Pergamon

Tetrahedron 56 (2000) 2247–2257

TETRAHEDRON

Palladium-Catalyzed Asymmetric Reduction of Racemic Allylic Esters with Formic Acid: Effects of Phosphine Ligands on Isomerization of π-Allylpalladium Intermediates and Enantioselectivity

Motoi Kawatsura, Yasuhiro Uozumi,† Masamichi Ogasawara and Tamio Hayashi*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

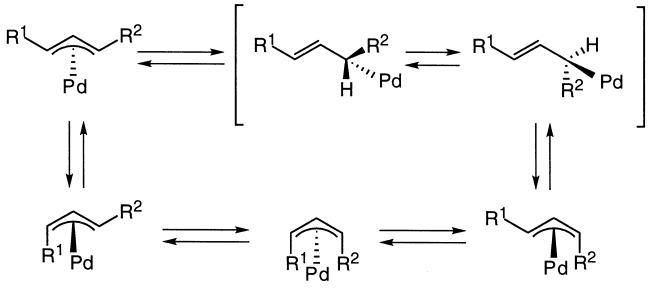
Accepted 7 December 1999

Abstract—A new MOP ligand (**1b**), (*R*)-(+)-2-(bis(3-trifluoromethylphenyl)phosphino)-2′-methoxy-1,1′-binaphthyl, was found to be more enantioselective than other MOP ligands for the palladium-catalyzed asymmetric reduction of α,α-disubstituted allylic esters with formic acid. The reduction of DL-2-(1-naphthyl)-3-buten-2-yl benzoate gave 3-(1-naphthyl)-1-butene of 90% ee. The higher enantioselectivity of **1b** is ascribed to fast *syn–anti* isomerization of π-allylpalladium intermediates formed by oxidative addition of allylic ester to a palladium(0) species. The rate of *syn–anti* isomerization was measured by the magnetization saturation transfer in ^{1}H NMR.

Introduction

Asymmetric allylic substitutions catalyzed by palladium complexes containing optically active phosphine ligands have attracted significant interest due to their synthetic utility.[1] The catalytic cycle of the reactions involves a π-allylpalladium complex as a key intermediate. Enantioselectivity in the asymmetric allylic substitutions is strongly dependent on the isomerization of π-allylpalladium intermediates which proceeds via well-known σ–π–σ mechanism. When a palladium atom shifts from one face to the other face, a substituent at the terminal position of π-allyl group coordinated to a palladium undergoes *syn-anti* interconversion with respect to the hydrogen at the center position by the σ–π–σ mechanism[2] (Scheme 1).

π-Allylpalladium complexes bearing a sterically bulky monodentate phosphine ligand (L), an anionic ligand (X), and π-allyl moiety that contains two alkyl substituents (R^1 and R^2) at 1-position take a *trans* geometry with respect to the phosphine ligand and the disubstituted π-allyl carbon due to a steric repulsion between them.[3] In this type of π-allylpalladium complexes where R^1 and R^2 are different to each other, there are three patterns of isomerization. They are (A) epimerization, (B) *syn-anti* isomerization and (C) *cis–trans* isomerization (Scheme 2). (A) The epimerization proceeds through a σ-allylpalladium intermediate that forms σ-bond at the C-3 position (*cis* to phosphorous atom). By the rotation around C2–C3 bond in this σ-allylpalladium intermediate, the palladium metal moves to the other face of π-allyl. During this isomerization, *syn* and *anti*



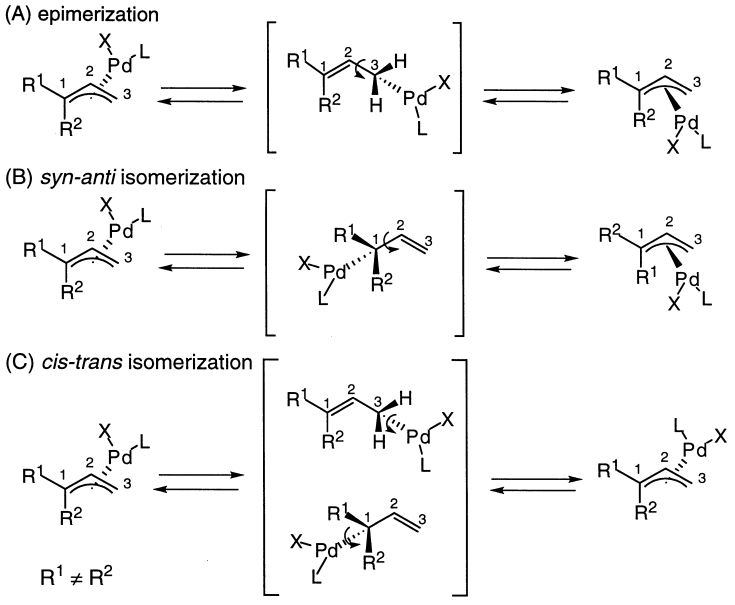
Scheme 1.

Keywords: isomerization; π-allylpalladium; enantioselectivity.

* Corresponding author. Tel.: +81-75-753-3983; fax: +81-75-753-3988; e-mail: thayashi@kuchem.kyoto-u.ac.jp

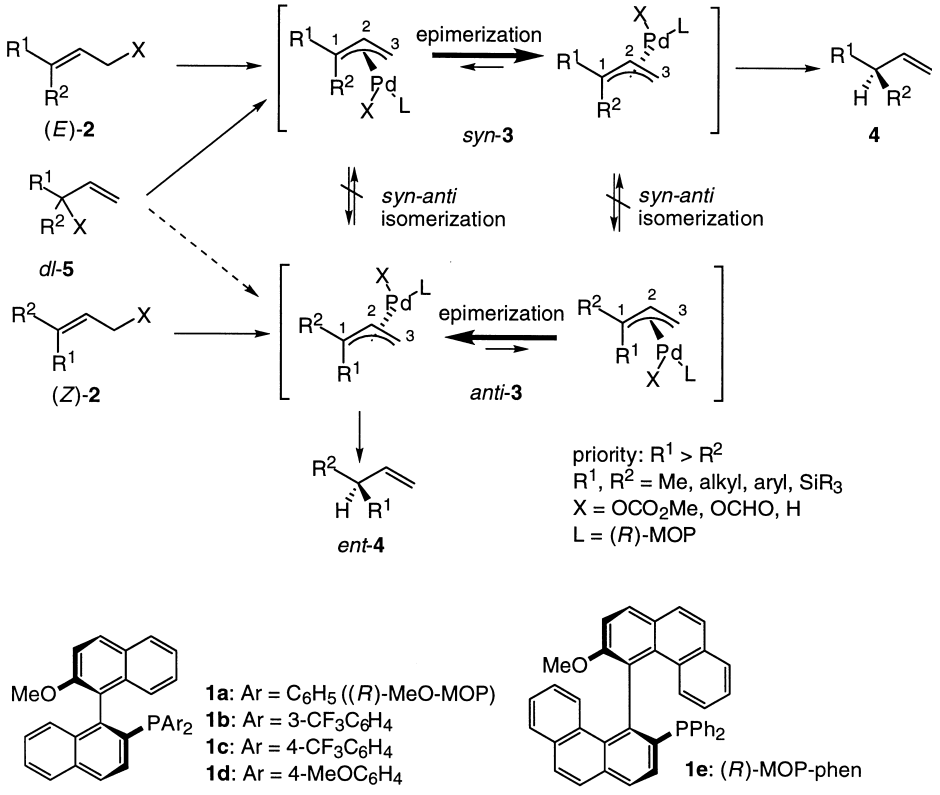
† Present address: Department of Organic Chemistry, Faculty of Pharmaceutical Sciences, Nagoya City University, Mizuho-ku, Nagoya 467-8603, Japan.

0040–4020/00/$ - see front matter
PII: S0040-4020(99)01107-2

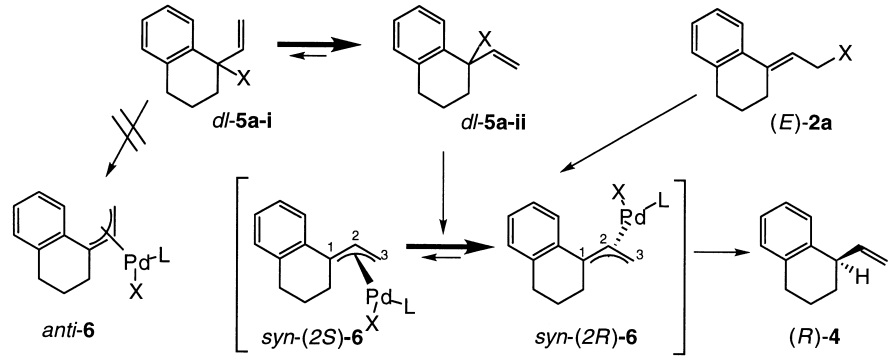


Scheme 2.

substituents on C-1 carbon stay at the original positions, so we call this one epimerization. (B) The *syn–anti* isomerization proceeds through a σ-allylpalladium intermediate that forms the σ-bond at the C-1 position (*trans* to phosphorous atom). The *syn–anti* interconversion takes place through rotation around C1–C2 bond in this σ-allylpalladium intermediate. The isomerization of the substituents from *syn* to *anti* and vice versa leads to the shift of palladium atom from one face to the other. (C) The *cis–trans* isomerization is an exchange of phosphine ligand (L) and anionic ligand (X) on the palladium atom. The *cis–trans* interconversion takes place through rotation of palladium–carbon bond in the σ-allylpalladium intermediates. It should be noted that the epimerization (A) and *syn–anti* isomerization (B) are the same type of isomerization occurring through the σ–π–σ mechanism, but the epimerization is generally much faster than the *syn–anti* isomerization because of the stability of the primary alkylpalladium intermediate



Scheme 3.



