Preparation of Axially Chiral Biphenyl Diphosphine Ligands and Their Application in Asymmetric Hydrogenation

Toshiaki MORIMOTO,* Kiyoshi YOSHIKAWA, Masanao MURATA, Naoko YAMAMOTO, and Kazuo ACHIWA

School of Pharmaceutical Sciences, University of Shizuoka; 52–1 Yada, Shizuoka 422–8526, Japan.
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Axially chiral biphenyldiphosphine ligands bearing diphenylphosphino group(s) and/or dicyclohexylphosphino group(s) were prepared in enantiomerically pure form starting from 2,6-dimethylnitrobenzene *via* 8 steps: iodination, reduction, methoxylation through diazotization, Ullmann coupling, bromination, phosphorylation, optical resolution, and silane reduction, and the obtained ligands were used in rhodium-catalyzed asymmetric hydrogenation.

Key words axially chiral ligand; diphosphine ligand; optical resolution; asymmetric hydrogenation; rhodium complex

Development of efficient methods for catalytic enantioselective synthesis has been an important subject for the practical synthesis of optically active organic compounds.[1] Numerous methods of enantioselective synthesis employing various catalysts such as transition metal complexes coordinated with many types of chiral ligands have been reported for more than three decades.[1—6] For the development of efficient chiral catalysts, creation of new types of ligands is a most significant strategy. Among various types of chiral ligands, diphosphines are the most effective and are widely applicable in the catalytic asymmetric hydrogenation of prochiral compounds such as olefins, ketones, and imines using transition metal (rhodium, ruthenium, iridium, *etc.*) complexes as catalyst. We previously proposed a novel idea, "respective control concept" for designing new chiral ligands,[7—10] and developed efficient diphosphine ligands such as (2*S*-*cis*)-4-(dicyclohexylphosphino)-2-[(diphenylphosphino)methyl]-1-pyrrolidinecarboxylic acid 1,1-dimethylethyl ester (BCPM) and its analogs,[8,11—13] (4*R*-*trans*)-[(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis[bis(4-methoxy-3,5-dimethylphenyl)phosphine] (MOD-DIOP) and its analogs,[14—17] *etc.* (Fig. 1) for rhodium-catalyzed asymmetric hydrogenation of some prochiral ketones (ketopantolactone, α- and β-amino ketones, *etc.*), and olefins (itaconic acid and its derivatives, *N*-acyldehydroamino acids, *etc.*). Furthermore, we revealed that phosphines bearing electron-donating groups such as cyclohexyl groups, *p*-(dimethylamino)phenyl groups, and *p*-methoxy-*m*,*m*′-dimethylphenyl groups enhance not only the catalytic activity but also the enantioselectivity in the rhodium-catalyzed hydrogenations. The *p*-methoxy-*m*,*m*′-dimethylphenyl (abbreviated to MOD) group was found to be a useful component for developing efficient ligands on the basis of its steric effect (*m*-Me) as well as its electronic effect (*p*-MeO, *m*-Me).[15] We also reported in preliminary communications the design and preparation of axially chiral diphosphines,[18—21] which were found to be very efficient ligands for ruthenium-catalyzed asymmetric hydrogenation of a β-keto ester or rhodium-catalyzed asymmetric hydrogenation of an α-amino ketone. In this article we describe in detail the synthesis of optically pure 3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyls **8a**—**c** bearing one or two 6,(6′)-dicyclohexylphosphino group(s) and/or 6,(6′)-diphenylphosphino group(s), and an application to rhodium-catalyzed asymmetric hydrogenation.

Results and Discussion

The synthetic route of axially dissymmetric biphenyldiphosphine ligands **8a**—**c** bearing one or two dicyclohexylphosphino group(s) and/or one or two diphenylphosphino group(s) is described in Chart 1 (**8a**—**c** were abbreviated to BIMOP, Cy-BIMOP, and MOC-BIMOP, respectively). Iodination of 2,6-dimethylnitrobenzene (**1**) was carried out selectively at the 3-position by heating with iodine at 90 °C for 4 d in the presence of periodic acid in acetic acid containing dil. sulfuric acid, yielding mono-iodide **2** in high isolated yield (95%). The nitro group of **2** was reduced by heating with iron powder in water for 48 h in the presence of a catalytic amount of sulfuric acid, and the corresponding amine was isolated as a hydrochloride **3** in high yield (92%). The amino group was converted to a methoxy group by diazotization with isoamyl nitrite followed by elimination of N_2 in methanol, and an anisole derivative **4** was obtained in good yield. The methoxy group was expected to be useful for introducing a bromo group at the *para*-position and for increasing the electron density of a phosphino group introduced later at the same position. Ullmann coupling of **4** was carried out by heating with copper powder in sulfolane at 220 °C for 15 h, affording the corresponding biphenyl **5**. Bromination of **5** was easily performed by the reaction with 2 eq of bromine in acetic acid, yielding selectively a 6,6′-di-

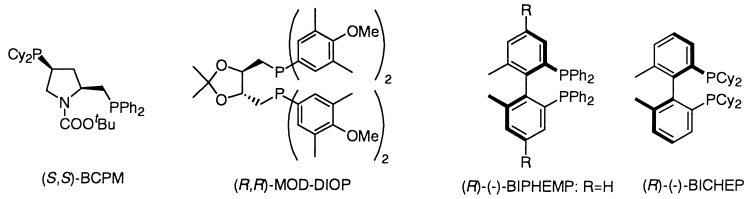
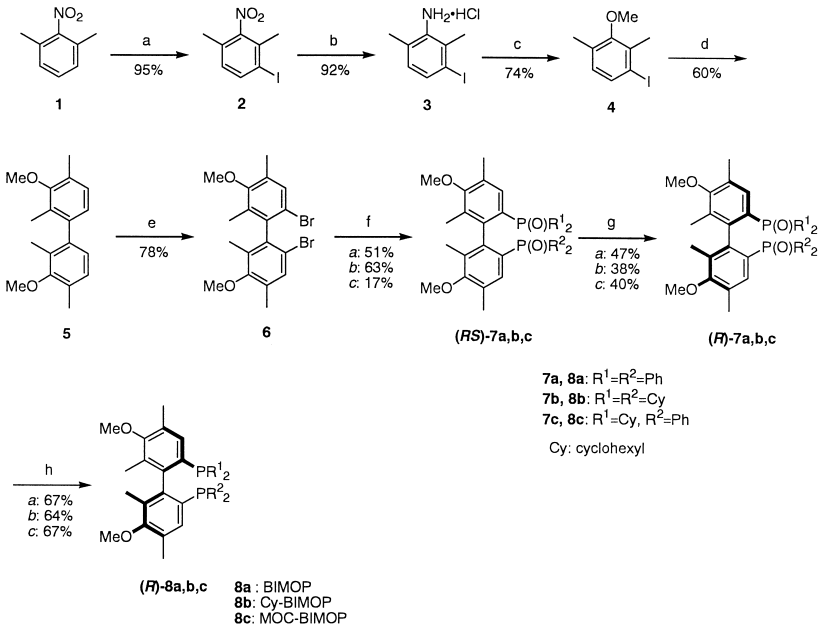


