Asymmetric Hydrogenation of Ketones Using a Ruthenium(II) Catalyst Containing BINOL-Derived Monodonor Phosphorus-Donor Ligands.

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Supporting Information

Contents

A) General	S2
B) Synthesis of (S)-BrXuPHOS	S3
C) Synthesis of (S)-MeO XuPHOS, (R)-biPh XuPHOS, (S)-Me XuPHOS and (S)-PhPHOS	S5
D) Synthesis of (S)-ethylPHOS	S9
E) Synthesis of (S)-monoPHOS	S10
F) Synthesis of (S)-iso propyl phosphite	S11
G) Synthesis of the Ru (II) complexes	S12
H) General experimental procedure for the asymmetric hydrogenation catalysed by (S, S, SS) Ru—BrXuPHOS	S15
I) HPLC, GC analysis and optical rotation data of the reduction products	S16
J) References	S17
K) X-ray crystallographic data for Ru(II) complex derived from 8	S19
L) ¹ H-NMR spectra for organic compounds lacking CHN analysis data	S22

A) General

All reactions, unless otherwise stated, were run under an atmosphere of argon in flame or oven dried glassware (round bottomed flasks or Schlenk tubes). Room temperature refers to ambient room temperature (20-22 °C), 0 °C refers to an ice slush bath and -78 °C refers to a dry ice-acetone bath. Heated experiments were conducted using thermostatically controlled oil baths. Reactions were monitored by Thin layer Chromatography (TLC) using aluminium backed silica gel 60 (F₂₅₄) plates, visualized using UV_{254 nm} and PMA, potassium permanganate or ninhydrin dips as appropriate. Flash column chromatography was carried out routinely using 60 Å silica gel (Merk). NMR spectra were recorded on Bruker DPX-300 (300 MHz) or DPX-400 (400 MHz) spectrometer. Chemical shifts are reported in δ units, parts per million downfield from (CH₃)₄Si. Coupling constants (J) are measured in hertz. IR spectra were recorded on a Nicolet Model Avatar 320 FTIR instrument. Mass spectra were recorded on a 7070E VG mass spectrometer. Enantiomeric excesses were determined by HPLC analysis (using a Merck-Hitachi L-6200 A intelligent pump, Merck-Hitachi L-4000 UV detector, Axxiom chromatography data system and controller model 727 and a Daicel Chiralcel OD 4.6 x 250 mm column) or GC analysis (Hewlett Packard 5890A gas chromatography, Cyclodextrin- β -236M-19 (CHROMPAC, 50m)) as stated. Elemental analyses were performed using the Exeter Analytical Model CE440. Melting points were recorded on a Stuart Scientific SMP 1 instrument. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

B) Synthesis of (S)-BrXuPHOS 8

1. Synthesis of *ortho*-diazo-bromobenzene **A** ¹

Tetra-fluoboric acid (40% in water) (232ml) and distilled water (232 ml) were charged into a three-neck flask (1000ml) equipped with a mechanical overhead stirrer and low temperature thermometer. The mixed solution was cooled to 0 °C and 2-bromoaniline (100g, 0.581mols) was dropwise charged in to the reaction mixture over a period of 10 mins. A solution of sodium nitrite (40g, 0.581mols) in 100ml water was added dropwise to the cooled reaction mixture, during the whole process, keeping the temperature of the mixture below 0°C. After stirring the reaction mixture for 30 mins, the viscous mixture was filtered and washed with: tetrafluoboric acid (5%, 2x 100ml), methanol (2x100ml) and diethyl ether (2x400ml). The pale yellow solid was blotted dry with filter papers and then dried on a high vacuum line for a minimum of 3 days. During the drying period, the pale yellow solid became slight pink which means slightly decomposition occurred (normal). After the drying the product was obtained (131g, 82.6%). The experimental data is as follows: IR: ν_{max} solid/cm⁻¹ = 3089, 2284, 1556, 1264, 1027, 770; ¹H NMR (300 MHz, DMSO) δ = 8.84 (1H, dd, *J* 8.4Hz, *J* 1.8Hz, CH), 8.31 (1H, dd, *J* 8.4Hz, *J* 1.1Hz, CH), 8.17 (1H, td, *J* 7.5Hz, *J* 1.5Hz, CH), 7.99 (1H, td, *J* 8.7Hz, *J* 0.7Hz, CH); ¹³C NMR (75 MHz, DMSO) 142.2 (s), 135.6 (s), 135.4(s), 130.7 (s), 124.8 (s), 119.0 (s);

2. Synthesis of *ortho*-dichlorophosphinobromobenzene **B** ²

Copper (I) bromide (1.88g, 0.0131mols) was charged in small portions to a solution of *ortho*-diazo-bromobenzene (60g, 0.219mols) in acetonitrile (300ml) at room temperature. On addition of copper (I) bromide, evolution of nitrogen was observed and the solution turned black. Phosphorus trichloride (33.5ml, 0.372mols) was added in one portion as the evolution of nitrogen continued. The solution was slowly warmed upto 30 °C and nitrogen evolution continued for a further 30 mins (**Caution!**

Control of the temperature must be very carefully to ensure the stable release of nitrogen). The reaction was slowly heated and refluxed for 30 mins and then allowed to cool down to room temperature. Aluminium powder (20 micron) (5.91g, 0.219mols) was added and stirred overnight. After this period the reaction mixture was refluxed for 1h and allowed to cool down to room temperature. Filtration of the reaction mixture through a piece of filtrate paper allowed the separation of the aluminium powder. The acetonitrile was removed by use of a high vacuum pump to leave a brown semi solid. Distillation under reduced pressure provided several lower boiling fractions with the product obtained at 97 °C / torr, (15.8g, 28%). The experimental data was in agreement with that reported in the literature.(21, 29) IR: ν_{max} solid/cm⁻¹ = 3062, 1559, 1426, 1100, 1021, 748; ¹H NMR (300 MHz, CDCl₃) δ = 8.11-8.08 (1H, dt, *J* 7.98Hz, Ar-H), 7.61-7.57 (1H, m, Ar-H), 7.52 (1H, t, *J* 6.83, Ar-H), 7.39 (1H, dt, *J* 6.08Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ = 133.5 (s), 132.7 (s), 131.6 (s), 128.2 (s), 126.5 (s), 125.9 (s); ³¹P NMR (162 MHz, CDCl₃) δ = 154.5; MS: *m/z* (EI) = 256 ([M]⁺, 78%), 223 (100%), 177 (80%), 107 (72%); HRMS: calc for C₆H₄BrCl₂P: 255.8606 ([M]⁺). Found 255.8606.

3. Synthesis of *ortho*-bis(dimethylaminophosphino)bromobenzene **C**³

Ortho-dichloride-phosphino bromobenzene was charged into normal degassed diethyl ether (400 ml) at 0 °C. After stirring for 10 mins, dimethylamine gas was charged into the reaction flask through a needle above the surface of the reaction mixture. The input time of the dimethylamine gas was about 15-20 mins, and during the period, more and more white inorganic salts came out, and the solution became a suspension. After the charge of the dimethylamine gas was complete, solution was stirred in the ice bath for 2 h. The inorganic salts were filtrated off and the resulting clear solution was evaporated under reduced pressure. The resulting oil was distilled at 106 °C/0.2 torr to obtain the final pure product which was a clear and colourless oil (5.24g, 98.6%). The experimental data was in agreement with that reported in the literature. ¹H NMR (300 MHz, CDCl₃) δ = 7.56-7.52 (1H, m, Ar-H), 7.48-7.44 (1H, m, Ar-H), 7.33-7.26 (1H, m, Ar-H), 7.15-7.11 (1H, m, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ = 143.5 (s), 134.02 (s), 133.1 (s), 129.66 (s), 127.28 (s), 126.95 (s), 41.57 (d, NMe₂); ³¹P NMR (162 MHz, CDCl₃) δ = 101.7. MS: *m/z* (EI) = 274 ([M]⁺, 40%), 230 (100%), 187 (65%), 107 (75%); HRMS: calc for C₁₀H₁₆BrN₂P: 274.0229 ([M]⁺). Found 274.0228.

