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Ferrocenylphosphine–imine ligands for Pd-catalyzed asymmetric allylic alkylation

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Abstract—Ferrocenylphosphine–imine ligands **6** derived from (*R*,*S*)-PPFNH$_2$-R **5** and a variety of benzaldehydes were applied in the Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate **7a** or pivalate **7b** with dimethyl malonate. The substituent effects on the catalytic reaction were investigated, and 96% e.e. with 99% yield was achieved when the *m*-nitro substituted ligand **6k** was used. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The asymmetric alkylation of allylic compounds catalyzed by palladium complexes has been investigated extensively due to its great potential use in asymmetric synthesis.[1] Among various chiral ligands developed for this reaction, *P*,*N* ligands have been used for a long time[2] and great progress has been made in the past decade in achieving high enantioselectivities. These *P*,*N* ligands include amino-phosphines,[3] oxazolino-phosphines,[4] pyridino-phosphines,[5] hydrazono-phosphines,[6] amidino-phosphines,[7] oxazolizino-phosphines,[8] oxazinano-phosphines,[9] and so on.

Phosphine–imine containing compounds have been attracting considerable attention in the past few years as an important class of *P*,*N* ligand. These *P*,*N* ligands are easily prepared and their electronic and steric properties can be readily modified. By appropriate electronic and steric modification, many phosphine–imine ligands have been developed and shown to be very effective in the Pd-catalyzed asymmetric allylic substitution.[10] Hashimoto et al. reported phosphine–imine ligands derived from 1-arylethylamines and 2-(diphenylphosphino)benzaldehyde.[11] When the sterically congested (*R*)-1-mesitylethylamine was used as the amine component, good enantioselectivity was achieved. Ligands derived from other bulky amines such as 1-ferrocenylbenzylamine were also very effective for this reaction.[12] Of the phosphine–imine ligands derived from (*S*)-1-(diphenylphosphino)-3-methyl-2-butanamine and benzaldehydes with different substituents at the *para*-position, the ligand bearing a more electron-donating dimethylamino group was demonstrated to induce the highest enantioselectivity in the Pd-catalyzed allylic alkylation reaction.[7c] These results suggest that, if an appropriate phosphine–imine skeleton is constructed, it is possible to explore efficient ligands for the Pd-catalyzed asymmetric allylic alkylation by tuning the electronic and steric properties.

Recently, a new type of ferrocenylphosphine–imine ligand was prepared by Hayashi et al. and successfully used in Rh-catalyzed asymmetric hydrosilylation of ketones.[13] By structural modification of this ferrocenylphosphine–imine skeleton, we report herein the synthesis of a series of new ferrocenylphosphine–imine ligands and their applications in the Pd-catalyzed asymmetric allylic alkylation reaction.

2. Results and discussion

2.1. Preparation of ferrocenylphosphine–imine ligands

The synthesis of the chiral ferrocenylphosphine–imine ligands **6** is shown in Scheme 1. The initial step in the synthesis involved the catalytic asymmetric reduction of ferrocenyl ketones **1** to the corresponding alcohols **2** with (*R*)-configuration using Corey's chiral B-methyl-

