Selected Papers

Preparation of Diastereomerically Pure and Mixed (S)-PhGly/BIPHEP/ Ru(II) Complexes and Their Catalytic Behavior with Li₂CO₃ in Asymmetric Cyanosilylation of Benzaldehyde

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A diastereomerically mixed complex $[Ru\{(S)-phgly\}_2\{(\pm)-biphep\}]$ is readily prepared from achiral diphosphine BIPHEP in two steps. These diastereomers are then separated by silica gel column chromatography. A 61:39 equilibrium mixture of $[Ru\{(S)-phgly\}_2\{(S)-biphep\}]$ and $[Ru\{(S)-phgly\}_2\{(R)-biphep\}]$ with Li₂CO₃ is used to catalyze cyanosilylation of benzaldehyde to afford the *R* cyanated product in 92% ee. The enantioselectivity is just slightly lower than that by using the pure $[Ru\{(S)-phgly\}_2\{(S)-biphep\}]/Li_2CO_3$ catalyst system of 96%. The high enantioselective ability of the diastereomerically mixed catalyst is revealed through a series of kinetic experiments in which the highly enantioselective $[Ru\{(S)-phgly\}_2\{(S)-biphep\}]/Li_2CO_3$ system is shown to catalyze the reaction 16.8 times faster than the less selective $[Ru\{(S)-phgly\}_2\{(R)-biphep\}]/Li_2CO_3$ system, affording the product in 2.6% ee. An equation is derived to approximate the relationship between the diastereomeric ratio of the catalyst and the ee value of the product.

Asymmetric cyanation of carbonyl and imino compounds is a facile and reliable method to introduce useful CN functionality with formation of a chiral center.¹ We have recently developed chiral catalyst systems consisting of amino acid/ BINAP/Ru(II) complexes and Li compounds, which exhibit excellent reactivity and enantioselectivity in hydrocyanation and cyanosilylation of aldehydes, ketones, and imines as well as the conjugate addition to α,β -unsaturated ketones (BINAP: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl).^{2–5} Scheme 1 exemplifies the asymmetric cyanosilylation of benzaldehyde (1) catalyzed by the [Ru{(*S*)-phgly}₂{(*S*)-binap}] [(*S*_A,*S*_P)-**3**]/ Li₂CO₃ system (PhGly: phenylglycinate).^{2,3a} The reaction with a substrate-to-catalyst molar ratio (S/C) of 10000 at -78 °C was completed in 12 h to afford the *R* cyanated product (*R*)-**2** in 97% ee.



Scheme 1. Enantioselective cyanosilylation of aldehyde 1 catalyzed by the (S_{A},S_{P}) -3/Li₂CO₃ system.

The simple biaryl diphosphine BIPHEP (2,2'-bis(diphenylphosphino)biphenyl) is achiral (*tropos*),⁶ but the chelate metal complex behaves as a chiral (*atropos*) compound, because the rotation around the biaryl axis is suppressed by the chelate structure (Scheme 2).^{7,8} The BIPHEP/metal complex is usually obtained as a racemic mixture, when the complexation is carried out without any regulation.⁹ The two isomers can be discriminated (preferably separated) as diastereomers, and then they show different chemical properties (e.g., catalytic effi-



BIPHEP/enantiomerically pure ligand/metal complexes a set of diastereomers

Scheme 2. Sequential transformation from achiral BIPHEP to diastereomeric BIPHEP/enantiomerically pure ligand/ metal complexes through racemic BIPHEP/metal complexes. X–Y: Enantiomerically pure ligand.



Scheme 3. Preparation and isolation of the diastereomeric (S)-PhGly/BIPHEP/Ru(II) complexes (S_A , S_P)-4a and (S_A , R_P)-4b.

ciency) from each other, when the second enantiomerically pure ligand(s) binds to the racemic complex.^{10–12} We here describe the preparation and isolation procedures for the diastereomerically pure and mixed (*S*)-PhGly/BIPHEP/Ru(II) complexes, and the catalytic performance with Li₂CO₃ examined in the enantioselective cyanosilylation of benzaldehyde.

