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Two Approaches in the Synthesis of Planar Chiral Azinylferrocenes

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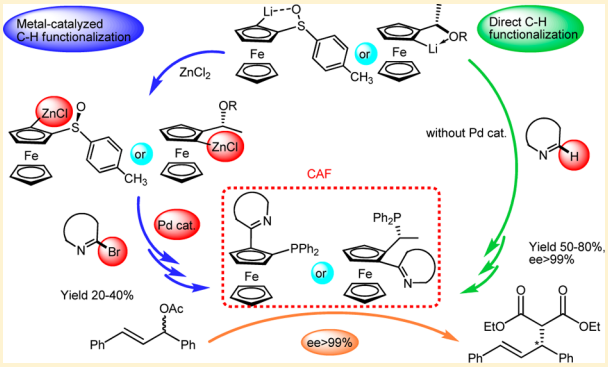
Supporting Information

ABSTRACT: Two synthetic routes to the chiral azinylferrocenes (CAFs) **5** and **15**, key intermediates for the synthesis of new enantiomerically enriched *P,N*-ligands, have been compared. The first approach is based on the palladium-catalyzed cross-coupling reaction of halogenated azines with organozinc derivatives of ferrocenes (the Negishi reaction). The second approach exploits a new synthetic methodology, which provides a shorter pathway, through the direct C−H functionalization of aromatics by the C−C coupling of halogen-free (hetero)arenes with lithium ferrocenes bearing stereogenic C and S atoms. The palladium complexes of *P,N*-ligands have been used as catalysts for the Tsuji−Trost reaction, which proceeds with high enantioselectivity to give allylic substitution products in good yields.



INTRODUCTION

Planar chiral ferrocenes have gained considerable interest from researchers working in the field of asymmetric synthesis due to the distinct advantage that the ferrocene core can rigidly sustain a mutual spatial arrangement of atoms. Additionally, ferrocene structures provide a good basis for the synthesis of compounds combining both the planar and central symmetry elements.[1] Among the best known compounds of this series are *P,S*-, *P,O*-, *P,P*-, and *P,N*-bidentate ligands used for palladium-catalyzed allylic substitution in the series of both cyclic and acyclic allyl acetates,[2] as well as for hydrogenations,[3] hydroborations,[4] cycloaddition reactions,[5] and others.[6]

One of the most versatile and powerful strategies for obtaining planar chiral homoannular substituted ferrocenes has involved exploiting the diastereoselective lithiation of the 2-position of the cyclopentadienyl ring bearing the chiral fragments, which are preliminarily introduced onto a side chain. The regio- and diastereoselectivity of this lithiation is achieved through the formation of a conformationally rigid five-, six-, or seven-membered ring in the transition state of the reaction. This phenomenon is well-known as the complex-induced proximity effect (CIPE)[7] and is exemplified by the coordination of a lithium atom with a lone electron pair of nitrogen or oxygen atoms of directing groups (X···Li bond, where X = N, O) in compounds **2**, **13**, and **16** (see Schemes 2 and 3). An impressive series of 1,2-directing groups can be used for the synthesis of planar chiral ferrocenes, such as dimethylaminoethyl-,[8] alkoxy-,[9] sulfoxide-,[10] oxazolinyl-,[11] imidazolinyl-,[12] pyrrolidinyl-,[13] and other ferrocenes.[14−20] Another important feature of diastereoselective lithiation is the specific spatial arrangement of atoms around an asymmetric center of the side chain of ferrocenes in the course of intermediate complex formation (Schemes 2 and 3, compounds **2**, **13**, **16**). Despite impressive efforts made by chemists working in this field, there is continuing interest in the development of new methods for the asymmetric synthesis of planar chiral ferrocenes to extend a variety of accessible derivatives and also to improve the schemes of their syntheses.

The chiral ligands of the ferrocene family are of great significance because, due to unshared electron pairs, they are capable of donor−acceptor interactions as well as the formation of complexes with metals and charged and neutral molecules. Hetaryl-substituted ferrocenes can be obtained either through the formation of heterocyclic fragments by using substituents preliminarily introduced into the metallocene structure or by cross-coupling reactions of heterocyclic compounds with ferrocenes.[21]

Currently, in the vast majority of cases, the synthesis of hetaryl-substituted ferrocenes, including chiral ones, is accomplished by using the cross-coupling methodology. Cross-coupling reactions are usually based on the interaction of haloheteroarenes or their synthetic equivalents (OTf, etc.) with organometallic derivatives of ferrocenes (magnesium, zinc, tin, etc.) in the presence of transition metal catalysts.[21] However, there is another synthetic methodology that appears to be effective for the direct introduction of readily available lithium derivatives of ferrocene[22] and cymantrene[23] into π-deficient azaheterocyclic compounds. These reactions have become