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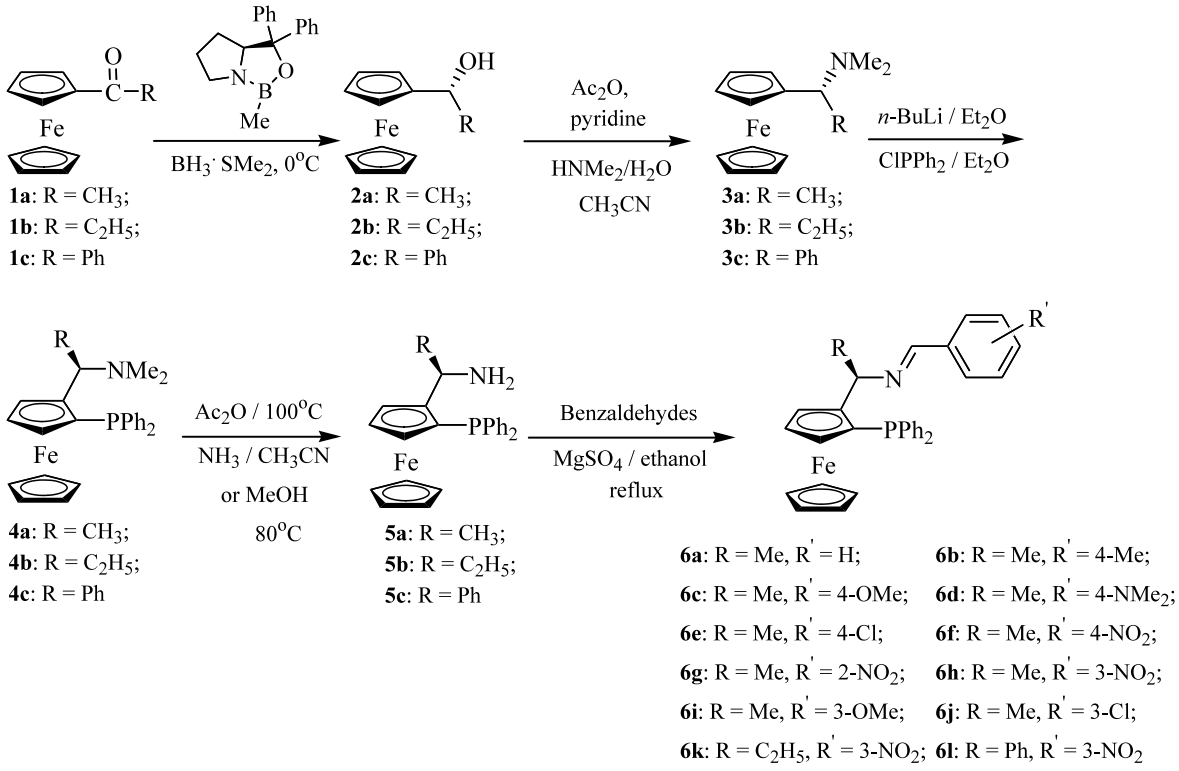
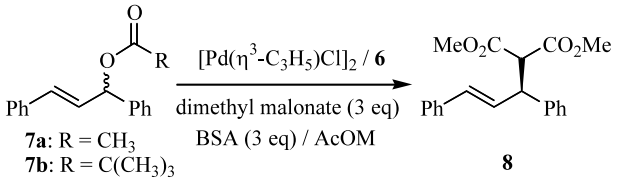


Scheme 1.

ated oxazaborolidine complex, which has been shown to be a highly effective reagent for the reduction of several ferrocenyl ketones.[14] All alcohols were obtained in high yields (>90%) and with very high enantioselectivities (>98% e.e.). Sequential treatment of chiral alcohols **2** with Ac_2O/pyridine and $HNMe_2/CH_3CN$, then afforded the optically active tertiary amines **3** with complete configurational retention in nearly quantitative yields. The highly diastereoselective *ortho*-lithiation of amines **3** followed by treatment with $ClPPh_2$ gave phosphine–amine compounds **4** (PPFA-R), which have (*R*,*S*)-configuration. After reaction of ferrocenylphosphine–amines **4** with Ac_2O at 100°C followed by treatment with a large excess of ammonia in methanol or acetonitrile in an autoclave at 80°C, the dimethylamino group of **4** was substituted by a primary amino group to form the key intermediate, (*R*,*S*)-PPFNH$_2$-R **5**. Nucleophilic substitution on the ferrocenylmethyl position was demonstrated to proceed with retention of configuration of the stereogenic carbon center.[15] The target ligands **6** were then prepared from (*R*,*S*)-PPFNH$_2$-R **5** and a variety of benzaldehydes in refluxing ethanol in the presence of anhydrous $MgSO_4$, following the modified procedure reported by Hayashi et al.[13]

2.2. Pd-catalyzed asymmetric allylic alkylation

The chiral ferrocenylphosphine–imine ligands **6** were then applied to the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate **7a** or pivalate **7b** with a dimethyl malonate (Scheme 2). This reaction was carried out in the presence of 2.0 mol% of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 5.0 mol% of chiral ligand, and a mixture of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of metal acetate.



