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# Preparation of Chiral Homoannularly Bridged N,P-Ferrocenyl Ligands by Intramolecular Coupling of 1,5-Dilithioferrocenes and Their Application in Asymmetric Allylic Substitution Reactions

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*Dedicated to the memory of Professor Yoshihiko Itoh*

**Keywords:** Asymmetric catalysis / Asymmetric synthesis / N,P ligands / Chirality / Allylation / Annulation

Homoannularly bridged ferrocene **6b** was prepared by intramolecular coupling of 1,5-dilithioferrocene **5b** mediated by $Fe(acac)_3$. Dilithioferrocene **5b** was prepared by lithium–halogen exchange of the corresponding diiodide, which was prepared by 1,5-dilithiation of the *o*-TMS-blocked ferrocene and followed by trapping with iodine and removal of the TMS group. Alternatively, **5b** could be readily prepared by the reaction of *o*-bromophenylferrocene **8** with *n*BuLi (>2 equiv.). The benzene ring of **6b** underwent *ortho* lithiation with *t*BuLi, and the resulting lithiated species was trapped with $Ph_2PCl$ to produce corresponding aminophosphane **7d**. Aminophosphane **13**, which has the phosphanyl group on the cyclopentadienyl ring, was prepared by intramolecular coupling of 1,5-dilithiated PhPPFA **11** mediated by $Fe(acac)_3$. New N,P ligands **7d** and **13** were used in the palladium-catalyzed allylic alkylation and amination of 1,3-diphenyl-2-propenyl acetate (**14**), and ligand **7d** was found to give good yields with enantioselectivities as high as 96% *ee*.
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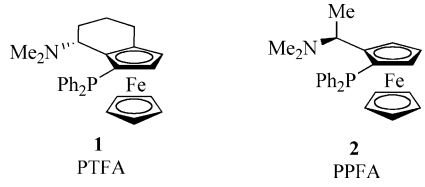
## Introduction

Chiral ferrocenes are a group of compounds that have central, planar, or $C_2$ chirality, and many of these compounds have a combination of these chiralities.[1] It is easy to introduce a chiral group onto ferrocene and stereospecifically carry out transformations of the functional group. The unique structure of ferrocenes allows one to design a variety of chiral ferrocenylphosphane ligands, which are useful tools for metal-catalyzed asymmetric reactions.[2] Although some useful chiral ferrocenyl phosphane ligands such as taniaphos[3] and josiphos[4] have already been reported, it is still of interest and a challenge to create new ferrocenyl phosphane ligands that produce more effective metal complex catalysts and/or to cover asymmetric reactions in which conventional ligands do not effectively work.

Weissensteiner et al. prepared homoannularly bridged chiral ferrocenes and studied their coordination chemistry.[5] These species possess lower conformational flexibility, and they can occasionally work more efficiently than flexible ferrocenes as ligands in certain metal-catalyzed asymmetric reactions. For example, PTFA {[(diphenylphosphanyl)tetramethyleneferrocenyl]dimethylamine, **1**} gave higher enantioselectivity (79% *ee*) than PPFA ({[(diphenylphopsphanyl)ferrocenyl]ethyl}dimethylamine, **2**; 63% *ee*) in the palladium-catalyzed Grignard cross-coupling reaction (Figure 1).[6]




**1** PTFA **2** PPFA

Figure 1. The PTFA and PPFA ligands.

We previously reported that *o*-TMS-blocked ferrocene **3** underwent 1,5-dilithiation upon treatment with more than one equivalent of *n*BuLi, and intramolecular coupling of resulting 1,5-dilithioferrocene **5a** occurred in the presence of $Fe(acac)_3$ to give homoannularly bridged ferrocene **6a** (Scheme 1).[7] We were interested in the unique structure of **6a** and designed a new ferrocenyl phosphane ligand based on its structure. Using the same intramolecular coupling methodology, we succeeded in the preparation of new chiral homoannularly bridged N,P-ferrocenyl ligands.[8] Palladium complexes containing these ligands catalyzed allylic substitutions with high enantioselectivities.[9]

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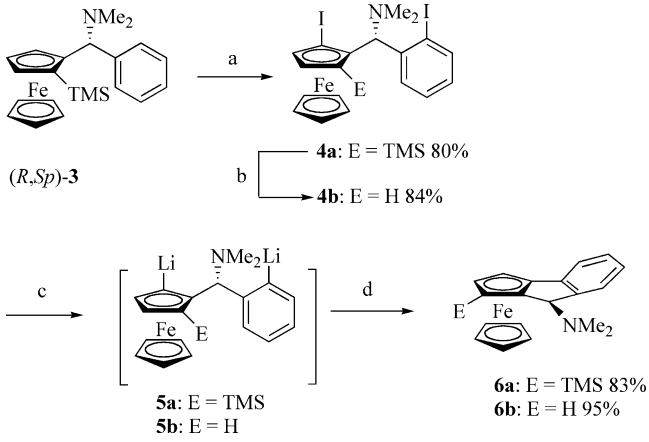



Scheme 1. Reagents and conditions: (a) *t*BuLi (2.4 equiv.) in diethyl ether, 0 °C, 2 h, then $I_2$ (2.5 equiv.); (b) *t*BuOK (1.1 equiv.) in DMSO, room temp., 15 h; (c) *n*BuLi (2.5 equiv.) in diethyl ether, 0 °C, 2 h; (d) $Fe(acac)_3$ (3.0 equiv.), 0 °C 10 min, then room temp., 22 h.