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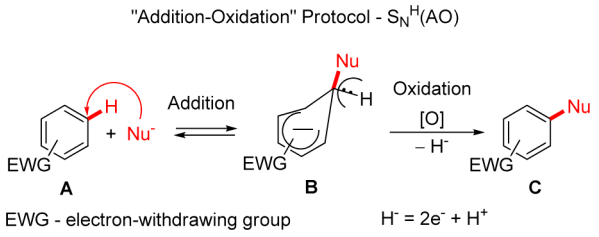
widespread over the last few decades and are currently known as nucleophilic aromatic substitution of hydrogen (S_NH) reactions.[24] These reactions are effective synthetic tools for C−C and C−X bond formations (X = N, O, S, P) in the series of arenes and heteroarenes because they do not require transition metal catalysis or the presence of an auxiliary group in the (hetero)aromatic ring. Scheme 1 demonstrates the oxidative

Scheme 1. Nucleophilic Substitution of Hydrogen through the "Addition−Oxidation" Steps



version of the S_NH reactions, the so-called "Addition−Oxidation" S_NH(AO) protocol. Because the spontaneous elimination of the hydride ion from σ^H-adducts **B** is scarcely possible, the presence of an oxidative agent (for instance, air oxygen often performs this role) is required to convert σ^H-adducts **B** into the S_NH products **C** by eliminating a proton and the pair of electrons.

The synthesis of planar chiral ferrocenes is somewhat limited by the need to use multistep schemes, which often involve laborious separation and purification procedures. Therefore, reducing the number of steps (or combining several steps into a one-pot procedure) appears to be both an attractive and beneficial approach. We have managed to obtain compounds **5** and **17** by using the S_NH methodology in three instead of four steps (Schemes 2 and 3), omitting the transmetalation reaction (exchange of lithium atoms with zinc). It should be noted that the S_NH reactions allow one to use azaheterocyclic compounds instead of their halogenated derivatives and also to avoid the application of metal catalysts.

The present paper reports the results of our comparative study concerning two plausible synthetic routes for the C−C coupling of azines with ferrocenes based on the Negishi and S_NH reactions. In both cases, ferrocene derivatives such as (*S*)-ferrocenyl-*p*-tolylsulfoxide and (*R*)-α-hydroxyethylferrocene, bearing asymmetric S and C atoms in the side chain, were used as nucleophiles. The synthesized *P,N*-ligands were further used in the Tsuji−Trost reaction.

