Supporting information

“Achiral” Benzophenone Ligand for Highly Enantioselective Ru-Catalysts in Ketone Hydrogenation

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General. ^1H and ^{31}P NMR spectra were measured on a Varian GEMINI 2000 (300MHz) and Varian UNITY INOVA (400MHz) spectrometers. Chemical shifts of ^1H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$) in CDCl_3 . Chemical shifts of ^{19}F NMR were expressed in parts per million downfield from BTF as an external standard ($\delta = -63.24$) in CDCl_3 . Chemical shifts of ^{31}P NMR were expressed in parts per million downfield from 85% H_3PO_4 as an external standard ($\delta = 0$) in CDCl_3 . Capillary GC analyses were conducted on a Shimadzu GC-14B instrument equipped with flame ionization detector by using N_2 (75 kPa) as a carrier gas. Peak areas were calculated by a Shimadzu C-R6A as an automatic integrator; a chiral column was CP-Cyclodextrin- β -2,3,6-M-19 (i.d. 0.25 mm x 25 m; Chrompack, GL Sciences, Tokyo). Analytical TLC was performed on glass plates (Merck Kieselgal 60 F₂₅₄; layer thickness, 0.25 and 0.2 mm). Visualization was accomplished by UV light (254 nm) and anisaldehyde. Column chromatography was performed on Kanto

Silica Gel 60N (spherical, neutral; Kanto Chemical Co., Tokyo).

Materials. (1*S*,2*S*)-(-)-diphenylethylenediamine ((*S,S*)-DPEN) was provided by Kankyo Kagaku Center Co., LTD. to which we are grateful.

Preparation of RuCl₂(dpbp)[(*S,S*)-dpen] (2).

To a mixture of [RuCl₂(C₆H₆)₂] (2.5 mg, 0.005 mmol) and DPBP (2,2'-bis(diphenylphosphino)benzophenone) (5.5 mg, 0.01 mmol) was added DMF (1 ml) at r.t. under argon atmosphere in Schlenk tube. After stirred for 20 min at 100 °C, the reaction mixture concentrated under reduced pressure, to give RuCl₂(dpbp)(dmf)_n.

To a mixture of RuCl₂(dpbp)(dmf)_n (8.7 mg, 0.01 mmol) and (*S,S*)-DPEN (2.1 mg, 0.01 mmol) was added CH₂Cl₂ (1 ml) at rt under argon atmosphere in Schlenk tube. After stirred for 10 min at rt, the reaction mixture concentrated under reduced pressure, to give RuCl₂(dpbp)[(*S,S*)-dpen].

¹H NMR (CDCl₃, 300 MHz) δ 2.94-3.15 (m, 4H), 4.45-4.64 (m, 2H), 6.91-7.33 (m, 32H), 7.42-7.54 (m, 2H), 7.68-7.80 (m, 2H), 8.03-8.11 (m, 2H); ³¹P NMR (CDCl₃, 162 MHz) δ 46.38 (d, *J* = 23.6 Hz, 1P), 47.23 (d, *J* = 23.6 Hz, 1P).

Anal. Calcd for C₅₁H₄₄Cl₂N₂OP₂Ru·CH₂Cl₂·DMF: C, 60.45; H, 4.89; N, 3.84%. Found: C, 60.08; H, 5.23; N, 3.75%.

Preparation of [RuCl(OTf)(dpbp){(*S,S*)-dpen}]₂AgOTf (3).

To a mixture of RuCl₂(dpbp)(dmf)_n (8.7 mg, 0.01 mmol) and (*S,S*)-dpen (2.1 mg, 0.01 mmol) was added CH₂Cl₂ (1 ml) at rt under argon atmosphere in Schlenk tube. After stirred for 10 min at r.t., the reaction mixture was added AgOTf (5.1

mg, 0.02 mmol) in one portion. After stirred for 3 h at rt, the reaction mixture was filtered through Celite to remove AgCl. The filtrate was concentrated under reduced pressure, to give [RuCl(OTf)(dpbp){(*S,S*)-dpen}]₂AgOTf.

¹H NMR (CDCl₃, 300 MHz) δ 2.86-2.94 (m, 4H), 3.29-3.45 (m, 4H), 4.50-4.63 (m, 4H), 6.91-7.51 (m, 68H), 7.65-7.77 (m, 4H), 7.99-8.07 (m, 4H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -78.45; ³¹P NMR (CDCl₃, 162 MHz) δ 46.51 (d, *J* = 22.9 Hz, 2P), 47.03 (d, *J* = 22.9 Hz, 2P).

