JOC Article

Role of Planar Chirality of *S,N*- and *P,N*-Ferrocene Ligands in Palladium-Catalyzed Allylic Substitutions

Shu-Li You,† Xue-Long Hou,*,† Li-Xin Dai,*,† Yi-Hua Yu,‡ and Wei Xia‡

State Key Laboratory of Organometallic Chemistry, and Laboratory of Analytical Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

xlhou@pub.sioc.ac.cn; dailx@pub.sioc.ac.cn

Received November 29, 2001

Palladium-catalyzed asymmetric allylic substitutions using thioether and phosphino derivatives of ferrocenyloxazoline as ligands have been investigated with a focus on studying the role of planar chirality. In allylic alkylation, up to 98% ee and 95% ee were achieved with *S,N*- and *P,N*-ligands, respectively. In allylic amination, 97% ee was realized with *P,N*-ligands in the presence of TBAF. Several palladium allylic complexes were characterized by X-ray diffraction and/or solution NMR. Thioether derivatives of ferrocenyloxazolines with only planar chirality showed lower enantioselectivity in the allylic alkylation except **5c** because of the formation of a new chirality on sulfur atom during the coordination of sulfur with palladium. On the other hand, in the planar chiral *P,N*-ligands without central chirality, (*Sp*)-**11a**−**c** there was no such disturbance and comparatively higher enantioselectivity in both palladium-catalyzed allylic alkylation and amination was provided.

Introduction

Chirotechnology is one of the most interesting and challenging technologies of recent years.[1] Great efforts have been made toward the establishment of asymmetric catalytic industrial processes. Therein, design and synthesis of chiral ligands are always the key point.[2] Ferrocene-containing[3] ligands are among the most interesting ligands because of their stability, easy introduction of planar chirality,[4−9] inherent special electronic and stereoproperties of the ferrocene skeleton. It is noteworthy that most ferrocene ligands contain planar chirality and/or central chirality (even axial chirality[10]). Synthesis and application of planar chiral ferrocene ligands culminated recently in two industrial asymmetric hydrogenation processes.[11] Although many excellent results were derived from planar chiral ferrocene ligands,[12] the understanding of the role of planar chirality is overlooked. Some examples showed that the planar chirality had significant effect on the enantioselectivity,[13] while in other examples it was not so apparent.[14] Kumada and Hayashi's results showed that the planar chirality was a decisive factor for exerting control over enantiomer excess and absolute configuration in the cross-coupling reaction catalyzed by (*R*,*Sp*)-PPFA, (*R*,*Rp*)-PPFA, and (*Sp*)-PPFA **1** with only planar chirality, respectively.[15] Bolm et al. found that on removal of the central chirality in hydroxyoxazolinyl ligand **2** the enantioselectivity in the diethylzinc addition reaction dropped significantly.[16]

† State Key Laboratory of Organometallic Chemistry.
‡ Laboratory of Analytical Chemistry.

(1) For some reviews: (a) Brunner, H. In *Topics in stereochemistry*; Eliel, E., Wilen, S. H., Eds.; Wiley: New York, 1988; Vol. 18, p 129. (b) Noyori, R.; Kitamura, M. In *Modern Synthetic Method*; Scheffold, R., Ed.; Springer: Berlin, 1989; p 115. (c) Ojima, I., Ed. *Catalytic Asymmetric Synthesis*; VCH: New York, 1993. (d) Seyden-Penne, J. *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*; Wiley: New York, 1995.

(2) Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.*Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999.

(3) Reviews: (a) Hayashi, T., Togni, A., Eds. *Ferrocenes*; VCH: Weinheim, 1995. (b) Schlögl, K. *Top. Stereochem*. **1967**, *1*, 39. (c) Richards, C. J.; Locke, A. J. *Tetrahedron*: *Asymmetry* **1998**, *9*, 2377. (d) Togni, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1475.

(4) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389.

(5) (a) Sammakia, T.; Latham, H. A.; Schaad, D. R. *J. Org. Chem*. **1990**, *55*, 1649. (b) Richards, C. J.; Damalidia, T.; Habbis, D. E.; Hursthouse, M. B. *Synlett* **1995**, 74. (c) Nishibayashi, Y.; Uemura, S. *Synlett* **1995**, 79.

(6) Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 5835.

(7) Enders, D.; Peters, R.; Lochtman, R.; Runsink, J. *Synlett* **1997**, 1462.

(8) Tsukazaki, M.; Tinkl, M.; Roglans, A.; Chapell, B. J.; Taylor, N. J.; Snieckus, V. *J. Am. Chem. Soc.* **1996**, *118*, 685.

(9) (a) Bolm, C.; Kesselgruber, M.; Muñiz-Fernández, K.; Raabe, G. *Organometallics*, **2000**, *19*, 1648. (b) Ireland, T.; Almena Perea, J.; Knochel, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1457.

(10) You, S.-L.; Zhu, X.-Z.; Luo, Y.-M.; Hou, X.-L.; Dai, L.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7471.

(11) (a) Blaser, H.-V.; Spindler, F. *Chimia* **1997**, *51*, 297; (b) Imwinkelried, R. *Chimia* **1997**, *51*, 300.

(12) Selected recent papers on chiral ferrocene ligands: (a) Zhou, X.-T.; Lin, Y.-R.; Dai, L.-X. *Tetrahedron*: *Asymmetry* **1999**, *10*, 855. (b) Deng, W.-P.; Hou, X.-L.; Dai, L.-X. *Tetrahedron*: *Asymmetry* **1999**, *10*, 4689. (c) Manoury, E.; Fossey, J. S.; Aït-Haddou, H.; Daran, J.-C.; Balavoine, G. G. A. *Organometallics* **2000**, *19*, 3736. (d) Bolm, C.; Hermanns, N.; Hildebrand, J. P.; Muñiz-Fernández, K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3465. (e) Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1999**, *18*, 2291.

(13) (a) Stangeland, E. L.; Sammakia, T. *Tetrahedron* **1997**, *53*, 16503. (b) Richards, C. J.; Hibbs, D. E.; Hurthouse, M. B. *Tetrahedron Lett*. **1995**, *36*, 3745. (c) Kuwano, R.; Uemura, T.; Saitoh, M.; Ito, Y. *Tetrahedron Lett*. **1999**, *40*, 1327. (d) Donde, Y.; Overman, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 2933. (e) Zhang, W.; Shimanuki, T.; Kida, T.; Nakatusuji, Y.; Ikeda, I. *J. Org. Chem*. **1999**, *64*, 6247. (f) Shintani, R.; Lo, M. M.-L.; Fu, G. C. *Org. Lett*. **2000**, *2*, 3695.

(14) (a) Pastor, S. D.; Togni, A. *J. Am. Chem. Soc.* **1989**, *111*, 2333. (b) Togni, A.; Pastor, S. D. *J. Org. Chem*. **1990**, *55*, 1649.

(15) (a) Hayashi, T.; Tajika, M.; Tamao, K.; Kumada, M. *J. Am. Chem. Soc.* **1976**, *98*, 3718. (b) Hayashi, T.; Konoshi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180.

(16) (a) Bolm, C.; Muñiz-Fernández, K.; Seger, A.; Raabe, G.; Gunther, K. *J. Org. Chem*. **1998**, *63*, 7860. (b) Bolm, C.; Muñiz-Fernández, K.; Hildebrand, J. P. *Org. Lett*. **1999**, *1*, 991. (c) Muñiz-Fernández, K.; Bolm, C. *Chem. Eur. J*. **2000**, *6*, 2309.

10.1021/jo016330z CCC: $22.00
Published on Web 05/21/2002

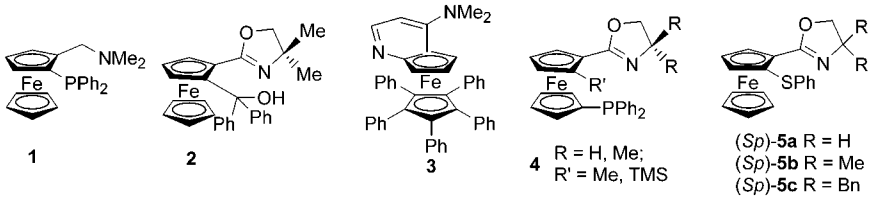


FIGURE 1. Structures of ligands **1**−**5**.

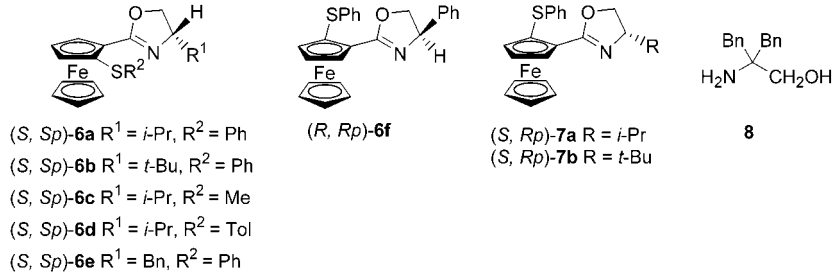


FIGURE 2. Structures of ligands **6**−**8**.

Recently, the work of Fu and co-workers on the single planar chiral ferrocene ligand **3** revealed that it is a highly efficient catalyst for asymmetric reactions.[17] For this reason, there is an urgent need to study the role of planar chirality in ferrocene systems for the purpose of new, efficient ligand design. In the course of studying the role of planar chirality,[18] we found that planar chirality dominated the enantiomer excess and absolute configuration in the palladium-catalyzed Heck reaction and allylic substitution reaction catalyzed by planar chiral 1,1′-*P*,*N*-2′-substituted ferrocene ligands **4**.[19,20] We also found that *S*,*N*-ligands **5a** and **5b** with only planar chirality showed very low enantioselectivity while the ligands with central and planar chiralities **6** gave the product with high ee (Figure 1).[21] Further studies showed that a new chiral center on the sulfur atom was formed during the coordination of **5a** and **5b** with metal, and two diastereomeric complexes were formed so that they gave the lower enantioselectivity. To reveal the role of planar chirality in 1,2-disubstituted ferrocenes and to avoid the formation of a new chiral center on a coordinated atom, *P*,*N*-ligands with or without central chirality were synthesized and tested. In this paper, we report the results of these studies in detail. With the aid of X-ray crystallographic and NMR studies, the role of planar chirality in 1, 2-disubstituted ferrocene ligands is discussed.

Results and Discussions

Synthesis of Ligands. Ligands (*S*,*Sp*)-**6a**−**e** were prepared in high diastereoselectivity from ferrocene and chiral amino alcohols by using known procedures.[21,22] For the purpose of studying the relative asymmetric inductive effect between planar chirality and central chirality, the ligands (*S*,*Rp*)-**7a** and (*S*,*Rp*)-**7b** with only a different configuration of planar chirality compared to (*S*,*Sp*)-**6a** and (*S*,*Sp*)-**6b** were also prepared. In addition, ligand (*R*,*Rp*)-**6f** with phenyl as substituent on the oxazoline ring was also prepared with high diastereoselectivity as a phenyl group on the oxazoline showed good stereocontrol in the asymmetric catalysis sometimes.[23] However, two kinds of chirality in the above two pairs of ligands, **6a** vs **7a** and **6b** vs **7b**, most likely may be matched or mismatched in reactions. To show the role of planar chirality more clearly, ligands (*Sp*)-**5a**, **-5b**, and **-5c** having a similar backbone but only planar chirality were synthesized. Ligand (*Sp*)-**5a** was synthesized in good yields from ligand (*S*,*Sp*)-**6a** and ethylamino alcohol in our previous paper,[21] and ligands (*Sp*)-**5b** and (*Sp*)-**5c** were synthesized by using corresponding amino alcohol and similar method. Geminal α-disubstituted **8** was synthesized according to the literature procedure (Figure 2).[24]

Also, ligands (*S*,*Sp*)-**9**, (*S*,*Rp*)-**10**, and (*Sp*)-**11a**−**c** were chosen to study the role of planar chirality in palladium-catalyzed allylic substitution reaction with *P*,*N*-ligands. Ligand (*S*,*Sp*)-**9** and (*S*,*Rp*)-**10** were prepared according

(17) (a) Ruble, J. C.; Latham, H. A.; Fu, G. C. *J. Am. Chem. Soc*, **1997**, *119*, 1492. (b) Fu, G. C. *Acc. Chem. Res.* **2000**, *33*, 412.

(18) (a) You, S.-L.; Hou, X.-L.; Dai, L.-X.; Cao, B.-X. J. Sun, *Chem. Commun*. **2000,** 1933. (b) You, S.-L.; Hou, X.-L.; Dai, L.-X.; Zhu, X.-Z. *Org. Lett.* **2001**, *3*, 149. (c) You, S.-L.; Hou, X.-L.; Dai, L.-X. *Tetrahedron*: *Asymmetry* **2000**, *11*, 1495. (d) Du, X.-D.; Dai, L.-X.; Hou, X.-L.; Xia, L.-J.; Tang, M.-H. *Chin. J. Chem*. **1998**, *16*, 90. (e) Dai, L.-X.; Hou, X.-L.; Deng, W.-P.; You, S.-L.; Zhou, Y.-G. *Pure Appl. Chem*. **1999**, *71*, 1401. (f) Zhou, X.-T.; Lin, Y.-R.; Dai, L.-X.; Sun, J.; Xia, L.-J.; Tang, M.-H. *J. Org. Chem*. **1999**, *64*, 1331. (g) You, S.-L.; Zhu, X.-Z.; Hou, X.-L.; Dai, L.-X. *Hua Xue Xue Bao* **2001**, *59*, 1667.