Scheme 4.

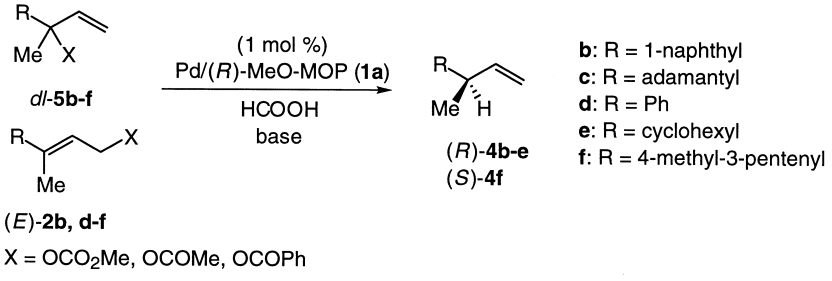
compared with the tertiary alkylpalladium. To obtain high stereoselectivity in palladium-catalyzed reaction that proceeds through monophosphine π-allylpalladium intermediates, it is important to control these three isomerizations. Palladium-catalyzed reduction of allylic esters with formic acid proceeds through this type of monophosphine π-allylpalladium intermediate.

Palladium-catalyzed reduction of allylic esters with formic acid developed by Tsuji and co-workers[4] provides a convenient method for regioselective synthesis of less-substituted olefins. Mechanistic studies[5] on the catalytic reduction have revealed that the olefin is produced by reductive elimination from the key intermediate, Pd(II)(π-allyl)(hydrido)(L), which is generated by the decarboxylation of the palladium formate complex, and that the use of monodentate phosphine ligand is essential for the high regioselectivity. We have previously reported[6,7] that the asymmetric reduction of γ,γ-disubstituted allylic carbonates **2** with formic acid in the presence of a palladium catalyst coordinated with axially chiral monodentate phosphine ligand, (*R*)-2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl ((*R*)-MeO–MOP)[8] (**1a**), or its biphenanthryl analog, (*R*)-MOP-phen[7] (**1e**) gives optically active olefins **4** of up to 91% ee (Scheme 3). The reduction of geometrically pure *E*- or *Z*- allylic esters of 3,3-disubstituted-2-propenols proceeds by way of Pd(II)X(π-allyl)L intermediates **3** where the epimerization is fast but the *syn–anti* isomerization is slow compared with the reductive elimination forming olefin **4** and the stereochemical outcome is mainly determined by the thermodynamic stability of the epimeric π-allylpalladium intermediates.

Recently, we found that some racemic tertiary allylic esters can also be used for the asymmetric reduction if one of the alkyl groups at the α-position is a sterically bulky group.[9] For example, racemic methyl 1-vinyl-1,2,3,4-tetrahydronaphthyl benzoate, obtained from tetralone, gave reduction product with 93% enantiomeric purity. The high enantioselectivity can be accounted for by the selective formation of a π-allylpalladium intermediate that contains the more bulky group at the *syn* position (Scheme 4). However, for the asymmetric reduction of α,α-disubstituted allylic esters where the selectivity in forming *syn* or *anti* π-allylpalladium intermediates is not high, the enantioselectivity was lower. Here we wish to report that high enantioselectivity is also attained for such allylic esters by use of new MOP ligand **1b** containing 3-$CF_3C_6H_4$ group on the phosphorous. The ligand **1b** accelerates the *syn–anti* isomerization to result in the reductive elimination from thermodynamically more stable *syn* isomer.

Results and Discussion

The results obtained for the asymmetric reduction of α,α-disubstituted allylic esters DL-**5** (Scheme 5) are summarized in Table 1, which also contains the data for γ,γ-disubstituted esters (*E*)-**2**. The asymmetric reduction of allyl carbonate DL-**5b** that contains sterically bulky 1-naphthyl group at 1-position in the presence of 1 mol% of palladium catalyst coordinated with (*R*)-MeO–MOP (**1a**) proceeded regioselectively to give 94% yield of terminal olefin (*R*)-3-(1-naphthyl)-1-butene (**4b**) of 65% ee (entry 1). Benzoate ester DL-**5b′** also underwent the asymmetric reduction to give (*R*)-**4b** in 72% ee (entries 2 and 3). The enantioselectivity was lower in the reaction of sterically less bulky esters, DL-**5d**, DL-**5e** and DL-**5f**, the enantioselectivities being 40% ee, 29% ee and 55% ee, respectively (entries 7, 9 and 11). On the other hand, (*E*)-3,3-disubstituted-2-propenyl



Scheme 5.

Table 1. Asymmetric reduction of racemic allylic esters (DL-**5b**–**f**) and (*E*)-3,3-disubstituted-2-propenyl esters ((*E*)-**2b**,**d**–**f**) catalyzed by palladium/(*R*)-MeO–MOP complex (the reaction was carried out with 2.2 equiv. of formic acid in dioxane (0.5 M) in the presence of 1.2 equiv. of base and 1.0 mol% of catalyst prepared in situ by mixing $Pd_2(dba)_3{\cdot}CHCl_3$ and (*R*)-MeO-MOP (P/Pd=2/1) at 20°C)

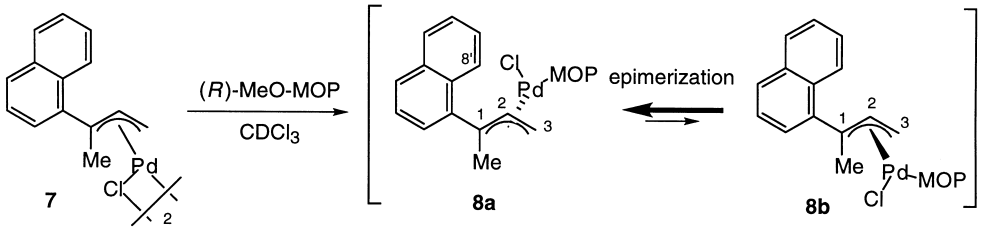
Entry	Allyl ester	X in **5**	Base	Conditions time (h)	Yield (%)[a] of **4**	% ee of **4** (config)[b]
1	DL-**5b**	OCO_2Me	P. S.	12	94	65[b] (*R*)
2	DL-**5b′**	OCOPh	P. S.	10	75	72[b] (*R*)
3	DL-**5b′**	OCOPh	Et_3N	36	73	72[b] (*R*)
4[c]	DL-**5b**	OCO_2Me	P. S.	36	92	71[b] (*R*)
5	(*E*)-**2b**	OCO_2Me	P. S.	144	84	88[b] (*R*)
6	DL-**5c**	OCO_2Me	P. S.	36	96	75[d]
7	DL-**5d**	OCOMe	P. S.	2	80	40[e] (*R*)
8	(*E*)-**2d**	OCO_2Me	P. S.	19	88	60[e] (*R*)
9	DL-**5e**	OCOMe	P. S.	2	99	29[e] (*R*)
10	(*E*)-**2e**	OCO_2Me	P. S.	15	99	71[e] (*R*)
11	DL-**5f**	OCO_2Me	P. S.	5	82	55[d] (*S*)
12	(*E*)-**2f**	OCO_2Me	P. S.	14	95	76[d] (*S*)

[a] Isolated yield by silica gel column chromatography.
[b] Determined by GLC analysis with chiral stationary phase column, CP Cyclodex β236M.
[c] Reaction with (*R*)-MOP-phen.
[d] Determined by HPLC analysis of dianilide of carboxylic acid, obtained by the oxidation ($NaIO_4$-$KMnO_4$) of **4f** with Sumichiral OA-4100 (hexane/dichloroethane/ethanol=50/15/1).
[e] Determined by HPLC analysis of anilide of carboxylic acid, obtained by the oxidation ($NaIO_4$-$KMnO_4$) of **4c**, **4d** and **4e** with Sumichiral OA-2000 (hexane/dichloroethane/ethanol=250/20/1).

esters (*E*)-**2b**, (*E*)-**2d**, (*E*)-**2e** and (*E*)-**2f**, which are regioisomeric esters of DL-**5** gave the olefins **4** of 88% ee, 60% ee, 71% ee and 76% ee, respectively (entries 5, 8, 10 and 12). Thus, the enantioselectivity is higher for (*E*) esters **2** than for the corresponding DL esters **5**. These results are as expected, because (*E*)-**2** should form only *syn* isomer of the π-allylpalladium intermediate at the oxidative addition while DL-**5** will form both *syn* and *anti* isomers. The reductive elimination from the *anti* isomer will produce an olefin of opposite absolute configuration to that from *syn* isomer.