Fig. 1. Diphosphine Ligands

* To whom correspondence should be addressed. e-mail: morimtt@u-shizuoka-ken.ac.jp



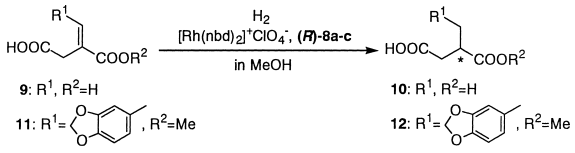
Reagents: (a) I_2, HIO_4, H_2SO_4/AcOH, H_2O; (b) 1)Fe, H_2SO_4/H_2O, 2) HCl/MeOH; (c) 1) *i*-AmylONO/AcOH, dioxane, 2) MeOH; (d) Cu/sulfolane; (e) Br_2/AcOH; (f) *a*) *t*-BuLi, $Ph_2P(O)Cl$/THF; *b*) 1) *t*-BuLi, Cy_2PCl/THF, 2) H_2O_2/CH_2Cl_2; *c*) 1) *t*-BuLi, $Ph_2P(O)Cl$/THF, 2) *t*-BuLi, Cy_2PCl/THF, 3) H_2O_2/CH_2Cl_2; (g) *a,b*) (-)-DBTA, *c*) HPLC with Chiralpack OT(+); (h) $HSiCl_3$, NEt_3/PhCl

Chart 1. Synthesis of (*R*)-6,6′-Bis(dialkylphosphino)-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl (**(*R*)-8a—c**)

brominated product **6** in good yield. Dilithiation of **6** with *tert*-butyllithium at −70 °C followed by treatment with 2 eq of diphenylphosphinic chloride resulted in the formation of a diphosphine dioxide, (*RS*)-6,6′-bis(diphenylphosphoryl)-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl **(*RS*)-7a** in 51% yield. An (*RS*)-6,6′-bis(dicyclohexylphosphoryl) derivative **(*RS*)-7b** was similarly prepared in 63% yield by the reaction of the dilithiate with chlorodicyclohexylphosphine followed by oxidation with hydrogen peroxide. An (*RS*)-6-dicyclohexylphosphoryl-6′-diphenylphosphoryl derivative **(*RS*)-7c** was also synthesized in 14% yield by stepwise diphenylphosphorylation and dicyclohexylphosphination followed by oxidation. Effective optical resolution of **(*RS*)-7a, b** was attained by using (2*R*,3*R*)-(−)-2,3-*O*,*O*′-dibenzoyltartaric acid (DBTA) as a resolving agent. When a hot solution of **(*RS*)-7a** and (−)-DBTA in chloroform was diluted with hot ethyl acetate, cooled, and seeded with a small amount of pure **(*R*)-7a**, a less soluble diastereomer precipitated as crystals. Repeated recrystallization from a mixed solvent of chloroform and ethyl acetate gave a diasteromerically pure complex of **(*R*)-7a** and the dibenzoyltartaric acid in a theoretical 47% isolated yield. Free **(*R*)-7a** was isolated quantitatively by treatment with alkaline. Optically pure **(*R*)-7b** was also isolated in 38% overall yield from **(*RS*)-7b** by resolution with (2*R*,3*R*)-(−)-2,3-*O*,*O*′-dibenzoyltartaric acid in methanol. Optical resolution of **(*RS*)-7c** was found to be difficult with the dibenzoyltartaric acid; therefore, **(*R*)-7c** was isolated by preparative HPLC with a chiral column, Chiralpack OT(+) using hexane/2-propanol (4/1) as an eluent. Reduction of the phosphine oxides **(*R*)-7a—c** was carried out without any racemization in a sealed tube by heating with an excess of trichlorosilane in the presence of triethylamine in chlorobenzene at 140 °C (bath temp.) for 5 h. Purification by silica gel column chromatography (eluent: chloroform for **8a** or toluene for **8b, c**) afforded the corresponding phosphines **(*R*)-8a—c** in good yields. The absolute configurations of **(*R*)-8a—c** were determined by comparison of their CD spectra on the shape and the signs of the major Cotton effects with that of (*R*)-BIPHEMP whose absolute configuration had been determined by X-ray crystallography.[22] The CD spectra of **(*R*)-8a—c** showed a nearly identical Cotton curve (exhibiting strong negative maxima at 230—240 nm and weaker positive maxima at 266—278 nm) with those of (*R*)-BIPHEMP and its analogs.[22] The absolute configurations of (*R*)- and (*S*)-BICHEP bearing a similar structure to **8b** had been also determined by comparison of their CD spectra with those of (*R*)- and (*S*)-BIPHEMP.[23]

