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Synthesis of novel P-ketimine bidentate ferrocenyl ligands with central and planar chirality and comparsion in the catalytic activity between P-ketimine and P-aldimine

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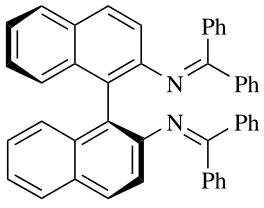
Abstract—A series of novel ferrocenylphosphine-ketimine ligands **6** were prepared by reaction of (R,S_p)-$PPFNH_2$-R or (S,S_p)-$PPFNH_2$ with a variety of *m*-substituted acetophenones. A different catalytic activity was observed between ferrocenylphosphine-ketimine ligands and corresponding aldimine ligands. The efficiency and diastereomeric impact of these ferrocenylphosphine-ketimine ligands in Pd-catalyzed asymmetric allylic alkylation were first investigated, and higher enantioselectivity of over 98% e.e. with 95% yield was obtained by the use of ferrocenylphosphine-ketimine ligands. However, in Rh-catalyzed asymmetric hydrosilylation of aryl ketones, only 42% e.e. was obtained by the use of ferrocenylphosphine-ketimine ligands compared to 90% e.e. with the use of aldimine ligands.

1. Introduction

Chiral *P*,*N*-ligands have been found widespread application in a variety of asymmetric catalysis in past decade.[1] As an important class of *P*,*N*-ligands, chiral phosphine-imine compounds have been attracting considerable attention recently since they are easily prepared and readily modified in electronic and steric properties. Recently, many fine-tuned chiral phosphine-imine based ligands have been found to be very effective in a variety of asymmetric catalytic reactions.[2] Recently, we have reported the application of some ferrocenylphosphine-imine ligands from (R,S_p)-$PPFNH_2$ and a variety of benzaldehydes, and found that ligands with *m*-electron-withdrawing substitutents tended to give higher catalytic activities and enantioselectivities in Pd-catalyzed asymmetric allylic alkylation.[3] Compared to the extensive application of aldimine ligands derived from aldehydes and primary amines, there are few reports on the synthesis of ketimine ligands from ketones and primary amines for asymmetric catalysis partly due to the difficult synthesis and instability of ketimine compounds.[4] However, the introduction of an alkyl or aryl group into the methylene moiety of aldimines could significantly affect the electronic and steric effect of the chiral ligand, which would lead to the dramatic changes in the reactivity and enantioselectivity of the catalytic reaction. Therefore, the investigation into the difference between aldimines and ketimines in catalytic activity is very meaningful for the design of efficient ligands for a variety of asymmetric catalysis.



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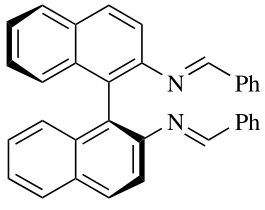

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Recently, Reetz and Angermund have reported the C_2-symmetric diketimines **1** and C_2-symmetric dialdimines **2** exhibited different reactivity and enantioselectivity in Pd–catalyzed asymmetric allylic alkylation.[4b] The Pd-complex derived from the diketimine **1** turned out to be a reasonably active catalyst, affording the allylic alkylation product in 78% yield with an e.e.-value of 92%, while the Pd-complex derived from the dialdimine **2** surprisingly showed no activity what-

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soever. This interesting result stimulated us to develop a series of novel ferrocenylphosphine-ketimine ligands and investigate the different reactivity and enantioselectivity between ferrocenylphosphine-ketimine and its aldimine analogues in catalytic asymmetric reaction. To the best of our knowledge, no reports have focused on the difference between P-aldimines and P-ketimines in the catalytic reaction before us.

In order to investigate the impact of diastereomeric ferrocenyl ligands in the catalytic asymmetric reactions, the synthesis of (S,S_p)-PPFNH$_2$ and its imine derivatives was carried out, and their efficiency in the catalytic reaction was also examined.