Results and Discussion

Preparation of the Diastereomerically Pure and Mixed (S)-PhGly/BIPHEP/Ru(II) Complexes. The PhGly/ BIPHEP/Ru(II) complexes were prepared according to the previous method for the synthesis of the PhGly/BINAP/Ru(II) complexes.^{3a} Thus, an achiral diphosphine BIPHEP (0.51 mmol) reacted with $[RuCl_2(\eta^6-C_6H_6)]_2$ (0.25 mmol) in DMF at 100 °C to give the chiral but racemic Ru(II) complex $[\operatorname{RuCl}_2\{(\pm)-\operatorname{biphep}\}(\operatorname{dmf})_n]^{13}$ (Scheme 3). The DMF solution of this crude complex was mixed with a methanol solution of sodium (S)-phenylglycinate (1.5 mmol) at ambient temperature to afford a 1:1 mixture of $[Ru\{(S)-phgly\}_2\{(S)-biphep\}]$ $[(S_A, S_P)-4\mathbf{a}]$ and $[\operatorname{Ru}\{(S)-\operatorname{phgly}\}_2\{(R)-\operatorname{biphep}\}]$ $[(S_A, R_P)-4\mathbf{b}]$. These complexes were sufficiently stable for isolation with silica gel column chromatography, so that 4a (40%) and 4b (39%) were obtained in a pure form (see the Experimental Section). When (S_A, S_P) -4a was mixed with LiBr, the Ru·Li combined complex $[Li(Ru\{(S)-phgly\}_2\{(S)-biphep\})]Br$ $[(S_A, S_P)-5a]$ was obtained as a crystalline compound. The structure was determined by a single-crystal X-ray analysis, as shown in Figure 1, and closely resembles that of the previously reported $[Li(Ru\{(S)-phgly\}_2\{(S)-binap\})]Br, including$ the position of the Li cation and Br anion.^{3c}

Isomerization of the (S)-PhGly/(R)-BIPHEP/Ru(II) Complex to the Equilibrium Mixture. The (S)-PhGly/(R)-BIPHEP/Ru(II) complex (S_A , R_P)-4b was a stable single isomeric compound at ambient temperature, but took the form of a diastereomeric equilibrium mixture of (S_A , S_P)-4a and (S_A , R_P)-4b under the appropriate thermodynamic conditions



Figure 1. ORTEP drawing of (*S*_A,*S*_P)-5a. This structure is optimized with THF molecules, which are omitted for clarity. Selected distances (Å) and bond angles (deg): Ru–O1 2.092(8), Ru–O3 2.109(7), Ru–N1 2.171(1), Ru–N2 2.207(1), Ru–P1 2.277(3), Ru–P2 2.286(3), C1–O1 1.290(1), C1–O2 1.266(8), Li–O2 1.937(3), N1–Br 3.399(1), N2–Br 3.480(1); O1–Ru–O3 162.4(3), N1–Ru–N2 88.4(4), P1–Ru–P2 90.4(1). Only amino and methyne protons of PhGly are shown for clarity.

(Table 1).⁸ When (S_A, R_P) -4b was heated at 120 °C for 3 h in 1,4-dioxane, a 61:39 mixture of (S_A, S_P) -4a and (S_A, R_P) -4b was obtained (Entry 1). The same ratio of the diastereomers was also achieved in the isomerization of (S_A, S_P) -4a, indicating that equilibrium between 4a and 4b was reached under these conditions. A longer period of 6 h was required to attain the equilibrium at 110 °C (Entry 2). The isomerization at 100 °C did not reach equilibrium even after 12 h (Entry 3). An acyclic polyether diglyme was somewhat less effective for this purpose (Entry 4). Messy compounds were obtained at 160 °C (Entry 5). The isomerization very sluggishly proceeded in THF or DME (Entries 6 and 7).

Table 1. Isomerization of (S_A, R_P) -4b to the Mixture of (S_A, S_P) -4a and (S_A, R_P) -4b^{a)}

(S_A, R_P) -4b \longrightarrow (S_A, S_P) -4a + (S_A, R_P) -4b						
single isomer		diastereomeric mixture				
Entry	Solvent	Temp/°C	Time/h	$4a/4b^{b)}$		
1	1,4-dioxane	120	3	61:39		
2	1,4-dioxane	110	6	61:39		
3	1,4-dioxane	100	12	58:42		
4	diglyme	110	5	42:58		
5	diglyme	160	2	c)		
6	THF	100 ^{d)}	12	1:99		
7	DME	100	12	3:97		

a) Isomerizations were conducted in 20 mM solution of the complex. b) Diastereomeric ratio of (S_A, S_P) -4a and (S_A, R_P) -4b determined by ³¹P NMR analysis. c) Messy compounds were observed. d) Reaction in a sealed tube.