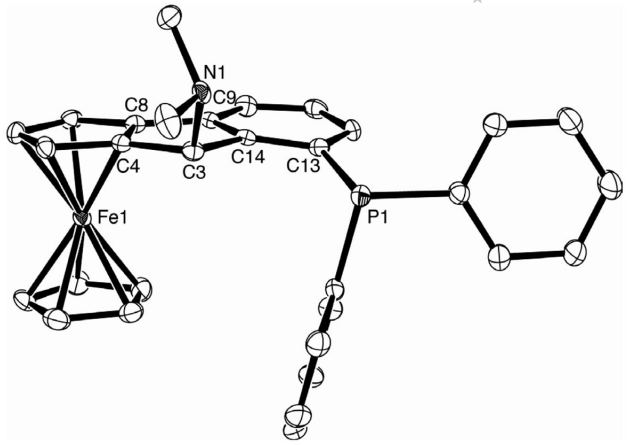
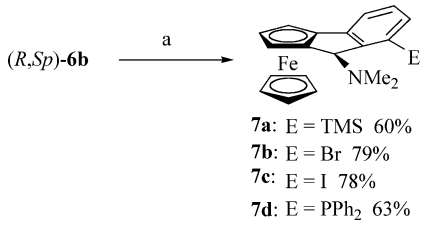



Figure 2. X-ray structure of **7d**. Selected bond lengths [Å]: C3–C4 1.511, C3–C14 1.537, C4–C8 1.428, C8–C9 1.473, C9–C14 1.411, C13–C14 1.388, N1–C3 1.524, P1–C13 1.842. Selected bond angles [°]: C3–C4–C8 110.3, C4–C3–C14 101.8, C8–C9–C14 107.8, C3–C14–C9 111.0, C9–C14–C13 121.7, C3–C14–C13 127.0, P1–C13–C14 116.14, N1–C3–C4 111.7, N1–C3–C14 111.5.

## Results and Discussion

We first carried out *ortho* lithiation of **6b**, which was readily prepared by intramolecular coupling of TMS-free ferrocenyl 1,5-diiodide **4b**.[7] Upon treatment of **6b** with *t*BuLi (1 equiv.) followed by trapping with TMSCl, the TMS group was exclusively introduced at the *ortho* position of the benzene ring to give **7a**. Contrary to our expectation, the *ortho* position of the cyclopentadienyl moiety was not silylated and the production of **6a** was not observed. The structure of **7a** was determined by spectroscopic analysis; the loss of the signal of one proton from the benzene ring in the $^1H$ NMR spectra and the downfield shift of one of the benzene carbon signals in the $^{13}C$ NMR spectra indicated that the replacement occurred at the benzene ring (Scheme 2). Similarly, bromine and iodine atoms could be introduced at the *ortho* position of the benzene ring to obtain corresponding halides **7b**,**c**. Thus, the preparation of chiral aminophosphane **7d** was accomplished by direct *ortho* lithiation of **6b** or lithiation of **7b**,**c** and subsequent trapping with diphenylphosphanyl chloride; compound **7d** was obtained in 63% yield. The structure of **7d** was confirmed by X-ray crystallographic analysis (Figure 2).




Scheme 2. Reagents and conditions: (a) *t*BuLi (1.3 equiv.) in diethyl ether, 0 °C, 2 h, then $E^+$ (1.0 equiv.).

We tried to prepare the diastereomer of **6b** − (*R*,*Rp*)-**10** − by successive 1,5-dilithiation of (*R*)-*o*-bromophenylferrocene **8** and annulation of (*R*,*Rp*)-1,5-dilithioferrrocene **9**, as shown in Scheme 3. Because taniaphos [thought to possess the (*R*,*Sp*) stereochemistry] could be prepared by trapping with $Ph_2PCl$,[3a] the intramolecular coupling of **9** should be expected to give (*R*,*Rp*)-**10**. However, the stereochemistry of the actual taniaphos product was not (*R*,*Rp*) but (*R*,*Sp*), which was confirmed by X-ray crystallographic analysis, that is, the stereochemistry of the product was identical to that of **6b** obtained by the annulation of **5b**. This result was confusing because the planar chirality of taniaphos is supposed to be (*Sp*), which could be derived from (*Rp*)-lithioferrocene **9** as was reported. One explanation could be that isomerization of the 1,5-dilithioferrocene might occur during the intramolecular coupling. This possibility, however, was refuted by examination of the structure of original taniaphos-Rh (CCDC-134965), which was carefully prepared by Knochel et al.[3a] The correct stereochemistry of taniaphos was found to be (*R*,*Rp*) as shown in Scheme 3; the long convention of illustrating it as the (*R*,*Sp*) form is incorrect.[10] Therefore, *ortho* lithiation of **8** proceeded with (*Sp*) stereochemistry to give **5b**, from which intramolecular coupling yielded (*R*,*Sp*)-**6b**. This process could provide a more convenient route to **6b** than that starting from *o*-TMS-blocked ferrocene **3** (method B in the Experimental Section).