Catalytic asymmetric hydrogenation of functionalized olefins such as itaconic acid (**9**), α-piperonylidenesuccinic acid monomethyl ester (**11**), and (*Z*)-α-acetamidocinnamic acid (**13**) was carried out by using cationic rhodium complexes of **(*R*)-8a—c**. The results are summarized in Tables 1 and 2. Using 0.1 mol% of cationic rhodium(I) complex catalysts which were prepared by mixing bis(norbornadiene)-rhodium(I) perchlorate $[[Rh(nbd)_2]^+ClO_4^-]$ and **(*R*)-8a—c** in dichloromethane and concentrated *in vacuo*, the hydrogenation of itaconic acid (**9**) was carried out in methanol under 5 atm of hydrogen, yielding the hydrogenation product **10** quantitatively in 51% ee (*S*) with **(*R*)-8a**, 80% ee (*R*) with **(*R*)-8b**, and 71% ee (*R*) with **(*R*)-8c**, respectively (Table 1). In the presence of triethylamine the enantioselectivity with **(*R*)-8a** was reduced to 19% ee (*S*). Analogous α-piperonylidenesuccinic acid monomethyl ester (**11**) was also hydrogenated under the same conditions as described above, and similar results were obtained (56% ee (*S*) with **(*R*)-8a**, 73% ee (*R*) with **(*R*)-8b**, 59% ee (*R*) with **(*R*)-8c**). To our surprise, the chirality of the products **10** and **12** ((*S*)-configuration) induced by **(*R*)-8a** was reversed in comparison with that induced by **(*R*)-8b, c**, although all the ligands **(*R*)-8a—c** have the same axial chirality backbone. (*R*)-BINAP did not show

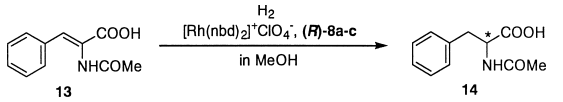
Table 1. Asymmetric Hydrogenation[a] of Itaconic Acid and α-Piperonylidenesuccinic Acid Monomethyl Ester Catalyzed by Rhodium(I) Complexes of Ligands **(*R*)-8a—c**



Substrate	Ligand	Yield (%)[b]	E.e. (%)[c]	Confign.[d]
9	**(*R*)-8a**	100	51	*S*
9	**(*R*)-8b**	100	80	*R*
9	**(*R*)-8c**	100	71	*R*
11	**(*R*)-8a**	72	56	*S*
11	**(*R*)-8b**	100	73	*R*
11	**(*R*)-8c**	61	59	*R*

a) The reaction was carried out using 0.5 M solution of the substrate in MeOH under the conditions: [Subst.]/[Rh]=1000, 5 atm (H_2), 30 °C, 20 h. *b*) Determined by ^{1}H-NMR analysis. *c*) Calculated on the basis of the specifical rotation value of the pure (*R*)-enantiomer **10**, $[\alpha]_D^{20}$ +16.88° (*c*=2.16, EtOH) [Berner E., Leonardsen R., *Ann. Chem.*, **1**, 538 (1939).] or by HPLC analysis of the corresponding morpholino derivative of **12** on a chiral column, Chiralcel OD. *d*) Determined by the sign of the specific rotation in comparison with that of **(*R*)-10** or **(*R*)-12**, $[\alpha]_D^{20}$ +30.4° (*c*=2, MeOH) [Brown E., Daugan A., *Tetrahetron Lett.*, **26**, 3997—3998 (1985).].

Table 2. Asymmetric Hydrogenation[a] of (*Z*)-2-Acetamidocinnamic Acid Catalyzed by Rhodium(I) Complexes of Ligands **(*R*)-8a—c**



Ligand	Yield (%)[b]	E.e. (%)[c]	Confign.[d]
(*R*)-8a	42	30	*R*
(*R*)-8b	100	79	*S*
(*R*)-8c	100	61	*S*

a) The reaction was carried out using 0.1 M solution of the substrate in MeOH under the conditions: [Subst.]/[Rh]=500, 10 atm (H_2), 50 °C, 24 h. *b*) Determined by ^{1}H-NMR analysis. *c*) Calculated on the basis of the specifical rotation value of the pure (*S*)-enantiomer **14**, $[\alpha]_D^{20}$ +40.1° (*c*=1.0, MeOH) [Vineyard B. D., Knowles W. S., Sabacky M. J., Bachman G. L., Weinkauff D. J., *J. Am. Chem. Soc.*, **99**, 5946—5952 (1977).]. *d*) Determined by the sign of the specific rotation.

good enantioselectivity (almost racemic) in the hydrogenation of **9** and **11** under the same reaction conditions. Contrary to these results, ruthenium complexes of both **(*R*)-8a** and (*R*)-BINAP showed the same chirality induction (*R*) in the hydrogenation of a β-keto ester, methyl 3-oxobutanoate (98—99% ee (*R*)) and an α,β-unsaturated carboxylic acid, tiglic acid (87—91% ee (*R*)).[18] Next, the hydrogenation of (*Z*)-α-acetamidocinnamic acid (**13**) was carried out with 0.2 mol% of the same rhodium complexes of **(*R*)-8a—c** under 10 atm of hydrogen, and the hydrogenation product was obtained quantitatively (except when using **(*R*)-8a**) in 30% ee (*R*) with **(*R*)-8a**, 79% ee (*S*) with **(*R*)-8b**, and 61% ee (*S*) with **(*R*)-8c**, respectively. In this case, reversal of chilarity induction was also observed between **(*R*)-8a** (*R*-selective) and **(*R*)-8b, c** (*S*-selective). It should be noted that the *R* and *S* selectivities (or *vice versa*) in hydrogenation of itaconic acids and (*Z*)-α-acetamidocinnamic acid, respectively, are the same in a stereochemical sense, though the *R* and *S* are superficially different.

