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Development of Chiral (*S*)-Prolinol-Derived Ligands for Palladium-Catalyzed Asymmetric Allylic Alkylation: Effect of a Siloxymethyl Group on the Pyrrolidine Backbone

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Received March 31, 2004

A series of novel chiral aminophosphine ligands are designed and readily prepared from (*S*)-prolinol. The reactivity and selectivity in the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with a dimethyl malonate−BSA−LiOAc system using these chiral ligands are evaluated, and the structural elucidation of ligands and palladium complex is also conducted. Moreover, a series of trialkylsilylated chiral aminophosphine ligands are prepared and applied to palladium-catalyzed asymmetric allylic alkylation (up to 98% ee).

Introduction

In recent years, palladium-catalyzed allylic alkylation has been extended to catalytic asymmetric synthesis by the use of chiral ligands,[1] and the development of highly efficient enantioselective catalysis for this reaction has been awaited with great anticipation.[2] Because chiral phosphine ligands can induce a high enantiomeric excess in the palladium-catalyzed reaction of racemic and achiral allylic substrates with nucleophiles, P,P-chelate chiral ligands such as BINAP,[3] chiraphos,[4] and Trost's ligand[5] play an important role in catalytic asymmetric synthesis.[6] Chiral P,N-chelate compounds have also been used as ligands for asymmetric allylic alkylation during the past decades,[6t,7] for instance, phosphinooxazolines,[8] iminophosphines,[9] phosphinohydrazones[10] (possessing sp^2 nitrogen[11]), and aminophosphines[6c,d,f,12] (possessing sp^3 nitrogen). In particular, pyrrolidinyl-containing aminophosphines[13] such as **1**[13h] and **2**[13d,g,m,14b] (Figure 1) have been found to be efficient chiral sources. Recently, we have reported palladium-catalyzed asymmetric allylic alkylation using pyrrolidinyl-containing chiral aminophosphines **3** as a ligand.[14] It has been proved that a series of aminophosphine ligands **3** possessing methoxyl groups in the terminal of the side chain induced high enantioselectivities. Herein, we report palladium-catalyzed asymmetric allylic alkylation using novel pyrrolidinyl-containing chiral aminophosphine ligands (*S*)-**4**[15] possessing hydroxyl groups in the terminal of the side chain.

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10.1021/jo049469t CCC: $27.50
Published on Web 09/04/2004

Results and Discussion

Synthesis of Chiral Aminophosphine Ligands (*S*)-4. The chiral aminophosphine ligands (*S*)-**4** were readily prepared from commercially available optically pure (*S*)-prolinol and various phosphine oxides **5** in two steps (Scheme 1). A nucleophilic aromatic substitution (S_NAr) reaction[16] of a phosphine oxide compound such as diphenyl(2-methoxyphenyl)phosphine oxide **5a** with bislithiated (*S*)-prolinol gave the corresponding aminophosphine oxide **6a**. This aminophosphine oxide **6a** was converted into the desired chiral aminophosphine ligand (*S*)-**4a** in good yield by reduction with trichlorosilane−triethylamine. The other ligands (*S*)-**4** were prepared in the same manner.

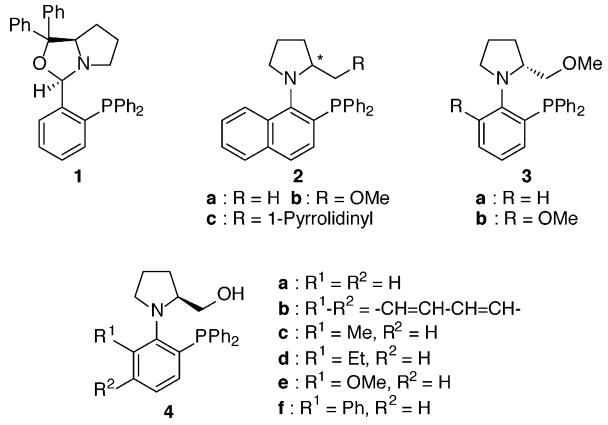

FIGURE 1. Pyrrolidinyl-containing aminophosphines.

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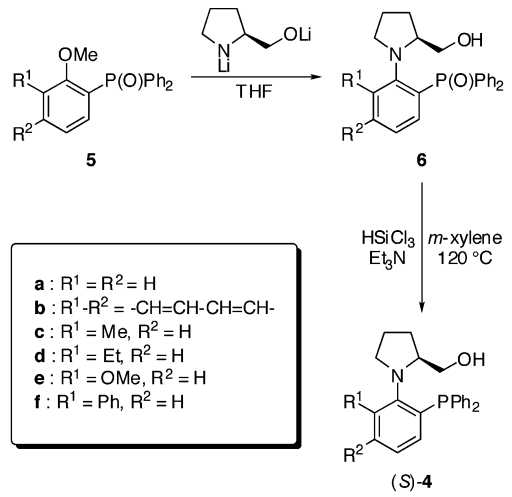
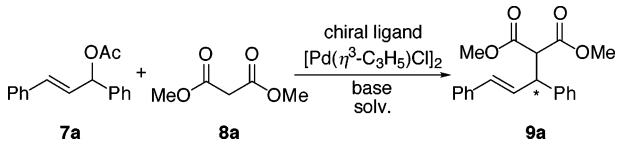
SCHEME 1. Synthesis of Chiral Aminophosphine Ligands (*S*)-4



Yield of **6** : **a** = 64 %, **b** = 75 %, **c** = 62 %, **d** = 36 %, **e** = 93 %, **f** = 63 %.
Yield of **4** : **a** = 90 %, **b** = 65 %, **c** = 91 %, **d** = 78 %, **e** = 83 %, **f** = 75 %.

SCHEME 2. Palladium-Catalyzed Asymmetric Allylic Alkylation (AAA Reaction)



Palladium-Catalyzed Asymmetric Allylic Alkylation. These chiral aminophosphine ligands (*S*)-**4** were applied to the palladium-catalyzed asymmetric allylic alkylation (AAA reaction) of 1,3-diphenyl-2-propenyl acetate (**7a**) with a dimethyl malonate (**8a**) (Scheme 2). This reaction was carried out in the presence of 2 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 4 mol % of a chiral ligand, and a mixture of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and 2 mol % of LiOAc in toluene to give the alkylated product **9a**;[14b] the results are summarized in Table 1.

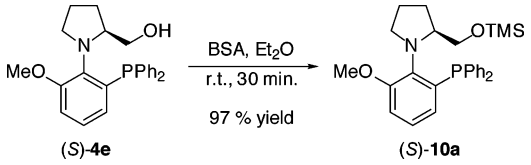
The reactions occurred successfully, and the alkylated product **9a** was obtained in good yields (entries 1−5 and 7). The ligand (*S*)-**4a** gave the product **9a** in low enantiopurity (entry 1), whereas ligands (*S*)-**4b**−**f**, 6′-substituted analogues of (*S*)-**4a**, brought about high asymmetric induction (entries 2−5 and 7). Although enantioselectivity was improved to 96% ee by decreasing the reaction temperature (−20 °C), the reaction rate became slow (entry 6). To our surprise, the ligand (*S*)-**4a** gave enantioselectivity higher than that with the ligand (*R*)-**3a** possessing methoxyl group in the terminal of the side chain (entry 1 vs 8), just as it appeared in the case of a 6′-methoxyl-type ligand such as (*S*)-**4e** versus (*R*)-**3b** (entry 5 vs 9). It was noteworthy that the asymmetric induction was emphasized, although the hydroxyl group of (*R*)-**3** is sterically less hindered than the methoxyl group of (*S*)-**4**.

TABLE 1. Palladium-Catalyzed AAA Reaction Using Chiral Ligands (*R*)-3 and (*S*)-4[a]

entry	ligand	R^1	R^2	yield %[b]	ee/%[c] (config)[d]
1	(*S*)-**4a**	H	H	98	58 (*S*)
2	(*S*)-**4b**	−CH=CH−CH=CH−		86	89 (*S*)
3	(*S*)-**4c**	Me	H	94	92 (*S*)
4	(*S*)-**4d**	Et	H	89	87 (*S*)
5	(*S*)-**4e**	OMe	H	91	93 (*S*)
6[e]	(*S*)-**4e**	OMe	H	41	96 (*S*)
7	(*S*)-**4f**	Ph	H	93	83 (*S*)
8[f]	(*R*)-**3a**	H	H	97	40 (*R*)
9[f]	(*R*)-**3b**	OMe	H	97	85 (*R*)

[a] The reaction was carried out at 0.5 mmol scale in toluene at rt for 24 h with 3.0 equiv of **8a** and BSA, in the presence of LiOAc (2 mol %), chiral ligand (4 mol %), and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2 mol %). [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Established from the optical rotation by comparison with the literature data.[17] [e] The reaction was carried out at −20 °C for 7 days. [f] See ref 14.

SCHEME 3. Silyl Etherification of (*S*)-4e by BSA



Although enantioselectivity was higher than that with the ligand (*R*)-**3a** possessing methoxyl group in the terminal of the side chain (entry 1 vs 8), just as it appeared in the case of a 6′-methoxyl-type ligand such as (*S*)-**4e** versus (*R*)-**3b** (entry 5 vs 9). It was noteworthy that the asymmetric induction was emphasized, although the hydroxyl group of (*R*)-**3** is sterically less hindered than the methoxyl group of (*S*)-**4**.

