Optically Pure 1,2-Bis[(*o*-alkylphenyl)phenylphosphino]ethanes and Their Use in Rhodium-Catalyzed Asymmetric Hydrogenations of α-(Acylamino)acrylic Derivatives

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This paper is dedicated to Dr. Joe P. Richmond on the occasion of his 60th birthday.

Abstract: Optically pure (*S,S*)-1,2-bis[(*o*-alkylphenyl)-phenylphosphino]ethanes **1a–d** were prepared in four steps from phenyldichlorophosphine *via* phosphine-boranes as the intermediates. The rhodium complexes **5a–d** of these diphosphines were used for the asymmetric hydrogenations of α-(acylamino)-acrylic derivatives including β-disubstituted derivatives. Markedly high enantioselectivity (78–>99%) was observed for the reduction of β-monosubstituted derivatives. β-Disubstituted derivatives were also reduced in considerably high enantioselectivity (up to 90%). The single crystal X-ray analysis of the rhodium complex **5c** of (*S,S*)-1,2-bis[phenyl(5′,6′,7′,8′-tetrahydronaphthyl)phosphino]ethane (**1c**) revealed its δ-type structure with face orientation of the two tetrahydronaphthyl groups and edge orientation of the two phenyl groups. This conformation corresponds to that of the rhodium complex of 1,2-bis[(*o*-methoxyphenyl)phenylphosphino]ethane (DIPAMP); the rhodium complex of (*R,R*)-DIPAMP, whose chirality at phosphorus is opposite that of **5c**, exhibits a λ-type structure with the face orientation of the two *o*-methoxyphenyl groups and the edge orientation of the two phenyl groups. The conformational similarity of these rhodium complexes as well as the stereochemical outcome in the asymmetric hydrogenations means that the coordinative interaction of the methoxy group of DIPAMP with rhodium metal is not the main factor that affects asymmetric induction.

Keywords: asymmetric catalysis; asymmetric hydrogenation; enantioselectivity; rhodium catalysts; P-stereogenic ligands

Introduction

Optically active phosphine ligands have played an important role in various catalytic asymmetric reactions, and numerous chiral phosphines have been designed and synthesized over the past three decades.[1,2] Most chiral phosphine ligands hitherto reported possess their chiral centers not at the phosphorus atoms but at the carbon backbones. On the other hand, a relatively small number of P-stereogenic phosphines has been reported so far, and some of them played an important role in the early stages of the history of homogeneous asymmetric hydrogenation.[3–8] This is largely ascribed to the fact that the phosphines of this class are not easily available using earlier methods.[2j] Apart from the synthetic difficulties, some P-stereogenic phosphines are potentially useful in catalytic asymmetric syntheses. For example, PAMP,[5] CAMP,[5] DIPAMP,[6–9] 1,3-bis[(*o*-methoxyphenyl)phenylphosphino]propane,[10] DIPAMP-PYRPHOS[11], and 1,1-bis[(*o*-methoxyphenyl)phenylphosphino]ferrocene[12–14] are known to provide high enantiomeric excesses of products in the asymmetric hydrogenation of α-(acylamino)acrylic derivatives.[15] It is noteworthy that these ligands possess an *o*-methoxyphenyl group at the phosphorus atoms. The role of the methoxy group in asymmetric induction remains unclear, but a weak interaction of the methoxy oxygen with a metal center is suggested as one of the factors that effects the enantioselectivity of the hydrogenation.[16] We questioned this explanation and decided to investigate the role of the methoxy group in the DIPAMP ligand.

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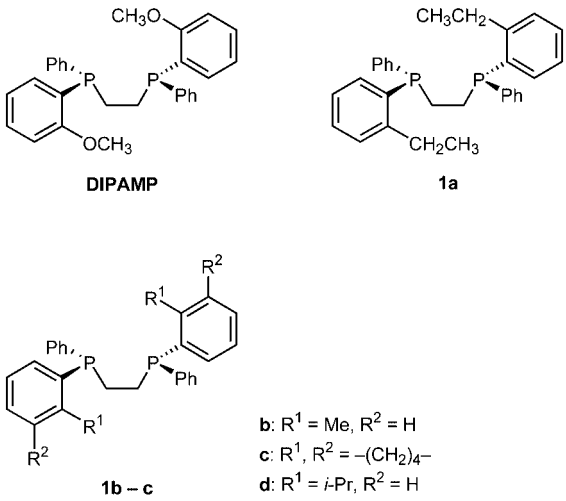


Figure 1. (*S,S*)-DIPAMP and (*S,S*)-bis[(*o*-alkylphenyl)phenylphosphino]ethanes.

In this paper we report the synthesis of a series of structurally similar diphosphines containing alkyl groups of various sizes in one of the two phenyl rings bonded to each phosphorus atom (Figure 1) as well as the comparison of the sense and order of enantioselection of their reactions with those catalyzed by Rh-DIPAMP.[17]

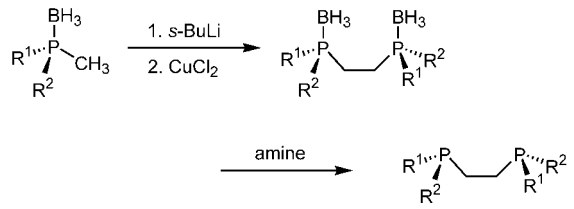
Results and Discussion

Synthesis of Optically Pure 1,2-Bis[(*o*-alkylphenyl)phenylphosphino]ethanes

Previously, we reported that the optically pure bidentate P-stereogenic phosphine ligands can be prepared by using phosphine-boranes as the intermediates (Scheme 1).[18] The method involves the following characteristic features: (1) The dimerization products, di(phosphine-boranes), are obtained as almost enantiomerically pure compounds, even though the enantiopurities of the starting phosphine-boranes are not very high, since the *meso*-isomers can be removed by recrystallization or chromatography. (2) Intermediate phosphine-boranes are stable in air and moisture and can be handled easily. (3) The final step of removing the boranato group proceeds under mild conditions without any racemization of the diphosphines.[19]

This methodology was applied to the preparation of the desired optically active bidentate phosphines. The overall reaction sequence is shown in Scheme 2.

Dichlorophenylphosphine was allowed to react sequentially with *o*-alkylphenylmagnesium bromide, lithium *l*-menthoxide, and borane-THF to afford a mixture of two diastereomers, **(S_P)-2a–d** and **(R_P)-2a–d**, in good yields. Each diastereomer was obtained by fractional re-



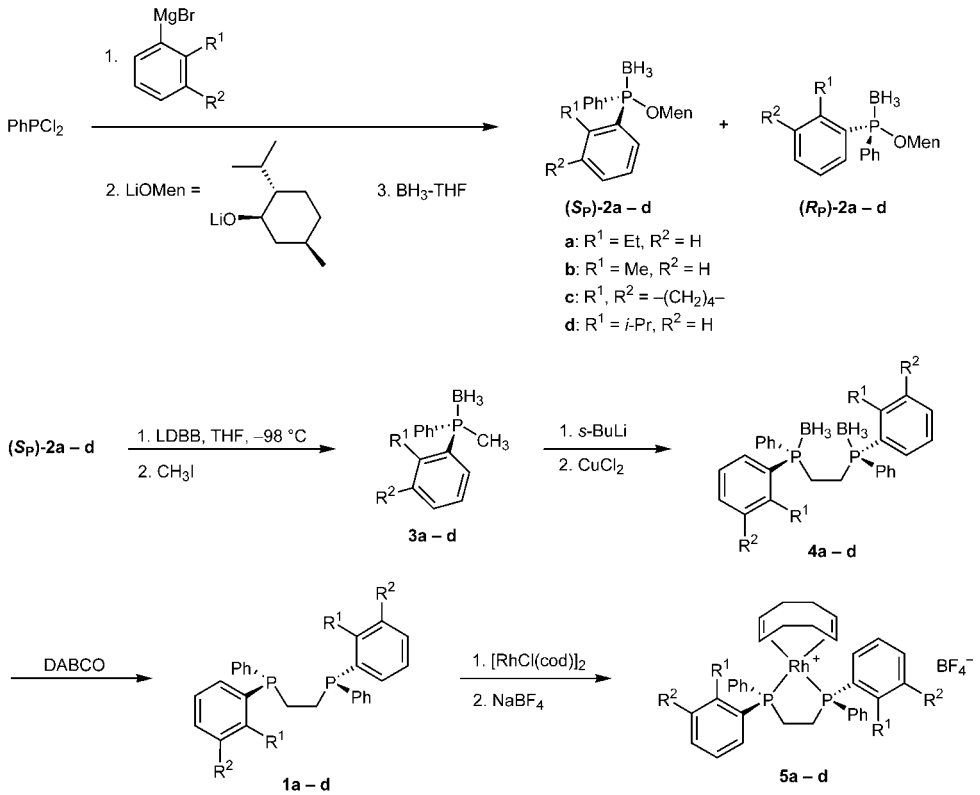
Scheme 1.

crystallization or preparative HPLC. The absolute configurations at asymmetric phosphorus atom of the four diastereomers **(S_P)-2a–d** were determined by single crystal X-ray analysis. Compounds **(S_P)-2a–d** were reduced by treatment with a large excess of lithium 4,4′-di-*t*-butylbiphenylide (LDBB)[20] at $-98\,^{\circ}C$, followed by reaction with iodomethane, to furnish **(*S*)-3a–d** with about 90% ee.[21] Without further purification, **(*S*)-3a–d** were converted to dimerization products *via* successive reactions with *s*-butyllithium and copper(II) chloride, and the resulting products were recrystallized to afford enantiomerically pure phosphine-boranes **(*S,S*)-4a–d**. The two boranato groups of these compounds were removed by reaction with 1,4-diazabicyclo[2.2.2]octane (DABCO) in toluene at $50\,^{\circ}C$ for 30 min to furnish the desired phosphine ligands **(*S,S*)-1a–d** in an almost quantitative yield.