4. Synthesis of (*S*)-Br XuPHOS **8**^{4, 5}

To a solution containing *ortho*-bis(dimethylamino)phosphinobromobenzene (0.822g, 0.003mol) dissolved in toluene (25ml) was charged a solution of (*S*)-bi-2-naphthol (0.859g, 0.003mol) in Toluene (25ml). The reaction flask was placed in an oil bath and kept stirring at room temperature for 10 mins, and then was heated up to reflux for 24 h. The reaction was monitored by ³¹P NMR, and the released dimethylamine gas was monitored by pH paper. After the reaction finished, it was allowed to cool down to room temperature. Solvent was removed to get a yellow solid. 30 ml of degassed pentane was charged into the oil above and stirred overnight. The resulting suspension was filtered and rinsed with further pentane. The off white solid was left to dry under high vacuum. The solid was purified by recrystallization with toluene to give slightly yellow crystals (1.17g, 82%). m.p. 225 - 227 °C; [α]_D²⁷ = +46.0 (*c* 0.2, CH₂Cl₂); IR: ν_{max} solid/cm⁻¹ = 3053, 1226, 1199, 948, 821, 803, 749; ¹H NMR (300

MHz, CDCl₃) δ = 8.05-8.02 (2H, m, Ar-H), 7.82-7.80 (1H, d, Ar-H), 7.62-7.59 (3H, m, Ar-H), 7.47-7.18 (8H, m, Ar-H), 7.03-6.96 (1H, m, Ar-H), 6.82-6.78 (1H, m, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ = 149.99 (s), 149.20 (s), 133.35 (s), 133.17 (d, J_{CP} 5.75Hz), 132.8 (s), 132.1 (s), 131.9 (d, J_{CP} 4.60Hz), 131.1 (s), 129.87 (s), 128.8 (d, J_{CP} 8.62 Hz), 128.2 (s), 127.2 (d, J_{CP} 5.17Hz), 126.7 (s), 126.5 (s), 125.5 (s), 125.2 (s), 121.9 (d, J_{CP} 5.75Hz); ³¹P NMR (162 MHz, CDCl₃) δ = 174.7. MS: m/z (EI) = 471([M+H]⁺, 100%), 286 (90%), 268 (30%), 239 (40%); HRMS: calc for C₂₆H₁₆BrO₂P: 468.9993 ([M-H]⁺). Found 468.9977.

C) Synthesis of (*S*)-MeO XuPHOS 7, (*R*)-biPh XuPHOS 6, (*S*)-Me XuPHOS 9 and (*S*)-PhPHOS 5.

1. Synthesis of *ortho*-bis(dimethylaminophosphino)anisole ⁴

In an oven dried 100 ml round bottom flask twice purged with nitrogen, 2-bromoanisole (1.00g, 5.3mmol) was dissolved in freshly distilled diethyl ether (25ml) and it was allowed to cool to -78°C . To the resulting solution was added *n*-butyllithium (1.6M, 5.8mmol, 3.63ml, 1.1eq) and the mixture was allowed to stir for 30 mins whilst being maintained at -78°C . The reaction mixture was then allowed to warm to 0°C and bis-(dimethylamino)chlorophosphane (5.8mmol, 0.897g, 0.85ml, 1.1 eq) was added dropwise *via* a nitrogen purged syringe and the reaction mixture was allowed to stir 20-30 mins at ambient temperature. The resulting white suspension was washed with saturated degassed sodium hydrogen carbonate solution (25ml), diluted with diethyl ether (25ml) and transferred to a separating funnel, the organic layer was collected and the aqueous layer back extracted with a further aliquot of ether (5ml). The combined organic layers were dried over magnesium sulphate for half an hour, filtered and concentrated under reduced pressure to give the crude product as a pale green oil (696mg, 58%). b.p. 95°C (0.5 Torr); IR: ν_{max} neat/cm⁻¹ = 2859, 2252, 1583, 1466, 1236, 948; ¹H NMR (300 MHz, CDCl₃) δ = 7.70-7.66 (1H, m, Ar-H), 7.29-7.22 (1H, m, Ar-H), 7.09-7.07 (1H, m, Ar-H), 6.65 (1H, dd, J 4.3Hz, J 8.1Hz, Ar-H), 3.77 (3H, s, CH₃), 2.58 (12H, d, J_{PH} 18.4Hz, 2NMe₂); ¹³C NMR (75 MHz, CDCl₃) δ = 161.5 (d, J_{CP} 14.9Hz, ipso C), 133.0 (d, J_{CP} 5.7Hz, Ar-C), 129.9 (Ar-C), 128.7 (d, J_{CP} 11.5Hz, *ipso* C), 121.2 (Ar-C), 110.8 (Ar-C), 55.7 (CH₃), 42.0 (d, J_{CP} 18.4Hz, N(CH₃)₂); ³¹P NMR (162 MHz, CDCl₃) δ = 97.7; MS: m/z (EI) = 226([M]⁺, 20%), 182 (100%), 139(70%); HRMS: calc for C₁₁H₁₉N₂OP: 226.1235 ([M]⁺). Found 226.1230.

2. Synthesis of (*S*)-MeO XuPHOS **7 a**^{4, 5}

To a solution containing 2-bis-(dimethylaminophosphino)-anisole (500mg, 2.2mmol) dissolved in toluene (25ml) was charged the (*S*)-bi-2-naphthol (630mg, 2.2mmol) dissolved in anhydrous toluene (25ml). The reaction flask was placed in an oil bath and stirred at room temperature for 10 mins. It was heated up to reflux for 24 hrs. The reaction was monitored by ³¹P NMR, and also the releasing dimethylamine gas was monitored by pH paper. After the reaction finished, it was allowed to cool down to room temperature. Solvent was removed to get a off-white solid and dried under high vacuum. The white solid was purified by recrystallization from toluene (604mg, 65%). m.p. 234 °C; $[\alpha]_D^{26} = +44.8$ (*c* 0.2, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 1588, 1430, 1228, 950, 822, 754; ¹H NMR (300 MHz, CDCl₃) δ = 7.96-7.93 (1H, m), 7.83-7.79 (1H, m), 7.60 (2H, t, *J* 8.1Hz), 7.49-7.35 (4H, m), 7.33-7.18 (3H, m), 7.13-7.09 (1H, m), 6.96-6.85 (1H, m), 6.80-6.77 (1H, m), 6.69-6.64 (1H, m), 3.96 (3H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ = 162.65 (d, *J* = 19.17 Hz), 152.56 (s), 150.31 (s), 149.25 (s), 132.98 (s), 132.80 (d, *J* 47.28 Hz), 131.26 (d, *J* 68.41 Hz), 130.57 (s), 130.33 (d, *J* 5.03 Hz), 128.38 (d, *J* 13.08 Hz), 126.94 (d, *J* 13.08 Hz), 126.05 (d, *J* 26.16 Hz), 124.71 (d, *J* 39.23 Hz), 122.02 (s), 120.50 (s), 110.49 (s), 55.95 (s); ³¹P NMR (162 MHz, CDCl₃) δ = 181; MS: *m/z* (EI) = 421 ([M-H]⁺, 100%), 286 (87%); HRMS: calc for C₂₇H₁₉O₃P: 421.0994 ([M-H]⁺). Found 421.1003; Anal. Calculated for C₂₇H₁₉O₃P: C, 76.77; H, 4.53; P, 7.33. Found: C, 76.56; H, 4.74; P, 7.16.

3. Synthesis of *Ortho*-bis-(dimethylaminophosphino)-biphenyl³

In an oven dried 250 ml round bottom flask twice purged with nitrogen, 2-bromobiphenyl (5.00g, 21.4 mmol, 3.698 ml) was dissolved in freshly distilled diethyl ether (100ml) and cooled to -78 °C. To the resulting solution was added *n*-butyllithium (2.5M, 23.6mmol, 9.44ml, 1.1eq) and the mixture was allowed to stir for 30 mins whilst being maintained at -78 °C. The reaction mixture was then allowed to warm to 0 °C and bis-(dimethylamino)-chloro-phosphane (23.6mmol, 3.63g, 3.43ml, 1.1 eq) was added dropwise *via* a nitrogen purged syringe and the reaction mixture was allowed to stir 20-30 mins at ambient temperature. The resulting white suspension was washed with saturated degassed sodium hydrogen carbonate solution (100ml), diluted with diethyl ether (100 ml) and transferred to a separating funnel, the organic layer was collected and the aqueous layer back extracted with a further aliquot of ether (20ml). The combined organic layers were dried over magnesium sulphate, filtered and concentrated under reduced pressure to give the crude product as a pale green oil. The resulting oil was taken up in hot methanol (50ml), the bottom of the flask scratched with a steel needle and crystallization allowed to occur at -20 °C in the freezer. Subsequently the crystals were filtered under nitrogen on a glass sinter, washed with small amounts of cold methanol and dried for eight hours under high vacuum in a Schlenk tube to furnish a large, colorless, crystals (0.73g, 25%). m.p. 38 °C. IR: $\nu_{\max}$ solid/cm⁻¹ = 3049, 2857, 2784, 1441, 1192, 950; ¹H NMR (300 MHz, CDCl₃) δ = 7.58-7.54 (1H, m, Ar-H), 7.49-7.46 (2H, m, 2Ar-H), 7.37-7.32 (4H, m, 4Ar-H), 7.27- 7.19 (2H, m, 2Ar-H), 2.39 (12H, d, *J* 9.00Hz, 2N(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ = 145.6 (C¹⁰, d, *J*_{CP} 16.67Hz), 143.6 (C⁵, s), 139.2 (C⁴, d, *J*_{CP} 6.32Hz), 132.1 (C⁹, d, *J*_{CP} 8.05Hz), 131.6 (Ar-C, s), 128.7 (C⁸, d, *J*_{CP} 5.17Hz), 128.6 (Ar-C), 128.2 (Ar-C), 127.9 (Ar-C), 126.8 (Ar-C), 41.7 (4C, d, *J*_{CP} 17.51Hz, 2NMe₂); ³¹P NMR (162 MHz, CDCl₃) δ = 100.5; Anal. Calculated for C₁₆H₂₁N₂P: C, 70.57; H, 7.77; N, 10.29. Found: C, 70.60; H, 7.76; N, 10.02.