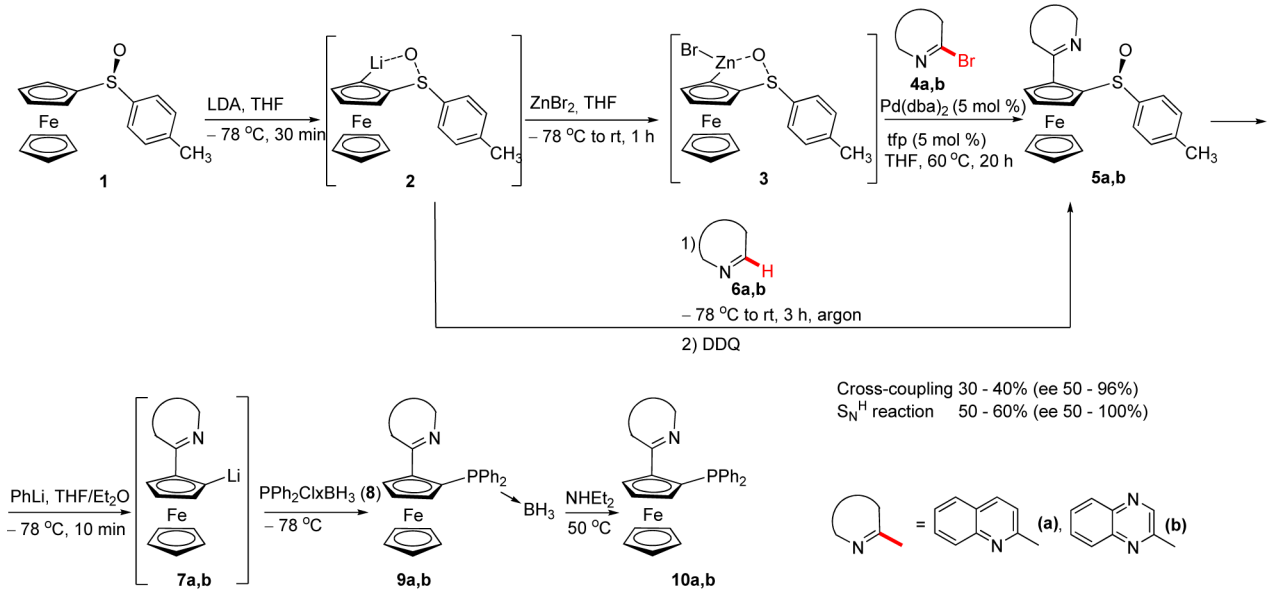
RESULTS AND DISCUSSION

Enantioselective syntheses based on (*S*)-ferrocenyl-*p*-tolylsulfoxide **1**[25] and (*R*)-α-hydroxyethylferrocene **11**[26] as starting materials were shown to produce a number of chiral ferrocene ligands. Knochel and co-workers suggested an approach to the palladium(0)-catalyzed (hetero)arylation of zinc derivatives of (*S*)-ferrocenyl-*p*-tolylsulfoxide[10a] and (*R*)-α-methoxyphenylmethyl-substituted ferrocene[9b] by using the Negishi reaction. This cross-coupling reaction enabled quinolin-8-yl and isoquinolin-1-yl fragments to be incorporated in sulfoxide **1**.[10a] It should be noted that enantiomerically enriched ether derivatives of ferrocene, e.g., compound **12**, can also enter the Negishi reaction. Indeed, the products derived from the C−C coupling of the zinc derivative of (*R*)-α-methoxyphenylmethylferrocene with 2-iodopyridine, 2-iodoquinoline, and 2-iodopyrimidine have been obtained.[9b]

According to Kagan's procedure, the synthesis of heteroaryl-substituted ferrocene derivatives **5** and **15** has been realized (Schemes 2 and 3). Lithioferrocene **2**[27] obtained from sulfoxide **1** was subjected to transmetalation with $ZnBr_2$ in anhydrous THF to give the intermediate **3**, which was involved in the C−C coupling reaction with 2-bromoquinoline and 2-bromoquinoxaline in the presence of bis(dibenzylideneacetone)palladium(0) to afford the target compounds **5a,b** in 40% and 60% yields, respectively (Scheme 2).

An alternative way to induce the C−C coupling of (hetero)arenes with ferrocenes is the direct C−H functionalization of aromatic compounds through the nucleophilic substitution of hydrogen in π-deficient azines **6** by lithioferrocene **2**. We have found that compound **2** readily reacts with azines **6a,b** at −78 °C to give chiral derivatives (S_{Fc},*S*)-[2-(quinolin-2-yl)-ferrocen-1-yl]-*p*-tolylsulfoxide **5a** and (S_{Fc},*S*)-[2-(quinoxalin-2-yl)-ferrocen-1-yl]-*p*-tolylsulfoxide **5b** in 80% and 75% yields, respectively (Scheme 2).

Scheme 2. Synthesis of Chiral Derivatives 5, 9, and 10



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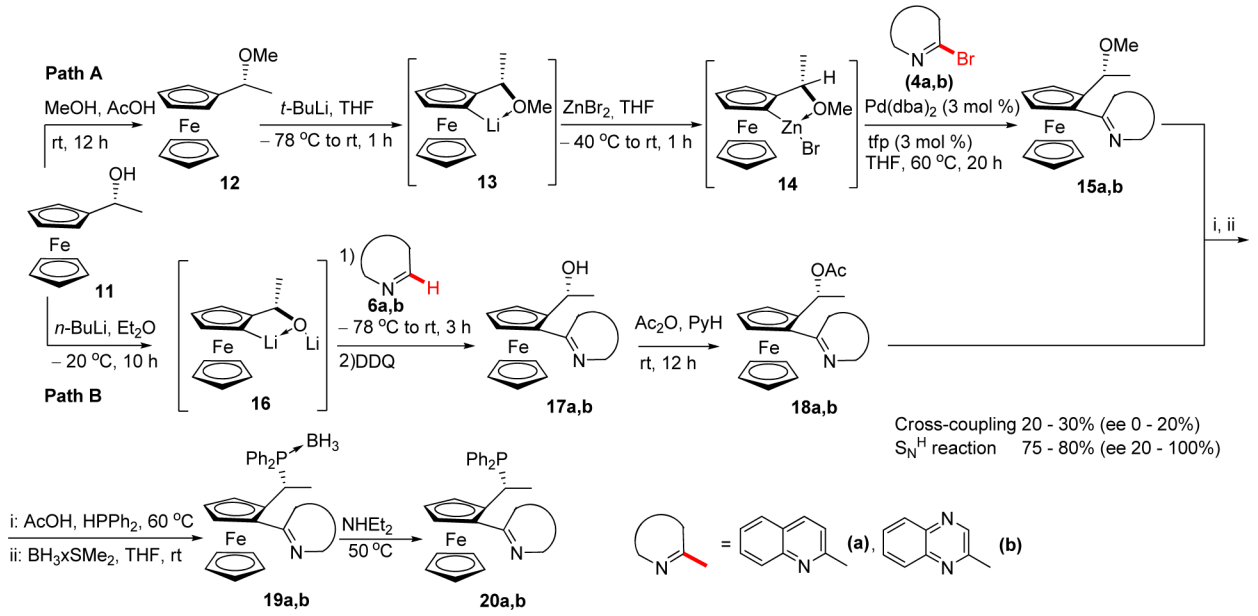
Scheme 3. Synthesis of Chiral Compounds 15, 18, and 19