Scheme 2.

Initially, the effects of the aryl ring substituent of the ferrocenylphosphine–imine ligands on the catalytic reaction were examined and the results are summarized in Table 1. Entries 1–6 show the results of those ligands **6a**–**f** with *para*-substituents. Comparison of the catalytic activities and enantioselectivities for the different R substituents indicated that ligands with electron-withdrawing substituents (chloro or nitro) tended to give higher catalytic activities and enantioselectivities than those with electron-donating substituents (methyl, methoxy and dimethylamino, entries 1–6). Of these *para*-substituted ligands, nitro substituted **6f** gave the best results (91% yield, 87% e.e.), as shown in entry 6. This interesting result prompted us to synthesize the *ortho*- and *meta*-nitro analogs and to investigate their efficiencies in the catalytic reaction. Replacing **6f** with **6g**, carrying a nitro group in the *ortho*-position of the aryl ring, gave the product **8** in merely 78% yield and 80% e.e. (entry 7). However, when the *meta*-nitro substituted ligand **6h** was employed, the e.e. was significantly raised to 93% with a 99% yield (entry 8). Good

Table 1. Asymmetric allylic alkylation of allylic acetate **7a** using ligands **6a**–**j**[a]

Entry	Ligand	Yield (%)[b]	% e.e.[c] (config.)[d]
1	**6a**	51	73 (*S*)
2	**6b**	59	83 (*S*)
3	**6c**	53	83 (*S*)
4	**6d**	56	84 (*S*)
5	**6e**	67	86 (*S*)
6	**6f**	91	87 (*S*)
7	**6g**	78	80 (*S*)
8	**6h**	99	93 (*S*)
9	**6i**	97	91 (*S*)
10	**6j**	96	90 (*S*)

[a] The reactions were carried out in toluene in the presence 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, 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.[16]

results were also obtained when *meta*-methoxy substituted ligand **6i** and *meta*-Cl substituted ligand **6j** were applied in the catalytic reaction compared with their *para*-substituted analogs (entry 9 versus entry 3, entry 10 versus entry 5).

Optimization of the reaction conditions was then examined by the use of ligand **6h** with a *meta*-nitro substituent and results are summarized in Table 2. The use of CsOAc or NaOAc as base gave a similar enantioselectivity to KOAc (entries 1 and 3 versus entry 2). However, upon use of LiOAc instead of KOAc, the enantioselectivity decreased dramatically to 79% e.e. (entry 4). The effect of solvents on this reaction was also investigated and a significant variation in the catalytic activity was observed. CH_2Cl_2 proved to be an inferior solvent for the reaction, and only 75% e.e. with 43% yield was obtained (entry 5). Using THF as solvent, the enantioselectivity decreased markedly with a slight decrease in the yield (entry 6). When the reaction was carried out in DMSO, DMF or benzene, a slight drop in enantioselectivity was observed (entries 7–9). It was also found that the reaction was sensitive to temperature. When the reaction temperature was lowered to 10°C, an increase in the enantioselectivity (95% e.e.) was obtained but longer time was required to complete the reaction (entry 10). Lowering the temperature further to 0°C caused a decrease in enantioselectivity to 91% e.e. with only 73% yield even after 96 h (entry 11). Replacing acetate **7a** with pivalate **7b** as substrate resulted in an increase in enantioselectivity to 94% e.e. (entry 12), and lowering the reaction temperature to 10°C could further improve the enantioselectivity (entry 13). The absolute configuration of product **8** from these reactions was proven to be *S* by comparing the specific rotation with a literature value.[16]

Under the optimized reaction conditions (toluene as solvent, **7b** as substrate, KOAc as base, and completing the reaction at rt), the influence of the substituent in the ferrocenylmethyl position on the catalytic activity and enantioselectivity was examined (Table 3). When the propyl analogue **6k** was used, the enantioselectivity rose to 96% e.e. (entry 2). However, when the substituent in the ferrocenylmethyl position was a phenyl group, the enantioselectivity decreased dramatically to 83% e.e. with a marked decrease in the yield (entry 3). It was noted that using PPFA-R **4** as ligands for the asymmetric allylic alkylation resulted in product **8** with much lower enantioselectivities and reactivities (entries 4–6).