2. Results and discussion

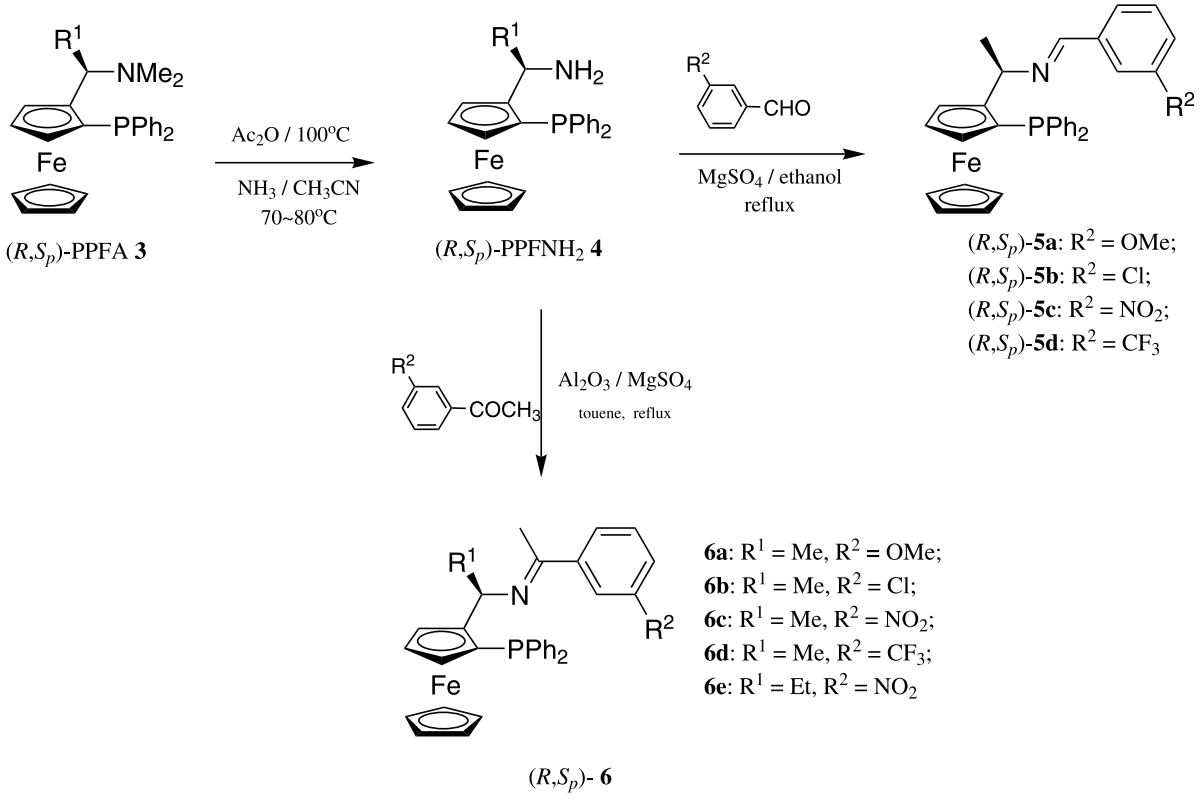
2.1. Synthesis of ferrocenylphosphine-aldimine 5 and P-ketimine ligands 6

The novel ferrocenylphosphine-ketimine ligands **6** were synthesized according to Scheme 1. As we have reported previously, the ferrocenylphosphine-aldimine **5** could be easily prepared in high yields from ferrocenylphosphine-amines **4** [(R,S_p)-PPFNH$_2$][5] with *m*-substituted benzaldehydes in refluxing ethanol in the presence of anhydrous MgSO$_4$.[3] However, compared to the easy synthesis of aldimines, the preparation of corresponding ferrocenylphosphine-ketimine **6** is more difficult. Under the same reaction conditions, no ferrocenylphosphine-ketimine products **6** were obtained by the reaction of PPFNH$_2$-R **4** with aryl alkyl ketones. The target ketimine compounds can be prepared when the reaction of PPFNH$_2$-R **4** with a variety of *m*-substituted acetophenones was carried out in the presence of active Al_2O_3, however, the yield was relatively low and no target compounds were obtained over 50% yield even after 2 days in refluxing toluene. It is fortunate that this difficulty can be easily resolved when a complex system of active Al_2O_3 and anhydrous MgSO$_4$ was used in synthetic reaction, and the reaction gave the target ferrocenylphosphine-ketimine ligands **6** in reasonable yields. However, an attempt to synthesize the ketimines from other ketones failed. All of these phosphine-imine ligands have the (R,S_p)-configurations.