These ligands were reacted with $[RhCl(cod)]_2$, followed by treatment with $NaBF_4$, to afford the corresponding rhodium cationic complexes **5a–d** as air-stable orange powders.

Asymmetric Hydrogenation of α-(Acylamino)acrylic Derivatives

Rhodium complexes **5a–d** were used in the catalytic asymmetric hydrogenation of α-(acylamino)acrylic derivatives (Eq. 1). In order to compare the hydrogenation results, the reactions were carried out under the same conditions as those employed by Knowles et al. in the experiments using DIPAMP.[6,7] The results are summarized with reported results in Table 1. It should be noted that the use of complex **5a** with the *o*-ethyl group as a catalyst provided remarkably high ees of the products, and the overall performance of this complex is comparable to that of Rh-DIPAMP. These results indicate that the *o*-ethyl group of **5a** is not less effective as a stereodiscriminating factor than the *o*-methoxy group of DIPAMP. Fairly high enantioselectivity with up to 92% ee was observed even when the least sterically congested ligand **1b** bearing an *o*-methylphenyl group was employed.[22] The ligands with larger alkyl substituents (**1c, d**) provided almost perfect enantioselectivity (> 99% ee). Another significant fact is that the catalysts prepared from **1a–d**, whose chirality at phosphorus atoms is (*S,S*), provided hydrogenation products with *R* configuration. This indicates the same sense of enan-



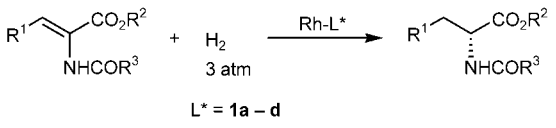
Scheme 2. Synthesis of optically active 1,2-bis[(*o*-alkylphenyl)phenylphosphino]ethanes and their rhodium complexes.

Table 1. Asymmetric hydrogenation of β-monosubstituted α-(acylamino)acrylic acids catalyzed by rhodium complexes of (*S,S*)-1,2-bis[(*o*-substituted phenyl)phenylphosphine]ethanes.

R^1	R^2	R^3	Solvent	Temperature	ee [%] of product[a]				
					5a	**5b**	**5c**	**5d**	**Rh–DIPAMP**[b]
Ph	H	CH_3	*i*-PrOH	50 °C	90	89	93	92	96
Ph	H	Ph	*i*-PrOH	50 °C	86	91	93	93	93
Ph	CH_3	CH_3	*i*-PrOH	50 °C	97	92	>99	>99	97
Ar[c]	H	CH_3	*i*-PrOH/H_2O (88/12)	50 °C	91	90	92	91	94
H	H	CH_3	EtOH	25 °C	93	90	94	96	90
H	CH_3	CH_3	MeOH	25 °C	91	84	90	78	95

[a] All hydrogenations using rhodium complexes **5a–d** prepared from ligands **1a–d** possessing (*S,S*)-configuration afforded (*R*)-amino acid derivatives.
[b] The original paper of Knowles et al. described that (*S*)-products were produced by the use of (*R,R*)-DIPAMP.[6,7] Therefore, the use of (*S,S*)-DIPAMP produces (*R*)-products.
[c] Ar = 4-AcO-3-$MeOC_6H_3$.

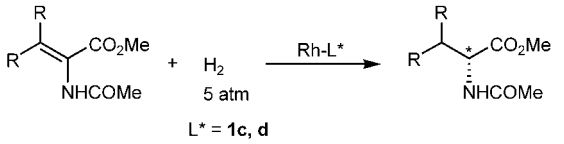
tioselection as in the case of DIPAMP [*S* products from (*R,R*)-DIPAMP]. Thus, the enantioselection of the same sense and comparable degree is observed for DIPAMP and **1a–d**. This means that the donating ability of the methoxy group of DIPAMP is not the main factor that effects the asymmetric induction.



(1)

We also tried the asymmetric hydrogenations of β,β-disubstituted α-(acylamino)acrylates to clarify the potential synthetic utility of **1a–d** (Eq. 2). While asymmetric hydrogenations of β-monosubstituted α-(acylamino)-acrylates usually give good results, the reduction of β,β-disubstituted α-(acylamino)acrylates in high enantioselectivity has been notoriously difficult with the exception of recent studies by several research groups.[23] For example, methyl β,β-dimethyl-α-(*N*-acetylamino)-acrylate has been reported with 55% ee by using the DIPAMP-Rh complex.[28] The results of using the rhodium complexes **5c, d** are summarized in Table 2. It is note-

worthy that higher enantioselectivities of up to 89% were obtained. These results indicate that it is possible to improve or tune enantioselectivity by changing the *o*-methoxy group to an alkyl group in the structure of P-stereogenic ligands.



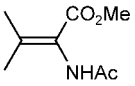
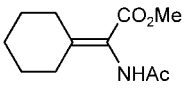
(2)

X-Ray Crystallographic Analysis of the Rhodium Complex 5c

The most attractive compound for this X-ray study would be the rhodium complex **5a**, since its molecular structure closely resembles that of DIPAMP. However, we failed to obtain good single crystals of **5a** for the X-ray analysis. Instead, we succeeded in the X-ray analysis of the complex **5c**. The ORTEP drawing is shown in Figure 2. The molecular structure is compared with the reported structure of the DIPAMP-Rh complex. Both structures possess C_2 symmetry, they closely resemble each other except for the opposite absolute configuration at the chiral phosphorus atoms. Selected interatomic distances and angles are listed in Table 3. The rhodium atom is nearly square planar, and the P–Rh–P angle of 83.6° is comparable to the values observed in DIPAMP-Rh complex (83°).[7] The distance between the rhodium and the benzylic carbon is 3.73 Å. This value is almost equal to the reported distance (3.7 Å) between the rhodium and the methoxy oxygen in the DIPAMP-Rh complex. This is particularly interesting because the distances do not change despite the lack of the coordination ability in **5c**.

Rhodium complex **5c** exhibits a δ-type conformation of the hydrocarbon backbone in the solid state. The rhodium complex of (*R,R*)-DIPAMP, whose chirality at phosphorus is opposite to that of **1c**, forms a λ-type structure. In both structures, the *o*-substituted phenyl groups are face-oriented and occupy the equatorial positions, and the edge-oriented phenyl groups are located at the

Table 2. Asymmetric hydrogenation of methyl β,β-disubstituted α-(acetylamino)acrylates by the use of **5c** or **5d**.[a]

Substrate	Precatalyst	Solvent	ee [%] (Config.)[b,c]
	**5c**	MeOH	87 (*R*)
"	**5c**	C_6H_6	90 (*R*)
"	**5d**	MeOH	79 (*R*)
"	**5d**	C_6H_6	89 (*R*)
	**5c**	MeOH	89 (*R*)
"	**5c**	C_6H_6	86 (*R*)
"	**5d**	MeOH	73 (*R*)
"	**5d**	C_6H_6	75 (*R*)

[a] All reactions were carried out at 50 °C and an initial H_2 pressure of 6 atm for 12–24 h with a substrate/catalyst ratio of 100.

[b] Enantiomeric excesses were determined by chiral capillary GC using a Chrompack Chirasil-L-Val column (25 m).

[c] Absolute configurations were assigned by comparison of chiral GC elution order with the one described in the literature.[24]

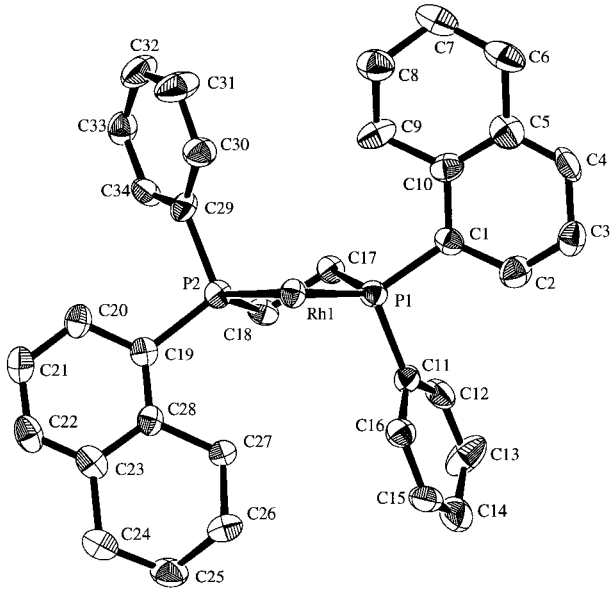


Figure 2. Molecular structure of cation complex **5c** (ORTEP). Coordinated cyclooctadiene and counter anion (BF_4^-) are omitted for clarity.

Table 3. Selected interatomic distances and intramolecular angles for **5c** {[Rh(cod)(**1c**)]$^+$[BF_4^-]}.

