Supporting Information

Synthesis and Application of Chiral *P,N*-Ligands with *Pseudo-meso* and *Pseudo-C_2* Symmetry

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General Procedures: All air-sensitive reactions were performed in oven dried glassware under argon using freshly distilled solvents. THF was dried and distilled from sodium-benzophenone under nitrogen. Methylene chloride was distilled over CaH_2. Column chromatography was performed using EM silica gel 60 (230-400 mesh). ^{1}H, ^{13}C, and ^{31}P NMR spectra were reccorded on Bruker AM 400 and AM 500 spectrometers. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as internal standard. Optical rotations were obtained on a Perkin-Elmer 343 polarimeter.

Diethyl (*S*)-{2-[(*S*)-4,5-dihydro-3H-dinaphtho[1,2-c:2´,1´-e]azepino}ethyl phosphonate (4).

To a solution of (*S*)-2,2´-di(bromomethyl)-1,1´-binaphthyl (1.5 g, 3.4 mmol) and triethylamine (1.1 mL) in THF (25 mL) was added a solution of (2-aminoethyl)phosphonic acid diethyl ester (643 mg, 3.4 mmol) in THF (25 mL). The mixture was heated to reflux for 12 h. The mixture was filtered, the filtrate was concentrated and purified by flash chromatography on silica gel with CH_2Cl_2/MeOH (98:2) as eluant to give **4** (91%) as a yellow oil. $[\alpha]_D^{20}$ = 228 (c = 1); ^{1}H NMR ($CDCl_3$) 400 MHz δ 7.88 (4H, d, *J* = 8.3 Hz), 7.48 (2H, d, *J* = 8.1 Hz), 7.39 (4H, m), 7.20 (2H, m), 4.05 (4H, m), 3.63 (2H, d, *J* = 12.3 Hz), 3.14 (2H, d, *J* = 12.3 Hz), 2.84 (1H, m), 2.62 (1H, m), 2.04 (2H, m), 1.26 (6H, q, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$) 100.6 MHz δ 135.37, 133.57, 131.75, 128.87, 128.71, 128.05, 127.84, 126.23, 125.90, 62.02 (d, $J_{C\text{-}P}$ = 9.5 Hz), 55.53 , 48.98, 25.84 (d, $J_{C\text{-}P}$ = 275 Hz), 16.91(2xC, d, $J_{C\text{-}P}$ = 11 Hz); ^{31}P NMR ($CDCl_3$) 202.5 MHz δ 30.7.

(*S*)-2-[(*S*)-4,5-dihydro-3H-dinaphtho[1,2-c:2´,1´-e]azepino]ethylphosphine (5).

To a degassed solution of **4** (1 g, 2.2 mmol) in THF (30 mL) was added $LiAlH_4$ (0.25 g, 6.6 mmol) in small portions at 0 °C. The mixture was stirred for 30 min at 0 °C, then diluted with THF (30 mL), quenched with a saturated aquous Na_2SO_4 solution (0.65 mL) and filtered though a plug of silica and concentrated to give **5** (94%) as a white solid that should be stored under nitrogen. $[\alpha]_D^{20}$ = 133 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 400 MHz δ 7.88 (4H, dd, *J* = 8.3, 1.3 Hz), 7.47 (2H, d, *J* = 8.3 Hz), 7.39 (4H, t, *J* = 7.8 Hz), 7.21-7.18 (2H, m), 3.64 (2H, d, *J* = 12.3 Hz), 3.12 (2H, d, *J* = 12.3 Hz), 2.70 (1H, m), 2.49 (1H, m), 2.24 (2H, dt, $J_{H\text{-}P}$ = 195 Hz, $J_{H\text{-}H}$ = 7.4 Hz), 1.73 (2H, m); ^{13}C NMR ($CDCl_3$) 100.6 MHz δ 133.41. 131.75, 131.58, 129.80, 126.83, 126.74, 126.14, 125.88, 124.28, 123.89, 56.65, 53.60, 11.33 (d, $J_{C\text{-}P}$ = 22 Hz); ^{31}P NMR ($CDCl_3$) 202.5 MHz δ -143 (t, $J_{H\text{-}P}$ = 195 Hz).

(*S*)-2-[(*S*)-4,5-dihydro-3H-dinaphtho[1,2-c:2´,1´-e]azepino-borane]ethylphosphine-borane (6).

