general procedure (A) from (S_P,S_P)-**1a** using iodomethane; Colorless crystals.

(R_P,R_P)-1,2-Bis[(2-ethoxyphenyl)(phenyl)phosphino-*P*-borane]ethane (1c).



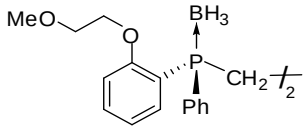
Prepared according to the general procedure (A) from (R_P,R_P)-**1a** using iodoethane (0.62 g, 0.32 mL, 4.0 mmol). Colorless crystals (485 mg, 94%): mp 158–160 °C; R_f: 0.72 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: +96.4 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.30–1.70 (br m, 6H; 2 BH_3), 1.07 (t, *J* = 7.1 Hz, 6H; 2 Me), 2.64 (m, 4H; 2 PCH_2), 3.75 (m, 4H; 2 CH_2), 6.74 (m, 2H; Ar-H), 7.02 (m, 2H; Ar-H), 7.31–7.48 (m, 8H; Ar-H), 7.63 (m, 4H; Ar-H), 7.91 (m, 2H; Ar-H); ^{13}C NMR: δ = 14.2, 17.4 (m), 63.8, 111.0, 114.9 (d, *J*(C,P) = 53 Hz), 120.6 (m), 128.3 (m), 129.4 (d, *J*(C,P) = 59 Hz), 130.5 (m), 131.7 (m), 133.8, 136.7 (m), 160.6; ^{31}P NMR: δ = +19.0 (br m); MS (FAB): *m/z* (%): 513 (15) [M^+−H]; anal. calcd. for $C_{30}H_{38}B_2O_2P_2$ (514.19): C 70.08, H 7.45; found: C 69.96, H 7.53.

(R_P,R_P)-1,2-Bis{[2-(9-anthrylmethoxy)phenyl](phenyl)phosphino-*P*-borane}ethane (1l).



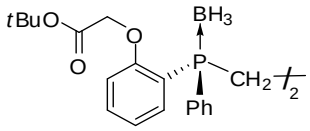
Prepared according to the general procedure (A) from (R_P,R_P)-**1a** using 9-chloromethylanthracene (0.68 g, 3.0 mmol), KI (10 mg) and stirred at r.t. The crude was purified by recrystallization from MeOH (20 mL). Yellow crystals (779 mg, 93%): mp 196–198 °C (dec.); R_f: 0.51 (toluene); $[\alpha]_D^{25}$: +281 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.15–1.50 (br m, 6H; 2 BH_3), 2.17 (m, 4H; 2 PCH_2), 5.63 (s, 4H; 2 OCH_2), 6.23 (t, *J* = 7.8 Hz, 4H; Ar-H), 6.53 (t, *J* = 7.5 Hz, 2H; Ar-H), 6.76 (m, 4H; Ar-H), 7.12 (m, 4H; Ar-H), 7.29–7.48 (m, 8H; Ar-H), 7.55 (m, 2H; ArH), 7.76–7.92 (m, 6H; Ar-H), 7.97 (dd, *J* = 0.9 and 5.4 Hz, 4H; Ar-H), 8.44 (s, 2H; Ar-H); ^{13}C NMR: δ = 16.5 (m), 62.9, 111.3, 116.3 (d, *J*(C,P) = 52 Hz), 120.9 (m), 123.6, 125.0, 125.4, 126.8, 127.1 (m), 127.9 (d, *J*(C,P) = 60 Hz), 128.8, 129.0, 129.3, 130.6 (m), 130.8, 131.2, 133.8, 136.4 (m), 160.8; ^{31}P NMR: δ = +17.5 (br s); anal. calcd. for $C_{56}H_{50}B_2O_2P_2$ (838.56): C 80.21, H 6.01; found: C 80.43, H 6.15.

(R_P,R_P)-1,2-Bis{[2-(2-methoxyethoxy)phenyl](phenyl)phosphino-*P*-borane}ethane (1p).



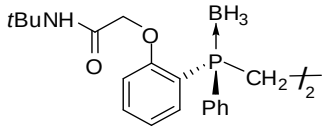
Prepared according to the general procedure (A) from (R_P,R_P)-**1a** using 2-methoxyethyl *p*-toluenesulfonate (0.92 g, 4.0 mmol). White powder (535 mg, 93%): mp 168–170 °C; R_f: 0.50 (toluene/EtOAc 8:2); $[\alpha]_D^{25}$: +48.0 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.25–1.80 (m, 6H; 2 BH_3), 2.67 (m, 4H; 2 PCH_2), 3.28 (s, 6H; 2 Me), 3.48 (m, 4H; 2 CH_2OMe), 3.85 (m, 4H; 2 CH_2CH$_2$OMe), 6.80 (br d, J = 8.3 Hz, 2H; Ar-H), 7.04 (m, 2H; Ar-H), 7.41 (m, 8H; Ar-H), 7.72 (m, 4H; Ar-H), 7.95 (m, 2H; Ar-H); ^{13}C NMR: δ = 17.8 (m), 58.9, 67.2, 70.1, 111.2, 115.3 (d, J(C,P) = 52 Hz), 121.0 (m), 128.3 (m), 129.3 (d, J(C,P) = 59 Hz), 130.6, 132.0 (m), 133.8, 136.8 (m), 160.5; ^{31}P NMR: δ = +18.7 (br s); MS (FAB): *m/z* (%): 573 (22) [M^+−H]; anal. calcd. for $C_{32}H_{42}B_2O_4P_2$ (574.24): C 66.93, H 7.37; found: C 67.12, H 7.53.

(R_P,R_P)-1,2-Bis{[2-(*tert*-butoxycarbonylmethoxy)phenyl](phenyl)phosphino-*P*-borane}ethane (1q).