π-Allylpalladium complex, PdCl[1-(1-naphthyl)-1-methyl-π-allyl](MeO-MOP) (**8**), was prepared by mixing $[PdCl\{1\text{-}(1\text{-naphthyl})\text{-}1\text{-methyl-}\pi\text{-allyl}\}]_2$ (**7**) with 1 equiv. (to Pd) of (*R*)-MeO–MOP and it was characterized by ^1H, ^{13}C and ^{31}P NMR spectra. In $CDCl_3$ at −50°C the complex exists as a mixture of isomers in a ratio of 3:2. These two isomers have substituted carbon (C-1) of the π-allyl *trans* to the phosphorus atom of MeO–MOP and the unsubstituted carbon (C-3) *cis* to phosphorous, which is determined by a large coupling constant (J=9.8 Hz) between methyl group and phosphorous and no coupling between C-3 protons and phosphorous. Both isomers contain 1-naphthyl and methyl groups *syn* and *anti* positions, respectively, which was determined by NOE's between the hydrogen on the C-2 position of π-allyl moiety and one of the hydrogens on the 1-naphthyl group, probably C-8′ hydrogen. Thus, the structures of the isomers are assigned to be **8a** and **8b** shown in Scheme 6. These results reveal that the *syn* isomers where 1-naphthyl is *syn* to the hydrogen on the C-2 carbon are thermodynamically much more stable than *anti* isomers. (*E*)-Allylic ester (*E*)-**2b**, which should form only *syn*-π-allylpalladium intermediate, gave optically active alkene **4b** of 88% ee. In this reaction, the enantioselectivity is determined by the epimerization of *syn*-π-allylpalladium intermediates. On the other hand, the reaction of racemic allyl ester DL-**5b** mainly forms the *syn*-π-allylpalladium intermediates but a minor amount of *anti*-π-allylpalladium intermediates are also formed. This *anti*-π-allylpalladium intermediate gives an opposite enantiomer after the epimerization and, as a result, the enantioselectivity in the catalytic reduction was reduced. In order to attain the higher enantioselectivity in the asymmetric reduction of α,α-disubstituted esters **5**, it is necessary to accelerate the *syn*–*anti* isomerization in the π-allylpalladium intermediates to reach the equilibrium where *syn* isomers are predominant.

Several reaction conditions were examined for the asymmetric reduction of DL-2-(1-naphthyl)-3-buten-2-yl benzoate (DL-**5b′**). The results are summarized in Table 2. Under the standard conditions so far used, where 2.2 equiv. (to allyl ester) of formic acid was added in one portion, the enantioselectivity was 73% ee (entry 1). A little higher enantioselectivity (76% ee) was observed in the reduction with 1.1 equiv. of formic acid (entry 2). The enantioselectivity was further increased by slow addition of formic acid over a period of 10 h, which gave (*R*)-**4b** of 80% ee (entry



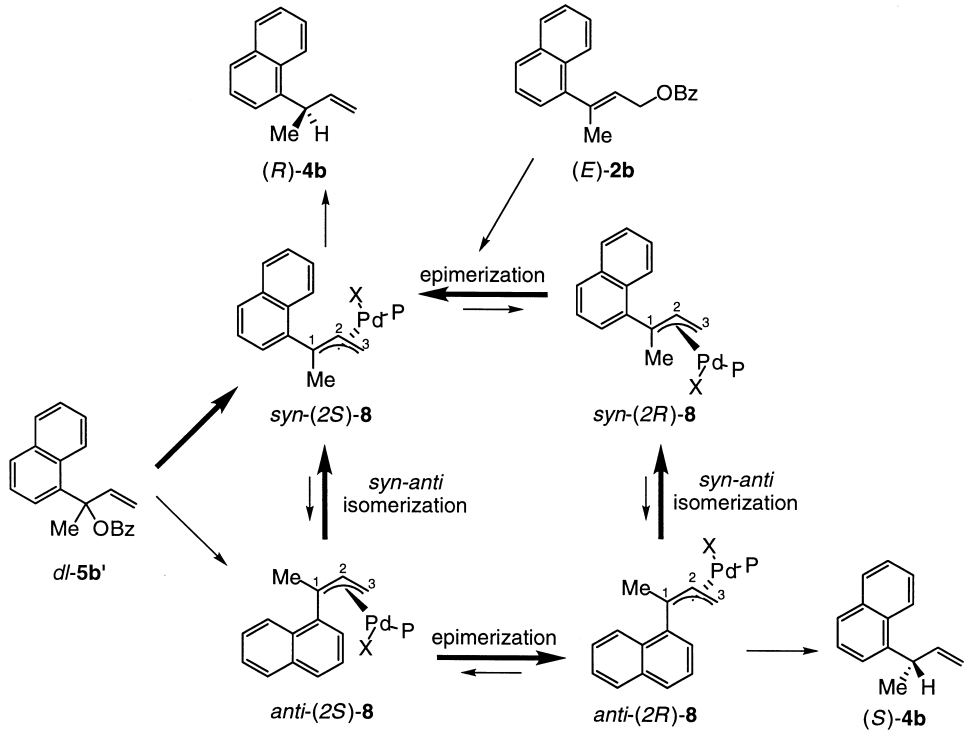
Scheme 6.

Table 2. Asymmetric reduction of DL-2-(1-naphthyl)-3-buten-2-yl benzoate (DL-**5b′**) and methyl (*E*)-3-(1-naphthyl)-2-buten-2-butenyl carbonate (*E*)-**2b** with formic acid catalyzed by palladium-MOP complexes (the reaction was carried out with 2.2 or 1.1 equiv. of formic acid in THF-dioxane (1:1) in the presence of 1.2 equiv. of Et_3N and 1.0 mol% of catalyst prepared in situ by mixing $Pd_2(dba)_3{\cdot}CHCl_3$ and MOP ligand (P/Pd=2/1) at 0°C)

Entry	Allyl ester	MOP ligand	HCOOH (equiv.)	Method[a]	Time (days)	Yield (%)[b] of **4b**	% ee of **4b**[c] (config)[d]
1	DL-**5b′**	**1a**	2.2	A	1.5	81	73 (*R*)
2	DL-**5b′**	**1a**	1.1	A	2.0	85	76 (*R*)
3	DL-**5b′**	**1a**	1.1	B	3.0	77	80 (*R*)
4	DL-**5b′**	**1e**	2.2	A	1.5	91	77 (*R*)
5	DL-**5b′**	**1e**	1.1	B	2.0	92	82 (*R*)
6	DL-**5b′**	**1d**	2.2	A	4.5	83	69 (*R*)
7	DL-**5b′**	**1c**	2.2	A	0.7	76	76 (*R*)
8	DL-**5b′**	**1b**	2.2	A	3.5	92	84 (*R*)
9	DL-**5b′**	**1b**	1.1	A	3.0	77	86 (*R*)
10	DL-**5b′**	**1b**	1.1	B	3.0	86	90 (*R*)
11[e]	(*E*)-**2b**	**1b**	2.2	A	6.0	86	88 (*R*)

[a] Method A; formic acid was added in one portion. Method B; formic acid was added slowly over 10 h.
[b] Isolated yield by silica gel column chromatography.
[c] Determined by GLC analysis with chiral stationary phase column, CP Cyclodex β236M.
[d] Specific rotation of **4b** in entry 10 is $[\alpha]_D^{20}=+16.3$ (c=0.35, chloroform)
[e] The reaction was carried out at 20°C.

3). These results suggest that the slow addition extends the lifetime of π-allylpalladium intermediates to provide a chance for the *syn–anti* isomerization. However, the enantioselectivity observed here (80% ee) is still lower than that in the reduction of (*E*)-**5b** which gave **4b** of 88% ee (entry 5 in Table 1). It follows that the equilibration to *syn*-π-allylpalladium intermediates is not reached in the reaction of DL-**5b′** and a certain amount of *anti* intermediates are still involved even in the reaction under the slow addition conditions. The asymmetric reduction of DL-**5b′** was also examined with some other axially chiral monophosphine ligands, (*R*)-MOP-phen (**1e**) and MeO-MOP analogues containing substituents on the diphenylphosphino group, **1b** (Ar=3-$CF_3C_6H_4$), **1c** (Ar=4-$CF_3C_6H_4$), and **1d** (Ar=4-$MeOC_6H_4$). Under the standard conditions, **1e**, **1d**, **1c**, and **1b** gave (*R*)-**4b** of 77, 69, 76, and 84% ee, respectively (entries 4, 6, 7 and 8). Thus, the order of enantioselectivity in the reaction with MeO–MOP analogues is **1b** (Ar=3-$CF_3C_6H_4$)>**1c** (Ar=4-$CF_3C_6H_4$)>**1a** (Ar=Ph)>**1d** (Ar=4-$MeOC_6H_4$). The highest enantioselectivity (90% ee) was obtained in the reaction with **1b** by the slow addition of formic acid, the enantioselectivity being essentially the same as that obtained in the reduction of (*E*)-**2b** catalyzed by palladium/**1b** (entry 11). It is expected that the *syn-anti* isomerization is accelerated by the introduction of trifluoromethyl group on the MeO–MOP