To a degassed solution of **5** (0.15 g, 0.42 mmol) in THF (5 mL) was added dropwise a solution of $BH_3{\cdot}Me_2S$ (2M in THF, 0.44 mL) at room temperature. The solution was stirred for 1 h and concentrated under reduced pressure to give **6** as a white solid in quantitative yield. $[\alpha]_D^{20}$ = 286 (c = 0.125, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 400 MHz 7.98 (1H, d, *J* = 8.4 Hz), 7.97-7.92 (3H, m), 7.68 (1H, d, *J* = 8.3 Hz), 7.50-7.39 (4H, m), 7.31 (1H, d, *J* = 8.0 Hz), 7.28-720 (2H, m), 4.7 (2H, dm, $J_{\text{H-P}}$ = 375 Hz), 3.93 (1H, d, *J* = 11.5 Hz), 3.71 (1H, d, *J* = 14.1 Hz), 3.65(1H, d, *J* = 14.1 Hz), 3.15 (1H, d, *J* = 11.4 Hz), 2.92 (1H, m), 2.83 (1H, m), 2.53 (2H, m), 0.33 (3H, broad); ^{13}C NMR ($CDCl_3$) 100.6 MHz δ 136.61, 135.50, 134.26, 134.23, 131.09, 130.45, 129.74, 129.63, 128.89, 128.86, 128.11, 127.73, 127.16, 127.04, 126.81, 126.57, 62.99, 60.37, 56.84, 12.47 (d, $J_{\text{C-P}}$ = 35 Hz); ^{31}P NMR ($CDCl_3$) 202.5 MHz δ 55.3 (broad).

Alkylation procedure of phosphine-borane 6.

To a suspension of NaH (10.5 mg, 0.44 mmol) in THF (0.5 mL) was added simultaneously **6** (77 mg, 0.2 mmol) and (*R*)- or (*S*)-2,2´-di(bromomethyl)-1,1´-binaphthyl **2** (88 mg, 0.2 mmol) and the solution was stirred for 2h at room temperature. After filtration, the filtrate was concentrated and purified by flash chromatography on silica gel with CH_2Cl_2/hexane (1:1) as eluent to give ***(S,S)*-7** (79%) or ***(R,S)*-7** (76%) as white solids.

(*S*,*S*)-2-[(*S*)-4,5-dihydro-3H-dinaphtho[1,2-c:2´,1´-e]azepino-borane]-1-[(*S*)-4,5-dihydro-3H-dinaphtho[1.2-c:2´,1´-e]phosphepino-borane]ethane ((***S*,*S***)**-7**): $[\alpha]_D^{20}$ = 218 (c = 0.95, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 400 MHz δ 8.01 (2H, dd, *J* = 8.3, 5.8 Hz), 7.95-7.86 (6H, m), 7.62 (2H, dd, *J* = 8.0, 4.5 Hz), 7.55 (1H, d, J = 8.0 Hz), 7.49-7.38 (6H, m), 7.33 (1H, d, *J* = 8.0 Hz), 7.26-7.16 (4H, m), 7.12 (2H, t, *J* = 8.4 Hz), 3.80 (1H, d, *J* = 11.1 Hz), 3.75(1H, d, *J* = 14.1 Hz), 3.69 (1H, d, *J* = 14.1 Hz), 3.10 (1H, d, *J* = 11.3 Hz), 2.97 (2H, m), 2.85 (1H, dd, *J* = 14.6, 5.0 Hz,), 2.79 (1H, dd, *J* = 14.6, 8.3 Hz,), 2.78 (1H, dd, *J* =17.1, 1.5 Hz), 2.64 (1H, dd, *J* = 17.1 Hz, 13.1 Hz), 2.50 (1H, qd, *J* = 12.3, 3.0 Hz), 1.96 (1H, qd, *J* = 12.3, 7.6 Hz), 1.23 (3H. broad), 0.32 (3H, broad); ^{13}C NMR ($CDCl_3$) 125.7 MHz δ 136.1, 135.2, 133.9, 133.8, 133.7, 133.4, 133.2, 133.1, 132.2, 132.0, 131.5, 131.2, 130.9, 130.1, 130.0, 129.6, 129.5, 129.3 (2 signals), 128.9, 128.6, 128.5 (2 signals), 128.4 (2 signals), 128.3, 128.1, 127.8, 127.7, 127.4, 126.8, 126.7, 126.6 (2 signals), 126.5, 126.4, 126.3, 126.1, 125.9, 125.8, 61.5 (2 signals), 55.1 (d, *J* = 9 Hz), 29.9 (d, *J* = 28 Hz), 29.0 (d, *J* = 24 Hz), 18.06 (d, *J* = 22 Hz); ^{31}P NMR ($CDCl_3$) 202.5 MHz δ 46.0.