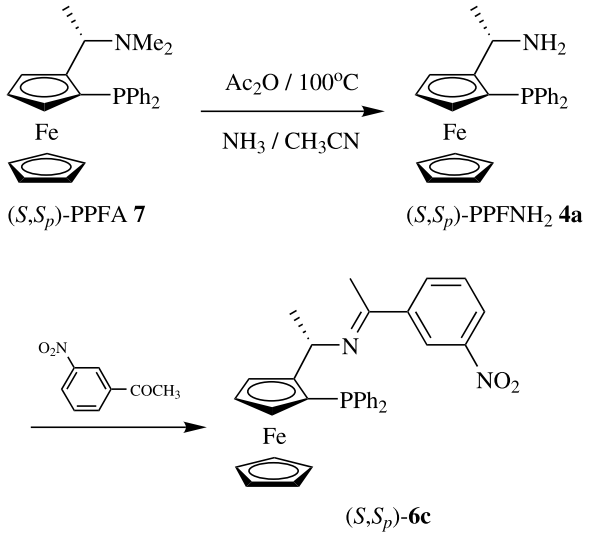
To examine the effect of diastereomeric ligands on the catalytic reactions, the corresponding ferrocenylphosphine-imine ligands (S,S_p)-**6c** was prepared in 57% yield in the same manner by employing (S,S_p)-PPFA as illustrated in Scheme 2.[6,7]

2.2. Catalytic activities of P-aldimine ligands 5 and P-ketimine ligands 6 in Pd-catalyzed asymmetric allylic alkylation

Palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenylprop-2-en-1-yl pivalate **8** with dimethyl malonate was first investigated using standard condition reported previously (Eq. (1)).[8] The results were summarized in Table 1.



Scheme 1. Synthesis of ferrocenylphosphine-imine ligands (R,S_p)-**5** and (R,S_p)-**6**.



Scheme 2. Synthesis of ketimine (S,S_p)-**6c**.

As we have reported previously, all of these *meta*-substituted ferrocenylphosphine-aldimines exhibited good catalytic activity and enantioselectivity (entries 1–4), and up to 94% e.e. with 99% yield was obtained by the use of *m*-NO_2 substituted ligand **5c** (entry 3). When a methyl group was introduced into the benzylidene position of the ferrocenylphosphine-aldimine skeleton, the resulting ketimine ligands chelated with Pd to form a more sterically encumbered catalyst, which was expected to exhibit lower catalytic activity. However, as shown in Table 1, all of the ferrocenylphosphine-ketimine ligands **6** from (R,S_p)-PPFNH_2-R and *meta*-substituted acetophenones surprisingly gave the allylic alkylation product **9a** in good yield and e.e. (entries 5-9). Compared to their aldimine analogues **5**, ketimine ligands **6** with a methyl group in benzylidene position exhibited higher enantioselectivity (entries 1–4 versus entries 5–8). When ketimine ligand **6e** was used, the best result was obtained in over 98% e.e. and 95% yield (entry 9). This result was consistent with that reported by Reetz based on C_2-symmetric diimine **1** and **2**. The reason why a sterically encumbered catalyst show higher activity than the seemingly less shielded homologue are explained by Reetz et al. based on the AMS model. This can be traced to a 'locking-in' effect of the phenyl group in **6**/Pd, in contrast, the phenyl group of **5**/Pd rotates much more freely, resulting in considerably enhanced steric shielding. The configuration of allylic alkylation product **9a** from these reactions was proved to be *S* by comparing the specific rotation with the literature values.[9] When diethyl methylmalonate instead of dimethyl malonate was used as the nucleophile, P-ketimine ligand **6c** also exhibited higher enantioselectivity than the corresponding P-aldimine **5c** (entry 11 versus entry 10), and up to 98% e.e.-value of allylic product **9b** was obtained (entry 11).