In an attempt to obtain effective ferrocene ligands for catalysis, we used sulfoxides **5** as precursors for the synthesis of (S_{Fc})-[2-(2-(hetero)aryl)-ferrocen-1-yl]-diphenylphosphines **10**. The lithium exchange in sulfoxides **5** with PhLi affords 1-lithium-2-hetarylferrocenes **7a,b**, which interact with $PPh_2Cl{\cdot}BH_3$ (**8**) to form complexes **9** (Scheme 2). The relatively stable borane-protected *P,N*-ligands **9** can be handled in air and purified by silica column chromatography. In addition, they can be easily deprotected by treatment with diethylamine,[27] thus giving ligands **10a** and **10b** in nearly quantitative yield.

In a similar way, the zinc compound **14** derived from ferrocene ether **12** (R_{Fc},*R*-isomer) was involved in the Negishi coupling with bromoazines **4**. The synthetic chain to prepare compounds **20** from the chiral alcohol **11** involves the following steps (Scheme 3, Path A): (a) the formation of ether **12** followed by treatment with *tert*-BuLi in dry THF to form the lithium derivative **13**; (b) the transmetalation of **13** with $ZnBr_2$ in THF to afford zinc derivative **14**; (c) the Negishi cross-coupling of **14** with bromoazines (**4a,b**) to form compounds **15**, which are then transformed into *P,N*-ligands **19** protected with a BH_3-group. Deprotection affords the target products **20a,b**.

We have found that the C−C coupling of azines with the starting ferrocene alcohol **11** can be achieved directly without the preliminary alkylation of the hydroxy group. Indeed, compound **16**, generated by the treatment of (*R*)-α-hydroxyethylferrocene **11** with *n*-BuLi at −20 °C in dry ether for 10 h,[28] reacts easily with azines **6a,b** to form (R_{Fc})-1-(quinolin-2-yl)-2-(α-(*R*)-hydroxyethyl)ferrocene **17a** (78%) and (R_{Fc})-1-(quinoxalin-2-yl)-2-(α-(*R*)-hydroxyethyl) ferrocene **17b** (75%) (Scheme 3, Path B). It should be noted that compounds **17a,b** can be used as ligands for the synthesis of metal complexes.

A conventional way to substitute the hydroxy group at an asymmetric carbon atom with a *P*-nucleophile is the reaction of alkyloxy/acyloxy derivatives **15** or **18** with diphenylphosphine.[26] To obtain acyloxy derivatives **18a,b**, compounds **17a,b** were treated with an acetic anhydride in pyridine at ambient temperature for 12 h. Heating 1-hetaryl-2-(α-(*R*)-methoxyethyl)-ferrocenes **15a,b** or 1-hetaryl-2-(α-(*R*)-acetyloxyethyl)ferrocenes **18a,b** with diphenylphosphine in acetic acid at 60 °C for 6 h followed by treatment with $BH_3{\cdot}SMe_2$ in dry THF gave rather stable borane complexes **19** (Scheme 3).

We have established that use of the S_N^H methodology for the synthesis of quinoline derivatives **9a** and **19a** allows one to increase significantly yields of compounds **9a** and **19a** and to provide a good enantiomeric excess for the major stereoisomer in these compounds (Table 1). Unfortunately, in the case of quinoxaline compounds **9b** and **19b** the S_N^H approach did not give an improvement in the stereoselectivity of the synthesis. A plausible reason is a lower temperature of the S_N^H reaction of quinoline derivatives in comparison with that for the cross-coupling process. Obviously, an enhanced temperature for the Negishi reactions leads to a lower stability of the intermediate **14**. Absence of stereoselectivity in the synthesis of quinoxaline derivatives can be explained by spontaneous racemization of ferrocene compounds[6b,29] or coordination by the additional nitrogen of the quinoxaline. Also an enhanced π-deficiency of the quinoxaline fragment can destabilize the ferrocene part of the molecule, thus facilitating isomerization of the ligand.