We previously reported the correlation between the chirality of bidentate ligands and the absolute configuration of the products obtained by rhodium-catalyzed asymmetric hydrogenation or palladium-catalyzed asymmetric allylic alkylation. We first proposed a *P*/*M* chirality concept,[24] where the positioning array of four phenyl rings of diphosphine ligands closely correlates with the absolute configuration of products in asymmetric hydrogenation, and later presented a more general concept, *Pr*/*Mr* chirality,[25] for showing all chiral bidentate ligands (*e.g.* P,P-ligand, P,N-ligand, S,N-ligand, N,N-ligand, *etc.*) (Chart 2). The ligands **(*R*)-8a—c** were classified to bear *Pr*-chirality by comparison with (*R*)- or (*S*)-BINAP, whose metal complexes had been structurally resolved by X-ray crystallography.[26,27] Based on our previous elucidation of the correlation between the *Pr*/*Mr* chirality of ligands and the hydrogenation products,[24,25] it is reasonable that *Pr*-chirality ligands show *R*- and *S*-selectivities in the hydrogenation of itaconic acids and (*Z*)-α-acetamidocinnamic acid, respectively. Therefore, the ligands **(*R*)-8b, c** have normal selectivity in the rhodium-catalyzed hydrogenation. Similar *R*- and *S*-selectivities were observed with (*R*)-BICHEP in the hydrogenation of itaconic acids and (*Z*)-α-acetamidocinnamic acid.[28] Although the reason why **(*R*)-8a** shows reversed chirality is not clearly demonstrated, the reversed chirality might be rationalized by a possible explanation that a dinuclear complex[26,29] of Rh(I) and a triaryl-type ligand **(*R*)-8a** (probably formed *in situ* from a diene coordinate starting complex) can show reversed chirality. Other reversal of chirality induced by MOD-DIOP in rhodium-catalyzed asymmetric hydrogenation of enamides was reported previously.[30] It is well known that the rhodium-catalyzed asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid proceeds by Halpern's mechanism[31] where an intermediate of a minor diasteromeric complex of the substrate and the catalyst is much more active for oxidative addition of hydrogen (a rate-determining step) than a major intermediate, and, therefore, the minor intermediate affords a predominant enantiomeric product. In the case of a possible dinuclear complex of **(*R*)-8a**, a minor diastereomeric complex may not be so active such that

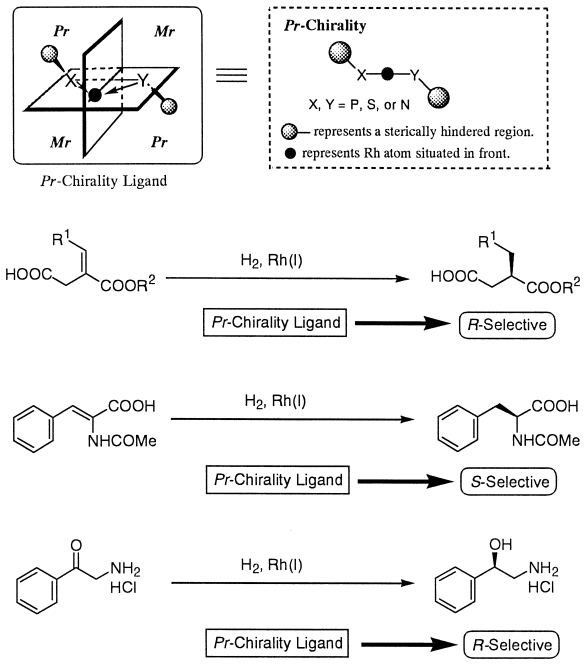
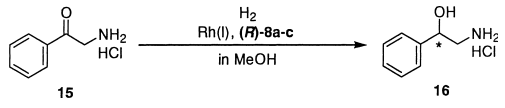


Chart 2. Correlation between the Chirality of Bidentate Ligands and the Absolute Configuration of the Asymmetric Hydrogenation Products

Table 3. Asymmetric Hydrogenation[a] of 2-Aminoacetophenone Hydrochloride Catalyzed by Rhodium(I) Complexes of Ligands **(*R*)-8a—c**



15 **16**

Ligand	Rh[b]	[**15**]/[Rh]	atm/°C/d	Yield (%)[c]	E.e. (%)[d]	Confign.[d]
(*R*)-8a	Rh^N	500	50/50/4	61	8	*S*
(*R*)-8b	Rh^N	500	50/50/4	100	55	*R*
(*R*)-8c	Rh^+	1000	90/50/7	100	93	*R*

a) The reaction was carried out using 0.5 M solution of the substrate in MeOH in the presence of triethylamine ([Et_3N]/[Rh]=5). *b*) Rh^+: $[Rh(nbd)_2]^+ClO_4^-$, Rh^N: $[Rh(nbd)Cl]_2$. *c*) Determined by ^{1}H-NMR analysis. *d*) Determined by HPLC analysis of the corresponding *N*-benzoyl derivative on a chiral column, Chiralcel OD, in comparison with an authentic specimen.

the chirality of the product might be controlled by a major diastereomer.

Furthermore, asymmetric hydrogenation of a functionalized ketone, 2-aminoacetophenone hydrochloride (**15**) was carried out in the presence of 0.1—0.2 mol% of a cationic or a neutral rhodium(I) complex of **(*R*)-8a—c** under the conditions described in Table 3. In this case a similar trend was observed for the chirality of the product **16** (8% ee (*S*) with **(*R*)-8a**, 55% ee (*R*) with **(*R*)-8b**, 93% (*R*) with **(*R*)-8c**). It is noteworthy that the ligand **(*R*)-8c** bearing both a diphenylphosphino group and a dicyclohexylphosphino group (electronically dissymmetrized phosphino groups) showed a very high enantioselectivity. It has been demonstrated that other backbone-type ligands, BCPMs bearing both dissymmetrized phosphino groups, also show high enantioselectivity in similar rhodium-catalyzed asymmetric hydrogenation of various amino ketones.[12,13]

In summary, we have described the synthesis of enantiopure biphenyl ligands bearing one or two diphenylphosphino group(s) and/or one or two dicyclohexylphosphino group(s), and their application to rhodium(I)-catalyzed asymmetric hydrogenation of itaconic acid and its analogs, (*Z*)-α-acetamidocinnamic acid, and 2-aminoacetophenone hydrochloride.

Experimental

Melting points were determined on a micro hot-stage apparatus and are uncorrected. ^{1}H-NMR spectra were recorded in a $CDCl_3$ solution using a JEOL JNM-EX 270 spectrometer. Chemical shift values are expressed in ppm based on tetramethylsilane for ^{1}H. IR spectra were measured on a JASCO IR-810 spectrometer. Optical rotations were measured on a JASCO DIP-140 digital polarimeter. CD spectra were recorded on a JASCO J-20 spectropolarimeter, and λ values are expressed in nm. Column chromatographic isolation was conducted using silica gel (Kieselgel 60, 70—230 mesh, Merck). Kieselgel 60 F254 aluminum plates (Merck) were employed for TLC. In general, all organic reagents were used as purchased. THF was distilled over sodium metal/benzophenone ketyl and used as peroxide-free. Sulfolane and chlorobenzene were dried over Molecular Sieves 4A. For the catalytic reactions, dehydrated methanol and dichloromethane were purchased and used after being degassed and filled with argon.

