Supplementary Material (ESI) for Chemical Communications

Supplementary Information

An Efficient and Highly Stereoselective Synthesis of New P-Chiral 1,5-Diphosphanylferrocene Ligands and Their Use in Some Enantioselective Hydrogenations

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(S_{Fc},αS)-(2-Diphenylphosphino)-1-[α-(2-diphenylphosphinophenyl)] ferrocenemethanol [(S_{Fc},αS)-5]:

A suspension of magnesium turnings (49 mg, 2.0 mmol) and 2-bromophenyl)diphenylphosphine (682 mg, 2.0 mmol) in THF (10 mL) was refluxed until the magnesium was dissolved (about 30 min). The resulting solution of Grignard reagent was cooled to -78 ºC, and (S)-α-(diphenylphosphino)ferrocenecarboxaldehyde **4** (597 mg, 1.5 mmol) was added. After stirring for 5 h at -78 ºC, the mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with saturated NH_4Cl solution, and extracted with Et_2O (2×10 mL). The combined extracts were washed with brine (20 mL), dried (MgSO4), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO2, hexane-EtOAc = 6:1) to give yellow crystals (951 mg, 96%) as a mixture of two diastereomers. Recrystallization from hexane afforded pure (S_{Fc},αS)-**5** (753 mg, 76%).^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.77 (m, 1H), 3.75 (m, 1H), 4.14 (s, 5H), 4.19 (t, 1H, J = 2.4 Hz), 4.32 (m, 1H), 6.58 (m, 1H), 6.79 (m, 1H), 7.15 ~ 7.56 (m, 23H); ^{31}P NMR ($CDCl_3$, 162 MHz): δ -16.80 (s), -21.32 (s).

(S_{Fc},αS)-Taniaphos (1b):

To a suspension of 30% KH (140 mg, 1.04 mmol) (previously washed with hexane under nitrogen) in THF (10 mL) was added (S_{Fc},αS)-**5** (530 mg, 0.8 mmol) at 0 ºC. After stirring for 2 h at 0 ºC, iodomethane (57 uL, 0.9 mmoL) was added via a syringe, and then the mixture was stirred for 1.5 h at 0 ºC. The reaction was quenched with MeOH (2

mL), and the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL), washed with water (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexane-EtOAc = 10:1) to give yellow crystals of **1b** (491 mg, 91%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.81 (s, 3H), 3.63 (m, 1H), 4.10 (m, 1H), 4.13 (t, 1H, J = 2.5 Hz), 4.16 (s, 5H), 5.77 (d, 1H, J = 6.8 Hz), 6.87 (m, 1H), 7.01 ~ 7.59 (m, 22H), 7.68 (m, 1H); ^{31}P NMR ($CDCl_3$, 101 MHz): δ -18.40 (d, J = 17.4 Hz), -19.33 (d, J = 17.4 Hz).

(S_{Fc},αS)-2-Bromo-1-[α-(2-diphenylphosphinophenyl)]ferrocenemethanol [(S_{Fc},αS)-7]:

A suspension of Mg (729 mg, 30 mmol) in THF (10 mL) was added dropwise a solution of 2-bromophenyldiphenylphosphine (9.42 g, 27.6 mmol) in THF (30 mL) at about 50 ºC. After addition, the mixture was refluxed for 1 h, cooled to room temperature, and added to a solution of (S)-2-bromoferrocenecarboxaldehyde **6** (6.74 g, 23 mmol) in Et_2O (20 mL) at -78 ºC. After stirring for 6 h at -78 ºC, the mixture was warmed to room temperature, and stirred overnight. The reaction was quenched with saturated NH_4Cl solution (50 mL), and diluted with EtOAc (100 mL). The organic layer was separated, washed with brine (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by chromatography (SiO_2, hexane-EtOAc = 5:1) to give yellow crystals of the title compound **7** (12.51 g, 98%) as a single diastereomer. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.67 (dd, 1H, J = 3.5 and 2.0 Hz), 4.04 (t, 1H, J = 2.5 Hz), 4.18 (m, 1H), 4.27 (s, 5H), 4.40 (m, 1H), 6.47 (dd, 1H, J = 6.5 and 3.5 Hz), 7.00 (m, 1H), 7.18 (m, 1H), 7.15 ~ 7.37 (m, 12H); ^{31}P NMR ($CDCl_3$, 101 MHz): δ -17.30.