Interatomic distances (Å)			
Rh(1)–P(1)	2.290(5)	Rh(1)–P(2)	2.274(5)
P(1)–C(1)	1.79(2)	P(1)–C(11)	1.82(2)
P(1)–C(17)	1.83(2)	P(2)–C(19)	1.84(2)
P(2)–C(29)	1.85(2)	P(2)–C(18)	1.82(2)
Intramolecular angles (deg)			
P(1)–Rh(1)–P(2)	83.6(2)	Rh(1)–P(1)–C(1)	118.6(6)
Rh(1)–P(1)–C(11)	113.8(6)	Rh(1)–P(1)–C(17)	108.0(5)
Rh(1)–P(2)–C(19)	116.5(5)	Rh(1)–P(2)–C(29)	111.1(6)
Rh(1)–P(2)–C(18)	110.0(6)		
Intramolecular non-bonding distances (Å)			
Rh(1)–C(9)	3.68	Rh(1)–C(27)	3.77

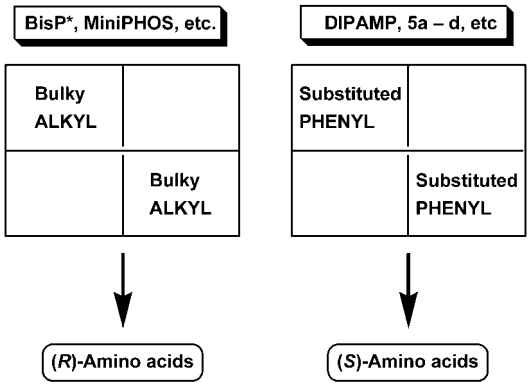


Figure 3. Quadrant diagrams.

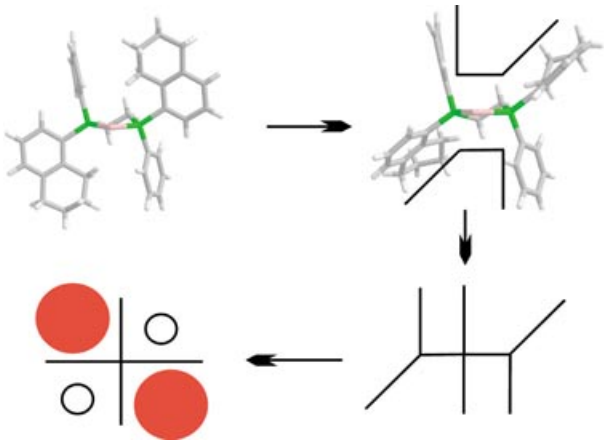


Figure 4. Schematic illustration of the possibility to regard unsubstituted phenyls of **5c** as "bulky" substituents. The X-ray-based structure of **5c** shown in the upper left corner is conformationally modified by rotation around two P–C bonds producing "pockets" appropriate for the coordination of a substrate in the upper right and lower left quadrants.

axial positions. The structural similarity of the rhodium complexes of **5c** and DIPAMP also demonstrates that a coordinative interaction of the methoxy group of DIPAMP with rhodium metal is not a main factor that effects the asymmetric induction.

Sense of Enantioselection in Asymmetric Hydrogenations with DIPAMP-Type Ligands and Other P-Stereogenic Diphosphines

The data described above demonstrate that even a minimal difference in size of the substituents of phosphorus (e.g., in the complex **5b**) is sufficient to secure enantioselectivities up to 92% ee, and increasing the size of the alkyl substituents results in the improved performance of the corresponding rhodium complexes. This clearly indicates the spatial control of the enantioselection. However, if the sense of enantioselection obtained with Rh-DIPAMP and **5a–d** is compared with that observed in asymmetric hydrogenations catalyzed with rhodium complexes of such ligands as DuPHOS, BisP*, MiniPHOS, BPE, BIPNOR, TangPHOS, etc., conclusions on the exact mechanism of stereoregulation become complicated. Indeed, a straightforward application of the quadrant diagrams would lead to the opposite conclusions for these two groups of ligands (Fig. 3).

In order to explain this contradiction, we suggest considering the difference in the conformational properties of these two groups. The aryl substituents of the DIPAMP-like ligands are conformationally flexible; the free rotation around the P–C bond can significantly change the asymmetric environment important for the enantioselectivity of hydrogenation. On the other hand, the asymmetric environment does not change upon any conformational change in the complexes of the ligands of the BisP* type. Hence, we suggest that the X-ray structures of the Rh complexes are not useful for the evaluation of the stereoregulating factors in the DIPAMP-like ligands, since, in solution, a favorable conformation acquired for any particular intermediate may be quite different from the solid-state conformation of the catalyst precursor.

In particular, the hindrance arising from the relatively bulky equatorial ligands can be almost eliminated by rotation around the P–C bonds, leaving in the corresponding quadrant a "pocket" appropriate for the coordination of the substrate (Fig. 4). However, the axial substituents hinder the access to the rhodium atom from above in any conformation of the phenyl ring. Thus, the hindrance from the unsubstituted phenyls in DIPAMP-like ligands can be rationalized, and the quadrant rule becomes generally applicable.

Conclusions

Synthesis of various C_2-symmetrical diphosphines **1a–d** has been accomplished *via* the phosphine-borane synthetic route. Testing their rhodium complexes as the catalysts for the asymmetric hydrogenation of representative dehydroamino acids demonstrated that the alkyl groups in the substituted phenyl rings of **1a–d** provide the same services in the asymmetric hydrogenations catalyzed by their rhodium complexes as the methoxy group in the *o*-methoxyphenyl rings of DIPAMP. Hence, the donating properties of the methoxy group in DIPAMP are an unlikely reason for its high efficiency, and the enantioselection in the asymmetric hydrogenations catalyzed by the rhodium complexes of DIPAMP and **1a–d** is induced by the spatial properties of the ligands. Comparing the sense of enantioselection provided by **5a–d** and Rh-DIPAMP with that observed in the asymmetric hydrogenations catalyzed by the rhodium complexes of the ligands with a conformationally stable asymmetric environment (BisP*, DuPHOS, etc.), we

conclude that the unsubstituted phenyls of Rh-DIPAMP and the rhodium complexes of **1a–d** actually hinder the substrate coordination.

Experimental Section

General Procedures

The NMR spectra were recorded on JEOL JNM-GSX-400 and JEOL JNM-GSX-500 spectrometers. The IR spectra were recorded on a JASCO FT/IR-200 spectrophotometer. Optical rotations were measured with a JASCO DIP-370 digital polarimeter with a 10-cm long cell. Analytical high-performance liquid chromatography (HPLC) was performed on a Shimazu LC-10AD pump and a Shimazu SPD-10A UV-VIS detector. Preparative HPLC was performed on a JAI LC-908 recycling preparative HPLC. Mass spectra were obtained on JEOL JMS-HX110 and JEOL JMS-DX-300 (FD-Mass) instruments. Microanalysis was performed on a Perkin-Elmer 240B instrument at the Chemical Analysis Center of Chiba University. GC analysis was performed using a Hewlett-Packard Model HP5890 series II and Shimadzu GC-8A. All reactions were performed under argon atmosphere. Dry THF was purchased from Kanto Chemical Co. Inc. and used without further purification. Hydrogenation reactions were performed using reagent grade solvents without further purification.

(S_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-ethylphenyl)phenylphosphine-borane [(S_P)-2a] and (R_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-ethylphenyl)phenylphosphine-borane [(R_P)-2a]

o-Ethylphenylmagnesium bromide (35.8 mL of a 1.40 mol/L THF solution, 50 mmol) was added dropwise over 30 min into a solution of freshly distilled dichlorophenylphosphine (6.8 mL, 50 mmol) in THF (50 mL) with vigorous stirring at −78 °C under argon. After addition, the cooling bath was removed, and temperature was elevated gradually to room temperature over 30 min, and stirring was continued for an additional 1.5 h. The mixture was cooled to 0 °C, and lithium *l*-menthoxide [prepared from *l*-menthol (7.83 g, 50 mmol) in THF (50 mL) and *n*-BuLi (29.6 mL of a 1.69 mol/L hexane solution) at 0 °C] was added dropwise over 30 min, then warmed to 50 °C for 1 h. The mixture was again cooled to 0 °C and a borane-THF complex (65 mL of a 1.0 mol/L solution) was added. The reaction mixture was poured into a mixture of ice/water and hexane. The organic layer was separated, and the aqueous layer was extracted with hexane. The combined extracts were washed with brine and dried (Na_2SO_4) and then concentrated under vacuum. The residual oil was subjected to column chromatography (silica gel, toluene:hexane, 1:4) as the eluent to give a mixture of (S_P1′*R*,2′*S*,5′*R*)-(2′-isopropyl-5′-methylcyclohexyloxy)(*o*-ethylphenyl)phenylphosphine-borane and (R_P1′*R*,2′*S*,5′*R*)-(2′-isopropyl-5′-methylcyclohexyloxy)(*o*-ethylphenyl)phenylphosphine-borane (*ca.* 5:2) as colorless crystals; yield: 13.4 g (70%). Attempts to separate each diastereomer by recrystallization from methanol resulted in the formation of colorless needles (mp 74–75 °C) consisting of (S_P)-**2a** and (R_P)-**2a** in a 1:1 molar ratio. The molecular structure of this substrate was determined by single crystal X-ray analysis. The X-ray crystallographic data are as follows: prismatic. $P2_1$ (#4), a = 14.733(2), b = 8.4430(6), c = 19.109(2) Å, β = 94.49(1)°, V = 2369.7 Å^3, Z = 4, D_{calc} = 1.072 g/cm^3, temperature of data collection 296 K, 3180 observed reflections ($I > 3.00\sigma(I)$), R = 0.065, R_W = 0.062. Separation of each diastereomer was accomplished by preparative HPLC (ODS, MeOH).