The mechanism for asymmetric induction with this type of ligand is rationalized on the basis of the stereochemical results obtained (Scheme 3). In the conformational

Table 2. Asymmetric allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate **7a** or pivalate **7b** using ligand **6h**[a]

Entry	Substrate	Solvent	Base	Temp. (°C)	Yield (%)[b]	% e.e.[c] (config.)[d]
1	**7a**	Toluene	BSA–CsOAc	25	99	93 (*S*)
2	**7a**	Toluene	BSA–KOAc	25	99	93 (*S*)
3	**7a**	Toluene	BSA–NaOAc	25	99	92 (*S*)
4	**7a**	Toluene	BSA–LiOAc	25	99	79 (*S*)
5	**7a**	CH_2Cl_2	BSA–KOAc	25	43	75 (*S*)
6	**7a**	THF	BSA–KOAc	25	95	86 (*S*)
7	**7a**	DMSO	BSA–KOAc	25	96	91 (*S*)
8	**7a**	DMF	BSA–KOAc	25	91	90 (*S*)
9	**7a**	Benzene	BSA–KOAc	25	99	93 (*S*)
10	**7a**	Toluene	BSA–KOAc	10	90	95 (*S*)[e]
11	**7a**	Toluene	BSA–KOAc	0	73	91 (*S*)[f]
12	**7b**	Toluene	BSA–KOAc	25	99	94 (*S*)
13	**7b**	Toluene	BSA–KOAc	10	91	96 (*S*)[e]

[a] Molar ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.02 equiv.), **6h** (0.05 equiv.), dimethyl malonate (3.0 equiv.), BSA (3.0 equiv.) and a catalytic amount of additive salts.
[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.[16]
[e] The reaction was carried out for 72 h.
[f] The reaction was carried out for 96 h.

Table 3. Asymmetric allylic alkylation of 1,3-diphenylprop-2-en-1-yl pivalate **7b** using ligand **6** and **4**[a]

Entry	Ligand	Yield (%)[b]	e.e. (%)[c] (config.)[d]
1	**6h**	99	94 (*S*)
2	**6k**	99	96 (*S*)
3	**6l**	89	83 (*S*)
4	**4a**	85	48 (*S*)
5	**4b**	84	20 (*S*)
6	**4c**	47	62 (*S*)

[a] The reactions were carried out in toluene in the presence 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, 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.[16]

equilibrium of sterically favored π-allyl palladium complexes *exo*-**9** and *endo*-**10**,[17] complex *exo*-**9** would be formed preferentially due to the key influence of the planar chirality of the ferrocenyl units on the 1,3-diphenylallyl orientation through interactions between the diphenylphosphinoferrocene unit and the allylic fragment, according to the recent research by Guiry et al.[18] The nucleophile attacks the allylic terminus *trans* to the phosphorus atom in the major diastereomer *exo*-**9**, from the back side of the palladium catalyst in the π-allyl system as designated in **9**,[19] affording the product (*S*)-**8**.

3. Conclusion

In conclusion, a series of new ferrocenylphosphine–imine ligands developed for the enantioselective Pd-catalyzed allylic alkylation and up to 96% e.e. was achieved by using the *meta*-nitro substituted ligand **6k**. Further studies on the applications of ferrocenylphosphine–imine ligands **6** are still in progress.