We consider this unexpected phenomenon to be caused by the effect of the 2-pyrrolidinyl substituent; if the hydroxyl groups in the Pd−ligand complexes could be easily converted into the silyl ether groups by excess BSA in situ,[18] then the 2-pyrrolidinyl substituent would be sterically more hindered than the methoxyl groups, resulting in an increase in the enantioselectivity of **9a**.

Synthesis and Application of Chiral Ligand (*S*)-10a to the Palladium-Catalyzed AAA Reaction. According to our anticipation, we attempted to react of (*S*)-**4e** with BSA. To a solution of (*S*)-**4e**, BSA was added at room temperature (Scheme 3), and the resulting product was a novel aminophosphine (*S*)-**10a** via the trimethylsilylation. Using (*S*)-**10a** as a ligand, we examined a palladium-catalyzed AAA reaction in the same manner (Table 2, entry 2). The reaction provided a level of chemical yield and enantioselectivity similar to that of entry 1.

We next examined reaction conditions of the palladium-catalyzed AAA reaction. Initially, using (*S*)-**10a**

(13) Some recent examples of Pd-catalyzed AAA reaction using pyrrolidinyl-containing aminophosphine ligands: (a) Cheng, X.; Hill, K. K. *Tetrahedron: Asymmetry* **2003**, *14*, 2045. (b) Mino, T.; Tanaka, Y.; Sato, Y.; Saito, A. Sakamoto, M.; Fujita, T. *Tetrahedron Lett.* **2003**, *44*, 4677 and 5759. (c) Lam, H.; Cheng, X.; Steed, J. W.; Aldous, D. J.; Hill, K. K. *Tetrahedron Lett.* **2002**, *43*, 5875. (d) Kondo, K.; Kazuta, K.; Fujita, H.; Sakamoto, Y.; Murakami, Y. *Tetrahedron* **2002**, *58*, 5209. (e) Farrell, A.; Goddard, R.; Guiry, P. J. *J. Org. Chem.* **2002**, *67*, 4209. (f) Wang, Y.; Li, X.; Ding, K. *Tetrahedron Lett.* **2002**, *43*, 159. (g) Mino, T.; Tanaka, Y.; Akita, K.; Anada, K.; Sakamoto, M.; Fujita, T. *Tetrahedron: Asymmetry* **2001**, *12*, 1677. (h) Okuyama, Y.; Nakano, H.; Hongo, H. *Tetrahedron: Asymmetry* **2000**, *11*, 1193. (i) Cahill, J. P.; Cunneen, D.; Guiry, P. J. *Tetrahedron: Asymmetry* **1999**, *10*, 4157. (j) Hiroi, K.; Suzuki, Y.; Abe, I. *Tetrahedron: Asymmetry* **1999**, *10*, 1173. (k) Hiroi, K.; Suzuki, Y.; Abe, I. *Chem. Lett.* **1999**, 149. (l) Suzuki, Y.; Abe, I.; Hiroi, K. *Heterocycles* **1999**, *50*, 89. (m) Hattori, T.; Komuro, Y.; Hayashizaka, N.; Takahashi, H.; Miyano, S. *Enantiomer* **1997**, *2*, 203.

(14) (a) Mino, T.; Tanaka, Y.; Sakamoto, M.; Fujita, T. *Tetrahedron: Asymmetry* **2001**, *12*, 2435. (b) Mino, T.; Tanaka, Y.; Sakamoto, M.; Fujita, T. *Heterocycles* **2000**, *53*, 1485.

(15) Mino, T.; Tanaka, Y.; Akita, K.; Sakamoto, M.; Fujita, T. *Heterocycles* **2003**, *60*, 9.

(16) Hattori, T.; Sakamoto, J.; Hayashizaka, N.; Miyano, S. *Synthesis* **1994**, 199.

(17) Hayashi, T.; Yamamoto, A.; Hagihara, T.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 191.

(18) (a) Galbraith, M. N.; Horn, D. H. S.; Middleton, E. J.; Hackney, R. J. *J. Chem. Soc., Chem. Commun.* **1968**, 466. (b) Klebe, J. F.; Finkbeiner, H.; White, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 3390.

TABLE 2. Palladium-Catalyzed AAA Reaction Using Chiral Ligands (*S*)-4e and (*S*)-10a[a]

entry	ligand	base	yield %[b]	ee/%[c] (config)[d]
1	(*S*)-**4e**	BSA-LiOAc	93	93 (*S*)
2	(*S*)-**10a**	BSA-LiOAc	93	93 (*S*)

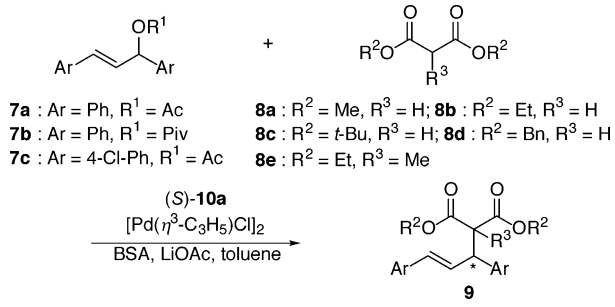
[a] The reaction was carried out at 0.5 mmol scale in toluene at rt for 24 h with 3.0 equiv of **8a** and BSA, in the presence of LiOAc (2 mol %), chiral ligand (4 mol %), and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2 mol %). [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Established from the optical rotation by comparison with the literature data.[17]

TABLE 3. Influence of Solvent on Palladium-Catalyzed AAA Reaction Using Chiral Ligand (*S*)-10a[a]

entry	solvent	time/h	yield %[b]	ee/%[c] (config)[d]
1	toluene	2	93	93 (*S*)
2	THF	3	98	91 (*S*)
3	Et_2O	2	93	92 (*S*)
4	CPME[e]	2	99	90 (*S*)
5	*n*-hexane	2	93	91 (*S*)
6	MeCN	24	90	87 (*S*)
7	DMF	24	88	82 (*S*)
8	Ph-CF_3	2	98	89 (*S*)

[a] The reaction was carried out at 0.5 mmol scale at rt with 3.0 equiv of **8a** and BSA, in the presence of LiOAc (2 mol %), (*S*)-**10a** (4 mol %), and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2 mol %). [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Established from the optical rotation by comparison with the literature data.[17] [e] Cyclopentyl methyl ether.

SCHEME 4. Palladium-Catalyzed AAA Reaction of Various Allylic Esters with Various Malonates Using (*S*)-10a as a Ligand



as a ligand, we conducted this reaction in various solvents, and the results are summarized in Table 3.

In the case of toluene, the reaction was almost finished within 2 h (entry 1). Changing the solvent to various ethers brought similar levels of chemical yields and enantioselectivities in comparison with entry 1 (entry 2−4). Using a low-polar solvent, such as *n*-hexane, also provided a similar level of catalytic activity (entry 5). However, use of non-ether-type polar solvents decreased not only the reactivities but also the enantioselectivities (entries 6 and 7). When α,α,α-trifluorotoluene was used as a solvent, high reactivity was observed, though the enantioselectivity was slightly lower (entry 8).

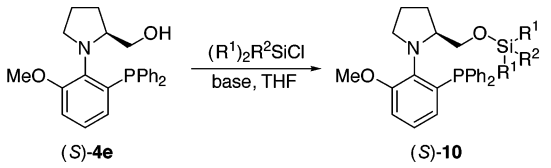
In addition, we examined AAA reactions of various dialkyl malonates and allyl esters using (*S*)-**10a** as a ligand (Scheme 4). As shown in Table 4, the reaction at −10 °C provided high enantiomeric excess compared to the case in which the reaction took place at room temperature (entry 1). Pivaroyl allylic ester **7b** was also converted to **9a** with high enantioselectivity (entry 2). The reaction using 4, 4′-dichloro-substituted allylic ester **7c** as a substrate provided the corresponding product **9b** at the same level of enantioselectivity as entry 2; however, the reaction rate became slow as a result of the temperature decreasing (entry 3). The enantioselectivity was improved when diethyl malonate **8b** was used as a sterically more-hindered nucleophile (entry 4), but the same effect did not occur in the case of di-*tert*-butyl malonate **8c** and dibenzyl malonate **8d** (entries 5 and 6). The enantioselectivity was achieved to 98% ee when diethylmethyl malonate **8e** was used at 0 °C. (entry 7).