Scheme 4. Proposed isomerization pathway between (S_A, R_P) -4b and (S_A, S_P) -4a. L: (S)-PhGly. S: Solvent.

The plausible isomerization pathway between (S_A, R_P) -**4b** and (S_A, S_P) -**4a** is shown in Scheme 4. One of two Ru–P bonds in (S_A, R_P) -**4b** is cleaved under the heating conditions to form an intermediate, which is stabilized by coordination of solvent(s) (1,4-dioxane for instance) to Ru. Rotation of the BIPHEP moiety around the biphenyl axis followed by reforming the chelate structure to afford the diastereomeric (S_A, S_P) -**4a**. The ratio of (S_A, S_P) -**4a** and (S_A, R_P) -**4b** (61:39) is dependent on the relative stability in the equilibrium. This explanation is consistent with the previously reported isomerization mechanism of [RuCl₂(biphep){ (S_aS) -dpen}].^{8b}

Asymmetric Cyanosilylation of Benzaldehyde with the (S)-PhGly/BIPHEP/Ru(II) Catalysts. We next examined the catalytic efficiency of the (S_A, S_P) -4a/Li₂CO₃ system (4a: Li₂CO₃ = 1:1) for asymmetric cyanosilylation of aldehyde 1 (Scheme 5). The reaction was carried out with a 1.2 equiv of (CH₃)₃SiCN in the presence of the 4a/Li₂CO₃ system at an S/C of 10000 in ether at $-78 \,^{\circ}$ C for 6 h to produce the *R* silylated cyanohydrin (*R*)-2 in 96% ee quantitatively (see the Experimental Section). The ee value was comparable to that observed in the reaction with the (S_A, S_P) -3/Li₂CO₃ catalyst system of 97%, and the sense of enantioselection was the same in both cases (Scheme 1).^{3a} This result suggested that the (S)-BIPHEP/Ru(II) structure of 4a was maintained through the

0 H + (CH ₃) 1 1:4:Li ₂ CO ₃ = 10000:1:1	∋₃SiCN -	4 , Li ₂ CO ₃ (C ₂ H ₅) ₂ O −78 °C	(CH ₃) ₃ SiO_CN (<i>R</i>)-2
4	Time, h	% Yield	% ee
(<i>S</i> _A , <i>S</i> _P)-4a	6	>99	96
(<i>S</i> _A , <i>R</i> _P)- 4b	6	30	2.6
(<i>S</i> _A , <i>S</i> _P) -4a /(<i>S</i> _A , <i>R</i> _P) -4b = 61:39	18	94	92

Scheme 5. Enantioselective cyanosilylation of 1 with the 4/Li₂CO₃ catalyst system.

catalytic performance, and the function was similar to that of the (S)-BINAP/Ru(II) moiety of **3**.

The reactivity and enantioselectivity were significantly decreased by using the (S_A, R_P) -4b/Li₂CO₃ system as a catalyst under the same conditions (Scheme 5). This result was consistent with that observed in the reaction using the corresponding BINAP complex.² When the cyanation was conducted using the 61:39 (S_A, S_P) -4a/ (S_A, R_P) -4b equilibrium mixture with Li₂CO₃ for 18 h, (R)-2 was obtained in 94% yield and 92% ee. The reaction rate and the enantioselectivity were lower than those obtained using pure (S_A, S_P) -4a and the Li₂CO₃ system, but the decrease in the ee value was much smaller than we expected based on the 4a/4b ratio. Then we measured the ee value of 2 in the reaction catalyzed by the (S_A, S_P) -4a/ (S_A, R_P) -4b mixture with various diastereometric ratios in the presence of Li_2CO_3 under the regular conditions (1:(CH₃)₃-SiCN:4:Li₂CO₃ = 10000:12000:1:1, -78 °C). These data were plotted on the graph of Figure 2a and are indicated by filled circles (). High ee values were obtained even by using the 4a/4b mixtures in low ratio. For instance, product 2 in 88% ee was obtained in the cyanation with a 40:60 (S_A, S_P) -4a/ (S_A, R_P) -4b mixture. Then, we performed kinetic studies to elucidate the nonlinear relationship between the diastereomeric purity of 4 and the ee value of 2.