(*R*,*S*)-2-[(*S*)-4,5-dihydro-3H-dinaphtho[1,2-c:2´,1´-e]azepino-borane]-1-[(*R*)-4,5-dihydro-3H-dinaphtho[1.2-c:2´,1´-e]phosphepino-borane]ethane ((***R*,*S***)**-7**): $[\alpha]_D^{20}$ = 68 (c = 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 400 MHz δ 7.81-7.72 (7H, m), 7.64 (1H, d, *J* = 8.3 Hz), 7.56 (1H, d, *J* = 8.5 Hz), 7.37 (1H, d, *J* = 7.4 Hz), 7.35-7.24 (6H, m), 7.17-7.03 (7H, m), 6.95 (1H, d, *J* = 8.3 Hz), 3.80 (1H, d, *J* = 11.3 Hz), 3.50 (1H, d, *J* = 13.9 Hz), 3.38 (1H, d, *J* = 13.9 Hz), 3.03 (1H, d, *J* = 11.3 Hz), 2.79-2.68 (3H, m), 2.62-2.56 (3H, m), 2.35 (1H, m), 1.91 (1H, m), 1.39 (3H, broad), 0.23 (3H, broad); ^{13}C NMR ($CDCl_3$) 100.6 MHz δ 136.1, 135.1, 133.9, 133.8, (2 signals), 133.4, 133.2, 133.0, 133.2, 132.0, 131.8, 131.5, 131.1, 131.0, 130.6, 130.4, 130.2, 130.0, 129.9, 129.6, 129.4, 129.3, 128.9, 128.6, 128.5 (2 signals), 128.4, 128.3, 127.8, 127.5, 127.4, 127.3, 126.8, 126.6, 126.5, 126.4, 126.3, 126.1, 126.0, 125.8, 63.5, 58.4, 54.5 (d, *J* = 8 Hz), 30.2 (d, *J* = 33 Hz), 28.5 (d, *J* = 26 Hz), 18.3 (d, *J* = 23 Hz); ^{31}P NMR ($CDCl_3$) 202.5 MHz δ 46.0.

N-deprotection procedure:

To a solution of ***(S,S)*-7** or **(*R*,*S*)-7** (74 mg, 0.11 mmol) in CH_2Cl_2 was added DABCO (12.5 mg, 0.11 mmol) and the solution was stirred for 4 h at room temperature. After evaporation of the solvent, the crude product was purified by flash chromatography on silica gel with CH_2Cl_2 then CH_2Cl_2/AcOEt (98:2) as eluent to give **(*S*,*S*)-1-BH_3** (96%) or **(*R*,*S*)-1-BH_3** (94%) as a white solids.

(*S*,*S*)-2-[(*S*)-4,5-dihydro-3H-dinaphtho[1,2-c:2´,1´-e]azepino]-1-[(*S*)-4,5-dihydro-3H-dinaphtho[1.2-c:2´,1´-e]phosphepino-borane]ethane ((*S*,*S*)-1-BH_3): $[\alpha]_D^{20}$ = 93 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 400 MHz δ 7.96 (1H, d, J = 8.3 Hz), 7.92-7.85 (7H, m), 7.51 (2H, d, *J* = 8.1 Hz), 7.49-7.34 (8H, m), 7.20-7.13 (5H, m), 7.07 (1H, d, *J* = 8.4 Hz), 3.60 (2H, d, *J* = 12.2 Hz), 3.10 (2H, d, *J* = 12.2 Hz), 2.91 (1H, dd, *J* = 13.1, 2.3 Hz), 2.88 (1H, m), 2.78 (2H, d, *J* = 7.0 Hz,), 2.59 (1H, dd, *J* = 17.1, 13.1 Hz,), 2.56 (1H, m), 1.94 (1H, m), 1.79 (1H, m), 0.48 (3H, broad); ^{13}C NMR ($CDCl_3$) 100.6 MHz δ 135.38, 134.30, 133.58, 133.55, 133.47, 133.24, 132.71, 132.39, 131.77, 131.25, 131.15, 130.84, 129.20, 128.94, 128.86, 128.79, 128.72, 128.68, 128.00, 127.82, 127.75, 127.30, 126.96, 126.63, 126.26, 126.00, 125.93, 55.41, 49 01, 30.84 (d, $J_{C\text{-}P}$ = 32 Hz), 30.42 (d, $J_{C\text{-}P}$ = 30.5 Hz), 23.23 (d, $J_{C\text{-}P}$ = 28.5 Hz); ^{31}P NMR ($CDCl_3$) 202.5 MHz δ 45.9.