We next investigated the impact of diastereomeric ferrocenyl ligands on the palladium-catalyzed asymmetric allylic alkylation. Compared to (R,S_p)-**6c**, (S,S_p)-**6c** showed lower enantioselectivity but gave the alkylation product **9a** with the same configuration (entry 7 versus

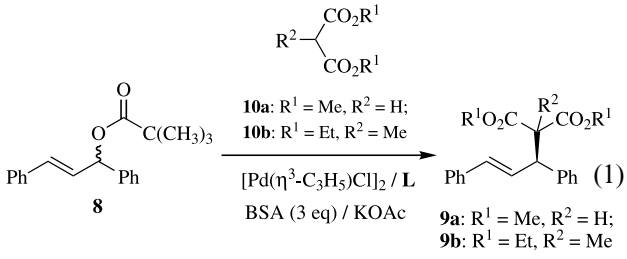


Table 1. Asymmetric allylic alkylation of 1,3-diphenylprop-2-en-1-yl pivalate **8** and cyclohexenyl acetate **11** using ligand **5** and **6**[a]

Entry	Ligand	Substrate	Nucleophile	Yield (%)[b]	E.e. (%)[c] config.[d]
1	(R,S_p)-**5a**	**8**	**10a**	98	90 (*S*)
2	(R,S_p)-**5b**	**8**	**10a**	95	90 (*S*)
3	(R,S_p)-**5c**	**8**	**10a**	99	94 (*S*)
4	(R,S_p)-**5d**	**8**	**10a**	94	91 (*S*)
5	(R,S_p)-**6a**	**8**	**10a**	91	93 (*S*)
6	(R,S_p)-**6b**	**8**	**10a**	90	93 (*S*)
7	(R,S_p)-**6c**	**8**	**10a**	94	98 (*S*)
8	(R,S_p)-**6d**	**8**	**10a**	90	92 (*S*)
9	(R,S_p)-**6e**	**8**	**10a**	95	>98 (*S*)
10	(R,S_p)-**5c**	**8**	**10b**	89	96[e]
11	(R,S_p)-**6c**	**8**	**10b**	91	98[e]
12	(S,S_p)-**6c**	**8**	**10a**	91	88 (*S*)
13	(R,S_p)-**5c**	**11**	**10a**	81	83[f]
14	(R,S_p)-**6c**	**11**	**10a**	95	62[f]

[a] The reactions were carried out in toluene in the present of 2.0 mol% $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 5.0 mol% of chiral ligand, 3.0 equiv. of dimethyl malonate or diethyl methylmalonate, 3.0 equiv. of BSA and a catalytic amount of KOAc at rt

[b] Isolated yields.

[c] Determined by HPLC analysis using a chiralpak AD column (eluent:hexane: 2-propanol = 90: 10, 1.0 mL/min).

[d] The *S*-configuration was confirmed by comparing the specific rotation with a literature value.[9]

[e] Determined by HPLC analysis using a chiralpak AD column (eluent:hexane: 2-propanol = 97.5:2.5, 0.5 mL/min).

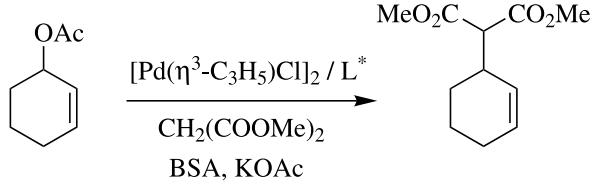
[f] Determined by GC analysis using a β-390 sationary capillary column.

Table 2. Asymmetric hydrosilylation of acetophenone **13** using ligand **5** and **6**[a]

Entry	Ligand	Yield (%)[b]	E.e. (%)[c] config.[d]
1	(R,S_p)-**5a**	92	90 (*R*)
2	(R,S_p)-**5b**	90	80 (*R*)
3	(R,S_p)-**5c**	89	81 (*R*)
4	(R,S_p)-**5d**	90	90 (*R*)
5	(R,S_p)-**6a**	76	42 (*R*)
6	(R,S_p)-**6b**	71	38 (*R*)
7	(R,S_p)-**6c**	59	29 (*R*)
8	(R,S_p)-**6d**	74	40 (*R*)
9	(R,S_p)-**6e**	54	31 (*R*)
10	(S,S_p)-**6c**	51	26 (*R*)