4. Synthesis of (*R*)-biph XuPHOS **6**^{4,5}

To a solution containing *Ortho*-bis-(dimethylaminophosphino) biphenyl (134mg, 0.49mmol) dissolved in toluene (25ml) was charged (*R*)-bi-2-naphthol (859mg, 0.003mol) dissolved in toluene (25ml). The reaction flask was placed in an oil bath and stirred at room temperature for 10 mins. It was heated up to reflux for 24 hrs. The reaction was monitored by ³¹P NMR, and also the releasing dimethylamine gas was monitored by pH paper. After the reaction finished, it was allowed to cool down to room temperature. Solvent was removed to get a off-white solid and dried under high vacuum. The white solid was purified by recrystallisation with 1ml of toluene to give white crystalline solid (158mg, 69%). The experimental data is as follows: m.p. 250-252 °C; [α]_D²⁷: -9.0 (c 0.1, CH₂Cl₂); IR: ν_{max} solid/cm⁻¹ = 3056, 1460, 1226, 947, 825, 801, 749; ¹H NMR (300 MHz, CDCl₃) δ= 7.96-7.87 (3H, m, Ar-H), 7.73 (1H, d, *J* 8.67, Ar-H), 7.65-7.62 (2H, m, Ar-H), 7.50-7.24 (13H, m, Ar-H), 7.07-7.01 (1H, m, Ar-H), 6.88 (1H, d, *J* 9.00Hz); ¹³C NMR (75 MHz, CDCl₃) δ= 150.4 (s), 149.0 (d, *J*_{CP} 6.32Hz), 147.8 (s), 140.2 (d, *J*_{CP} 7.47Hz), 133.2 (d, *J*_{CP} 17.82Hz), 132.0 (s), 131.8 (d, *J*_{CP} 8.05Hz), 131.5 (s), 130.92 (s), 130.7 (d, *J*_{CP} 4.60Hz), 130.5 (d, *J*_{CP} 3.45Hz), 129.8 (s), 129.5 (d, *J*_{CP} 3.45Hz), 128.6 (s), 128.3 (s), 127.3 (d, *J*_{CP} 2.30Hz), 126.6 (s), 126.5 (s), 125.2 (d, *J*_{CP} 12.65Hz), 122.6 (s), 122.0 (s); ³¹P NMR (162 MHz, CDCl₃) δ= 178.7; MS: *m/z* (EI) = 467 ([M-H]⁺, 100%), 268 (26%); HRMS: calc for C₃₂H₂₁O₂P: 467.1201 ([M-H]⁺). Found 467.1192.

5. Synthesis of bisdimethylaminophenylphosphine **3**

Dichlorophosphinobenzene (2.5 g, 0.013967 mol) was charged into normal degassed diethyl ether (400 ml) at 0 °C. After stirring for 10 mins, dimethylamine gas was charged into the reaction flask through a needle above the surface of the reaction mixture. The input time of the dimethylamine gas was about 15-20 mins. During the period, white inorganic salts came out, and the solution became a suspension. After the charge of the dimethylamine gas was complete, solution was stirred in the ice bath for 2 h. The inorganic salts were filtrated off and the resulting clear solution was evaporated under reduced pressure. The resulting oil was distilled at 106 °C/0.2 torr to obtain the final pure product which was a clear and colourless oil (2.74g, 99%). The experimental data was in agreement with that reported in the literature. IR: ν_{max} neat/cm⁻¹ = 2875, 2828, 2784, 1186, 952, 667; ¹H NMR (300 MHz, CDCl₃) δ= 7.41-7.39 (2H, m, Ar-H), 7.38-7.31 (2H, m, Ar-H), 7.26-7.21 (1H, m, Ar-H), 2.66 (12H, d, *J* 9.15 Hz, 2N(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ= 141.2 (d, *J* 4.02 Hz, Ar-C), 132.6 (d, *J* 9.20 Hz, Ar-C), 131.6 (s, Ar-C), 131.4 (s, Ar-C), 128.7 (d, *J* 2.87 Hz, Ar-C), 127.9 (s, Ar-C), 42.2 (d, *J* 14.9 Hz, NMe₂); ³¹P NMR (162 MHz, CDCl₃) δ= 100.25.

6. Synthesis of (*S*)-phPHOS **6**^{4,5}

To a solution containing bis(dimethylamino)phosphino benzene (1.00 g, 5.096 mmol) dissolved in toluene (25ml) was charged a solution of (*S*)-bi-2-naphthol (1.459 g, 5.096 mmol) in Toluene (25ml). The reaction flask was placed in an oil bath and kept stirring at room temperature for 10 mins, and then was heated up to reflux for 24 h. The reaction was monitored by ³¹P NMR, and the released dimethylamine gas was monitored by pH paper. After the reaction finished, it was allowed to cool down to room temperature. Solvent was removed to get a yellow oil. 30 ml of degassed

pentane was charged into the oil above and stirred overnight. The resulting suspension was filtered and rinsed with further pentane. The off white solid was left to dry under high vacuum. The solid was purified by recrystallization with toluene to give slightly yellow crystals (1.78g, 89%). m.p. 165 °C; $[\alpha]_D^{19} = +180.3$ (*c* 0.2, CH₂Cl₂); IR: ν_{max} solid/cm⁻¹ = 3054, 1587, 1228, 948, 819, 743; ¹H NMR (300 MHz, CDCl₃) δ = 8.03 (1H, d, *J* 8.85 Hz, Ar-H), 7.95 (1H, d, *J* 8.28 Hz, Ar-H), 7.85 (1H, d, *J* 8.85 Hz, Ar-H), 7.66 (1H, d, *J* 8.85 Hz, Ar-H), 7.59 (1H, d, *J* 8.67 Hz, Ar-H), 7.48- 7.38 (6H, m, Ar-H), 7.31- 7.23 (4H, m, Ar-H), 7.17 (1H, d, *J* 7.53 Hz, Ar-H), 6.70 (1H, d, *J* 8.64 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ = 150.4 (s), 149.0 (d, *J* 5.75 Hz), 139.3 (d, *J* 37.80 Hz), 133.2 (d, *J* 24.7 Hz), 132.4 (s), 131.8 (d, *J* 46.0 Hz), 131.1 (d, *J* 2.88 Hz), 130.7 (s), 129.8 (s), 128.8 (d, *J* 7.47 Hz), 128.5 (d, *J* 6.90 Hz), 127.3 (d, *J* 3.45 Hz), 126.6 (d, *J* 18.40 Hz), 125.3 (d, *J* 17.82 Hz), 122.7 (s), 121.9 (s); ³¹P NMR (162 MHz, CDCl₃) δ = 185.0.