(S_{Fc},αS)-2-Bromo-1-[α-methoxy-(2-diphenylphosphinophenylmethyl)]ferrocene [(S_{Fc},αS)-8]:

To a suspension of KH (30%, 3.75 g, 28.1 mmol) (washed with hexane) in THF (20 mL) was added a solution of (S_P,αS)-2-bromo-1-[α-(2-diphenylphosphinophenyl)] ferrocenemethanol [(S_{Fc},αS)-**7**] (12.00 g, 21.6 mmol) in THF (180 mL) at 0 ºC. After

stirring for 2 h at 0 ºC, iodomethane (1.48 mL, 23.8 mmoL) was added via a syringe, then the mixture was stirred for 1 h at 0 ºC. The reaction was quenched with MeOH (5 mL), and the solvents were removed under reduced pressure. The residue was dissolved in EtOAc (150 mL), washed with water (100 mL) and brine (100 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexane-EtOAc = 5:1) to give yellow crystals of compound **8** (12.10 g, 98%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 3.29 (s, 3H), 3.96 (t, 1H, J = 2.5 Hz), 4.01 (m, 1H), 4.27 (s, 5H), 4.33 (m, 1H), 6.09 (d, 1H, J = 7.8 Hz), 7.04 (m, 1H), 7.15 ~ 7.37 (m, 12H), 7.44 (m, 1H); ^{31}P NMR ($CDCl_3$, 101 MHz): δ -18.46.

(S_{Fc},αS)-Taniaphos (1b):

To a solution of (S_P,αS)-2-bromo-1-[α-methoxy-(2-diphenylphosphinophenylmethyl)] ferrocene [(S_{Fc},αS)-**8**](1.43 g, 2.5 mmol) in THF (10 mL) was added 1.7 M t-BuLi (pentane solution, 3.24 mL, 5.5 mmol) at -78 ºC. After stirring for 10 min at -78 ºC, chlorodiphenylphosphine (493 uL, 2.75 mmoL) was added. After stirring for 2 h at -78 ºC, the mixture was warmed to room temperature and stirred overnight. The reaction was quenched with saturated $NaHCO_3$ solution (5 mL), and diluted with CH_2Cl_2 (50 mL). The organic layer was separated, washed with brine (20 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by chromatography (SiO_2, hexane-EtOAc = 10:1) to give yellow crystals (1.59 g, 94%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.81 (s, 3H), 3.63 (m, 1H), 4.10 (m, 1H), 4.13 (t, 1H, J = 2.5 Hz), 4.16 (s, 5H), 5.77 (d, 1H, J = 6.8 Hz), 6.87 (m, 1H), 7.01 ~ 7.59 (m, 22H), 7.68 (m, 1H); ^{31}P NMR ($CDCl_3$, 101 MHz): δ -18.40 (d, J = 17.4 Hz), -19.33 (d, J = 17.4 Hz).

(S_{Fc},S_P,αS)-2-[(2-Methoxyphenyl)phenylphosphino]-1-[α-methoxy-(2-diphenylphosphinophenylmethyl)]ferrocene [(S_{Fc},S_P,αS)-2a]:

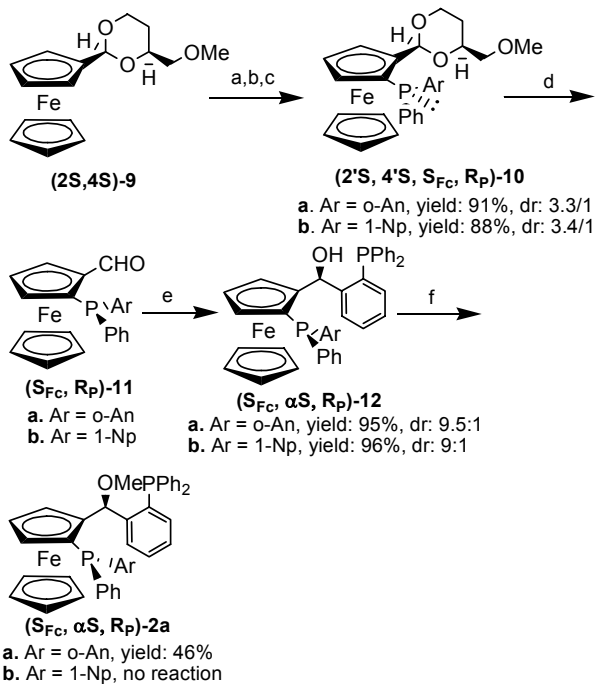
To a solution of bromide [(S_{Fe},αS)-**8**] (2.85 g, 5 mmol) in THF (30 mL) was added slowly 1.7 M t-BuLi (6.5 mL, 11 mmol) via a syringe at -78 ºC. After stirring for 10 min at -78 ºC, $PhPCl_2$ (746 uL, 5.5 mmoL) was added via a syringe, After stirring for 30 min at -78

ºC, the mixture was warmed to room temperature and stirred for 1 h at room temperature. the mixture was cooled to -78 ºC again, and a suspension of o-AnLi [prepared from 2-bromoanisole (805 uL, 6.5 mmol) and 1.7 M t-BuLi (7.6 mL, 13 mmol) in Et_2O (30 mL) at -78 ºC] was added via a cannula, then the mixture was stirred overnight at -78 ºC to room temperature. The reaction was quenched with water (20 mL), The organic layer was separated, washed with brine (30 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexane-EtOAc = 10:1) to give yellow crystals (3.21 g, 91%) as a single diastereomer. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.71 (s, 3H), 3.67 (m, 1H), 3.90 (m, 1H), 3.96 (s, 3H), 4.06 (t, 1H, J = 2.3 Hz), 4.22 (s, 5H), 5.52 (d, 1H, J = 6.5 Hz), 6.80~6.98 (m, 4H), 7.08~7.36 (m, 14H), 7.76 (m, 1H); ^{31}P NMR ($CDCl_3$, 101 MHz): δ -17.98 (d, J = 10.0 Hz), -33.15 (d, J = 10.0 Hz).

(S_{Fc},S_P,αS)-2-[(1-Naphthyl)phenylphosphino]-1-[α-methoxy-(2-diphenylphosphino phenylmethyl)]ferrocene [(S_{Fc},S_P,αS)-2b] and (S_{Fc},R_P,αS)-2-[(1-naphthyl)phenyl phosphino]-1-[α-methoxy-(2-diphenylphosphinophenylmethyl)]ferrocene [(S_{Fc},R_P,αS)-2b]:

To a solution of bromide **[(S_{Fc},αS)-8]** (2.85 g, 5 mmol) in THF (30 mL) was added slowly 1.7 M t-BuLi (6.5 mL, 11 mmol) via a syringe at -78 ºC. After stirring for 10 min at -78 ºC, $PhPCl_2$ (746 uL, 5.5 mmoL) was added via a syringe, After stirring for 30 min at -78 ºC, the mixture was warmed to room temperature and stirred for 1 h at room temperature. Tthe mixture was cooled to -78 ºC again, and a suspension of o-AnLi [prepared from 1-bromonaphthalene (900 uL, 6.5 mmol) and 1.7 M t-BuLi (7.6 mL, 13 mmol) in Et_2O (30 mL) at -78 ºC] was added via a cannula, then the mixture was stirred overnight at -78 ºC to room temperature. The reaction was quenched with water (20 mL), The organic layer was separated, washed with brine (30 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexane-EtOAc = 10:1) to give yellow crystals (3.30 g, 91%) as a mixture of two diastereomers (ratio: ~9:1), which was recrystallised from hexane to give pure major product [(S_{Fe},S_P,αS)-**2b**] (2.83 g, 78%) as yellow crystals. The mother liquor was concentrated, and the residue was recrystallized from MeOH to afford pure minor