[a] The reaction was carried out in 2.0 mL of THF in the presence of $[Rh(NBD)Cl]_2$ (0.01 mmol), ligand (0.03 mmol), acetophenone (2.0 mmol), Ph_2SiH_2 (2.5 mmol).
[b] Isolated yield.
[c] Determined by GC analysis with a capillary chiral column (cyclodex-β,2-,3-,6-methylated, 30 m×0.25 mm (i.d.)).
[d] The absolute configuration was determined by comparison of the retention time of the enantiomers on the GC analysis with literature values.

entry 12). This result indicated that (*R*)-central chirality and (S_p)-planar chirality were matched in these ferrocenylphosphine-imine ligands for the palladium-catalyzed asymmetric allylic alkylation.



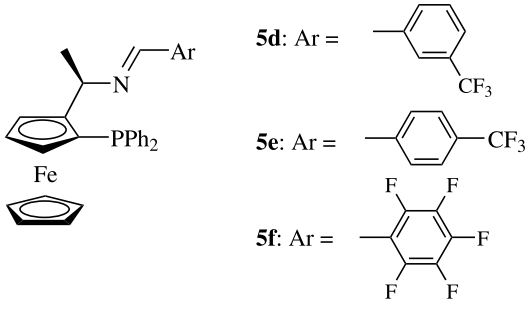
(2)

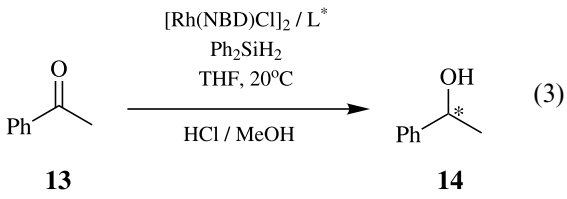
11 **12**

In order to show the validity of the developed ligands, the applications to other substrates such as cyclohexenyl acetate were then investigated. Although the Pd-catalyzed asymmetric allylic alkylation of acyclic substrates is one of the most thoroughly investigated C–C bond forming reactions, the corresponding substitution of cycloalkenyl esters is still a major challenge.[10] The reaction of cyclohexenyl acetate **11** with dimethyl malonate was catalyzed by **5**/Pd and **6**/Pd complexes to give the dimethyl (cyclohexen-2-yl)malonate **12** (Eq. (2)). The results, summarized in Table 1 (entries 13 and 14), indicated that the more effective ligand in this reaction was the ferrocenylphosphine-aldimine ligand **5c**, and up to 83% e.e. of allylic product **12** was achieved, which was in contrast to the results obtained in the alkylation of 1,3-diphenylprop-2-en-1-yl pivalate **8**.

2.3. Catalytic activity of P-aldimine ligands 5 and P-ketimine ligands 6 in Rh-catalyzed asymmetric hydrosilylation of acetophenone

We next examined the difference in catalyst activity between the chiral ferrocenylphosphine-aldimine ligands **5** and ketimine ligands **6** in the Rh-catalyzed asymmetric hydrosilylation of acetophenone.[11] In 1995, Hayashi et al. reported that ferrocenylphosphine-aldimine ligands **5d–f** were very effective ligands for rhodium-catalyzed asymmetric hydrosilylation of prochiral ketones.[5a] On the basis of the good results obtained in Pd-catalyzed asymmetric allylic alkylation by the use of ferrocenylphosphine-ketimine ligands, we then presumed that these P-ketimine ligands are perphaps more effective ligands than corresponding aldimine for Rh-catalyzed asymmetric hydrosilylation of prochiral ketones. However, the results obtained by the use of ferrocenylphosphine-ketimine ligands **6** are very depressed, and the reaction gave the chiral alcohol with unexpectedly low enantioselectivity compared to the corresponding aldimine **5**.