7. Synthesis of *ortho*-bis(dimethylaminophosphino) toluene ³

In an oven dried 100 ml round bottom flask twice purged with nitrogen, 2-bromotoluene (5.00g, 29.2 mmol) was dissolved in freshly distilled diethyl ether (125ml) and it was allowed to cool to -78 °C. To the resulting solution was added *t*-butyllithium (1.7M, 59.9 mmol, 35 ml, 2.05 eq) and the mixture was allowed to stir for 30 mins whilst being maintained at -78 °C. The reaction mixture was then allowed to warm to 0 °C and bis-(dimethylamino)chlorophosphane (29.2 mmol, 4.51 g, 4.27 ml, 1.0 eq) was added dropwise *via* a nitrogen purged syringe and the reaction mixture was allowed to stir 20-30 mins at ambient temperature. The resulting white suspension was washed with saturated degassed sodium hydrogen carbonate solution (125ml), diluted with diethyl ether (125ml) and transferred to a separating funnel, the organic layer was collected and the aqueous layer back extracted with a further aliquot of ether (5ml). The combined organic layers were dried over magnesium sulphate for half an hour, filtered and concentrated under reduced pressure to give the crude product as a colourless oil (696mg, 58%). b.p. 72.5-74.0 °C (0.05 Torr); IR: ν_{max} neat/cm⁻¹ = 3052, 2858, 1445, 1189, 952, 665; ¹H NMR (300 MHz, CDCl₃) δ = 6.90-6.86 (1H, m, Ar-H), 6.69-6.57 (3H, m, Ar-H), 2.17 (12H, d, *J*_{PH} 9.06Hz, 2NMe₂), 1.74 (3H, s, ArCH₃); ¹³C NMR (75 MHz, CDCl₃) δ = 140.2 (d, *J*_{CP} 21.84Hz, Ar-C), 138.6 (d, *J*_{CP} 2.88Hz, Ar-C), 130.65 (d, *J* 2.88Hz, Ar-C), 130.4 (d, *J*_{CP} 6.90Hz, Ar-C), 127.7 (s, Ar-C), 125.2 (s, Ar-C), 41.2 (d, *J* 16.09Hz, N(CH₃)₂), 20.3 (d, *J*_{CP} 12.64Hz, ArCH₃); ³¹P NMR (162 MHz, CDCl₃) δ = 98.3; Anal. Calculated for C₁₁H₁₉N₂P: C, 62.84; H, 9.11; N, 13.32. Found: C, 62.87; H, 9.13; N, 13.12; P, 14.63.

8. Synthesis of (*S*)-Me XuPHOS **9** ^{4,5}

To a solution containing 2-bis-(dimethylaminophosphino)toluene (734mg, 3.49mmol) dissolved in toluene (25ml) was charged the (*S*)-bi-2-naphthol (1g, 3.49mmol) dissolved in anhydrous toluene (25ml). The reaction flask was placed in an oil bath and stirred at room temperature for 10 mins. It was heated up to reflux for 24 hrs. The reaction was monitored by ³¹P NMR, and also the releasing dimethylamine gas was monitored by pH paper. After the reaction finished, it was allowed to cool down to room temperature. Solvent was removed to get a off-white solid and dried under high vacuum. The white solid was purified by recrystallization from toluene (1.20g, 85%). m.p. 186 °C; $[\alpha]_D^{25} = +89.5$ (*c* 0.2, CH₂Cl₂); IR: ν_{max} solid/cm⁻¹ = 3048, 1588, 1231,

949, 816, 746; ^1H NMR (300 MHz, CDCl_3) δ = 8.03 (1H, d, J 8.85Hz, Ar-H), 7.95 (1H, d, J 8.10Hz, Ar-H), 7.82 (1H, d, J 8.64Hz, Ar-H), 7.63-7.58 (2H, m, Ar-H), 7.47-7.36 (4H, m, Ar-H), 7.32-7.14 (5H, m, Ar-H), 6.89 (1H, t, J 6.96Hz, Ar-H), 6.68 (1H, d, J 8.85Hz, Ar-H), 2.79 (3H, d, J 2.07Hz, Ar-CH₃); ^{13}C NMR (75 MHz, CDCl_3) δ = 149.8 (d, J 94.27Hz, Ar-C), 142.2 (d, J 29.89Hz, Ar-C), 133.2 (d, J 32.2Hz, Ar-C), 131.72 (s, Ar-C), 131.70 (d, J 48.86Hz, Ar-C), 131.0 (s, Ar-C), 130.9 (d, J 3.45Hz, Ar-C), 129.7 (d, J 5.18Hz, Ar-C), 128.8 (d, J 8.63Hz, Ar-C), 127.3 (d, J 9.20Hz, Ar-C), 126.5 (d, J 20.12Hz, Ar-C), 125.7 (s, Ar-C), 125.2 (d, J 22.42Hz, Ar-C), 122.33 (s, Ar-C), 122.0 (s, Ar-C), 20.2 (d, J 23.56Hz, Ar-CH₃); ^{31}P NMR (162 MHz, CDCl_3) δ = 183.0; MS: m/z (EI) = 406 ($[\text{M}]^+$, 100%), 239 (32%); HRMS: calc for $\text{C}_{27}\text{H}_{19}\text{O}_2\text{P}$: 406.1123 ($[\text{M}]^+$). Found 406.1112.

D) Synthesis of (S)-ethylPHOS 4

1. Synthesis of bis-dimethylaminophosphino ethane³

Dichlorophosphino ethane (2.0g, 1.59ml, 0.0153mol) was charged into normal degassed diethyl ether (120 ml) at 0 °C. After stirring for 10 min, dimethyl amine gas was charged into the reaction flask through a needle above the surface of the reaction mixture. The input time of the dimethylamine gas was about 15-20 mins, and during the period, more and more white inorganic salts came out, and the solution became a white suspension. After the charge of the dimethylamine gas was complete, solution was stirred in the ice bath for 2h—2.5h. The white inorganic salt was filtrated off under magnesium sulfate powder under argon and the resulting clear solution was evaporated under reduced pressure. The resulting clear oil was the final product (2.24g, 99%). IR: ν_{max} neat/ cm^{-1} = 2962, 2876, 2783, 1260, 949, 754; The experimental data was in agreement with that reported in the literature. ^1H NMR (400 MHz, CDCl_3) δ = 2.56 (12H, dd, J 4.56 Hz, J 9.11 Hz, $\text{N}(\text{CH}_3)_2$), 1.52 (2H, dq, J 7.72 Hz, J 1.89 Hz, CH_2), 0.88 (3H, dt, J 17.71 Hz, J 7.54 Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 40.45 (d, J 12.3 Hz, NMe_2), 19.26 (d, J 0.9 Hz, CH_2), 8.13 (d, J 21.4, CH_3); ^{31}P NMR (162 MHz, CDCl_3) δ = 97.3;

2. Synthesis of (S)-ethylPHOS 4^{4, 5}

To a solution containing *bis*-dimethylaminophosphino ethane (1.00g, 0.0067mol) dissolved in anhydrous toluene (25ml) was charged the (S)-bi-2-naphthol (1.92g, 0.0067mol) dissolved in anhydrous toluene (25ml). The reaction flask was placed under argon in an oil bath and stirred at room temperature for 10 min. It was heated up to reflux for 24 hrs. The reaction was monitored by ^{31}P NMR, and also the releasing dimethyl amine gas was monitored by wet pH paper. After the reaction finished, it was allowed to cool down to room temperature. Solvent was removed to get a yellow solid and dried under high vacuum. The yellow solid was purified by washing with cold Et_2O to give light yellow solid (1.95g, 85%). m.p. 200 °C; $[\alpha]_{\text{D}}^{18}$ =

+506.6 (*c* 0.1, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 3058, 2959, 1229, 952, 820, 748; Anal. Calculated for C₂₂H₁₇O₂P: C, 76.74; H, 4.98; P, 9.00; Found: C, 76.39; H, 4.99; P, 8.84; ¹H NMR (400 MHz, CDCl₃) δ = 7.88 (1H, d, *J* 8.83 Hz, Ar-H), 7.81 (3H, dd, *J* 4.28 Hz, *J* 8.83 Hz, Ar-H), 7.41 (1H, d, *J* 8.83 Hz, Ar-H), 7.31 (2H, td, *J* 1.24 Hz, *J* 6.72 Hz, Ar-H), 7.25 (3H, t, *J* 8.19 Hz, Ar-H), 7.15 (2H, t, *J* 6.68 Hz, Ar-H), 1.53 (2H, m, CH₂), 1.08 (3H, m, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 150.28 (d, *J* 3.45 Hz, Ar-C), 148.34 (d, *J* 6.90 Hz, Ar-C), 132.72 (s, Ar-C), 131.08 (d, *J* 33.91 Hz, Ar-C), 129.96 (d, *J* 71.14 Hz, Ar-C), 128.15 (d, *J* 9.19 Hz, Ar-C), 126.72 (d, *J* 5.75 Hz, Ar-C), 126.05 (s, Ar-C), 124.68 (d, *J* 2.88 Hz, Ar-C), 121.57 (d, *J* 59.20 Hz, Ar-C), 26.53 (d, *J* 32.18 Hz, CH₂), 5.09 (d, *J* 18.97 Hz, CH₃); ³¹P NMR (162 MHz, CDCl₃) δ = 215.7; MS: *m/z* (EI) = 343 ([M-H]⁺, 100%), 212 (25%); HRMS: calc for C₂₂H₁₇O₂P: 343.0888 ([M-H]⁺). Found: 343.0887.