(S_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-ethylphenyl)phenylphosphine-borane [(S_P)-2a]: Colorless prisms; mp 80.0–80.5 °C (MeOH); $[\alpha]_D^{26}$: −103 (*c* 0.97, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.48 (d, J = 6.9 Hz, 3H), 0.63–1.72 (m, 11H), 0.75 (d, J = 6.9 Hz, 3H), 0.78 (t, J = 7.7 Hz, 3H), 0.89 (d, J = 6.5 Hz, 3H), 2.14–2.17 (m, 1H), 2.51–2.58 (m, 2H), 4.33–4.40 (m, 1H), 7.24–7.26 (m, 1H), 7.29–7.33 (m, 1H), 7.37–7.50 (m, 4H), 7.55–7.60 (m, 2H), 8.11 (ddd, J = 13.7, 7.7, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.4 (d, J = 6.6 Hz), 15.2 (s), 20.9 (d, J = 5.7 Hz), 22.1 (d, J = 8.2 Hz), 22.6 (s), 25.4 (d, J = 8.2 Hz), 26.5 (d, J = 4.1 Hz), 31.5 (s), 34.1 (s), 43.6 (s), 48.9 (s), 80.4–80.5 (m), 125.3 (d, J = 13.1 Hz), 128.3 (d, J = 10.7 Hz), 129.5 (d, J = 7.4 Hz), 130.4 (d, J = 61.5 Hz), 130.4 (d, J = 11.5 Hz), 130.8 (s), 132.3 (s), 134.1 (d, J = 9.8 Hz), 135.3 (d, J = 68.1 Hz), 147.7 (d, J = 4.9 Hz); ^{11}B NMR ($CDCl_3$): δ −55.4 (d, J = 62.4 Hz); ^{31}P NMR ($CDCl_3$): δ = 105.6 (m); IR (KBr): ν = 3040, 2920, 2370, 1585, 1445, 1085, 975, 885 cm^{-1}; FAB-MS: *m/z* (rel intensity) = 369 (M^+−BH_3, 25), 379 (M^+−3H, 51); anal. calcd. for $C_{24}H_{36}BOP$: C 75.40, H 9.49; found: C 75.66, H 9.69.

The absolute configuration at the asymmetric phosphorus atom of this diastereomer was determined to be *S* by single crystal X-ray analysis.

X-Ray Crystallographic Data: FW = 382.33, prismatic $P2_12_12_1$ (#19), a = 14.368(2), b = 17.042(1), c = 9.8810(8) Å, V = 2419.4(4) Å^3, Z = 4, D_{calc} = 1.050 g/cm^3, temperature of data collection 196 K, 1428 observed reflections ($I > 3.00\sigma(I)$), R = 0.064, R_W = 0.069.

(R_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-ethylphenyl)phenylphosphine-borane [(R_P)-2a]: Colorless crystals; mp 57.5–58.5 °C; $[\alpha]_D^{24}$: −25.0 (*c* 1.05, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.67 (d, J = 6.9 Hz, 3H), 0.67–1.42 (m, 8H), 0.80 (d, J = 6.3 Hz, 3H), 0.86 (d, J = 7.3, 3H), 0.86 (t, J = 7.4 Hz, 3H), 1.63–1.66 (m, 2H), 2.00–2.03 (m, 2H), 2.53–2.64 (m, 2H), 4.30–4.40 (m, 1H), 7.26–7.69 (m, 8H), 8.07 (dd, J = 11.7, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.8 (d, J = 7.4 Hz), 15.4 (d, J = 4.1 Hz), 21.0 (d, J = 7.4 Hz), 22.0 (d, J = 6.6 Hz), 22.7 (s), 25.5 (d, J = 4.9 Hz), 26.7 (d, J = 4.1 Hz), 31.4 (s), 34.1 (s), 43.2 (s), 49.1 (s), 79.6–79.7 (m), 125.5 (d, J = 11.5 Hz), 128.3 (d, J = 10.7 Hz), 129.6 (d, J = 9.0 Hz), 130.8 (d, J = 11.5 Hz), 130.9 (d, J = 55.0 Hz), 131.1 (s), 132.1 (s), 133.4 (d, J = 8.2 Hz), 133.5 (d, J = 9.0 Hz), 134.3 (d, J = 68.9 Hz), 147.7 (d, J = 8.2 Hz); ^{11}B NMR ($CDCl_3$): δ = −60.4 (d, J = 62.2 Hz); ^{31}P NMR ($CDCl_3$): δ = 103.0 (m); IR (KBr): ν = 3020, 2915, 2360, 1580, 1430, 1060, 960 cm^{-1}; FAB-MS: *m/z* (rel intensity) = 369 (M^+−BH_3, 25), 379 (M^+−3H, 48); anal. calcd. for $C_{24}H_{36}BOP$: C 75.40, H 9.49; found: C 75.22, H 9.47.

(*S*)-*o*-Ethylphenyl(methyl)phenylphosphine-borane (3a)

A solution of (S_P1′*R*,2′*S*,5′*R*)-(2′-isopropyl-5′-methylcyclohexyloxy)(*o*-ethylphenyl)phenylphosphine-borane (2.68 g, 7.0 mmol) in THF (15 mL) was added to a solution of lithium

4,4′-di-*tert*-butylbiphenylide [prepared from 4,4′-di-*tert*-butylbiphenyl (7.47 g, 28 mmol) and lithium (218 mg, 31 mmol) in THF (130 mL) at 0 °C] with vigorous stirring at −98 °C under argon. After 5 min, iodomethane (2.0 mL, 32 mmol) was added at the same temperature, and stirring was continued for 10 min. The reaction was quenched with methanol, and the mixture was partitioned between hexane and brine. The organic layer was separated, and the aqueous layer was extracted with hexane. The combined extracts were washed with brine and dried (Na_2SO_4) and concentrated under vacuum. The residue was passed through a short column (silica gel, hexane) to remove 4,4′-di-*tert*-butylbiphenyl. The product was isolated by column chromatography (silica gel, toluene) to afford (*S*)-*o*-ethylphenyl(methyl)phenylphosphine-borane; yield: 1.55 g (91%). The enantiomeric excess of the product was determined to be 88% ee by HPLC analysis [DAICEL CHIRALCEL OJ, hexane:2-propanol = 9:1, 1.0 mL/min, (*R*) t_1 = 10.4 min, (*S*) t_2 = 12.3 min]. Colorless oil; $[\alpha]_D^{26}$: +21.2 (*c* 1.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.72–1.59 (m, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.86 (d, *J* = 9.7 Hz, 3H), 2.48–2.72 (m, 2H), 7.25–7.33 (m, 2H), 7.34–7.47 (m ,4H), 7.57–7.62 (m, 2H), 7.67 (dd, *J* = 13.5, 7.7 Hz); ^{13}C NMR ($CDCl_3$): δ = 13.2–13.8 (m), 14.9 (d, *J* = 6.6 Hz), 27.1 (d, *J* = 5.7 Hz), 125.9–126.0 (m), 127.5 (d, *J* = 55.0 Hz), 128.8 (d, *J* = 9.8 Hz), 129.9 (brs), 130.9 (s), 131.5 (s), 131.6 (s), 131.7 (s), 131.8 (d, *J* = 54.9 Hz), 131.5 (s), 132.2 (d, *J* = 9.8 Hz), 148.5 (d, *J* = 9.0 Hz); ^{11}B NMR ($CDCl_3$): δ = −58.1 (d, *J* = 54.6 Hz); ^{31}P NMR ($CDCl_3$): δ = 10.1 (m); IR (neat): ν = 3025, 2940, 2360, 1585, 1435, 1085, 895 cm^{-1}; HRMS (FAB): calcd. for $C_{15}H_{20}BKP$ ($M+K^+$): 281.1028; found: 281.1037.

(*S*,*S*)-1,2-Bis[boranato(*o*-ethylphenyl)-phenylphosphino]ethane (4a)

A solution of (*S*)-*o*-ethylphenyl(methyl)phenylphosphine-borane (90% ee) (324 mg, 1.34 mmol) was dissolved in THF (7 mL) was cooled to −78 °C under argon. To this solution *sec*-BuLi (1.4 mL of 1.05 M/L cyclohexane solution) was added, and stirring was continued for 2 h. Freshly dried, well-powdered anhydrous copper(II) chloride (270 mg, 2.0 mmol) was added with vigorous stirring. The temperature was kept at this level for 30 min, and then elevated over 2 h to room temperature. After stirring for an additional 1 h, water and ethyl acetate were added and the mixture was passed through Celite. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined extracts were washed with 5% ammonia and brine, dried (Na_2SO_4), and concentrated under vacuum. The product was isolated by preparative TLC (silica gel, hexane:AcOEt = 5:1) to give (*S*,*S*)-1,2-bis[boranato(*o*-ethylphenyl)phenylphosphino]ethane; yield: 255 mg (79%); colorless needles; mp 151.5–152.5 °C (hexane:CH_2Cl_2 = 5:1); $[\alpha]_D^{26}$: +51.8 (*c* 1.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.84–1.61 (m, 6H), 0.86 (t, *J* = 8.2 Hz, 6H), 2.21–2.28 (m, 2H), 2.46–2.68 (m, 6H), 7.26–7.60 (m, 18H); ^{13}C NMR ($CDCl_3$): δ = 14.8–14.9 (m), 19.9–20.3 (m), 27.0 (s), 125.8 (d, *J* = 54.1 Hz), 126.1 (s), 128.9 (d), 129.4 (d, *J* = 55.0 Hz), 130.2 (s), 131.2 (s), 131.8 (s), 132.0 (s), 132.5 (s), 148.8 (d, *J* = 4.3 Hz), 148.8 (d, *J* = 4.3 Hz); ^{11}B NMR ($CDCl_3$): δ = −59.9 (brs); ^{31}P NMR ($CDCl_3$): δ = 18.0 (m); IR (KBr): ν = 3040, 2935, 2360, 1585, 1430, 1185, 1115, 1070 cm^{-1}; FAB MS (rel intensity): *m*/*z* = 455 (M^+-2BH_3+H, 31), 467 (M^+-BH_3-H, 90), 477 (M^+-5H, 54), 481 (M^+-H, 45); anal. calcd. for $C_{30}H_{38}B_2P_2$: C 74.73, H 7.94; found: C 74.47, H 7.88.