(3)

13 **14**

As shown in Table 2, all of ferrocenylphosphine-aldimine ligands **5** exhibited good catalytic activity (entries 1–4), and up to 90% e.e. was obtained by the use of ligands **5a** and **5d** (entries 1 and 4). Compared to the results obtained in Pd-catalyzed asymmetric allylic alkylation, where ferrocenylphosphine-ketimines **6** exhibited higher enantioselectivity than their aldimine analogues **5**, extremely low enantioselectivity was obtained in the Rh-catalyzed asymmetric hydrosilylation by the use of ketimine ligands **6** (entries 1–4 versus entries 5–8). Only 42% e.e. was observed by the use of ketimine ligand **6a**, compared to an e.e.-value of 90% with the corresponding aldimine **5a** (entry 5 versus entry 1). The reason why ketimine **6** and aldimine **5** showed dramatically different activity can be rationalized by mechanistic studies on the stereochemistry and reaction course of Rh-catalyzed hydrosilylation by Brunner et al.[12] Using ketimine **6** as cocatalyst, the methyl group in the benzylidene position blocked the coordination site by a steric interaction. Therefore, the complex of substrate with the central metal and subsequent addition of Ph_2SiH_2 to rhodium atom was limited, which resulted in the low enantioselectivity and reactivity.

In addition, the impact of diastereomeric ferrocenyl ligands on the rhodium-catalyzed asymmetric hydrosilylation was also examined, and the experimental data showed that the combination of (*R*)-central chirality and (S_p)-planar chirality in these ferrocenylphosphine-

imine ligands were also advantageous to the catalytic reaction. The configuration of alcohol product **14** from these reactions was proved to be *R*.

3. Conclusion

In conclusion, we have developed a series of new ferrocenylphosphine-ketimine ligands **6** and investigated the difference in the catalytic activity between P-ketimines and P-aldimines in asymmetric catalysis. An extreme difference in catalytic activity between aldimine ligands 5 and ketimine ligands **6** was observed. In Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenylprop-2-en-1-yl pivalate **8**, ferrocenylphosphine-ketimine ligands **6** exhibited higher enantioselectivity than the corresponding aldimine ligands **5**. When *m*-NO_2 substituted ketimine ligand **6e** was used in the test reaction, over 98% e.e. with 95% yield of allylic alkylation product was obtained. However, in Pd-catalyzed asymmetric allylic alkylations of cyclohexenyl acetate, the more effective ligand was the ferrocenylphosphine-aldimine ligand **5c**, and up to 83% e.e. was achieved. While in Rh-catalyzed asymmetric hydrosilylation of prochiral ketones, ferrocenylphosphine-ketimine ligands **6** gave lower enantioselectivity, only 42% e.e. of alcohol was obtained. This research also indicated that (*R*)-central chirality and (S_p)-planar chirality in these ferrocenylphosphine-ketimine ligands were matched for the test reactions. Further application and modification of ligands are in progress.

4. Experimental

4.1. General methods

Melting points were measured on a Yazawa micro melting point apparatus (uncorrected). Optical rotations were measured on a HORIBA SEPA-200 high sensitive polarimeter. The ^{1}H NMR spectra were recorded on a BRUKER DRX 400 system with TMS as an internal standard. The ^{31}P NMR spectra were recorded using a BRUKER DRX 400 system with 85% phosphoric acid as the external standard. Enantiomeric excesses (% e.e.) were determined by HPLC (Agilent 1100 series) analysis. All experiments were carried out under an argon atmosphere. All solvents were dried using standard procedures. 1,3-Diphenylprop-2-en-1-yl pivalate **8** was derived from the reaction of 1,3-diphenylprop-2-en-1-ol with pivaloyl chloride in pyridine. **4** and **7** were synthesized following the literature method.

4.2. General procedure for the synthesis of (R,S_p)-ferrocenylphosphine-ketimine 6

To a solution of (R,S_p)-PPFNH$_2$-R **4** (1.0 mmol) in toluene (8.0 mL) were added the corresponding acetophenones (1.0 mmol), active Al_2O_3 (500 mg) and anhydrous $MgSO_4$ (200 mg). The reaction mixture was heated to reflux. After the reaction was complete (detected by TLC after 24 h), the reaction mixture was diluted with toluene. $MgSO_4$ and Al_2O_3 were removed by filtration and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography.