(*R*,*S*)-2-[(*S*)-4,5-dihydro-3H-dinaphtho[1,2-c:2´,1´-e]azepino]-1-[(*R*)-4,5-dihydro-3H-dinaphtho[1.2-c:2´,1´-e]phosphepino-borane]ethane ((*R*,*S*)-1-BH_3): $[\alpha]_D^{20}$ = 12 (c = 0.25, $CHCl_3$) ^{1}H NMR ($CDCl_3$) 400 MHz δ 7.90-7.81 (8H, m), 7.51 (1H, d, *J* = 8.4 Hz), 7.41-7.35 (8H, m), 7.29 (1H, d, *J* = 8.5 Hz), 7.23-7.12 (5H, m), 7.05 (1H, d, *J* = 8.5 Hz), 3.60 (2H, d, *J* = 12.2 Hz), 3.16 (2H, d, *J* = 12.2 Hz), 2.92-2.82 (3H, m), 2.77-2.6 (3H, m), 1.91 (1H, m), 1.66 (1H, m), 0.48 (3H, broad); ^{13}C NMR ($CDCl_3$) δ 100.6 MHz δ 135.37, 134.37, 133.58, 133.46, 133.21, 132.72, 132.40, 131.76, 131.33, 131.23, 130.77, 130.70, 129.17, 128.96, 128.93, 128.89, 128.78, 128.74, 128.69, 127.98, 127.84, 127.77, 127.73, 127.31, 126.95, 126.62, 126.27, 126.19, 126.00, 125.93, 55.71, 49.40, 3.89 (d, $J_{C\text{-}P}$ = 62.5 Hz), 30.13 (d, $J_{C\text{-}P}$ = 30 Hz), 22.51 (d, $J_{C\text{-}P}$ = 28.5 Hz); ^{31}P NMR ($CDCl_3$) 202.5 MHz δ 46.0.

Typical procedure for catalytic asymmetric allylic substitution using palladium acetate as palladium source.

Ligand (***S,S)*-1**-BH_3. (5 mg, 0.0077 mmol) and *rac*-1.3-diphenyl-2-propenyl acetate (78 mg, 0.31 mmol) were mixed in degassed CH_2Cl_2 (0.7 mL) in a dry flask. Palladium acetate (1.73 mg, 0.0077 mmol) was added and the solution was degassed and stirred for 15 min at room temperature. A solution of dimethyl malonate (91.8 mg, 0.69 mmol) and BSA (189 mg, 0.93 mmol) in degassed CH_2Cl_2 (0.7 mL) was added at –78 °C. Potassium acetate (few crystals) was added, the solution was degassed and stirred at room temperature. After complete reaction (monitored by HPLC), a saturated solution of NH_4Cl in water was added, and the aquous layer was extracted with Et_2O. The organic phases were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with hexane/EtOAc (4:1) as eluent to give the product (95%, 98.5% ee (*S))* as a white solid. The enantiomeric excess was mesured using HPLC (chiralcel OD-H, flow rate =0.5 mL/min, hexane:isopropanol = 99:1, t_R = 21.30 min, t_S = 22.85 min.

The same procedure was used for the dimethyl(3-cyclohexenyl)malonate, but the product was purified by flash chromatography on silica gel with hexane/EtOAc (95:5) as eluent The enantiomeric excess was mesured using GC: Chrompack Permethyl-β-CD.

Typical procedure for catalytic asymmetric allylic substitution using allylpalladium chloride dimer as palladium source.

To a degassed solution of (***S,S)*-1**-BH_3 (7.15 mg, 11 µmol) in toluene (0.3 mL) was added a degassed solution of DABCO (2.5 mg, 22.1 µmol) in toluene (0.1 mL) and the mixture was stirred for 8 h at 80 °C. The solvent was removed under reduced pressure. CH_2Cl_2 (0.5 mL) was added, the solution was degassed and allyl palladium chloride dimer (1.05 mg, 2.9 µmol) was added and the solution was stirred at room temperature for 20 min. *Rac*-1.3-diphenyl-2-propenyl acetate (138.8 mg, 0.55 mmol) in degassed CH_2Cl_2 (0.6 mL) was added at –78 °C, then a solution of dimethyl malonate (163 mg, 1.24 mmol) and BSA (335 mg, 1.65 mmol) in degassed CH_2Cl_2 (0.8 mL) was added at –78 °C. Potassium acetate (few crystals) was added, the solution was degassed and stirred at room temperature. After complete reaction, a saturated solution of NH_4Cl in water was added, and the aqueous layer was extracted with Et_2O. The organic phases were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with hexane/EtOAc (4:1) as eluent to give the product (93%, 98.4% ee (*S*)*)* as a white solid.