Supplementary Information

Commercially available diamines DPEN (Fluka) and AMP (Aldrich) were used as received. Enantiomerically pure DACH[1] and DAIPEN[2] were prepared according to literature procedures. Enantiomerically pure p*seudo-ortho*-dibromo-paracyclophane (for the synthesis of ligands **1a** and **1b**) was prepared according to literature procedure.[3]

General procedure for crude PhanePhos-Ru-diamine precatalysts **2**

Method A: PhanePhos **1a-b** (0.1 mmol) and $[(C_6H_6)RuCl_2]_2$ (0.05 mmol) were dissolved in anhydrous and degassed DMF (2 mL) under nitrogen. The reaction was heated to 100 °C for 3-4 hours, then the diamine (0.105 mmol) was added and the reaction was allowed to reach room temperature while stirring overnight (14-16 hours). The solvent was removed under high vacuum and the crude residue was used for hydrogenations without any further purification.

Method B: PhanePhos **1a-b** (0.1 mmol) and $[(C_6H_6)RuCl_2]_2$ (0.05 mmol) were dissolved in anhydrous toluene (3-5 mL and DMF (0.5-0.8 mL) under nitrogen. The reaction was heated to 100 °C for 3-4 hours and then the diamine (0.105 mmol) was added. The reaction was allowed to reach room temperature while stirring overnight (14-16 hours). The reaction was filtered over Celite™ to remove turbidity, then the solvent was evaporated under high vacuum and the crude residue was used for hydrogenations without any further purification.

^{31}P NMR (162 MHz, $CDCl_3$) of precatalysts **2**
[((*S*)-**1a**)$RuCl_2$((*S*,*S*)-DPEN)]: δ = 45.6 (s); [((*S*)-**1a**)$RuCl_2$((*R*,*R*)-DPEN)]: δ= 45.2 (s); [((*R*)-**1b**)$RuCl_2$((*R*,*R*)-DPEN)]: δ= 48.1 (s); [((*S*)-**1b**)$RuCl_2$((*S*,S)-DACH)]: δ= 45.6 (s); [((*S*)-**1b**)$RuCl_2$((*S*)-AMP)]: δ= 40.9 (d), 41.4 (d); [(*R*)-**1b**)$RuCl_2$((*S*)-AMP)]: δ = 49.1 (s); [((*S*)-**1b**)$RuCl_2$((*S*)-DAIPEN)]: δ= 44.9 (d) 47.6 (d); [((*R*)-**1b**)$RuCl_2$((*S*)-DAIPEN)]: δ = 45.5 (d), 48.9 (d).

Synthesis of [((*R*)-**1b**)$RuCl_2$((*S*,*S*)-DPEN)]
$[(C_6H_6)RuCl_2]_2$ (0.436 mmol, 218 mg), (*R*)-xylyl-PhanePhos (0.871 mmol, 0.60 g), toluene (8 mL) and anhydrous DMF (6 mL) were heated at 100°C for 4 h. To the clear red reaction mixture was added (*S*,*S*)-DPEN (0.871 mmol, 185 mg) and it was heated at 100°C for 1.5 h. The supernatant was separated from, the insoluble yellow residue and the solvent was evaporated under reduced pressure. Diethylether (10 mL) and methanol (10 mL) were added, a pale yellow precipitate was formed, filtered off and washed with methanol (12 mL). A pale yellow solid was obtained (0.42 g, 45%).
^1H-NMR ($CDCl_3$, 400 MHz): δ = 1.78 (1H, ddd, *J* = 15.0, 10.5, 4.5 Hz), 2.07 (6H, s), 2.27 (6H, s), 2.27 (6H, s), 2.59 (1H, m), 2.78 (1H, m), 4.01 (1H, m), 4.40 (1H, m), 4.49 (1H, m), 6.36 (1H, d, *J* = 8.0 Hz), 6.42 (1H, d, *J* = 8.0 Hz), 6.60 (2H, m), 6.79 (1H, m), 6.96 (2H, m), 7.06 (1H, s), 7.13 (3H, m), 8.04 (2H, m), 8.21 (1H, m).
^{31}P-NMR ($CDCl_3$,162 MHz): δ = + 46.06 (s).
The performance in hydrogenation of the isolated precatalyst was indistinguishable from that of the crude precatalysts.