E) Synthesis of (*S*)-monoPHOS 2 ⁶

To a solution containing tris-(dimethylaminophosphino)phosphine (0.360g, 0.4ml 0.00222mol) dissolved in anhydrous toluene (20ml) was charged the (*S*)-bi-2-naphthol (0.500g, 0.00175mol) dissolved in anhydrous toluene (20ml). The reaction flask was placed under argon in an oil bath and stirred at room temperature for 10 mins. It was heated up to reflux for 12 hrs. The reaction was monitored by ³¹P NMR, and also the releasing dimethylamine gas was monitored by wet pH paper. After the reaction finished, it was allowed to cool down to room temperature. Solvent was removed under reduced pressure to give a yellow solid and dried under high vacuum. The resulting dry solid was purified to give a light yellow solid (424mg, 68%). mp 208 - 210 °C; The following data is in agreement with published data. $[\alpha]_D^{22} = +683.7$ (*c* 0.03, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 2775, 1229, 944, 821, 751, 686; ¹H NMR (300 MHz, CDCl₃) δ = 7.88 (1H, d, *J* 8.60 Hz, Ar-H), 7.84-7.80 (3H, m, Ar-H), 7.42 (1H, d, *J* 8.64 Hz, Ar-H), 7.37-7.24 (5H, m, Ar-H), 7.22-7.12 (2H, m, Ar-H), 2.46 (6H, d, *J* 9.06 Hz, Ar-CH₃); ¹³C NMR (75 MHz, CDCl₃) δ = 131.12 (Ar-C), 130.66 (Ar-C), 130.40 (Ar-C), 128.73 (Ar-C), 128.65 (Ar-C), 127.39 (Ar-C), 127.31 (Ar-C), 126.48 (Ar-C), 125.17 (Ar-C), 124.98 (Ar-C), 122.49 (Ar-C), 122.36 (Ar-C), 36.36 (d, NMe₂); ³¹P NMR (121 MHz, CDCl₃) δ = 149.9; MS: *m/z* (EI) = 359 ([M]⁺, 100%), 313 (50%); HRMS: calc for C₂₂H₁₈NO₂P: 359.1075 ([M]⁺). Found 359.1077.

F) Synthesis of (*S*)-*iso* propyl phosphite 3^{7,8}

Trichloro phosphine PCl_3 (575mg, 0.36ml, 4.19mmol, 1.2e.q.) was dissolved in anhydrous toluene (50ml), and the solution was cooled to $-78\text{ }^\circ\text{C}$. Et_3N (2.43ml, 1.77g, 17.45e.q.) was added slowly, and the reaction mixture was stirred for 5min. (*S*)-BINOL (1.0g, 3.49mmol, 1.0e.q.) was added in. The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 90min, and then stirred at room temperature for 3h. Reaction was monitored by ^{31}P NMR until it indicated no presence of starting material. *Isopropanol* (210mg, 0.27ml, 3.49mmol, 1.0e.q.) and Et_3N (1.22ml, 833mg, 8.73mmol, 2.5e.q.) were added slowly. The reaction mixture was stirred for 18h until ^{31}P NMR indicated no starting material left. The crude product was purified after column and gave the final product as a white powder (686mg, 52.5%). mp $80\text{--}82\text{ }^\circ\text{C}$. $[\alpha]_{\text{D}}^{18} = +254.7$ (c 0.1, CH_2Cl_2); IR: ν_{max} solid/ $\text{cm}^{-1} = 3054, 2967, 1588, 1212, 938, 746$; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.97\text{--}7.89$ (4H, m, Ar-H), 7.51 (1H, d, J 8.64Hz, Ar-H), 7.44–7.34 (5H, m, Ar-H), 7.24 (2H, t, J 7.65Hz, Ar-H), 4.58–4.47 (1H, m, CH), 1.31 (6H, dd, J 6.21Hz, J 12.82Hz, 2 CH_3); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 148.72$ (s, Ar-C), 148.10 (s, Ar-C), 133.19 (d, J 10.35Hz, Ar-C), 131.69 (d, J 34.49Hz, Ar-C), 130.42 (d, J 43.69Hz, Ar-C), 128.72 (d, J 6.90Hz, Ar-C), 127.45 (s, Ar-C), 126.56 (d, J 9.20Hz, Ar-C), 125.31 (d, J 14.37Hz, Ar-C), 122.26 (d, J 9.77Hz, Ar-C), 69.96 (d, J 12.65Hz, CH), 25.01 (d, J 28.74Hz, CH_3); ^{31}P NMR (162 MHz, CDCl_3) $\delta = 147.3$; MS: m/z (EI) = 374 ($[\text{M}]^+$, 100%), 331 (80%); HRMS: calc for $\text{C}_{23}\text{H}_{19}\text{O}_3\text{P}$: 374.1072. Found: 374.1079.

G) Synthesis of the Ru (II) complexes ⁹

1. Synthesis of (S, S, SS) Ru—EthylPHOS **4** complex

[RuCl₂(C₆H₆)₂] (100mg, 0.200mmol) and (*S*)-Et PHOS **4** (275.5mg, 0.800mmol, 4e.q.) were placed in a 50-ml Schlenk flask. After the air in the flask was replaced with argon, anhydrous DMF (9 ml) was added, the mixture was degassed and stirred under argon at 100 °C for 15 min to form a reddish brown solution. After the solution was cooled to room temperature, (*S*, *S*)-DPEN (85mg, 0.400mmol, 2e.q.) was added and the mixture was degassed again before it was stirred for 3h. After the reaction finished, DCM (30—60ml) was added into the reaction mixture, and at each time it was turned on the high vacuum and back to argon, to do azeotrope to get rid of remaining DMF. The resulting dark brown solid was dried under the high vacuum to give the final product (*S*, *S*, *SS*) Ru—Et PHOS (321mg, 75%). mp 210 °C (dec.); [α]_D²² = -77.9 (c 0.1, CH₂Cl₂); IR: ν_{max} solid/cm⁻¹ = 2926, 1666, 1224, 945, 747, 697; ¹H NMR (300 MHz, CDCl₃) δ= 7.95-7.84 (6H, m, Ar-H), 7.59 (4H, dd, *J* 8.85Hz, *J* 14.89Hz, Ar-H), 7.48 (2H, d, *J* 8.85Hz, Ar-H), 7.44-7.35 (6H, m, Ar-H), 7.22-7.17 (6H, m, Ar-H), 7.11-7.06 (6H, m, Ar-H), 7.05-7.02 (4H, m, Ar-H), 4.27-4.24 (2H, m, 2NH₂CH), 4.20-4.15 (2H, m, 2NHH), 3.73-3.67 (2H, m, 2NHH), 2.82-2.74 (2H, m, 2PCHH), 2.54-2.40 (2H, m, 2PCHH), 1.00-0.90 (6H, m, 2CH₃); ³¹P NMR (162 MHz, CDCl₃) δ= 228.8; LSIMS: *m/z* (FAB) = 1072 ([M]⁺, 100%), 1037 (60%), 905 (20%); HRMS: calc for C₅₈H₅₀Cl₃³⁵N₂O₄P₂Ru¹⁰²: 1072.1666 ([M]⁺). Found: 1072.1707.