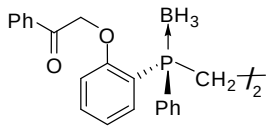
Prepared according to the general procedure (A) from (R_P,R_P)-**1a** using *tert*-butyl bromoacetate (0.78 g, 0.59 mL, 4.0 mmol). Colorless crystals (645 mg, 94%): mp 147–149 °C; R_f: 0.56 (toluene/EtOAc 8:2); $[\alpha]_D^{25}$: +10.6 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.25–1.75 (m, 6H; 2 BH_3), 1.35 (s, 18H; 6 Me), 2.71 (m, 4H; 2 PCH_2), 4.31 (s, 4H; 2 OCH_2), 6.65 (m, 2H; Ar-H), 7.04 (m, 2H; Ar-H), 7.39 (m, 8H; Ar-H), 7.75 (m, 4H; Ar-H), 7.92 (m, 2H; Ar-H); ^{13}C NMR: δ = 18.2 (m), 27.9, 65.3, 82.5, 111.2 (m), 115.6 (d, J(C,P) = 52 Hz), 121.7 (m), 128.3 (m), 129.0 (d, J(C,P) = 59 Hz), 130.6, 132.2 (m), 133.5, 137.0 (m), 159.6 (m), 166.6; ^{31}P NMR: δ = +19.7 (br s); MS (FAB): *m/z* (%): 685 (5) [M^+−H]; anal. calcd. for $C_{38}H_{50}B_2O_6P_2$ (686.37): C 66.50, H 7.34; found: C 66.55, H 7.49.

(R_P,R_P)-1,2-Bis{[2-(*N*-*tert*-butylcarbamoylmethoxy)phenyl](phenyl)phosphino-*P*-borane}ethane (1r).



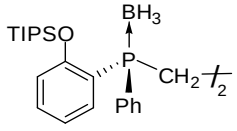
Prepared according to the general procedure (B) from (R_P,R_P)-**1a** using bromo-(*N*-*tert*-butyl)acetamide (0.78 g, 4.0 mmol). White powder (625 mg, 91%): mp 171–173 °C; R_f: 0.16 (toluene/EtOAc 6:4); $[\alpha]_D^{25}$: +20.10 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.35–1.60 (m, 6H; 2 BH_3), 1.19 (s, 18H; 6 Me), 2.35 and 2.58 (2 m, 4H; 2 PCH_2), 3.96 and 4.18 (2 d, J = 14.5 Hz, 2x 2H; 2 OCH_2), 5.90 (br s, 2H; NH), 6.83 (m, 2H; Ar-H), 7.14 (m, 2H; Ar-H), 7.37–7.69 (m, 14H; Ar-H); ^{13}C NMR: δ = 18.6 (m), 28.5, 51.4, 67.6, 112.1 (m), 115.0 (d, J(C,P) = 54 Hz), 122.5 (m), 128.2 (d, J(C,P) = 57 Hz), 128.9 (m), 131.4, 131.6 (m), 134.3, 135.3 (m), 158.7, 165.7; ^{31}P NMR: δ = +18.8 (br s); MS (FAB): *m/z* (%): 683 (30) [M^+−H]; anal. calcd. for $C_{38}H_{52}B_2N_2O_4P_2$ (684.40): C 66.69, H 7.66, N 4.09; found: C 66.86, H 7.82, N 4.26.

(R_P,R_P)-1,2-Bis[(2-phenacyloxyphenyl)(phenyl)phosphino-*P*-borane]ethane (1s).



Prepared according to the general procedure (A) from (R_P,R_P)-**1a** using 2-bromoacetophenone (0.44 g, 2.2 mmol). White powder (655 mg, 94%): mp 184–186 °C; R_f: 0.45 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: +14.0 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.35–1.65 (br m, 6H; 2 BH_3), 2.56–3.02 (m, 4H; 2 PCH_2), 5.09 and 5.19 (2d, J = 16.7 Hz, 4H; 2 OCH_2), 6.66 (m, 2H; Ar-H), 6.99 (m, 2H; Ar-H), 7.26–7.50 (m, 12H; Ar-H), 7.59 (m, 2H; Ar-H), 7.70–7.95 (m, 10H; Ar-H); ^{13}C NMR: δ = 18.2 (m), 70.5, 112.0 (m), 115.9 (d, J(C,P) = 52 Hz), 121.7 (m), 127.7, 128.4 (m), 128.8, 129.1 (d, J(C,P) = 59 Hz), 130.6, 132.0 (m), 133.6, 133.9, 134.0, 136.8 (m), 159.9 (m), 192.4; ^{31}P NMR: δ = +19.8 (br s); MS (FAB): *m/z* (%): 693 (7) [M^+−H]; anal. calcd. for $C_{42}H_{42}B_2O_2P_2$ (694.35): C 72.65, H 6.10; found: C 72.65, H 6.14.

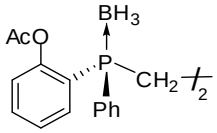
(R_P,R_P)-1,2-Bis[(phenyl)(2-triisopropylsiloxyphenyl)phosphino-*P*-borane]ethane (1t).