TABLE 4. Palladium-Catalyzed AAA Reaction of Various Allylic Esters with Various Malonates Using (*S*)-10a as a Ligand[a]

entry	Ar	R^1	R^2	R^3	prod.	temp °C	time h	yield %[b]	ee/%[c] (config)
1	Ph	Ac	Me	H	**9a**	−10	24	97	95 (*S*)[d]
2	Ph	Piv	Me	H	**9a**	rt	24	92	92 (*S*)[d]
3	4-Cl-Ph	Ac	Me	H	**9b**	−30	120	79	93
4	Ph	Ac	Et	H	**9c**	−10	48	95	97 (*S*)[e]
5	Ph	Ac	*t*-Bu	H	**9d**	0	72	95	80 (*S*)[f]
6	Ph	Ac	Bn	H	**9e**	−20	72	90	95
7	Ph	Ac	Et	Me	**9f**	0	48	98	98 (*R*)[g]

[a] The reaction was carried out at 0.5 mmol scale in toluene with 3.0 equiv of **8** and BSA, in the presence of LiOAc (2 mol %), (*S*)-**10a** (4 mol %), and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2 mol %). [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Established from the optical rotation by comparison with the literature data.[17] [e] Established from the optical rotation by comparison with the literature data.[19] [f] Established from the optical rotation by comparison with the literature data.[20] [g] Established from the optical rotation by comparison with the literature data.[14a]

SCHEME 5. Synthesis of Chiral Aminophosphine Ligands (*S*)-10



Chiral Aminophosphine Ligands 10; Preparation and Their Catalytic Activities. The above results prompted us to search for sterically more-hindered ligands. Accordingly, we have designed a series of silylated chiral aminophosphine ligands **10** readily prepared from (*S*)-**4e** with the corresponding silyl chlorides (Scheme 5) and applied them to the palladium-catalyzed AAA reaction in the same manner as described above (Scheme 2). The results are summarized in Table 5.

The reactions were successfully carried out with high enantioselectivities at room temperature, except for when (*S*)-**10c** was used as a ligand (entry 3). In particular, using chiral ligand (*S*)-**10b** slightly increased the enantioselectivity (entry 2). To improve the enantioselectivity, we further examined the effect of decreasing the temperature. At −20 °C, enantioselectivity was achieved to 98% ee in Et_2O (entry 6), although its reaction rate became slow compared to the reaction carried out in toluene at the same temperature (entry 5).

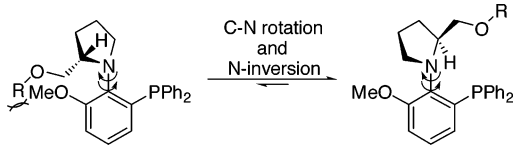
Structural Elucidation of Chiral Aminophosphine Ligands and Their Palladium Complexes. On

TABLE 5. Palladium-Catalyzed AAA Reactions Using Chiral Ligands (*S*)-10[a]

entry	ligand	solvent	temp/°C	yield %[b]	ee/%[c] (config)[d]
1	(*S*)-**10a**	toluene	rt	93	93 (*S*)
2	(*S*)-**10b**	toluene	rt	90	94 (*S*)
3	(*S*)-**10c**	toluene	rt	98	78 (*S*)
4	(*S*)-**10d**	toluene	rt	90	91 (*S*)
5	(*S*)-**10b**	toluene	−20	69	97 (*S*)
6	(*S*)-**10b**	Et_2O	−20	46	98 (*S*)

[a] The reaction was carried out at 0.5 mmol scale for 24 h with 3.0 equiv of **8a** and BSA, in the presence of LiOAc (2 mol %), chiral ligand (4 mol %), and [Pd(η^3-C_3H_5)Cl]$_2$ (2 mol %). [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Established from the optical rotation by comparison with the literature data.[17]

SCHEME 6. C(aryl)−N(amine) Bond Rotation of (*S*)-4e and (*S*)-10a



the basis of these results, we investigated the 2-pyrrolidinyl sidechain of (*S*)-**4** and (*S*)-**10** further from the viewpoint of structural studies. Recently, we discovered the C(aryl)−N(amine) bond atropisomeric aminophosphines and applied them to the palladium-catalyzed AAA reaction.[21] The results demonstrated that the high asymmetric induction was urged to the C(aryl)−N(amine) axial chirality. Those results indicate that there are two types of candidates in the configuration of (*S*)-**4** and (*S*)-**10**, and they are of the (a*R*)- or (a*S*)-configuration on their C(aryl)−N(amine) axis (Scheme 6). However, neither of the diastereomers derived from C(aryl)−N(amine) axial chirality and 2-pyrrolidinyl chirality were observed from the result of TLC nor by determining the NMR at various temperatures in toluene-*d*. Thus, despite the fact that these observations suggest the C(aryl)−N(amine) axis in (*S*)-**4** and (*S*)-**10** is configurationally flexible, the high asymmetric induction was urged to the ligands (*S*)-**4** and (*S*)-**10**. We considered that the 2-pyrrolidinyl side chains of (*S*)-**4** and (*S*)-**10** would be distant from the aryl moiety containing methoxyl and phosphino groups as a result of their steric stability; therefore, the (a*S*)-configuration is more favorable than the (a*R*)-configuration on their C(aryl)−N(amine) axis when the ligand coordinates with the palladium atom. Furthermore, it appears that the 2-pyrrolidinyl chirality induces the C(aryl)−N(amine) axial chirality in the molecule. To confirm our anticipation, we examined the single-crystal X-ray diffraction analysis of (*S*)-**4e** and (*S*)-**10a**.

The structures of the chiral ligands, both (*S*)-**4e** and (*S*)-**10a** containing a 2-pyrrolidinyl moiety, were determined by single-crystal X-ray diffraction analysis, with the results (Figures S1 and S2, Supporting Information)

SCHEME 7. Preparation of Palladium Complexes with Chiral Ligands (*S*)-4e and (*S*)-10a

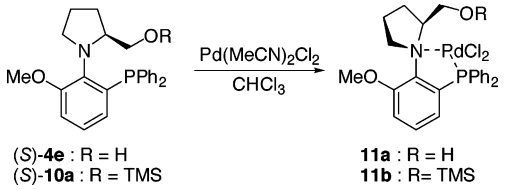


TABLE 6. Palladium-Catalyzed AAA Reactions Using Chiral Ligands (*S*)-4e and (*S*)-10a[a]

entry	ligand	base	yield %[b]	ee/%[c] (config)[d]
1	(*S*)-**4e**	NaH	68	68 (*S*)
2	(*S*)-**10a**	NaH	79	79 (*S*)

[a] The reaction was carried out at 0.5 mmol scale in toluene at rt for 24 h with 3.0 equiv of **8a** and NaH, in the presence of chiral ligand (4 mol %) and [Pd(η^3-C_3H_5)Cl]$_2$ (2 mol %). [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Established from the optical rotation by comparison with the literature data.[17]

indicating that the more stable structures feature the a*S*-type configuration of their C(aryl)−N(amine) axis.[22] These configurations clearly suggest that both of the 2-pyrrolidinyl side chains approach the diphenyl phosphinyl groups.

Treating the corresponding chiral ligand with Pd(MeCN)$_2$Cl$_2$ in chloroform, we next prepared the palladium complexes **11a** and **11b** (Scheme 7). Although the attempt at X-ray analysis of the palladium complex **11b** was unsuccessful, we were eventually able to obtain X-ray diffraction patterns by exchanging the complex **11b** to **11a**. As a result, the ligand (*S*)-**4e** is P,N-coordinated with a palladium atom by (a*S*)-configuration, and the 2-pyrrolidinyl side chain expectantly approaches the central palladium atom (Figure S3, Supporting Information).[22] The unit cells of (*S*)-**4e**, (*S*)-**10a**, and **11a** contain two independent molecules, but another molecule also shows the a*S*-type configuration of its C(aryl)−N(amine) axis. These results clearly suggest that the (a*S*)-configuration is more favorable than the (a*R*)-configuration on the C(aryl)−N(amine) axis when the ligand coordinates to the palladium atom, as if the 2-pyrrolidinyl chirality disturbs the N-inversion in molecules.

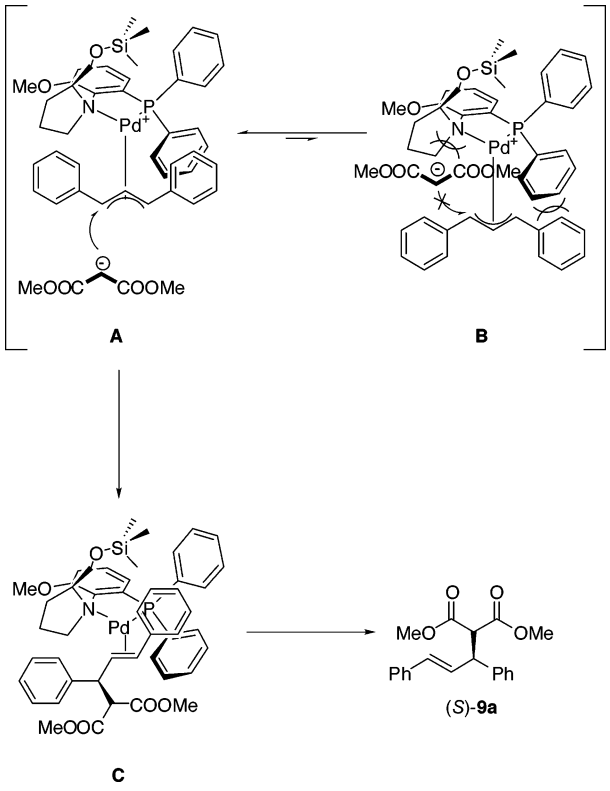
In addition, we prepared the chloroform-*d* solution of complex **11a** and gradually analyzed ^{1}H NMR spectra involving addition of BSA in portions. Following that, we compared these spectra to the spectrum of the complex **11b** (Figure S4, Supporting Information).[22] The spectrum of the complex **11a** was gradually approximated to that of the complex **11b** each time BSA was added.