We next outlined a synthesis for the preparation of aminophosphane **13**, which has the phosphanyl group in the cyclopentadienyl ring *ortho* to the amino group. We first unsuccessfully attempted a classical *ipso* substitution to exchange the silyl group for a halogen atom[11] en route to the phosphane moiety. Our next synthetic route involved intramolecular coupling of 1,5-dilithio-PhPPFA **11**[12] in an analogous manner to the successive 1,5-dilithiation and intramolecular coupling of **3** but with a phosphane moiety in place of the TMS group. PhPPFA **11** could be 1,5-dilithiated upon treatment with *t*BuLi (>2 equiv.) and subsequently trapped with $BrCF_2CF_2Br$ to give corresponding 1,5-dibromide **12** in 78% yield. Compound **12** was then

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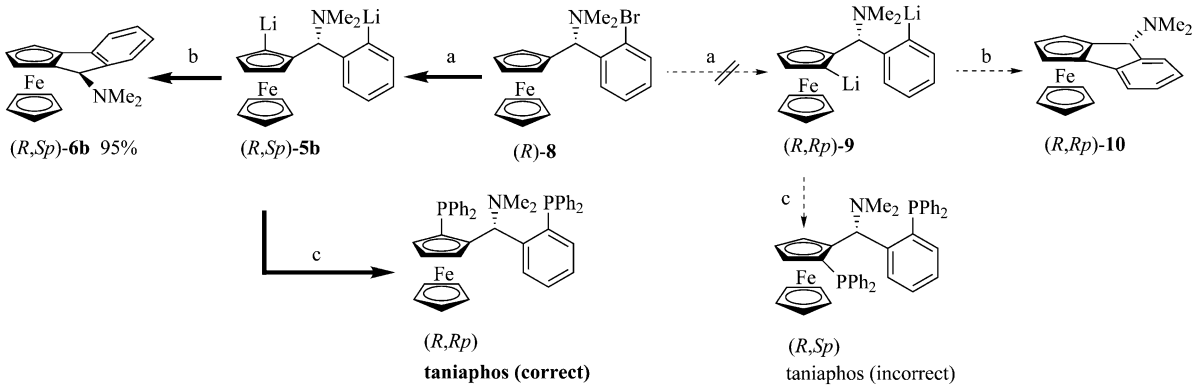
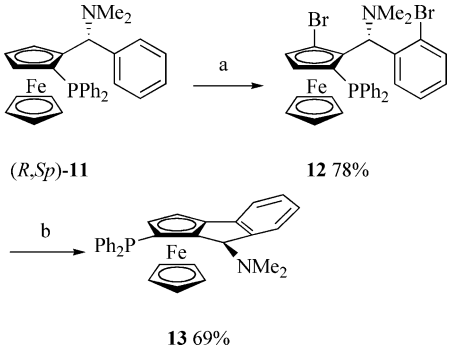



Scheme 3. Reagents and conditions: (a) *t*BuLi (3 equiv.) in diethyl ether, 0 °C, 2 h; (b) $Fe(acac)_3$ (3 equiv.), 0 °C 10 min, then room temp., 22 h; (c) $Ph_2PCl$ (2.5 equiv.), –78 °C, 1 h.

treated with *t*BuLi (2 equiv.) and subsequently with $Fe(acac)_3$, and the intramolecular coupling then proceeded to give aminophosphane **13** in 69% yield (Scheme 4).




Scheme 4. Reagents and conditions: (a) *t*BuLi (2.5 equiv.) in diethyl ether, 0 °C, 2 h, then $BrCF_2CF_2Br$ (3.0 equiv.); (b) *t*BuLi (2.5 equiv.) in diethyl ether, 0 °C, 2 h, then $Fe(acac)_3$ (3.0 equiv.), 0 °C 10 min, then room temp., 22 h.

Having achieved the preparation of homoannularly bridged chiral aminophosphanes **7d** and **13**, we used them in the benchmark palladium-catalyzed asymmetric allylic alkylation reaction to demonstrate their ability as ligands.[13] Table 1 summarizes the results of the reaction of (±)-(*E*)-1,3-diphenyl-2-propenyl acetate (**14**) with dimethyl malonate (**15**). The reaction was carried out under conditions that included a catalytic amount of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and either ligand **7d** or **13** in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of potassium acetate as the base. Detailed conditions are indicated in Table 1.[14] The results of reactions involving other related chiral N,P ligands, such as **1**, **2**, **11**, **12**, and taniaphos, are also shown in Table 1 for comparison. These results show that **7d** was the most effective as product **16** was obtained in good yield with high enantiomeric excess (96% *ee*; Table 1, Entry 3). N,P-ferrocenyl ligand **13** was less effective and gave a lower *ee* value relative to homoannularly bridged N,P-ferrocenyl ligands **1** (PTFA) and **7d**. However, **13** seems to give a somewhat higher selectivity than corresponding flexible ligand **11** (Table 1, Entries 5, 7).