2. Synthesis of (S, S, SS) Ru—PhPHOS **5** complex

[RuCl₂(C₆H₆)₂] (100 mg, 0.200 mmol) and (*S*)-PhPHOS **5** (314 mg, 0.800 mmol, 4e.q.) were placed in a 50-ml Schlenk flask. After the air in the flask was replaced with argon, anhydrous DMF (7 ml) was added, the mixture was degassed and stirred under argon at 100 °C for 15 min to form a reddish brown solution. After the solution was cooled to room temperature, (*S*, *S*)-DPEN (85 mg, 0.400 mmol, 2e.q.) was added and the mixture was degassed again before it was stirred for 3h. After the reaction

finished, DCM (30—60ml) was added into the reaction mixture, and at each time it was turned on the high vacuum and back to argon, to do azeotrope to get rid of remaining DMF. The resulting dark brown solid was dried under the high vacuum to give the final product (*S, S, SS*) Ru—PhPHOS (378 mg, 81%). m.p. 185 °C (dec.); $[\alpha]_D^{22} = -287.8$ (*c* 0.1, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 3056, 2922, 1661, 1225, 945, 696; ¹H NMR (300 MHz, CDCl₃) δ = 8.29 (2H, d, *J* 8.85 Hz, Ar-H), 8.03- 7.58 (10H, m, Ar-H), 7.40- 7.11 (12H, m, Ar-H), 7.07- 6.90 (16H, m, Ar-H), 6.78 (2H, d, *J* 8.49 Hz, Ar-H), 6.60 (2H, d, *J* 8.85 Hz, Ar-H), 4.35-4.32 (2H, m, 2NH₂CH), 3.75-3.68 (2H, m, 2NHH), 3.40-3.34 (2H, m, 2NHH); ³¹P NMR (162 MHz, CDCl₃) δ = 205.7; MS: *m/z* (FAB) = 1168 ([M]⁺, 100%), 1133 (42%); HRMS: calc for C₆₆H₅₀Cl³⁵N₂O₄P₂Ru¹⁰²: 1168.1636 ([M]⁺). Found: 1168.1666.

3. Synthesis of (*S, S, SS*) Ru—monoPHOS **2** complex

[RuCl₂(C₆H₆)₂] (100mg, 0.200mmol) and (*S*)-monophos (287mg, 0.800mmol, 4e.q.) were placed in a 50-ml Schlenk flask. After the air in the flask was replaced with argon, anhydrous DMF (10 ml) was added, the mixture was degassed and stirred under argon at 100 °C for 10 min to form a reddish brown solution. After the solution was cooled to 25 °C, (*S, S*)-DPEN (85mg, 0.400mmol) was added and the mixture was degassed again before it was stirred for 3h. After the reaction finished, the supernatant was removed, and DCM was added in for several times into the reaction mixture, and at each time it was turned on the high vacuum and back to argon. The resulting dark yellow solid was dried under the high vacuum to give (*S, S*)-DPEN Ru (II) complex (390mg, 89%). m.p. 245 – 247 °C (dec.); $[\alpha]_D^{20} = -392.7$ (*c* 0.1, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 2917, 2359, 1668, 1226, 944, 823; ¹H NMR (300 MHz, CDCl₃) δ = 8.31 (2H, d, *J* 8.85Hz, Ar-H), 8.02-7.84 (8H, m, Ar-H), 7.47-7.39 (4H, m, Ar-H), 7.34-7.07 (10H, m, Ar-H), 6.94-6.92 (6H, m, Ar-H), 6.73-6.72 (4H, m, Ar-H), 4.23-4.20 (2h, m, 2NH₂CH), 3.99-3.96 (2H, m, 2NHH), 3.32-3.26 (2H, m, 2NHH), 2.91 (12H, d, *J* 21.85Hz, 2NMe₂); ³¹P NMR (162 MHz, CDCl₃) δ = 172.7; LSIMS: *m/z* (FAB) = 1102 ([M]⁺, 100%), 1067 (50%), 743 (30%); HRMS: calc for C₅₈H₅₂Cl³⁵N₄O₄P₂Ru¹⁰²: 1102.1884 ([M]⁺). Found 1102.1895.

4. Synthesis of (*R, R, RR*) Ru—biphenyl XuPHOS **6** complex

[RuCl₂(C₆H₆)₂] (79mg, 0.158mmol) and (*R*)-biphenyl XuPHOS **6** (297mg, 0.633mmol, 4e.q.) were placed in a 50-ml Schlenk flask. After the air in the flask was replaced with argon, anhydrous DMF (7 ml) was added, the mixture was degassed and stirred under argon at 100 °C for 15 min to form a reddish brown solution. After the solution was cooled to room temperature, (*R, R*)-DPEN (67mg, 0.316mmol, 2e.q.) was added and the mixture was degassed again before it was stirred for 3h. After the reaction finished, DCM (30—60ml) was added into the reaction mixture, and at each time it was turned on the high vacuum and back to argon, to do azeotrope to get rid of remaining DMF. The resulting dark brown solid was dried under the high vacuum to give the final product (*R, R, RR*) Ru—biphenyl XuPHOS (240mg, 58%). m.p. 210 °C (dec.); $[\alpha]_D^{19} = +331.8$ (*c* 0.1, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 3049, 1668, 1225, 948, 747, 695; ¹H NMR (300 MHz, CDCl₃) δ = 8.00-7.87 (2H, m, Ar-H), 7.71-7.66 (4H, m, Ar-H), 7.57-7.50 (6H, m, Ar-H), 7.41-7.34 (4H, m, Ar-H), 7.28-6.93 (24H, m, Ar-H), 6.85-6.66 (10H, m, Ar-H), 6.35 (2H, d, *J* 8.83Hz, Ar-H), 4.44-4.42 (2H, m, 2NH₂CH), 3.84-3.79 (2H, m, 2NHH), 3.28-3.26 (2H, m, 2NHH); ³¹P NMR (162

MHz, CDCl₃) δ = 210.0; MS: m/z (EI) = 1321 ([M+H]⁺, 100%), 1037 (70%); HRMS: calc for C₇₈H₅₈Cl₂N₂O₄P₂Ru: 1320.2292. Found 1320.2329.

5. Synthesis of (*S, S, SS*) Ru—*iso*-propyl phosphite **3** complex

[RuCl₂(C₆H₆)₂] (77mg, 0.154mmol) and (*S*)-isopropyl phosphite **3** (230mg, 0.616mmol, 4e.q.) were placed in a 50-ml Schlenk flask. After the air in the flask was replaced with argon, anhydrous DMF (5 ml) was added, the mixture was degassed and stirred under argon at 100 °C for 15 min to form a reddish brown solution. After the solution was cooled to room temperature, (*S, S*)-DPEN (65mg, 0.307mmol, 2 e.q.) was added and the mixture was degassed again before it was stirred for 3h. After the reaction finished, DCM (30—60ml) was added into the reaction mixture, and at each time it was turned on the high vacuum and back to argon, to do azeotrope to get rid of remaining DMF. The resulting dark brown solid was dried under the high vacuum to give the final product (*S, S, SS*) Ru—*iso*-propyl phosphite (224mg, 64%). m.p. 160-162 °C (dec.). [α]_D²³ = -306.6 (*c* 0.1, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 2360, 1662, 1228, 942, 807, 695; ³¹P NMR (162 MHz, CDCl₃) δ = 155.4; LSIMS: m/z (FAB) = 1132 ([M]⁺, 100%), 1099 (30%), 935 (35%); HRMS: calc for C₆₀H₅₄O₆Cl₂N₂P₂Ru¹⁰²: 1132.1878. Found: 1132.1887.

6. Synthesis of (*S, S, SS*) Ru—MeO XuPHOS **7** complex

[RuCl₂(C₆H₆)₂] (100mg, 0.200mmol) and (*S*)-MeO XuPHOS **7** (338mg, 0.800mmol, 4e.q.) were placed in a 50-ml Schlenk flask. After the air in the flask was replaced with argon, anhydrous DMF (10 ml) was added, the mixture was degassed and stirred under argon at 100 °C for 10 min to form a reddish brown solution. After the solution was cooled to 25 °C, (*S, S*)-DPEN (85mg, 0.400mmol) was added and the mixture was degassed again before it was stirred for 3h. After the reaction finished, the supernatant was removed, and DCM was added in for several times into the reaction mixture, and at each time it was turned on the high vacuum and back to argon. The resulting dark yellow solid was dried under the high vacuum to give the metal complex (*S, S, SS*) Ru—MeO XuPHOS (438mg, 89%). m.p. 270-272 °C (dec.); [α]_D¹⁹ = -237.5 (*c* 0.02, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 3328, 2934, 1669, 1221, 945, 750; ¹H NMR (400MHz, CDCl₃): δ = 7.72 (2H, d, *J* 7.95Hz, Ar-H), 7.66 (2H, d, *J* 7.91Hz, Ar-H), 7.61 (2H, t, *J* 12.00Hz, Ar-H), 7.49 (2H, d, *J* 8.83Hz, Ar-H), 7.44 (2H, t, *J* 8.23Hz, Ar-H), 7.35 (2H, t, *J* 7.99Hz, Ar-H), 7.28-7.24 (8H, m, Ar-H), 7.16-7.13 (8H, m, Ar-H), 7.10-7.06 (6H, m, Ar-H), 7.02-7.00 (6H, m, Ar-H), 6.87 (2H, t, Ar-H), 4.58 (2H, m, 2NH₂CH), 4.47-4.45 (2H, m, 2NH), 4.14-4.10 (2H, m, 2NH), 3.97 (6H, s, 2OCH₃); ³¹P NMR (162 MHz, CDCl₃) δ = 206.3. LSIMS: m/z (FAB) = 1228 ([M]⁺, 100%), 1193 (71%); HRMS: calc for C₆₈H₅₄O₆Cl₂N₂P₂Ru¹⁰²: 1228.188. Found: 1228.188. (Note: other isotope peaks observed within 10 ppm: 1228.192 (45%), 1228.190 (20%), 1228.185 (25%)).