Hydrogenation of acetophenone

Standard procedure at S/C 3000/1: the catalyst (0.002 mmol) was placed in a 50 mL Parr hydrogenation vessel. The vessel was evacuated and refilled with nitrogen three times, then purged with hydrogen by pressurising to 8 bar and releasing the pressure. The procedure was repeated at least three times. A solution of acetophenone (0.72 g, 6 mmol) in anhydrous *i*-propanol (3 mL) was introduced with a syringe via the vessel injection port and the vessel was purged with hydrogen. A solution of *t*-BuOK in *i*-PrOH (0.1 mL, 0.1 mmol) was added through the injection port, the vessel was purged with hydrogen and pressurised to 8 bar. The reaction was stirred at room temperature for 40 minutes. A reaction sample was diluted with methyl-*t*-butyl ether and analysed by chiral GC: Chirasil DEX CB, 100°C for 7 min, then 30°C/min to 200°C: 9.3 min (*R*), 9.5 min (*S*). The stereochemistry of 1-phenyl-ethanol was assigned by comparison with commercially available (*R*)- 1-phenyl-ethanol (Aldrich).

Reaction with [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] at 3000/1: (2.1 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 0.5 hour, (*R*)-1-phenylethanol: > 99 % conversion, 99 % ee.

Reaction with [((*S*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] at 3000/1: (2.1 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 1 hour, (*R*)-1-phenylethanol: > 99 % conversion, 41 % ee.

Reaction with KOH at S/C 5000/1: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **3** (1.20 g, 10 mmol), *i*-PrOH (5 mL), KOH in *i*-PrOH (2 M, 0.1 mL, 0.2 mmol), room temperature, 1.5 hours, 5.5 bar initial hydrogen pressure, the reaction was periodically recharged with hydrogen to maintain the pressure between 3.5 and 5.5 bar. (*R*)-1-phenylethanol: > 99 % conversion, 99 % ee. The same reaction with K_2CO_3 (28 mg, 0.2 mmol) gave, after 2 hours, 20% conversion and 96 % ee.

Reaction in neat acetophenone: S/C 5000/1: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (9.2 mg, 0.0086 mmol), acetophenone (5.15 g, 42.9 mmol), *t*-BuOK (48 mg, 0.43 mmol), room temperature, 22 hours, 5.5 bar initial hydrogen pressure, the reaction was recharged twice with hydrogen to maintain the pressure between 2.0 and 5.5 bar. (*R*)-1-phenylethanol: 57 % conversion, 95.5 % ee.

Reaction at S/C 10000/1: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), acetophenone (2.40 g, 20 mmol), *i*-PrOH (10 mL), *t*-BuOK in *i*-PrOH (1 M, 0.5 mL, 0.5 mmol), room temperature, 1 hour, 5.5 bar initial hydrogen pressure, the reaction was periodically recharged with hydrogen to maintain the pressure between 3.5 and 5.5 bar. (*R*)-1-phenylethanol: > 99 % conversion, 99 % ee.

Reaction at S/C 20000/1: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN] (2.1 mg, 0.002 mmol), acetophenone (4.80 g, 40 mmol), *i*-PrOH (8 mL), *t*-BuOK in *i*-PrOH (1 M, 1 mL, 1 mmol), room temperature, 1.5 hours, 5.5 bar initial hydrogen pressure, the reaction was periodically recharged with hydrogen to maintain the pressure between 3.5 and 5.5 bar. (*R*)-1-phenylethanol: > 99 % conversion, 99 % ee.

Reaction at S/C 40000/1: a solution of **3** (96.1 g, 0.8 mol, stirred over K_2CO_3, filtered and freshly distilled) in anhydrous *i*-PrOH (150 mL) was charged into a 600 mL hydrogenation vessel equipped with mechanical stirrer. The vessel was evacuated and refilled with nitrogen three times, then purged with hydrogen by pressurising to 8 bar (under stirring) and releasing the pressure. The procedure was repeated five times. The vessel was thermostated at 25°C. [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN] (21 mg, 0.02 mmol) was placed in a 50 mL Schlenk flask under nitrogen and a solution of *t*-BuOK in *i*-propanol (1 M, 20 mL, 20 mmol) was added. The reaction was stirred to allow complete dissolution of the solid and the resulting clear yellow solution was transferred into the hydrogenation vessel with a syringe through the injection port. The vessel was purged three times with hydrogen and pressurised to 8 bar. The reaction was stirred at 25°C and periodically recharged with hydrogen in order to maintain the pressure between 7 and 8 bar. After 4 hours the pressure was released and analysis of the crude by chiral GC indicated that (*R*)-1-phenylethanol was formed with > 99% conversion and 98.5% ee. The solvent was evaporated and the product was obtained as a colourless oil by short path distillation (93.6 g, yield 97%, 98.5 % ee, $[\alpha]_D^{20}$= 43.36°(neat)).