(19) (a) Deng, W.-P.; Hou, X.-L.; Dai, L.-X.; Yu, Y.-H.; Xia, W. *Chem. Commun*. **2000**, 285. (b) Deng, W.-P.; Hou, X.-L.; Dai, L.-X.; Dong, X.-W. *Chem. Commun*. **2000**, 1483. (c) Deng, W.-P.; You, Shu-Li; Hou, X.-L.; Dai, L.-X.; Yu, Y.-H.; Xia, W. *J. Am. Chem. Soc*. **2001**, *123*, 6518.

(20) For reviews of asymmetric allylic substitution reactions: (a) Consiglio, G.; Waymouth, R. M. *Chem. Rev*. **1989**, *89*, 257. (b) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron*: *Asymmetry* **1992**, *3*, 1089. (c) Trost, B. M.; Van Vranken, D. L. *Chem. Rev*. **1996**, *96*, 395. (d) Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH Publishers: New York, 1993. (e) Pfaltz, A.; Lautens, M. in ref 2, Vol. 2, p 833.

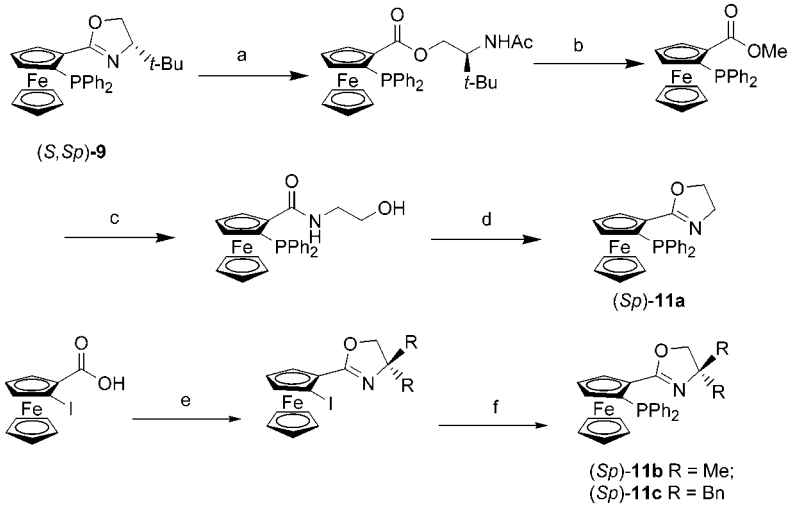
(21) You, S.-L.; Zhou, Y.-G.; Hou, X.-L.; Dai, L.-X. *Chem. Commun*. **1998**, 2765.

(22) Ahn, K. H.; Cho, C.-W.; Beak, H.-H.; Park, J.; Lee, S. *J. Org. Chem*. **1996,** *61*, 4937.

(23) (a) Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc*. **1993**, *115*, 5328. (b) Kanemasa, S.; Oderaotoshi, Y.; Tanaka, J.; Wada, E. *J. Am. Chem. Soc*. **1998**, *120*, 12355. (c) Andrus, M. B.; Asgari, D.; Sclafani, J. A. *J. Org. Chem*. **1997**, *62*, 9365.

(24) O'Donnell, M. J.; Polt, R. L. *J. Org. Chem*. **1982**, *47*, 2663.

SCHEME 1[a]



[a] Condition and reagent: (a) (1) TFA, H_2O, Na_2SO_4, THF; (2) Ac_2O, Pyr, DCM 63%; (b) MeONa, THF/MeOH, 55 °C 94%; (c) Na, $NH_2(CH_2)_2OH$, 100 °C 92%; (d) Et_3N, MsCl, DCM 85%; (e) (1) $(ClCO)_2$, $NH_2CR_2CH_2OH$, Et_3N, DCM; (2) PPh_3, CCl_4, Et_3N, CH_3CN; (f) (1) *n*-BuLi; (2) Ph_2PCl.

TABLE 1. Asymmetric Palladium-Catalyzed Allylic Alkylations with Planar Chiral *S,N*-Ligands[a]

entry	ligand	time (h)	yield[b] (%)	ee[c] (%)	configuration[d]
1	(*S,Sp*)-**6a**	3	98	89.4	*S*
2	(*S,Sp*)-**6b**	10	98	98.0	*S*
3	(*S,Sp*)-**6c**	3	98	81.9	*S*
4	(*S,Sp*)-**6d**	3	98	89.9	*S*
5	(*S,Sp*)-**6e**	5	98	87.8	*S*
6	(*R,Rp*)-**6f**	1	98	89.1	*R*
7	(*S,Rp*)-**7a**	3	98	90.4	*S*
8	(*S,Rp*)-**7b**	1	98	89.8	*S*
9	(*Sp*)-**5a**	48	90	8.3	*R*
10	(*Sp*)-**5b**	48	92	12.5	*R*
11	(*Sp*)-**5c**	5	98	71.8	*S*

[a] See the Experimental Section. [b] Isolated yield based on **12**. [c] Determined by chiral HPLC (Chiracel OD column). [d] Absolute configuration of product was assigned through comparison of the sign of specific rotations with the literature data.[27]

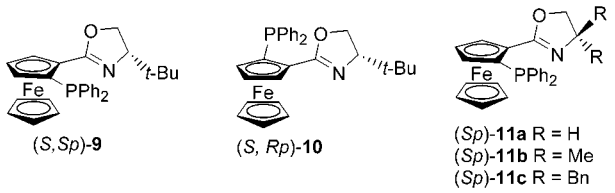
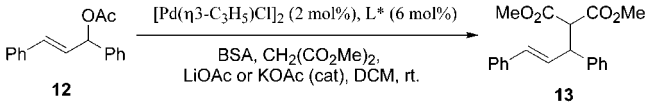


FIGURE 3. Structures of ligands **9**−**11**.

to the reported methods.[22] (*Sp*)-**11a**−**c** were also synthesized from (*S,Sp*)-**9** or (*Sp*)-2-iodine-1-(4,4-dibenzyloxazolinyl)ferrocene (Scheme 1, Figure 3).

Asymmetric Alkylation. The allylic substitutions of *rac*-1,3-diphenylprop-2-enyl acetate with dimethyl malonate or benzylamine as nucleophile were used in this paper as the model reaction because the mechanism of these reactions is fairly understood and the efficiency of the ligands can be quickly deciphered.[25] Lithium acetate, instead of potassium acetate, was used as the additive in palladium-catalyzed allylic alkylation with *S,N*-ligands,[26] which accelerated the reaction and improved the enantioselectivity a little.[21] Using the above conditions, the palladium-catalyzed asymmetric allylic alkylation with *S,N*-ligands was carried out (eq 1), and the



results are summarized in Table 1. The sense of enantio induction was determined by HPLC and specific rotation of the reaction product, methyl 2-carbomethoxy-3,5-diphenylpent-4-enoate.[27] Ligands **6b**−**f** show high catalytic efficiency and high to excellent enantioselectivities (81.9−98.0% ee). Ligand **6d** with a *p*-methylphenylthio group provides almost equal enantioselectivity given by ligand **6a** with a phenylthio group (entry 4 vs entry 1 in Table 1). It seems that ligands with an arylthio group give higher enantioselectivity than ligand **6c** with a methylthio group does (entry 3 in Table 1). The results also indicate that the ligand with R^1 = *t*-Bu (entry 2 in Table 1) is superior to R^1 = *i*-Pr (entry 1 in Table 1), Bn (entry 5 in Table 1), or Ph (entry 6 in Table 1).

To disclose the role of planar chirality, ligands (*S,Rp*)-**7a**, (*S,Rp*)-**7b**, and (*Sp*)-**5a**−**c** are tested in this reaction under the above conditions. We noticed that products are always in the *S* configuration, no matter if the planar chirality of the ligand is *S* (**6a**,**b**) or *R* (**7a**,**b**). That is, the absolute configuration of the product in this reaction

(25) (a) Allen, J. V.; Coote, S. J.; Dawson, G. J.; Frost, G. C.; Williams, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2065. (b) Matt, P. V.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T.; Helmchen, G. *Tetrahedron*: *Asymmetry* **1994**, *5*, 573.

(26) Selected S,N-ligands in Pd-catalyzed allylic substitutions: (a) Wu, X.-W.; Hou, X.-L.; Dai, L.-X.; Cao, B.-X. J. Sun, *Chem. Commun.* **2000**, 1195. (b) Dawson, G. J.; Frost, C. G.; Martin, C. J.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1993**, *34*, 7793. (c) Allen, J. V.; Bower, J. F.; Williams, J. M. J. *Tetrahedron*: *Asymmetry* **1994**, *5*, 1895. (d) Koning, B.; Meetsma, A.; Kellogg, R. M. *J. Org. Chem.* **1998**, *63*, 5533. (e) Adams, H.; Anderson, J. C.; Cubbon, R.; James, D. S.; Mathias, J. P. *J. Org. Chem.* **1999**, *64*, 8256. (f) Imai, Y.; Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Synlett* **1999**, 1319.

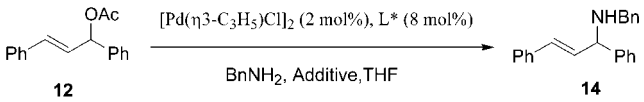
(27) Wimmer, P.; Widhalm, M. *Tetrahedron*: *Asymmetry* **1995**, *6*, 657.

TABLE 2. Asymmetric Palladium-Catalyzed Allylic Alkylations with Planar Chiral *P,N*-Ligands[a]

entry	ligand	time (h)	yield[b] (%)	ee (%)[c]	configuration[d]
1	(*S,Sp*)-**9**	12	96	92.3	*S*
2	(*S,Rp*)-**10**	48	94	94.6	*S*
3	(*Sp*)-**11a**	3	98	76.6	*R*
4	(*Sp*)-**11b**	48	90	54.0	*R*
5	(*Sp*)-**11c**	4	96	5.9	*S*

[a] See the Experimental Section. [b] Isolated yield based on **12**. [c] Determined by chiral HPLC (Chiracel OD column). [d] Absolute configuration of product was assigned through comparison of the sign of specific rotations with the literature data.[27]

is governed by the central chirality. This conclusion is further supported as follows: (1) when the central chirality of ligand **6f** is *R*, the configuration of the product is also changed to *R* (entry 6 in Table 1); (2) the very low ee values from ligands **5a**,**b** with only planar chirality (entries 9 and 10, 8.3% and 12.5%, respectively) also indicate the smaller influence of planar chirality on asymmetric induction. Based on these results, we might conclude that the planar chirality has little effect on the enantioselectivity in our preliminary communication.[21] On further comparison of the results in entries 2 and 8 of Table 1, (*S,Sp*)-**6b** is apparently a matched one and (*S,Rp*)-**7b** is not. Thus, the effect of planar chirality should not be overlooked. However, a jump of ee values was observed by using ligand (*Sp*)-**5c** with two benzyl groups as substituent (71.8% ee in entry 11, Table 1). In addition, the absolute configuration was *S*, while that for ligands (*Sp*)-**5a** and (*Sp*)-**5b** was *R* ,although three ligands have the same *S* configuration of planar chirality. On careful examination of the structure of the ligands, we reasoned that a new chirality on the sulfur atom was produced when ligands **5** coordinated with palladium, which disturbed the asymmetric induction. In the ligands with central chirality, a substituent on the oxazoline ring would exert a definite asymmetric induction during the coordination and direct the phenyl group on sulfur in the opposite position due to the steric effect. In the ligands without central chirality, there will be almost no diastereoselectivity in the coordinating process and the chirality on the S-atom will be easily racemized, causing the very low ee value of the product. To exclude this disturbance, the diphenylphosphinoferrocenyloxazolines were chosen as ligands and the same reaction was carried out (eq 2). The reaction conditions were almost the same



as above, but KOAc was used as the additive and 8 mol % ligand was used. The results are summarized in Table 2. Ligand (*S,Rp*)-**10** was found to be better than (*S,Sp*)-**9** and gave a higher enantioselectivity (94.6% ee in entry 2 vs 92.3% ee in entry 1, Table 2).[28] The product obtained with both ligands is in the *S* configuration despite their different planar chirality. It was noteworthy that the ligands (*Sp*)-**11a**,**b** with only planar chirality provided good ee, which is far better than that by using the corresponding *S,N*-ligands (*Sp*)-**5a** and **5b** (entries 3 and 4, Table 2 vs entries 9 and 10, Table 1). For these ligands, it seemed that enantioselectivity was higher when the groups on the oxazolines became less steric (entries 3 and 4 in Table 2). It was interesting that an unexpected low ee value was observed by using ligand (*Sp*)-**11c** with two benzyl groups (entry 5 in Table 2). (*Sp*)-**11a** gave the product with highest ee up to 76.6% in the *R* configuration, which indicated also that (*S,Rp*)-**10** should have one pair of matched chiralities.

TABLE 3. Asymmetric Palladium-Catalyzed Allylic Aminations with Planar Chiral *P,N*-ligands[a]

entry	ligand	*T* (°C)	TBAF (equiv)	yield[b] (%)	ee[c] (%)	configuration[d]
1	(*S,Sp*)-**9**	40	none	95	47.7	*R*
2	(*S,Rp*)-**10**	40	none	67	86.1	*R*
3	(*S,Rp*)-**10**	40	2	96	95.8	*R*
4	(*S,Rp*)-**10**	50	2	96	97.2	*R*
5	(*S,Rp*)-**10**	50	4	90	96.6	*R*
6	(*S,Sp*)-**9**	50	2	83	91.3	*R*
7	(*Sp*)-**11a**	50	2	96	73.7	*S*
8	(*Sp*)-**11b**	50	2	95	60.3	*S*
9	(*Sp*)-**11c**	50	2	71	52.7	*S*

[a] See the Experimental Section. [b] Isolated yield based on **12**. [c] Determined by chiral HPLC (Chiracel OD column). [d] Absolute configuration of product was assigned through comparison of the sign of specific rotations with the literature data.[30]

Planar chiral *P,N*-ligands were also subjected in asymmetric palladium-catalyzed allylic amination reaction[29] (eq 2), and the results are listed in Table 3.