Moreover, we examined the palladium-catalyzed AAA reaction under the condition that trimethylsilylation of (*S*)-**4e** does not occur in situ, such as when using NaH instead of BSA-LiOAc, and found that the enantioselectivity of **9a** was higher than that in the case of (*S*)-**4e** (Table 6). This result indicate that the hydroxyl group of the (*S*)-**4**-palladium complexes was trimethylsilylated by excess BSA in the AAA reaction system; that the resulting trimethylsiloxyl group was sterically more hindered than the methoxyl group emphasized the enantioselectivity of the alkylated product.

(19) Vyskocil, S.; Smrcina, M.; Hanus, V.; Polasek, M.; Kocovsky, P. *J. Org. Chem*. **1998**, *63*, 7738.
(20) Seebach, D.; Devaquet, E.; Ernst, A.; Hayakawa, M.; Kuehnle, F. N. M.; Schweizer, W. B.; Weber, B. *Helv. Chim. Acta* **1995**, *78*, 1636.
(21) Mino, T.; Tanaka, Y.; Yabusaki, T.; Okumura, D.; Sakamoto, M.; Fujita, T. *Tetrahedron: Asymmetry* **2003**, *14*, 2503.

(22) See Supporting Information.

SCHEME 8. Plausible Asymmetric Induction Process of Palladium-Catalyzed AAA Reaction Using Chiral Ligands (*S*)-4e and (*S*)-10a



Finally, we suggested the plausible asymmetric induction process of the palladium-catalyzed AAA reaction of **7a** with **8a** using chiral ligands (*S*)-**4e** and (*S*)-**10a** in Scheme 8. There are two candidates, **A** and **B**, which are considerable reaction intermediates formed from chiral ligands (*S*)-**4e** and (*S*)-**10a**. However, **B** has been proved unstable as a result of steric hindrance of the phenyl rings between the allylic substrate and the ligand. In addition, the nucleophilic attack of **8a** is hypothesized to be difficult because of steric hindrance of the bulky 2-pyrrolidinyl trimethylsiloxymethyl group. Therefore, the reaction probably proceeds through a W-type intermediate **A** rather than an M-type intermediate **B**. The nucleophilic attack occurs predominantly at the allyl terminus from the trans to the better π-acceptor (P > N).[23] As a result, the (*S*)-product **9a** was obtained in this reaction using the chiral aminophosphines (*S*)-**4** and (*S*)-**10** as ligands.

Conclusion

In summary, we were able to achieve highly enantioselective palladium-catalyzed asymmetric allylic alkylation using a novel chiral pyrrolidinyl-containing aminophosphine ligands (*S*)-**4** possessing a hydroxyl group. Furthermore, the trialkylsilylated aminophosphine ligand (*S*)-**10** also produced good results in the palladium-catalyzed asymmetric allylic alkylation. Moreover, by employing various structural methods, we were able to reveal that the (a*S*)-configuration of chiral pyrrolidinyl-containing aminophosphine ligands are more favorable than the (a*R*)-configuration on their C(aryl)−N(amine) axis, and the hydroxyl group of the palladium complex formed by (*S*)-**4e** was trimethylsilylated by excess BSA in situ. We are currently investigating other asymmetric reactions further using aminophosphines such as (*S*)-**4e** and (*S*)-**10** as the chiral ligands or chiral base catalysts.

Experimental Section

Preparation of Phosphine Oxides 5. Diphenyl(2-methoxyphenyl)phosphine oxide **5a** is commercially available. 1-Methoxy-2-diphenylphosphinonaphthalene oxide **5b**,[13g,16] 2-methoxy-3-methylphenyldiphenylphosphine oxide **5c**,[14a] 2,3-dimethoxyphenyldiphenylphosphine oxide **5e**,[14a] and 2-methoxy-3-phenylphenyldiphenylphosphine oxide **5f**[14a] were prepared according to the literature method.

2-Methoxy-3-ethylphenyldiphenylphosphine Oxide (5d). To mixture of 2-ethylanisole (10.0 mmol), TMEDA (1.51 mL, 10.0 mmol), and ether (25 mL) was added dropwise *n*-BuLi in hexane (9.2 mL, 14.7 mmol, 1.66 M) over 10 min. The mixture was stirred at room temperature for 2 h and then treated with chlorodiphenylphosphine (1.8 mL, 10.0 mmol), and the resulting mixture was diluted with ether and quenched with 2 M aqueous HCl. The organic layer was washed with 2 M aqueous Na_2CO_3 and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in AcOH (50 mL), treated with 30% aqueous H_2O_2 (1.5 mL), and then gradually heated to 80 °C for 2 h. The mixture was cooled to room temperature, diluted with ether (100 mL), and then treated with 2 M aqueous NaOH at 0 °C. The water layer was extracted with ether, and the combined extracts were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with *n*-hexane/EtOAc = 1/3): 33%; mp 108−111 °C; ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.24 (t, J = 7.6 Hz, 3H), 2.68 (q, J = 7.6 Hz, 2H), 3.47 (s, 3H), 7.05−7.13 (m, 1H), 7.15−7.24 (m, 1H), 7.40−7.56 (m, 7H), 7.67−7.77 (m, 4H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 14.5, 22.39, 62.0, 123.9 (d, J_{cp} = 12.9 Hz), 125.8, 127.2, 128.2, 128.4, 131.5 (d, J_{cp} = 2.8 Hz), 131.6, 131.8, 132.1 (d, J_{cp} = 9.2 Hz), 132.8, 134.2, 134.6 (d, J_{cp} = 2.1 Hz), 137.9 (d, J_{cp} = 6.2 Hz), 160.8 (d, J_{cp} = 2.8 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ 28.0; EI-MS *m*/*z* (rel intensity) 336 (M^+, 98); HRMS (FAB-MS) *m*/*z* calcd for $C_{21}H_{21}O_2P$ + H 337.1357, found 337.1355.

Typical Procedure for Preparation of Aminophosphine Oxides 6. To the solution of (*S*)-prolinol (1.03 mmol) in THF (1 mL) was added slowly *n*-BuLi in hexane (1.4 mL, 2.2 mmol, 1.56 M) at −80 °C for 10 min and then room temperature for 2 h under an argon atmosphere. After phosphine oxide **5** (1.0 mmol) was added at 0 °C, stirring was continued for 20 h at room temperature. The mixture was diluted with ether and quenched with saturated aqueous NH_4Cl. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography. (*S*)-1-[2′-(Diphenylphosphinyl)-1′-naphthalenyl]-2-(hydroxymethyl)pyrrolidine **6b** was prepared according to the literature method.[13g]

(*S*)-1-[2′-(Diphenylphosphinyl)phenyl]-2-(hydroxymethyl)pyrrolidine (6a): 64%; mp 179−181 °C; $[\alpha]^{25}_D$ −112 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.14−1.31 (m, 1H), 1.43−1.57 (m, 1H), 1.71−1.85 (m, 1H), 1.85−2.06 (m, 2H), 2.29−2.42 (m, 1H), 3.25−3.39 (m, 2H), 3.56 (d, J = 10.8 Hz, 1H), 6.36 (br-s, 1H), 6.98−7.17 (m, 2H), 7.38−7.59 (m, 8H), 7.67−7.85 (m, 4H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 24.8, 26.3, 58.1, 61.5, 69.1, 125.5, 125.7, 127.2, 127.3, 128.6, 128.8 (d, J_{cp} = 4.4 Hz), 128.9, 131.5, 131.7, 132.1, 132.6, 132.7, 133.3, 134.4, 134.6, 157.5; ^{31}P NMR (121 Mz, $CDCl_3$) δ 28.8; EI-MS *m*/*z* (rel intensity) 377 (M^+, 1); HRMS (FAB-MS) *m*/*z* calcd for $C_{23}H_{24}NO_2P$ + H 378.1623, found 378.1602.

(23) Åkermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679.

(*S*)-1-[2′-(Diphenylphosphinyl)-6′-methylphenyl]-2-(hydroxymethyl)pyrrolidine (6c): 76%; mp 163−166 °C; $[\alpha]^{25}_D$ −81.5 (*c* 0.27, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.37−1.49 (m, 1H), 1.49−1.68 (m, 2H), 1.80−2.04 (m, 2H), 2.30 (s, 3H), 2.61 (dd, *J* = 8.4 and 15.5 Hz, 1H), 3.38 (ddd, *J* = 5.5, 8.8 and 14.3 Hz, 1H), 3.45−3.56 (m, 1H), 3.56−3.66 (m, 1H), 6.72−6.81 (m, 1H), 6.89 (ddd, *J* = 1.3, 7.7 and 14.5 Hz, 1H), 7.06 (dt, *J* = 3.2 and 7.6 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.40−7.56 (m, 6H), 7.61−7.72 (m, 2H), 7.72−7.82 (m, 2H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 19.8, 26.0, 28.1, 53.9, 63.5, 65.9, 125.8 (d, J_{cp} = 14.7 Hz), 128.7 (d, J_{cp} = 5.1 Hz), 128.8 (d, J_{cp} = 4.4 Hz), 131.6, 131.8, 132.8 (d J_{cp} = 8.8 Hz), 133.2 (d, J_{cp} = 13.6 Hz), 134.2, 134.6, 135.1, 136.5, 138.1 (d, J_{cp} = 2.0 Hz), 139.8 (d, J_{cp} = 7.9 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ 30.1; FAB-MS *m*/*z* (rel intensity) 392 (M^+ + 1, 100); HRMS (FAB-MS) *m*/*z* calcd for $C_{24}H_{26}NO_2P$ + H 392.1779, found 392.1777.