Reaction with [((*S*)-**1a**)$RuCl_2$((*R,R*)-DACH)] at 3000/1: (1.9 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 0.5 hour, (*S*)-1-phenylethanol: > 99 % conversion, 97 % ee.

Reaction with [((*S*)-**1a**)$RuCl_2$((*S,S*)-DACH)] at 3000/1: (1.9 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 0.5 hour, (*S*)-1-phenylethanol: > 99 % conversion, 45 % ee.

Reaction with [((*S*)-**1a**)$RuCl_2$((*R,R*)-DPEN)] at 3000/1: (1.9 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 0.5 hour, (*S*)-1-phenylethanol: > 99 % conversion, 98 % ee.

Reaction with [((*S*)-**1a**)$RuCl_2$((*S,S*)-DPEN)] at 3000/1: (2.0 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 1.25 hours, (*S*)-1-phenylethanol: > 99 % conversion, 43 % ee.

Reaction with [((*S*)-**1b**)$RuCl_2$((*R,R*)-DACH)] at 3000/1: (2.0 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 0.5 hour, (*R*)-1-phenylethanol: > 99 % conversion, 98 % ee.

Reaction with [((*S*)-**1b**)$RuCl_2$((*S,S*)-DACH)] at 3000/1: (2.0 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 2 hours, (*R*)-1-phenylethanol: > 99 % conversion, 8 % ee.

Reaction with [((*R*)-**1b**)$RuCl_2$((*S*)-DAIPEN)] at 3000/1: (2.1 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 2 hours, (*R*)-1-phenylethanol: > 99 % conversion, 80 % ee.

Reaction with [((*S*)-**1b**)$RuCl_2$((*S*)-DAIPEN)] at 3000/1: (2.3 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 2 hours, (*R*)-1-phenylethanol: 50 % conversion, 25 % ee.

Reaction with [((*S*)-**1b**)$RuCl_2$((*S*)-AMP)] at 3000/1: (2.0 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 2 hours, (*S*)-1-phenylethanol: > 99 % conversion, 53 % ee.

Reaction with [((*R*)-**1b**)$RuCl_2$((*S*)-AMP)] at 3000/1: (2.0 mg, 0.002 mmol), acetophenone (0.72 g, 6 mmol), *i*-PrOH (3 mL), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), 8 bar, 2.5 hours, (*R*)-1-phenylethanol: > 99 % conversion, 92 % ee.

Hydrogenation of ketones

The same standard procedure as for acetophenone was used. When the reaction was complete the solvent was evaporated and the residue was analysed by NMR and by chiral GC or HPLC. The stereochemistry was assigned by comparing the optical rotation with literature data.[4]

(*R*)-1-(4'-Trifluoromethylphenyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **5a** (1.25 g, 6.6 mmol, S/C 3300/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (3 mL), 8 bar, 1 hour. Chirasil DEX CB, 100°C for 7 min, then 30°C/min to 200°C: 9.9 min (*R*), 10.2 min (*S*). > 99% conversion, 97% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*R*)-1-(4'-Bromophenyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **5b** (1.19g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (3 mL), 8 bar, 1 hour. Chirasil DEX CB, 150°C for 20 min, then 15°C/min to 200°C: 9.9 min (*R*), 10.2 min (*S*). >99 % conversion, 99 % ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*R*)-1-(4'-Methoxyphenyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **5c** (0.9g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 1.5 hours. Chirasil DEX CB, 160 °C for 8.5 min, then 20°C/min to 200°C: 22.3 min (*R*), 22.7 min (*S*). >99 % conversion, 97 % ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*R*)-1-(3'-Trifluoromethyphenyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **5d** (1.13 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (3 mL), 8 bar, 30 minutes. Chirasil DEX CB, 100°C for 7 min, then 30°C/min to 200°C: 9.5 min (*R*), 9.8 min (*S*). >99% conversion, 99% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*R*)-1-(2'-Trifluoromethylphenyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN] (2.1 mg, 0.002 mmol), **5e** (1.13 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (3 mL), 8 bar, 1 hour. Chirasil DEX CB, 100°C for 7 min, then