The allylic amination reaction was performed at 40 °C in THF. The enantioselectivity of product obtained from (*S,Rp*)-**10** was higher than that from (*S,Sp*)-**9** (entry 1 vs 2, Table 3). The reaction was completed very quickly, and the enantioselectivity was improved greatly when 2 equiv of TBAF was added as additive (entry 3 vs 2, Table 3).[31] In addition, the enantioselectivity was improved by increasing the temperature to 50 °C but affected little by increasing the amount of TBAF to 4 equiv (entries 4 and 5 in Table 3). At the same time, product with higher enantioselectivity could be achieved also from (*S,Sp*)-**9** when 2 equiv of TBAF was added (entry 6 vs 1, Table 3). Ligands with only planar chirality showed good enantioselectivity in the optimized allylic amination similar to that in the allylic alkylation reaction. The same conclusion as for the allylic alkylation reaction could be drawn that enantioselectivity was higher when the groups on the oxazolines was smaller (entries 7−9 in Table 3). (*Sp*)-**11a** gave the product with highest 73.7% ee in *S* configuration, which indicated also that (*S,Rp*)-**10** should contain one pair of matched chiralities. For *P,N*-ligands in these two reactions, it is evident that the planar chirality plays an important role in asymmetric induction and the matching of central and planar chiralities may offer excellent enantioselectivity. The very low ee values for **5a** and **5b** are a special case due to the formation of a new chiral center on S atom.

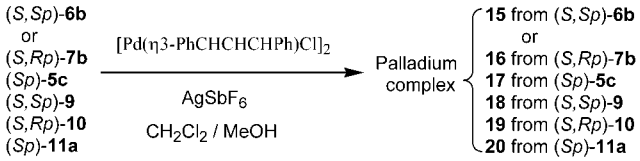
(28) Ahn, K. H.; Cho, C.-W.; Park, J.; Lee,S. *Tetrahedron*: *Asymmetry* **1997**, *8*, 1179.

(29) Malone, Y. M.; Guiry, P. J. *J. Organomet. Chem.* **2000**, *603*, 110.

(30) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301.

(31) Burckhardt, U.; Baumann, M.; Togni,A. *Tetrahedron*: *Asymmetry* **1997**, *8*, 155.

X-ray Crystallographic Study of the Intermediate Complex: *S,N*-Ligands and *P,N*-Ligands. To investigate the relative inductive effect of planar chirality and central chirality and the role of planar chirality through studying the mechanism in this reaction,[32,33] palladium allylic complexes **15**−**20** were prepared (eq 3).



Crystals of complexes **15**, **17**, **19**, and **20** were obtained by slow evaporation from the proper organic solvents. The crystals were stable for several months in air without any additional precautions. The crystal structure of **15** was found to be the allylic intermediate **15A** with M-type (endo-syn-syn). (Nomenclature note: the endo-isomer is defined as the isomer in which the central allyl proton points to the ferrocene core.) The phenyl group on the sulfur is trans to *tert*-butyl group on the oxazoline ring due to the steric effect. In line with the structural evidence for nitrogen−phosphorus or nitrogen−sulfur ligands, we found that the two palladium-terminal allylic carbon bond distances are slightly different from each other, with the bond trans to sulfur longer than the bond trans to nitrogen. The actual bond distances for Pd−C30 and Pd−C32 are 2.21 and 2.15 Å, respectively.

The crystal of complex **17** was given as a dark red crystal containing one EtOAc molecule from hexane/CH_2Cl_2/EtOAc. Consistent with **15**, the crystal structure of **17** was found to be the M type (endo-syn-syn) allylic intermediate **17A**. In addition, the bond trans to sulfur is longer than that trans to nitrogen in the crystal structure; the actual bond distances are 2.26 and 2.18 Å, respectively. The data show that the sulfur atom is a better π-acceptor than the oxazoline nitrogen atom. The phenylthio group was also trans to the nonsubstituted Cp ring, and the most interesting thing is that the two benzyl groups mount across the 1,3-diphenyl allylic moiety. The plane of phenyl in one of the benzyl groups was almost perpendicular with the plane of the allylic moiety (the angle is 86°). The plane of allylic moiety was almost parallel with the skeleton of the ferrocene (the angle between plane C(40)−C(41)−C(42) and Cp ring is 70°). The two geminal benzyl groups on the oxazoline ring have a significant effect on the conformation of the allylic intermediate **17A**. This is the reason for the rather high ee value of allylic alkylation reaction by using ligand **5c**, even there is still a new chiral center on the S atom (entry 11 in Table 1).

The crystal structure of **19** was found to be **19B** (exo-syn-syn). That of **20** was found to be exo-syn-syn also. Comparing these two complexes, the 94.5° angle of P−Pd−N in **20** is larger than that in **19**; in addition to that, the bonds of Pd−P and Pd−N in **20** were shorter than that in **19**. From these data, we can see that the π-allyl moiety is closer to the ferrocene backbone in **20** than that in **19**.

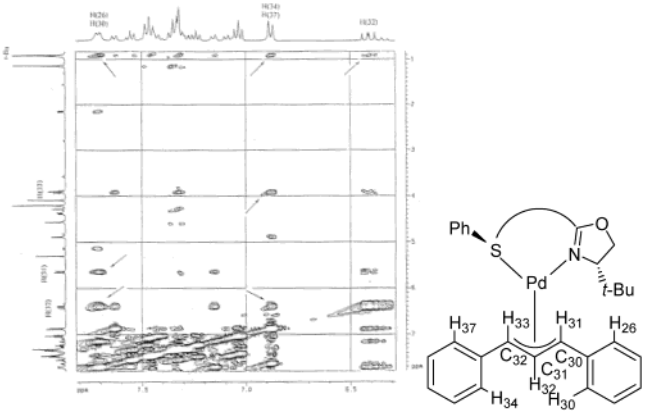


FIGURE 4. Sections of the NOESY spectrum of complex **15** showing the cross-peaks due to the interactions of the *t*-Bu protons with H32, with H26 (or 30), and with H34 (or 37), respectively. The arrows show the NOEs (400 MHz, mixing time 0.7 s, 273 K, CD_2Cl_2). Though the NOE between the *t*-Bu protons and H32 is weak, it can be easily found when the mixing time changes to 1.0 or 1.3 s (see also the text).

NMR Study of the Intermediate Complexes. The ^{1}HNMR spectrum of the complex **15** at the same temperature of the reaction (25 °C) in CD_2Cl_2 showed that there was a mixture of two conformers in a ratio of 3.1:1 and their conformations were assigned by a combination of COSY, ^{13}C−^{1}H correlation, and two-dimensional NOE experiments. The ^{1}HNMR manifested only the syn,syn arrangement of the allylic unit, as evidenced by the coupling constants between the allyl protons H(31), H(32), and H(33) of ∼12 Hz and no apparent NOE between H(31) [or H(33)] and H(32) in the 2D NOESY spectrum. The major structure was deduced to be in the M conformation in solution, which is the same as the solid-state conformation of **15A** (Figure 4). To confirm this conclusion, two important evidences were provided in the relevant NOE experiment. First, we found that H(32) showed NOE relevant with the protons of *tert*-butyl in the major structure. Though the NOE was weak, it was distinct in the 2D NOESY spectra with different exchange times such as 0.7, 1.0, and 1.3 s (Figure 4). The shortest distance between them is 3.10 Å in the X-ray structure, which was responsible to the weak NOE here.[34] Second, the doublet peak at 7.63 ppm was deduced to be H(26) and H(30) in the major component, for it had NOE with H(31) and H(32). Similarly, the doublet peak at 6.81 ppm was deduced to be H(34) and H(37) in the major intermediate, for it had NOE with H(32) and H(33). At the same time, both of them had NOE with a *tert*-butyl group in the major component, which indicated that the major intermediate was M type (endo-syn-syn).

From the results listed in Table 1, we found that **6b** showed a better stereocontrol over that of **7b**, which has the same central chirality but opposite planar chirality. Palladium allylic complex **16** was investigated in order to give a proper explanation. The solution NMR of **16** was

(32) (a) Steinhagen, H.; Reggelin, M.; Helmchen,G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2108. (b) Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelin, M.; Huttner, G.; Walter, O.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523. (c) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. (d) Selvakumar, K.; Valentini, M.; Wörle, M.; Pregosin, P. S.; Albinati, A. *Organometallics* **1999**, *18*, 1207.

(33) Boog-wick, K.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1998**, *17*, 3254.

(34) Pregosin, P. S.; Valentini, M. *Enantiomer* **1999**, *4*, 529.

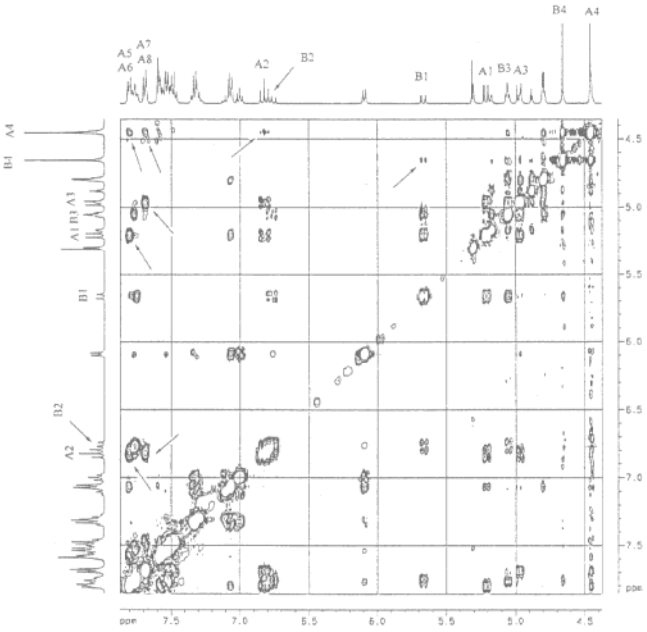


FIGURE 5. Sections of the NOESY spectrum of complex **16** (A, endo-syn-syn isomer; B, exo-syn-syn isomer). H4 indicates the unsubstituted cp ring protons. The arrows show the NOEs (400 MHz, mixing time 1.0 s, 273 K, CD_2Cl_2) (see also text).

studied in detail though a suitable X-ray structure of **16** was not obtained. CD_2Cl_2 was also chosen as the solvent. The ^{1}H NMR spectrum of the complex at 25 °C showed that it was a mixture of two conformers in a ratio of 2.2:1, and their conformations were assigned by a combination of COSY, $^{13}C-^1H$ correlation, and dimensional NOE experiments. The ^{1}HNMR manifested only the syn,syn arrangement of the allylic unit. Consistent with **15**, the results revealed that the M-type allylic moiety (endo-syn-syn) was the major conformer (Figure 5).

Some evidence supports our conclusion. First, the nonsubstituted Cp ring [H(4)] showed NOE with H(2) in the major component. Second, the H(1) (doublet peak at 5.67 ppm) showed NOE relevant with a nonsubstituted Cp ring [H(4)] in the minor component. Third, a multiple peak at 7.81 ppm was deduced to be H(5) or H(6) for it showed NOE relevant with H(1) and H(2) in the major component. A multiple peak at 7.69 ppm was deduced to be H(7) or H(8) for it showed NOE relevant with H(2) and H(3) in the major component. At the same time, both of them showed NOE relevant with the nonsubstituted Cp ring [H(4)]. As a result, the major component is the M type (endo-syn-syn). We are surprised by this result, for the product should have an *R* configuration when the two components reacted with nucleophile at the same rate, and it is in contrast with our experimental results. Again, an identical alkylation reaction was performed with 2 mol % intermediate **16** as the catalyst and the product was isolated in 90% ee and 98% yield with *S* configuration, showing that **16** is actually the intermediate. One reasonable explanation is two conformers may have different reactivity with the nucleophile.[35]

(35) (a) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033. (b) Mackenzie, P. B.; Whelan, J.; Bosnish, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033.

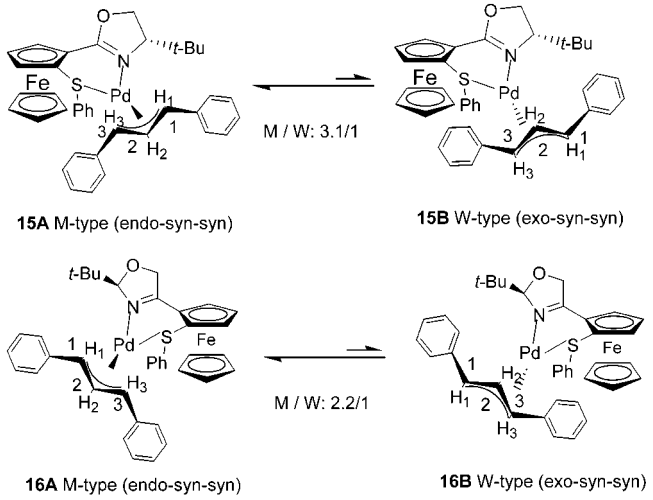


FIGURE 6. Equilibrium of complexes **15** and **16**.