Table 1. Palladium-catalyzed asymmetric allylic alkylation with chiral ferrocenyl N,P ligands.[a]

| Entry | Ligand | Yield [%] | *ee* [%][b] (Config.) |
|---|---|---|---|
| 1[c] | **1** (PTFA) | 75 | 71 (*S*) |
| 2[c] | **2** (PPFA) | – | 54 (*R*) |
| 3 | **7d** | 92 | 96 (*R*) |
| 4 | (*R*,*Sp*)-**13** | 99 | 14 (*S*) |
| 5 | **11** (PhPPFA) | 99 | 30 (*S*) |
| 6 | **12** | 99 | 30 (*S*) |
| 7 | taniaphos | 99 | 37 (*S*) |

[a] **14** (0.5 mmol), **15** (1.5 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.01 mmol, 2 mol-%), ligand (0.03 mmol, 6 mol-%), BSA (1.5 mmol), KOAc (0.015 mmol); room temp., 13 h, in $CH_2Cl_2$ (3.0 mL). [b] Determined by HPLC (Chiralpack AD-H). [c] See ref.[5e]

Because **7d** was revealed to be the most successful N,P-ferrocenyl ligand examined here for asymmetric allylic alkylations, it was then further used for the asymmetric allylic amination of **14** with benzylamine **17**. The results of the reaction under several conditions are summarized in Table 2. We first carried out the reaction using a 2:1 ratio of **17**/**14** and palladium/**7d** complex (2 mol-%) in THF at room temperature, but amination product **18** was hardly obtained (Table 2, Entry 1). However, the reaction proceeded smoothly in $CH_2Cl_2$ under similar conditions to give (*S*)-configured product **18** in moderate yield with moderate *ee* (Table 2, Entry 3). Finally, the use of a 4:1 ratio of **17**/**14** and the addition of tetrabutylammonium fluoride (TBAF)

Table 2. Palladium-catalyzed asymmetric allylic amination in the presence of **7d** as ligand.[a]

| Entry | Solvent | Additive | Yield [%] | *ee* [%][b] (Config.) |
|---|---|---|---|---|
| 1[c] | THF | TBAF | 0 | – |
| 2[c,d] | THF | TBAF | 87 | 67 (*S*) |
| 3[c] | $CH_2Cl_2$ | – | 60 | 76 (*S*) |
| 4 | $CH_2Cl_2$ | – | 67 | 84 (*S*) |
| 5 | $CH_2Cl_2$ | TBAF | 94 | 90 (*S*) |

[a] **14** (0.5 mmol), **17** (2.0 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.01 mmol. 2 mol-%), ligand (0.03 mmol, 6 mol-%), TBAF (1.0 mmol); room temp., 18–24 h. [b] Determined by HPLC (Chiralpack AD-H). [c] **14** (2.0 mmol). [d] Reflux for 24 h.

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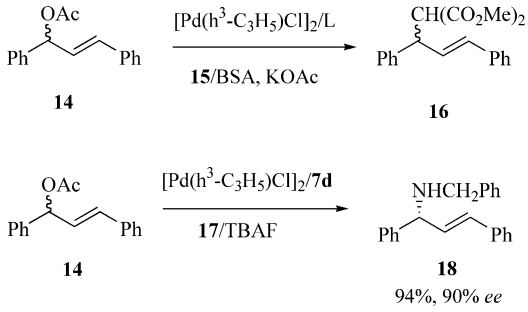
improved the results to 90% *ee* and 94% yield (Table 2, Entry 5; Scheme 5). The addition of TBAF was essential to obtain high enantioselectivity.[11b]




Scheme 5.

## Conclusion

In conclusion, we prepared homoannularly bridged N,P-ferrocenyl ligands by intramolecular coupling of 1,5-dilithioferrocene. In particular, **7d** was the most successful ligand in the palladium-catalyzed allylic substitution of 1,3-diphenyl-2-propenyl acetate (**14**), and produced products with up to 96% *ee*. Further studies of the application of **7d** to metal-catalyzed asymmetric reactions are in progress.