30°C/min to 200°C: 9.4 min (*R*), 9.6 min (*S*). >99% conversion, 98% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*S*)-(2'-Methylphenyl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (2.1 mg, 0.002 mmol), **5f** (0.800 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 1 hour. Chirasil DEX CB, 100 °C for 15 min, then 5°C/min to 200°C: 23.5 min (*R*), 24.6 min (*S*). >99% conversion, 97% ee.

(*R*)-(2'-Bromophenyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **5g** (1.20g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (3 mL), 5.5 bar, 1.5 hours. Chirasil DEX CB, 120 °C for 20 min, then 15°C/min to 200°C: 6.0 min (*R*), 7.0 min (*S*). >99 % conversion, 99 % ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*S*)-(2'-Methoxyphenyl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (6.4 mg, 0.006 mmol), **5h** (0.450g, 3.0 mmol, S/C 500/1), *t*-BuOK in *t*-BuOH (1 M, 0.3 mL, 0.3 mmol), *i*-PrOH (5 mL), 5.5 bar, 2.5 hours. Chirasil DEX CB, 120 °C for 20 min, then 15°C/min to 200°C: 21.7 min (*S*), 22.4 min (*R*). >99 % conversion, 94 % ee.

(*S*)-1-(4'-Methylphenyl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (2.1 mg, 0.002 mmol), **5i** (0.805 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 1.75 hours. Chirasil DEX CB, 120 °C for 20 min, then 15°C/min to 200°C: 9.9 min (*R*), 10.0 min (*S*). >99 % conversion, 98 % ee.

(3', 4'-Dichlorophenyl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (2.1 mg, 0.002 mmol), 3', 4'-Dichloroacetophenone (1.13g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 8 bar, 0.5 hour. Chirasil DEX CB, 160 °C for 8.5 min, then 15°C/min to 200°C: 9.5 min, 9.6 min. >99 % conversion, 98 % ee. Stereochemistry not assigned.

(3', 4'-Difluorophenyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), 3', 4'-Difluoroacetophenone (0.94g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 0.5 hour. Chirasil DEX CB, 160 °C for 8.5 min, then 15°C/min to 200°C: 2.4 min, 2.5 min. >99 % conversion, 99 % ee. Stereochemistry not assigned.

(*S*)-1-Phenylpropanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (2.1 mg, 0.002 mmol), **6a** (0.805 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 1.5 hours. Chirasil DEX CB, 160 °C for 8.5 min, then 20°C/min to 200°C: 12.9 min (*R*), 13.3 min (*S*). >99 % conversion, 99 % ee.

(*S*)-1-Phenylpentanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (2.1 mg, 0.002 mmol), **6b** (0.970 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 3 hours. Chirasil DEX CB, 100 °C for 15 min, then 5°C/min to 200°C: 26.6 min (*S*), 26.9 min (*R*). >99 % conversion, 96 % ee.

(*S*)-1,2-Diphenylethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **6c** (1.18 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 5 hours. Chiralcel OD column, heptane/*i*-propanol 96/4, 1 mL/min, 12.4 min (*R*), 16.2 (*S*). > 99% conversion, 98% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*S*)-1-Phenyl-2-methyl-propan-1-ol: [((*S*)-**1a**)$RuCl_2$((*R,R*)-DPEN] (2.9 mg, 0.003 mmol), **6d** (0.44 g, 3.0 mmol, S/C 1000/1), *t*-BuOK in *i*-PrOH (1 M, 0.15 mL, 0.15 mmol), *i*-PrOH (3 mL), 8 bar, 2.5 hours. Chirasil DEX CB, 110°C for 30 min, then 5°C/min to 200°C: 29.2 min (*R*), 30.1 min (*S*). >99% conversion, 71% ee. [((*S*)-**1a**)$RuCl_2$((*R,R*)-DACH] (2.5 mg, 0.003 mmol), **6d** (0.45 g, 3.0 mmol, S/C 1000/1), *t*-BuOK in *i*-PrOH (1 M, 0.15 mL, 0.15 mmol), *i*-PrOH (3 mL), 8 bar, 2.5 hours. >99% conversion, 53%ee. [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (6.4 mg, 0.006 mmol),), **6d** (0.45 g, 3.0 mmol, S/C 500/1), *t*-BuOK in *i*-PrOH (1 M, 0.3 mL, 0.3 mmol), *i*-PrOH (5 mL), 5.5 bar, 3.5 hours. >99% conversion, 31%ee.