2,4-Dimethyl-3-nitroiodobenzene (2) To a mixture of 2,6-dimethylnitrobenzene (**1**) (151 g, 1.0 mol), acetic acid (1200 ml), and conc. H_2SO_4 (60 ml) were added iodine (102 g, 0.4 mol) and periodic acid dihydrate (205 g, 0.90 mol), and the mixture was stirred and heated at 90 °C for 4 d. After cooling to room temperature, the reaction mixture was diluted with water (2000 ml) and extracted with dichloromethane (1000 ml). The extract was ice-cooled and washed successively with aqueous 2 M NaOH (3×500 ml), water (3×500 ml), and brine (300 ml), and dried over $MgSO_4$. Evaporation of the solvent *in vacuo* gave **2** as a yellowish solid (263 g, 95%). The product was pure enough to be used in the next step. An analytical sample of **2** was obtained by recrystallization from ethanol as pale yellow needles, mp 69—70 °C. IR (KBr) cm^{-1}: 1520, 1370, 860. ^{1}H-NMR δ ($CDCl_3$): 2.24 (3H, s, CH_3), 2.38 (3H, s, CH_3), 6.86 (1H, d, J=8 Hz), 7.81 (1H, d, J=8 Hz). *Anal.* Calcd for $C_8H_8INO_2$: C, 34.68; H, 2.91; N, 5.06. Found: C, 34.80; H, 2.75; N, 4.73.

3-Iodo-2,6-dimethylaniline Hydrochloride (3) A mixture of **2** (277 g, 1.0 mol), water (500 ml), conc. H_2SO_4 (20 g, 0.2 mol), and iron powder (168 g, 3.0 mol) was mechanically stirred and heated under reflux for 48 h. After the reaction mixture was cooled to 70 °C, toluene (400 ml) was added and the mixture was stirred for 5 min at the same temperature. Precipitated inorganic materials were filtered off and washed successively with toluene (300 ml) and water (200 ml). The filtrates were combined and the organic layer was separated. The aqueous layer was ice-cooled and aq. 1 M NaOH was added until the pH of the solution became 9—10. The alkaline solution was extracted with toluene. The toluene extract and the above organic layer were combined and dried over $MgSO_4$. Evaporation of the solvent *in vacuo* left a crude aniline as a red oil. To a solution of the crude aniline in methanol (500 ml) under ice-cooling was added a methanol solution containing 25% dry HCl enough for forming its hydrochloride as precipitates. Evaporation of the solvent left a solid. After three-times dissolution in methanol (300 ml) followed by evaporation, ether (700 ml) was added to the residue and the mixture was stirred and heated under reflux for 1 h. After cooling to room temperature, the precipitates were collected by filtration, washed with ether (300 ml), and dried, affording **3** as a white solid (261 g, 92%) (pure enough to be used in the next step). An analytical sample of **3** was obtained by recrystallization from methanol as colorless needles, mp 185—186 °C. IR (KBr) cm^{-1}: 2770, 1970, 1590, 1515. ^{1}H-NMR δ ($CDCl_3$): 2.40 (3H, s, CH_3), 2.56 (3H, s, CH_3), 6.97 (1H, d, J=8 Hz), 7.83 (1H, d, J=8 Hz). *Anal.* Calcd for $C_8H_{11}ClIN$: C, 33.89; H, 3.91; N, 4.94. Found: C, 33.89; H, 3.54; N, 4.66.

3-Iodo-2,6-dimethylanisole (4) To a stirred and cooled (−5—0 °C) solution of **3** (142 g, 0.5 mol) in acetic acid (250 ml) and 1,4-dioxane (250 ml) was added dropwise isoamyl nitrite (64.5 g, 0.55 mol) during 1 h, and the stirring was continued at 0 °C for another 1 h. Ice-cooled 1,4-dioxane (250 ml) was added to the reaction mixture containing precipitates of the corresponding diazonium salt formed. The precipitates were collected by filtration and washed with cooled 1,4-dioxane (250 ml). [Caution: Since the diazonium salt is thermally quite unstable (explosive), it should be isolated with much care and used immediately in the next step.] The obtained diazonium salt was carefully added into cooled methanol (1000 ml), and the mixture was stirred at 0 °C for 1 h and at room temperature for 1 h, and then heated under reflux for 15 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo*. Purification of the residue by silica gel column chromatography (eluent: hexane/toluene=2/1) afforded **4** (97 g, 74%) as an oil. ^{1}H-NMR δ ($CDCl_3$): 2.23 (3H, s, CH_3), 2.39 (3H, s, CH_3), 3.68 (3H, s, OCH_3), 6.73 (1H, d, J=8 Hz), 7.47 (1H, d, J=8 Hz). *Anal.* Calcd for $C_9H_{11}IO$: C, 41.25; H, 4.23. Found: C, 40.96; H, 4.20.

3,3′-Dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl (5) A mixture of **4** (52.4 g, 0.5 mol), sulfolane (50 ml), and copper powder (20.4 g, 0.32 mol) was mechanically stirred and heated at 220 °C for 15 h. After cooling to 70 °C, the reaction mixture was diluted with toluene (80 ml). Precipitates were filtered by suction and washed with toluene (2×60 ml). The combined filtrates were washed successively with water (2×100 ml) and saturated brine (60 ml), dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by silica gel column chromatography (eluent: hexane/toluene=2/1) gave the corresponding biphenyl (**5**) (16.2 g, 60%) as a white solid: mp 81—82 °C. ^{1}H-NMR δ ($CDCl_3$): 1.98 (6H, s, 2×CH_3), 2.34 (6H, s, 2×CH_3), 3.75(6H, s, 2×OCH_3), 6.79 (2H, d, J=7.5 Hz), 7.03 (2H, d, J=7.5 Hz). *Anal.* Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.69; H, 8.16.