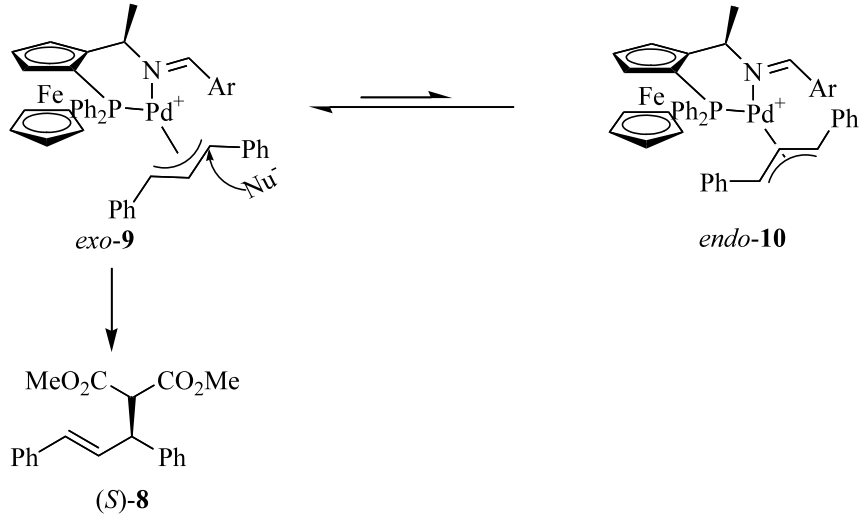
4. Experimental

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-Diphenyl-2-propenyl acetate **7a** was prepared according to the reported method.[20] 1,3-Diphenyl-2-propenyl pivalate **7b** was derived from the reaction of 1,3-diphenylprop-2-en-1-ol with pivaloyl chloride in pyridine. **4a**,[15b] **4b**[21] and **4c**[22] were synthesized following the literature method. (*R*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]ethylamine **5a** and **6a** were prepared according to Hayashi's procedure.[13]

4.2. General procedure for the synthesis of $PPFNH_2$-R, 5

Amine **4** (5.0 mmol) was sealed in an air-free tube with acetic anhydride (3.0 mL). The tube was heated to 100°C for 2 h. After cooling to rt, the reaction mixture was poured into 10% aqueous potassium carbonate (150 mL) with vigorous stirring. The oily material solidified about 10 min later and was extracted with Et_2O (2×50 mL). The ethereal extract was successively washed with 2N 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 saturated solution of NH_3 in MeOH (25 mL) or a solution of 25% aqueous ammonia (10 mL) in CH_3CN (20 mL). The mixture was then placed in a 100 mL autoclave and heated at 80°C for 8 h. The reaction mixture was



Scheme 3.

diluted with CH_2Cl_2 (10 mL) and the solvent was evaporated. The residue was chromatographed on an alumina column to give the product **5**.

4.2.1. (*R*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]-ethylamine, 5a. Recrystallized from *n*-hexane in 63% yield; mp 132–133°C; $[\alpha]_D^{25}$ −296 (*c* 0.51, benzene); ^{1}H NMR (DMSO-d_6) δ 1.35 (d, J=6.4 Hz, 3H), 3.28 (br, 1H), 3.69(s, 1H), 3.98 (s, 5H), 4.01 (m, 1H), 4.32 (t, J=2.4 Hz, 1H), 4.47 (s, 1H), 7.15–7.52 (m, 10H); ^{31}P NMR δ −24.6.

4.2.2. (*R*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]propylamine, 5b. Recrystallized from *n*-hexane in 57% yield; mp 118–119°C; $[\alpha]_D^{25}$ −354 (*c* 0.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.97 (t, J=7.2 Hz, 3H), 1.47–1.90 (m, 2H), 1.85 (br, 2H), 3.76 (s, 1H), 3.78–3.80 (m, 1H), 4.03 (s, 5H), 4.27 (s, 1H), 4.39 (s, 1H), 7.24–7.55 (m, 10H); ^{31}P NMR δ −21.8.

4.2.3. (*R*)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]-benzylamine, 5c. Recrystallized from *n*-hexane in 46% yield; mp 119–121°C; $[\alpha]_D^{25}$ −305 (*c* 0.20, $CHCl_3$); ^{1}H NMR (CCl_4) δ 1.44 (br, 2H), 3.86 (s, 1H), 3.87 (s, 5H), 4.32 (s, 1H), 4.34 (s, 1H), 5.31 (m, 1H), 7.30–7.68 (m, 15H); ^{31}P NMR δ −23.5.

