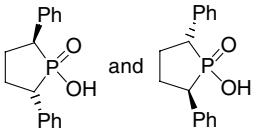
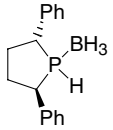
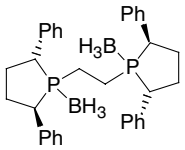
Supporting Information Available:



(*R*,*R*)- and (*S*,*S*)-1-hydroxy-1-oxo-2,5-*trans*-diphenylphospholane. Both (*R*,*R*)- and (*S*,*S*)-1-hydroxy-1-oxo-2,5-*trans*-diphenylphospholane were prepared according to the methods described by Fiaud and co-workers (Guillen *et al*. Tetrahedron, **2002**, *58*, 5895). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (m, 2H), 2.30-2.4 (m, 2H), 3.13 (m, 2H), 7.10-7.20 (m, 10H), OH shift dependent on concentration; ^{31}P NMR (162 MHz, $CDCl_3$) δ 67.8; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.77 (d, J_{CP} = 12.3 Hz, CH_2), 45.64 (d, J_{CP} = 87.5 Hz, CH), 127.05 (s), 128.66 (d, J_{CP} = 5.4 Hz), 128.77 (s), 136.26 (d, J_{CP} = 5.8 Hz, *ipso*-C_{Ar}); (*S*,*S*) $[\alpha]_D$ = –108.0 (*c* = 0.6, CH_2Cl_2) [lit. $[\alpha]_D$ = –102.7 (*c* = 0.6, CH_2Cl_2)], (*R*,*R*) $[\alpha]_D$ = +105.9 (*c* = 0.6, CH_2Cl_2).

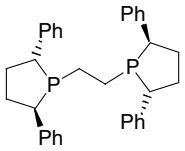


(*R*,*R*)-2,5-*trans*-Diphenylphospholane-borane adduct. To a stirred suspension of (*R*,*R*)-1-hydroxy-1-oxo-2,5-*trans*-diphenylphospholane (3.50 g, 12.0 mmol) in toluene (20 mL) at room temperature, under an atmosphere of nitrogen, was added phenylsilane (1.68 g, 15.5 mmol) drop-wise *via* syringe. Once the addition was complete the reaction was heated to 110°C. After 16 h at 110°C the reaction was allowed to cool to room temperature and then concentrated *in vacuo* to give an opaque gum. The gum was placed under an atmosphere of nitrogen, taken up in de-gassed THF (20 mL) and the resulting solution cooled to 0°C. Borane-methyl sulfide complex (4.88 mL, 51.4 mmol) was added drop-wise *via* syringe and once the addition was complete the reaction was allowed to warm to room temperature. After 16 h at room temperature the reaction was concentrated *in vacuo* to yield a white solid. The solid was purified by flash column chromatography (9:1 heptane:EtOAc) to give the product as a white solid (3.12 g, 95%): R_f = 0.25 (9:1 heptane:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.1-0.9 (br q, 3H, BH_3), 2.15-2.25 (m, 2H), 2.55-2.65 (m, 2H), 3.52 (m, 1H), 3.95 (m, 1H), 4.82 (dq, J_{HP} = 361 Hz, J_{HH} = 11.1 Hz, 1H, PH), 7.25 (m, 4H), 7.35 (m, 6H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.13 (d, J_{PH} = 359 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 33.86 (s, CH_2), 34.66 (d, J_{CP} = 3.7 Hz, CH_2), 40.66 (d, J_{CP} = 29.3 Hz, CH), 44.47 (d, J_{CP} = 32.7 Hz, CH), 127.31 (s), 127.36 (s), 128.52 (d, *J* = 2.0 Hz), 128.62 (s), 128.67 (s), 129.02 (s), 136.51 (s, *ipso*-C_{Ar}), 137.73 (d, *J* = 4.8 Hz, *ipso*-C_{Ar}).

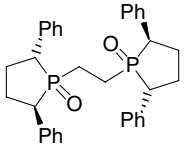


1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane-borane adduct. To a stirred solution of (*R*,*R*)-2,5-*trans*-diphenylphospholane-borane adduct (2.00 g, 7.87 mmol) in THF (20 mL) at –78°C, under an atmosphere of nitrogen, was added a 1.6 M solution of *n*-BuLi in hexanes (4.86 mL, 7.87 mmol) drop-wise *via* syringe. The reaction was then allowed to warm to -20°C and after stirring for 1 h a solution of 1,2-ethylene ditosylate (1.45 g, 3.94 mmol) in THF (20 mL) was added drop-wise *via* cannula. Once the addition was complete the reaction was allowed to warm to room temperature and stirred for a further 40 h. The reaction was quenched at 0°C by the slow addition of a 1 M aqueous solution of HCl (15 mL). The reaction was concentrated *in vacuo* and resulting white solid residue partitioned between water (30 mL) and CH_2Cl_2 (30 mL). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 x 30 mL). The organic fractions were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a white solid. Purification by flash column chromatography (9:1 heptane:EtOAc) yielded the product as a white solid (1.44 g, 69%): R_f = 0.50 (3:1 heptane:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.2-0.7 (br m, 6H, BH_3), 1.29 (m, 4H, CH_2), 2.00-2.10 (m, 4H, CH_2), 2.30-2.40 (m, 4H, CH_2), 3.03 (m, 2H, CH), 3.48 (m, 2H, CH), 7.05 (m, 4H), 7.10-7.20 (m, 8H), 7.25-7.35 (m, 8H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.22 (br. s); ^{13}C