TABLE 4. Selected NMR Data for Palladium Allylic Complexes 15 and 16

	^{1}H NMR (ppm)			^{13}C NMR (ppm)		
	H1	H2	H3	C1	C2	C3
15A	5.58	6.34	3.85	94.2	108.6	76.5
15B	5.07	6.32	4.81	86.5	107.0	83.8
16B	5.67	6.77	5.06	92.2	105.5	75.3
16A	5.21	6.83	4.97	86.8	107.0	81.9

It was reported that there was a correlation between the downfield shifts in the ^{13}C NMR and relative positive charge of the carbon nuclear.[36] With such a correlation, the ^{13}C NMR was used for predicting the reactivity of carbon termini of the palladium allylic complexes.[37] For **15** there are two isomers, **15A** and **15B**, in a ratio of 3.1:1 (Figure 6). Chemical shifts for terminal carbons of allyl are $\delta = 94.2$ (allylic carbon trans to S, C1) and 76.5 (trans to N, C3) for **15A** ($\Delta\delta = 17.7$) and $\delta = 86.5$ (allyl carbon trans to S, C1) and 83.8 (trans to N, C3) for **15B** ($\Delta\delta = 2.7$). It means that C1 of both **15A** and **15B** is more sensitive than C3 for nucleophilic attack. We can also reason that **15A** is more reactive than **15B** by comparison of their ^{13}C chemical shifts of C1 (Table 4). Because nucleophilic attack at diastereomer **15A** is more favored, the product will be given in *S* configuration. It is consistent with our experimental results. For **16**, there are also two conformers, **16A** and **16B**, in a ratio of 2.2:1 (Figure 6). Terminal allyl carbon chemical shifts are $\delta = 86.8$ (allyl carbon trans to S) and 81.9 (trans to N) for **16A** ($\Delta\delta = 4.9$) and $\delta = 92.2$ (allyl carbon trans to S) and 75.3 (trans to N) for **16B** ($\Delta\delta = 16.9$), suggesting that **16B** is the more reactive conformer (Table 4). Although **16A** occupies a higher population and is a favorable diastereomer during the thermodynamic equilibrium, it

(36) (a) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano,A. *Organometallics* **1987**, *6*, 620. (b) Åkermark, B.; Zetterberg, K.; Hansson, S.; Krakenberger, B.; Vitagliano, A. *J. Organomet. Chem.* **1987**, *335*, 133. (c) Macsár, i I.; Szabó, K. J. *Organometallics* **1999**, *18*, 701. (d) Malet, R.; Moreno-Mañas, M.; Parella, T.; Pleixats, R. *Organometallics* **1995**, *14*, 2463.

(37) (a) Macsári, I.; Hupe, E.; Szabó,K. J. *J. Org. Chem.* **1999**, *64*, 9547. (b) Aranyos, A.; Szabó, K. J.; Castaño, A. M.; Bäckvall, J.-E. *Organometallics* **1997**, *16*, 1058. (c) Moreno-Mañas, M.; Pajuelo, F.; Parella, T.; Pleixats, R. *Organometallics* **1997**, *16*, 205.

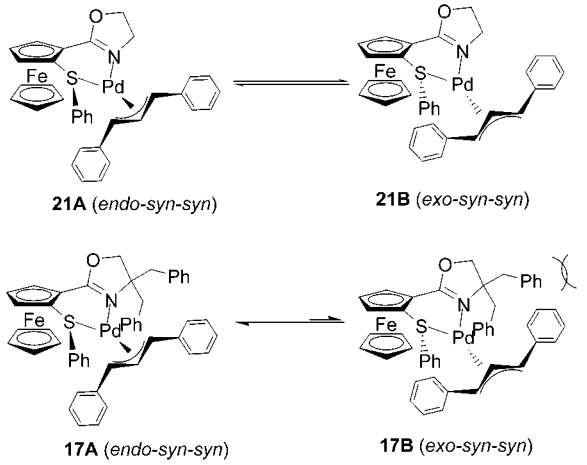


FIGURE 7. Proposed mechanism in palladium-catalyzed allylic substitution reaction with planar chiral ligands **5a** and **5c**.

is a less reactive species. The *S* product was obtained by kinetic control.

Palladium allylic complex **17** synthesized from ligand (*Sp*)-**5c** was studied also. The allylic moiety was M type (endo-syn-syn) in the X-ray structure. Unfortunately, the ^{1}H NMR gave all wide and broad peaks. The allylic protons were difficult to assign. We think that it may be caused by the fast equilibrium between the two isomers of complex **17**. In the ligands without central chirality, the phenyl group on the sulfur will become more flexible. For all the palladium allyl complexes with planar chiral *S*,*N*-ligands, there would exist four intermediates caused by the chirality of sulfur and the conformation of the allyl. However, only two major intermediates were discussed since the other two were less stable as steric reason caused by phenyl group on sulfur and the phenyl group of the allyl when they were on the same direction (Figure 7). With the ligands (*Sp*)-**5a**, **21A** (endo-syn-syn) and **21B** (exo-syn-syn) represented the two major components, in which a chiral center on sulfur was formed. The product was given in low ee value because the difference was small between **21A** and **21B**. The situation was changed greatly in complex **17**. For the two benzyl groups mounted across the diphenyl allyl moiety, component **17A** (endo-syn-syn) was more stable than **17B** (exo-syn-syn). As a result, the product could be given in high ee with *S* configuration by using (*Sp*)-**5c** as ligand. It also explained the difference between the ee values provided by *P*,*N*-ligands **11** and *S*,*N*-ligands **5a** and **5b**. Higher ee values were obtained for *P*,*N*-ligands **11** because no new chiral center was formed on the phosphorus atom during the coordination of them with palladium. NMR spectra of complexes derived from *P*,*N*-ligands **18**−**20** have also been studied. On the basis of the NMR data of the complexes, it is difficult to assign the conformation of the intermediates. All the complexes except **19** reached equilibrium between the two conformers as soon as they dissolved in the solvent. It took 9 h to reach equilibrium for complex **19**, and only one conformer was observed immediately after dissolution of the complex. Because the X-ray structure of complex **19** was determined as **19A** (endo-syn-syn), we elucidated that it was the major component in the solution. For complex **18**, the ratio of

TABLE 5. Selected NMR Data for Palladium Allylic complexes 18 and 19

	^{1}H NMR (ppm)			^{13}C NMR (ppm)		
	H1	H2	H3	C1	C2	C3
18A	5.84	6.47	3.44	104.4	111.3	69.9
18B	6.14	6.41	5.07	109.6	111.1	74.4
19A	5.21	6.89	3.89	94.0	108.8	78.0
19B	5.69	6.69	4.57	103.7	132.9	66.3

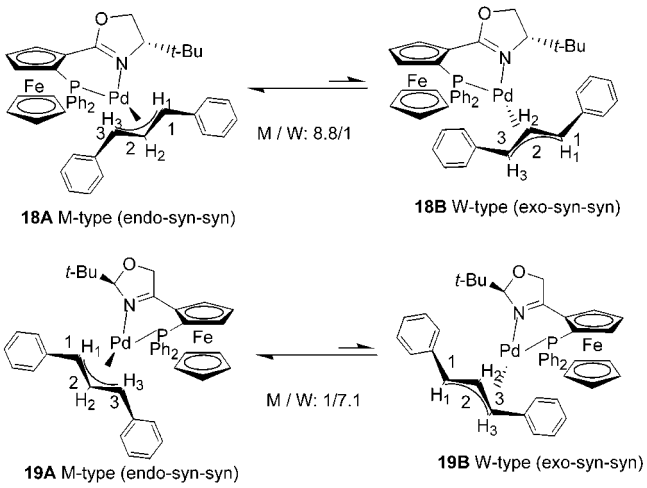


FIGURE 8. Equilibrium of complexes **18** and **19**.

the two conformers is 8.8:1. Terminal ^{13}C allyl chemical shifts are δ = 104.4 (allyl carbon trans to P) and 69.9 (trans to N) for the major component ($\Delta\delta$ = 34.5) and δ = 109.6 (allyl carbon trans to P) and 75.3 (trans to N) for the minor one ($\Delta\delta$ = 35.2), suggesting that the minor conformer was the more reactive species (Table 5). When the product was given in high ee in the *S* configuration, the minor component was probably **18A** (endo-syn-syn). For **19** there are two isomers, **19A** and **19B**, in a ratio of 1:7.1 (Figure 8). Terminal ^{13}C allyl chemical shifts are δ = 94.0 (allyl carbon trans to P) and 78.0 (trans to N) for **19A** ($\Delta\delta$ = 26.0) and δ = 103.7 (allyl carbon trans to P) and 66.3 (trans to N) for **19B** ($\Delta\delta$ = 37.4) (Table 5). Again, ^{13}C chemical shifts of C1 for **18** and **19** showed that both **18B** and **19B** were more reactive species compared with that of **18A** and **19A** (Table 5). The fact that the major component **19B** is the more reactive one suggested that **19** should be a better catalyst than complex **18**, giving high enantioselectivity.

P,*N*-ligands with only planar chirality (*Sp*)-**11a**−**c** showed moderate enantioselectivity in both allylic alkylation and amination reaction. (*Sp*)-**11a** with two H-atoms on the oxazoline gave highest enantioselectivity. For complex **20** there are two isomers in a ratio of 2.8:1. Terminal ^{13}C allyl chemical shifts are δ = 100.7 (allyl carbon trans to P) and 71.1 (trans to N) for the major component ($\Delta\delta$ = 29.6) and δ = 96.3 (allyl carbon trans to P) and 75.5 (trans to N) for the minor one ($\Delta\delta$ = 20.8), suggesting that the major component has a higher reactivity. When the product of the allylic alkylation was in the*R* configuration, the major component was assigned as W type (exo-syn-syn) which is just the same as the structure of the X-ray.

Conclusion

High enantioselectivity was obtained in palladium-catalyzed allylic alkylation and amination reactions by thioether and phosphino derivatives of ferrocenyloxazolines with central and planar chiralities. The importance of planar chirality in 1,2-disubstituted ferrocene systems was showed both in alkylation and amination reactions.[19] Newly formed central chirality on sulfur atom of ligands **5a** and **5b** during the complexation with palladium might be the reason for their poor enantiocontrol. Comparatively higher enantioselectivities were obtained for *P*,*N*-ligands (*Sp*)-**11** with only planar chirality, since there was no such disturbance. The matching of planar and central chiralities is essential for excellent asymmetric induction and the absolute configuration of the product are mainly governed by the central chirality.

Experimental Section

General Methods. The commercially available reagents were used as received without further purification. Chiral amino alcohols were synthesized from the amino acids following a standard procedure.[38] $PhSO_2Me$, PhSSPh, TolSSTol,[39] $[Pd(C_3H_5)Cl]_2$,[40] $[Pd(\eta^3\text{-PhCHCHCHPh})Cl]_2$,[29] **8b**, **9b**, **10b**, **17**, **18**,[22] **11**,[24] **23**, and **24a**[16a] were prepared by using literature procedures.

All reactions were performed under an atmosphere of either argon or nitrogen using oven-dried glassware. Solvents were treated prior to use according to the standard methods. Melting points are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ at room temperature. Chemical shifts are given in parts per million relative to TMS as an internal standard. Optical rotations were measured using a polarimeter with a thermally jacketed 10 cm cell at 25 °C (concentration *c* given as g/100 mL). IR spectra were measured in cm^{-1} Ee values were determined by chiral HPLC on Chiracel OD and OJ columns.

(*S*,*Sp*)-2-(Methylthio)-1-(4-isopropyloxazolinyl)ferrocene (*S*,*Sp*)-6c. To a solution of [4-(*S*)-isopropyl-2-oxazolinyl]ferrocene (311 mg, 1 mmol) in dry ether (15 mL) was added TMEDA (0.2 mL, 1.3 mmol) at 25 °C. The resulting mixture was cooled to −78 °C, and *n*-BuLi (0.8 mL, 1.6M in hexane, 1.3 mmol) was added dropwise and stirred for 2 h at this temperature. The mixture was treated with $PhSO_2SMe$ (282 mg, 1.5 mmol) and stirred for another 1 h at rt. The reaction mixture was diluted with Et_2O and quenched with saturated aqueous $NaHCO_3$ solution. The organic layer was extracted twice with Et_2O. The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo to give the crude product, which was purified by column chromatography (EtOAc/petroleum ether = 1/10) to give **6c** (274 mg, 80%) as an orange solid: mp 83−84 °C; $[\alpha]^{20}_D = -280$ (*c* = 0.21 in $CHCl_3$); ^{1}H NMR δ 4.72 (dd, *J* = 1.6, 2.6 Hz, 1H), 4.40 (dd, *J* = 1.6, 2.4 Hz, 1H), 4.26−4.33 (m, 2H), 4.19 (s, 5H), 4.01−4.14 (m, 2H), 2.40 (s, 3H), 1.88 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H); MS (EI) *m*/*z* 343 (M^+, 100), 328 (38), 300 (10), 242 (18), 190 (21), 121 (29); IR (KBr, cm^{-1}) 2959 (w), 1660 (s), 1361 (w), 1147 (m), 977 (m). Anal. Calcd for $C_{17}H_{21}FeNOS$: C, 59.48; H, 6.17; N, 4.08. Found: C, 59.44; H, 6.07; N, 3.88.