## Experimental Section

**(Cyclopentadienyl){(*R*,*Sp*)-η$^5$-8-(dimethylamino)dihydrocyclopenta-[*a*]indenyl}iron(II) (6b)**

**Method A:** To a 200-mL three-neck round-bottom flask containing a magnetic stirring bar was added (*Rp*)-1-iodo-2-[(*R*)-1-(dimethylamino)-*o*-iodophenylmethyl]ferrocene[7] (**4b**; 5.71 g, 10.0 mmol) and dry diethyl ether (70 mL) under a slight pressure of nitrogen. The flask was cooled in an ice bath and a solution of *n*BuLi (1.6 M in hexane, 15.8 mL, 25.0 mmol) was then added by syringe through the septum whilst stirring. After 2 h, a solution of $Fe(acac)_3$ (10.6 g, 30.0 mmol) in dry benzene (45 mL) was injected into the solution, and the mixture was stirred at 0 °C for 10 min. The ice bath was then removed, and the mixture was warmed to room temp. and stirred for an additional 22 h. The reaction was quenched with a 10% aqueous solution of NaOH, and the precipitate was removed by filtration through a Celite pad. The filtrate was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined extracts were washed (brine), dried ($K_2CO_3$), and filtered, and the solvent was removed under reduced pressure. The crude dark orange solid was purified by column chromatography on silica gel (hexane/ethyl acetate/triethylamine, 20:4:1) to give pure (*R*,*Sp*)-**6b** as orange crystals. Yield: 3.0 g, 9.5 mmol, 95%. M.p. 92 °C. $[a]_D^{25}$ = –774 (*c* = 0.16, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ = 2.13 (s, 6 H, $NMe_2$), 3.87 (s, 5 H, Cp), 4.25 (t, *J* = 2.3 Hz, 1 H, Cp-H), 4.51 (d, *J* = 1.9 Hz, 1 H, Cp-H), 4.56 (d, *J* = 2.2 Hz, 1 H, Cp-H), 4.99 (s, 1 H, C*H*N), 7.14 (d, *J* = 7.3 Hz, 1 H), 7.22 (t, *J* = 7.3 Hz, 1 H), 7.31 (d, *J* = 7.3 Hz, 1 H), 7.42 (d, *J* = 7.3 Hz, 1 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 40.8 ($NMe_2$), 59.2 (*C*$NMe_2$), 65.1, 68.5, 70.1, 70.3, 90.6, 91.4, 119.6, 125.0 125.4, 127.9, 141.6, 147.5 ppm. HRMS: calcd. for $C_{19}H_{19}FeN$ $[M + H]^+$ 318.0914; found 318.0939.

**Method B:** To a 200-mL three-neck round-bottom flask containing a magnetic stirring bar was added [(*R*)-1-(dimethylamino)-*o*-bromophenylmethyl]ferrocene (**8**; 1.9 g, 4.8 mmol) and dry diethyl ether (30 mL) under a slight pressure of nitrogen. The flask was cooled in a dry-ice bath, and a solution of *t*BuLi (1.58 M in hexane, 9.5 mL, 15.0 mmol) was then added by syringe through the septum whilst stirring. The mixture was warmed to room temp. and stirred for 2 h. A solution of $Fe(acac)_3$ (5.1 g, 14 mmol) in dry benzene (30 mL) was then injected into the solution at 0 °C. The mixture was stirred at 0 °C for 10 min, the ice bath was then removed, and the mixture was warmed to room temp. and stirred for an additional 22 h. The reaction was quenched with a 10% aqueous solution of NaOH, and the precipitate was removed by filtration through a Celite pad. The filtrate was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined extracts were washed (brine), dried ($K_2CO_3$), and filtered, and the solvent was removed under reduced pressure. The crude dark orange solid was purified by column chromatography on silica gel (hexane/ethyl acetate/triethylamine, 20:4:1) to give pure (*R*,*Sp*)-**6b**. Yield: 1.4 g, 4.4 mmol, 92%.

**Typical Experimental Procedure for the Lithiation of 6b Followed by Trapping with Electrophiles ($Ph_2PCl$, TMSCl, $BrCF_2CF_2Br$, $I_2$)**

**7d:** To a 50-mL Schlenk tube containing a magnetic stirring bar was added (*R*,*Sp*)-**6b** (1.0 g, 3.2 mmol) and dry diethyl ether (20 mL) under a slight pressure of nitrogen. The tube was cooled in an ice bath, and a solution of *t*BuLi (1.6 M in hexane, 2.6 mL, 4.2 mmol) was added by syringe through the septum whilst stirring. After 2 h, $Ph_2PCl$ (0.61 mL, 3.3 mmol) was added to the mixture; the ice bath was then removed, and the mixture was warmed to room temp. and stirred for an additional 20 h. The reaction was quenched with saturated aqueous $NaHCO_3$, and the solution was then extracted with diethyl ether (3 × 30 mL). The combined extracts were washed (brine), dried ($K_2CO_3$), and filtered, and the solvent was removed under reduced pressure. The brown residue was purified by column chromatography on silica gel (hexane/ethyl acetate/triethylamine, 20:2:1) to give pure **7d** as a yellow solid. Yield: 1.0 g, 2.0 mmol, 63%. M.p. 39 °C. $[a]_D^{25}$ = –864 (*c* = 0.14, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ = 1.78 (s, 6 H, $NMe_2$), 3.87 (s, 5 H, Cp), 4.20 (t, *J* = 2.2 Hz, 1 H, Cp-H), 4.44 (d, *J* = 2.2 Hz, 1 H, Cp-H), 4.46 (d, *J* = 2.2 Hz, 1 H, Cp-H), 4.79 (s, 1 H, C*H*N), 6.70 (dd, *J* = 4.6, 7.6 Hz, 1 H), 7.1 (t, *J* = 7.6 Hz, 1 H), 7.2–7.5 (m, 11 H, aromatic signals) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 39.7 ($NMe_2$), 59.1 (*C*$NMe_2$), 64.9, 68.1, 69.9, 70.2, 90.3, 91.3, 119.4, 127.8–128.7 (several aromatic signals), 129.5, 133.9, 134.1, 134.2, 134.4, 135.7 (d, $J_{P,C}$ = 19.1 Hz), 137.2 (d, $J_{P,C}$ = 10.8 Hz), 138.0 (d, $J_{P,C}$ = 11.4 Hz), 141.2 (d, $J_{P,C}$ = 6.30 Hz), 151.7 (d, $J_{P,C}$ = 20.7 Hz) ppm. $^{31}$P NMR (202 MHz, $CDCl_3$): δ = –13.7 ($J_{P,H}$ = 11.0 Hz) ppm. HRMS: calcd. for $C_{31}H_{28}FeNP$ $[M + H]^+$ 502.1387; found 502.1356. Crystals suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$/hexane.