Table 1. Total Yields of Chiral Derivatives 9 and 19

entry	Negishi cross-coupling, total yield (ratio, %)	direct C−H functionalization (S_N^H reactions), total yield (ratio, %)
9a	30 (98:2 er)	58 (>99:1 er)
9b	40 (74:26 er)	51 (74:26 er)
19a	26 (50:50 er)	78 (>99:1 er)
19b	23 (60:40 er)	75 (60:40 er)

It has been suggested that compounds **5** and **17** are formed according to a commonly accepted scheme of the S_N^H reactions.[24a] The first step is the addition of lithium derivatives **2** and **16** to azines, resulting in the formation of the σ^H-adducts **Li-21**, which then undergo hydrolysis into the corresponding dihydro compounds **H-22**. Finally, the aromatization of the latter into the S_N^H products **5** and **17** occurs (Scheme 4). Yields of compounds **5** and **17** are increased about 15% if a mild oxidizing agent such as DDQ (2,3-dichloro-5,6-dicyanobenzo-quinone) is used instead of air oxygen.

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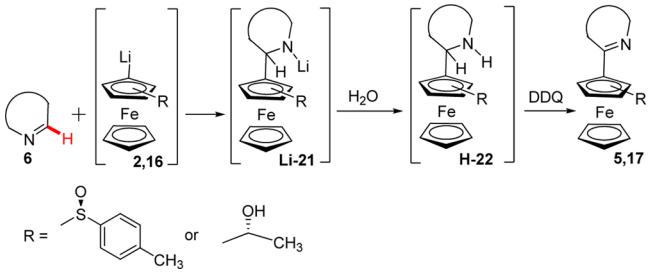
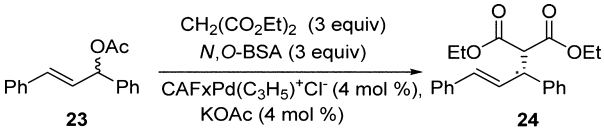
Scheme 4. Plausible Mechanism for the S_N^H Synthetic Pathway to Compounds 5 and 17



Asymmetric Catalysis. It has been established that ligands **10a** and **20a** can be used in widespread palladium-catalyzed allylic substitution (Scheme 5). The reaction of 1,3-diphenyl-2-propenyl acetate **23** with diethyl malonate as a nucleophilic agent (the Tsuji–Trost reaction) was performed in various solvents (THF, toluene, CH_2Cl_2) in the presence of allylpalladium(II) chloride (2 mol %), a ligand (4 mol %), *N*,*O*-bis(trimethylsilyl)-acetamide (BSA, 2 equiv), and a catalytic amount of KOAc. The complex was prepared in situ from an allylpalladium(II) chloride dimer and an appropriate ligand (CAF) (**10a**, **20a**) in the ratio 1:2. On mixing of the ligand and the allylpalladium(II) chloride, the reaction solution exhibited an acute deepening in color. Metal complexes of other chiral ferrocene ligands with palladium[13b] were shown to first form intermediate complexes with diphenylallyl, which favor regio- and stereoselective attack by diethyl malonate. In the absence of chiral ligands, stereoselectivity is not observed, whereas the substitution of the acetoxy group with a nucleophilic reagent occurs.[30]

Scheme 5. Allylic Alkylation



Both ligands (**10a** and **20a**) demonstrated better efficiency (90% to >99%) than those obtained with ferrocene (56–91%).[9b,10a] Table 2 provides the data concerning the solvent effects on the reaction selectivity. The ligands were tested at 22 °C for 24 h. The highest yield of (*S*)-diethyl-2-(1,3-diphenylallyl)malonate was reached when the reaction was performed in CH_2Cl_2 (Table 2, entry 2 for **10a** and entry 5 for **20a**). For **10a**, the highest stereoselectivity was also achieved in CH_2Cl_2 (Table 2, entry 2), whereas the highest stereoselectivity for ligand **20a** was achieved in THF (Table 2, entry 6).

Table 2. Palladium-Catalyzed Allylic Alkylation in the Presence of Ligands 10a and 20a

entry	ligand (4 mol %)	solvent	yield[a] (%)	enantiomeric[b] ratio (% er)
1	**10a**	toluene	99	97:3
2		CH_2Cl_2	99	>99:1
3		THF	85	96:4
4	**20a**	toluene	99	97:3
5		CH_2Cl_2	99	98:2
6		THF	45	>99:1

[a]The reaction was performed at 22 °C. Isolated yield after purification by column chromatography. [b]Determined by HPLC (Chiralcel OD-H).