Prepared according to the general procedure (A) from (R_P,R_P)-**1a** using chlorotriisopropylsilane (0.58 g, 0.64 mL, 3.0 mmol). Colorless crystals (725 mg, 94%): mp 164–166 °C; R_f: 0.60 (toluene); $[\alpha]_D^{25}$ = +65.2 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.20–1.70 (m, 6H; 2 BH_3), 0.78 and 0.81 (2d, J = 7.5 Hz, 36H; 12 Me), 1.09 (sept, J = 7.5 Hz, 6H; 6 CH), 2.44–2.79 (m, 4H; 2 CH_2), 6.78 (m, 2H; Ar-H), 7.04 (m, 2H; Ar-H), 7.28–7.49 (m, 12H; Ar-H), 7.86 (m, 2H; Ar-H); ^{13}C NMR: δ = 13.1, 17.8, 17.9, 19.4 (m), 115.5 (d, J(C,P) = 55 Hz), 117.9, 120.8 (m), 128.6 (m), 130.4, 130.7 (d, J(C,P) = 60 Hz), 130.9 (m),

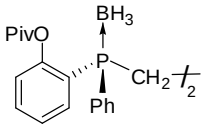
133.6, 137.1 (m), 158.4; ^{31}P NMR: δ = +20.0 (br m); MS (FAB): *m/z* (%): 769 (25) [M^+−H]; anal. calcd. for $C_{44}H_{70}B_2O_2P_2Si_2$ (770.77): C 68.56, H 9.15; found: C 68.53, H 9.43.

(R_P,R_P)-1,2-Bis[(2-acetoxyphenyl)(phenyl)phosphino-*P*-borane]ethane (1u).



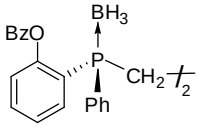
Prepared according to the general procedure (C) from (R_P,R_P)-**1a** using acetyl chloride (0.17 g, 0.16 mL, 2.2 mmol). Colorless crystals (530 mg, 97%): mp 143–144 °C; R_f: 0.43 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: +70.5 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.25–1.70 (br m, 6H; 2 BH_3), 1.84 (s, 6H; 2 Me), 2.52 (m, 4H; 2 CH_2), 7.18 (m, 2H; Ar-H), 7.30–7.60 (m, 14H; Ar-H), 7.79 (m, 2H; Ar-H); ^{13}C NMR: δ = 18.4 (m), 20.7, 119.7 (d, *J*(C,P) = 52 Hz), 123.7 (m), 126.1 (m), 128.3 (d, *J*(C,P) = 59 Hz), 129.0 (m), 131.4 (m), 133.3, 135.1 (m), 152.6, 167.6; ^{31}P NMR: δ = +19.3 (br m); anal. calcd. for $C_{30}H_{34}B_2O_4P_2$ (542.16): C 66.46, H 6.32; found: C 66.51, H 6.35.

(R_P,R_P)-1,2-Bis[(phenyl)(2-pivaloyloxyphenyl)phosphino-*P*-borane]ethane (1v).



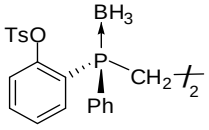
Prepared according to the general procedure (C) from (R_P,R_P)-**1a** using pivaloyl chloride (0.26 g, 0.27 mL, 2.2 mmol). Colorless crystals (610 mg, 97%): mp 177–179 °C; R_f: 0.64 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: +50.3 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.25–1.80 (br m, 6H; 2 BH_3), 0.85 (s, 18H; 6 Me), 2.49 (m, 4H; 2 CH_2), 7.02 (m, 2H; Ar-H), 7.26–7.49 (m, 12H; Ar-H), 7.57 (m, 2H; Ar-H), 7.85 (m, 2H; Ar-H); ^{13}C NMR: δ = 18.9 (m), 26.6, 38.8, 118.6 (d, *J*(C,P) = 52 Hz), 123.6 (m), 125.8 (m), 128.4 (d, *J*(C,P) = 57 Hz), 128.9 (m), 131.0 (m), 131.1 (d, *J*(C,P) = 5 Hz), 133.4, 136.1 (m), 153.5, 175.6; ^{31}P NMR: δ = +21.3 (br m); MS (FAB): *m/z* (%): 625 (12) [M^+−H]; anal. calcd. for $C_{36}H_{46}B_2O_4P_2$ (626.32): C 69.04, H 7.40; found: C 69.33, H 7.56.

(R_P,R_P)-1,2-Bis[(2-benzoyloxyphenyl)(phenyl)phosphino-*P*-borane]ethane (1w).



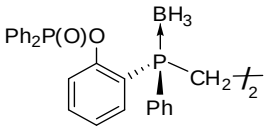
Prepared according to the general procedure (C) from (R_P,R_P)-**1a** using benzoyl chloride (0.31 g, 0.26 mL, 2.2 mmol). Colorless crystals (650 mg, 98%): mp 167–169 °C; R_f: 0.62 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: +97.1 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.35–1.65 (br m, 6H; 2 BH_3), 2.55 (m, 4H; 2 PCH_2), 7.05–7.45 (m, 18H; Ar-H), 7.58 (m, 4H; Ar-H), 7.72 (m, 4H; Ar-H), 7.92 (m, 2H; Ar-H); ^{13}C NMR: δ = 18.0 (m), 120.4 (d, *J*(C,P) = 52 Hz), 124.1, 126.1 (m), 127.5 (d, *J*(C,P) = 58 Hz), 128.0, 128.3, 128.5 (m), 130.1, 130.9, 131.3 (m), 133.4, 133.7, 135.1 (m), 152.7, 163.5; ^{31}P NMR: δ = +18.8 (br s); MS (FAB): *m/z* (%): 665 (16) [M^+−H]; anal. calcd. for $C_{40}H_{38}B_2O_4P_2$ (666.30): C 72,10, H 5.75; found: C 72.33, H 5.80.

(R_P,R_P)-1,2-Bis{(phenyl)[2-(*p*-tosyloxy)phenyl]phosphino-*P*-borane}ethane (1x).