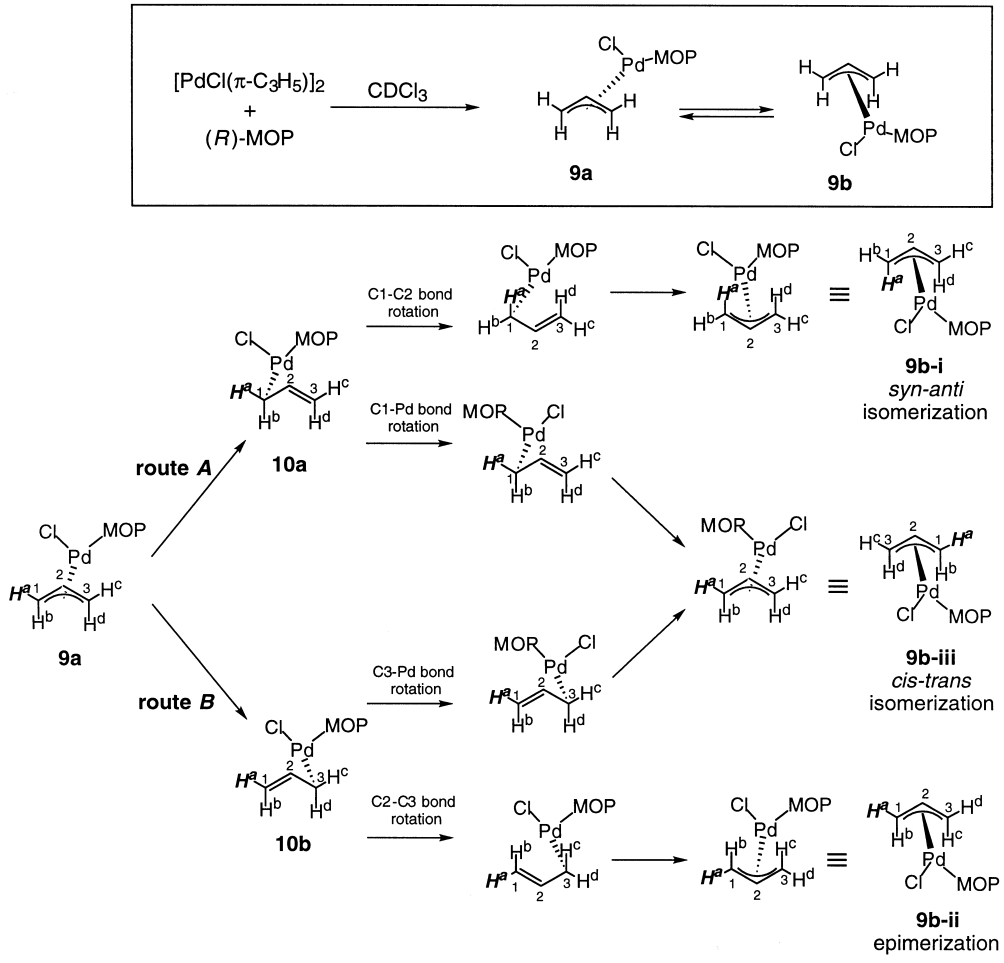
Scheme 7.

ligand and that the reaction of DL-**5b**′ produces olefin **4b** from *syn*-π-allylpalladium intermediates after the equilibration.

The stereochemical results in the reduction of DL-**5b**′ and (*E*)-**2b** with MOP are illustrated in Scheme 7. The π-allylpalladium intermediate resulting from (*E*)-**2b** should be *syn*-**8**, which contains 1-naphthyl group at the *syn* position. After the epimerization between *syn*-(2*R*)-**8** and *syn*-(2*S*)-**8**, the product (*R*)-**4b** is formed from thermodynamically more stable *syn*-(2*S*)-**8**. On the other hand, DL-**5b**′ forms both *syn*-π-allylpalladium intermediate (*syn*-**8**) and *anti*-π-allylpalladium intermediate (*anti*-**8**) in a certain ratio, *syn*-**8** being predominant. To attain the high enantioselectivity in the reduction of DL-**5b**, the isomerization of *anti*-**8** to *syn*-**8** is necessary. The experimental results indicate that the slow addition of formic acid extends the lifetime of π-allylpalladium intermediates to reach the equilibration and that MOP ligand **1b** accelerates the *syn–anti* isomerization.

Rate constants for the isomerization of π-allylpalladium complexes coordinated with MOP ligands were measured by the magnetization saturation transfer technique in ^{1}H NMR.[10] As a model of the π-allylpalladium intermediates, we chose nonsubstituted π-allylpalladium complexes PdCl(π-C_3H_5)(MOP) (**9**) where MOP ligands are **1a**, **1b**, and **1d** (Scheme 8). These MOP ligands showed a remarkable difference in the enantioselectivity for reduction of DL-**5b**′. It would be better to use π-allylpalladium-MOP complexes bearing 1,1-disubstituted π-allyl groups, but the *syn–anti* isomerization is too slow to measure the rate by the saturation transfer.

In complex **9a**, *syn* and *anti* protons on the C-1 position of the π-allyl group which is *trans* to phosphorus, are named $\boldsymbol{H^a}$ and H^b, respectively, and *syn* and *anti* protons on the C-3 position are named H^c and H^d, respectively. The isomerization which corresponds to the *syn–anti* isomerization of π-(1,1-disubstituted allyl)palladium, (B) in Scheme 2, is that proceeds through route *A*. By this conversion of **9a** to **9b–i**, protons $\boldsymbol{H^a}$ and H^b on the C-1 position exchange their *syn* and *anti* positions while H^c and H^d on the C-3 position stay at the original positions. By the isomerization which corresponds to the epimerization, (A) in Scheme 2, **9a** is converted into **9b-ii** through route *B*, where $\boldsymbol{H^a}$ and H^b stay at the original positions while H^c and H^d are exchanged. In the *cis–trans* isomerization, (C) in Scheme 2, all protons remain on the original positions, but palladium moves from one π-allyl face to the other. As a result, it appears that protons $\boldsymbol{H^a}$ and H^c exchange their positions. It is possible to measure the rate constants of the three isomerizations by the magnetization saturation transfer technique in ^{1}H NMR because the $\boldsymbol{H^a}$ proton on **9a** shifts to the different positions on **9b** depending on the type of isomerization. The rate



Scheme 8.

Table 3. Rate constants (k) for exchange of π-allylpalladium complexes [PdCl(π-C_3H_5)L] (**9a** and **9b**); *syn–anti* isomerization (k_1), epimerization (k_2) and *cis–trans* isomerization (k_3) (the rate constants were measured by saturation of $\mathbf{H}^a$ proton in **9a** at 0°C in $CDCl_3$)

Entry	MOP ligand (L)	k_1 (s^{-1}) *syn–anti* isomerization	k_2 (s^{-1}) epimerization	k_3 (s^{-1}) *cis–trans* isomerization
1	**1b** (Ar=3-$CF_3C_6H_4$)	1.7	3.1	3.3
2	**1a** (Ar=Ph) (MeO-MOP)	0.4	8.0	2.0
3	**1d** (Ar=4-$MeOC_6H_4$)	0.08	17	1.3

constants of the isomerization of π-allylpalladium complexes **9** are summarized in Table 3. In the complex coordinated with (*R*)-MeO–MOP (**1a**), the rate constants for *syn–anti* isomerization, epimerization, and *cis–trans* isomerization were 0.4 s^{-1}, 8.0 s^{-1}, and 2.0 s^{-1}, respectively. The rate of *syn–anti* isomerization (k_1) was strongly dependent on the MOP ligands coordinated to palladium. Thus, the rate constants (k_1) for the palladium complex of **1b** (Ar=3-$CF_3C_6H_4$) and **1d** (Ar=4-$MeOC_6H_4$) are 1.7 s^{-1} and 0.08 s^{-1}, respectively. The isomerization with **1b** is fastest, four times faster than that with **1a** and twenty times faster than that with **1d**. The order of the rate constants (k_2) for the epimerization was reverse, slowest with **1b** and fastest with **1d**, though the difference was not so large as the rate constants for the *syn-anti* isomerization.

The fast rate of the *syn–anti* isomerization observed for the π-allylpalladium complex **9** coordinated with **1b** (Ar=3-$CF_3C_6H_4$) is in good agreement with the high enantioselectivity in the catalytic asymmetric reduction of α,α-disubstituted allylic ester DL-**5b′**. The *syn* and *anti* π-allylpalladium intermediates **8** formed by the oxidative addition of DL-**5** to palladium(0) coordinated with **1b** undergo the *syn–anti* isomerization, faster than those of other MOP ligands, to reach the equilibration where *syn* intermediates are predominant. The *syn* intermediates will produce the reduction product **4b** of high enantiomeric excess. The slow addition of formic acid will also increase the enantioselectivity by providing a chance for the isomerization to *syn*-intermediates.

Experimental

General

All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a JEOL JNM-EX270 spectrometer (270 MHz for ^1H and 109 MHz for ^{31}P), JEOL JNM-AL400 spectrometer (400 MHz for ^1H NMR), or JEOL JNM LA500 spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR, and to an external 85% H_3PO_4 standard for ^{31}P NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25°C unless otherwise noted. HPLC analysis was performed on a Shimadzu LC-6A liquid chromatograph system and a JASCO PU-980 liquid chromatograph system with chiral stationary phase column Sumitomo Chemical Co. Ltd., Sumipax OA series. GLC analysis was performed on a HEWLETT PACKARD HP 6890 series with a chiral stationary phase column, CP Cyclodex β-236M (50 m). Optical rotation were measured on a JASCO DIP-370 polarimeter.

Materials

THF was dried over sodium benzophenone ketyl and distilled prior to use. [PdCl(π-C_3H_5)]$_2$,[11] $Pd_2(dba)_3$·$CHCl_3$,[12] (*R*)-MeO-MOP,[8] **1d** (Ar=4-$MeOC_6H_4$),[8b] (*R*)-MOP-phen,[7] (*E*)-3-cyclohexyl-2-butenol,[13] (*E*)-3-phenyl-2-butenol[14] and ethyl 3-(1-naphthyl) crotonate[15] were prepared according to the reported procedures. New MOP analogues **1b** (Ar=3-$CF_3C_6H_4$) and **1c** (Ar=4-$CF_3C_6H_4$) were prepared by the modified procedure of MOP synthesis (see below).