product [(S_{Fe},R_P,αS)-**2b**] (217 mg, 6%) as yellow crystals. Major product [(S_{Fe},S_P,αS)-**2b**] **:** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.96 (s, 3H), 3.74 (m, 1H), 3.84 (s, 5H), 4.13 (t, 1H, J = 2.5 Hz), 4.20 (m, 1H), 6.04 (d, 1H, J = 7.3 Hz), 6.89~7.41 (m, 20H), 7.55 (ddd, 1H, J = 8.0, 6.8 and 1.3 Hz), 7.64 (dd, 1H, J = 6.8 and 1.5 Hz), 7.69 (ddd, 1H, J = 5.3, 3.5 and 1.7 Hz), 7.89 (t, 2H, J = 8.0 Hz), 9.32 (dd, 1H, J = 7.5 and 6.8 Hz). ^{31}P NMR ($CDCl_3$, 101 MHz): δ -18.83 (d, J = 21.3 Hz), -35.08 (d, J = 21.3 Hz). Minor product S_{Fe},R_P,αS)-**2b**]**:** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.73 (s, 3H), 3.61 (m, 1H), 4.21 (t, 1H, J = 2.5 Hz), 4.22 (s, 5H), 4.28 (m, 1H), 5.86 (d, 1H, J = 7.3 Hz), 6.67 (ddd, 1H, J = 7.8, 4.3 and 1.3 Hz), 6.79~7.61 (m, 23H), 7.75 (br. d, 1H, J = 8.0 Hz), 8.29 (m, 1H). ^{31}P NMR ($CDCl_3$, 101 MHz): δ -18.52 (d, J = 18.4 Hz), -27.69 (d, J = 18.4 Hz).



(2'S, 4'S, S_{Fc}, R_P)-2-[4'-(Methoxymethyl-1,3-dioxan-2'-yl]-1-[(2-methoxyphenyl) phenylphosphino]ferrocene [(2'S, 4'S, S_{Fc}, R_P)-10a]:

To a solution of (2S,4S)-4-(methoxymethyl)-2-ferrocenyl-1,3-dioxane [**(2S,4S)-9**] (1.58 g, 5 mmol) in Et_2O (20 mL) was added 1.7 M t-BuLi solution in pentane (3.23 mL, 5.5 mmol) at –40 ºC. After stirring for 10 min, the cooling bath was removed and the mixture was warmed to room temperature, and stirred for 1.5 h at room temperature. The

resulting orange suspension was cooled to –78 ºC, and dichlorophenylphosphine (750 uL, 5.5 mmol) was added in one portion. After stirring for 10 min, the cooling bath was removed and the mixture was warmed to room temperature, and stirred for 1.5 h at room temperature. The mixture was cooled to –78 ºC again, a solution of 2-methoxyphenyllithium [prepared from 2-bromoanisole (1.22 mL, 6.5 mmol) and 1.7 M t-BuLi solution in pentane (7.6 mL, 13 mmol) in Et_2O (40 mL) at –78 ºC] was added slowly via a cannula. The mixture was warmed to room temperature overnight, and filtered through a pad of Celite. The filtrate was concentrated. The residue was purified by chromatography (SiO_2, hexane-EtOAc = 6:1) to afford the title compound (2.41 g, 91%) as a mixture of two diastereomers (in about 3.3:1 ratio). Recrystallising from hexane, the major product [(2'S, 4'S, S_{Fc}, R_P)-**10a**] (1.41 g, 53%) was obtained. The absolute configuration of (2'S, 4'S, S_{Fc}, R_P)-**10a** was determined by single-crystal X-ray diffraction analysis. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 1.42 (dm, 1H, *J* = 13.3 Hz); 1.74 (m, 1H,); 2.89 (d, 2H, *J* = 5.1 Hz); 3.03 (s, 3H); 3.59 (m, 1H); 3.60 (s, 3H); 3.74 (m, 1H); 3.91 (td, 1H, *J* = 12.2 and 2.5 Hz); 4.08 (s, 5H); 4.24 ~4.27 (m, 2H); 4.70 (m, 1H); 5.71 (d, 1H, *J* = 2.5 Hz); 6.74 (dd, 1H, *J* = 7.9 and 4.6 Hz); 6.80 ~ 6.86 (m, 2H); 7.22 (m, 1H); 7.31 ~ 7.35 (m, 3H); 7.51 ~7.56 (m, 2H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ – 31.46 (s).