The evidence for the structure of 1,2-disubstituted hetarylferrocenes and palladium complexes derived from the ligands **10a** and **20a** has been provided by NMR, IR, mass spectrometry, X-ray analysis, and elemental analysis. The optical purity of all chiral compounds was determined by HPLC on an analytical column using the chiral sorbent Chiralcel OD-H (Table 2).

The structure of compound **9a** has been unequivocally determined by X-ray analysis (see Supporting Information, Figure S1). The crystals of **9a** were obtained by crystallization from a mixture of dichloromethane and diethyl ether.

CONCLUSIONS

In summary, a new synthetic pathway to the chiral *P*,*N*-ligands **10** and **20** by using a straightforward noncatalytic functionalization of the C(sp^2)-H-bond in (hetero)arenes (the S_N^H methodology) has been advanced. This approach enabled us to reduce the number of steps in the synthesis of ferrocene ligands by omitting the transmetalation of lithium organometallic compounds into zinc-containing compounds and to avoid the use of halogenated azines and catalysis by metal complexes. Whereas lithium ferrocenes are able to react with a variety of mono-, di-, and triazines, as well as their benzo analogues, this method can be exploited widely for the synthesis of planar chiral ferrocene derivatives.[22] The ligands obtained were used in palladium-catalyzed allylic substitution reactions. The Tsuji–Trost allylic alkylation proceeded easily to give the target chiral compounds in quantitative yields and with ee > 99%. It is noteworthy that the use of a palladium catalyst with the ligands **10** and **20** was efficient and selective at 22 °C.

EXPERIMENTAL SECTION

General. All reactions were carried out under argon using standard Schlenk techniques. The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{31}P NMR (162 MHz), and ^{13}C and ^{1}H 2D NMR spectra were recorded on a NMR spectrometer (400 MHz). Chemical shifts are given in δ values (ppm) using TMS as the internal standard and $CDCl_3$ as the solvent. The mass spectra were measured on a mass spectrometer equipped with an orthogonal electrospray ionization (ESI) source, a six-port divert valve and a syringe pump (kd Scientific) with the flow rate of 180 μL/h. The IR spectra were recorded using a infrared spectrometer equipped with a diffuse reflection attachment. The elemental analysis was carried out on an automated analyzer. Analytical HPLC was performed using a reverse-phase column and a Chiralcel OD-H column (250 mm × 4.6 mm), detection at 230 and 254 nm, 0.02 mL/min flow rate. The angle of rotation was measured on a spectrophotopolarimeter. The course of the reactions was monitored by TCL on 0.25 mm silica gel plates (60F 254). The column chromatography was performed on silica gel (silica gel 60, 0.035–0.070 mm, 220–440 mesh).

Ferrocene, acetylferrocene, diethylmalonate, *N*,*O*-bis(trimethylsilyl)-acetamide, allylpalladium chloride (dimer), 3-acetoxy-1,3-diphenylpropene, and compounds of the azine family were purchased.

Bromoferrocene,[10f] (*R*)-α-hydroxyethylferrocene,[25,10e] $Ph_2PCl{\cdot}BH_3$,[10] (α-(*R*)-metoxyethyl)ferrocene[9] were prepared according to the published procedures.

Crystallographic Data for 9a. Crystals of **9a** were obtained by crystallization from a mixture of dichloromethane and heptanes to give yellow single crystals. X-ray diffraction analysis was performed on an X-ray diffractometer equipped with a CDD detector (Mo Kα graphite-monochromated radiation, λ = 0.71073 Å, ω-scanning technique, the scanning step was 1° and the exposure time per frame was 10 s at 295(2) K). Analytical absorption correction was used in the reflection

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intensities integration.[31] The structure was solved by the direct method and refined applying the full matrix least-squares against F2hkl with anisotropic displacement parameters for all non-hydrogen atoms using the SHELX97 program package.[32] All hydrogen atoms were located in different electron density maps and refined using a riding model with fixed thermal parameters.

CCDC 997473 contains the corresponding crystallographic data of **9a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(S)-Ferrocenyl-*p*-tolylsulfoxide (1). A 1.6 M solution of *n*-BuLi in hexane (0.63 mL, 1.0 mmol) was added to a solution of bromoferrocene (1 mmol) in anhydrous THF (6 mL) under an atmosphere of argon at 0 °C. After 20 min of stirring, the reaction mixture was cooled to −78 °C, and a solution of (1*R*,2*S*,5*R*)-(−)-mentyl-(*S*)-*p*-toluenesulfinate (1.1 mmol) in anhydrous THF (15 mL) was added. The reaction solution was stirred for 0.5 h at −78 °C. Finally, the reaction mixture was purified on silica gel. The eluate was concentrated to dryness in vacuo. Yield: 0.217 g (67%). Yellow solid. R_f = 0.3 (eluent hexane/EtOAc, 7:3). All physicochemical characteristics of compound **1** are in good agreement with the earlier reported data.[2S,10e]