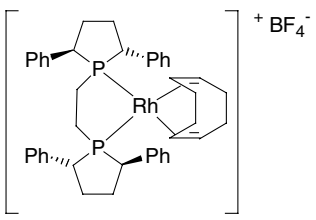
NMR (100.6 MHz, $CDCl_3$) δ 17.19 (m, bridge CH_2), 30.61 (s, ring CH_2), 33.62 (s, ring CH_2), 45.16 (m, ring CH), 46.91 (m, ring CH) 127.26 (s), 128.47 (s), 128.57 (s), 128.86 (s), 134.81 (s, *ipso*-C_{Ar}), 136.93 (s, *ipso*-C_{Ar}); MS (APCI) *m/z* 534 (M^+).



1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane. To a stirred solution of 1,2-bis[(*R*,*R*)-2,5-diphenylphospholano]ethane-borane adduct (1.10 g, 2.06 mmol) in CH_2Cl_2 (30 mL) at room temperature, under an atmosphere of nitrogen, was added $HBF_4.OMe_2$ (2.51 mL, 20.6 mmol) drop-wise *via* syringe. After 16 h at room temperature a de-gassed saturated aqueous solution of $NaHCO_3$ (30 mL) was added *via* syringe. Once effervescence had ceased the biphasic mixture was stirred for a further 15 min. The organic layer was removed *via* syringe and stored under nitrogen. The aqueous layer was extracted with de-gassed CH_2Cl_2 (4 x 20 mL) and all organic fractions were combined, dried ($MgSO_4$) and filtered under nitrogen. Concentration *in vacuo* gave a white solid that was recrystallised from de-gassed *i*-PrOH (40 mL) to give the product as white crystals (0.96 g, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57 (m, 2H), 0.96 (m, 2H), 1.76-1.86 (m, 2H), 2.05-2.15 (m, 2H), 2.27 (m, 2H), 2.48 (m, 2H), 2.95 (m, 2H), 3.59 (m, 2H), 7.08 (m, 6H), 7.16 (m, 4H), 7.21 (m, 6H), 7.30 (m, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.01; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.45 (dd, J_{CP} = 36.0 Hz, J_{CCP} = 27.1 Hz, bridge CH_2), 31.92 (s, ring CH_2), 37.38 (s, ring CH_2), 46.15 (m, ring CH), 50.57 (m, ring CH), 125.75 (s), 125.83 (s), 127.25 (s), 127.86 (m), 128.30 (s), 128.53 (s), 138.33 (m, *ipso*-C_{Ar}), 144.65 (m, *ipso*-C_{Ar}); HRMS (EI) *m/z* calcd for $C_{34}H_{36}P_2$ 506.2292, found 506.2269; $[\alpha]_D$ = -174.9 (*c* = 0.3, CH_2Cl_2).



1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane oxide. To a vigorously stirred solution of 1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane (40 mg, 0.08 mmol) in CH_2Cl_2 (5 mL) at room temperature was added a 27.5 wt. % solution of H_2O_2 in H_2O (5 mL) drop-wise *via* syringe. After 16 h the biphasic mixture was cooled to 0°C and a saturated aqueous solution of $Na_2S_2O_5$ was added carefully until effervescence ceased. The aqueous layer was separated and extracted with CH_2Cl_2 (3 x 5 mL). The orgainc fractions were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the product as a white solid (42 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (m, 2H), 1.46 (m, 2H), 1.82 (m, 2H), 2.14 (m, 2H), 2.25-2.45 (m, 4H), 2.77 (m, 2H), 3.40-3.50 (m, 2H), 7.10 (m, 4H), 7.24 (m, 8H), 7.30-7.40 (m, 8H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.56; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.62 (m, bridge CH_2), 26.38 (s, ring CH_2), 31.64 (s, ring CH_2), 45.50 (m, ring CH), 48.43 (m, ring CH), 126.05 (s), 126.15 (s), 127.65 (s), 127.97 (s), 128.03 (s), 134.06 (s, *ipso*-C_{Ar}), 135.26 (s, *ipso*-C_{Ar}); MS (ES) *m/z* 538 (M^+); Chiral HPLC, Chialpak AD-H (250 x 4.6 mm), heptane/EtOH 80/20, 1 mL/min, 25°C, detection by UV at 210 nm: 9.5 min (*S*,*S*), 15.2 min (*R*,*R*), 22.9 min (*meso*). >98% ee [(*R*,*R*)-enantiomer].