(2'S, 4'S, S_{Fc}, R_P)-2-[4'-(methoxymethyl-1,3-dioxan-2'-yl]-1-[(1-naphthyl)phenyl phosphino]ferrocene [(2'S, 4'S, S_{Fc}, R_P)-10b]:

To a solution of (2S,4S)-4-(methoxymethyl)-2-ferrocenyl-1,3-dioxane [**(2S,4S)-9]** (3.16 g, 10 mmol) in Et_2O (40 mL) was added 1.5 M t-BuLi solution in pentane (7.4 mL, 11 mmol) at –40 ºC. After stirring for 10 min, the cooling bath was removed and the mixture was warmed to room temperature, and stirred for 1.5 h at room temperature. The resulting orange suspension was cooled to –78 ºC, and dichlorophenylphosphine (1.49 mL, 11 mmol) was added in one portion. After stirring for 10 min, the cooling bath was removed and the mixture was warmed to room temperature, and stirred for 1.5 h at room temperature. The mixture was cooled to –78 ºC again, a solution of 1-naphthyllithium [prepared from 1-bromonaphthalene (1.67 mL, 12 mmol) and 1.5 M t-BuLi solution in pentane (16 mL, 24 mmol) in Et_2O (60 mL) at –78 ºC] was added slowly via a cannula.

The mixture was warmed to room temperature overnight, and filtered through a pad of Celite. The filtrate was concentrated. The residue was purified by chromatography (SiO_2, hexane-EtOAc = 6:1) to afford the title compound (4.95 g, 90%) as a mixture of two diastereomers (in about 3.4:1 ratio), which was recrystallised from hexane to give the pure major product [(2'S, 4'S, S_{Fc}, R_P)-**10b**] (2.53 g, 51%) as yellow needles. The absolute configuration of (2'S, 4'S, S_{Fc}, R_P)-**10b** was determined by single-crystal X-ray diffraction analysis. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 1.33 (dm, 1H, *J* = 13.3 Hz); 1.63 (m, 1H); 2.56 (dd, 1H, *J* = 10.3 and 4.8 Hz); 2.67 (dd, 1H, *J* = 10.3 and 5.6 Hz); 2.76 (s, 3H); 3.58 (m, 1H); 3.67 (m, 1H); 3.86 (td, 1H, *J* = 12.2 and 2.5 Hz); 4.15 (s, 5H); 3.74 (m, 1H); 4.21 (ddd, 1H, *J* = 11.4, 5.1 and 1.0 Hz); 4.31 (t, 1H, *J* = 2.5 Hz); 4.74 (m, 1H); 5.69 (d, 1H, *J* = 2.5 Hz); 7.16 (ddd, 1H, *J* = 7.1, 5.1 and 1.2 Hz); 7.29 ~ 7.40 (m, 6H); 7.54 ~ 7.58 (m, 2H); 7.74 (d, 1H, *J* = 8.3 Hz); 7.78 (d, 1H, *J* = 8.0 Hz); 8.25 ~8.28 (m, 1H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ – 28.03 (s).