(*RS*)-6,6′-Dibromo-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*RS*)-6) To a stirred solution of **5** (27.0 g, 0.10 mol) in acetic acid (100 ml) was added bromine (12 ml, 0.24 mol) with cooling in an ice-bath, and the mixture was stirred at room temperature for 3 h. To the reaction mixture was added saturated sodium bisulfite solution until the orange color of the remaining bromine disappeared. White precipitates were collected by filtration, washed with water (300 ml), and dried *in vacuo*. Recrystallization from 2-propanol gave pure **(*RS*)-6** (33.4 g, 78%) as colorless prisms: mp 122—123 °C. ^{1}H-NMR δ ($CDCl_3$): 1.93 (6H, s, 2×CH_3), 2.32 (6H, s, 2×CH_3), 3.73 (6H, s, 2×OCH_3), 7.36 (2H, s). *Anal.* Calcd for $C_{18}H_{20}Br_2O_2$: C, 50.49; H, 4.71. Found: C, 50.85; H, 4.73.

(*RS*)-6,6′-Bis(diphenylphosphoryl)-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*RS*)-7a) To a stirred solution of **(*RS*)-6** (4.28 g,

0.01 mol) in THF (90 ml) at −70 °C under an argon atmosphere was added dropwise a solution of *tert*-butyllithium (1.5 M in pentane, 28 ml, 0.042 mol), and the mixture was stirred at the same temperature for 1 h. To the stirred and cooled reaction mixture was added a solution of diphenylphosphinic chloride (10.4 g, 0.044 mol) in THF (10 ml). After stirring for 1 h, the reaction temperature was slowly raised up to room temperature during more than 3 h. The solvent was removed *in vacuo* and dichloromethane (100 ml) was added to the residue. The dichloromethane solution was washed successively with aq. 1 M NaOH solution (100 ml), water (3×50 ml), and saturate brine (30 ml), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by silica gel column chromatography (eluent: chloroform/acetone=9/1) followed by recrystallization from methanol gave pure **(*RS*)-7a** (3.42 g, 51%) as colorless leaflets: mp >320 °C. IR (KBr) cm^{-1}: 1195 (P=O). ^{1}H-NMR δ ($CDCl_3$): 1.29 (6H, s, 2×CH_3), 2.20 (6H, s, 2×CH_3), 3.59 (6H, s, 2×OCH_3), 6.90 (2H, d, J_{HCCP}=14 Hz), 7.26—7.51 (12H, m), 7.60—7.76 (8H, m). *Anal.* Calcd for $C_{42}H_{40}O_4P_2\cdot 1/2H_2O$: C, 74.21; H, 6.08. Found: C, 73.88; H, 5.93.

(*RS*)-6,6′-Bis(dicyclohexylphosphoryl)-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*RS*)-7b) To a stirred solution of **(*RS*)-6** (4.28 g, 0.01 mol) in THF (90 ml) at −70 °C under an argon atmosphere was added dropwise a solution of *tert*-butyllithium (1.5 M in pentane, 28 ml, 0.042 mol), and the mixture was stirred at the same temperature for 1 h. To the stirred and cooled reaction mixture was added a solution of chlorodicyclohexylphosphine (8.38 g, 0.036 mol) in THF (10 ml). After stirring for 1 h, the reaction temperature was slowly raised up to room temperature during more than 6 h. The solvent was removed *in vacuo* and dichloromethane (100 ml) and water (10 ml) were added to the residue. The two-phase solution was ice-cooled and a solution of 31% hydrogen peroxide (11 ml, 0.1 mol) was added. The mixture was stirred at room temperature for 3 h. The organic layer was separated, washed successively with aq. 1 M NaOH (50 ml), water (3×50 ml), and saturated brine (30 ml), dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by silica gel column chromatography (eluent: toluene/ethyl acetate=9/1) gave pure (**(*RS*)-7b**) (4.38 g, 63%) as a white solid: mp 249—250 °C. IR (KBr) cm^{-1}: 1182 (P=O). ^{1}H-NMR δ ($CDCl_3$): 1.10—1.91 (40H, m), 1.81 (6H, s, 2×CH_3), 1.97—2.11 (4H, m, 4×CH), 2.33 (6H, s, 2×CH_3), 3.74 (6H, s, 2×OCH_3), 6.99 (2H, d, J_{HCCP}=11 Hz). *Anal.* Calcd for $C_{42}H_{64}O_4P_2$: C, 72.59; H, 9.28. Found: C, 73.07; H, 9.52.

(*RS*)-6-Dicyclohexylphosphoryl-6′-diphenylphosphoryl-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*RS*)-7c) To a stirred solution of **(*RS*)-6** (1.00 g, 2.3 mmol) in THF (30 ml) at −70 °C under an argon atmosphere was added dropwise a solution of *tert*-butyllithium (1.5 M in pentane, 2 ml, 3.5 mmol), and the mixture was stirred at the same temperature for 0.5 h. To the reaction mixture was added a solution of diphenylphosphinic chloride (0.51 g, 2.3 mmol) in THF (5 ml). After 0.5 h the reaction temperature was gradually raised up to room temperature during more than 3 h. The reaction mixture was chilled again at −70 °C and a solution of *tert*-butyllithium (1.5 M in pentane, 2 ml, 3.5 mmol) was added dropwise. After 0.5 h a solution of chlorodicyclohexylphosphine (0.55 g, 2.3 mmol) in THF (5 ml) was added, and the mixture was stirred at −70 °C for 0.5 h. Then the temperature was gradually raised up to room temperature during more than 6 h, and the solvent was removed by evaporation. The residue was dissolved in a mixed solvent of dichloromethane (30 ml) and water (5 ml). To the solution with ice-cooling was added 31% hydrogen peroxide (5 ml, 45 mmol), and the mixture was stirred at room temperature for 3 h. The organic layer was separated, washed successively with aq. 1 M NaOH (10 ml), water (3×20 ml), and saturated brine (20 ml), dried over $MgSO_4$, and concentrated *in vacuo*. Isolation by silica gel column chromatography (eluent: ethyl acetate) gave pure **(*RS*)-7c** in 17% yield as a white solid: mp 225—227 °C. IR (KBr) cm^{-1}: 1190 (P=O). ^{1}H-NMR δ ($CDCl_3$): 1.36 (3H, s, CH_3), 1.51—2.07 (22H, m), 1.85 (3H, s, CH_3), 2.33 (3H, s, CH_3), 2.35 (3H, s, CH_3), 3.68 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 6.98 (1H, d, J_{HCCP}=13 Hz), 7.03 (1H, d, J=8 Hz), 7.58—7.71 (4H, m), 7.26—7.47 (6H, m). *Anal.* Calcd for $C_{42}H_{52}O_4P_2$: C, 73.88; H, 7.68. Found: C, 73.57; H, 8.05.