(*S*,*S*)-1,2-Bis[(*o*-ethylphenyl)phenylphosphino]ethane (1a)

(*S*,*S*)-1,2-Bis[boranato(*o*-ethylphenyl)phenylphosphino]ethane (72 mg, 0.15 mmol) and DABCO (67 mg, 0.60 mmol) was dissolved in 1 mL of degassed toluene and the solution was maintained at 50 °C for 30 min. The mixture was subjected to a short column (silica gel, degassed toluene) under argon to give (*S*,*S*)-1,2-bis[(*o*-ethylphenyl)phenylphosphino]ethane diphosphine in almost quantitative yield. Colorless oil; $[\alpha]_D^{24}$: −10.8° (*c* 0.50, toluene); ^{1}H NMR ($CDCl_3$): δ = 1.13 (t, *J* = 7.5 Hz, 6H), 2.07–2.09 (m, 4H), 2.80–2.95 (m, 4H), 7.10–7.30 (m, 18H); IR (neat): ν = 3020, 2925, 1575, 1460, 1425, 1260, 1025 cm^{-1}; HRMS (FAB): calcd. for $C_{30}H_{33}P_2$ ($M+H^+$): 455.2050; found: 455.2068.

(S_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-methylphenyl)phenylphosphine-borane [(S_P)-2b] and (R_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)(*o*-methylphenyl)phenylphosphine-borane [(R_P)-2b]

o-Methylphenylmagnesium bromide (47 mL of 1.06 M/L THF solution, 50 mmol) was added dropwise over 30 min into a solution of freshly distilled dichlorophenylphosphine (6.8 mL, 50 mmol) in THF (50 mL) with vigorous stirring at −78 °C under argon. After addition, the cooling bath was removed, the mixture was warmed to room temperature over *ca.* 30 min, and stirring was continued for an additional 1.5 h. The flask was immersed in an ice bath, and a solution of lithium menthoxide [prepared from *l*-menthol (7.83 g, 50 mmol) in THF (50 mL) and *n*-BuLi (29.6 mL of 1.69 mol/L hexane solution at 0 °C) was added dropwise over 30 min, and the mixture was warmed to 50 °C and stirring was continued for 1 h. The flask was again immersed in an ice-water bath, and borane-THF complex (65 mL of 1.0 mol/L) was added. The reaction mixture was poured into a mixture of ice/water and hexane. The organic layer was separated, and the aqueous layer was extracted with hexane. The combined extracts were washed with brine and dried (Na_2SO_4), and the solvents were removed under vacuum to leave a crystalline solid (yield: 16.1 g) consisting of (S_P1′*R*,2′*S*,5′*R*)-(2′-isopropyl-5′-methylcyclohexyloxy)(*o*-methylphenyl)phenylphosphine-borane and (R_P1′*R*,2′*S*,5′*R*)-(2′-isopropyl-5′-methylcyclohexyloxy)(*o*-methylphenyl)phenylphosphine-borane (88:12). Each diastereomer was separated by fractional crystallization or preparative HPLC (ODS, MeOH).

(S_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-methylphenyl)phenylphosphine-borane [(S_P)-2b]: Colorless prisms; mp 85.5–86.5 °C (MeOH); $[\alpha]_D^{26}$: −112 (*c* 0.92, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.47 (d, *J* = 6.8 Hz, 3H), 0.68–1.71 (m, 11H), 0.76 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H), 2.10 (s, 3H), 2.15–2.26 (m, 1H), 4.31–4.39 (m, 1H), 7.13–7.20 (m, 1H), 7.30–7.46 (m, 5H), 7.54–7.59 (m, 2H), 8.12 (ddd, *J* = 13.8 7.7 1.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 15.2 (s), 21.0 (d, *J* = 5.4 Hz), 21.2–21.3 (m), 22.1 (d, *J* = 7.4 Hz), 25.5 (d, *J* = 8.2 Hz), 31.5 (s), 34.1 (s), 43.7 (s), 49.0

(s), 80.4–80.5 (m), 125.5 (d, J = 13.1 Hz), 128.3 (d, J = 10.7 Hz), 130.4 (d, J = 11.5 Hz), 130.6 (d, J = 60.7 Hz), 130.9 (s), 131.3–131.4 (m), 132.2 (s), 134.1–134.4 (m), 134.6 (d, J = 58.2 Hz), 141.7 (d, J = 4.9 Hz); ^{11}B NMR ($CDCl_3$): δ = −60.7 (d, J = 62.8 Hz); ^{31}P NMR ($CDCl_3$): δ = 105.6 (m); IR (KBr): ν = 3050, 2920, 2380, 1585, 1445, 1085, 990, 885 cm^{-1}; FAB MS (rel intensity): m/z = 365 (M^+−3H, 37), 355 (M^+−BH_3, 22); anal. calcd. for $C_{23}H_{34}BOP$: C 75.01, H 9.31; found: C 74.79, H, 9.22. The absolute configuration at the asymmetric phosphorus atom of this diastereomer was determined to be *S* by single crystal X-ray analysis.

X-Ray Crystallographic Data: FW = 368.30, prismatic $P2_12_12_1$ (#19), a = 13.283(1), b = 17.079(2), c = 10.026(1) Å, V = 2274.4(4) Å^3, Z = 4, D_{calc} = 1.076 g/cm^3, temperature of data collection 296 K, 1615 observed reflection ($I > 2.00\sigma(I)$), R = 0.060, R_W = 0.067.

(R_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-methylphenyl)phenylphosphine-borane [(R_P)-2b]: Colorless prisms; mp 73.5–74.5 °C (hexane); $[\alpha]_D^{26}$: −23.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.69 (d, J = 6.8 Hz, 3H), 0.69–1.67 (m, 10H), 0.79 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 7.0 Hz, 3H), 1.95–2.08 (m, 2H), 2.16 (s, 3H), 4.32–4.35 (m, 1H), 7.15–7.18 (m, 1H), 7.32–7.46 (m, 5H), 7.53–7.58 (m, 2H), 8.09 (ddd, J = 13.0, 7.5, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 15.4 (s), 21.1 (d, J = 6.6 Hz), 21.4 (s), 22.0 (s), 22.7 (s), 25.5 (s), 31.3 (s), 34.1 (s), 42.9 (s), 49.1 (s), 79.7 (d, J = 2.5 Hz), 125.6 (d, J = 10.7 Hz), 128.3 (d, J = 9.8 Hz), 130.8 (d, J = 11.5 Hz), 131.1 (s), 131.2 (d, J = 50.0 Hz), 131.5 (s), 131.9 (s), 133.5 (s, J = 69.7 Hz), 133.7–133.8 (m), 141.6 (d, J = 6.6 Hz); ^{11}B NMR ($CDCl_3$): δ −60.8 (d, J = 57.5 Hz); ^{31}P NMR ($CDCl_3$): δ = 103.6 (m); IR (KBr): ν = 3020, 2915, 2375, 1580, 1440, 1075, 980 cm^{-1}; FAB MS (rel intensity): m/z = 365 (M^+−3H, 56), 355 (M^+−BH_3, 33); anal. calcd. for $C_{23}H_{34}BOP$: C 75.01, H 9.31; found: C 74.95, H 9.04.

(*S*)-*o*-Methylphenyl(methyl)phenylphosphine-borane (3b)

A solution of (S_P1′*R*,2′*S*,5′*R*)-(2′-isopropyl-5′-methylcyclohexyloxy)(*o*-methylphenyl)phenylphosphine-borane (3.68 g, 10 mmol) in THF (20 mL) was added into a solution of lithium 4,4′-di-*tert*-butylbiphenylide [prepared from 4,4′-di-*tert*-butylbiphenyl (10.7 g, 40 mmol) and lithium (305 mg, 44 mmol) and THF (150 mL)] with vigorous stirring at −98 °C under argon. After 5 min, iodomethane (3.1 mL, 50 mmol) was added and stirring was continued at the same temperature for 10 min. The reaction was quenched by the addition of methanol and the mixture was partitioned between hexane and brine. The aqueous layer was extracted with hexane, and the combined organic layers were washed with brine and dried over sodium sulfate. The solvents were evaporated, and the residue was passed through a short column of silica gel to remove 4,4′-di-*tert*-butylbiphenyl using hexane as the eluent. The product was isolated by column chromatography (silica gel, toluene) to afford (*S*)-*o*-methylphenyl(methyl)phenylphosphine-borane; yield: 1.85 g (81%). The enantiomeric excess of the product was determined to be 77% ee by HPLC analysis [DAICEL CHIRALPAK AS, hexane:2-propanol = 9:1, 1.0 mL/min, (*R*) t_1 = 7.4 min, (*S*) t_2 = 10.0 min]. Colorless oil; $[\alpha]_D^{23}$: +27.8 (*c* 1.05, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.86–1.58 (m, 3H), 1.87 (t, J = 9.9 Hz, 3H), 2.19 (s), 7.19–7.22 (m, 1H), 7.30–7.34 (m, 1H), 7.39–7.49 (m, 4H), 7.56–7.61 (m, 2H), 7.69 (ddd, J = 12.1, 7.7, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): d = 12.7–13.2 (m), 21.7 (d, J = 4.9 Hz), 126.0 (d, J = 11.5 Hz), 127.8 (d, J = 55.0 Hz), 128.8 (d, J = 10.7 Hz), 130.9 (s), 131.0 (d, J = 55.8 Hz), 131.4 (s), 131.5 (s), 131.7 (d, J = 8.2 Hz), 132.3 (d, J = 10.7 Hz), 142.4 (d, J = 8.2 Hz); ^{11}B NMR ($CDCl_3$): δ = −58.7 (d, J = 56.3 Hz); ^{31}P NMR ($CDCl_3$): δ = 10.9 (m); IR (neat): ν = 3020, 2350, 1580, 1430, 1060, 895 cm^{-1}; HRMS (FAB): calcd. for $C_{14}H_{18}BKP$ ($M+K^+$): 267.0876; found: 267.0879.