7. Synthesis of (*S, S, SS*) Ru—Br XuPHOS **8** complex

[RuCl₂(C₆H₆)₂] (100mg, 0.200mmol) and (*S*)-Br XuPHOS **8** (377mg, 0.800mmol, 4e.q.) were placed in a 50-ml Schlenk flask. After the air in the flask was replaced with argon, anhydrous DMF (10 ml) was added, the mixture was degassed and stirred under argon at 100 °C for 10 min to form a reddish brown solution. After the solution was cooled to 25 °C, (*S, S*)-DPEN (85mg, 0.400mmol) was added and the mixture

was degassed again before it was stirred for 3h. After the reaction finished, the supernatant was removed, and DCM was added in for several times into the reaction mixture, and at each time it was turned on the high vacuum and back to argon. The resulting dark yellow solid was dried under the high vacuum and recrystallised in hot DMF (100mg/3.3ml) at 100°C to give the final bright golden crystals (*S, S, SS*) Ru—Br XuPHOS (345mg, 65%). mp 235 - 237 °C (dec.); $[\alpha]_D^{19} = -496.8$ (*c* 0.1, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 2927, 2360, 1673, 1224, 954, 809; ¹H NMR (300 MHz, CDCl₃) δ = 8.43-8.41 (2H, m, Ar-H), 8.15-8.14 (2H, m, Ar-H), 7.92-7.86 (4H, m, Ar-H), 7.51-7.26 (6H, m, Ar-H), 7.12-7.10 (10H, m, Ar-H), 6.98-6.84 (12H, m, Ar-H), 6.55-6.30 (6H, m, Ar-H), 4.55-4.53 (2H, m, 2NH₂CH), 4.23-4.20 (2H, m, 2NH₂CH), 2.88-2.83 (2H, m, 2NH₂CH); ³¹P NMR (162 MHz, CDCl₃) δ = 203.9; LSIMS: *m/z* (FAB) = 1291 ([M-Cl]⁺, 100%), 1247 (65%), 1196 (50%), 1079 (35%); HRMS: calc for C₆₆H₄₈Br⁷⁹Br⁸¹Cl³⁵N₂O₄P₂Ru¹⁰²: 1291.0168 ([M-Cl]⁺). Found 1291.0167.

8. Synthesis of (*S, S, SS*) Ru—Me XuPHOS **9** complex

[RuCl₂(C₆H₆)₂] (92 mg, 0.185 mmol) and (*S*)-Me XuPHOS **9** (303 mg, 0.738 mmol, 4e.q.) were placed in a 50-ml Schlenk flask. After the air in the flask was replaced with argon, anhydrous DMF (9 ml) was added, the mixture was degassed and stirred under argon at 100 °C for 10 min to form a reddish brown solution. After the solution was cooled to 25 °C, (*S, S*)-DPEN (78 mg, 0.370 mmol) was added and the mixture was degassed again before it was stirred for 3h. After the reaction finished, the supernatant was removed, and DCM was added in for several times into the reaction mixture, and at each time it was turned on the high vacuum and back to argon. The resulting dark yellow solid was dried under the high vacuum to give the final product (*S, S, SS*) Ru—Me XuPHOS (100 mg, 23%). mp 250 - 252 °C (dec.); $[\alpha]_D^{19} = -460$ (*c* 0.1, CH₂Cl₂); IR: $\nu_{\max}$ solid/cm⁻¹ = 3689, 2359, 1668, 1225, 947, 696; ¹H NMR (300 MHz, CDCl₃) δ = 8.35 (2H, d, *J* 8.28Hz, Ar-H), 8.00 (4H, d, *J* 9.00Hz, Ar-H), 7.87-7.78 (2H, m, Ar-H), 7.73-7.66 (2H, m, Ar-H), 7.45 (2H, d, *J* 7.92Hz, Ar-H), 7.34-7.24 (4H, m, Ar-H), 7.12-6.82 (19H, m, Ar-H), 6.61-6.58 (5H, m, Ar-H), 6.37-6.35 (2H, m, Ar-H), 4.13-4.11 (2H, m, 2NH₂CH), 3.75-3.49 (2H, m, 2NH₂CH), 2.56-2.48 (2H, m, 2NH₂CH), 2.22 (6H, s, 2Ar-CH₃); ³¹P NMR (162 MHz, CDCl₃) δ = 215.6; LSIMS: *m/z* (FAB) = 1196 ([M]⁺, 100%), 1125 (30%); HRMS: calc for C₆₈H₅₄Cl³⁵N₂O₄P₂Ru¹⁰²: 1196.1979 ([M-Cl]⁺). Found 1291.2028.

H) General experimental procedure for the asymmetric hydrogenation catalysed by (*S, S, SS*) Ru—BrXuPHOS **9**

In an oven dried round bottom flask (250 mL), acetophenone (2.10 mL, 2.17 g, 18.08 mmol) and (CH₃)₃COK (10 mg, 0.0904 mmol, 0.5 mol%) were dissolved in dry and degassed 2-propanol (120 mL). (*S, S, SS*) Ru—BrXuPHOS (12 mg, 0.00904 mmol, 0.05 mol%) was dissolved in anhydrous and degassed CH₂Cl₂ (6 mL), which was used as the catalyst stock solution and was transferred into the reaction solution above under argon. The mixture was degassed by three vacuum-filling with argon cycles and then it was quickly transferred into the autoclave. It was purged with hydrogen for 10 seconds at 2, 5 and 8 atm respectively, and finally the hydrogen was introduced to 10 atm. The reaction mixture was stirred vigorously at 20-22 °C for 20h. The mixture was filtered through a pad of silica gel and the pad was washed with a 50% solution of ethyl acetate in hexane (150 mL). The filtrate was concentrated under reduced

pressure to afford the reduction product. Purification by flash chromatography was applied when appropriate.

I) HPLC, GC analysis and optical rotation data of the reduction products

1. Data of reduction products (reactions catalyzed by (S, S, SS) Ru—BrXuPHOS at room temperature)

(*R*)-1-phenylethanol: $[\alpha]_D^{22} +45.2$ (*c* 0.5, CH₂Cl₂) (lit.¹⁰ $[\alpha]_D^{23} +48.6$ (*c* 1.0, CH₂Cl₂), 96% e.e. (*R*)), 90.2 % e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 115 °C, *R* isomer 19.2 min, *S* isomer 20.6 min).

(*R*)-1-(4'-methylphenyl)ethanol: $[\alpha]_D^{25} +53.2$ (*c* 0.236, CHCl₃) (lit.¹¹ $[\alpha]_D^{22} -54.1$ (*c* 0.0532, CHCl₃), 96 % e.e. (*S*)), 96.0 % e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 125 °C, *R* isomer 19.6 min, *S* isomer 20.7 min).

(*R*)-1-(1'-naphthyl)ethanol: $[\alpha]_D^{21} +74.2$ (*c* 0.3, ether) (lit.⁹ $[\alpha]_D^{25} +77.0$ (*c* 1.02, ether), 98 % e.e. (*R*)), 94.2 % e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 155 °C, *S* isomer 59.6 min, *R* isomer 61.7 min).

(*R*)-1-(2'-bromophenyl)ethanol: $[\alpha]_D^{23} +54.9$ (*c* 0.340, CH₂Cl₂) (lit.⁹ $[\alpha]_D^{24} -60.5$ (*c* 0.57, CH₂Cl₂), 98 % e.e. (*S*)), 91.0 % e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 145 °C, *R* isomer 24.8 min, *S* isomer 29.1 min).

(*R*)-1-(4'-methoxyphenyl)ethanol: $[\alpha]_D^{24} +39.8$ (*c* 0.300, CHCl₃) (lit.¹² $[\alpha]_D^{23} -51.9$ (*c* 1.04, CHCl₃), 97 % e.e. (*S*)), 85.2 % e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 130 °C, *R* isomer 38.3 min, *S* isomer 39.9 min).