Preparation of new MOP analogues 1b (Ar=3-$CF_3C_6H_4$) and 1c (Ar=4-$CF_3C_6H_4$)

New MOP analogues were prepared from (*R*)-2-hydroxy-2′-methoxybinaphthyl by the sequence of (1) sulfonylation, (2) palladium-catalyzed phosphinylation, and (3) reduction.

(*R*)-(−)-2-Methoxy-2′-((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl

To a solution of (*R*)-2-hydroxy-2′-methoxybinaphthyl[16] (10.6 g, 35.3 mmol) and pyridine (3.6 g, 45.5 mmol) in $CHCl_3$ (100 mL) at 0°C was added dropwise trifluoromethanesulfonic anhydride (14.3 g, 50.7 mmol). The mixture was stirred at 0°C for 2 h. The reaction mixture was evaporated. The residue was diluted with EtOAc and washed with 5% hydrochloric acid, saturated sodium bicarbonate and brine, dried over anhydrous sodium sulfate and evaporated. The residue was chromatographed on silica gel (hexane/EtOAc=1/1) to give 13.5 g (89%) of (*R*)-(−)-2-methoxy-2′-((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl: $[\alpha]_D^{20}=-92.5$ (c=1.7, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.82 (s, 3H), 7.00–8.20 (m, 12H). Anal. Calcd for $C_{22}H_{15}F_3SO_4$: C, 61.11; H, 3.50. Found: C,60.88; H, 3.51.

(*R*)-(+)-2-(Bis(3-trifluoromethylphenyl)phosphinyl)-2′-methoxy-1,1′-binaphthyl

To a mixture of (*R*)-(−)-2-((trifluoromethanesulfonyl)oxy)-2′-methoxy-1,1′-binaphthyl (1.03 g, 2.61 mmol), bis(3-trifluoromethylphenyl)phosphine oxide (1.35 g, 3.99 mmol), palladium diacetate (115 mg, 0.51 mmol) and 1,4-bis(diphenylphosphino)butane (dppb) (228 mg, 0.54 mmol) were added 40 mL of dimethyl sulfoxide and diisopropylethylamine (1.8 mL, 10.2 mmol) and the mixture was heated with stirring at 100°C for 12 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure to give a dark brown residue. The residue was diluted with EtOAc, washed with water, dried

over anhydrous sodium sulfate and evaporated. The residue was chromatographed on silica gel (hexane/EtOAc=1/1) to give 1.36 g (80%) of (*R*)-(+)-2-(bis(3-trifluoromethylphenyl)phosphinyl)-2′-methoxy-1,1′-binaphthyl: $[\alpha]_D^{20}$=+116.1 (*c*=0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.68 (s, 3H), 6.79–8.06(m, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 Hz, RT) δ 26.9. Anal. Calcd for $C_{35}H_{23}F_6O_2P$: C, 67.75; H, 3.74. Found: C, 68.01; H, 3.77.

(*R*)-(+)-2-(Bis(3-trifluoromethylphenyl)phosphino)-2′-methoxy-1,1′-binaphthyl (1b)

To a mixture of (*R*)-(+)-2-(bis(3-trifluoromethylphenyl)-phosphinyl)-2′-methoxy-1,1′-binaphthyl (700 mg, 1.13 mmol) and Et_3N (1.14 g, 11.3 mmol) in toluene (10 mL) was added Cl_3SiH (765 mg, 5.65 mmol) at 0°C. The reaction mixture was stirred at 120°C for 30 h. After being cooled to room temperature, the mixture was diluted with ether and quenched with a small amount of saturated sodium bicarbonate. The resulting suspension was filtered through Celite, and the solid was washed with ether. The combined organic layer was dried over anhydrous magnesium sulfate and evaporated. The crude product was chromatographed on silica gel (hexane/EtOAc=9/1) to give 624 mg (92%) of (*R*)-(+)-2-(bis(3-trifluoromethylphenyl)phosphino)-2′-methoxy-1,1′-binaphthyl (**1b**): $[\alpha]_D^{20}$=+47.7 (*c*=0.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.48 (s, 3H), 6.85–8.03 (m, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 Hz, RT) δ −12.0. Anal. Calcd for $C_{35}H_{23}F_6OP$: C, 69.54; H, 3.84. Found: C,69.38; H, 3.89.

(*R*)-(+)-2-(Bis(4-trifluoromethylphenyl)phosphinyl)-2′-methoxy-1,1′-binaphthyl

$[\alpha]_D^{20}$=+96.3 (*c*=2.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.68 (s, 3H), 6.78–8.06 (m, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 Hz, RT) δ 27.1. Anal. Calcd for $C_{35}H_{23}F_6O_2P$: C, 67.75; H, 3.74. Found: C, 68.01; H, 3.41.

(*R*)-(+)-2-(Bis(4-trifluoromethylphenyl)phosphino)-2′-methoxy-1,1′-binaphthyl (1c). $[\alpha]_D^{20}$=+61.1 (*c*=0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.43 (s, 3H), 6.83–8.02 (m, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 Hz, RT) δ −12.5. Anal. Calcd for $C_{35}H_{23}F_6OP$: C, 69.54; H, 3.84. Found: C,69.32; H, 4.04.

Preparation of 3,3-disubstituted propenyl esters ((*E*)-2b,d,e and f)

Methyl (*E*)-3-(1-naphthyl)-2-butenyl carbonate ((***E*)-2b**), methyl (*E*)-3-phenyl-2-butenyl carbonate ((***E*)-2d**), methyl (*E*)-3-cyclohexyl-2-butenyl carbonate ((***E*)-2e**) and geranyl methyl carbonate ((*E*)-**2f**) were obtained by treatment of the corresponding alcohols with methyl chloroformate and pyridine.[17] (*E*)-3-(1-Naphthyl)-2-butenol was prepared from the corresponding alcohol which was readily prepared by reduction of ethyl 3-(1-naphthyl) crotonate[12] with $LiAlH_4$, and used without purification. A typical procedure is given for the preparation of methyl (*E*)-3-cyclohexyl-2-butenyl carbonate ((***E*)-2e**). Experimental procedures: To a solution of (*E*)-3-cyclohexyl-2-butenol and pyridine (522 mg, 6.6 mmol) in benzene (10 mL) was added methyl chloroformate (467 mg, 4.9 mmol) dropwise at 0°C and stirred for 1.5 h. The reaction was quenched with brine and extracted with ether. The organic layer was washed with saturated sodium bicarbonate solution, dried over anhydrous sodium sulfate and evaporated. The crude product was purified by silica gel column chromatography (hexane/ EtOAc=10/1) to give 657 mg (94%) of methyl (*E*)-3-cyclohexyl-2-butenyl carbonate ((***E*)-2e**): ^1H NMR ($CDCl_3$) δ 1.15–1.92 (m, 11H), 1.70 (s, 3H), 3.79 (s, 3H), 4.66 (d, *J*=7.0 Hz, 2H), 5.36 (t, *J*=7.0 Hz, 1H). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.49. Found: C, 67.78; H, 9.47.

Methyl (*E*)-3-(1-naphthyl)-2-butenyl carbonate ((*E*)-2b). ^1H NMR ($CDCl_3$) δ 2.16 (s, 3H), 3.78 (s, 3H), 4.91 (d, *J*=6.7 Hz, 2H), 5.71 (t, *J*=6.7 Hz, 1H), 7.23–7.91 (m, 7H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 202 Hz, RT) δ 19.2, 54.6, 64.5, 123.6, 124.6, 125.2, 125.3, 125.6, 125.8, 127.3, 128.2, 130.5, 133.6, 141.6, 142.2, 155.7. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.99; H, 6.18.

Methyl (*E*)-3-cyclohexyl-2-butenyl carbonate ((*E*)-2d). ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H), 3.80 (s, 3H), 4.85 (d, *J*=6.9 Hz, 2H), 5.91 (t, *J*=6.9 Hz, 1H), 7.24–7.42 (m, 5H). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.73; H, 6.82.

Geranyl methyl carbonate ((*E*)-2f).[17] ^1H NMR ($CDCl_3$) δ 1.60 (s, 3H), 1.68 (s, 3H), 1.71 (s, 3H), 2.02–2.18 (m, 4H), 3.77 (s, 3H), 4.63 (d, *J*=7.0 Hz, 2H), 5.07 (m, 1H), 5.38 (t, *J*=7.0 Hz, 1H).