(*S*,*S*)-1,2-Bis[boranato(*o*-methylphenyl)-phenylphosphino]ethane (4b)

To a solution of (*S*)-*o*-methylphenyl(methyl)phenylphosphine-borane (77% ee) (1.30 g, 5.7 mmol) in THF (23 mL) was added *sec*-BuLi (6.5 mL of 0.96 mol/L cyclohexane solution) at −78 °C with stirring. After 2 h, freshly dried, well-powdered anhydrous copper(II) chloride (1.15 g, 8.6 mmol) was added with vigorous stirring and the mixture was gradually warmed to room temperature over 2 h. After stirring for an additional 1 h, water and ethyl acetate were added and the mixture was passed through Celite. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined extracts were washed with 5% ammonia and brine, and dried (Na_2SO_4). Purification by column chromatography (silica gel, toluene) and by subsequent recrystallization (toluene-hexane) afforded (*S*,*S*)-1,2-bis[boranato(*o*-methylphenyl)phenylphosphino]ethane; yield: 773 mg (57%); colorless crystals; mp 152.0–153.0 °C (toluene:hexane = 1:2); $[\alpha]_D^{23}$: +57.0 (*c* 1.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.55–1.63 (m, 6H), 2.11 (s, 6H), 2.22–2.30 (m, 2H), 2.50–2.57 (m, 2H), 7.18–7.20 (m, 2H), 7.28–7.32 (m, 2H), 7.37–7.54 (m, 12H), 7.63 (dd, J = 11.8, 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 19.1–19.5 (m), 21.7 (brs), 126.0 (d, J = 53.3 Hz), 126.2 (brs), 128.7 (d, J = 54.1 Hz), 129.0 (s), 131.3 (s), 131.8–132.0 (m), 132.9–133.4 (m), 142.6 (d, J = 4.1 Hz), 142.7 (d, J = 4.1 Hz); ^{11}B NMR ($CDCl_3$): δ = −60.4 (brs); ^{31}P NMR ($CDCl_3$): δ = 19.1 (brs); IR (KBr): ν = 3020, 2885, 2340, 1575, 1430, 1185, 1105, 1055 cm^{-1}; FAB MS (rel intensity): m/z = 427 (M^+−2BH_3 + H, 18), 439 (M^+−BH_3−H, 52), 449 (M^+−5H, 30), 453 (M^+−H , 19); anal. calcd. for $C_{28}H_{34}B_2P_2$: C 74.05, H 7.55; found: C 74.00, H 7.61.

(*S*,*S*)-1,2-Bis[(*o*-methylphenyl)phenylphosphino]ethane (1b): ^{1}H NMR ($CDCl_3$): δ = 1.95–2.20 (m, 4H), 2.37 (s, 6H), 7.1–7.3 (m, 18H); IR (KBr): ν = 3020, 2940, 1430, 760 cm^{-1}; HRMS (FAB): calcd. for $C_{28}H_{28}P_2$ (M^+): 426.1708; found: 426.1664.

(S_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(phenyl)(5″,6″,7″,8″-tetrahydro-1″-naphthyl)-phosphine-borane [(S_P)-2c] and (R_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)(phenyl)-(5″,6″,7″,8″-tetrahydro-1″-naphthyl)phosphine-borane [(R_P)-2c]

Dichlorophenylphosphine (7.4 mL, 54 mmol) was subsequently reacted with 5,6,7,8-tetrahydro-1-naphthylmagnesium bromide (56 mL of 0.97 mol/L THF solution, 54 mmol), lithium menthoxide (54 mmol), and borane-THF complex (70 mL of

1.0 mol/L) in a similar manner to that described above to give a mixture of (S_P)-diastereomer and (R_P)-diastereomer (*ca.* 3:1) as colorless crystals; yield: 17.7 g (80%). Each diastereomer was separated by recrystallization from hexane or preparative HPLC (ODS, MeOH).

(S_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(phenyl)(5″,6″,7″,8″-tetrahydro-1″-naphthyl)phosphine-borane [(S_P)-2c]: Colorless prisms; mp 143.5–144.5 °C (hexane); $[\alpha]_D^{26}$: −103 (*c* 0.92, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.42 (d, *J* = 6.8 Hz, 3H), 0.76–1.69 (m, 15H), 0.76 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 2.18–2.28 (m, 2H), 2.70–2.77 (m, 3H), 4.28–4.37 (m, 1H), 7.20–7.26 (m, 2H), 7.37–7.46 (m, 3H), 7.53–7.59 (m, 2H), 7.98 (ddd, *J* = 14.5, 8.0, 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 15.2 (s), 21.1 (s), 22.2 (s), 22.4 (s), 22.6 (s), 22.7 (s), 25.6 (s), 28.2 (d, *J* = 4.1 Hz), 30.0 (s), 31.6 (s), 34.2 (s), 43.8 (s), 49.1 (d, *J* = 4.9 Hz), 80.3 (d, *J* = 3.3 Hz), 125.2 (d, *J* = 14.8 Hz), 128.4 (d, *J* = 10.7 Hz), 129.9 (d, *J* = 59.1 Hz), 130.3 (s), 130.8 (d, *J* = 2.5 Hz), 132.6 (d, *J* = 19.7 Hz), 133.7 (d, *J* = 2.5 Hz), 134.9 (d, *J* = 68.9 Hz), 138.3 (d, *J* = 7.4 Hz), 141.0 (d, *J* = 4.9 Hz); ^{11}B NMR ($CDCl_3$): δ = −60.2 (d, *J* = 56.9 Hz); ^{31}P NMR ($CDCl_3$): δ = 106.0 (m); IR (KBr): ν = 2925, 2380, 1435, 1200, 1155, 1135, 1065, 980, 830, 755 cm^{-1}; FAB MS (rel intensity): *m*/*z* = 395 (M^+−BH_3, 10), 405 (M^+−3H, 36); HRMS (FAB): calcd. for $C_{26}H_{37}BOP$ (M^+−H): 407.2677; found: 407.3087; anal. calcd. for $C_{26}H_{38}BOP$: C 76.47, H 9.38; found: C 76.08, H 9.49. The absolute configuration at the asymmetric phosphorus atom of this diastereomer was determined to be *S* by single crystal X-ray analysis.

X-Ray Crystallographic Data: FW = 408.37, monoclinic $P2_1$ (#4), *a* = 8.089(1), *b* = 15.658(9), *c* = 10.125(3) Å, β = 109.88(2)°, *V* = 1206.1100 $Å^3$, *Z* = 2, D_{calc} = 1.124 g/cm^3, temperature of data collection 288 K, 1426 observed reflection ($I > 3.00\sigma(I)$), R = 0.053, R_W = 0.058.

(R_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(phenyl)(5″,6″,7″,8″-tetrahydro-1″-naphthyl)phosphine-borane [(R_P)-2c]: Colorless crystals; mp 103.0–103.5 °C; $[\alpha]_D^{25}$: −21.5 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.67 (d, *J* = 7.1 Hz, 3H), 0.71–1.70 (m, 14H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 7.1 Hz, 3H), 1.97–2.06 (m, 2H), 2.53 (t, *J* = 6.3 Hz, 2H), 2.77 (t, *J* = 6.3 Hz, 2H), 4.29–4.38 (m, 1H), 7.24–7.25 (m, 2H), 7.35–7.46 (m, 3H), 7.55–7.58 (m, 2H), 7.94 (ddd, *J* = 16.8, 9.3, 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 15.5 (s), 21.1 (s), 22.1 (s), 22.3 (s), 22.5 (s), 22.7 (s), 28.2 (d, *J* = 4.1 Hz), 29.2 (s), 31.4 (s), 34.2 (s), 43.0 (s), 49.1 (d, *J* = 5.8 Hz), 79.6 (d, *J* = 4.1 Hz), 125.2 (d, *J* = 12.4 Hz), 128.3 (d, *J* = 9.9 Hz), 130.7 (d, *J* = 11.6 Hz), 130.8 (d, *J* = 56.2 Hz), 131.1 (s), 131.6 (d, *J* = 16.5 Hz), 133.3 (d, *J* = 2.5 Hz), 133.9 (d, *J* = 68.6 Hz), 138.3 (d, *J* = 8.3 Hz), 140.9 (d, *J* = 7.4 Hz); ^{11}B NMR ($CDCl_3$): δ = −60.5 (d, *J* = 55.8 Hz); ^{31}P NMR ($CDCl_3$): δ = 103.5 (m); IR (KBr): ν = 3050, 2930, 2380, 1570, 1440, 1230, 1065, 990, 750 cm^{-1}; FAB MS (rel intensity): *m*/*z* = 395 (M^+−BH_3, 15), 405 (M^+−3H, 46); HRMS (FAB): calcd. for $C_{26}H_{37}BOP$ (M−H): 407.2677; found: 407.3121; anal. calcd. for $C_{26}H_{38}BOP$: C 76.47, H 9.38; found: C 76.32, H 9.46.