(*S*,*Sp*)-2-(Phenylthio)-1-(4-isopropyloxazolinyl)ferrocene (*S*,*Sp*)-6a. Similar procedures as for **6c** (except for being quenched with PhSSPh) give **6a** in 93% yield (1 mmol scale) as an orange solid: mp 78−79 °C; $[\alpha]^{20}_D = +69$ (*c* = 0.26 in $CHCl_3$); ^{1}H NMR δ 7.07−7.19 (m, 5H), 4.88 (m, 1H), 4.39−4.40 (m, 2H), 4.28 (s, 5H), 4.27−4.30 (m, 1H), 3.93−4.02 (m, 2H), 1.79 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); MS (EI) *m*/*z* 405 (M^+, 27), 361 (5), 263 (14), 121 (10); IR (KBr, cm^{-1}) 2964 (w), 1658 (s), 1480 (m), 1147 (m), 981 (m). Anal. Calcd for $C_{22}H_{23}FeNOS$: C, 65.19; H, 5.72; N, 3.46. Found: C, 65.18; H, 5.62; N, 3.46.

(*S*,*Sp*)-2-(*p*-Methylphenylthio)-1-(4-isopropyloxazolinyl)-ferrocene (*S*,*Sp*)-6d. Similar procedures as for **6c** (except for being quenched with TolSSTol) give **6d** in 76% yield (1 mmol scale) as an orange solid: mp 69−70 °C; $[\alpha]^{20}_D = -60$ (*c* = 0.35 in $CHCl_3$); ^{1}H NMR δ 7.16 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.82−4.84 (m, 1H), 4.31−4.35 (m, 3H), 4.25 (s, 5H), 3.97−4.03 (m, 2H), 1.81 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); MS (EI) *m*/*z* 419 (M^+, 100), 375 (4), 263 (16), 177 (10), 121 (16); IR (KBr, cm^{-1}) 2960 (w), 1659 (s), 1492 (m), 1147 (w), 977 (m). Anal. Calcd for $C_{23}H_{25}FeNOS$: C, 65.87; H, 6.01; N, 3.34. Found: C, 66.03; H, 5.95; N, 3.15.

(*S*,*Sp*)-2-(Phenylthio)-1-(4-benzyloxazolinyl)ferrocene (*S*,*Sp*)-6e. Similar procedures as for **6c** (except for being quenched with PhSSPh) give **6e** in 76% yield (1 mmol scale) as a red oil: $[\alpha]^{20}_D = +119$ (*c* = 1.13 in $CHCl_3$); ^{1}H NMR δ 7.18−7.30 (m, 10H), 4.89 (m, 1H), 4.38−4.47 (m, 3H), 4.25 (s, 5H), 4.22−4.33 (m, 1H), 3.94−4.00 (m, 1H), 3.18 (dd, *J* = 4.6, 13.7 Hz, 1H), 2.61 (dd, *J* = 8.9, 13.7 Hz, 1H); MS (EI) *m*/*z* 453 (M^+, 100), 361 (24), 319 (20), 253 (27), 121 (39), 91 (50); IR (KBr, cm^{-1}) 3084 (w), 2924 (m), 1657 (s), 1478 (m), 1142 (m), 983 (s); HRMS calcd for $C_{26}H_{23}FeNOS$ 453.0849, found 453.0816.

(*S*,*Sp*)-2-(Phenylthio)-1-(4-phenyloxazolinyl)ferrocene (*S*,*Sp*)-6f. Similar procedures as for **6c** (except for being quenched with PhSSPh) give **6f** in 57% yield (1 mmol scale) as an orange solid: mp 72−73 °C; $[\alpha]^{20}_D = -83$ (*c* = 0.31 in $CHCl_3$); ^{1}H NMR δ 7.14−7.29 (m, 10H), 5.21 (dd, *J* = 8.2, 9.7 Hz, 1H), 4.96 (dd, *J* = 1.5, 2.7 Hz, 1H), 4.70 (dd, *J* = 8.5, 9.9 Hz, 1H), 4.44−4.48 (m, 2H), 4.33 (s, 5H), 3.18 (t, *J* = 8.3 Hz, 1H); MS (EI) *m*/*z* 439 (M^+, 100), 297 (20), 269 (31), 177 (38), 121 (56); IR (KBr, cm^{-1}) 3081 (w), 2897 (w), 1653 (s), 1580 (m), 1477 (m), 1139 (m), 992 (s). Anal. Calcd for $C_{25}H_{21}FeNOS$: C, 68.39; H, 4.78; N, 3.19. Found: C, 68.27; H, 4.99; N, 3.17.

(*S*,*Rp*)-**2-(phenylthio)-1-(4-isopropyloxazolinyl)ferrocene 7a.** To a solution of 2-(*S*,*Sp*)-(trimethylsilyl)-1-(4-isopropyloxazolinyl)ferrocene (369 mg, 1 mmol) in dry ether (15 mL) at 25 °C was added *n*-BuLi (0.8 mL, 1.6M in hexane). The reaction mixture was stirred at the same temperature for 1 h before treatment with PhSSPh (327 mg, 1.5 mmol). After usual workup and column chromatography (EtOAc/petroleum ether = 1/10), (*S*)-2-(*Rp*)-(phenylthio)-5-(*Sp*)-(trimethylsilyl)-1-(4-isopropyloxazolinyl)ferrocene was given (334 mg, 76%) as an orange solid: mp 93−94 °C; $[\alpha]^{20}_D = -16$ (*c* = 0.20 in $CHCl_3$); ^{1}H NMR δ 7.07−7.26 (m, 5H), 4.52 (d, *J* = 2.5 Hz, 1H), 4.31 (d, *J* = 2.5 Hz, 1H), 4.27 (s, 5H), 4.19−4.25 (m, 1H), 3.86−4.02 (m, 1H), 1.71 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.31 (s, 9H); MS (EI) *m*/*z* (rel intensity) 477 (M^+, 100), 462 (47), 375 (17), 121 (11), 73 (13); IR (KBr, cm^{-1}) 2956 (m), 1651 (m), 1477 (m), 1168 (m), 992 (m). Anal. Calcd for $C_{25}H_{31}FeNOSSi$: C, 62.88; H, 6.54; N, 2.93. Found: C, 63.10; H, 6.62; N, 2.69.

To a solution of (trimethylsilyl)-1-(4-isopropyloxazolinyl)-ferrocene (477 mg, 1 mmol) in THF (5 mL) at 25 °C was added tetrabutylammonium fluoride (5 mL, 1M in THF). The resulting reaction mixture was refluxed for 3 h. After usual workup and column chromatography (EtOAc/petroleum ether = 1/10), title compound **7a** was afforded (356 mg, 88%) as a red oil: $[\alpha]^{20}_D = -252$ (*c* = 0.45 in $CHCl_3$); ^{1}H NMR δ 7.04−7.26 (m, 5H), 4.94 (br, 1H), 4.47 (m, 1H), 4.44 (m, 1H), 4.29 (s, 5H), 4.19 (m, 1H), 4.08 (m, 1H), 3.98 (m, 1H), 1.75 (m, 1H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); MS (EI) *m*/*z* (rel intensity) 405 (M^+, 27), 253 (10), 177 (11), 121 (12); IR (KBr, cm^{-1}) 2958 (m), 1659 (s), 1479 (m), 1143 (w), 1002 (w), 983

(38) Mckennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. *J. Org. Chem.* **1993**, *58*, 3568.

(39) (a) Hayashi, S.; Furukawa, M.; Yamamoto, J.; Niigata, K. *Chem. Pharm. Bull.* **1967**, *15*, 1188. (b) Mikolajczyk, M.; Drabowicz, *Synthesis* **1980**, 32.

(40) Dent, W. T.; Wilkinson, A. I. *J. Chem. Soc.* **1964**, 1585.

(m). Anal. Calcd for $C_{22}H_{23}FeNOS$: C, 65.19; H, 5.72; N, 3.46. Found: C, 65.38; H, 5.63; N, 3.30.

1-Phenyl-2-amino-2-benzylpropanol 8. (1) *N*-[1-(Methoxycarbonyl)-1-benzyl-2-phenylethyl]benzophenone Imine. A solution of KHMDS (8 mL, 1 M in THF, 8 mmol) was added to the methyl 1-[*N*-(diphenylmethylene)]phenylalanate (2.3 g, 6.7 mmol) in THF (35 mL) at −78 °C to give a red solution that was allowed to stir for 1 h. BnBr (1.1 mL, 9 mmol) was added, and the reaction mixture was allowed to warm to rt and stir for 3 h. The resulting yellow solution was poured into water (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed with brine (30 mL), dried (Na_2SO_4), and filtered. The filtrate was concentrated to give the crude product, which was recrystallized from EtOAc to give pure product (3.1 g, 72% yield) as a white solid: mp 144−145 °C; ^{1}H NMR δ 7.56−7.58 (m, 2H), 7.19−7.38 (m, 16H), 6.62−6.64 (m, 2H), 3.32 (dd, J = 14.0, 19.9 Hz, 4H), 3.05 (s, 3H); MS (EI) m/z 434 (M+1, 5), 342 (100), 251 (35), 165 (52), 91 (50), 77 (6); IR (KBr, cm^{-1}) 3055 (w), 2926 (w), 1730 (s), 1641 (m), 1494 (m), 1215 (m), 1087 (m), 698 (s). Anal. Calcd for $C_{30}H_{27}NO_2$: C, 83.21; H, 6.24; N, 3.23. Found: C, 82.95; H, 6.11; N, 3.06.

(2) Methyl (1-Phenyl-2-amino-2-benzyl)propanoate. Hydrochloric acid (20 mL, 1 M, 20 mmol) was added dropwise to a solution of benzophenone imine prepared in a previous experiment (5.6 g, 12.9 mmol) in Et_2O/CH_2Cl_2 (50 mL/10 mL) at 0 °C, and the two-phase mixture was allowed to stir at rt overnight. The aqueous layer was removed and washed with CH_2Cl_2 (2 ω 15 mL). The combined organic layers were extracted with 2 M hydrochloric acid (2 × 15 mL), and the aqueous layers were combined and concentrated to give a solid mass, which was dissolved in a saturated aqueous solution of $NaHCO_3$ (50 mL) and stirred for 30 min. The resulting suspension was extracted with CH_2Cl_2 (4 × 20 mL). The organic phase was combined, dried (Na_2SO_4), and filtered. The filtrate was concentrated to give propanoate (2.3 g, 66% yield) as a white solid: mp 72−73 °C; ^{1}H NMR δ 7.16−7.31 (m, 10H), 3.66 (s, 3H), 3.37 (d, J = 13.1 Hz, 2H), 2.85 (d, J = 13.1 Hz, 2H), 1.55 (br, 2H); MS (EI) m/z 270 (M + 1, 7), 178 (100), 118 (69), 91 (96); IR (KBr, cm^{-1}) 3381 (w), 3028 (w), 2931 (w), 1737 (s), 1494 (m), 1209 (m), 1177 (s), 1083 (s). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.90; H, 7.06; N, 5.20. Found: C, 75.75; H, 7.13; N, 5.03.

(3) 1-Phenyl-2-amino-2-benzylpropanol 8. A solution of propanoate obtained from the last procedure (1.88 g, 7 mmol) in Et_2O (30 mL) was added to a solution of lithium aluminum hydride (1.33 g, 35 mmol) in Et_2O (15 mL) at such a rate as to maintain gentle reflux. The reaction mixture was then stirred at rt overnight, cooled to 0 °C, and quenched by cautious addition of water (1.6 mL), followed by 15% aqueous NaOH solution (1.6 mL) and finally water (4.8 mL). The mixture was allowed to stir for 2 h and filtered, and the salts were washed with Et_2O. The Et_2O fractions were combined, dried (Na_2SO_4), and concentrated to give aminopropanol **8** (1.5 g, 89%) as a white solid: mp 134−135 °C; ^{1}H NMR δ 7.13−7.25 (m, 10H), 3.19 (s, 2H), 2.73 (dd, J = 13.3, 19.5 Hz, 4H), 2.08 (br, 3H); MS (EI) m/z 242 (M+1, 2), 210 (32), 150 (100), 91 (88); IR (KBr, cm^{-1}) 3341 (w), 3155 (s), 1577 (s), 1167 (m), 1064 (s). Anal. Calcd for $C_{16}H_{19}NO$: C, 79.73; H, 7.88; N, 5.81. Found: C, 79.38; H, 7.88; N, 5.56.

(*Sp*)-2-(Phenylthio)-1-(4, 4-dimethyl)ferrocenyloxazoline (*Sp*)-5b. 1) (*S*,*Sp*)-[2′-(*N*-Acetyl)amino-3′-methylbutyl]-2-(phenylthio)ferrocene-1-carboxylate. A solution of **6a** (81 mg, 0.2 mmol) in THF (22 mL) was treated with powdered Na_2SO_4 (1.48 g, 10 mmol), water (0.2 mL, 11 mmol), and trifluoroacetic acid (0.08 mL, 1 mmol). The suspension was stirred for 12 h, and anhydrous Na_2SO_4 (0.4 g, 2.8 mmol) was added. Filtration and concentration at <30 °C afforded the unstable ammonium salt, which was dissolved in CH_2Cl_2 (4 mL), cooled in an ice bath, and treated sequentially with acetic anhydride (0.7 mL, 7 mmol) and pyridine (1.1 mL, 14 mmol). The reaction mixture was allowed to warm to ambient temperature over 7 h. The solution was washed with cold 3 N HCl (3 ω 5 mL) and saturated $NaHCO_3$ (5 mL). The organic layer was dried, and the solvent was removed. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1/3) to afford (*S*,*Sp*)-[2′-(*N*-acetyl)amino-3′-methylbutyl]-2-(phenylthio)ferrocene-1-carboxylate (82 mg, 88%) as a yellow solid: mp 102−103 °C; $[\alpha]^{20}_D = +37$ (c = 0.31 in $CHCl_3$); ^{1}H NMR δ 7.22 (d, J = 7.7 Hz, 2H), 7.05−7.13 (m, 3H), 5.30 (br, 1H), 5.11 (m, 1H), 4.56−4.58 (m, 2H), 4.46 (dd, J = 2.9, 11.4 Hz, 1H), 4.30 (s, 5H), 4.01 (dd, J = 2.9, 11.4 Hz, 1H), 3.90 (m, 1H), 2.10 (m, 1H), 1.60 (s, 3H), 1.03 (d, J = 6.7 Hz, 3H), 0.94 (d, J = 6.71 Hz, 3H); MS (EI) m/z 465 (M$^+$, 17), 338 (100), 292 (9), 200 (18), 171 (13); IR (KBr, cm^{-1}) 3304 (m), 3084 (w), 2960 (w), 1726 (s), 1644 (s), 1479 (m), 1154 (m), 1004 (m). Anal. Calcd for $C_{24}H_{27}FeNOS$: C, 61.94; H, 5.85; N, 3.01. Found: C, 61.76; H, 5.88; N, 2.84.