4.2.1. (*R*)-*N*-[1-(3-Methoxyphenyl)ethylidene]-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine 6a. Recrystallized from *n*-hexane to afford orange needle solid; 54.8% yield; mp 130–131°C; $[\alpha]_D^{25}=-351$ (*c* 0.10, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 1.44 (d, $J=6.4$ Hz, 3 H), 2.07 (s, 3 H), 3.69 (s, 3 H), 3.69 (s, 1 H), 4.02 (s, 5 H), 4.38 (s, 1 H), 4.66 (s, 1 H), 4.99–5.00 (m, 1 H), 6.82–7.52 (m, 14 H); ^{31}P NMR δ −21.4. HRMS calcd for $C_{33}H_{32}NOPFe$ 545.1570, found 545.1569.

4.2.2. (*R*)-*N*-[1-(3-Chlorophenyl)ethylidene]-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine 6b. Orange viscous liquid; 57.6% yield; $[\alpha]_D^{25}=-366$ (*c* 0.13, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.57 (d, $J=6.8$ Hz,3 H), 2.16 (s, 3 H), 3.73 (s, 1 H), 4.06 (s, 5 H), 4.32 (s, 1 H), 4.67–4.68 (m, 1 H), 5.12–5.13 (m, 1 H), 6.85–7.48 (m, 14 H); ^{31}P NMR δ −28.0. HRMS calcd for $C_{32}H_{29}ClNPFe$ 549.1075, found 549.1072.

4.2.3. (*R*)-*N*-[1-(3-Nitrophenyl)ethylidene]-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine 6c. Recrystallized from *n*-hexane to afford brown needle solid; 51.6% yield; mp 132–133°C; $[\alpha]_{25}^{D}=-381$ (*c* 0.13, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 1.47 (d, $J=6.6$, 3 H), 2.23 (s, 3 H), 3.67 (s, 1 H), 4.07 (s, 5 H), 4.39 (s, 1 H), 4.70 (s, 1 H), 5.08–5.12 (m, 1 H), 6.73–8.11 (m, 14 H); ^{31}P NMR δ −19.8. HRMS calcd for $C_{32}H_{29}N_2O_2PFe$ 560.1311, found 560.1292.

4.2.4. (*R*)-*N*-[1-(3-Trifluoromethylphenylethylidene]-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine 6d. Orange viscous liquid; 49.5% yield; $[\alpha]_D^{25}=-348$ (*c* 0.11, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 1.55 (d, $J=4.0$ Hz, 3 H), 2.59 (s, 3 H), 3.72 (s, 1 H), 4.06 (s, 5 H), 4.26 (s, 1 H), 4.68 (s, 1 H), 5.08–5.09 (m, 1 H), 6.94–7.91 (m, 14 H); ^{31}P NMR δ −28.0. HRMS calcd for $C_{33}H_{29}F_3NPFe$ 583.1339, found 583.1337.

4.2.5. (*R*)-*N*-[1-(3-Nitrophenyl)ethylidene]-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]propylamine 6e. Orange foam solid; 61.2% yield; $[\alpha]_D^{25}=-369$ (*c* 0.11, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 0.83 (t, $J=7.2$ Hz, 3 H), 1.81–1.86 (m, 1 H), 2.20 (s, 3 H), 2.25–2.30 (m, 1 H), 3.63 (s, 1 H), 4.07 (s, 5 H), 4.39 (s, 1 H), 4.68 (s, 1 H), 4.84–4.86 (m, 1 H), 6.75–8.12 (m, 14 H); ^{31}P NMR δ −22.1. HRMS calcd for $C_{33}H_{31}N_2O_2PFe$ 574.1472, found 574.1474.

4.3. Synthesis of (S,S_p)-ferrocenylphosphine-ketimine

4.3.1. Synthesis of (*S*)-1-[(*S*)-2-(diphenylphosphino)-ferrocenyl]ethylamine 4a. The amine **7** (2.0 mmol) was sealed in an air-free tube with acetic anhydride (1.5 mL). The tube was heated to 100°C for 2 h. After cooled to rt, the reaction mixture was poured into 50 mL of 10% aqueous potassium carbonate with vigorous stirring. Oil material was extracted with Et_2O (20 mL× 2). The ether extract was successively washed with 2 M