General Procedure for the Synthesis of (S_{Fc},*S*)-[2-(Quinolin-2-yl)-ferrocen-1-yl]-*p*-tolylsulfoxide (5a) and (S_{Fc},*S*)-[2-(Quinoxalin-2-yl)-ferrocen-1-yl]-*p*-tolylsulfoxide (5b) by Negishi Cross-Coupling Reaction. Sulfoxide **1** (0.324 g, 1 mmol) in anhydrous THF (10 mL) was cooled to −78 °C. A 2.0 M solution of LDA in THF (0.6 mL, 1.1 mmol) was added, and the reaction mixture was stirred for 30 min at −78 °C. A solution of $ZnBr_2$ in THF (0.8 mL, 1.7 M, 1.3 mmol) was added. The mixture was warmed to room temperature and stirred for 1 h. The solvent was removed under reduced pressure. For the cross-coupling reaction, bis(dibenzylideneacetone)palladium(0) (0.029 g, 5 mol %), tris-*o*-furylphosphine (0.012 g, 5 mol %), and the corresponding azine **4** (1.4 mmol) in anhydrous THF (5 mL) were stirred for 5 min at room temperature. The prepared zinc reagent was added in anhydrous THF (10 mL). The reaction mixture was heated to 60 °C for 20 h. After addition of saturated NH_4Cl soln., the mixture was extracted with diethyl ether (60 mL). The organic layer was washed with water, and dried over Na_2SO_4. Purification was performed by a flash chromatography on silica gel (using an appropriate solvent as eluent). The eluate was concentrated to dryness in *vacuo*.

General Procedure for the Synthesis of (S_{Fc},*S*)-[2-(Quinolin-2-yl)-ferrocen-1-yl]-*p*-tolylsulfoxide (5a) (previously published method[33] for the synthesis of 5a was modified) and (S_{Fc},*S*)-[2-(Quinoxalin-2-yl)-ferrocen-1-yl]-*p*-tolylsulfoxide (5b) by S_N^H Reaction. A 2.0 M solution of LDA in THF (0.55 mL, 1.1 mmol) was added to a solution of sulfoxide **1** (0.324 g, 1 mmol) in anhydrous THF (5 mL) under argon at −78 °C. After 40 min of stirring the reaction mixture, a solution of the corresponding azine **11** (2.0 mmol) in anhydrous THF (7 mL) was added. The reaction mixture was stirred for 30 min at −78 °C and subsequently warmed to room temperature for 2.5 h. Then water (1.0 mmol) and a solution of DDQ (1.0 mmol) in THF (10 mL) was added and the reaction mixture was filtrated off through the neutral alumina. The eluate was concentrated to dryness in vacuo. Finally, the residue was purified by using a column chromatography on silica gel (using an appropriate solvent as eluent). The eluate was concentrated to dryness in *vacuo*.

General Procedure for the Synthesis of (S_{Fc})-[2-(2-Quinolin-2-yl)-ferrocen-1-yl]-diphenylphosphine Borane Complex (9a)[34] and (S_{Fc})-[2-(2-Quinoxalin-2-yl)-ferrocen-1-yl]-diphenylphosphine Borane Complex (9b). The reaction was carried out under the atmosphere of argon at −78 °C. a 1.8 M solution of PhLi in dibutyl ether (1.11 mL, 2.0 mmol) was added to a precooled solution of hetarylferrocenyl-*p*-sulfoxide 5 (1.0 mmol) in THF (5 mL). After 10 min of stirring, $Ph_2PCl{\cdot}BH_3$ (**8**) (3.0 mmol) was added. The reaction mixture was exposed at −78 °C for 5 min, and then it was warmed to room temperature for 1 h. Water (0.5 mL) and triethylamine (0.3 mL) were added, and the reaction mixture was evaporated under reduced pressure. Finally, the reaction mixture was purified on silica gel (using an appropriate solvent as eluent). The eluate was concentrated to dryness in *vacuo*.

General Procedure for the Synthesis of (α-(*R*)-Metoxyethyl)-ferrocene (12). A solution of (*R*)-α-hydroxyethylferrocene **11** in a mixture of methanol (15 mL) and acetic acid (0.5 mL) was stirred for 12 h at room temperature. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$ solution. The remaining suspension was extracted with diethyl ether. The organic layers were washed with water and brine and dried over $MgSO_4$. The acetate was further purified by a rapid column chromatography on silica gel. The eluate was concentrated to dryness *in vacuo*.