**7a:** Orange solid. Yield: 0.75 g, 60%. M.p. 84 °C. $[a]_D^{25}$ = –972 (*c* = 0.65, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.35 (s, 9 H, $SiMe_3$), 2.00 (br. s, 6 H, $NMe_2$), 3.86 (s, 5 H, Cp), 422 (t, *J* = 2.3 Hz, 1 H, Cp-H), 4.48 (d, *J* = 2.3 Hz, 1 H, Cp-H), 4.54 (d, *J* = 2.3 Hz, 1 H, Cp-H), 4.97 (s, 1 H, C*H*N), 7.15–7.35 (m, 3 H, aromatic signals) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): δ = –0.31 ($SiMe_3$), 40.1 ($NMe_2$), 58.9 (*C*$NMe_2$), 64.9, 68.5, 69.6, 70.2, 90.7, 91.0, 121.0, 127.0, 131.3, 137.3, 140.3, 153.9 ppm. $C_{22}H_{27}FeNSi$ (389.39): calcd. C 67.86, H 6.99, N 3.60; found C 67.64, H 7.13, N 3.44.

**7b:** Orange solid. Yield: 1.0 g, 79%. M.p. 46 °C. $[a]_D^{25}$ = –1303 (*c* = 0.20, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ = 2.09 (s, 6 H, $NMe_2$), 3.89 (s, 5 H, Cp), 4.29 (t, *J* = 2.2 Hz, 1 H, Cp-H), 4.54 (d, *J* = 2.2 Hz, 1 H, Cp-H), 4.56 (d, *J* = 2.2 Hz, 1 H, Cp-H), 4.95 (s, 1 H, C*H*N), 7.09 (t, *J* = 7.7 Hz, 1 H), 7.23 (d, *J* = 7.7 Hz, 1 H),

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7.28 (d, $J$ = 7.7 Hz, 1 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 40.4 ($NMe_2$), 59.7 ($CNMe_2$), 65.2, 69.2, 70.3, 70.4, 89.6, 90.1, 118.2, 120.5, 129.1, 129.6, 144.3, 146.1 ppm. HRMS: calcd. for $C_{19}H_{18}BrFeN$ [M + H]$^+$ 396.0019; found 396.0110.

**7c:** Orange oil. Yield: 1.1 g, 78%. $[a]_D^{25}$ = –1198 ($c$ = 0.30, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 2.05 (s, 6 H, $NMe_2$), 3.87 (s, 5 H, Cp-H), 4.26 (t, $J$ = 2.2 Hz, 1 H, Cp-H), 4.51 (d, $J$ = 2.2 Hz, 1 H, Cp-H), 4.54 (d, $J$ = 2.2 Hz, 1 H, Cp-H), 4.75 (s, 1 H, C*H*N), 6.91 (t, $J$ = 7.7 Hz, 1 H), 7.23 (d, $J$ = 7.7 Hz, 1 H), 7.52 (d, $J$ = 7.7 Hz, 1 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 40.2 ($NMe_2$), 59.7 ($CNMe_2$), 65.1, 70.3, 70.4, 71.1, 89.7, 90.2, 93.7, 118.9, 129.6, 135.3, 143.7, 149.7 ppm. HRMS: calcd. for $C_{19}H_{18}FeIN$ [M + H]$^+$ 443.9880; found 443.9864.