4.3. General procedure for the synthesis of ligands, 6

To a solution of (*R*,*S*)-PPFNH$_2$-R **5** (1.0 mmol) in ethanol (5.0 mL) was added the corresponding benzaldehyde (1.0 mmol) and anhydrous $MgSO_4$ (600 mg). The reaction mixture was heated to reflux. After the reaction was complete (detected by TLC), the reaction mixture was diluted with CH_2Cl_2. $MgSO_4$ was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography.

4.3.1. (*R*)-*N*-(4-Methylbenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine, 6b. Yellow solid; 71% yield; mp 119–121°C; $[\alpha]_D^{25}$ −446 (*c* 0.13, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.68 (d, J=5.2 Hz, 3H), 2.28 (s, 3H), 3.76 (s, 1H), 4.07 (s, 5H), 4.34 (s, 1H), 4.69 (s, 1H), 4.81 (m, 1H), 6.80–7.52 (m, 14H), 7.93 (s, 1H); ^{31}P NMR δ −23.5. HRMS (FAB) calcd for $C_{32}H_{30}NPFe$+H 516.1536, found 516.1538.

4.3.2. (*R*)-*N*-(4-Methoxybenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine, 6c. Yellow solid; 67% yield; mp 145–146°C; $[\alpha]_D^{25}$ −454 (*c* 0.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.70 (d, 3H), 3.75 (s, 1H), 3.77 (s, 3H), 4.06 (s, 5H), 4.34 (s, 1H), 4.70 (s, 1H), 4.83 (m, 1H), 6.64–7.53 (m, 14H), 7.91 (s, 1H); ^{31}P NMR δ −23.5. HRMS (FAB) calcd for $C_{32}H_{30}NOPFe$+H 532.1485, found 532.1480.

4.3.3. (*R*)-*N*-(4-Dimethylaminobenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine, 6d. Golden solid; 66% yield; mp 136–138°C; $[\alpha]_D^{25}$ −540 (*c* 0.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.67 (d, J=5.2 Hz, 3H), 2.93 (s, 6H), 3.73 (s, 1H), 4.05 (s, 5H), 4.31 (s, 1H), 4.68 (br, 2H), 6.42–7.53 (m, 14H), 7.87 (s, 1H); ^{31}P NMR δ −23.2. HRMS (FAB) calcd for $C_{33}H_{33}N_2PFe$+H 545.1803, found 545.1810.

4.3.4. (*R*)-*N*-(4-Chlorobenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine, 6e. Golden solid; 74% yield; mp 126–127°C; $[\alpha]_D^{25}$ −372 (*c* 0.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.66 (d, J=6.4 Hz, 3H), 3.74 (s, 1H), 4.07 (s, 5H), 4.33 (s, 1H), 4.66 (s, 1H), 4.81 (m, 1H), 6.81–7.51 (m, 14H), 7.96 (s, 1H); ^{31}P NMR δ −23.2. HRMS (FAB) calcd for $C_{31}H_{27}ClNPFe$+H 536.0992, found 536.0995.

4.3.5. (*R*)-*N*-(4-Nitrobenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine, 6f. Dark red solid; 81% yield; mp 196–198°C; $[\alpha]_D^{25}$ −500 (*c* 0.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.69 (d, J=1.7 Hz, 3H), 3.77 (s, 1H), 4.08 (s, 5H), 4.36 (s, 1H), 4.68 (s, 1H), 4.90 (m, 1H), 6.74–7.97 (m, 14H), 8.09 (s, 1H); ^{31}P NMR δ −24.1. HRMS (FAB) calcd for $C_{31}H_{27}N_2O_2PFe$+H 547.1232, found 547.1230.

4.3.6. (*R*)-*N*-(2-Nitrobenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine, 6g. Orange solid; 91% yield; mp 174–176°C; $[\alpha]_D^{25}$ −354 (*c* 0.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.71 (d, J=6.4 Hz, 3H), 3.83 (s, 1H), 4.08 (s, 5H), 4.38 (s, 1H), 4.68 (s, 1H), 5.00 (m, 1H), 6.84–7.83 (m, 14H), 8.50 (s, 1H); ^{31}P NMR δ −25.2. HRMS (FAB) calcd for $C_{31}H_{27}N_2O_2PFe$+H 547.1232, found 547.1229.