Preparation of racemic 1,1-disubstituted propenyl esters (DL-5b–f)

A typical procedure is given for DL-2-(1-naphthyl)-3-butene-2-yl benzoate (DL-**5b′**). To a solution of vinylmagnesium bromide (7.2 mL of 0.9 M, 6.5 mmol) in diethyl ether at 0°C was added dropwise a solution of 1′-acetonaphthone (1.0 g, 5.9 mmol) in THF (30 mL). The mixture was stirred at room temperature for 12 h. It was quenched with 0.5% sulfuric acid solution and extracted with ether. The ether extracts were dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crude product. To a solution of this crude allyl alcohol and 1,10-phenanthroline (ca. 5 mg) in THF (10 mL) was added 1.5 M *n*-butyllithium in hexane (4.7 mL, 7.1 mmol) at −78°C and stirred for 0.5 h. To this reaction mixture was added benzoyl chloride (993 mg, 7.1 mmol). The mixture was allowed to warm to room temperature and stirred for 1 h. The reaction was quenched with saturated sodium bicarbonate solution and extracted with ether. The organic layer was washed with saturated sodium bicarbonate solution and brine, dried over anhydrous sodium sulfate and evaporated. The crude product was purified by alumina column chromatography (hexane/Et_3N=10/1) to give 1.3 g (73%) of DL-2-(1-naphthyl)-3-butene-2-yl benzoate (DL-**5b′**): ^1H NMR ($CDCl_3$) δ 2.26 (s, 3H) 5.27 (d, *J*=17.6 Hz, 1H), 5.33 (d, *J*=17.6 Hz, 1H), 6.56 (dd, *J*=10.7 and 17.6 Hz, 1H), 7.28–8.41 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 202 Hz, RT) δ 25.1, 114.5, 123.9, 124.2, 124.6, 125.4, 126.0, 127.1, 127.7, 128.5, 128.9, 129.8, 130. 2, 131.0, 132. 1, 133.3, 134.6, 138.2, 142.0, 143.1, 164.4. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.50; H, 5.97.

DL-Methyl 2-(1-naphthyl)-3-butene-2-yl carbonate (DL-5b). ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3H), 3.54 (s, 3H), 5.18 (d, J=17.4 Hz, 1H), 5.24 (d, J=10.7 Hz, 1H), 6.44 (dd, J=10.7 and 17.4 Hz, 1H), 7.41–8.37 (m, 7H). ^{13}C{^{1}H} NMR ($CDCl_3$, 202 Hz, RT) δ 26.1, 54.2, 85.8, 114.9, 124.6, 124.8, 125.2, 126.5, 129.0, 129.4, 130.3, 134.6, 137.4, 141.8, 153.3. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.23; H, 5.96.

DL-Methyl 2-adamantyl-3-buten-2-yl carbonate (DL-5c). ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 3H), 1.60–1.80 (m, 15H), 1.95–2.05 (m, 3H), 3.72 (s, 3H), 5.01 (d, J=16.5 Hz, 1H), 5.26 (d, J=9.5 Hz, 1H), 5.92 (dd, J=9.5, 16.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 202 Hz, RT) δ 28.4, 35.8, 36.9, 39.5, 53.9, 89.2, 115.0, 138.7, 154.2. Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C,72.60; H, 9.30.

DL-2-Phenyl-3-buten-2-yl acetate (DL-5d). ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 3H), 2.05 (s, 3H), 5.22 (d, J=9.5 Hz, 1H), 5.25 (d, J=16.0 Hz, 1H), 6.26 (dd, J=9.5 and 16.0 Hz, 1H), 7.21–7.38 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 202 Hz, RT) δ 21.6, 24.2, 85.6, 117.1, 124.6, 126.6, 128.0, 128.2, 144.4, 169.9. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 68.00; H, 7.20.

DL-2-Cyclohexyl-3-buten-2-yl acetate (DL-5e). ^{1}H NMR ($CDCl_3$) δ 0.82–1.86 (m, 11H), 1.57 (s, 3H), 2.02 (s, 3H), 5.10 (d, J=16.5 Hz, 1H), 5.16 (d, J=9.5 Hz,1H), 5.97 (dd, J=9.5, 16.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 202 Hz, RT) δ 21.0, 24.9, 26.5, 27.0, 27.3, 47.9, 75.1, 111.8, 144.3, 170.0. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.62; H, 9.96.

DL-Methyl linalyl carbonate (DL-5f). ^{1}H NMR ($CDCl_3$) δ 1.64 (s, 3H), 1.66 (s, 3H), 1.70 (s, 3H), 0.92 (t, J=7.0 Hz, 3H), 1.90–2.00 (m, 2H), 2.10–2.20 (m, 3H), 3.80 (s, 3H), 5.17–5.22 (m, 1H), 5.24 (d, J=9.5 Hz, 1H), 5.34 (d, J=16.2 Hz, 1H), 5.79 (dd, J=9.5 and 16.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 202 Hz, RT) δ 17.5, 22.0, 22.8, 25.2, 39.2, 53.5, 83.9, 113.6, 123.3, 131.4, 140.8, 153.5. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.49. Found: C, 68.16; H, 9.78.

Catalytic asymmetric reduction of racemic allylic esters DL-5

Typical procedures are given for the reaction of DL-2-(1-naphthyl)-3-buten-2-yl benzoate (DL-5b′) (entries 8 and 10 in Table 2).

Method A. (entry 8): To a solution of $Pd_2(dba)_3{\cdot}CDCl_3$ (3.4 mg, 0.0033 mmol) and ligand **1b** (8.1 mg, 0.013 mmol) in THF/dioxane (0.15 mL/0.15 mL) was added DL-2-(1-naphthyl)-3-buten-2-yl benzoate (**DL-5b′**) (101.3 mg, 0.34 mmol) in THF/dioxane (0.15 mL/0.15 mL) and Et_3N (40.4 mg, 0.40 mmol). Formic acid (16.1 mg, 0.35 mmol) was added and the mixture was stirred at 0°C. The reaction was monitored by TLC and diluted with hexane. The catalyst was removed by filtration through a short silica gel (hexane). The filtrate was evaporated to give 47.0 mg (77%) of (*R*)-3-(1-naphthyl)-1-butene ((***R***)-**4b**).

Method B. (entry 10): To a solution of $Pd_2(dba)_3{\cdot}CDCl_3$ (5.1 mg, 0.0049 mmol) and ligand **1b** (12.2 mg, 0.020 mmol) in THF/dioxane (0.25 mL/0.25 mL) was added DL-2-(1-naphthyl)-3-buten-2-yl benzoate (DL-**5b′**) (152.9 mg, 0.51 mmol) in THF/dioxane (0.25 mL/0.25 mL) and Et_3N (60.2 mg, 0.60 mmol). Formic acid (24.3 mg, 0.53 mmol) was added slowly over 10 h at 0°C and the mixture was stirred at 0°C. The reaction was monitored by TLC and dilute with hexane. The catalyst was removed by filtration through a short silica gel (hexane). The filtrate was evaporated to give 79.3 mg (86%) of (*R*)-3-(1-naphthyl)-1-butene ((***R***)-**4b**):[18] ^{1}H NMR ($CDCl_3$, 400 MHz, RT) δ 1.51 (d, J=6.8 Hz, 1H), 4.31 (quintet, J=6.8 Hz, 1H), 5.12 (dt, J=11.7, 1.5 Hz, 1H), 5.13 (dt, J=17.6, 1.5 Hz, 1H), 6.16 (ddd, J=6.8, 11.7, 17.6 Hz, 1H), 7.04–8.54 (m, 7H). $[\alpha]_D^{20}$=+16.3 (c=0.35, $CDCl_3$); 90% ee. The enantiomeric purity was determined by GLC analysis with CP Cyclodex β236M. The absolute configuration was assigned to be (*R*)-(+) by correlation with known (*S*)-(+)-2-(1-naphthyl)propionic acid. ^{1}H NMR and analytical data for other reduction products **4c**–**f** are shown below.

3-Adamantyl-1-butene[19] (**4c**) (75% ee). $[\alpha]_D^{20}$=+3.5 (c=1.0, chloroform) ^{1}H NMR ($CDCl_3$) δ 0.90 (d, J=7.3 Hz, 3H), 1.20–2.00 (m, 16H), 1.95–2.05 (m, 3H), 4.87–4.96 (m, 2H), 5.26 (d, J=10.5 Hz, 1H), 5.38 (d, J=17.5 Hz, 1H), 5.92 (dd, J=10.5 and 17.5 Hz, 1H).

(*R*)-3-Phenyl-1-butene ((*R*)-4d) (60% ee). ^{1}H NMR ($CDCl_3$) δ 1.39 (d, J=6.8 Hz, 3H), 2.48 (quintet, J=6.8 Hz, 1H), 5.00–5.08 (m, 2H), 6.02 (ddd, J=6.8, 10.5 and 16.0 Hz, 1H), 7.19–7.34 (m, 5H). $[\alpha]_D^{22}$=−2.2 (c=0.74, chloroform). *lit.*[20] (*R*)-(−): $[\alpha]_D^{22}$=−6.39 (neat).

(*R*)-3-Cyclohexyl-1-butene ((*R*)-4e) (71% ee). ^{1}H NMR ($CDCl_3$) δ 0.98 (d, J=6.9 Hz, 3H), 0.92–1.78 (m, 11H), 1.91–2.04 (m, 1H), 4.88–4.94 (m, 2H), 5.68 (m, 1H). $[\alpha]_D^{20}$=+3.6 (c=0.9, chloroform). *lit.*[21] (*R*)-(+): $[\alpha]_D^{24}$=+4.1 (c=0.67, chloroform).