(*R*)-1-(1'-Naphtyl)-ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **7a** (1.02 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (3 mL), 8 bar, 1 hour. Chirasil DEX CB, 165°C for 15 min, then 15°C/min to 200°C: 13.2 min (*S*), 13.9 min (*R*). >99% conversion, 99% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*R*)-1-(2'-Naphtyl)-ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **7b** (1.02 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (3 mL), 8 bar, 1 hour. Chirasil DEX CB, 165°C for 15 min, then 15°C/min to 200°C: 11.9 min (*R*), 12.7 min (*S*). >99% conversion, 99% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*R*)-1-Ferrocenylethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (3.2 mg, 0.003 mmol), **7c** (0.68 g, 3.0 mmol, S/C 1000/1, recrystallysed from heptane/MTBE 10/1), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (5 mL), 5.5 bar, 1 hour. Daicel Chiralpack AS column (250x.6mm), heptane/*i*-PrOH 94/6, 0.65 mL/min, 12.8 min (minor), 15.4 min (major); >99% conversion, 92% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*R*)-1-(2-Furyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **7d** (0.66g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 2.5 hours. Chirasil DEX CB, 120°C for 20 min, then 15°C/min to 200°C: 6.4 min (*S*), 6.5 min (*R*). >99% conversion, 96% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*S*)-1-(2-Thienyl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (2.1 mg, 0.002 mmol), **7e** (0.750 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 4.0 hours. . Chirasil DEX CB, 100 °C for 15 min, then 5°C/min to 200°C: 19.5 min (*R*), 20.1 min (*S*). 99 % conversion, 96 % ee.

(*S*)-1-(3-Thienyl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (2.1 mg, 0.002 mmol), **7f** (0.760 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-

PrOH (10 mL), 5.5 bar, 3.0 hours. . Chirasil DEX CB, 100 °C for 15 min, then 5°C/min to 200°C: 20.3 min (*R*), 20.8 min (*S*). >99 % conversion, 98 % ee.

(*R*)-1-(2'-Pyridyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (4.3 mg, 0.004 mmol), **7g** (0.73 g, 6.0 mmol, S/C 1500/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (3 mL), 8 bar, 18 hours. Chirasil DEX CB (as trifluoroacetate), 100°C for 10 min, then 45°C/min to 200°C: 4.5 min (*R*), 4.8 min (*S*). >99% conversion, 78% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*R*)-1-(3'-Pyridyl)ethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (4.2 mg, 0.004 mmol), **7h** (0.73 g, 6.0 mmol, S/C 1500/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (3 mL), 8 bar, 3 hours. Chirasil DEX CB, 40°C for 15 min, then 3°C/min to 180°C: 46.4 min (*R*), 47.3 min (*S*). >99% conversion, 99% ee. The opposite enantiomer of precatalyst afforded the opposite enantiomer of product.

(*S*)-1-(4'-Pyridyl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (6.4 mg, 0.006 mmol), **7i** (0.725 g, 6.0 mmol, S/C 1000/1), *t*-BuOK in *t*-BuOH (1 M, 0.3 mL, 0.3 mmol), *i*-PrOH (3 mL), 5.5 bar, 16 hours. Chirasil DEX CB (as trifluoroacetate), 100°C for 10 min, then 45°C/min to 200°C: 7.0 min (*R*), 7.3 min (*S*). >99% conversion, 96% ee.

1-(2,5-Dimethyl-3-furyl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (2.1 mg, 0.002 mmol), 2,5-Dimethyl-3-acetylfurane (0.83 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *i*-PrOH (1 M, 0.3 mL, 0.3 mmol), *i*-PrOH (10 mL), 5.5 bar, 15 hours. Chirasil DEX CB, 100°C for 7 min, then 30°C/min to 200°C: 8.8 min (*major*), 9.1 min (*minor*). >99% conversion, 95% ee. Stereochemistry not assigned.