(*S*)-Methylphenyl(5′,6′,7′,8′-tetrahydro-1′-naphthyl)-phosphine-borane (3c)

A solution of (S_B1′*R*,2′*S*,5′*R*)-(2′-isopropyl-5′-methylcyclohexyloxy)(phenyl)(5″,6″,7″,8″-tetrahydro-1″-naphthyl)phosphine-borane (6.53 g, 16 mmol) in THF (80 mL) was added to a solution of LDBB (210 mL of 0.3 M THF solution, 64 mmol) at −98 °C. After 5 min, diiodomethane (6.0 mL, 96 mmol) was added. The product was isolated by column chromatography (silica gel, toluene) to afford (*S*)-methylphenyl(5′,6′,7′,8′-tetrahydro-1′-naphthyl)phosphine-borane; yield: 4.22 g (98%). The enantiomeric excess of the product was determined to be 84% ee by HPLC analysis [DAICEL CHIRALCEL OJ, hexane: 2-propanol = 9:1, 0.25 mL/min, (*R*) t_1 = 41.3 min, (*S*) t_2 = 44.8 min]. Colorless oil; $[\alpha]_D^{26}$: +10.8 (*c* 0.88, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.70–1.42 (m, 3H), 1.58–1.85 (m, 4H), 1.84 (t, *J* = 9.9 Hz, 3H), 2.17–2.21 (m, 1H), 2.76–2.78 (m, 2H), 2.88–2.92 (m, 1H), 7.22–7.26 (m, 2H), 7.38–7.52 (m, 4H), 7.57–7.62 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 13.7 (d, *J* = 41.8 Hz), 22.2 (s), 22.5 (s), 28.6 (d, *J* = 5.7 Hz), 125.6 (d, *J* = 10.7 Hz), 127.6 (d, *J* = 54.1 Hz), 128.8 (d, *J* = 9.78 Hz), 129.9 (d, *J* = 9.8 Hz), 130.9 (d, *J* = 2.5 Hz), 131.4 (d, *J* = 9.8 Hz), 131.5 (d, *J* = 55.0 Hz), 132.8 (d, *J* = 2.5 Hz), 138.8 (d, *J* = 9.0 Hz), 141.6 (d, *J* = 9.0 Hz); ^{11}B NMR ($CDCl_3$): δ −53.6 (d, *J* = 52.8 Hz); ^{31}P NMR ($CDCl_3$): δ = 10.6 (m); IR (neat): ν = 3055, 2935, 2370, 1435, 1065, 890 cm^{-1}; HRMS (FAB): calcd. for $C_{17}H_{22}BKP$ ($M + K^+$): 307.1189; found: 307.1182.

(*S*,*S*)-1,2-Bis[boranatophenyl(5′,6′,7′,8′-tetrahydro-1′-naphthyl)phosphino]ethane (4c)

(*S*)-Methylphenyl(5′,6′,7′,8′-tetrahydro-1′-naphthyl)phosphine-borane (84% ee) (2.98 g, 11.1 mmol) was subsequently treated with *sec*-BuLi (12 mL of 1.0 mol/L cyclohexane-hexane solution) and anhydrous copper(II) chloride (2.4 g, 18 mmol) in the same procedure as described above. Purification by column chromatography (silica gel, toluene) and recrystallization (toluene-hexane) afforded (*S*,*S*)-1,2-bis[boranatophenyl(5′,6′,7′,8′-tetrahydro-1′-naphthyl)phosphino]ethane; yield: 1.62 g (55%); colorless crystals; mp 195.0–195.5 °C (toluene : hexane = 2:3); $[\alpha]_D^{23}$: +36.6 (*c* 0.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.77–1.50 (m, 6H), 1.51–1.85 (m, 8H), 2.15–2.22 (m, 4H), 2.50–2.57 (m, 2H), 2.71–2.85 (m, 6H), 7.18–7.25 (m, 4H), 7.36–7.58 (m, 12H); ^{13}C NMR ($CDCl_3$): δ = 19.8–20.2 (m), 22.1 (s), 22.4 (s), 28.6 (s), 29.9 (s), 125.7 (d, *J* = 4.9 Hz), 125.7 (d, *J* = 5.7 Hz), 125.8 (d, *J* = 53.3 Hz), 128.6–129.4 (m), 130.5 (brs), 131.2 (s), 131.8 (d, *J* = 4.1 Hz), 131.9 (d, *J* = 4.9 Hz), 139.0 (d, *J* = 4.1 Hz), 139.1 (d, *J* = 4.1 Hz), 141.9 (d, *J* = 4.1 Hz), 141.9 (d, *J* = 4.9 Hz); ^{11}B NMR ($CDCl_3$): δ = −60.0 (brs); ^{31}P NMR ($CDCl_3$): δ = 18.2 (brs); IR (KBr): ν = 2935, 2370, 1435, 1060, 845 cm^{-1}; FAB MS (rel intensity): *m*/*z* = 507 (M^+−$2BH_3$ + H, 2), 519 (M^+−BH_3−H, 6); anal. calcd. for $C_{34}H_{42}B_2P_2$: C 76.43, H 7.92; found: C 76.26, H 7.92.

(S_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-isopropylphenyl)phenylphosphine-borane [(S_P)-2d] and (R_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)(*o*-isopropylphenyl)phenylphosphine-borane [(R_P)-2d]

Dichlorophenylphosphine (19 mL, 140 mmol) was successively reacted with *o*-isopropylphenylmagnesium bromide (140 mL of 1.0 M/L THF solution, 140 mmol), lithium menthoxide (140 mmol), and borane-THF complex (182 mL of 1.0 mol/L) in a similar manner to that described above to give a mixture of (S_P)-diastereomer and (R_P)-diastereomer as

colorless crystals; yield: 46.6 g (84%). Each diastereomer was separated by fractional crystallization from hexane.

(S_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-isopropylphenyl)phenylphosphine-borane [(S_P)-2d]: Colorless prisms; mp 134.5–135.0 °C (hexane); $[\alpha]_D^{18}$: −82.6 (*c* 1.39, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.52–1.80 (m, 11H), 0.61 (d, *J* = 7.0 Hz, 3H), 0.67 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 7.3 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 2.05–2.08 (m, 1H), 3.12–3.18 (m, 1H), 4.38–4.47 (m, 1H), 7.28–7.32 (m, 2H), 7.35–7.44 (m, 3H), 7.47–7.51 (m, 1H), 7.55–7.61 (m, 2H), 8.10 (ddd, *J* = 9.4, 7.7, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 15.3 (d, *J* = 4.1 Hz), 21.0 (d, *J* = 5.7 Hz), 22.1 (d, *J* = 8.2 Hz), 22.5 (brs), 23.3 (d, *J* = 8.2 Hz), 23.4 (d, *J* = 4.9 Hz), 25.4 (d, *J* = 8.2 Hz), 31.0 (dd, *J* = 4.9, 4.9 Hz), 31.5 (brs), 34.1 (brs), 43.6 (s), 48.9 (s), 80.5–80.6 (m), 125.4 (d, *J* = 12.3 Hz), 127.1 (d, *J* = 8.2 Hz), 128.2 (d, *J* = 10.2 Hz), 130.1 (d, *J* = 75.5 Hz), 130.4 (s), 130.8 (s), 132.4 (s), 133.2 (d, *J* = 9.8 Hz), 133.4 (d, *J* = 9.8 Hz), 135.9 (d, *J* = 66.5 Hz), 152.6 (d, *J* = 6.6 Hz); ^{11}B NMR ($CDCl_3$): δ −60.4 (d, *J* = 45.8 Hz); ^{31}P NMR ($CDCl_3$): δ = 104.3 (m); IR (KBr): ν = 3055, 2950, 2390, 1590, 1570, 1435, 1060, 990, 765 cm^{-1}; FAB MS (rel intensity): *m*/*z* = 393 (M^+−3H, 23), 395 (M^+−H, 10); anal. calcd. for $C_{25}H_{38}BOP$: C 75.76, H 9.66; found: C 75.80, H 9.72. The absolute configuration at the asymmetric phosphorus atom of this diastereomer was determined to be *S* by single crystal X-ray analysis.

X-Ray Crystallographic Data: FW = 396.36, monoclinic $P2_1$ (#4), *a* = 8.4609(6), *b* = 10.761(1), *c* = 13.858(1) Å, β = 98.473(7)°, *V* = 1248.0(2) Å^3, *Z* = 2, D_{calc} = 1.055 g/cm^3, temperature of data collection 296 K, 1609 observed reflection (*I* > 3.00σ(*I*)), *R* = 0.065, R_W = 0.065.