(*R*)-6,6′-Bis(diphenylphosphoryl)-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*R*)-7a) A mixture of **(*RS*)-7a** (6.71 g, 0.01 mol) and (2*R*,3*R*)-(−)-2,3-*O*,*O*′-dibenzoyltartaric acid monohydrate (4.14 g, 0.011 mol) in chloroform (10 ml) was heated to form a clear solution. To the hot solution was added hot ethyl acetate (20 ml), and the solution was cooled to room temperature. After addition of a small amount of pure **(*R*)-7a** as a seed, additional hot ethyl acetate (10 ml) was added, and the whole solution was allowed to stand for 15 h. Precipitated crystals were collected by filtration, and repeatedly recrystallized from hot chloroform (5 ml) and ethyl acetate (10 ml), affording a pure complex of **(*R*)-7a** and *O*,*O*′-dibenzoyltartaric acid (2.42 g, 47%): mp 216—217 °C (decomp.), $[\alpha]_D^{21}$ +20.0° (*c*=0.63, $CHCl_3$). IR (KBr) cm^{-1}: 1730 (C=O). ^{1}H-NMR δ ($CDCl_3$): 1.28 (6H, s, 2×CH_3), 2.15 (6H, s, 2×CH_3), 3.52 (6H, s, 2×OCH_3), 5.02 (2H, br, 2×COOH), 5.81 (2H, s, 2×CH), 6.90 (2H, d, J_{HCCP}=15 Hz), 7.19—7.56 (26H, m), 8.00—8.02 (4H, m). *Anal.* Calcd for $C_{60}H_{54}O_{12}P_2$: C, 70.03; H, 5.29. Found: C, 70.46; H, 5.29. The complex was dissolved in dichloromethane (150 ml) and stirred with aq. 1 M NaOH (50 ml) for 0.5 h. The organic layer was separated, washed successively with water (3×50 ml) and saturated brine (30 ml), and dried over $MgSO_4$. Removal of the solvent *in vacuo* left **(*R*)-7a** as a white solid (1.58 g, 47% from **(*RS*)-7a**). An analytical sample of **(*R*)-7a** was obtained by recrystallization from methanol/isopropyl ether as colorless prisms, mp 268—269 °C, $[\alpha]_D^{20}$ +77.9° (*c*=0.72, $CHCl_3$). IR (KBr) cm^{-1}: 1195 (P=O). ^{1}H-NMR spectral data were in good agreement with those of **(*RS*)-7a**. *Anal.* Calcd for $C_{42}H_{40}O_4P_2\cdot 1/2CH_3OH$: C, 74.33; H, 6.17. Found: C, 74.63; H, 6.09.

(*R*)-6,6′-Bis(dicyclohexylphosphoryl)-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*RS*)-7b) A mixture of **(*RS*)-7b** (6.95 g, 0.01 mol) and (2*R*,3*R*)-(−)-2,3-*O*,*O*′-dibenzoyltartaric acid monohydrate (4.14 g, 0.011 mol) in methanol (170 ml) was heated to form a clear solution, and then left at room temperature. Precipitated crystals were collected by filtration and repeatedly recrystallized from methanol (80 ml), affording a pure complex of **(*R*)-7b** and *O*,*O*′-dibenzoyltartaric acid (2.11 g, 40%): mp 213—214 °C (decomp.), $[\alpha]_D^{21}$ −63.5° (*c*=1.02, $CHCl_3$). IR (KBr) cm^{-1}: 1730 (C=O). ^{1}H-NMR δ ($CDCl_3$): 0.82—1.90 (40H, m, 4×$(CH_2)_5$), 1.75 (6H, s, 2×CH_3), 2.24 (6H, s, 2×CH_3), 2.12—2.38 (4H, m, 4×CH), 3.65 (6H, s, 2×OCH_3), 5.72 (2H, s, 2×CH), 6.86 (2H, d, J_{HCCP}=12 Hz), 7.37—7.43 (4H, m), 7.52—7.57 (2H, m), 7.47 (2H, br, 2×COOH), 8.04—8.07 (4H, m). *Anal.* Calcd for $C_{60}H_{78}O_{12}P_2$: C, 68.42; H, 7.46. Found: C, 68.37; H, 7.75. The complex was dissolved in dichloromethane (150 ml) and stirred with aq. 1 M NaOH (50 ml) for 0.5 h. The organic layer was separated, washed successively with water (3×50 ml) and saturated brine (30 ml), and dried over $MgSO_4$. Removal of the solvent *in vacuo* left **(*R*)-7b** as a solid (1.32 g, 38% from **(*RS*)-7b**): mp 99—100 °C, $[\alpha]_D^{21}$ −42.6° (*c*=1.10, $CHCl_3$). IR (KBr) cm^{-1}: 1182 (P=O). ^{1}H-NMR spectral data were in good agreement with those of **(*RS*)-7b**. *Anal.* Calcd for $C_{42}H_{64}O_4P_2\cdot 1/2H_2O$: C, 71.66; H, 9.31. Found: C, 71.43; H, 9.43.

(*R*)-6-Dicyclohexylphosphoryl-6′-diphenylphosphoryl-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*R*)-7c) Optically pure **(*R*)-7c** was isolated in 80% yield by preparative HPLC with a chiral column (Chiralpack OT(+), Daicel) using hexane/2-propanol (4/1): $[\alpha]_D^{20}$ +25.7° (*c*=1.00, $CHCl_3$). ^{1}H-NMR spectral data were in good agreement with those of **(*RS*)-7c**.