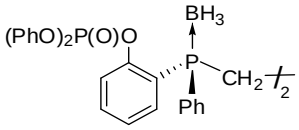
Prepared according to the general procedure (C) from (R_P,R_P)-**1a** using *p*-toluenesulfonyl chloride (0.42 g, 2.2 mmol). Colorless crystals (710 mg, 93%): mp 169–171 °C; R_f: 0.22 (toluene); $[\alpha]_D^{25}$: +80.2 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.20-1.51 (br m, 6H; 2 BH_3), 2.32–2.56 (m, 10H; 2 PCH_2 and 2 Me), 7.10–7.59 (m, 24H; Ar-H), 7.97 (m, 2H; Ar-H); ^{13}C NMR: δ = 17.7 (m), 21.7, 118.5 (d, *J*(C,P) = 49 Hz), 119.0, 125.9 (m), 128.1, 128.2 (d, *J*(C,P) = 59 Hz), 128.8, 129.8, 130.9, 131.4, 132.4, 134.0, 136.8 (m), 145.6, 152.3; ^{31}P NMR: δ = +19.9 (br s); anal. calcd. for $C_{40}H_{42}B_2O_6P_2S_2$ (766.46): C 62.68, H 5.52; found: C 62.52, H 5.53.

(R_P,R_P)-1,2-Bis[(2-(diphenylphosphinyloxy)phenyl)(phenyl)phosphino-*P*-borane]ethane (1y).



Prepared according to the general procedure (C) from (R_P,R_P)-**1a** using diphenylphosphinic chloride (0.52 g, 0.42 mL, 2.2 mmol). White powder (810 mg, 94%): mp 116–118 °C; R_f: 0.51 (EtOAc); $[\alpha]_D^{25}$: +126.9 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.55–1.55 (br m, 6H; 2 BH_3), 2.47 (m, 4H; 2 PCH_2), 7.08–7.58 (m, 36H; Ar-H), 7.86 (m, 2H; Ar-H); ^{13}C NMR: δ = 17.8 (m), 117.5 (m), 119.5 (m), 124.1 (m), 127.5–135.8 (m), 153.9 (m); ^{31}P NMR: δ = +18.2 (br m, 2P; PBH_3), +33.7 (s, 2P; PO); MS (FAB): *m/z* (%): 859 (16) [M^++H]; anal. calcd. for $C_{50}H_{48}B_2O_4P_4$ (858.43): C 69.96, H 5.64; found: C 70.27, H 5.68.

(R_P,R_P)-1,2-Bis[(2-(diphenylphosphoryloxy)phenyl)(phenyl)phosphino-*P*-borane]ethane (1z).

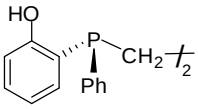


Prepared according to the general procedure (C) from (R_P,R_P)-**1a** using diphenyl phosphoryl chloride (0.59 g, 0.45 mL, 2.2 mmol). Colorless foam (790 mg, 86%): R_f: 0.33 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: +41.6 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 0.25–1.75 (m, 6H; 2 BH_3), 2.74 (m, 4H; 2 CH_2), 6.97 (m, 8H; Ar-H), 7.09–7.39 (m, 20H; Ar-H), 7.44 (m, 2H; Ar-H), 7.62 (m, 6H; Ar-H), 7.93 (m, 2H; Ar-H); ^{13}C NMR: δ = 18.3 (m), 118.6 (dd, J(C,P) = 50 and 11 Hz), 118.8 (m), 119.9 (m), 125.2 (m), 125.5 (m), 127.9 (d, J(C,P) = 58 Hz), 128.6 (m), 129.6 (m), 131.0 (m), 131.5 (m), 133.9 (m), 136.0 (m), 149.7 (m), 152.5 (d, J(C,P) = 5 Hz); ^{31}P NMR: δ = −17.9 (s, 2P; PO), +19.3 (br m, PBH_3); MS (FAB): *m/z* (%): 921 (2) [M^+−H]; anal. calcd. for $C_{50}H_{48}B_2O_8P_4$ (922.43): C 65.10, H 5.24; found: C 65.00, H 5.34.

General Procedure for the Synthesis of 1,2-Bis[(*o*-RO-phenyl)(phenyl)phosphino]ethane "R-SMS-Phos" (2b,c,l,p–r,t–y) - Scheme 1, *step b*: 1,2-Bis[(*o*-RO-phenyl)(phenyl)phosphino-*P*-borane]ethane in Et_2NH (10 mL/1 mmol of **1**) was refluxed for 2–3 h under inert atmosphere. After concentration, purification on silica gel and/or recrystallization under inert atmosphere the title compound **2** was obtained.

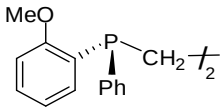
"R-SMS-Phos" (2t,u) - Scheme 1, *step d*: To a stirred solution of **2a** (1 mmol) in THF (10 mL) was added NaH (60 mg, 2.5 mmol) at 0 °C. After 15 min, TIPSCl or AcCl (2.5 mmol) was added and left to stir at r.t. for 1 h under inert atmosphere. The mixture was quenched with H_2O (0.1 mL), concentrated, and the residue was filtered trough a pad of silica gel and the product was recrystallized under inert atmosphere.

(R_P,R_P)-1,2-Bis[(*o*-hydroxyphenyl)(phenyl)phosphino]ethane (2a) ((R_P,R_P)-SMS-Phos).



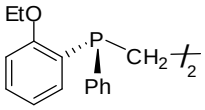
For its preparation from (R_P,R_P)-DiPAMP (**2b**) (Scheme 1, *step e*), see above. It was also prepared from (R_P,R_P)-**1a** (0.46 g, 1.00 mmol) according to the general procedure (Scheme 1, *step b*). The product was isolated as a diethylamine complex. The free ligand was obtained upon stirring with Amberlite® IRC-50 (1.2 g) in MeOH (5 mL) for 3 h. Purification on silica gel eluting with toluene/EtOAc 8:2 yielded (R_P,R_P)-**2a** as white powder (375 mg, 87%). Its characteristics were identical to the product obtained by demethylation of (R_P,R_P)-DiPAMP.