**1,5-Dibromo PhPPFA (12):** To a 300-mL three-neck round-bottom flask containing a magnetic stirring bar was added (*R*,*Sp*)-**11** (PhPPFA; 1.7 g, 3.4 mmol) and dry diethyl ether (30 mL) under a slight pressure of nitrogen. The flask was cooled in an ice bath, and a solution of *t*BuLi (1.6 M in hexane, 5.4 mL, 8.5 mmol) was then added by syringe through the septum whilst stirring. After 2 h, a solution of $BrCF_2CF_2Br$ (1.2 mL, 10 mmol) in THF (40 mL) was injected into the mixture; the ice bath was then removed, and the mixture was warmed to room temp. and stirred for an additional 16 h. The reaction was quenched with saturated aqueous $NH_4Cl$, and extracted with $CH_2Cl_2$ (3 × 30 mL). The combined extracts were washed (brine), dried ($K_2CO_3$), and filtered, and the solvent was removed under reduced pressure. The orange residue was purified by column chromatography on silica gel (hexane/ethyl acetate/triethylamine, 20:4:1) to give pure **12** as an orange solid. Yield: 1.75 g, 2.6 mmol, 78%. M.p. 177 °C. $[a]_D^{25}$ = –266 ($c$ = 0.20, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 2.04 (s, 6 H, $NMe_2$), 3.68 (s, 5 H, Cp), 3.88 (d, $J$ = 2.0 Hz, 1 H, C*H*N), 4.57 (d, $J$ = 2.2 Hz, 1 H, Cp-H), 5.13 (d, $J$ = 4.6 Hz, 1 H, Cp-H), 7.08–7.90 (m, 14 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 45.1 ($NMe_2$), 68.4, 69.6 (d, $J_{P,C}$ = 3.6 Hz), 72.6, 73.2, 77.8 (d, $J_{P,C}$ = 19.2 Hz), 78.9, 93.1 (d, $J_{P,C}$ = 20.0 Hz), 127.8 (d, $J_{P,C}$ = 6.0 Hz), 132.4 (d, $J_{P,C}$ = 6.0 Hz), 139.0 (d, $J_{P,C}$ = 15.6 Hz), 139.2 (d, $J_{P,C}$ = 11.2 Hz), 125.6–143.1 (several aromatic signals) ppm. $^{31}$P NMR (202 MHz, $CDCl_3$): $\delta$ = –23.7 ($J_{P,H}$ = 9.9 Hz) ppm. HRMS: calcd. for $C_{31}H_{28}Br_2FeNP$ [M + H]$^+$ 661.9722; found 661.9429.

**(Cyclopentadienyl)({(*R*,*Sp*,*Sp*)-η$^5$-{8-(dimethylamino)-1-(diphenylphosphanyl)dihydrocyclopenta[*a*]indenyl})iron(II) (13):** To a 300-mL three-neck round-bottom flask containing a magnetic stirring bar was added **12** (1.0 g, 1.5 mmol) and dry diethyl ether (25 mL) under a slight pressure of nitrogen. The flask was cooled in an ice bath, and a solution of *t*BuLi (1.58 M in hexane, 2.4 mL, 3.8 mmol) was then added by syringe through the septum whilst stirring. After 2 h, a solution of $Fe(acac)_3$ (1.6 g, 4.5 mmol) in benzene (10 mL) was added to the reaction solution; the ice bath was then removed, and the mixture was warmed to room temp. and stirred for an additional 22 h. The reaction was quenched with a 10% aqueous solution of NaOH, and the precipitate was removed by filtration through a Celite pad. The filtrate was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined extracts were washed (brine), dried ($K_2CO_3$), and filtered, and the solvent was removed under reduced pressure. The dark orange residue was purified by column chromatography on silica gel (hexane/ethyl acetate/triethylamine, 20:4:1) to give pure **13** as an orange solid. Yield: 0.53 g, 1.06 mmol, 70%. M.p. 47 °C. $[a]_D^{25}$ = –460 ($c$ = 0.1, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.98 (s, 6 H, $NMe_2$), 3.37 (s, 1 H, C*H*N), 3.67 (t, 5 H, Cp), 4.74 (s, 1 H), 5.08 (s, 1 H), 7.11–7.59 (m, 14 H, aromatic signals) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 40.6 ($NMe_2$), 62.1 ($CNMe_2$), 68.7, 70.0 (d, $J_{P,C}$ = 19.2 Hz), 71.7, 72.3 (d, $J_{P,C}$ = 14.4 Hz), 93.5, 99.5 (d, $J_{P,C}$ = 28.8 Hz), 119.2, 125.0–140.8 (several aromatic signals), 138.2 (d, $J_{P,C}$ = 8.4 Hz), 140.1 (d, $J_{P,C}$ = 8.4 Hz), 147.8 ppm. $^{31}$P NMR (202 MHz, $CDCl_3$): $\delta$ = –21.1 ($J_{P,H}$ = 9.2 Hz) ppm. HRMS: calcd. for $C_{31}H_{28}FeNP$ [M + H]$^+$ 502.1356; found 502.1418.