(*R*)-6,6′-Bis(diphenylphosphino)-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*R*)-BIMOP, (*R*)-8a) In a sealed tube were placed **(*R*)-7a** (671 mg, 1.00 mmol), degassed chlorobenzene (30 ml), and triethylamine (4.86 g, 48 mg), and cooled in an ice bath under argon. To the mixture was added trichlorosilane (5.42 g, 40 mmol). After the tube was sealed, the whole mixture was stirred and heated at a bath temperature of 140 °C for 5 h. The reaction mixture was ice-cooled, and a degassed solution of aq. 30% NaOH was added slowly enough to decompose white precipitates. The mixture was stirred and heated at 70 °C for 0.5 h under argon, and cooled to room temperature. After chlorobenzene (70 ml) was added, the organic layer was separated, washed successively with water (3×50 ml) and saturated brine (30 ml), dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by silica gel column chromatography (eluent: chloroform) gave pure **(*R*)-8a** (428 mg, 67%) as a white solid: mp 265—266 °C, $[\alpha]_D^{19}$ +37.4° (*c*=0.50, $CHCl_3$); CD λ nm: 240 (neg. max.), 278 (pos. max.) (*c*=0.002, EtOH/CH_2Cl_2=22/3). ^{1}H-NMR δ ($CDCl_3$): 1.24 (6H, s, 2×CH_3), 2.21 (6H, s, 2×CH_3), 3.48 (6H, s, 2×OCH_3), 6.84 (2H, s, 2×CH), 7.24—7.27 (20H, m, 4×C_6H_5). *Anal.* Calcd for $C_{42}H_{40}O_2P_2$: C, 78.98; H, 6.31. Found: C, 78.73; H, 6.25.

(*R*)-6,6′-Bis(dicyclohexylphosphino)-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*R*)-Cy-BIMOP, (*R*)-8b) Reduction of **(*R*)-7b** (695 mg, 1.00 mmol) with trichlorosilane was carried out in a similar manner as described for the preparation of **(*R*)-8a**. Purification by silica gel column chromatography (eluent: toluene) gave pure **(*R*)-8b** (424 mg, 64%) as a white solid: mp 185—186 °C, $[\alpha]_D^{19}$ −56.5° (*c*=1.16, $CHCl_3$); CD λ nm: 230 (neg. max.), 266 (pos. max.) (*c*=0.002, EtOH). ^{1}H-NMR δ ($CDCl_3$): 0.90—1.90 (44H, m, 4×C_6H_{11}), 1.80 (6H, s, 2×CH_3), 2.35 (6H, s, 2×CH_3), 3.72 (6H, s, 2×OCH_3), 7.09 (2H, s, 2×CH). *Anal.* Calcd for $C_{42}H_{64}O_2P_2$: C, 76.10; H, 9.73. Found: C, 76.04; H, 9.59.

(*R*)-6-Dicyclohexylphosphino-6′-diphenylphosphino-3,3′-dimethoxy-2,2′,4,4′-tetramethyl-1,1′-biphenyl ((*R*)-MOC-BIMOP, (*R*)-8c) Reduction of **(*R*)-7c** (110 mg, 0.16 mmol) with trichlorosilane (800 mg, 6.5 mmol)

was carried out in a similar manner as described for the preparation of **(*R*)-8a**. Purification by silica gel column chromatography (eluent: toluene) gave pure **(*R*)-8c** (72 mg, 67%) as a white solid: mp 226—229 °C, $[\alpha]_D^{20}$ −2.1° (c=1.00, benzene); CD λ nm: 238 (neg. max.), 274 (pos. max.) (c=0.001, EtOH). ^{1}H-NMR δ ($CDCl_3$): 1.11—2.12 (22H, m, 2×C_6H_{11}), 1.56 (3H, s, CH_3), 1.81 (3H, s, CH_3), 2.23 (3H, s, CH_3), 2.35 (3H, s, CH_3), 3.52 (3H, s, OCH_3), 3.71 (3H, s, OCH_3), 6.86 (1H, s, CH), 6.88 (1H, s, CH), 7.18—7.29 (10H, m, 2×C_6H_5). *Anal.* Calcd for $C_{42}H_{52}O_2P_2$: C, 77.51; H, 8.05. Found: C, 77.04; H, 8.23.

Catalytic Asymmetric Hydrogenation of Itaconic Acid (9) and Its Analog (11) A rhodium(I) complex catalyst solution was prepared by mixing bis(norbornadiene)rhodium(I) perchlorate $[Rh(nbd)_2]^+ClO_4^-$ (0.8 mg, 0.002 mmol) and a chiral ligand **(*R*)-8a—c** (0.0022 mmol) in degassed dichloromethane (2 ml) at room temperature for 3 h under an argon atmosphere followed by concentration *in vacuo* and dissolution in methanol (2 ml). To a glass tube equipped with a stirring bar were placed itaconic acid (**9**) (260 mg, 2.0 mmol) (or α-piperonylidenesuccinic acid monomethyl ester (**11**) (528 mg, 2.0 mmol)), degassed methanol (2 ml), and the above catalyst solution. The hydrogenation was carried out with stirring in an autoclave under 5 atm of hydrogen at 30 °C for 20 h. According to the procedures reported previously,[15,16] the hydrogenation product **10** or **12** was isolated and the enantiomeric excess was determined. All the results are summarized in Table 1.

Catalytic Asymmetric Hydrogenation of (*Z*)-α-Acetamidocinnamic Acid (13) The hydrogenation of **13** was carried out in a similar manner as described above except hydrogen pressure (10 atm), temperature (50 °C), and reaction time (24 h). According to the procedure reported previously,[32,33] the hydrogenation product **14** was isolated and the enantiomeric excess was determined. All the results are summarized in Table 2.

Catalytic Asymmetric Hydrogenation of 2-Aminoacetophenone Hydrochloride (15) The hydrogenation of **15** (685 mg, 5.0 mmol) was carried out in methanol (10 ml) with a cationic rhodium(I) catalyst prepared from $[Rh(nbd)_2]^+ClO_4^-$ (1.9 mg, 0.005 mmol) and **(*R*)-8c** (3.6 mg, 0.0055 mmol) or a neutral catalyst prepared *in situ* from $[Rh(nbd)Cl]_2$ (0.005 mmol) and **(*R*)-8a, b** (0.011 mmol) in the presence of triethylamine (0.025 mmol) under the conditions described in Table 3. According to the procedure reported previously,[32,33] the hydrogenation product **16** was isolated and the enantiomeric excess was determined by HPLC after conversion to its *N*-benzoyl derivative. All the results are summarized in Table 3.

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