We measured the time-conversion data for the cyanosilylation of 1 catalyzed by the $4a/Li_2CO_3$ and the $4b/Li_2CO_3$ systems. As shown in Figure 2b, there was a huge difference in the rate between these two catalytic reactions. The reaction rate ratio $\alpha (k_{4a}/k_{4b})^{14}$ was calculated to be 16.8. When the reaction is conducted with an x:(100 - x) mixture of (S_A, S_P) -4a and (S_A, R_P) -4b, we here introduce the imaginary 4a/4b diastereomeric ratio y:(100 - y) considering the factor of the reaction rate, where

$$y = \frac{100x}{x + \frac{100 - x}{\alpha}}$$
(1)

The theoretical % ee of product 2 ($ee_{2/cal}$) is given by

$$ee_{2/cal} = \frac{ee_{2/4a}y + ee_{2/4b}(100 - y)}{100}$$
(2)

in which $e_{2/4a}$ and $e_{2/4b}$ indicate the % ee of 2 in the reaction catalyzed by the $4a/Li_2CO_3$ and the $4b/Li_2CO_3$ systems, respectively. As shown in Scheme 5, the $e_{2/4a}$ and $e_{2/4b}$ are



Figure 2. Enantioselective cyanosilylation of 1. a) Relationship between the 4a/4b ratio and the evalue of the product 2; •: Experimental data; \triangle : Theoretical data. b) Reaction time-conversion relationship; \bigcirc : The reaction with the (S_A, S_P) - $4a/Li_2CO_3$ catalyst; \times : The reaction with the (S_A, R_P) - $4b/Li_2CO_3$ catalyst.

experimentally determined to be 96% and 2.6%, respectively. Thus,

$$ee_{2/cal} = 0.934y + 2.6$$
 (3)

The eqs 1 and 3, and $\alpha = 16.8$ afford the relationship between $e_{2/cal}$ and *x*:

$$ee_{2/cal} = \frac{93.4}{1 + \frac{1}{16.8} \left(\frac{100}{x} - 1\right)} + 2.6$$
(4)

The values of eq 4 were plotted on the graph of Figure 2a and are indicated with open triangles (\triangle), and these findings agree well with the experimental data shown with \bullet . These results suggest that the cyanation is catalyzed by the monomeric species, and the product ee value is primarily determined by the **4a/4b** ratio as well as the reactivity and enantioselectivity of each catalytic species.

Conclusion

A 1:1 diastereomeric mixture of $[Ru\{(S)-phgly\}_2\{(S)-biphep\}]$ $[(S_A,S_P)-4a]$ and $[Ru\{(S)-phgly\}_2\{(R)-biphep\}]$ $[(S_A,R_P)-4b]$ is readily prepared from the achiral (*tropos*) diphosphine BIPHEP in two steps. The chiral (*atropos*) structure of the BIPHEP/Ru(II) moiety due to the suppression of rotation around the biphenyl axis with the two Ru–P coordination bonds of the complexes is sufficiently stable at the ambient temperature. The diastereomeric complexes $(S_A,S_P)-4a$ and $(S_A,R_P)-4b$ are separated by silica gel column chromatography into pure compounds. $(S_A,S_P)-4a$ and LiBr form the Ru-Li bimetallic complex [Li(Ru{(S)-phgly}_2{(S)-biphep})]Br [$(S_A,S_P)-5a$]. The structure determined by a single-crystal X-ray analysis closely resembles the corresponding (S)-BINAP complex.

Isomerization of (S_A, R_P) -**4b** occurs at 120 °C in 1,4-dioxane to give a 61:39 equilibrium mixture of (S_A, S_P) -**4a** and (S_A, R_P) -**4b** in 3 h. The rate of isomerization depends on the temperature and solvent, suggesting that the isomerization proceeds through a monodentate BIPHEP/Ru(II) intermediate stabilized by the coordination of solvent(s).

The catalyst system of (S_A, S_P) -**4a** and Li₂CO₃ exhibits high reactivity and enantioselectivity for asymmetric cyanosilylation of benzaldehyde (1) to afford the product (*R*)-**2** in 96% ee. The catalyst performance is comparable to that of the previously reported [Ru{(*S*)-phgly}₂{(*S*)-binap}]/Li₂CO₃ system, suggesting that the chiral function of the (*S*)-BIPHEP/Ru(II) moiety resembles that of the (*S*)-BINAP/Ru(II) group.