(*S*)-1-[2′-(Diphenylphosphinyl)-6′-ethylphenyl]-2-(hydroxymethyl)pyrrolidine (6d): 36%; mp 142−144 °C; $[\alpha]^{25}_D$ −85.0 (*c* 1.01, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.24 (t, *J* = 7.5 Hz, 3H), 1.35−1.47 (m, 1H), 1.47−1.61 (m, 1H), 1.61−1.70 (m, 1H), 1.85−2.06 (m, 2H), 2.50−2.70 (m, 3H), 3.30−3.41 (m, 1H), 3.41−3.49 (m, 1H), 3.59−3.68 (m, 1H), 6.78 (ddd, *J* = 1.7, 5.0 and 9.3 Hz, 1H), 6.89 (ddd, *J* = 1.5, 7.6 and 14.7 Hz, 1H), 7.12 (dt, *J* = 3.1 and 7.7 Hz, 1H), 7.40−7.55 (m, 7H), 7.62−7.73 (m, 2H), 7.73−7.82 (m, 2H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 15.2, 24.0, 25.5, 27.6, 54.7, 62.9, 67.1, 125.7 (d, J_{cp} = 14.6 Hz), 128.3 (d, J_{cp} = 6.0 Hz), 128.4 (d, J_{cp} = 5.13 Hz) 131.2, 131.4, 132.3 (d, J_{cp} = 8.7 Hz), 132.5, 132.7 (d, J_{cp} = 13.4 Hz), 134.0 (d, J_{cp} = 21.1 Hz), 134.8, 135.9, 136.2, 145.9 (d, J_{cp} = 7.7 Hz), 151.9; ^{31}P NMR (121 Mz, $CDCl_3$) δ 30.0; FAB-MS *m*/*z* (rel intensity) 406 (M^+ + 1, 99); HRMS (FAB-MS) *m*/*z* calcd for $C_{25}H_{28}NO_2P$ + H 406.1936, found 406.1915.

(*S*)-1-[2′-(Diphenylphosphinyl)-6′-methoxyphenyl]-2-(hydroxymethyl)pyrrolidine (6e): 93%; mp 171−172 °C; $[\alpha]^{25}_D$ −111.8 (*c* 1.04, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.18−1.38 (m, 1H), 1.38−1.68 (m, 2H), 1.68−1.90 (m, 2H), 2.5−2.70 (m, 1H), 3.26−3.46 (m, 1H), 3.46−3.70 (m, 2H), 3.82 (s, 3H), 6.52−6.70 (m, 2H), 7.05−7.17 (m, 2H), 7.40−7.56 (m, 6H), 7.62−7.73 (m, 2H), 7.73−7.84 (m, 2H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 25.4, 27.4, 53.3, 55.1, 63.0, 65.3, 116.7 (d, J_{cp} = 2.3 Hz), 125.8 (d, J_{cp} = 12.7 Hz), 126.4 (d, J_{cp} = 15.9 Hz), 128.2 (d, J_{cp} = 9.2 Hz), 128.3 (d, J_{cp} = 8.3 Hz) 131.1, 131.1, 131.2, 131.4 (d, J_{cp} = 2.6 Hz), 132.0, 132.3 (d, J_{cp} = 8.8 Hz), 132.7, 133.4, 134.2, 135.3, 136.7, 143.4 (d, J_{cp} = 3.0 Hz), 159.1 (d, J_{cp} = 11.5 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ 30.0; FAB-MS *m*/*z* (rel intensity) 408 (M^+ + 1, 100); HRMS (FAB-MS) *m*/*z* calcd for $C_{24}H_{26}NO_3P$ + H 408.1729, found 408.1728.

(*S*)-1-[2′-(Diphenylphosphinyl)-6′-phenylphenyl]-2-(hydroxymethyl)pyrrolidine (6f): 63%; mp 175−177 °C; $[\alpha]^{25}_D$ +4.4 (*c* 0.79, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.09−1.26 (m, 2H), 1.26−1.50 (m, 1H), 1.62−1.80 (m, 1H), 2.52−2.72 (m, 2H), 2.98 (br-s, 1H), 3.06−3.22 (m, 1H), 3.48 (d, *J* = 12.0 Hz, 1H), 6.33 (d, *J* = 8.7 Hz, 1H), 6.97−7.13 (m, 2H), 7.18−7.26 (m, 2H), 7.26−7.41 (m, 5H), 7.41−7.61 (m, 5H), 7.61−7.73 (m, 2H), 7.73−7.85 (m, 2H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 25.3, 27.0, 56.2, 63.2, 64.5, 124.0 (d, J_{cp} = 14.4 Hz), 127.8, 128.6, 128.8, 128.9, 129.6, 132.0 (d, J_{cp} = 9.8 Hz), 132.1 (d, J_{cp} = 10.6 Hz), 132.2, 132.6 (d, J_{cp} = 9.2 Hz), 132.8, 133.5, 133.8, 134.2, 135.2 (d, J_{cp} = 13.1 Hz), 137.6 (d, J_{cp} = 2.4 Hz), 141.7, 144.4 (d, J_{cp} = 8.1 Hz), 151.6 (d, J_{cp} = 4.3 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ 32.3; FAB-MS *m*/*z* (rel intensity) 454 (M^+ + 1, 100); HRMS (FAB-MS) *m*/*z* calcd for $C_{27}H_{26}NO_2P$ + H 454.1936, found 454.1943.

Typical Procedure for Preparation of Aminophosphine Ligands 4. To a mixture of phosphine oxide **6** (0.3 mmol) and triethylamine (0.17 mL, 1.2 mmol) in *m*-xylene (2 mL) was added trichlorosilane (0.12 mL, 1.2 mmol) at 0 °C under an argon atmosphere. The reaction mixture was refluxed for 6 h. After being cooled to room temperature, the mixture was diluted with ether and quenched with 2 M aqueous NaOH solution. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with *n*-hexane/EtOAc = 6/1). (*S*)-1-[2′-(Diphenylphosphino)-1′-naphthalenyl]-2-(hydroxymethyl)pyrrolidine **4b** was prepared according to the literature method.[13g]

(*S*)-1-[2′-(Diphenylphosphino)phenyl]-2-(hydroxymethyl)pyrrolidine (4a): 90%; mp 69−70 °C; $[\alpha]^{25}_D$ +0.3 (*c* 0.31, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.50−1.76 (m, 2H), 1.84−2.07 (m, 2H), 2.38−2.53 (m, 1H), 2.53−2.68 (m, 1H), 3.25−3.47 (m, 2H), 3.47−3.66 (m, 2H), 6.86 (ddd, *J* = 1.5, 3.8 and 7.7 Hz, 1H), 7.09 (dt, *J* = 0.7 and 7.6 Hz, 1H), 7.21−7.31 (m, 3H), 7.31−7.41 (m, 9H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 24.6, 26.9, 56.9, 61.7, 66.1, 124.2 (d, J_{cp} = 2.2 Hz), 125.8, 128.4, 128.5, 128.5, 128.5, 128.6, 129.0, 130.4, 133.3, 133.7, 133.9, 134.3, 134.6, 136.4 (d, J_{cp} = 5.6 Hz), 137.1 (d, J_{cp} = 9.2 Hz), 138.3, 154.0 (d, J_{cp} = 20.1 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ −16.9; EI-MS *m*/*z* (rel intensity) 361 (M^+, 7.5); HRMS (FAB-MS) *m*/*z* calcd for $C_{23}H_{24}NOP$ + H 362.1674, found 362.1659.

(*S*)-1-[2′-(Diphenylphosphino)-6′-methylphenyl]-2-(hydroxymethyl)pyrrolidine (4c): 91%; mp 76−79 °C; $[\alpha]^{25}_D$ +83.7 (*c* 1.04, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.60−1.80 (m, 2H), 1.90−2.18 (m, 3H), 2.28 (s, 3H), 2.81 (dd, *J* = 7.8 and 16.0 Hz, 1H), 3.41 (dt, *J* = 1.5 and 11.7 Hz, 1H), 3.53 (dt, *J* = 1.1 and 6.0 Hz, 1H), 3.72 (d, *J* = 12.0 Hz, 1H), 4.50 (dt, *J* = 3.2 and 12.4 Hz, 1H), 6.71 (ddd, *J* = 1.1, 3.0 and 6.9 Hz 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.14−7.24 (m, 3H), 7.27−7.38 (m, 8H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 19.2, 25.9, 28.5, 53.3, 63.2, 64.1, 126.9, 128.8, 128.8 (d, J_{cp} = 6.3 Hz), 128.9 (d, J_{cp} = 8.0 Hz), 129.6, 131.7, 134.1 (d, J_{cp} = 18.8 Hz), 134.9 (d, J_{cp} = 20.6 Hz), 136.6 (d, J_{cp} = 3.7 Hz), 137.9, 138.2 (d, J_{cp} = 8.2 Hz), 141.7 (d, J_{cp} = 6.6 Hz), 149.7 (d, J_{cp} = 20.7 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ −17.2; FAB-MS *m*/*z* (rel intensity) 376 (M^+ + 1, 98); HRMS (FAB-MS) *m*/*z* calcd for $C_{24}H_{26}NOP$ + H 376.1830, found 376.1821.