(R_P,R_P)-1,2-Bis[(*o*-anisyl)(phenyl)phosphino]ethane (2b) ((R_P,R_P)-DiPAMP).



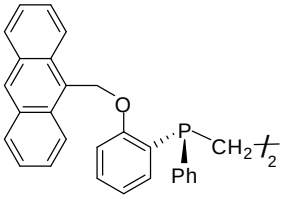
Prepared from (R_P,R_P)-**1b** (0.37 g, 0.75 mmol) according to the general procedure. Colorless crystals (335 mg, 97%). ^{1}H NMR: δ = 1.95 and 2.29 (2 m, 4H; 2 PCH_2), 3.74 (s, 6H; 2 Me), 6.77–6.97 (m, 6H; Ar-H), 7.21–7.41 (m, 12H; Ar-H).

(R_P,R_P)-1,2-Bis[(2-ethoxyphenyl)(phenyl)phosphino]ethane (2c).



Prepared from (R_P,R_P)-**1c** (0.39 g, 0.75 mmol) according to the general procedure. Colorless crystals (355 mg, 98%): mp 82–84 °C; R_f: 0.42 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$: −67.0 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 1.19 (t, J = 7.0 Hz, 6H; 2 Me), 1.97 and 2.32 (2 m, 4H; 2 PCH_2), 3.91 (m, 4H; 2 OCH_2), 6.77 (m, 2H; Ar-H), 6.84 (m, 2H; Ar-H), 7.01 (m, 2H; Ar-H), 7.20–7.41 (m, 12H; Ar-H); ^{13}C NMR: δ = 14.4, 21.8 (m), 63.6, 110.9, 120.5. 126.5 (m), 128.2 (m), 128.6, 129.8, 132.2 (m), 133.3 (m), 137.0 (m), 160.2 (m); ^{31}P NMR: δ = −19.6 (s); MS (FAB): *m/z* (%): 487 (100) [M^++H]; HR-MS (EI): *m/z* = 486.189, calcd. for $C_{30}H_{32}O_2P_2$ [M^+]: 486.188; anal. calcd. for $C_{30}H_{32}O_2P_2$ (486.52): C 74.06, H 6.63; found: C 74.39, H 6.73.

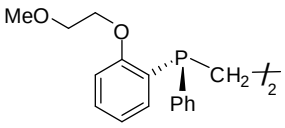
(R_P,R_P)-1,2-Bis{[2-(9-anthrylmethoxy)phenyl](phenyl)phosphino}ethane (2l).



Prepared from (R_P,R_P)-**1l** (0.626 g, 0.75 mmol) according to the general procedure. Yellow crystals (575 mg, 95%): mp 183–185 °C; R_f: 0.71 (toluene); $[\alpha]_D^{25}$: −31.0 (c 0.5 in $CHCl_3$); ^{1}H NMR: δ = 1.60 and 1.93 (2 m, 4H; 2 PCH_2), 5.67 and 5.82 (2 d, J = 10.8 Hz, 4H; 2 CH_2), 6.65–6.93 (m, 12H; Ar-H), 7.02 (m, 2H; Ar-H), 7.11 (m, 2H; Ar-H), 7.26–7.41 (m, 10H; Ar-H), 7.97 (m, 8H;

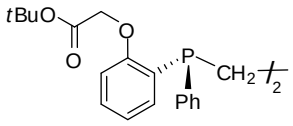
Ar-H), 8.42 (s, 2H; Ar-H); ^{13}C NMR: δ = 21.4 (m), 63.0, 111.5, 121.1, 124.1, 124.9, 126.4, 126.8, 127.6 (m), 127.8, 128.7, 128.8, 130.0, 130.9, 131.3, 132.5, 132.6, 132.7, 132.8, 137.2 (m), 160.7 (m); ^{31}P NMR: δ = −21.8 (s); anal. calcd. for $C_{56}H_{44}O_2P_2$ (810.89) C 82.95, H 5.47; found: C 82.91, H 5.52.

(R_P,R_P)-1,2-Bis{[2-(2-methoxyethoxy)phenyl](phenyl)phosphino}ethane (2p).



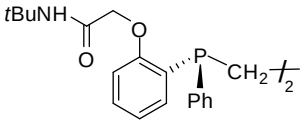
Prepared from (R_P,R_P)-**1p** (431 mg, 0.75 mmol) according to the general procedure. Colorless oil (400 mg, 98%): R_f: 0.33 (toluene); $[\alpha]_D^{25}$: −9.4 (c 0.6 in $CHCl_3$); ^{1}H NMR: δ = 1.96 and 2.33 (m, 4H; 2 PCH_2), 3.31 (s, 6H; 2 Me), 3.50 (t, J = 5.2 Hz, 4H; 2 CH_2OMe), 3.99 (m, 4H; 2 CH_2CH_2OMe), 6.81 (d, J = 8.1 Hz, 2H; Ar-H), 6.87 (m, 2H; Ar-H), 7.04 (m, 2H; Ar-H), 7.22–7.40 (m, 12H; Ar-H); ^{13}C NMR: δ = 22.0 (m), 59.1, 67.5, 70.5, 111.3, 120.9, 127.1 (m), 128.2 (m), 128.4, 129.7, 132.2 (m), 133.1 (m), 137.4 (m), 160.1 (m); ^{31}P NMR: δ = −20.2 (s); MS (FAB): m/z (%): 547 (91) [M^++H]; HR-MS (EI): m/z = 546.210, calcd. for $C_{32}H_{36}O_4P_2$ [M^+]: 546.209.

(R_P,R_P)-1,2-Bis{[2-(*tert*-butoxycarbonylmethoxy)phenyl](phenyl)phosphino}ethane (2q).