Typical procedure for Ru-catalyzed hydrogenation of ketones.

To a solution of RuCl₂(dpbp)[(*S,S*)-dpen] (11.2 mg, 0.012 mmol) in 2-propanol (3.3 ml) was added ketone substrate (3.0 mmol) under argon atmosphere in Schlenk tube. 100-ml autoclave was charged with this reaction mixture under a stream of argon. After addition of KOH/2-propanol (0.5 M, 60 μl, 0.03 mmol), hydrogen was introduced at a pressure of 15 atm. The solution was vigorously stirred for 4 h at rt. After the reaction mixture concentrated under reduced pressure, the residue was filtered through a short column of silica gel (hexane/ethyl acetate = 1/3) to give alcohol product.

Analysis of enantio excess of hydrogenation products

(*R*)-1-Phenylethanol

GC (column, CP-Cyclodextrin-β-2,3,6-M-19, i.d. 0.25 mm x 25 m, Chrompack,

carrier gas, N₂ (75 kPa), column temp 105 °C, injection and detection temp 135 °C, split rate, 100:1), t_R of *R*-isomer 21.7 min, t_R of *S*-isomer 23.5 min, t_R of ketone 13.4 min.

(*R*)-1-(2-Tolyl)ethanol

GC (column, CP-Cyclodextrin-β-2,3,6-M-19, i.d. 0.25 mm x 25 m, Chrompack, carrier gas, N₂ (75 kPa), column temp 130 °C, injection and detection temp 160 °C, split rate, 100:1), t_R of *R*-isomer 16.1 min, t_R of *S*-isomer 18.1 min, t_R of ketone 8.94 min.

(*R*)-1-(3-Tolyl)ethanol

GC (column, CP-Cyclodextrin-β-2,3,6-M-19, i.d. 0.25 mm x 25 m, Chrompack, carrier gas, N₂ (75 kPa), column temp 115 °C, injection and detection temp 145 °C, split rate, 100:1), t_R of *R*-isomer 23.7 min, t_R of *S*-isomer 25.7 min, t_R of ketone 16.4 min.

(*R*)-1-(4-Tolyl)ethanol

GC (column, CP-Cyclodextrin- β -2,3,6-M-19, i.d. 0.25 mm x 25 m, Chrompack, carrier gas, N₂ (75 kPa), column temp 120 °C, injection and detection temp 150 °C, split rate, 100:1), t_R of *R*-isomer 17.4 min, t_R of *S*-isomer 19.1 min, t_R of ketone 14.8 min.

(*R*)-1-(1-Naphthyl)ethanol

GC (column, CP-Cyclodextrin- β -2,3,6-M-19, i.d. 0.25 mm x 25 m, Chrompack, carrier gas, N₂ (75 kPa), column temp 160 °C, injection and detection temp 190 °C, split rate, 100:1), t_R of *S*-isomer 37.6 min, t_R of *R*-isomer 38.9 min, t_R of ketone 25.9 min.

Crystal data of [RuCl(OTf)(dpbp){(*S,S*)-dpen}]₂AgOTf (3)

Empirical formula	C ₁₀₇ H _{90.50} AgCl _{9.50} F _{7.50} N ₄ O _{9.50} P ₄ Ru ₂ S _{2.50}	
Formula weight	2577.65	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2	
Unit cell dimensions	a = 20.9715(16) Å	α = 90°

	$b = 39.437(3) \text{ \AA}$	$\beta = 90^\circ$
	$c = 13.8177(10) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$11428.0(15) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.498 Mg/m^3	
Absorption coefficient	0.823 mm^{-1}	
F(000)	5202	
Crystal size	$0.29 \times 0.27 \times 0.13 \text{ mm}^3$	
Theta range for data collection	$1.47 \text{ to } 27.93^\circ$	
Index ranges	$-27 \leq h \leq 26, -51 \leq k \leq 50, -18 \leq l \leq 18$	
Reflections collected	135463	
Independent reflections	26825 [R(int) = 0.0511]	
Completeness to $\theta = 27.93^\circ$	99.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9006 and 0.7963	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	26825 / 2307 / 1448	
Goodness-of-fit on F^2	1.145	
Final R indices [I > 2sigma(I)]	$R_1 = 0.0754, wR_2 = 0.2099$	
R indices (all data)	$R_1 = 0.0821, wR_2 = 0.2145$	
Absolute structure parameter	0.04(3)	
Largest diff. peak and hole	$10.390 [2.99 \text{ \AA from H1VA}] \text{ and } -1.310$ $[1.01 \text{ \AA from RU3}] \text{ e.\AA}^{-3}$	