(*S*)-1-[2′-(Diphenylphosphino)-6′-ethylphenyl]-2-(hydroxymethyl)pyrrolidine (4d): 78%; mp 82−85 °C; $[\alpha]^{25}_D$ +72.6 (*c* 1.06, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.24 (t, *J* = 7.5 Hz, 3H), 1.55−1.75 (m, 2H), 1.90−2.20 (m, 1H), 2.59 (q, *J* = 7.4 Hz, 2H), 2.77 (dd, *J* = 8.0 and 16.0 Hz, 1H), 3.30−3.53 (m, 2H), 3.75 (d, *J* = 12.0 Hz, 1H), 4.53 (t, *J* = 10.7 Hz, 1H), 6.71 (ddd, *J* = 1.4, 3.7 and 7.4 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.16−7.24 (m, 2H), 7.28−7.39 (m, 9H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 15.2, 23.6, 25.4, 28.0, 54.1, 62.7, 65.1, 126.7, 128.4, 128.4, 128.5, 129.1, 131.1, 131.7, 133.7 (d, J_{cp} = 19.0 Hz), 134.5 (d, J_{cp} = 20.6 Hz), 136.1 (d, J_{cp} = 3.8 Hz), 137.9 (d, J_{cp} = 8.2 Hz), 141.3 (d, J_{cp} = 7.2 Hz), 144.0, 148.7 (d, J_{cp} = 20.3 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ −17.0; EI-MS *m*/*z* (rel intensity) 389 (M^+, 9); HRMS (FAB-MS) *m*/*z* calcd for $C_{25}H_{28}NOP$ + H 390.1987, found 390.1964.

(*S*)-1-[2′-(Diphenylphosphino)-6′-methoxyphenyl]-2-(hydroxymethyl)pyrrolidine (4e): 83%; mp 119−120 °C; $[\alpha]^{25}_D$ +68.1 (*c* 1.04, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.47−1.76 (m, 2H), 1.85−2.03 (m, 3H), 2.80 (dd, *J* = 7.6 and 15.6 Hz, 1H), 3.39 (t, *J* = 10.5 Hz, 1H), 3.55−3.70 (m, 2H), 3.81 (s, 3H), 4.26 (t, *J* = 11.4 Hz, 1H), 6.38−6.45 (m, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 7.18−7.28 (m, 2H), 7.28−7.40 (m, 8H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 25.3, 27.8, 52.8, 55.0, 62.9, 63.7, 112.8, 124.6, 127.1 (d, J_{cp} = 2.1 Hz), 128.4, 128.4 (d, J_{cp} = 6.6 Hz,), 128.4 (d, J_{cp} = 5.1 Hz,), 133.8 (d, J_{cp} = 19.2 Hz,), 134.5 (d, J_{cp} = 20.9 Hz,), 136.3 (d, J_{cp} = 3.8 Hz), 137.6 (d, J_{cp} = 9.1 Hz), 140.3 (d, J_{cp} = 20.6 Hz), 141.9 (d, J_{cp} = 4.1 Hz), 158.2 (d, J_{cp} = 3.8 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ −17.2; FAB-MS *m*/*z* (rel intensity) 392 (M^+ + 1, 77); HRMS (FAB-MS) *m*/*z* calcd for $C_{24}H_{26}NO_2P$ + H 392.1779, found 392.1777.

(*S*)-1-[2′-(Diphenylphosphino)-6′-phenylphenyl]-2-(hydroxymethyl)pyrrolidine (4f): 71%; mp 65−68 °C; $[\alpha]^{25}_D$ +90.9 (*c* 1.11, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.19−1.51 (m, 1H), 1.51−1.70 (m, 2H), 1.70−1.85 (m, 1H), 2.70−3.08 (m, 3H), 3.16 (t, *J* = 11.3 Hz, 1H), 3.43 (d, *J* = 11.6 Hz, 1H), 3.96 (br-s, 1H), 6.95 (ddd, *J* = 1.8, 3.8 and 7.2 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.17−7.50 (m, 16H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 24.9, 27.6, 56.7, 56.8, 63.1, 125.5, 127.2, 128.1, 128.4, 128.5, 128.6, 129.0, 129.3, 133.6 (d, J_{cp} = 4.5 Hz), 133.9, 134.1, 134.3,

136.2 (d, J_{cp} = 5.9 Hz), 138.2 (d, J_{cp} = 8.3 Hz), 140.2, 141.4 (d, J_{cp} = 1.9 Hz), 142.9, 149.5 (d, J_{cp} = 22.7 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ −17.7; FAB-MS *m/z* (rel intensity) 438 (M^+ + 1, 85); HRMS (FAB-MS) *m/z* calcd for $C_{29}H_{28}NOP$ + H 438.1987, found 438.1980.

(*S*)-1-[2′-(Diphenylphosphino)-6′-methoxyphenyl]-2-(trimethylsilanoxymethyl)pyrrolidine (10a). To a solution of (*S*)-1-[2′-(diphenylphosphino)-6′-methoxyphenyl]-2-(hydroxymethyl)pyrrolidine **4e** (0.20 g, 0.5 mmol) in $CHCl_3$ (1.5 mL) was added *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (0.5 mL, 2.0 mmol) at room temperature. The mixture was stirred for 1 h under an argon atmosphere and concentrated under reduced pressure, and the residue was purified by silica gel chromatography (elution with *n*-hexane/EtOAc = 20/1): 95%; mp 105−108 °C; $[\alpha]^{25}_D$ +51.0 (*c* 1.02, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ −0.08 (s, 9H), 1.55−1.68 (m, 3H), 1.90−2.07 (m, 1H), 2.47 (br-s, 1H), 2.72 (dd, *J* = 7.3 and 15.4 Hz, 1H), 3.05 (t, *J* = 10.0 Hz, 1H), 3.29 (dd, *J* = 4.0 and 10.0 Hz, 1H), 3.48−3.60 (m, 1H), 3.73 (s, 3H), 6.31 (ddd, *J* = 1.3, 2.8 and 7.6 Hz, 1H), 6.80 (dd, *J* = 0.6 and 8.0 Hz, 1H), 6.99 (dt, *J* = 0.8 and 7.9 Hz, 1H), 7.12−7.30 (m, 10H); ^{13}C NMR (75 Mz, $CDCl_3$) δ −0.5, 24.4, 29.7, 52.7, 55.0, 63.8, 66.3 (d, J_{cp} = 5.0 Hz), 112.3, 124.9, 126.5, 128.2 (d, J_{cp} = 9.7 Hz), 128.2, 128.3 (d, J_{cp} = 7.0 Hz), 133.9 (d, J_{cp} = 20.6 Hz), 134.3 (d, J_{cp} = 21.1 Hz), 138.7, 138.9, 139.1, 141.2 (d, J_{cp} = 21.0 Hz), 142.1 (d, J_{cp} = 4.5 Hz), 157.9 (d, J_{cp} = 3.6 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ −15.7; EI-MS *m/z* (rel intensity) 463 (M^+, 7.5); HRMS (FAB-MS) *m/z* calcd for $C_{27}H_{34}NO_2PSi$ + H 464.2175, found 464.2139.

(*S*)-1-[2′-(Diphenylphosphino)-6′-methoxyphenyl]-2-[dimethyl(1″,1″-dimethylethyl)silanoxymethyl]pyrrolidine (10b). To a solution of (*S*)-1-[2′-(diphenylphosphino)-6′-methoxyphenyl]-2-(hydroxymethyl)pyrrolidine **4e** (0.12 g, 0.3 mmol) and triethylamine (0.1 mL, 0.7 mmol) in $CHCl_3$ (2 mL) was added the solution of *tert*-butyldimethylsilyl chloride (0.1 g, 0.66 mmol) in $CHCl_3$ (2 mL) at room temperature. The mixture was stirred for 18 h under an argon atmosphere and concentrated under reduced pressure, and the residue was purified by silica gel chromatography (elution with *n*-hexane/EtOAc = 15/1): 90%; mp 79−80 °C; $[\alpha]^{25}_D$ +52.5 (*c* 0.99, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ −0.07 (d, *J* = 4.8 Hz, 6H), 0.82 (s, 9H), 1.57−1.75 (m, 3H), 1.92−2.10 (m, 1H), 2.48 (br-s, 1H), 2.78 (dd, *J* = 7.8 and 15.2 Hz, 1H), 3.21 (t, *J* = 9.8 Hz, 1H), 3.44 (dd, *J* = 4.2 and 9.9 Hz, 1H), 3.52−3.65 (m, 1H), 3.80 (s, 3H). 6.37 (ddd, *J* = 1.3, 2.8 and 7.7 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 7.05 (dt, *J* = 0.8 and 7.9 Hz, 1H), 7.19−7.36 (m, 10H); ^{13}C NMR (75 Mz, $CDCl_3$) δ −5.3, −5.2, 18.3, 24.4, 26.0, 29.6, 52.6, 55.0, 64.0, 66.9 (d, J_{cp} = 5.3 Hz), 112.4, 124.9, 126.5, 128.2 (d, J_{cp} = 9.7 Hz), 128.2, 128.3 (d, J_{cp} = 9.6 Hz), 133.9 (d, J_{cp} = 20.5 Hz), 134.3 (d, J_{cp} = 21.2 Hz), 138.8 (d, J_{cp} = 13.3 Hz), 139.1 (d, J_{cp} = 15.0 Hz), 141.3 (d, J_{cp} = 21.9 Hz), 142.3 (d, J_{cp} = 4.5 Hz), 157.9 (d, J_{cp} = 3.4 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ −15.7; FAB-MS *m/z* (rel intensity) 504 (M^+ − 1, 30); HRMS (FAB-MS) *m/z* calcd for $C_{30}H_{40}N_2PSi$ + H 506.2644, found 506.2599.