(*S*)-(2-Benzofuryl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (2.1 mg, 0.002 mmol), **7j** (0.96 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *i*-PrOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 3 hours. Chiralcel OJ column (250*4.6mm), CO_2/MeOH 96/4, 3 mL/min, temperature:35°C, 6.6 min (*R*), 7.8 min (*S*), >99% conversion, 97%ee.

(*R*)-(*E*)-4-Phenyl-3-buten-2-ol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (2.1 mg, 0.002 mmol), **8** (0.88 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), 5.5 bar, 1 hour. Chirasil DEX CB, 115°C for 20 min, then 15°C/min to 200°C: 22.8 min (*R*), 9.1 min (*S*). >99% conversion, 97% ee.

(*S*)-(*E*)-4-Phenyl-3-buten-2-ol: [((*S*)-**1a**)$RuCl_2$((*R,R*)-DACH)] (1.8 mg, 0.002 mmol), **8** (0.88 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 2 hours. >99% conversion, 96% ee.

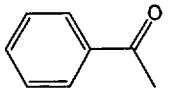
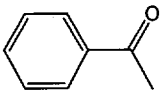
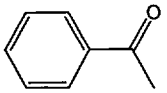
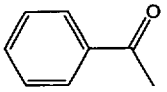
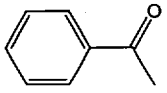
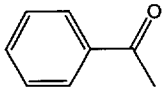
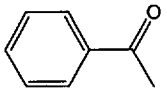
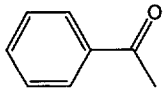
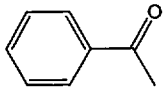
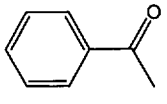
(*S*)-(*E*)-4-Phenyl-3-buten-2-ol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DACH)] (2.0 mg, 0.002 mmol), **8** (0.88 g, 6.0 mmol, S/C 3000/1), *t*-BuOK in *t*-BuOH (1 M, 0.1 mL, 0.1 mmol), *i*-PrOH (10 mL), 5.5 bar, 22 hours. >99% conversion, 85% ee.

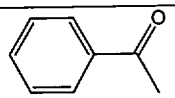
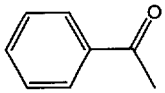
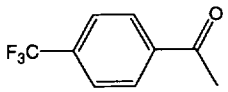
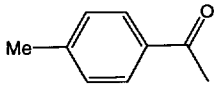
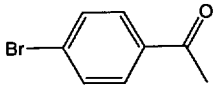
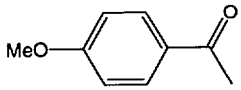
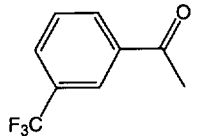
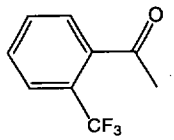
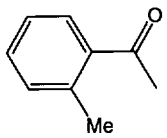
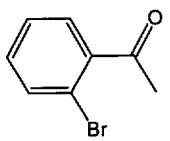
(*S*)-1-(1'-Cyclohexenyl)ethanol: [((*S*)-**1b**)$RuCl_2$((*R,R*)-DPEN)] (3.2 mg, 0.003 mmol), **9** (0.375 g, 3.0 mmol, S/C 1000/1), *t*-BuOK in *t*-BuOH (1 M, 0.15 mL, 0.15 mmol), *i*-PrOH (3 mL), 5.5 bar, 2 hours. Chirasil DEX CB, 100 °C for 15 min, then 5°C/min to 200°C: 17.9 min (*S*), 18.3 min (*R*). >99% conversion, 94% ee.