(R_P1′*R*,2′*S*,5′*R*)-(2′-Isopropyl-5′-methylcyclohexyloxy)-(*o*-isopropylphenyl)phenylphosphine-borane [(R_P)-2d]: Colorless needles; mp 116.0–116.5 °C (hexane); $[\alpha]_D^{24}$: −29.6 (*c* 0.99, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.43–1.66 (m, 10H), 0.64 (d, *J* = 6.8 Hz, 3H), 0.81–0.86 (m, 12H), 1.93–2.00 (m, 1H), 2.07–2.17 (m, 1H), 3.11–3.20 (m, 1H), 4.28–4.40 (m, 1H); 7.31–7.46 (m, 5H), 7.49–7.59 (m, 3H), 8.06 (dd, *J* = 10.9, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 15.4 (s), 21.1 (d, *J* = 7.4 Hz), 22.0 (d, *J* = 5.4 Hz), 22.7 (brs), 23.3 (d, *J* = 9.0 Hz), 23.6 (d, *J* = 8.2 Hz), 25.5 (d, *J* = 5.7 Hz), 30.9 (dd, *J* = 5.7, 5.7 Hz), 31.4 (s), 34.2 (s), 43.5 (s), 49.1 (s), 79.8 (brs), 125.6 (d, *J* = 11.5 Hz), 127.1 (d, *J* = 7.4 Hz), 128.2 (d, *J* = 10.7 Hz), 130.5 (d, *J* = 73.0 Hz), 130.7 (s), 131.1 (s), 132.2 (s), 132.9 (d, *J* = 9.8 Hz), 133.0 (d, *J* = 9.0 Hz), 134.7 (d, *J* = 68.0 Hz), 152.6 (d, *J* = 8.2 Hz); ^{11}B NMR ($CDCl_3$): δ = −60.4 (d, *J* = 56.4 Hz); ^{31}P NMR ($CDCl_3$): δ = 102.3 (m); IR (KBr): ν = 3020, 2920, 2390, 1580, 1560, 1435, 1120, 1070, 985, 960, 930, 870, 770 cm^{-1}; FAB MS (rel intensity): *m*/*z* = 393 (M^+−3H, 38), 395 (M^+−H, 14); anal. calcd for $C_{25}H_{38}BOP$: C 75.76, H 9.66; found: C 75.78, H 9.84.

(*S*)-(*o*-Isopropylphenyl)phenylmethylphosphine-borane (3d)

A solution of (S_P1′*R*,2′*S*,5′*R*)-(2′-isopropyl-5′-methylcyclohexyloxy)(*o*-isopropylphenyl)phenylphosphine-borane (7.93 g, 20 mmol) in THF (100 mL) was added to a solution of LDBB (270 mL of 0.3 M THF solution, 80 mmol) at −98 °C. After 5 min, diiodomethane (7.0 mL, 112 mmol) was added. The product was isolated by column chromatography (silica gel, toluene) to afford (*S*)-(*o*-isopropylphenyl)phenylmethylphosphine-borane; yield: 5.06 g (99%). The enantiomeric excess of the product was determined to be 94% ee by HPLC analysis [DAICEL CHIRALPAK AS, hexane : 2-propanol = 30 : 1, 0.5 mL/min, (*R*) t_1 = 14.1 min, (*S*) t_2 = 18.4 min]. Colorless plates; mp 80.5–81.5 °C (toluene-hexane); $[\alpha]_D^{18}$: +8.7 (*c* 2.30, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.73 (d, *J* = 6.8 Hz, 3H), 0.88–1.56 (m, 3H), 1.08 (d, *J* = 6.83, 3H), 1.86 (d, *J* = 9.8 Hz, 3H), 3.13–3.19 (m, 1H), 7.29–7.53 (m, 6H), 7.57–7.67 (m, 3H) 2.19 (s); ^{13}C NMR ($CDCl_3$): δ = 13.7 (d, *J* = 41.4 Hz), 23.3 (s), 24.1 (s), 31.7 (d, *J* = 6.6 Hz), 126.1 (d, *J* = 9.9 Hz), 127.1 (d, *J* = 55.4 Hz), 127.6 (d, *J* = 8.3 Hz), 128.8 (d, *J* = 9.9 Hz), 130.9 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 9.1 Hz), 131.8 (d, *J* = 9.9 Hz), 131.9 (d, *J* = 1.7 Hz), 132.2 (d, *J* = 55.4 Hz), 153.6 (d, *J* = 9.1 Hz); ^{11}B NMR ($CDCl_3$): δ = −58.1 (d, *J* = 45.7 Hz); ^{31}P NMR ($CDCl_3$): δ 9.7 (m); IR (KBr): ν = 3020, 2935, 2380, 1580, 1470, 1430, 1070, 910, 895 cm^{-1}; FAB MS (rel intensity): *m*/*z* = 242 (M^+−BH_3−H, 46), 253 (M^+−3H, 100); anal. calcd. for $C_{16}H_{22}BP$: C 75.03, H 8.66; found: C 75.14, H 8.75.

(*S*,*S*)-1,2-Bis[boranato(*o*-isopropylphenyl)-phenylphosphino]ethane (4d)

(*S*)-(*o*-Isopropylphenyl)phenylmethylphosphine-borane (94% ee) (2.56 g, 10 mmol) was subsequently treated with *sec*-BuLi (10.6 mL of 0.96 mol/L cyclohexane-hexane solution) and anhydrous copper(II) chloride (2.0 g, 15 mmol) using the same procedure as described above. Purification by column chromatography (silica gel, toluene) and recrystallization (toluene-hexane) afforded (*S*,*S*)-1,2-bis[boranato(*o*-isopropylphenyl)-phenylphosphino]ethane; yield: 1.64 g (64%); colorless crystals; mp 160.5–161.5 °C (hexane : toluene = 10 : 1); $[\alpha]_D^{18}$: +55.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.68 (d, *J* = 6.8 Hz, 6H), 0.71–1.55 (m, 6H), 1.05 (d, *J* = 6.5 Hz, 6H), 2.19–2.27 (m, 2H), 2.55–2.63 (m, 6H), 3.12–3.19 (m, 6H), 7.26–7.30 (m, 2H), 7.33–7.40 (m, 5H), 7.43–7.53 (m, 7H), 7.58 (dd, *J* = 11.4, 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 20.1–20.4 (m), 23.2 (s), 24.0 (s), 31.6 (d, *J* = 3.3 Hz), 31.6 (d, *J* = 3.3, Hz), 125.6 (d, *J* = 55.0 Hz), 126.2 (d, *J* = 4.9 Hz), 126.2 (d, *J* = 4.9 Hz), 127.7 (d, *J* = 4.1 Hz), 127.8 (d, *J* = 4.1 Hz), 128.8 (d, *J* = 4.9 Hz), 128.9 (d, *J* = 4.9 Hz), 129.7 (d, *J* = 55.0 Hz), 131.2 (s), 131.9–132.1 (m) , 153.7 (d, *J* = 4.9 Hz) , 153.7 (d, *J* = 4.9 Hz); ^{11}B NMR ($CDCl_3$): δ = −59.9 (brs); ^{31}P NMR ($CDCl_3$): δ = 17.4 (m); IR (KBr): ν = 3020, 2935, 2340, 1580, 1470, 1430, 1165 cm^{-1}; FAB MS (rel intensity): *m*/*z* = 483 (M^+−2BH_3 + H, 27), 495 (M^+−BH_3−H, 100), 505 (M^+−5H, 40), 509 (M^+−H, 25), 510 (M^+, 14), 511 (M^+ + H, 28); anal. calcd. for $C_{32}H_{42}B_2P_2$: C 75.33, H 8.30; found: C 75.19, H 8.36.

(*S*,*S*)-1,2-Bis[(*o*-isopropylphenyl)phenylphosphino]ethane (1d): Mp 106–107 °C; $[\alpha]_D^{25}$: −10.0 (*c* 1.0, toluene); ^{1}H NMR ($CDCl_3$): δ = 0.98 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.8 Hz, 6H), 2.06–2.09 (m, 4H), 3.73–3.81 (m, 2H), 7.1–7.3 (m, 18H); ^{13}C NMR ($CDCl_3$): δ = 23.96, 23.99, 24.06, 24.11, 30.76, 30.89, 31.02, 125.49, 125.51, 125.97, 128.29, 128.34, 128.37, 129.19, 131.11, 132.49, 132.58, 132.68, 134.65, 134.70, 134.77, 138.98, 139.05, 139.12, 153.65, 153.76, 153.88 cm^{-1}; IR (KBr): ν = 3050, 2960, 1470, 1435, 745, 695 cm^{-1}; HRMS (FAB): calcd for $C_{32}H_{37}P_2$ (M − H): 438.2371; found: 483.2354.

Preparation of Rhodium Complexes 5a–d

Complexes **5a–d** were obtained as orange powders using the procedure described in the literature.[7] Single crystals of **5c** for X-ray analysis were prepared by recrystallization from dichloromethane.

X-Ray Crystallographic Data for 5c: Empirical formula = $C_{42.5}H_{53}BF_4P_2RhClO_2$ {[Rh(1c)(cod)]$BF_4 \cdot 1/2\ CH_2Cl_2 \cdot 2\ H_2$)}, FW = 881.99, monoclinic $P2_1$ (#4), $a = 11.558(2)$, $b = 22.07(2)$, $c = 16.671(4)$ Å, $\beta = 93.51(2)^\circ$, $V = 4244.54$ Å^3, $Z = 2$, $D_{calc} = 1.380$ g/cm^3, temperature of data collection 173 K, 4217 observed reflection ($I > 4.50\sigma(I)$), $R = 0.066$, $R_W = 0.082$.

General Procedure for Asymmetric Hydrogenation of α-Acylaminoacrylic Derivatives

A 50-mL Fischer–Porter tube was charged with the substrate (1 mmol) and the catalyst precursor (0.002 mmol or 0.001 mmol). The tube was connected to the hydrogen tank *via* stainless steel tubing. The vessel was evacuated and filled with hydrogen gas (Nippon Sanso, 99.9999%) to a pressure of about 2 atm. This operation was repeated and the bottle was immersed in a dry ice-ethanol bath. The upper cock of the bottle was opened and degassed solvent was added quickly using a syringe. After four vacuum/H_2 cycles, the tube was pressurized to the desired initial pressure and immersed in a constant-temperature bath. The solution or suspension was magnetically stirred at 50 °C until no further hydrogen uptake was observed. The resulting solution was passed through silica gel using ethyl acetate as the eluent, and the filtrate was submitted to direct analysis of the ee values by HPLC or GC.

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