The 61:39 equilibrium mixture of (S_A, S_P) -4a and (S_A, R_P) -4b with Li₂CO₃ catalyzes the reaction of 1 to yield (*R*)-2 in 92% ee. The enantioselectivity is just slightly lower than that with the pure (S_A, S_P) -4a/Li₂CO₃ catalyst system. Based on kinetic experiments, the high enantioselective ability of the diastereomerically mixed catalyst is elucidated: the highly enantioselective (S_A, S_P) -4a/Li₂CO₃ system catalyzes the reaction 16.8 times faster than the less selective (S_A, R_P) -4b/Li₂CO₃ system, giving (*R*)-2 in 2.6% ee. The relationship between the 4a/4b ratio (4a:4b = x:(100 - x)) and the % ee value of 2 (ee_{2/cal}) is approximated by eq 4.

Experimental

General. The commercially available benzaldehyde and $(CH_3)_3SiCN$ from Wako Pure Chemical Industries, Ltd. were used after distillation. Anhydrous $(C_2H_5)_2O$, THF, DME, 1,4-

dioxane, diglyme, DMF, pentane, CH₂Cl₂, and methanol were purchased from Kanto Chemical Co., Inc. and used without further purification. Li₂CO₃ was purchased from Aldrich Co. and used as a 0.1 M aqueous solution. NMR spectra were recorded on a JEOL JNM-ECS400 or LA400 (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR, 161.7 MHz for ³¹P NMR) spectrometer. The chemical shifts were reported downfield from TMS ($\delta = 0$) for ¹H NMR. For ¹³C NMR, the chemical shifts were reported on a scale relative to the solvent used as an internal reference. Carbon multiplicity was assigned by DEPT experiments. ³¹P NMR was carried out with phosphoric acid as an external standard. Gas chromatography (GC) analysis was conducted on a Shimadzu GC-17A or GC-2010 instrument using helium carrier gas. Mass-spectrometric measurements and elemental analysis were carried out at the Instrumental Analysis Division, Equipment Measurement Center, Creative Research Institution, Hokkaido University.

Preparation of Ruthenium Complexes [Ru{(S)-phgly}2- $\{(S)\text{-biphep}\}$ [(S_A,S_P)-4a] and [Ru $\{(S)\text{-phgly}\}_2$ {(R)-biphep}] $[(S_{A}, R_{P})-4b].$ $[RuCl_2(\eta^6-C_6H_6)]_2$ (127 mg, 0.25 mmol) and BIPHEP (262 mg, 0.51 mmol) were placed in a 50-mL Schlenk flask. After the air in the flask was replaced with argon, degassed DMF (10 mL) was added, and the mixture was heated at 100 °C for 10 min with stirring to give a reddish brown solution. After the solution was cooled to 25 °C, a degassed methanol solution (10 mL) of sodium (S)-phenylglycinate (260 mg, 1.5 mmol) was added and the mixture was stirred for 12 h. After removal of the solvent under reduced pressure, the residue was dissolved with ethyl acetate (80 mL). The solution was washed with water (100 mL \times 3) and brine, and then dried over MgSO₄. After evaporation of the solvent, the crude complex $((S_A, S_P)-4a:(S_A, R_P)-4b = 1:1.06$ determined by ¹Hand ³¹P NMR measurement) was purified by silica gel column chromatography (eluent: ethyl acetate to 1:9 methanol/ethyl acetate, R_f of (S_A, S_P) -4a = 0.47–0.63 (eluent: ethyl acetate), R_f of (S_A, R_P) -4b = 0.26–0.39 (eluent: ethyl acetate)). Each complex was precipitated with a mixture of CH2Cl2 (2mL) and pentane (50 mL) to afford (S_A, S_P) -4a (light yellow powder, 187 mg, 40% yield) and (S_A, R_P) -4b (light yellow powder, 182 mg, 39% yield), respectively. (S_A, S_P) -4a: mp (decomp) 212 °C; ¹H NMR (400 MHz, CDCl₃): δ 2.60 (m, 2H, NHH), 3.31 (m, 2H, NHH), 3.74 (t, 2H, J = 8.3 Hz, 2PhCH), 6.03 (d, 2H, J = 6.8 Hz, aromatic H), 6.73–9.02 (m and br, 36H, aromatic H); ³¹P NMR (161.7 MHz, CDCl₃): δ 51.4 (s); HRMS (ESI): *m/z* calcd for C₅₂H₄₄N₂O₄P₂Ru: 924.1834 ([M]⁺); found: 942.1826. (S_A, R_P) -4b: mp (decomp) 210 °C; ¹H NMR (400 MHz, CDCl₃): δ 2.21 (br, 2H, NHH), 2.53 (br, 2H, NHH), 4.68 (br, 2H, 2PhCH), 5.93 (d, 2H, J = 6.8 Hz, aromatic H), 6.41–8.67 (m, 36H, aromatic H); ³¹P NMR (161.7 MHz, CDCl₃): δ 50.7 (s); HRMS (ESI): m/z calcd for C₅₂H₄₄N₂O₄P₂Ru: 924.1834 ([M]⁺); found: 942.1832.