(2) (*Sp*)-2-(Phenylthio)-1-ferrocenecarboxylic Acid. A solution of carboxylate obtained in the last step (70 mg, 0.15 mmol) in THF (4 mL) and water (3.5 mL) was treated with aqueous 2.5 N NaOH solution (0.39 mL, 0.97 mmol) and heated at 55 °C for 8 h. The mixture was cooled, and the THF was removed in vacuo. The aqueous layer was extracted with $CHCl_3$ (2 × 10 mL), cooled in an ice bath, acidified (pH ∼1) with 3 N HCl, and extracted with CH_2Cl_2 (2 × 10 mL). The CH_2Cl_2 extract was dried (Na_2SO_4) and evaporated in vacuo. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1/2) to afford ferrocene carboxylic acid (43 mg, 87%) as an orange crystalline solid: mp 115−116 °C; $[\alpha]^{20}_D = +68$ (c = 0.29 in $CHCl_3$); ^{1}H NMR δ 7.14−7.28 (m, 5H), 5.13 (dd, J = 1.6, 2.7 Hz, 1H), 4.65 (dd, J = 1.5, 2.5 Hz, 1H), 4.61 (dd, J = 2.62.7 Hz, 1H), 4.30 (s, 5H); MS (EI) m/z 338 (M$^+$, 23), 258 (44), 200 (45), 171 (39), 121 (9); IR (KBr, cm^{-1}) 3150−2700 (s), 1739 (m), 1681 (s), 1457 (w), 1265 (m); HRMS calcd for $C_{17}H_{14}FeNO_2S$ 338.0064, found 338.0056.

(*Sp*)-2-(Phenylthio)-1-(4, 4-dimethyl)ferrocenyloxazoline 5b: A solution of (*Sp*)-ferrocene carboxylic acid (338 mg, 1 mmol) in 8 mL CH_2Cl_2 under argon was treated at ambient temperature by dropwise addition of oxalyl chloride (0.17 mL, 2 mmol) via syringe. After about 0.5h, all gas evolution had ceased, and the solvent was directly removed into a trap. After drying for 2 h, the red solid was dissolved in 4 mL CH_2Cl_2 under argon, and the resulting solution was transferred via cannula to a second Schlenk tube, which contained a solution of 2-amino-2-methylpropanol (107 mg, 1.2 mmol) and triethylamine (0.24 mL, 1.6 mmol) in 8 mL CH_2Cl_2. The resulting mixture was allowed to stir at rt overnight and then quenched with 20 mL of distilled water. The organic phase was separated, and the aqueous phase was extracted twice with 10 mL CH_2Cl_2. After the combined organic phases were dried over Na_2SO_4, the solvent was removed in vacuo. The crude product was purified by column chromatography (EtOAc/Petroleum ether = 1/1) to afford the corresponding amide (342 mg, 84%) as an orange solid: mp 123−124 °C; $[\alpha]_D^{20} = +60.2$ (c = 0.31 in $CHCl_3$); ^{1}H NMR δ 7.95 (s, 1H), 7.02−7.27 (m, 5H), 5.18−5.19 (m, 1H), 4.60−4.61 (m, 1H), 4.56−4.58 (m, 1H), 4.31 (s, 5H), 4.01 (br, 1H), 3.55 (dd, J = 12.0, 19.5 Hz, 2H), 1.31 (s, 3H), 1.09 (s, 3H); MS (EI) m/z 409 (M$^+$, 30), 408 (M-1, 100), 321 (48), 292 (19), 195 (13), 121 (14); IR (KBr, cm^{-1}) 3299 (s), 2966 (w), 1627 (s), 1545 (s), 1476 (m), 1077 (m), 1026 (m). Anal. Calcd for $C_{21}H_{23}FeNO_2S$: C, 61.62; H, 5.66; N, 3.42. Found: C, 61.47; H, 5.51; N, 3.28. To a solution of the above amide (345 mg, 0.6 mmol) in 5 mL of CH_2Cl_2 were added TsCl (191 mg, 1 mmol), triethylamine (0.14 mL, 1 mmol), and a catalytic amount of DMAP. Then the reaction mixture was allowed to stir at rt overnight. After complete conversion of the amide, the reaction was quenched with 20 mL of distilled water. The organic phase was separated, and the aqueous phase was extracted twice with 10 mL CH_2Cl_2. After the combined organic phases were dried over Na_2SO_4, the solvent was removed in vacuo. The crude product was purified by column chromatography (EtOAc/Petroleum ether = 1/10) to afford the title compound (217 mg, 92%) as an orange solid: mp 105−106 °C;

$[\alpha]^{20}_D = +340$ ($c = 0.36$ in $CHCl_3$); ^{1}H NMR δ 7.09−7.19 (m, 5H), 4.97 (m, 1H), 4.43−4.44 (m, 2H), 4.29 (s, 5H), 4.07 (d, J = 8.0 Hz, 1H), 3.86 (d, J = 8.0 Hz, 1H), 1.31 (s, 3H), 1.28 (s, 3H); MS (EI) m/z 391 (M^+, 34), 319 (32), 249 (12), 177 (13), 121 (32); IR (KBr, cm^{-1}) 2959 (w), 1636 (s), 1581 (m), 1481 (m), 1284 (m), 1122 (s), 1059 (m). Anal. Calcd for $C_{21}H_{21}$FeNOS: C, 64.46; H, 5.41; N, 3.58. Found: C, 64.50; H, 5.21; N, 3.46.

(*Sp*)-2-(Phenylthio)-1-ferrocenyloxazoline 5a. Following the procedure of synthesis **5b** as above by using corresponding amino alcohol give **5a** (63% yield for over two steps) as an orange solid: mp 136−137 °C; $[\alpha]^{20}_D = +36$ ($c = 0.23$ in $CHCl_3$); ^{1}H NMR δ 7.10−7.23 (m, 5H), 4.91 (m, 1H), 4.42−4.46 (m, 2H), 4.29 (s, 5H), 4.25−4.36 (m, 2H), 3.87−3.95 (m, 2H); MS (EI) m/z 363 (M^+, 25), 222 (13), 177 (19), 121 (13); IR (KBr, cm^{-1}) 2964 (w), 1658 (s), 1479 (m), 1142 (m), 987 (s); HRMS calcd for $C_{19}H_{17}$FeNOS 363.0383, found 363.0380.

(*Sp*)-2-(Phenylthio)-1-(4, 4-dibenzyloxazolinyl)ferrocene 5c. The corresponding amide was synthesized following a procedure similar to that for the synthesis of **5b** (1 mmol scale) by using amino alcohol **8**. The crude amide was dissolved in 20 mL of acetonitrile. To this solution were added PPh_3 (1.57 g, 6 mmol), Et_3N (0.65 mL, 5 mmol), and CCl_4 (1.45 mL, 15 mmol), and the mixture was stirred overnight. The deep red solution was worked up with 100 mL of distilled water. This mixture was extracted with hexane until the organic layer showed no orange color. The combined organic phases were dried over Na_2SO_4, and the solvent was removed in vacuo. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1/10) to afford the title compound (341 mg, 62%) as an orange solid: mp 115−116 °C; $[\alpha]^{20}_D = +186$ (c = 0.48 in $CHCl_3$); ^{1}H NMR δ 7.05−7.23 (m, 15H), 4.76 (m, 1H), 4.37−4.41 (m, 2H), 4.09 (dd, J = 8.6, 16.1 Hz, 1H), 3.99 (s, 5H), 3.06 (dd, J = 13.8, 19.5 Hz, 1H), 2.80 (dd, J = 13.7, 15.4 Hz, 1H); MS (EI) m/z 543 (M^+, 47), 452 (58), 361 (13), 121 (22), 91 (100); IR (KBr, cm^{-1}) 3083 (w), 2919 (w), 1656 (s), 1477 (m), 1026 (s). Anal. Calcd for $C_{33}H_{29}$FeNOS: C, 72.99; H, 5.34; N, 2.58. Found: C, 72.90; H, 5.28; N, 2.63.

(*Sp*)-2-(Diphenylphosphino)-1-ferrocenyloxazoline 11a. (1) (*S*,*Sp*)-[2′-(*N*-Acetyl)amino-3′,3′-dimethylbutyl]-2-(diphenylphosphino)-1-ferrocenecarboxylate. A solution of (*S*,*Sp*)-**9** (1.98 g, 4 mmol) in THF (40 mL) was treated with powdered Na_2SO_4 (29 g, 60 mmol), water (4 mL, 220 mmol), and CF_3COOH (1.74 mL, 22 mmol), The suspension was stirred for 3 d, and anhydrous Na_2SO_4 (8.4 g, 60 mmol) was added. Filtration and concentration at <30 °C afforded the unstable ammonium salt, which was dissolved in CH_2Cl_2 (70 mL), cooled in an ice bath, and treated sequentially with acetic anhydride (14 mL, 15 mmol) and pyridine (22 mL, 27 mmol). The reaction mixture was allowed to warm to ambient temperature over 7 h. The solution was washed with cold 3 N HCl (3 ω 100 mL) and saturated $NaHCO_3$ (100 mL). The organic layer was dried and condensed. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1/3) to afford [2′-(*N*-Acetyl)amino-3′,3′-dimethylbutyl]-2-(diphenylphosphino)-1-ferrocenecarboxylate (1.40 g, 63%) as a yellow solid: mp 188−189 °C dec; $[\alpha]^{20}_D = -231$ ($c = 0.33$ in $CHCl_3$); ^{1}H NMR δ 7.52 (m, 2H), 7.39−7.41 (m, 3H), 7.22−7.24 (m, 3H), 7.14−7.15 (m, 2H), 5.92 (d, J = 9.4 Hz, 1H), 5.08 (m, 1H), 4.64 (dd, J = 6.8, 11.5 Hz, 1H), 4.48 (t, J = 2.6 Hz, 1H), 4.17 (s, 5H), 4.09 (m, 1H), 3.95 (dd, J = 4.0, 11.5 Hz, 1H), 3.80 (m, 1H), 1.74 (s, 3H), 1.01 (s, 9H); MS (EI) m/z 555 (M^+, 100), 490 (14), 414 (73), 369 (51), 213 (26); IR (KBr, cm^{-1}) 3332 (m), 3057 (w), 2966 (m), 1702 (s), 1652 (s), 1434 (m), 1254 (s), 1165 (s), 696 (m). Anal. Calcd for $C_{31}H_{34}FeNO_3P$: C, 67.00; H, 6.13; N, 2.52. Found: C, 66.57; H, 6.23; N, 2.32.

(2) (*Sp*)-Methyl 2-(Diphenylphosphino)-1-ferrocenecarboxylate. To a solution of 2-(diphenylphosphino)-1-ferrocenecarboxylate prepared above (555 mg, 1.0 mmol) in THF (15 mL) was added a sodium methoxide solution prepared from sodium metal (1.0 g, 46 mmol) and 50 mL of methanol/THF (v/v 40:10). After being stirred for 2 h at 55 °C, the mixture was neutralized with methanolic acetic acid, and the solvent was removed by evaporation in vacuo. The residue was dissolved in dichloromethane, and the resulting solution was washed with water and then with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography with ethyl acetate/petroleum (1:20) as an eluent to afford 2-(diphenylphosphino)-1-ferrocenecarboxylate as an orange solid (402 mg, 94%): mp 206−207 °C; $[\alpha]^{20}_D = -251.0°$ ($c = 0.33$ in $CHCl_3$); ^{1}H NMR δ 7.48−7.50 (m, 2H), 7.36−7.38 (m, 3H), 7.20−7.25 (m, 5H), 5.05 (m, 1H), 4.44 (t, J = 2.5 Hz, 1H), 4.22 (s, 5H), 3.72 (m, 1H), 3.69 (s, 3H); ^{31}P NMR (161.92 MHz, $CDCl_3$) δ −16.36. MS m/z 428 (M^+, 100), 413 (36), 385 (71), 275 (6), 229 (8); IR (KBr) 3065 (w), 2950 (w), 1707 (s), 1447 (m), 1254 (s), 1162 (s), 746 (m). Anal. Calcd for $C_{24}H_{21}O_2$PFe: C, 67.35; H, 4.91. Found: C, 67.37; H, 4.85.