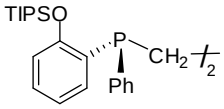
Prepared from (R_P,R_P)-**1q** (0.515 g, 0.75 mmol) according to the general procedure. Colorless oil (485 mg, 98%): R_f: 0.66 (toluene); $[\alpha]_D^{25}$: −47.7 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 1.42 (s, 18H; 6 Me), 2.00 and 2.39 (2m, 4H; 2 PCH_2), 4.42 (s, 4H; 2 OCH_2), 6.65 (m, 2H; Ar-H), 6.86 (m, 2H; Ar-H), 6.97 (m, 2H; Ar-H), 7.16–7.43 (m, 12H; Ar-H); ^{13}C NMR: δ = 22.0 (m), 28.0, 66.0, 82.1, 111.0, 121.5, 127.5 (m), 128.2 (m), 128.9, 129.5, 132.3, 133.5 (m), 136.9 (m), 159.5 (m), 167.6; ^{31}P NMR: δ = −21.0 (s); MS (EI): m/z (%): 658 (91) [M^+]; HR-MS (EI): m/z = 658.264, calcd. for $C_{38}H_{44}O_6P_2$ [M^+]: 658.261; anal. calcd. for $C_{38}H_{44}O_6P_2$ (658.70): C 69.29, H 6.73; found: C 69.52, H 7.03.

(R_P,R_P)-1,2-Bis{[2-(*N*-*tert*-butylcarbamoylmethoxy)phenyl](phenyl)phosphino}ethane (2r).



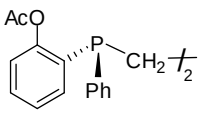
Prepared from (R_P,R_P)-**1r** (0.513 g, 0.75 mmol) according to the general procedure. Colorless crystals (470 mg, 95%): mp 149–150 °C; R_f: 0.50 (toluene/EtOAc 8:2); $[\alpha]_D^{25}$: +21.2 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 1.33 (s, 18H; 6 Me), 2.02 and 2.19 (2m, 4H; 2 PCH_2), 4.27 and 4.35 (2d, J = 14.4 Hz, 4H; 2 OCH_2), 6.70 (br s, 2H; NH), 6.80 (m, 2H; Ar-H), 6.98 (m, 2H; Ar-H), 7.09 (m, 2H; Ar-H), 7.31 (m, 12H; Ar-H); ^{13}C NMR: δ = 22.6 (m), 28.7, 51.2, 67.9, 111.8, 122.2, 125.8 (m), 128.5 (m), 128.9, 130.5, 131.8 (m), 132.5 (m), 136.6 (m), 158.9 (m), 166.7; ^{31}P NMR: δ = −24.4 (s); MS (FAB): m/z (%): 657 (100) [M^++H]; HR-MS (EI): m/z = 656.296, calcd. for $C_{38}H_{46}N_2O_4P_2$ [M^+]: 656.293; anal. calcd. for $C_{38}H_{46}N_2O_4P_2$ (656.73): C 69.50, H 7.06, N 4.27; found: C 69.47, H 7.37, N 4.12.

(R_P,R_P)-1,2-Bis[(phenyl)(2-triisopropylsiloxyphenyl)phosphino]ethane (2t).



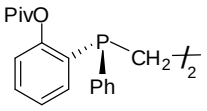
Prepared from (R_P,R_P)-**1t** (578 mg, 0.75 mmol) according to the general procedure. Colorless crystals (545 mg, 98%): mp 86–88 °C; R_f: 0.90 (hexane/toluene 1:1); $[\alpha]_D^{25}$: +5.7 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 1.01 and 1.02 (2d, J = 7.5 Hz, 36H; 12 Me), 1.22 (sept, J = 7.5 Hz, 6H; 6 CH), 1.86 and 2.12 (2 m, 4H; 2 CH_2), 6.75 (m, 2H; Ar-H), 6.82 (m, 2H; Ar-H), 6.95 (m, 2H; Ar-H), 7.15 (m, 2H; Ar-H), 7.23 (m, 10H; Ar-H); ^{13}C NMR: δ = 13.1, 18.0, 22.9, 117.5, 120.8, 128.1 (m), 128.2, 128.6 (m), 129.4, 131.9, 133.0 (m), 138.1 (m), 158.1 (m); ^{31}P NMR: δ = −23.9 (s); MS (FAB): m/z (%): 743 (96) [M^++H]; HR-MS (EI): m/z = 742.395, calcd. for $C_{44}H_{64}O_2P_2Si_2$ [M^+]: 742.392; anal. calcd. for $C_{44}H_{64}O_2P_2Si_2$ (743.10): C 71.12, H 8.68; found: C 71.23, H 8.88.

(R_P,R_P)-1,2-Bis[(2-acetoxyphenyl)(phenyl)phosphino]ethane (2u).



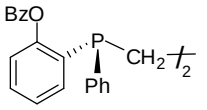
Prepared from (R_P,R_P)-**1u** (406 mg, 0.75 mmol) according to the general procedure. Colorless oil (370 mg, 96%): R_f: 0.54 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: −6.0 (c 0.5 in $CHCl_3$); ^{1}H NMR: δ = 1.91–2.20 (m, 10H; 2 CH_2; 2 Ac), 7.05 (m, 2H; Ar-H), 7.14–7.22 (m, 4H; Ar-H), 7.25–7.40 (m, 12H; Ar-H); ^{13}C NMR: δ = 20.7, 22.5 (m), 122.7, 126.2, 128.5 (m), 128.9, 130.0, 130.8 (m), 132.4 (m), 132.7 (m), 136.9 (m), 153.2 (m), 169.0; ^{31}P NMR: δ = −31.2 (s); HR-MS (EI): m/z = 514.147, calcd. for $C_{30}H_{28}O_4P_2$ [M^+]: 514.146.