**Palladium-Catalyzed Allylic Alkylation of (±)-1,3-Diphenyl-2-propenyl Acetate (14):** To a Schlenk tube containing a stirring bar was added $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.8 mg, 0.01 mmol, 2 mol-%) and ligand **7d** (15 mg, 0.03 mmol) dissolved in $CH_2Cl_2$ (3.0 mL). The mixture was stirred under an atmosphere of argon at room temp. for 30 min. Compound **14** (126 mg, 0.5 mmol), dimethyl malonate (**15**; 170 mL, 1.5 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (370 mL, 1.5 mmol), and potassium acetate (1.5 mg, 0.015 mmol) were successively added to this solution. The mixture was stirred at room temp. and monitored by TLC. After completion (13 h), the mixture was diluted with $CH_2Cl_2$ (20 mL), washed with saturated aqueous $NH_4Cl$, dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure, and the brown residue was subjected to PTLC (hexane/ethyl acetate, 40:3) to give pure **16**. Yield: 150 mg, 0.46 mmol, 93%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.51 (s, 3 H, $CH_3$), 3.70 (s, 3 H, $CH_3$), 3.96 (d, $J$ = 10.9 Hz, 1 H, C*H*CO), 4.26 (dd, $J$ = 8.7, 10.9 Hz, 1 H, C*H*Ph), 6.33 (dd, $J$ = 8.7, 15.7 Hz, 1 H, =C*H*CH), 6.46 (d, $J$ = 15.7 Hz, 1 H, PhC*H*=), 7.2–7.3 (m, 10 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 49.0 (*C*HPh), 52.3 ($CH_3$), 52.5 ($CH_3$), 57.5 (*C*HCO), 126.3, 127.1, 127.5, 127.6, 127.7, 127.8, 128.1, 128.4, 128.5, 128.6, 129.0, 131.7, 136.7, 140.0, 167.5 (CO), 168.1 (CO) ppm. The *ee* of the product (96%) was determined by HPLC [Chiralpack AD-H, 25 cm; hexane/2-propanol, 90:10, 1.0 mL/min, $t_R$(*R*) = 11.5 min, $t_R$(*S*) = 16.1 min].

**Palladium-Catalyzed Allylic Amination of 14:** To a Schlenk tube containing a stirring bar was added $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.8 mg, 0.01 mmol, 2 mol-%) and ligand **7d** (15 mg, 0.03 mmol) dissolved in dry $CH_2Cl_2$ (2.0 mL), and the mixture was stirred under an atmosphere of argon at room temp. for 30 min. Compound **14** (126 mg, 0.5 mmol), benzylamine **17** (0.43 g, 4.0 mmol), and TBAF (1 M in THF, 1.0 mL, 1.0 mmol) were successively added to this solution. The mixture was stirred at room temp. and monitored by TLC. After completion (18 h), the mixture was diluted with diethyl ether (20 mL), washed with saturated aqueous $NH_4Cl$, dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure. The brown residue was subjected to PTLC (hexane/ethyl acetate, 40:3) to give pure **18**. Yield: 140 mg, 0.47 mmol, 94%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.74 (br. s, 1 H), 3.74 (d, $J$ = 13.3 Hz, 1 H, one of PhC$H_2$N), 3.78 (d, $J$ = 13.3 Hz, 1 H, one of PhC$H_2$N), 4.37 (d, $J$ = 7.4 Hz, 1 H, C*H*NH), 6.30 (dd, $J$ = 7.4, 15.9 Hz, 1 H, =C*H*CH), 6.56 (d, $J$ = 15.9 Hz, 1 H, PhC*H*=), 7.2–7.4 (m, 15 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 51.3 ($CH_2$NH), 64.5 (*C*HNH), 126.4–129.0 (several aromatic signals), 130.3, 132.5, 136.8, 140.3, 142.8 ppm. The *ee* of the product (90%) was determined by HPLC [Chiracel OJ-H, 25 cm; hexane/2-propanol, 90–10, 0.6 mL/min, $t_R$(*S*) = 18.1 min, $t_R$(*R*) = 22.7 min].

**Crystallographic Data:** CCDC-641401 (for **7d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[10] In our previous work (see ref.[7]) we reported that (*R*,*Rp*)-1,5-diphosphane was prepared by the reaction of 1,5-dilithioferrocene **3b** with $Ph_2PCl$, and we stated that it was the diastereomer of taniaphos. The present study revealed that the correct stereochemistry of taniaphos is (*R*,*Rp*) as illustrated in Scheme 3, so the 1,5-diphosphane we prepared is in fact taniaphos and not *dia*-taniaphos. The incorrect structure of taniaphos as it has long been illustrated corresponds to *dia*-taniaphos. It is still not known why the stereochemistry of *o*-lithiation of (*R*)-**8** is (*Sp*), whereas that of *ortho* lithiation of bromo-free (*R*)-(1-dimethylamino)phenylmethylferrocene is (*Rp*), even though both of them have the same stereochemistry at the amino carbon. The *ortho* lithiation of (*R*)-configured amino carbons usually gives (*Rp*) planar chirality. D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, I. Ugi, *J. Am. Chem. Soc.* **1970**, *92*, 5389–5393. See also ref.[3c]

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[14] The reaction conditions were optimized by examining several additives. The *ee* values for additives are as follows: LiOAc: 80% *ee*, NaOAc: 81% *ee*, KOAc: 96% *ee*, $Cs_2CO_3$: 82% *ee*, and KOAc: in THF 90% *ee*.


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