(*S*)-3,7-Dimethyl-1,6-octadiene ((*S*)-4f) (76% ee). ^{1}H NMR ($CDCl_3$) δ 0.98 (d, J=7.0 Hz, 3H), 1.27–1.36 (m, 2H), 1.60 (s, 3H), 1.67 (s, 3H), 1.96 (q, J=7.0 Hz, 2H), 2.12 (septet, J=7.0 Hz, 1H), 4.90 (d, J=10.1 Hz, 1H), 4.92 (d, J=17.1 Hz, 1H), 5.05–5.15 (m, 1H), 5.70 (ddd, J=17.1, 10.1 and 7.0 Hz, 1H). $[\alpha]_D^{23}$=+7.0 (c=1.10, chloroform). *lit.*[22] (*R*)-(−): $[\alpha]_D$=−9.82 (c=6.18, chloroform).

Determination of the absolute configuration of 3-(1-naphthyl)-1-butene ((*R*)-4b)

To a solution of 3-(1-naphthyl)-1-butene ((***R***)-**4b**) (80 mg, 0.44 mmol; 61% ee) in *t*-BuOH (8 mL) and water (20 mL) were added $KMnO_4$ (175 mg, 1.11 mmol), $NaIO_4$ (1.52 g, 7.11 mmol) and K_2CO_3 (396 mg, 2.87 mmol), and the mixture was adjusted to pH 8 with 3 N aq NaOH. After stirring at rt for 2 h, the mixture was acidified with conc. hydrochloric acid to pH 1 and sodium hydrogen sulfite was added to reduce MnO_2. The mixture was extracted with ether, and the ether layer was extracted with 3 N aq. NaOH. The aqueous solution was acidified with conc. hydrochloric acid and extracted with ether. The ether

extracts were dried ($MgSO_4$) and evaporation of the solvent gave 2-(1-naphthyl)propionic acid (17 mg). $[\alpha]_D^{20}=+47.1$ (c=0.65, ethanol). *lit.*[23] (*S*)-(+)-2-(1-naphthyl)propionic acid (96% ee): $[\alpha]_D^{20}=+120.0$ (c=1.0, ethanol).

Determination of absolute configuration and enantiomeric purities of 4c–f

Olefins **4d–f** were converted into *N*-phenyl-2-adamantylpropanamide, *N*-phenyl-2-phenylpropanamide,[24] *N*-phenyl-2-cyclohexylpropanamide[25] and *N*,*N*′-diphenyl-2-methylpentane-1,5-dicarboxamide,[26] respectively, by oxidation with $NaIO_4/KMnO_4$ followed by treatment of the resulting carboxylic acids with aniline and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (WSC). The conditions for the determination of the enantiomeric purities of anilides with chiral stationary phase columns were as follows. *N*-phenyl-2-adamantylpropanamide: Sumichiral OA-2500I; hexane/1,2-dichloroethane/EtOH=1000/20/1; (+) isomer eluted faster than (−) isomer. *N*-Phenyl-2-cyclohexylpropanamide and *N*-phenyl-2-phenylpropanamide: Sumichiral OA-2000; hexane/1,2-dichloroethane/EtOH=250/20/1; *S* isomers eluted faster than *R* isomers. *N*,*N*′-Diphenyl-2-methylpentane-1,5-dicarboxamide: Sumichiral OA-4100; hexane/1,2-dichloroethane/EtOH=50/15/1; *R* isomer eluted faster than *S* isomer. A typical procedure for the conversion is given for the reaction of **2f**. To a solution of (*S*)-**2f** (61 mg, 0.44 mmol) in *t*-BuOH (10 mL) and water (20 mL), were added $KMnO_4$ (185 mg, 1.17 mmol), $NaIO_4$ (1.46 g, 6.86 mmol) and K_2CO_3 (366 mg, 2.64 mmol), and the mixture was adjusted to pH 8 with 3 N aq NaOH. After stirring at room temperature for 2 h, the mixture was acidified with conc. hydrochloric acid to pH 1 and sodium hydrogen sulfite was added to reduce MnO_2. The mixture was extracted with ether and the ether layer was extracted with 3N aq NaOH. The aqueous solution was acidified with conc. hydrochloric acid and extracted with ether. The ether extracts were dried ($MgSO_4$) and evaporation of the solvent gave 2-methylpentanedioic acid (38 mg). To a solution of the carboxylic acid (10 mg) obtained above in THF (0.5 mL), were added aniline (15 mg, 0.16 mmol) and WSC (30 μL), and the mixture was stirred at 40°C for 1 h. Conc. hydrochloric acid was added and the mixture was extracted with EtOAc. Evaporation of the solvent followed by silica gel column chromatography (hexane/EtOAc=1/1) gave *N*,*N*′-diphenyl-2-methylpentane-1,5-dicarboxamide (11 mg).

Preparation of [PdCl{1-(1-naphthyl)-1-methyl-π-allyl}]$_2$ (7)

Palladium chloride (900.4 mg, 5.0 mmol) and lithium chloride (430.2 mg, 10.1 mmol) was dissolved in hot water (1.5 mL) and to this solution were added ethanol (3 mL), 2-(1-naphthyl)-3-buten-2-ol (1.0 g, 5.0 mmol) in THF (15 mL) and aqueous hydrochloric acid (0.8 mL, 12 N). Carbon monoxide was passed through the solution at room temperature and, after 1 h, a clear yellow orange solution was obtained. The reaction mixture began to precipitate as orange–yellow crystals. After 4 h under carbon monoxide, the solvent was removed under reduced pressure and the residue was dissolved in $CHCl_3$ which was washed with water and dried over anhydrous sodium sulfate and evaporated to give 940 mg (58%) of [PdCl[π-(1-naphthyl)-1-methylallyl]]$_2$: ^{1}H NMR ($CDCl_3$) δ 1.79 (brs, 3H), 2.60 (brs, 1H), 3.95 (brs, 1H), 5.91 (brs, 1H), 7.41–8.66 (m, 7H). ^{13}C{^{1}H} NMR ($CDCl_3$, 202 Hz, RT) δ 28.8, 58.6, 95.1, 108.5, 125.0, 125.6, 125.8, 126.2, 127.6, 127.8, 128.5, 131.9, 133.7, 137.7. Anal. Calcd for $C_{28}H_{26}Cl_2Pd_2$: C, 52.04; H, 4.06. Found: C, 51.84; H, 4.10.

NMR study of PdCl{1-(1-naphthyl)-1-methyl-π-allyl}((*R*)-MeO-MOP) (8)

In an NMR sample tube were placed (*R*)-MeO-MOP (**1a**) (13.8 mg, 0.030 mmol) and [PdCl{1-(1-naphthyl)-1-methyl-π-allyl}]$_2$ (**7**) (9.6 mg, 0.015 mmol). The tube was filled with nitrogen and $CDCl_3$ (0.5 mL) was added. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were measured. *major isomer*: ^{1}H NMR ($CDCl_3$, 500 MHz, RT) δ 1.74 (d, J=12.7 Hz, 1H, *anti*-H on C^3), 2.11 (d, $J_{H\text{-}P}$= 9.8 Hz, Me), 2.55 (d, J=7.3 Hz, 1H, *syn*-H on C^3), 3.14 (s, 3H, OMe), 5.08 (dd, J=7.3, 12.7 Hz, 1H, H on C^2), 6.22–8.72 (m, 29H, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 Hz, RT) δ 27.5 (Me), 54.5 (C^3), 54.9 (OMe), 112.3 (d, $J_{C\text{-}P}$=2.1 Hz, C^2), 112.3 (d, $J_{C\text{-}P}$=24.8 Hz, C^1), 113.5–138.0 (aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, RT) δ 28.3 *minor isomer*: ^{1}H NMR ($CDCl_3$, 500 MHz, RT) δ 2.21 (d, $J_{H\text{-}P}$= 9.8 Hz, 1H, Me), 2.26 (d, J=12.7 Hz, *anti*-H on C^3), 2.75 (d, J=7.3 Hz, 1H, *syn*-H on C^3), 3.55 (s, 3H, OMe), 5.70 (dd, J=7.3, 12.7 Hz, 1H, H on C^2), 6.22–8.72 (m, 29H, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 Hz, RT) δ 27.8 (Me), 53.5 (C^3), 55.1 (OMe), 111.7 (d, $J_{C\text{-}P}$=3.1 Hz, C^2), 113.9 (d, $J_{C\text{-}P}$=23.8 Hz, C^1), 111.9–137.6 (aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, RT) δ 32.4.

NMR study of [PdCl(π-C_3H_5)]L (9a and 9b)

A typical procedure is given for the study of **[PdCl(π-C_3H_5)]((*R*)-MeO–MOP)**. In an NMR sample tube were placed (*R*)-MeO–MOP (12.8 mg, 0.027 mmol) and [PdCl(π-C_3H_5)]$_2$ (5.0 mg, 0.014 mmol). The tube was filled with nitrogen and $CDCl_3$ (0.5 mL) was added. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were measured.