(R_P,R_P)-1,2-Bis[(phenyl)(2-pivaloyloxyphenyl)phosphino]ethane (2v).



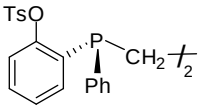
Prepared from (R_P,R_P)-**1v** (470 mg, 0.75 mmol) according to the general procedure. White solid (430 mg, 96%): R_f: 0.18 (toluene); $[\alpha]_D^{25}$: +5.9 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 1.25 (s, 18H; 6 Me), 2.02 (m, 4H; 2 CH_2), 7.01 (m, 2H; Ar-H), 7.13 (m, 4H; Ar-H), 7.20–7.38 (m, 12H; Ar-H); ^{13}C NMR: δ = 22.9 (m), 27.1, 39.1, 122.4, 126.0, 128.4 (m), 128.6, 129.9, 130.6 (m), 132.3, 132.7 (m), 137.0 (m), 153.8 (m), 176.6; ^{31}P NMR: δ = −25.3 (s); HR-MS (EI): *m/z* = 598.242, calcd. for $C_{36}H_{40}O_4P_2$ [M^+]: 598.240; anal. calcd. for $C_{36}H_{40}O_4P_2$ (598.65): C 72.23, H 6.73; found: C 72.41, H 6.85.

(R_P,R_P)-1,2-Bis[(2-benzoyloxyphenyl)(phenyl)phosphino]ethane (2w).



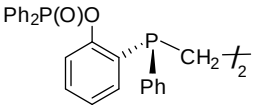
Prepared from (R_P,R_P)-**1w** (500 mg, 0.75 mmol) according to the general procedure. Colorless crystals (450 mg, 94%): mp 139–141 °C; R_f: 0.36 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$: +44.8 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 1.97 and 2.15 (2 m, 4H; 2 PCH_2), 7.21 (m, 16H; Ar-H), 7.41 (m, 6H; Ar-H), 7.58 (m, 2H; Ar-H), 7.96 (m, 4H; Ar-H); ^{13}C NMR: δ = 22.5 (m), 122.7, 126.2, 128.3 (m), 128.7, 129.1, 129.9, 130.2, 131.0 (m), 132.2 (m), 132.9 (m), 133.4, 136.6, 153.2 (m), 164.5; ^{31}P NMR: δ = −23.5 (s); MS (FAB): *m/z* (%): 639 (61) [M^++H]; HR-MS (EI): *m/z* = 638.179, calcd. for $C_{40}H_{32}O_4P_2$ [M^+]: 638.178; anal. calcd. for $C_{40}H_{32}O_4P_2$ (638.63): C 75.23, H 5.05; found: C 75.63, H 5.16.

(R_P,R_P)-1,2-Bis{(phenyl)[2-(*p*-tosyloxy)phenyl]phosphino}ethane (2x).



Prepared from (R_P,R_P)-**1x** (575 mg, 0.75 mmol) according to the general procedure. White solid (530 mg, 96%): R_f: 0.58 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$: +10.4 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 1.88 (m, 4H; 2 PCH_2), 2.38 (s, 6H; 2 Me), 6.98 (m, 2H; Ar-H), 7.06–7.35 (m, 20H; Ar-H), 7.76 (m, 4H; Ar-H); ^{13}C NMR: δ = 21.6, 22.7 (m), 121.6, 127.0, 128.4 (m), 128.6 (m), 128.7, 129.5, 130.0, 132.3 (m), 132.7 (m), 132.8, 132.9, 136.4 (m), 145.2, 152.3 (m); ^{31}P NMR: δ = −24.7 (s); MS (FAB): *m/z* (%): 739 (36) [M^++H]; anal. calcd. for $C_{40}H_{36}O_6P_2S_2$ (738.79): C 65.03, H 4.91; found: C 65.27, H 4.80.

(R_P,R_P)-1,2-Bis[(2-(diphenylphosphinyloxy)phenyl)(phenyl)phosphino]ethane (2y).



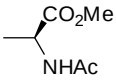
Prepared from (R_P,R_P)-**1y** (644 mg, 0.75 mmol) according to the general procedure. White solid (610 mg, 98%): R_f: 0.64 (toluene/EtOAc 6:4); $[\alpha]_D^{25}$: −3.4 (c 1.0 in $CHCl_3$); ^{1}H NMR: δ = 1.96 and 2.16 (m, 4H; 2 PCH_2), 6.96 (m, 4H; Ar-H), 7.11–7.58 (m, 26H; Ar-H), 7.69 (m, 4H; Ar-H), 7.96 (m, 4H; Ar-H); ^{13}C NMR: δ = 22.6 (m), 119.6 (m), 124.4 (m), 128.1–133.4 (m's), 136.6 (m), 153.8 (m); ^{31}P NMR: δ = −24.4 (s, 2P; PCH_2), +31.2 (s, 2P; PO); MS (FAB): *m/z* (%): 834 (90) [M^++H]; anal. calcd. for $C_{50}H_{42}O_4P_4$ (830.76): C 72.29, H 5.10; found: C 72.25, H 5.17.

***In situ* Preparation of [Rh((R_P,R_P)-R-sms-phos)(MeOH)$_2$]BF$_4$ Complex.** To a solution of [Rh(nbd)$_2$]BF$_4$ (2.3 mg, 6.3 μmol) in MeOH (0.5 mL), a solution of the (R_P,R_P)-R-SMS-phos ligand (0.8 equiv. to Rh-atom) in MeOH (0.5 mL) was added dropwise at r.t. The resulting solution was hydrogenated under 1 bar of H_2 for *ca*. 15 min. Elimination of metallic rhodium by filtration through a No. 3 sintered-glass filter afforded a clear brown solution of the title complex.