1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane-(1,5-cylcooctadiene) rhodium(I) tetrafluoroborate. An orange solution of 1,2-bis[(*R*,*R*)-2,5-diphenylphospholano]ethane (119 mg, 0.23 mmol) and bis(1,5-cyclooctadiene) rhodium(I) tetrafluoroborate (92 mg, 0.23 mmol) in de-gassed CH_2Cl_2 (8 mL), under an atmosphere of nitrogen, was stirred at room

temperature. After 2 h the reaction was concentrated *in vacuo* to give an orange residue. The residue was washed with de-gassed Et_2O (5 x 5 mL) under nitrogen and then dried *in vacuo* to give the product as an orange solid (187 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20-1.30 (m, 4H), 1.65-1.75 (m, 4H), 2.04 (m, 2H), 2.10-2.25 (m, 4H), 2.50-2.60 (m, 6H), 3.46 (m, 2H), 3.55 (m, 2H), 4.27 (m, 2H), 5.38 (m, 2H), 6.81 (d, J = 11.2 Hz, 4H), 7.07 (t, J = 11.2 Hz, 4H), 7.16 (t, J = 11.2 Hz, 2H), 7.33 (d, J = 11.2 Hz, 4H), 7.36 (t, J = 11.2 Hz, 2H), 7.51 (t, J = 11.2 Hz, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.62 (d, J_{PRh} = 153.9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.21 (m, bridge CH_2), 26.92 (s), 31.37 (s), 31.59 (s), 32.98 (s), 47.06 (m, ring CH), 49.69 (m, ring CH), 94.23 (d, J_{CRh} = 4.9 Hz, COD-CH), 101.45 (d, J_{CRh} = 2.5 Hz, COD-CH), 126.94 (s), 127.46 (s), 127.88 (s), 128.64 (s), 128.70 (s), 129.38 (s), 135.35 (s, *ipso*-C_{Ar}), 139.06 (s, *ipso*-C_{Ar}).

Rhodium-catalyzed asymmetric hydrogenation of dimethyl itaconate at S/C = 100,000. The reaction was carried out in a 300 mL pressure vessel equipped with a mechanical stirrer, cooling/heating coil, injection port, temperature probe and pressure transducer and fitted with a glass liner. The glass liner was charged with dimethyl itaconate (39.54 g, 250 mmol, 97% purity, Acros) and deoxygenated, nitrogen saturated MeOH (90 mL). The reactor was assembled, stirring commenced and the temperature set at 25°C. The reactor was pressurised up to 10 bar with nitrogen and depressurised once nitrogen uptake had ceased. The cycle was repeated 4 times and the reactor then charged with nitrogen to 10 bar and left for 30 min whilst the temperature equilibrated. The reactor was depressurised and a solution of 1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane-(1,5-cylcooctadiene) rhodium(I) tetrafluoroborate (2 mg, 0.0025 mmol), prepared under nitrogen, in deoxygenated, nitrogen saturated MeOH (10 mL) was injected *via* syringe. The reactor was then purged with hydrogen (5 times), and finally pressurised to 10 bar with hydrogen. Hydrogen uptake commenced immediately and the pressure was reset to 10 bar periodically over the course of 8 h. The reaction was left for a further 12 h, by which time hydrogen uptake had ceased. The reactor was flushed with nitrogen and dismantled. An aliquot was removed from the reaction liquor and analyzed by chiral GC: Chiradex GTA (30m x 0.25mm), 40°C for 7 min, then 10°C/min to 170°C: 13.1 min (*R*), 13.4 min (*S*). 100% conversion, 99% ee (*S* enantiomer).

Analytical data for hydrogenation of other substrates.

Using 1,2-Bis[(*R*,*R*)-2,5-diphenylphospholano]ethane-(1,5-cylcooctadiene) rhodium(I) tetrafluoroborate:

Hydrogenation of methyl acetamidocinnamate, Chiral GC. Chirasil DEX CB (25m x 0.25mm), 150°C for 25 min, then 15°C/min to 200°C: 17.9 min (*R*), 18.4 min (*S*). 100% conversion, 99% ee (*S* enantiomer).

Hydrogenation of *N*-(1-phenylvinyl)acetamide, Chiral GC. Chirasil DEX CB (25m x 0.25mm), 60°C for 2 min, then 10°C/min to 200°C: 16.4 min (enantiomer 1), 16.6 min (enantiomer 2). 100% conversion, 99% ee (enantiomer 1).

Hydrogenation of Candoxatril precursor, Chiral HPLC (of free acid). Chialpak AD-H (250 x 4.6 mm), heptane/EtOH 97/3, 1 mL/min, 25°C, detection by UV at 210 nm: 12.1 min (*S*), 14.4 min (*R*). 100% conversion, >98% ee (*R* enantiomer).

Using 1,2-Bis[(*S*,*S*)-2,5-diphenylphospholano]ethane-(1,5-cylcooctadiene) rhodium(I) tetrafluoroborate:

Hydrogenation of methyl 2-acetamidoacrylate, Chiral GC. Chirasil DEX CB (25m x 0.25mm), 60°C for 5 min, then 5°C/min to 135°C, then 15°C/min to 200°C: 16.4 min (*S*), 16.6 min (*R*). 100% conversion, 99% ee (*R* enantiomer).