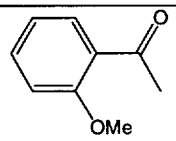
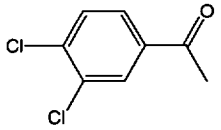
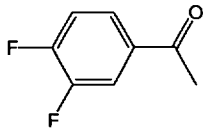
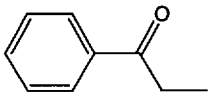
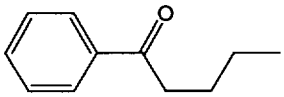
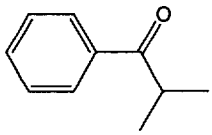
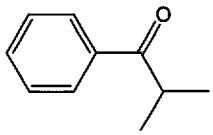
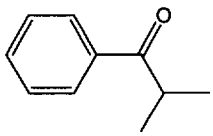
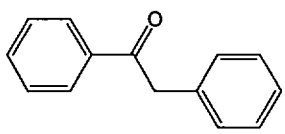
(*S*)-1-Cyclohexylethanol: [((*R*)-**1b**)$RuCl_2$((*S,S*)-DPEN)] (3.2 mg, 0.003 mmol), **10** (0.38 g, 3.0 mmol, S/C 1000/1), *t*-BuOK in *t*-BuOH (1 M, 0.15 mL, 0.15 mmol), *i*-PrOH (5 mL), 5.5 bar, 2 hours. BTA (as trifluoroacetate derivative): >99% conversion, 49% ee.

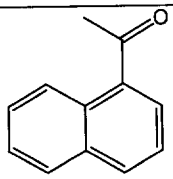
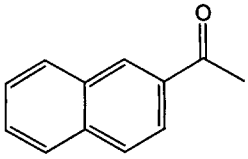
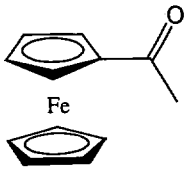
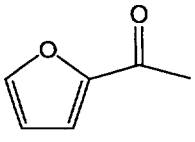
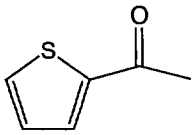
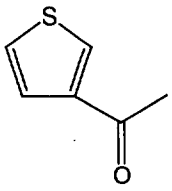
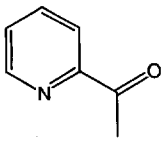
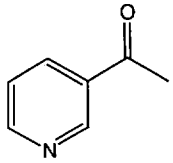
References:

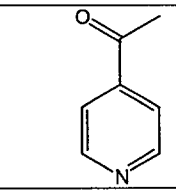
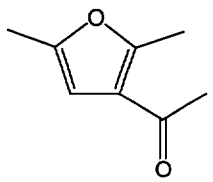
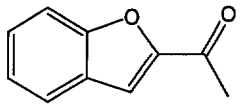
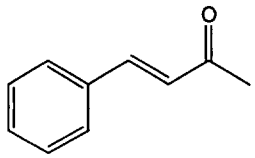
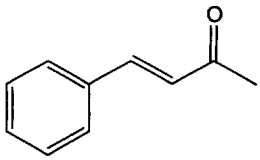
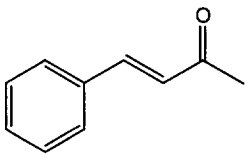
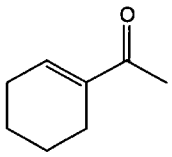
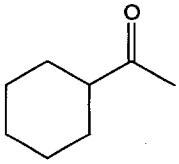
1) J.F. Larrow, E. N. Jacobsen, Y. Gao, Y. Hong, X. Nie, C. M. Zepp *J. Org. Chem.* **1994**, *59*, 1939.
2) S.-J. Wey, K. J. O'Connor, C. J. Burrows *Tetrahedron Lett.* **1993**, *34*, 1905.
3) a) P. J. Pye, K. Rossen, R. A. Reamer, N. N. Tsou, R. P. Volante, P. J. Reider *J. Am. Chem. Soc.* **1997**, *119*, 6207. b) Pye, P. J.; Rossen, K.; Volante, R. P. Merck & Co., PCT Appl. WO 97/47632, 1997.
4) a) (Optical rotations for alcohols derived from ketones: **5a**, **5d**, **5e**, **5f**, **5i**, **6d**) K. Nakamura, T. Matsuda *J. Org. Chem.* **1998**, *63*, 8957; b) (**5b**, **8**, **9**, **10**) T. Ohkuma, M. Koizumi, H. Doucet, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya, R. Noyori *J. Am. Chem. Soc.* **1998**, *120*, 13529. c) (**5c**) Z.-L. Wei, Z.-Y. Li, G.-Q. Lin *Tetrahedron* **1998**, *54*, 13059. d) (**5g**, **5h**) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya, R. Noyori *Angew. Chem.* **1998**, *37*, 1703. e) (**6a**) R. Noyori, S. Suga, K. Kawai, S. Okada, M. Kitamura *J. Organomet. Chem.* **1990**, *382*, 19. f) (**6b**) B. Weber, D. Seebach *Tetrahedron* **1994**, *50*, 7473. g) (**6c**) K. Yamamoto, H. Fukushima, M. Nakazaki *J. Chem. Soc., Chem. Comm.* **1984**, 1490. h) (**7a**) K. Suginaka, Y. Hayashi, Y. Yamamoto *Tetrahedron: Asymmetry* **1996**, *7*, 1153. i) (**7b**) J. Chandrasekharan, P. V. Ramachandran, H. C. Brown *J. Org. Chem.* **1985**, *50*, 5446. j) (**7c**) M. Watanabe *Synlett* **1995**, 1050. k) (**7d**, **7e**, **7f**, **7g**, **7h**, **7i**) T. Ohkuma, M. Koizumi, M. Yoshida, R. Noyori *Org. Lett.* **2000**, *2*, 1749. k) (**7j**) M. Kusakabe, Y. Kitano, Y. Kobayashi, F. Sato *J. Org. Chem.* **1989**, *54*, 2085.