HCl, 5% K_2CO_3, and water, and dried over Na_2SO_4. The solvent was removed under reduced pressure, the residue was dissolved in a solution of 10 mL 25% aqueous ammonia in 20 mL of CH_3CN. The mixture was then placed in a 100 mL autoclave and heated at 80°C for 8 h. The reaction mixture was diluted with 10 mL of CH_2Cl_2, and the solvent was evaporated. The residue was extracted with CH_2Cl_2 (10 mL×2) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel modified by 2% Et_3N, elution by hexanes:ethyl acetate:Et_3N, 20:10:1 to 10:20:1) to give 443 mg (53.6% yield) of (*S*)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]-ethylamine [(S,S_p)-**4a**] as an orange crystals. mp 127–128°C; $[\alpha]_D^{25} = -341$ (*c* 0.11, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 0.78 (d, $J = 6.4$ Hz, 3 H), 3.34 (br, 2 H), 3.72 (s, 1 H), 4.02 (s, 1 H), 4.02 (s, 5 H), 4.31 (s, 1 H), 4.60 (s, 1 H), 7.10–7.13 (m, 2 H), 7.25–7.29 (m, 3 H), 7.43 (s, 3 H), 7.50–7.52 (m, 2 H); ^{31}P NMR δ −23.2.

4.3.2. (*S*)-*N*-[1-(3-nitrophenyl)ethylidene]-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine 6c. Yellow solid; 57.1% yield; mp 147–149°C; $[\alpha]_D^{25} = -31.2$ (*c* 0.076, $CHCl_3$); ^{1}H NMR (DMSO-d^6) δ 0.96 (d, $J = 6.4$ Hz, 3 H), 2.38 (s, 3 H), 3.70 (s, 1 H), 3.90 (s, 5 H), 4.41 (s, 1 H), 4.81 (s, 1 H), 4.88–4.91 (m, 1 H), 7.16–8.81 (m, 14 H); ^{31}P NMR δ −22.5. HRMS calcd for $C_{32}H_{29}N_2O_2PFe$ 560.1311, found 560.1302.

4.4. General procedure for asymmetric allylic alkylations

A solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.7 mg, 0.01 mmol) and chiral ferrocenylphosphine-ketimine **6** or phosphine-aldimine **5** (0.025 mmol) in toluene (1.5 mL) was stirred at room temperature for one hour under argon. To this Pd-catalyst was added allylic pivalate **8** (0.50 mmol) or cyclohexenyl acetate **11** (0.50 mmol) in toluene (1.5 mL), followed by dimethyl malonate (170 μL, 1.5 mmol) or diethyl methylmalonate (260 μL, 1.5 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (BSA, 0.37 mL, 1.5 mmol), and a catalytic amount of KOAc sequentially. After stirring for 24 h, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and diluted with CH_2Cl_2. The organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure. E.e. value for **9a** determined by HPLC (Chiralpak AD, hexanes: 2-propanol = 90: 10, 1.0 mL/min); **9b** by HPLC (Chiralpak AD, hexanes: 2-propanol = 97.5: 2.5, 0.5 mL/min); **12** by GC (β-390 sationary capillary column). The absolute configuration was determined by the specific rotation with a literature value.[9]

4.5. General procedure for asymmetric hydrosilylation of acetophenone

A solution of $[Rh(NBD)Cl]_2$ (2.3 mg, 0.005 mmol) and chiral ferrocenylphosphine-imine ligand **5** and **6** (0.015 mmol) in THF (1.5 mL) was stirred at room temperature for 30 min under argon. To this Rh-catalyst was added acetophenone (120 mg, 110 μL, 1.0 mmol) and Ph_2SiH_2 (230 μL, 230 mg, 1.25 mmol) sequentially, and the mixture was stirred at rt for 1.5 h. The reaction mixture was then quenched with 1.0 ml of methanol, stirred at rt for 1 h, and subsequently hydrolysed by the addition of 1 N HCl aq. This solution was extracted with diethyl ether (50 mL×3) and the extract was dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (hexane:ethyl acetate, 9:1) to afford a pure product 14. The enantiomeric excess was determined by GC analysis with a capillary chiral column (cyclodex-β,2-,3-,6-methylated, 30 m×0.25 mm (i.d.)).

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