(S_{Fc}, R_P)-2-[(2-Methoxyphenyl)phenylphosphino]ferrocenecarboxaldehyde [(S_{Fc}, R_P)-11a]:

A mixture of acetal [(2'S, 4'S, S_{Fc}, R_P)-**10a**] (4.0 g, 7.5 mmol), p-TsOH.H_2O (2.0 g), CH_2Cl_2 (50 mL) and H_2O (30 mL) was stirred for 24 h at room temperature. The organic layer was separated, washed with saturated $NaHCO_3$ solution (20 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give the crude product (3.20 g, 100%) as red crystals, which was used directly in next step. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 3.66 (s, 3H); 3.96 (m, 1H); 4.22 (s, 5H); 4.71 (t, 1H, *J* = 2.3Hz); 5.13 (m, 1H); 6.72 (m, 1H); 6.78 ~ 6.87 (m, 2H); 7.29 (m, 1H); 7.41 (m, 3H); 7.54 (m, 2H); 10.24 (d, 1H, *J* = 3.3 Hz). ^{31}P NMR ($CDCl_3$, 101 MHz): δ – 34.66 (s).

(S_{Fc}, R_P)-2-[(1-Naphthyl)phenylphosphino]ferrocenecarboxaldehyde [(S_{Fc}, R_P)-11b]:

A mixture of acetal [(2'S, 4'S, S_{Fc}, R_P)-**10b**] (4.73 g, 7.5 mmol), p-TsOH.H_2O (2.0 g), CH_2Cl_2 (50 mL) and H_2O (30 mL) was stirred for 24 h at room temperature. The organic layer was separated, washed with saturated $NaHCO_3$ solution (20 mL), dried ($MgSO_4$),

and evaporated under reduced pressure to give the crude product (3.36 g, 100%) as red crystals, which was used directly in next step. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 4.04 (m, 1H); 4.28 (s, 5H); 4.76 (t, 1H, *J* = 2.3Hz); 5.17 (m, 1H); 7.02 (m, 1H); 7.29 ~ 7.48 (m, 6H); 7.52~7.59 (m, 2H); 7.80 (t, 2H, *J* = 7.5 Hz); 8.26 (m, 1H); 10.20 (d, 1H, *J* = 3.0 Hz). ^{31}P NMR ($CDCl_3$, 101 MHz): δ – 30.50 (s).

(S_{Fc},R_P,αS)-2-[(2-Methoxyphenyl)phenylphosphino]-1-[(diphenylphosphinophenyl)] ferrocenemethanol [(S_{Fc},R_P,αS)-12a]:

A suspension of magnesium turnings (63 mg, 2.6 mmol) and 2-bromophenyl)diphenylphosphine (887 mg, 2.6 mmol) in THF (10 mL) was refluxed until magnesium was dissolved (about 30 min). The resulting Gragnard reagent solution was cooled to -78 ºC, and a solution of (S_{Fc}, R_P)-2-[(2-methoxyphenyl)phenylphosphino] ferrocenecarbaoxaldehyde [(S_{Fc}, R_P)-**11a**] (856 mg, 2.0 mmol) in THF (10 mL) was added slowly via a syringe. After stirring for 5 h at -78 ºC, the mixture was allowed to warm to room temperature and stirred overnight at room temperature. The reaction was quenched with saturated NH_4Cl solution, and extracted with CH_2Cl_2 (2×20 mL). The combined extracts were washed with brine (20 mL), dried (MgSO4), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexane-EtOAc = 6:1) to give yellow crystals (1.297 g, 96%) as a mixture of two diastereomers (~9:1). Major product: ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.91 (br. s, 1H), 3.57 (m, 1H), 3.59 (s, 3H), 4.05 (m, 1H), 4.14 (t, 1H, J = 2.4 Hz), 4.18(s, 5H), 4.22 (m, 1H), 6.48~4.56 (m, 2H), 6.68~6.80 (m, 2H), 7.02 ~ 7.37 (m, 13H); 7.49~7.58 (m, 2H), 7.67 (m, 1H). ^{31}P NMR ($CDCl_3$, 101 MHz): δ -18.69 (d, J = 14.6 Hz), -32.85 (d, J = 14.6 Hz).