4.3.7. (*R*)-*N*-(3-Nitrobenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine, 6h. Red solid; 73% yield; mp 129–131°C; $[\alpha]_D^{25}$ −483 (*c* 0.12, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.68 (d, J=6.8 Hz, 3H), 3.75 (s, 1H), 4.08 (s, 5H), 4.35 (s, 1H), 4.68 (s, 1H), 4.89 (m, 1H), 6.67–8.07 (m, 15H); ^{31}P NMR δ −24.1. HRMS (FAB) calcd for $C_{31}H_{27}N_2O_2PFe$+H 547.1232, found 547.1230

4.3.8. (*R*)-*N*-(3-Methoxybenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine, 6i. Yellow solid; 54% yield; mp 98–99°C; $[\alpha]_D^{25}$ −430 (*c* 0.10, $CHCl_3$); ^{1}H NMR (CCl_4) δ 1.78 (d, J=6.4 Hz, 3H), 3.82 (s, 1H), 3.88 (s, 3H), 4.14 (s, 5H), 4.40 (s, 1H), 4.74 (s, 1H), 4.83 (m, 1H), 6.77–7.59 (m, 14H), 7.99 (s, 1H); ^{31}P NMR δ −20.9. HRMS (FAB) calcd for $C_{32}H_{30}NOPFe$+H 532.1487, found 532.1479.

4.3.9. (*R*)-*N*-(3-Chlorobenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine, 6j. Brown solid; 63% yield; mp 123–125°C; $[\alpha]_D^{25}$ −458 (*c* 0.12, $CHCl_3$); ^{1}H NMR (CCl_4) δ 1.77 (d, J=6.4 Hz, 3 H), 3.82 (s, 1H), 4.15 (s, 5H), 4.40 (s, 1H), 4.72 (s, 1H), 4.83 (m, 1H), 6.92–7.59 (m, 14H), 7.96 (s, 1H); ^{31}P NMR δ −21.1. HRMS (FAB) calcd for $C_{31}H_{27}ClNPFe$+H 536.0992, found 536.0996.

4.3.10. (*R*)-*N*-(3-Nitrobenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]propylamine, 6k. Golden solid; 54% yield; mp 133–134°C; $[\alpha]_D^{25}$ −300 (*c* 0.10, $CHCl_3$); ^{1}H NMR (CCl_4) δ 1.08 (t, J=7.2 Hz, 3H), 2.10–2.56 (m, 2H), 3.84 (s, 1H), 4.16 (s, 5H), 4.43 (s, 1H), 4.53–4.56 (m, 1H), 4.73 (s, 1H), 6.82–8.20 (m,

15H); ^{31}P NMR δ –24.0. HRMS (FAB) calcd for $C_{32}H_{29}N_2O_2PFe$+H 561.1393, found 561.1387.

4.3.11. (*R*)-*N*-(3-Nitrobenzylidene)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]phenylmethylamine, 6l. Yellow solid; 51% yield; mp 152–154°C; $[\alpha]_D^{25}$ –450 (*c* 0.22, $CHCl_3$); ^{1}H NMR (CCl_4) δ 3.91 (s, 1H), 3.96 (s, 5H), 4.37 (s, 1H), 4.47 (s, 1H), 5.88 (d, J=2.8 Hz, 1H), 6.95–8.14 (m, 20H); ^{31}P NMR δ –24.1. HRMS (FAB) calcd for $C_{36}H_{29}N_2O_2PFe$+H 609.1393, found 609.1380.

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 phosphine–imine **6** (0.025 mmol) in toluene (1.5 mL) was stirred at room temperature for 1 h under argon. To this Pd-catalyst was added allylic acetate **7a** or pivalate **7b** (0.50 mmol) in toluene (1.5 mL), followed by dimethyl malonate (170 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 a 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. The residue was purified by column chromatography (hexane:ethyl acetate, 8:1) to afford a pure product **8**. The enantiomeric excess was determined by HPLC (Chiralpak AD, hexanes:2-propanol=90:10, 1.0 mL/min). The absolute configuration was determined by the specific rotation with a literature value.[16]

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