Preparation of Bimetallic Complex [Li(Ru{(*S*)-phgly}₂-{(*S*)-biphep})]Br [(*S*_A,*S*_P)-5a]. A THF solution of LiBr (0.1 M, 150 μ L, 15 μ mol) was added to (*S*_A,*S*_P)-4a (12 mg, 13 μ mol) in a 20-mL Schlenk tube under an argon atmosphere. The clear orange solution was stored at ambient temperature for 10 h and at -11 °C (normal freezer) for 7 h. The precipitated yellow solid was filtered and washed with a small amount of cold THF followed by drying under reduced pressure to afford (*S*_A,*S*_P)-**5a** as yellow needles (8 mg, 8.6 μmol, 66% yield). Mp (decomp) 153 °C; ¹H NMR (400 MHz, THF-*d*₈): δ 2.96 (m, 2H, N*H*H), 3.63 (m, 2H, 2PhC*H*, partially overlapped to a peak of THF), 4.98 (t, 2H, *J* = 8.3 Hz, NH*H*), 6.02 (d, 2H, *J* = 7.6 Hz, aromatic H), 6.74 (t, 2H, *J* = 7.6 Hz, aromatic H), 6.97–7.58 (m and br, 32H, aromatic H), 7.75–8.89 (br, 2H, aromatic H); ³¹P NMR (161.7 MHz, THF-*d*₈): δ 53.1 (s); HRMS (ESI⁺) *m/z* calcd for C₅₂H₄₄LiN₂O₄P₂¹⁰²Ru: 931.1980 ([**3a** + Li]⁺); found: 931.1975.

The crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 910499. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Isomerization of (S_A, R_P) -4b to the Equilibrium 4a/4b Mixture. A degassed 1,4-dioxane (0.5 mL) solution of (S_A, R_P) -4b (9.2 mg, 10 µmol, 20 mM) was stirred and heated at 120 °C (oil bath temperature) for 3 h under argon atmosphere. After cooling to room temperature, ³¹P NMR measurement of the solution was carried out to estimate the ratio of (S_A, S_P) -4a/ (S_A, R_P) -4b. The data are listed in Table 1.

General Procedure of Asymmetric Cyanosilylation of Benzaldehyde (1). Caution: (CH₃)₃SiCN must be used in a well-ventilated hood due to its high toxicity.

A 50-mL Schlenk flask equipped with a Teflon-coated magnetic stirring bar was filled with argon. (CH₃)₃SiCN (1.19 g, 12.0 mmol) and 0.10 M aqueous solution of Li₂CO₃ (10 µL, 1.0 µmol) were placed in the flask, and the mixture was stirred for 30 min at 25 °C. To the pale yellow solution were added $(C_2H_5)_2O$ (10 mL), a 20 mM-THF solution of (S_A, S_P) -4a (50 µL, 1.0µmol), and tetralin (0.97 g, 7.34 mmol) as an internal standard for GC analysis. The resulting yellow solution was cooled down to -78 °C. Then 1 (1.06 g, 10.0 mmol) was charged into the flask, and the mixture was stirred for 12 h. The product was identified in accordance with the literature,^{3a} and the yield and ee of the product were determined by GC analysis (>99% yield, 96% ee). The ee of 2 was determined by GC analysis: column, CP-Chirasil-Dex (0.32 mm i.d. \times 25 m, df = 0.25 µm; Varian); column temp, 110 °C; injection temp, 220 °C; retention time (t_R) of (R)-2, 22.8 min (98.0%); t_R of (S)-2, 22.3 min (2.0%).

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Supporting Information

Copies of the ¹H and ³¹P NMR spectra of the Ru complexes **4** and the chiral GC charts of the compounds **2**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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