(S_{Fc},R_P,αS)-2-[(1-Naphthyl)phenylphosphino]-1-[α-[(diphenylphosphinophenyl)] ferrocenemethanol [(S_{Fe},R_P,αS)-12b]:

A suspension of magnesium turnings (63 mg, 2.6 mmol) and 2-bromophenyl)diphenylphosphine (887 mg, 2.6 mmol) in THF (10 mL) was refluxed until

magnesium was dissolved (about 30 min). The resulting Gragnard reagent solution was cooled to -78 ºC, and a solution of (S_{Fc}, R_P)-2-[(1-naphthyl)phenylphosphino] ferrocenecarbaoxaldehyde [(S_{Fc}, R_P)-**11b**] (897 mg, 2.0 mmol) in THF (10 mL) was added slowly via a syringe. After stirring for 5 h at -78 ºC, the mixture was allowed to warm to room temperature and stirred overnight at room temperature. The reaction was quenched with saturated NH_4Cl solution, and extracted with CH_2Cl_2 (2×20 mL). The combined extracts were washed with brine (20 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexane-EtOAc = 6:1) to give yellow crystals (1.322 g, 93%) as a mixture of two diastereomers (~9:1). Major product: ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.39 (br. s, 1H), 3.66 (m, 1H), 4.24(s, 5H), 4.29 (t, 1H, J = 2.4 Hz), 4.57 (m, 1H), 4.22 (m, 2H), 6.40~4.49(m, 3H), 6.61~6.67 (m, 2H), 6.83 ~ 7.01 (m, 4H); 7.10~7.59 (m, H), 7.75 (br. D, 1H, J = 7.8 Hz), 8.28 (m, 1H). ^{31}P NMR ($CDCl_3$, 101 MHz): δ -18.54 (d, J = 21.0 Hz), -29.56 (d, J = 21.0 Hz).

(S_{Fc},R_P,αS)-2-[(2-Methoxyphenyl)phenylphosphino]-1-[α-methoxy-(2-diphenyl phosphinophenylmethyl)]ferrocene [(S_{Fc},R_P,αS)-2a]:

To a suspension of KH (30%, 174 mg, 1.3 mmol washed with hexane) in THF (10 mL) was added alcohol [(S_{Fc},R_P,αS)-**12a**] (690 g, 1.0 mmol) at 0 ºC. After stirring for 2 h at 0 ºC, iodomethane (68 uL, 1.1 mmoL) was added via a syringe, then the mixture was stirred for 2 h at 0 ºC. The reaction was quenched with MeOH (0.5 mL), and the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL), washed with water (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexane-EtOAc = 10:1) to give yellow crystals (463 mg, 66%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.82 (s, 3H), 3.50 (m, 1H), 3.57 (s, 3H), 4.11 (t, 1H, J = 2.3 Hz), 4.17 (s, 5H), 4.19 (m, 1H), 5.79 (d, 1H, J = 6.8 Hz), 6.54~6.64 (m, 2H), 6.69 (m, 1H), 6.84 (ddd, 1H, J =7.8, 4.3 and 1.5 Hz), 7.02~7.37 (m, 12H), 7.52 (m, 2H), 7.66 (m, 1H); ^{31}P NMR ($CDCl_3$, 101 MHz): δ -18.44 (d, J = 18.7 Hz), -31.19 (d, J = 18.7 Hz).

Supplementary Material (ESI) for Chemical Communications

Asymmetric Hydrogenation-General Procedure:

Bis(1,5-cyclooctadiene)rhodium trifluoromethanesulfonate [$Rh(COD)_2TfO$] (2.3 mg, 5 umol) and the desired ligand (6 umol)) were placed in a vessel. Methanol (5.0 mL) was added to the reaction vessel via syringe. This solution was stirred at 25 ºC. under argon for 15 minutes. The desired substrate (1.0 mmol) was then added to the catalyst solution. The solution was then purged five times with argon and pressurized with hydrogen to the desired pressure and stirred at room temperature. The reactions were run for the desired time at the desired pressure, and then depressurized. Samples were taken and analyzed for conversion and enantiomeric excess using standard analytical techniques.