[PdCl(π-C_3H_5)]L (L=1a (*R*)-MeO–MOP). *major isomer:* ^{1}H NMR ($CDCl_3$, 500 MHz, −20°C) δ 0.82 (d, J=11.7 Hz, 1H, *anti*-H on C^3), 2.03 (dd, J=10.7 Hz, $J_{H\text{–}P}$=13.2 Hz, 1H, anti-H on C^1), 2.10 (d, J=6.4 Hz, 1H, *syn*-H on C^3), 3.65 (s, 3H, OMe), 4.13 (dd, J=4.9 Hz, $J_{H\text{–}P}$=7.3 Hz, 1H, *syn*-H on C^1), 4.99 (m, 1H, H on C^2), 6.88–7.90 (m, 22H, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 Hz, −20°C) δ 55.4 (OMe), 64.7 (C^3), 81.3 (d, $J_{C\text{–}H}$=31.0, C^1), 117.9 (d, $J_{C\text{–}H}$= 4.1, C^2), 113.9–155.7 (aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, −20°C) δ 20.2. *minor isomer*: ^{1}H NMR ($CDCl_3$, 500 MHz, −20°C) δ 1.48 (d, J=12.2 Hz, 1H, *anti*-H on C^3), 2.80 (d, J=6.4 Hz, 1H, *syn*-H on C^3), 2.99 (dd, J=8.8 Hz, $J_{H\text{–}P}$=13.7 Hz, 1H, *anti*-H on C^1), 3.24 (m, 1H, H on C^2), 3.27 (s, 3H, OMe), 3.99 (dd, J=6.8 Hz, $J_{H\text{–}P}$= 4.9 Hz, 1H, *syn*-H on C^1), 6.88–7.90 (m, 22H, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 Hz, −20°C) δ 54.9 (OMe), 60.6 (C^3), 80.0 (d, $J_{C\text{–}H}$=30.0, C^1), 117.8 (d, $J_{C\text{–}H}$= 4.1, C^2), 113.9–155.7 (aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, −20°C) δ 17.8.

[PdCl(π-C_3H_5)]L (L=1d) (Ar=4-MeOC_6H_4). *major*

isomer: ^{1}H NMR ($CDCl_3$, 500 MHz, −20°C) δ 1.18 (d, J=11.7 Hz, 1H, *anti*-H on C^3), 2.35 (m, 2H, *anti*-H on C^1 and *syn*-H on C^3), 3.74 (s, 3H, OMe), 3.79 (s, 6H, OMe), 4.26 (dd, J=5.9 Hz, J_{H-P}= 7.2 Hz, 1H, *syn*-H on C^1), 5.48 (m, 1H, H on C^2), 6.76–8.16 (m, 20H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 Hz, −20°C) δ 55.1 (OMe), 55,5 (OMe), 63.3 (C^3), 80.5 (d, J_{C-H}= 32.1, C^1), 117.4 (d, J_{C-H}=5.2, C^2), 112.8–160.3 (aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz, −20°C) δ 16.5. *minor isomer:* ^{1}H NMR (CDCl3, 500 MHz, −20°C) δ 1.76 (d, J=12.2 Hz, 1H, *anti*-H on C^3), 2.95 (d, J=6.9 Hz, 1H, *syn*-H on C^3), 3.13 (dd, J=8.8 Hz, J_{H-P}= 13.7 Hz, 1H, *anti*-H on C^1), 3.43 (s, 3H, OMe), 3.79 (m, 1H, H on C^2), 3.8 (s, 6H, OMe), 4.14 (dd, J=5.9 Hz, J_{H-P}= 7.0 Hz, 1H, *syn*-H on C^1), 6.76–8.16 (m, 20H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 Hz, −20°C) δ 54.9 (OMe), 55.1 (OMe), 69.5 (C^3), 79.5 (d, J_{C-H}=30.0 Hz, C^1), 117.1 (d, J_{C-H}=5.2 Hz, C^2), 113.9–155.7 (aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz, −20°C) δ 14.2.

[PdCl(π-C_3H_5)]L (L=1b) (Ar=3-$CF_3C_6H_4$). *major isomer:* ^{1}H NMR ($CDCl_3$, 500 MHz, −20°C) δ 1.00 (d, J=12.2 Hz, 1H, *anti*-H on C^3), 2.20 (d, J=7.0 Hz, 1H, *syn*-H on C^3), 2.32 (dd, J=10.7 Hz, J_{H-P}=13.4 Hz, 1H, anti-H on C^1), 3.76 (s, 3H, OMe), 4.36 (dd, J=7.3 Hz, J_{H-P}=9.4 Hz, 1H, *syn*-H on C^1), 5.16 (m, 1H, H on C^2), 6.97–8.00 (m, 20H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 Hz, −20°C) δ 55.4 (OMe), 60.0 (C^3), 81.3 (d, J_{C-H}= 31.0 Hz, C^1), 117.9 (d, J_{C-H}=5.2 Hz, C^2), 113.7–155.6 (aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz, −20°C) δ 19.8. *minor isomer:* ^{1}H NMR ($CDCl_3$, 500 MHz, −20°C) δ 1.71 (d, J=12.2 Hz, 1H, *anti*-H on C^3), 2.90 (d, J=6.4 Hz, 1H, syn-H on C^3), 3.20 (dd, J=9.1 Hz, J_{H-P}=13.7 Hz, 1H, *anti*-H on C^1), 3.41 (s, 3H, OMe), 3.63 (m, 1H, H on C^2), 4.23 (dd, J=7.0 Hz, J_{H-P}=9.4 Hz, 1H, *syn*-H on C^1), 6.97–8.00 (m, 20H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 Hz, −20°C) δ 55.0 (OMe), 64.7 (C^3), 80.0 (d, J_{C-H}=29.0, C^1), 117.9 (d, J_{C-H}=7.2, C^2), 113.7–155.6 (aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz, −20°C) δ 17.1.

Acknowledgements

This work was supported by 'Research for the Future' Program, the Japan Society for the Promotion of Science and a Grant-in-Aid for Scientific Research, the Ministry of Education, Japan.

References

1. For a review on catalytic allylic substitutions, see: J. Tsuji, *Palladium Reagents and Catalysts*, Chichester 1995. For reviews on catalytic asymmetric allylic substitutions, see: (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Hayashi, T. *In Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; p 325. (c) Frost, C. G.; Howarth, J.; Williams, J. M. *J. Tetrahedron Asymmetry* **1992**, *3*, 1089. (d) Consiglio, G.; Waymouth, M. *Chem. Rev.* **1989**, *89*, 257.

2. Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046.

3. Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775.

4. (a) Tsuji, J.; Yamakawa, T. *Teterahedron Lett.* **1979**, 613. (b) Tsuji, J.; Shimizu, I.; Minami, I. *Chem. Lett.* **1984**, 1017. (c) Tsuji, J.; Minami, I.; Shimizu, I. *Synthesis* **1986**, 623. (d) Mandai, T.; Matsumoto, T.; Kawada, M.; Tsuji, J. *J. Org. Chem.* **1992**, *57*, 1326. For a review: Tsuji, J.; Mandai, T. *Synthesis* **1996**, 1.

5. Oshima, M.; Shimizu, I.; Yamamoto, A.; Ozawa, F. *Organometallics* **1991**, *10*, 1221.

6. Hayashi, T.; Iwamura, H.; Uozumi, Y. *Tetrahedron Lett.* **1994**, *35*, 4813.

7. Hayashi, T.; Iwamura, H.; Uozumi, Y.; Matsumoto, Y.; Ozawa, F. *Synthesis* **1994**, 526.

8. (a) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887. (b) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945. (c) Uozumi, Y.; Suzuki, N.; Ogiwara, A.; Hayashi, T. *Tetrahedron* **1994**, *50*, 4293

9. Hayashi, T.; Kawatsura, M.; Iwamura, H.; Yamaura, Y.; Uozumi, Y. *Chem. Commun.* **1996**, 1767.

10. For examples: (a) Cho, H.; Iwashita, T.; Ueda, M.; Mizuno, A.; Mizukawa, K.; Hamaguchi, M. *J. Am. Chem. Soc.* **1988**, *110*, 4832. (b) Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067. (c) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681.

11. Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033.

12. Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.

13. Bellucci, C.; Glualtieri, F.; Scapecchi, S.; Teodori, E.; Budriesi, R.; Chiarini, A. *Farmaco* **1989**, *44*, 1167.

14. Bussas, R.; Muenster, H.; Kresze, G. *J. Org. Chem.* **1983**, *47*, 2828.

15. Kagabu, S.; Shimizu, Y.; Ito, C.; Moriya, K. *Synthesis* **1992**, 830.

16. Yashima, E.; Yamamoto, C.; Okamoto, Y.; *J. Am. Chem. Soc.*, **1996**, *118*, 4036, and references cited therein.

17. Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugita, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523.

18. Obora, Y.; Tsuji, Y. *J. Org. Chem.* **1995**, *60*, 4647.

19. Masuyama, Y.; Maekawa, K.; Kurusu, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2311.

20. (a) Hayashi, T.; Konishi, M.; Mise, T.; Kagotani, M.; Takaji, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180. (b) Cram, D. J. *J. Am. Chem. Soc.* **1952**, *74*, 2141.

21. Denmark, S. E.; Marble, L. K. *J. Org. Chem.* **1990**, *55*, 1984.

22. Arigoni, D.; Jeger, O. *Helv. Chim. Acta* **1945**, *37*, 881.

23. (a) Folli, U.; Iarossi, D.; Montanari, F.; Torre, G. *J. Chem. Soc.* (*C*) **1968**, 1317. (b) Fredga, A. *Ark. Kemi.* **1956**, *9*, 322.

24. Aaron, C.; Dull, D. L.; Schmiegel, J. L.; Jaeger, D.; Ohashi, Y.; Mosher, H. S. *J. Org. Chem.* **1967**, *32*, 2797.

25. Hoberg, H.; Guhl, D. *Angew. Chem.* **1989**, *101*, 1091.

26. Hoberg, H.; Baerhausen, D. *J. Organomet. Chem.* **1991**, *403*, 401.