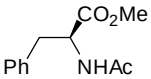
Hydrogenation Procedure for Substrates in Table 1. To a solution of the substrate in MeOH, three freeze-pump-thaw cycles were applied and the system was filled with Ar. Then to the substrate solution was added under Ar a solution of the preformed [Rh((R_P,R_P)-R-sms-phos)(MeOH)$_2$]BF$_4$ solvate in MeOH. A vacuum was applied to this system then it was backfilled with H_2. The mixture was stirred at the temperature and H_2 pressure as indicated. Progress of the hydrogenation was monitored by the diminution of the volume of the closed reaction system at 1 bar (until H_2 uptake ceased and the colour change of the solution); for reactions at 10 bar (**S7**) analyses were carried out at the indicated times.
The reaction mixture was analyzed by chiral GC (prior to analysis carboxylic groups were esterified with $TMSCHN_2$ in hexanes). Absolute configurations were assigned by comparison with the literature data of optical rotation of isolated products (90–98% yield) and/or of the t_R on chiral GC.

The following hydrogenation products with the mentioned absolute configuration were obtained using (R_P,R_P)-R-SMS-Phos ligands:

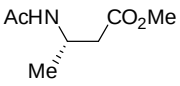
(*S*)-*N*-Acetyl-alanine methyl ester. ^{1}H NMR: δ = 1.41 (d, J = 7 Hz, 3H; CH*Me*), 2.02 (s, 3H; Ac), 3.76 (s, 3H; CO_2Me), 4.60 (m, 1H; CH), 6.26 (br s, 1H; NH); $[\alpha]_D^{25}$: −91.4 (c 1.0 in H_2O), >99% ee (*R*-enantiomer: $[\alpha]_D^{25}$: +91.2 (c 1.0 in H_2O)[4]); GC (Lipodex-E), 130 °C: 2.3 min (*S*), 2.6 min (*R*).



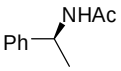
(*S*)-*N*-Acetyl-phenylalanine methyl ester. ^{1}H NMR: δ = 1.99 (s, 3H; Ac), 3.13 (m, 2H; CH_2), 3.73 (s, 3H; OMe), 4.90 (dt, J = 6 and 8 Hz, 1H; CH), 5.90 (br d, J = 6 Hz, 1H; NH), 7.09 (m, 2H; Ar-H), 7.28 (m, 3H; Ar-H); $[\alpha]_D^{25}$: +15.7 (c 1.0 in MeOH), >99% ee (*R*-enantiomer: $[\alpha]_D^{25}$: −15.8 (c 1.0 in MeOH)[4]); GC (Chiralsil-L-Val), 190 °C: 3.2 min (*R*), 3.4 min (*S*).



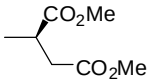
Methyl (*S*)-3-acetamidobutanoate. ^{1}H NMR: δ = 1.22 (d, J = 7 Hz, 1H; CH*Me*), 1.96 (s, 3H; Ac), 2.52 (dd, J = 5 and 16 Hz, 1H; CH_aH$_b$), 2.55 (dd, J = 5 and 16 Hz, 1H; CH$_a$$H_b$), 3,70 (s, 3H; OMe), 4.35 (m, 1H; CH), 6.09 (br s, 1H; NH); $[\alpha]_D^{25}$: −17.1 (c 1.4 in MeOH), 80% ee (*R*-enantiomer: $[\alpha]_D^{25}$: +21.4 (c 1.4 in MeOH)[5]); GC (CP-Chiralsil-DEX CB), 135 °C: 4.5 min (*S*), 4.7 min (*R*).



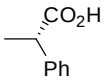
(*S*)-*N*-(1-Phenylethyl)acetamide. ^{1}H NMR: δ = 1.48 (d, J = 6.9 Hz, 3H; CH*Me*), 1.97 (s, 3H; Ac), 5.12 (m, 1H; CH), 5.84 (br s, 1H; NH), 7.22–7.39 (m, 5H; Ph); $[\alpha]_D^{25}$: −145 (c 1.0 in EtOH), >99% ee (*S*-enantiomer: $[\alpha]_D^{25}$: −148 (c 2.8 in EtOH)[6]); GC (CP-Chiralsil-DEX CB), 140 °C: 9.9 min (*S*), 10.4 min (*R*).



(*R*)-2-Methylsuccinic acid dimethyl ester. ^{1}H NMR: δ = 1.23 (d, J = 7 Hz, 3H; CH*Me*), 2.42 (dd, J = 6 and 16 Hz, 1H; CH_a), 2.75 (dd, J = 8 and 16 Hz, 1H; CH_b), 2.93 (m, 1H; CH), 3.68 (s, 3H; OMe), 3.70 (s, 3H; OMe); $[\alpha]_D^{25}$: +4.4 (c 3.0 in $CHCl_3$), 91% ee (*R*-enantiomer: $[\alpha]_D^{25}$: +4.8 (c 2.9 in $CHCl_3$)[7]); GC (Lipodex-E), 80 °C: 8.2 min (*S*), 8.5 min (*R*).



(*S*)-2-Phenylpropanoic acid. ^{1}H NMR: δ = 1.52 (d, J = 7 Hz, 3H; Me), 3.74 (q, J = 7 Hz, 1H; CH), 7.31 (m, 5H; Ph); $[\alpha]_D^{25}$: +63.2 (c 1.6 in $CHCl_3$), 88% ee (*R*-enantiomer: $[\alpha]_D^{25}$: −71.8 (c 1.57 in $CHCl_3$)[8]); GC after esterification with $TMSCHN_2$ (CP-Chiralsil-DEX CB), 90 °C: 16.1 min (*S*), 16.6 min (*R*).



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