(*S*)-1-[2′-(Diphenylphosphino)-6′-methoxyphenyl]-2-[(1″,1″-dimethylethyl)diphenylsilanoxymethyl]pyrrolidine (10c). To a solution of (*S*)-1-[2′-(diphenylphosphino)-6′-methoxyphenyl]-2-(hydroxymethyl)pyrrolidine **4e** (0.12 g, 0.3 mmol) and imidazole (0.04 g, 0.6 mmol) in DMF (1 mL) was added *tert*-butyldiphenylsilyl chloride (0.16 mL, 0.6 mmol) at room temperature. The mixture was stirred for 4.5 h under an argon atmosphere, diluted with ether, and quenched with water. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure, and the residue was purified by silica gel chromatography (elution with *n*-hexane/EtOAc = 40/1): 90%; $[\alpha]^{25}_D$ +35.8 (*c* 0.52, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 0.98 (s, 9H), 1.45−1.68 (m, 2H), 1.68−1.82 (m, 1H), 1.91−2.10 (m, 1H), 2.36 (br-s, 1H), 2.73 (dd, *J* = 7.7 and 15.3 Hz, 1H), 3.43 (dt, *J* = 0.6 and 10.6 Hz, 1H), 3.60−3.80 (m, 2H), 3.74 (s, 3H), 6.31 (ddd, *J* = 1.2, 2.7 and 7.64 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.95−7.12 (m, 3H), 7.12−7.18 (m, 3H), 7.18−7.42 (m, 11H), 7.50−7.63 (m, 4H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 19.2, 24.4, 26.9, 29.6, 52.4, 55.0, 64.1, 67.7, 112.3, 124.8, 126.4, 125.4 (d, J_{cp} = 3.9 Hz), 128.0 (d, J_{cp} = 13.6 Hz), 128.0, 128.2 (d, J_{cp} = 4.4 Hz), 129.2 (d, J_{cp} = 3.9 Hz), 133.7, 133.9, 134.2, 134.4 (d, J_{cp} = 5.8 Hz), 134.5, 135.5 (d, J_{cp} = 3.6 Hz), 138.7 (d, J_{cp} = 13.3 Hz), 139.1 (d, J_{cp} = 15.4 Hz), 142.3, 157.9; ^{31}P NMR (121 Mz, $CDCl_3$) δ −15.8; FAB-MS *m/z* (rel intensity) 630 (M^+ + 1, 33); HRMS (FAB-MS) *m/z* calcd for $C_{40}H_{44}NO_2PSi$ + H 630.2957, found 630.2985.

(*S*)-1-[2′-(Diphenylphosphino)-6′-methoxyphenyl]-2-[dimethyl(1″,1″,2″-trimethylpropyl)silanoxymethyl]pyrrolidine (10d). To a solution of (*S*)-1-[2′-(diphenylphosphino)-6′-methoxyphenyl]-2-(hydroxymethyl)pyrrolidine **4e** (0.12 g, 0.3 mmol) and triethylamine (0.1 mL, 0.7 mmol) in $CDCl_3$ (2 mL) was added dimethylthexylsilyl chloride (0.12 mL, 0.6 mmol) at room temperature. The mixture was stirred for 21 h under an argon atmosphere and concentrated under reduced pressure, and the residue was purified by silica gel chromatography (elution with *n*-hexane/EtOAc = 8/1): 46%; mp 66−68 °C; $[\alpha]^{25}_D$ +41.0 (*c* 0.10, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ −0.05 (d, *J* = 9.6 Hz, 6H), 0.76 (d, *J* = 1.8 Hz, 6H), 0.83 (d, *J* = 6.9 Hz, 6H), 1.45−1.75 (m, 4H), 1.91−2.08 (m, 1H), 2.50 (br-s, 1H), 2.77 (dd, *J* = 8.0 and 15.6 Hz, 1H), 3.18 (t, *J* = 9.8 Hz, 1H), 3.41 (dd, *J* = 4.2 and 9.9 Hz, 1H), 3.51−3.65 (m, 1H), 3.80 (s, 3H), 6.38 (ddd, *J* = 1.3, 2.8 and 7.6 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 7.05 (dt, *J* = 0.8 and 7.9 Hz, 1H), 7.20−7.35 (m, 10H); ^{13}C NMR (75 Mz, $CDCl_3$) δ −3.4, −3.3, 1.0, 18.5 (d, J_{cp} = 1.7 Hz), 20.4 (d, J_{cp} = 4.9 Hz), 24.4, 25.0, 29.6, 34.1, 52.7, 55.0, 64.0, 66.6 (d, J_{cp} = 5.5 Hz), 112.4, 124.9, 126.4, 128.1 (d, J_{cp} = 10.1 Hz), 128.2, 128.3 (d, J_{cp} = 6.5 Hz), 133.9 (d, J_{cp} = 20.5 Hz), 134.3 (d, J_{cp} = 21.3 Hz), 138.9 (d, J_{cp} = 13.4 Hz), 139.1 (d, J_{cp} = 15.2 Hz), 141.2, 141.5, 142.3 (d, J_{cp} = 4.5 Hz), 158.0 (d, J_{cp} = 3.5 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ −15.6; FAB-MS *m/z* (rel intensity) 534 (M^+ + 1, 32); HRMS (FAB-MS) *m/z* calcd for $C_{32}H_{44}NO_2PSi$ + H 534.2957, found 534.2933.

Preparation of Palladium Complex 11a. To a solution of $Pd(MeCN)_2Cl_2$ (0.013 g, 0.05 mmol) in $CHCl_3$ (0.5 mL) was added (*S*)-1-[2′-(diphenylphosphino)-6′-methoxyphenyl]-2-(hydroxymethyl)pyrrolidine **4e** (0.018 g, 0.05 mmol) at room temperature, The reaction mixture was stirred for 30 min under an atmosphere, filtered, and evaporated under reduced pressure, and purified by recrystallization from EtOH. The unit cell contains two independent molecules and one solvent molecule (EtOH): 45%; mp 153−156 °C (dec); $[\alpha]^{25}_D$ +223.1 (*c* 0.11, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 2.10−2.55 (m, 4H), 2.85−3.15 (m, 1H), 3.77 (dt, *J* = 2.8 and 10.8 Hz, 1H), 3.89−4.04 (m, 1H), 3.99 (s, 3H), 4.17 (dd, *J* = 4.9 and 10.9 Hz, 1H), 4.57 (dd, *J* = 7.7 and 7.8 Hz, 1H), 5.38 (dt, *J* = 8.7 and 11.0 Hz, 1H), 6.86 (ddd, *J* = 1.1, 7.8 and 9.6 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.32−7.64 (m, 7H), 7.70−7.84 (m, 2H), 7.84−8.00 (m, 2H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 26.3, 30.4, 56.0, 66.9, 69.2, 76.8, 116.4, 117.3, 124.9, 126.2, 127.1, 128.6, 128.8, 129.0, 129.5, 130.4, 130.6 (d, J_{cp} = 8.8 Hz), 131.5, 131.9 (d, J_{cp} = 2.9 Hz), 132.2 (d, J_{cp} = 3.1 Hz), 133.9, 134.0, 149.2 (d, J_{cp} = 18.7 Hz), 153.5 (d, J_{cp} = 17.7 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ 42.6; FAB-MS *m/z* (rel intensity) 534 ($[M - Cl]^+$ + 1, 100). Anal. Calcd for $C_{25}H_{23}Cl_2NO_{2.5}PPd$: C, 50.74; H, 4.94; N, 2.37. Found: C, 50.74; H, 4.94; N, 2.30.