(*R*)-1-(4'-bromophenyl)ethanol: $[\alpha]_D^{26} +32.8$ (*c* 1.600, CHCl₃) (lit.¹³ $[\alpha]_D^{24} -37.6$ (*c* 1.13, CHCl₃), 99% e.e. (*S*)), 80.0% e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 145 °C, *R* isomer 30.5 min, *S* isomer 31.9 min).

(*R*)-1-(4'-fluorophenyl)ethanol: $[\alpha]_D^{21} +32.7$ (*c* 0.880, CH₃OH) (lit.¹³ $[\alpha]_D^{25} -37.9$ (*c* 1.0, CH₃OH), 99% e.e. (*S*)), 94% e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 120 °C, *R* isomer 18.8 min, *S* isomer 20.2 min).

(*R*)-1-(2'-naphthyl)ethanol: $[\alpha]_D^{24} +36.3$ (*c* 0.580, EtOH) (lit.¹⁴ $[\alpha]_D^{27} +45.4$ (*c* 1.00, EtOH), 90% e.e. (*R*)), 85% e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 155 °C, *R* isomer 57.3 min, *S* isomer 58.7 min).

2. Data of reduction products (reactions catalyzed by (S, S, SS) Ru—BrXuPHOS in the ice bath)

(*R*)-1-phenylethanol: $[\alpha]_D^{26} +46.0$ (*c* 0.84, CH₂Cl₂) (lit.¹⁰ $[\alpha]_D^{23} +48.6$ (*c* 1.0, CH₂Cl₂), 96% e.e. (*R*)), 93.0 % e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 115 °C, *R* isomer 20.0 min, *S* isomer 21.3 min).

(*R*)-1-(1'-naphthyl)ethanol: $[\alpha]_D^{28} +77.2$ (*c* 0.67, ether) (lit.⁹ $[\alpha]_D^{25} +77.0$ (*c* 1.02, ether), 98 % e.e. (*R*)), 99.0 % e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 155 °C, *S* isomer 60.4 min, *R* isomer 62.3 min).

(*R*)-1-(2'-bromophenyl)ethanol: $[\alpha]_D^{25} +54.1$ (*c* 1.18, CHCl₃) (lit.¹³ $[\alpha]_D^{24} -54.6$ (*c* 1.23, CHCl₃), 99 % e.e. (*S*)), 99.0 % e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 145 °C, *R* isomer 26.2 min, *S* isomer 30.7 min).

3. Data of reduction products (reactions catalyzed by (*S*, *S*, *SS*) Ru—MeOXuPHOS at room temperature)

(*R*)-1-phenylethanol: $[\alpha]_D^{26} +43.6$ (*c* 0.934, CH₂Cl₂) (lit.¹⁰ $[\alpha]_D^{23} +48.6$ (*c* 1.0, CH₂Cl₂), 96% e.e. (*R*)), 88% e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 115 °C, *R* isomer 19.2 min, *S* isomer 20.5 min).

(*R*)-1-(4'-methylphenyl)ethanol: $[\alpha]_D^{29} +50.2$ (*c* 0.92, CHCl₃) (lit.¹¹ $[\alpha]_D^{22} -54.1$ (*c* 0.0532, CHCl₃), 96% e.e. (*S*)), 94% e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 125 °C, *R* isomer 19.2 min, *S* isomer 20.2 min).

(*R*)-1-(1'-naphthyl)ethanol: $[\alpha]_D^{18} +71.8$ (*c* 0.99, ether) (lit.⁹ $[\alpha]_D^{25} +77.0$ (*c* 1.02, ether), 98 % e.e. (*R*)), 88.0 % e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 155 °C, *S* isomer 59.0 min, *R* isomer 61.2 min).

(*R*)-1-(4'-fluorophenyl)ethanol: $[\alpha]_D^{19} +26.1$ (*c* 0.880, CH₃OH) (lit.¹³ $[\alpha]_D^{25} -37.9$ (*c* 1.0, CH₃OH), 99% e.e. (*S*)), 89% e.e. (*R*) by GC (Cyclodextrin- β -236M-19 (CHROMPAC, 50m), T = 120 °C, *R* isomer 18.9 min, *S* isomer 20.4 min).

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K) X-ray crystallographic data for Ru(II) complex derived from **8** (local name YJ4ort).

Yj4ort solid state structure

Yj4ort showing internal H bonds between the phenyl bromide and one of the NHs of each amine (hydrogens not involved in the interaction removed for clarity)

Experimental data for yj4ort

The asymmetric unit contains the complex and some diffuse electron density. This was modelled as disordered solvent, a methanol disordered over two positions (55:45 major minor) and a methanol occupying a similar position as a molecule of water. (45:55 methanol to water).

The torsion angle along the Ru-P1-C501-C502(Br5) bond is -46.36 (0.74) Ru1 - P1 - C501 - C502

The torsion angle along the Ru-P1-C601-C602(Br6) bond is -39.69 (1.55) Ru1 - P2 - C601 - C602

There are short contacts between some of the NHs of the amine ligand and the bromine of the bromophenyl group. These are tabulated below
Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	$\angle(\text{DHA})$	
0.92	2.91	3.533(15)	126.2	N7-H7C...Br5
0.92	3.05	3.615(15)	121.1	N8-H8C...Br6

Crystal Data

C₆₇H₅₄Br₂Cl₂N₂O₆P₂Ru, M = 1383.36, Monoclinic, space group C2(1)(c-unique)
a = 16.649(2), b = 19.163(2), c = 27.224(3) Å,
alpha = 90 deg., beta = 90 deg., gamma = 89.58 deg.,
U = 8685.0(19) Å³ (by least squares refinement on 8192 reflection positions),
T = 180(2) K, lambda = 0.71073 Å, Z = 4,
D(cal) = 1.058 Mg/m³, F(000) = 2798.
mu(MoK-alpha) = 1.237 mm⁻¹.
Crystal character: yellow block.
Crystal dimensions 0.32 x 0.28 x 0.12 mm,

Data Collection and Processing.

Siemens SMART (Siemens, 1994) three-circle system with CCD area detector.
The crystal was held at 180(2)
K with the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986).
Maximum theta was 29.07 deg.
The hkl ranges were -12/ 21, -26/ 25, -35/ 36.
27051 reflections measured, 18346 unique [R(int) = 0.1274].
Absorption correction by Semi-empirical from equivalents;
minimum and maximum transmission factors: 0.36; 0.91.

No crystal decay

Structure Analysis and Refinement.

The unit cell metric suggested the possibility of a C-centred orthorhombic lattice, rather than the apparent monoclinic lattice and systematic absences suggested that the space group might be C222(1). The structure could only be solved with monoclinic symmetry and space group C112(1) was used to allow ready comparison with the possible orthorhombic lattice. After refinement, it became clear that the asymmetric unit did not contain any additional symmetry, but there was extensive pseudo-orthorhombic twinning (twin factor 0.432(2)). Only with refinement of this twinning parameter could the R-value be reduced below about 0.2.

The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods. Disordered solvent atoms were interpreted as one MeOH molecule disordered over two positions and one sharing a site with a water molecule.

Hydrogen atoms were added at calculated positions and refined using a riding

model; H atoms were not found for the solvent molecules. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

The expected chirality of the ligands was confirmed by the value of the Flack parameter.

Absolute structure parameter $x = 0.00(2)$.

Floating origin constraints were generated automatically.

The weighting scheme was calc $w=1/[\sigma^2(F_o^2)+(0.0946P)^2]$ where $P=(F_o^2+2F_c^2)/3$.

Goodness-of-fit on F^2 was 0.850,

R_1 [for 6829 reflections with

$I > 2\sigma(I)$] = 0.0962, $wR_2 = 0.2447$.

Data / restraints / parameters 18346/ 583/ 647.

Extinction coefficient 0.00128(14).

Largest difference Fourier peak and hole 1.312 and -0.811 e.Å⁻³.

The relatively large final R-value was not unexpected because of the extensive twinning, not

all of which could be compensated for through refinement of the twin factor, in view of the

significant deviation of gamma from 90 deg which must have led to imprecise overlap of

the reflections with their twin equivalents.

Refinement used SHELXTL (Sheldrick, 1997).

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Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

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L) ¹H-NMR spectra for organic compounds lacking CHN analysis data.

Compound 8

Compound 6

Compound 9