(3) (*Sp*)-1-[*N*-(2′-Hydroxyethyl)amido]-2-(diphenylphosphino)ferrocene. A mixture of 2-(diphenylphosphino)-1-ferrocenecarboxylate (86 mg, 0.2 mmol), 2 mL of 2-aminoethanol, and a small amount of sodium was heated at 100 °C for 1 h. The mixture was diluted with dichloromethane and neutralized with acetic acid. The neutralized solution was washed with water and then with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography with ethyl acetate/petroleum (1:2) as an eluent to afford compound (*Sp*)-1-[*N*-(2′-hydroxyethyl)-amido]-2-(diphenylphosphino)ferrocene as a yellow solid (97 mg, 92%): mp 73−75 °C; $[\alpha]^{20}_D = -223.2$ ($c = 0.65$ in $CHCl_3$); ^{1}H NMR δ 7.15−7.58 (m, 11H), 5.15−5.16 (m, 1H), 4.48 (t, J = 2.6 Hz, 1H), 4.14 (s, 5H), 3.83 (m, 1H), 3.63−3.68 (m, 2H), 3.48−3.51 (m, 2H), 2.79 (br, 1H); ^{31}P NMR (161.92 MHz, $CDCl_3$) δ −20.07; MS m/z 457 (M^+, 25), 392 (100), 374 (39), 361 (21), 201 (15), 121 (4); IR (KBr) 3318 (s), 2924 (w), 1628 (s), 1533 (s), 1433 (m), 1273 (m), 1068 (m); HRMS calcd for $C_{25}H_{24}NO_2$PFe 457.08934, found 457.08998.

(4) (*Sp*)-2-(Diphenylphosphino)-1-ferrocenyloxazoline (*Sp*)-11a. To a solution of (*Sp*)-1-[*N*-(2′-hydroxyethyl)amido]-2-(diphenylphosphino)ferrocene (137 mg, 0.3 mmol) and triethylamine (0.23 mL, 1.5 mmol) in dichloromethane (3 mL) was added methanesulfonyl chloride (0.02 mL, 0.3 mmol) at 0 °C. After being stirred at rt for 5 h, the reaction solution was washed with distilled water (10 mL) and then with brine, dried over Na_2SO_4, and concentrated under reduced pressure to provide a residue that was purified by column chromatography with ethyl acetate/petroleum (1:5) as an eluent to afford (*Sp*)-**11a** as a yellow solid (112 mg, 85%): mp 177−178 °C; $[\alpha]^{20}_D = -65.0$ ($c = 0.45$ in $CHCl_3$); ^{1}H NMR δ 7.18−7.52 (m, 10 H), 4.99 (m, 1 H), 4.39 (t, J = 2.6 Hz, 1 H), 4.29 (dt, J = 10.2, 8.0 Hz, 1 H), 4.19 (s, 5 H), 4.04 (dd, J = 9.5, 17.5 Hz, 1 H), 3.75−3.87 (m, 2 H), 3.68 (m, 1 H); ^{31}P NMR (161.92 MHz, $CDCl_3$) δ −17.27; MS m/z 439 (M^+, 100), 410 (60), 362 (26), 348 (19), 183 (9); IR (KBr) 2877 (w), 1658 (m), 1639 (s), 1432 (m), 1257 (w), 1122 (m), 699 (s). Anal. Calcd for $C_{25}H_{22}$NOPFe: C, 68.39; H, 5.01; N, 3.19. Found: C, 68.11; H, 4.98; N, 3.17.

(*Sp*)-2-(Diphenylphosphino)-1-(4,4-dibenzyloxazolinyl)ferrocene 11c. (1) (*Sp*)-2-Iodine-1-(4,4-dibenzyloxazolinyl)ferrocene. A solution of (*Sp*)-2-iodine-1-ferrocenecarboxylic acid (356 mg, 1 mmol) in 8 mL of CH_2Cl_2 under argon was treated at ambient temperature by dropwise addition of oxalyl chloride (0.17 mL, 2 mmol) via syringe. After about 0.5 h, all gas evolution had ceased, and the solvent was directly removed into a trap. After drying for 2 h, the red solid was dissolved in 4 mL of CH_2Cl_2 under argon, and the resulting solution was transferred via cannula to a second Schlenk tube, which contained a solution of amino alcohol **8** (289 mg, 1.2 mmol) and Et_3N (0.24 mL, 1.6 mmol) in 8 mL of CH_2Cl_2. The resulting mixture was allowed to stir at rt overnight and then quenched with 20 mL of distilled water. The organic phase was separated, and the aqueous phase was extracted twice with 10 mL of CH_2Cl_2. After the combined organic phases were dried over Na_2SO_4, the solvent was removed in vacuo. The crude product was used without purification. The crude amide

was dissolved in 20 mL of acetonitrile. To this solution were added PPh_3 (0.78 g, 3 mmol), Et_3N (0.32 mL, 2.5 mmol), and CCl_4 (0.72 mL, 7.5 mmol) subsequently, and the mixture was stirred overnight. The deep red solution was worked up with 100 mL of distilled water. This mixture was extracted with hexane until the organic layer showed no orange color. The combined organic phases were dried over Na_2SO_4, the solvent was removed in vacuo. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:10) to afford the title compound (415 mg, 73%) as an orange solid: mp 45−46 °C; $[\alpha]^{20}_D = +0.4$ ($c = 0.62$ in $CHCl_3$); ^{1}H NMR δ 7.19−7.36 (m, 10H), 4.57 (m, 1H), 4.52 (m, 1H), 4.28 (t, J = 2.6 Hz, 1H), 4.15 (s, 5H), 3.90 (s, 5H), 3.17 (t, J = 13.7 Hz, 1H), 2.91 (d, J = 5.0 Hz, 1H), 2.86 (d, J = 4.9 Hz, 1H); MS (EI) m/z 561 (M^+, 28), 470 (39), 342 (100), 209 (8), 91 (82); IR (KBr, cm^{-1}) 3027 (w), 2916 (m), 1658 (s), 1454 (m), 1107 (m), 987 (m), 701 (s). Anal. Calcd for $C_{27}H_{24}FeNOI$: C, 57.80; H, 4.28; N, 2.50. Found: C, 57.86; H, 4.36; N, 2.35.

(2) (*Sp*)-2-(Diphenylphosphino)-1-(4,4-dibenzyloxazolinyl)ferrocene 11c. 2-Iodine-1-(4,4-dibenzyloxazolinyl)ferrocene (561 mg, 1 mmol) was dissolved in 15 mL of dry diethyl ether and cooled to −78 °C. *n*-BuLi (0.7 mL, 1.6 M in *n*-hexane, 1.1 mmol) was added at this temperature. The resulting mixture was stirred for 2 h, and chlorodiphenylphosphine (0.22 mL, 1.3 mmol) was added. The reaction mixture was allowed to warm to rt for 2 h, and the reaction solution was washed with distilled water (10 mL) and then with brine, dried over Na_2SO_4, and concentrated under reduced pressure to provide a residue that was purified by column chromatography with ethyl acetate/petroleum (1:10) as an eluent to afford (*Sp*)-**11c** as a yellow solid (192 mg, 31%): mp 150−151 °C; $[\alpha]^{20}_D = -31.0$ ($c = 0.42$ in $CHCl_3$); ^{1}H NMR δ 6.93−7.48 (m, 20 H), 4.77 (m, 1H), 4.29 (t, J = 2.4 Hz, 1H), 4.00 (d, J = 8.5 Hz, 1H), 3.93 (s, 5H), 3.87 (d, J = 8.4 Hz, 1H), 3.61 (m, 1H), 2.87 (d, J = 13.5 Hz, 1H), 2.80 (s, 2H), 2.65 (d, J = 13.5 Hz, 1H); ^{31}P NMR (161.92 MHz, $CDCl_3$) δ −17.33; MS m/z 619 (M^+, 73), 528 (53), 450 (22), 410 (30), 343 (100), 121 (20); IR (KBr) 2911 (w), 1655 (s), 1433 (m), 1126 (m), 986 (m), 699 (s). Anal. Calcd for $C_{39}H_{34}NOPFe$: C, 75.67; H, 5.49; N, 2.26. Found: C, 75.48; H, 5.32; N, 2.12.

(*Sp*)-2-(Diphenylphosphino)-1-(4,4-dimethyloxazolinyl)-ferrocene 11b. (*Sp*)-2-Iodine-1-(4,4-methyloxazolinyl)-ferrocene (409 mg, 1 mmol) was dissolved in 15 mL of dry diethyl ether and cooled to −78 °C. *n*-BuLi (0.7 mL, 1.6 M in *n*-hexane, 1.1 mmol) was addedat this temperature. The resulting mixture was stirred for 2 h, and chlorodiphenylphosphine (0.22 mL, 1.3 mmol) was added. The reaction mixture was allowed to warm to rt for 2 h, and the reaction solution was washed with distilled water (10 mL) and then with brine, dried over Na_2SO_4, and concentrated under reduced pressure to provide a residue that was purified by column chromatography with ethyl acetate/petroleum (1:10) as an eluent to afford compound **11b** as a yellow solid (296 mg, 63%): mp 127−128 °C; $[\alpha]^{20}_D = +81.6$ ($c = 0.57$ in $CHCl_3$); ^{1}H NMR δ 7.21−7.51 (m, 10 H), 5.02 (m, 1H), 4.37 (t, J = 2.5 Hz, 1H), 4.22 (s, 5H), 3.99 (d, J = 8.0 Hz, 1H), 3.61 (m, 1H), 3.50 (d, J = 8.0 Hz,1H), 1.20 (s, 3H), 1.15 (s, 3H); ^{31}P NMR (161.92 MHz, $CDCl_3$) δ −15.73; MS m/z 467 (M^+, 96), 411 (100), 409 (93), 318 (35), 121 (33); IR (KBr) 2964 (w), 1649 (s), 1434 (m), 1115 (m), 698 (s). Anal. Calcd for $C_{27}H_{26}NOPFe$: C, 69.44; H, 5.57; N, 3.00. Found: C, 69.08; H, 5.66; N, 2.88.

[(*S,Sp*)-2-(Phenylthio)-1-(4-*tert*-butyloxazolinyl)ferrocene]-(η^3-*trans*-1,3-diphenylallyl)palladium Hexafluoroantimonate 15. To a solution of 1,3-diphenylallylpalladium chloride dimmer (134 mg, 0.2 mmol) and **6b** (168 mg, 0.4 mmol) in MeOH/CH_2Cl_2 (v/v 1:1, 10 mL) was added silver hexafluoroantimonate (137 mg, 0.4 mmol) at rt in the absence of light. After 2 h, the reaction mixture was filtered through a 2-cm plug of Celite and washed with MeOH/CH_2Cl_2 (v/v 1:1). The filtrate was concentrated in vacuo to give Pd complex **15** (366 mg, 96%) as a red crystal: mp 238 °C dec; $[\alpha]^{20}_D = +63$ ($c = 0.15$ in $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 400 MHz) two isomers (3.1/1), major, δ 7.64 (d, J = 6.8 Hz, 2 H), 7.23−7.50 (m, 5H), 7.49 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.9 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 7.9 Hz, 2H), 6.81 (d, J = 7.2 Hz, 2H), 6.34 (dd, J_1 = 10.6 Hz; J_2 = 13.1 Hz, 1H), 5.58 (d, J = 13.1 Hz, 1H), 4.82 (dd, J_1 = 1.4 Hz; J_2 = 2.6 Hz, 1H), 4.50 (t, J = 2.7 Hz, 1H), 4.31 (dd, J = 3.5, 9.4 Hz, 1H), 4.21 (dd, J = 1.5, 2.6 Hz, 1H), 4.14 (s, 5H), 3.85 (d, J = 11.9 Hz, 1H), 3.83 (t, J = 9.4 Hz, 1H), 2.08 (dd, J = 3.4, 9.4 Hz, 1H), 0.84 (s, 9H); minor, δ 7.56 (d, J = 7.1 Hz, 2 H), 7.23−7.50 (m, 5H), 7.35 (dd, J = 7.2, 9.1 Hz, 2H), 7.25−7.30 (m, 1H), 7.20−7.24 (m, 1H), 7.09 (d, J = 7.3 Hz, 2H), 7.01 (t, J = 7.9 Hz, 2H), 6.32 (dd, J = 11.7, 13.1 Hz, 1H), 5.07 (d, J = 12.3 Hz, 1H), 4.81 (d, J = 11.2 Hz, 1H), 4.75 (m, 1H), 4.48 (t, J = 2.7 Hz, 1H), 4.28 (m, 1H), 4.24 (dd, J = 3.2, 10.1 Hz, 1H), 4.02 (s, 5H), 3.51 (t, J = 9.3 Hz, 1H), 2.71 (dd, J = 3.3, 9.3 Hz, 1H), 1.07 (s, 9H); ^{13}C NMR (CD_2Cl_2, 100 MHz) major isomers, δ 94.2 (allyl trans to S), 108.6 (central allyl), 76.5 (allyl trans to N); minor isomers, δ 86.5 (allyl trans to S), 107.0 (central allyl), 83.8 (allyl trans to N); MS (EI) m/z (rel intensity) 419 (100), 362 (43), 253 (39), 121 (42), 91 (13); IR (KBr, cm^{-1}) 2965 (w), 1627 (s), 1487 (m), 1256 (m), 1172 (m), 1028 (w), 656 (s). Anal. Calcd for $C_{38}H_{38}F_6NOSSbFePd$: C, 47.80; H, 3.98; N, 1.47; S, 3.36. Found: C, 47.69; H, 3.88; N, 1.44; S, 3.46.