Ketone	Ru-Complex	S/C	H_2, Bar	Time, h	% ee	config.
	((*S*)-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	3000	8	0.5	98	*S*
	((*S*)-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	3000	8	2	43	*S*
	((*S*)-PhanePhos)$RuCl_2$((*R*,*R*)-DACH)	3000	8	0.5	97	*S*
	((*S*)-PhanePhos)$RuCl_2$((*S*,*S*)-DACH)	3000	8	0.5	45	*S*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	3000	8	0.5	99	*R*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	3000	8	1	41	*R*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DACH)	3000	8	0.5	98	*R*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DACH)	3000	8	2	8	*R*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*)-DAIPEN)	3000	8	2	80	*R*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*S*)-DAIPEN)	3000	8	2	25	*R*

	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*)-AMP)	3000	8	2.5	92	*R*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*S*)-AMP)	3000	8	2	53	*S*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S,S*)-DPEN)	3300	8	1	97	*R*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R,R*)-DPEN)	3000	5.5	1.75	98	*S*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S,S*)-DPEN)	3000	8	1	99	*R*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S,S*)-DPEN)	3000	5.5	1.5	97	*R*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S,S*)-DPEN)	3000	8	0.5	99	*R*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S,S*)-DPEN)	3000	8	1	98	*R*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R,R*)-DPEN)	3000	5.5	1	97	*S*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S,S*)-DPEN)	3000	5.5	1.5	99	*R*

	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	500	5.5	2.5	94	*S*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	3000	8	0.5	98	(*)
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	3000	5.5	0.5	99	(*)
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	3000	5.5	1.5	99	*S*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	3000	5.5	3	96	*S*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	500	5.5	3.5	31	*S*
	((*S*)-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	1000	8	2.5	71	*S*
	((*S*)-PhanePhos)$RuCl_2$((*R*,*R*)-DACH)	1000	8	2.5	53	*S*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	3000	5.5	5	98	*R*

	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	3000	8	1	99	*R*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	3000	8	1	99	*R*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	1000	5.5	1	92	*R*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	3000	5.5	2.5	96	*R*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	3000	5.5	4	96	*S*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	3000	5.5	3	98	*S*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	1500	8	18	78	*R*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	1500	8	3	99	*R*

	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	1000	5.5	16	96	*S*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	3000	5.5	15	95	(*)
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	3000	5.5	3	97	*S*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	3000	5.5	1	97	*R-(E)*
	((*S*)-PhanePhos)$RuCl_2$((*R*,*R*)-DACH)	3000	5.5	2	96	*R-(E)*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DACH)	3000	5.5	22	85	*S-(E)*
	((*S*)-xylyl-PhanePhos)$RuCl_2$((*R*,*R*)-DPEN)	1000	5.5	2	94	*S*
	((*R*)-xylyl-PhanePhos)$RuCl_2$((*S*,*S*)-DPEN)	1000	5.5	2	49	*S*

>99% conversion to product was observed in each case. (*): Absolute configuration was not determined.