Preparation of Palladium Complex 11b. To a solution of $Pd(MeCN)_2Cl_2$ (0.013 g, 0.05 mmol) in $CHCl_3$ (0.5 mL) was added (*S*)-1-[2′-(diphenylphosphino)-6′-methoxyphenyl]-2-(trimethylsilanoxymethyl)pyrrolidine **10a** (0.023 g, 0.05 mmol) at room temperature. The reaction mixture was stirred for 30 min under an argon atmosphere, filtered, and evaporated under reduced pressure: 44%; mp 155−158 °C (dec); $[\alpha]^{25}_D$ +176.9 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ −0.22 (s, 3H), 2.12−2.45 (m, 3H), 3.06−3.28 (m, 1H), 3.66−3.92 (m, 2H), 3.99 (s, 1H), 4.09 (dd, *J* = 5.6 and 10.0 Hz, 1H), 4.47 (dd, *J* = 7.4 and 10.0 Hz, 1H), 5.37 (dt, *J* = 8.6 and 11.2 Hz, 1H), 6.91 (ddd, *J* = 1.1, 7.9 and 9.4 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.30−7.44 (m, 3H), 7.44−7.53 (m, 3H), 7.53−7.64 (m, 3H), 7.96−8.10 (m, 2H); ^{13}C NMR (75 Mz, $CDCl_3$) δ −0.9, 26.1, 31.1, 56.0, 66.2, 68.5, 77.0, 116.4, 117.1, 124.9, 126.3, 127.1, 128.6

(d, J_{cp} = 12.5 Hz), 128.9 (d, J_{cp} = 11.9 Hz), 129.3, 130.2, 130.6 (d, J_{cp} = 8.6 Hz), 131.7 (d, J_{cp} = 3.1 Hz), 131.9, 132.2 (d, J_{cp} = 2.9 Hz), 132.6, 133.6 (d, J_{cp} = 11.2 Hz), 134.3 (d, J_{cp} = 10.8 Hz), 148.6 (d, J_{cp} = 18.9 Hz), 153.6 (d, J_{cp} = 17.5 Hz); ^{31}P NMR (121 Mz, $CDCl_3$) δ 42.4; FAB-MS *m*/*z* (rel intensity) 604 ([M − Cl]$^+$, 98); HRMS (FAB-MS) *m*/*z* calcd for $C_{27}H_{34}Cl_2NO_2PPdSi$ − Cl 604.0820, found 604.0841.

Gradually Analyzed ^{1}H NMR Spectra of 11a Involving Addition of BSA by Portion.[22] To a solution of $Pd(MeCN)_2Cl_2$ (0.026 g, 0.1 mmol) in $CDCl_3$ (0.6 mL) was added (*S*)-1-[2′-(diphenylphosphino)-6′-methoxyphenyl]-2-(hydroxymethyl)-pyrrolidine **4e** (0.036 g, 0.1 mmol) at room temperature under an argon atmosphere. After being stirred for 30 min, the reaction mixture was displaced to a NMR tube and elucidated by ^{1}H NMR (300 Mz) analyses. To this solution was added the solution of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) in $CDCl_3$ (0.063 mL, 0.025 mmol, 0.4 M). After being shaken, the solution was elucidated by ^{1}H NMR (300 Mz) analyses; this action was repeated 4 times.

General Procedure for Palladium-Catalyzed Allylic Alkylation. To a mixture of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.004 g, 0.01 mmol), chiral aminophosphine **4** or **10** (0.02 mmol), and lithium acetate (0.001 g, 0.01 mmol) in a solvent (1 mL) were added *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (0.37 mL, 1.5 mmol), racemic allylic ester **7** (0.5 mmol), and 1,3-dicarbonyl compound **8** (1.5 mmol) under an argon atmosphere. After being stirred the corresponding times, the reaction mixture was diluted with ether and quenched with saturated aqueous NH_4Cl. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography.

***(S)*-Methyl-2-carbomethoxy-3,5-diphenylpent-4-enoate (9a):**[17] (Table 5, entry 6) 46% yield; 98% ee; $[\alpha]^{25}_D$ −20.6 (*c* 1.01, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 3.52 (s, 3H), 3.70 (s, 3H), 3.96 (d, *J* = 11.0 Hz, 1H), 4.26 (dd, *J* = 8.5 and 11.0 Hz, 1H), 6.32 (dd, *J* = 8.5 and 15.8 Hz, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 7.21−7.33 (m, 10H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 49.2, 52.5, 52.7, 57.7, 126.4, 127.2, 127.6, 127.9, 128.5, 128.8, 129.1, 131.9, 136.8, 140.2, 167.8, 168.2; EI-MS *m*/*z* (rel intensity) 324 (M^+, 11).

Methyl-2-carbomethoxy-3,5-bis(4′-chlorophenyl)pent-4-enoate (9b):[6x,9n] 79% yield; 93% ee; mp 65−68 °C; $[\alpha]^{25}_D$ −2.8 (*c* 1.12, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 3.54 (s, 3H), 3.70 (s, 3H), 3.91 (d, *J* = 10.8 Hz, 1H), 4.25 (dd, *J* = 8.4 and 10.7 Hz, 1H), 6.27 (dd, *J* = 8.3 and 15.7 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 7.15−7.35 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 48.3, 52.5, 52.6, 57.3, 127.5, 128.6, 128.9, 129.1, 129.2, 131.0, 133.0, 133.3, 135.0, 138.4; EI-MS *m*/*z* (rel intensity) 392 (M^+, 12).

***(S)*-Ethyl-2-carboethoxy-3,5-diphenylpent-4-enoate (9c):**[19] 95% yield; 97% ee; $[\alpha]^{25}_D$ −17.2 (*c* 1.02, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.01 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 3.90−4.01 (m, 3H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.26 (dd, 8.4 and 11.0 Hz, 1H), 6.33 (dd, *J* = 8.4 and 15.8 Hz, 1H), 7.19−7.33 (m, 10H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 13.8, 14.1, 49.2, 57.8, 61.4, 61.6, 126.4, 127.1, 127.5, 128.0, 128.5, 128.7, 129.4, 131.7, 136.9, 140.3, 167.4, 167.9; EI-MS *m*/*z* (rel intensity) 352 (M^+, 29).

***(S)*-1′,1′-Dimethylethyl-2-carbo-1″,1″-dimethylethoxy-3,5-diphenylpent-4-enoate (9d):**[20] 95% yield; 80% ee; mp 63−64 °C; $[\alpha]^{25}_D$ −9.3 (*c* 1.01, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.22 (s, 9H), 1.47 (s, 9H), 3.73 (d, *J* = 11.0 Hz, 1H), 4.15 (dd, *J* = 8.1 and 10.9 Hz, 1H), 6.33 (dd, *J* = 8.1 and 15.8 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 7.18−7.32 (m, 10H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 27.6, 27.9, 49.0, 59.3, 81.5, 81.8, 126.3, 126.8, 127.3, 128.2, 128.4, 128.5, 130.1, 131.2, 137.1, 140.8, 166.7, 167.2; FAB-MS *m*/*z* (rel intensity) 409 (M^+ + 1, 4).

Phenylmethyl-2-carbophenylmethoxy-3,5-diphenylpent-4-enoate (9e):[6x] 90% yield; 95% ee; $[\alpha]^{25}_D$ −4.5 (*c* 1.07, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 4.05 (d, *J* = 10.9 Hz, 1H), 4.30 (dd, *J* = 8.2 and 10.9 Hz, 1H), 4.92 (dd, *J* = 12.3 and 14.2 Hz, 2H), 5.10 (dd, *J* = 12.2 and 14.4 Hz, 2H), 6.30 (dd, 8.1 and 15.7 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.97−7.08 (m, 2H), 7.11−7.33 (m, 18H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 49.2, 57.7, 67.1, 67.3, 126.4, 127.1, 127.5, 127.9, 128.0, 128.1, 128.3, 128.3, 128.4, 128.5, 128.7, 128.9, 131.8, 135.0, 135.1, 136.7, 140.0, 167.1, 167.5; FAB-MS *m*/*z* (rel intensity) 477 (M^+ + 1, 2).

***(R)*-Ethyl-2-carboethoxy-2-methyl-3,5-diphenylpent-4-enoate (9f):**[14a] 98% yield; 98% ee; $[\alpha]^{25}_D$ +41.1 (*c* 1.02, $CHCl_3$); ^{1}H NMR (300 Mz, $CDCl_3$) δ 1.16 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.47 (s, 3H), 4.07 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.29 (d, *J* = 8.9 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.71 (dd, *J* = 8.9 and 15.8 Hz, 1H), 7.18−7.34 (m, 10H); ^{13}C NMR (75 Mz, $CDCl_3$) δ 14.0, 14.0, 18.8, 53.7, 58.9, 61.4, 126.3, 127.1, 127.3, 128.2, 128.4, 128.9, 129.6, 132.6, 137.3, 139.5, 171.0, 171.2; EI-MS *m*/*z* (rel intensity) 366 (M^+, 10).

Acknowledgment. We thank Prof. Katsuyuki Ogura (Chiba University) for generously sharing their Bruker DPX-300 system and Prof. Kentaro Yamaguchi (Chemical Analysis Center, Chiba University) for performing the X-ray diffraction analysis of **11a**.

Supporting Information Available: ORTEP diagrams of **4e**, **10a**, and **11a**; gradually analyzed ^{1}H NMR spectra of **11a** involving addition of BSA by portion; copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra of **4a**, **4c**−**f**, **5d**, **6a**, **6c**−**d**, **10a**−**d**, **11a**, and **11b**; copies of H−H and C−H COSY NMR spectra of **4e**, **11a**, and **11b**; copies of ^{1}H and ^{31}P VT NMR spectra of **4e**; copies of ^{1}H and ^{13}C NMR spectra of **9a**−**f**; copies of HPLC charts of **9a-f**; three X-ray crystallographic files in CIF format; and ORTEP diagrams for **4e**, **10a**, and **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049469T