[(*S,Rp*)-2-(Phenylthio)-1-(4-*tert*-butyloxazolinyl)ferrocene]-(η^3-*trans*-1, 3-diphenylallyl)palladium Hexafluoroantimonate 16. Similar procedures as for **15** from (*S,Rp*)-**7b** give complex **16** in 94% yield (0.4 mmol scale) as an orange solid: mp 248 °C dec; $[\alpha]^{20}_D = +333$ ($c = 0.58$ in $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 400 MHz) two isomers (2.2/1), major, δ 6.99−7.82 (m, 14H), 6.83 (t, J = 11.7 Hz, 1H), 5.21 (d, J = 11.9 Hz, 1H), 5.06 (dd, J = 1.5, 2.6 Hz, 1H), 4.97 (d, J = 11.5 Hz, 1H), 4.80 (m, 2H), 4.45 (s, 5H), 4.20 (dd, J = 3.1, 12.7 Hz, 1H), 3.57 (t, J = 9.3 Hz, 1H), 2.68 (dd, J = 3.1, 9.1 Hz, 1H), 0.61 (s, 9H); minor, δ 6.99−7.82 (m, 13H), 6.77 (dd, J = 11.0, 12.9 Hz, 1H), 6.08−6.10 (m, 2H), 5.67 (d, J = 12.8 Hz, 1H), 5.17 (dd, J = 1.5, 2.8 Hz, 1H), 5.06 (d, J = 10.7 Hz, 1H), 4.96−4.97 (m, 1H), 4.88 (dd, J = 2.7, 2.9 Hz, 1H), 4.66 (s, 5H), 4.22 (dd, J = 3.1, 10.0 Hz, 1H), 3.96 (t, J = 9.2 Hz, 1H), 2.17 (dd, J = 3.1, 9.0 Hz, 1H), 0.28 (s, 9H); ^{13}C NMR (CD_2Cl_2, 100 MHz) major isomers, δ 86.8 (allyl trans to S), 107.0 (central allyl), 81.9 (allyl trans to N); minor isomers, δ 92.2 (allyl trans to S), 105.5 (central allyl), 75.3 (allyl trans to N); MS (EI) m/z (rel intensity) 419 (100), 362 (26), 193 (96), 186 (16), 121 (42); IR (KBr, cm^{-1}) 2957 (w), 1626 (s), 1486 (m), 1181 (m), 988 (m), 657 (s). Anal. Calcd for $C_{38}H_{38}F_6NOSSbFePd$: C, 47.80; H, 3.98; N, 1.47; S, 3.36. Found: C, 47.64; H, 4.17; N, 1.30; S, 3.53.

[(*Sp*)-2-(Phenylthio)-1-(4, 4-dibenzyloxazolinyl)ferrocene]-(η^3-*trans*-1, 3-diphenylallyl)palladium Hexafluoroantimonate 17. By using (*Sp*)-**5c** and similar procedures as for **15** give the title compound in 94% yield (0.4 mmol scale) as a red solid. After slowly crystallized from hexane/dichloromethane/ethyl acetyl ester give **30**·EtOAc as a dark-red crystal: mp136−138 °C; $[\alpha]^{20}_D = +16.5$ ($c = 0.41$ in $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.19−7.67 (m, 27H), 6.55 (m, 1H), 4.76 (br, 1H), 4.61−4.63 (m, 2H), 4.34 (s, 5H), 4.22 (d, J = 9.3 Hz, 1H), 4.07 (d, J = 9.6 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H), 3.00 (br, 1H), 2.61 (br, 2H), 2.38 (br, 1H), 1.99 (s, 1H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CD_2Cl_2, 100 MHz) major isomers, δ 171.5, 135.9, 131.4, 131.0, 130.8, 130.7, 129.5, 129.4, 128.1, 106.1, 78.1, 77.8, 74.6, 73.4, 73.2; MS (EI) m/z (rel intensity) 753 (23), 543 (72), 452 (61), 218 (100), 91 (60); IR (KBr, cm^{-1}) 3028 (w), 1727 (m), 1612 (s), 1479 (m), 1251 (m), 657 (s). Anal. Calcd for $C_{48}H_{42}F_6NOSSbFePd$·EtOAc: C, 53.52; H, 4.29; N, 1.20; S, 2.74. Found: C, 53.27; H, 4.32; N, 1.20; S, 2.81.

[(*S,Sp*)-2-(Diphenylphosphino)-1-(4-*tert*-butyloxazolinyl)-ferrocene]-(η^3-*trans*-1,3-diphenylallyl)palladium Hexafluoroantimonate 18. Similar procedures as for **15** give the title compound in 96% yield (0.4 mmol scale) as an orange solid: mp 256−258 °C; $[\alpha]^{20}_D = -186$ ($c = 0.48$ in $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 400 MHz) two isomers (8.8/ 1), major, δ 6.70−7.72 (m, 20H), 6.47 (dd, J = 10.9, 13.5 Hz, 1H), 5.84 (dd, J =

8.1, 14.0 Hz, 1H), 5.15 (s, 1H), 4.83 (s, 1H), 4.51 (s, 1H), 4.36 (dd, J = 3.7, 9.2 Hz, 1H), 4.01 (t, J = 9.4 Hz, 1H), 3.71 (s, 5H), 3.44 (d, J = 10.3 Hz, 1H), 2.60 (dd, J = 3.2, 9.3 Hz, 1H), 0.87 (s, 9H); minor, δ 6.70−8.12 (m, 20H), 6.41 (dd, J = 7.6, 11.9 Hz, 1H), 6.14 (t, J = 11.9 Hz, 1H), 5.17 (m, 1H), 5.07 (d, J = 7.6 Hz, 1H), 5.05 (s, 1H), 4.74 (m, 1H), 4.33−4.38 (m, 1H), 3.78 (s, 5H), 3.59 (t, J = 9.3 Hz, 1H), 3.15 (dd, J = 3.2, 9.3 Hz, 1H), 1.11 (s, 9H); ^{31}P NMR (161.92 MHz, $CDCl_3$) δ 17.1 (major), 20.8 (minor); ^{13}C NMR (CD_2Cl_2, 100 MHz) major isomers, δ 104.4 (allyl trans to P), 111.3 (central allyl), 69.9 (allyl trans to N); minor isomers, δ 109.6 (allyl trans to P), 111.1 (central allyl), 74.4 (allyl trans to N); MS (EI) *m*/*z* (rel intensity) 495 (6), 368 (6), 193 (100), 115 (24), 91 (6); IR (KBr, cm^{-1}) 2962 (w), 1619 (s), 1482 (w), 1439 (m), 1175 (m), 1104 (m), 657 (s). Anal. Calcd for $C_{44}H_{43}F_6NOPSbFePd$: C, 51.27; H, 4.17; N, 1.36. Found: C, 51.23; H, 4.15; N, 1.40.

[(*S*,*Rp*)-2-(Diphenylphosphino)-1-(4-*tert*-butyloxazolinyl)-ferrocene]-(η^3-*trans*-1,3-diphenylallyl)palladium Hexafluoroantimonate 19. Similar procedures as for **15** give the title compound in 98% yield (0.4 mmol scale) as an orange solid: mp 267−269 °C; $[\alpha]^{20}_D$ = +490 (c = 0.19 in $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 400 MHz) two isomers (7.1/1), major, δ 7.04−7.74 (m, 18H), 6.69 (dd, J = 10.3, 14.0 Hz, 1H), 6.48 (dd, J = 7.5, 11.7 Hz, 2H), 6.04 (dd, J = 8.2, 14.0 Hz, 2H), 5.22 (s, 1H), 4.86 (t, J = 2.5 Hz, 1H), 4.69 (d, J = 10.3 Hz, 2H), 4.57 (s, 5H), 4.19 (dd, J = 3.1, 9.4 Hz, 1H), 4.12 (m, 1H), 3.86 (dd, J = 9.2, 9.4 Hz, 1H), 2.21 (dd, J = 3.1, 9.2 Hz, 1H), 0.31 (s, 9H); minor, δ 6.98−7.74 (m, 20H), 6.89 (m, 1H), 5.31 (m, 1H), 5.21 (m, 1H), 5.11 (m, 1H), 4.76 (t, J = 2.6 Hz, 1H), 4.41 (s, 5H), 4.17 (dd, J = 3.0, 9.3 Hz, 1H), 3.89 (m, 1H), 3.50 (dd, J = 9.3, 9.2 Hz, 1H), 3.13 (dd, J = 3.0, 9.2 Hz, 1H), 0.50 (s, 9H); ^{31}P NMR (161.92 MHz, $CDCl_3$) δ 15.7 (major), 20.1 (minor); ^{13}C NMR (CD_2Cl_2, 100 MHz) major isomers, δ 103.7 (allyl trans to P), 132.9 (central allyl), 66.3 (allyl trans to N); minor isomers, δ 94.0 (allyl trans to P), 108.8 (central allyl), 78.0 (allyl trans to N); MS (EI) *m*/*z* (rel intensity) 687 (5), 495 (23), 336 (26), 203 (69), 165 (100); IR (KBr, cm^{-1}) 2956 (w), 1622 (s), 1546 (w), 1484 (m), 1435 (m), 1179 (m), 1099 (w), 756 (m), 658 (s). Anal. Calcd for $C_{44}H_{43}F_6NOPSbFePd$: C, 51.27; H, 4.17; N, 1.36. Found: C, 50.91; H, 4.15; N, 1.33.

[(*Sp*)-2-(Diphenylphosphino)-1-(oxazolinyl)ferrocene]-(η^3-*trans*-1,3-diphenylallyl)palladium Hexafluoroantimonate 20. Similar procedures as for **15** give the title compound in 96% yield (0.4 mmol scale) as an orange solid: mp 266 °C dec; $[\alpha]^{20}_D$ = −494.4 (c = 0.35 in $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 400 MHz) two isomers (2.8/1), major, δ 6.92−7.78 (m, 18H), 6.57 (t, J = 11.7 Hz, 1H), 6.22 (dd, J = 8.0, 11.1 Hz, 2H), 5.84 (dd, J = 8.2, 10.1 Hz, 2H), 5.13 (s, 1H), 4.82 (d, J = 11.1 Hz, 1H), 4.74 (s, 1H), 4.18−4.33 (m, 3H), 4.15 (s, 5H), 3.25 (dd, J = 10.3, 20.7 Hz, 1H), 2.96 (dd, J = 10.2, 20.9 Hz, 1H); minor, δ 6.78 (t, J = 11.1 Hz, 1H, central allylic proton), 5.47 (dd, J = 10.3, 11.1 Hz, 1H, allylic proton trans to P), 4.69 (d, J = 11.1 Hz, 1H, allylic proton trans to N); ^{31}P NMR (161.92 MHz, $CDCl_3$) δ 16.9 (major), 17.9 (minor); ^{13}C NMR (CD_2Cl_2, 100 MHz) major isomers, δ 100.6 (allyl trans to P), 112.1 (central allyl), 71.1 (allyl trans to N); minor isomers, δ 96.3 (allyl trans to P), 111.5 (central allyl), 75.5 (allyl trans to N); MS (EI) *m*/*z* (rel intensity) 683 (23), 611 (7), 541 (12), 399 (100), 326 (20), 242 (24); IR (KBr, cm^{-1}) 3055 (w), 1629 (s), 1482 (w), 1438 (m), 1309 (w), 1177 (s), 1102 (m), 996 (m), 660 (s). Anal. Calcd for $C_{40}H_{35}F_6NOPSbFePd$: C, 46.55; H, 3.34; N, 1.32. Found: C, 46.52; H, 3.56; N, 1.18.

General Procedure for the Palladium-Catalyzed Allylic Substitutions of *rac*-1,3-Diphenyl-2-propenyl Acetate. $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.7 mg, 0.01 mmol) and the proper ligand (0.03 or 0.04 mmol) were dissolved in dry CH_2Cl_2 (2 mL), and the mixture was stirred for 30 min at rt under an atmosphere of argon. To this solution were successively added *rac*-1, 3-diphenyl-2-propenyl acetate (126 mg, 0.5 mmol), dimethylmalonate (0.17 mL, 1.5 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.37 mL, 1.5 mmol), and lithium acetate or Potassium acetate (0.015 mmol). The reaction mixture was stirred at rt and monitored by TLC. After completion, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed twice with ice-cold saturated aqueous ammonium chloride. The organic phase was dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by preparative TLC (EtOAc/petroleum ether = 1/15) to give the pure product. The enantiomeric purities were determined by HPLC analysis (Chiracel OD column, hexane/2-propanol (80:20); flow rate = 0.7 mL/min; t_R = 18.7 min, t_S = 20.4 min).

General Procedure for the Palladium-Catalyzed Allylic Amination of *rac*-1,3-Diphenyl-2-propenyl Acetate. $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.7 mg, 0.01 mmol) and ligand (0.04 mmol) were dissolved in dry THF (2 mL), and the mixture was stirred for 30 min at rt under an atmosphere of argon. To this solution were successively added *rac*-1,3-diphenyl-2-propenyl acetate (126 mg, 0.5 mmol), $BnNH_2$ (0.11 mL, 1.0 mmol), and TBAF (1 M in THF, 1 mL, 1 mmol). The reaction mixture was stirred at 50 °C and monitored by TLC. After completion, the reaction mixture was diluted with Et_2O (20 mL) and washed twice with ice-cold saturated aqueous ammonium chloride. The organic phase was dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by preparative TLC (EtOAc/petroleum ether = 1:10) to give the pure product. The enantiomeric purities were determined by HPLC analysis (Chiracel OJ column, hexane/2-propanol (87:13); flow rate = 0.6 mL/min; t_S = 20.3 min, t_R = 24.3 min).

Acknowledgment. This research was financially supported by the Major Basic Research Development Program (Grant No. G2000077506), National Natural Science Foundation of China, National Outstanding Youth Fund, Chinese Academy of Sciences, and Shanghai Committee of Science and Technology.

Supporting Information Available: ORTEP drawings andX-ray crystallographic files (CIF) of compounds **15**, **17**, **19**, and **20** and selected bond distances and angles for compound **15**, **17**, **19**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016330Z