General Procedure for the Synthesis of (R_{Fc})-1-(Quinolin-2-yl)-2-(α-(*R*)-metoxyethyl)ferrocene (15a) and (R_{Fc})-1-(Quinoxalin-2-yl)-2-(α-(*R*)-metoxyethyl)ferrocene (15b) by Negishi Cross-Coupling Reaction. A solution of compounds **12** (1 mmol) in diethyl ether (10 mL) was cooled to −78 °C. *t*-BuLi in pentane (1.7 M, 1.1 mmol) was added dropwise, and the mixture was warmed to room temperature and stirred for 1 h. After the mixture was cooled to −40 °C, a solution of $ZnBr_2$ in THF (1.7 M, 1.3 mmol) was added. The mixture was warmed to room temperature and stirred for 1 h. The solvent was then removed under reduced pressure. For the cross-coupling reaction, a solution of catalyst was prepared in THF (10 mL) from bis(dibenzylideneacetone)palladium(0) (3 mol %) and tris-*o*-furylphosphine (3 mol %) and stirred for 5 min at room temperature. A solution of the heterocyclic compound **4a** or **4b** (1 mmol) in anhydrous THF (5 mL) was added, and the reaction mixture was stirred for another 5 min. A solution of the zinc reagent solution in anhydrous THF (10 mL) was added, and the resulting mixture was heated to 60 °C and kept for 20 h. After addition of water, the mixture was extracted with diethyl ether (60 mL). The organic layers were washed with water and dried over Na_2SO_4. Purification was performed by using a flash chromatography on silica gel (using an appropriate eluent). The eluate was concentrated to dryness *in vacuo*.

General Procedure for the Synthesis of (R_{Fc})-1-(Quinolin-2-yl)-2-(α-(*R*)-hydroxy-ethyl)ferrocene (17a) and (R_{Fc})-1-(Quinoxalin-2-yl)-2-(α-(*R*)-hydroxyethyl)ferrocene (17b) by S_N^H Reaction. A 1.6 M solution of *n*-BuLi in hexane (1.38 mL, 2.2 mmol) was added to a solution of (*R*)-α-hydroxyethylferrocene 11 (0.230 g, 1 mmol) in diethyl ether (10 mL) under the atmosphere of argon at −20 °C. After intense stirring at −20 °C for 10 h, the solution of azine in diethyl ether (5 mL) was added to a precooled up to −78 °C reaction mixture, which was then warmed to room temperature for 3 h. Then water (1.0 mmol) and a solution of DDQ (1.0 mmol) in THF (10 mL) were added, and the reaction mixture was filtrated off through neutral alumina. Finally, the residue was purified by column chromatography on silica gel (using an appropriate solvent as eluent). The eluate was concentrated to dryness *in vacuo*.

General Procedure for the Synthesis of (R_{Fc})-1-(Quinolin-2-yl)-2-(α-(*R*)-acetoxy-ethyl)ferrocene (18a) and (R_{Fc})-1-(Quinoxalin-2-yl)-2-(α-(*R*)-acetoxyethyl)ferrocene (18b). An acetic anhydride (2 mL) was added to a solution of **17a** or **17b** (1 mmol) in pyridine (2 mL) under an atmosphere of argon at room temperature. The reaction mixture was exposed at room temperature for 12 h. The reaction solution was concentrated under reduced pressure. The acetates were further purified by using a rapid column chromatography on silica gel, deactivated by addition of NEt_3 to the eluent. The eluate was concentrated to dryness *in vacuo*.

General Procedure for the Synthesis of (R_{Fc})-1-(Quinolin-2-yl)-2-(α-(*R*)-diphenyl-phosphinoethyl)ferrocene Borane Complex (19a) and (R_{Fc})-1-(Quinoxalin-2-yl)-2-(α-(*R*)-diphenylphosphinoethyl)ferrocene Borane Complex (19b). Diphenylphosphine (1.2 mmol) was added under an argon atmosphere to a solution of **15a,b** or **18a,b** (1 mmol) in acetic acid (7 mL). After stirring for 6 h at 60 °C, the reaction mixture was cooled to room temperature, the solvent used was evaporated under reduced pressure, and the residual solid was dissolved in anhydrous THF (10 mL). An excess of solution of $BH_3{\cdot}SMe_2$ in THF (2 M, 8 mmol) was added dropwise, and the reaction mixture was stirred for 14 h at room temperature. The unreacted borane was destroyed by a careful hydrolysis. After extraction of the target products with CH_2Cl_2, the organic layers were collected, and the extract was dried over Na_2SO_4. After concentration, the crude reaction mixture was purified by a column chromatography on silica gel to give the diphenylphosphine complex of borane.

Deprotection. The borane complexes **9a** and **19a** (0.010 g, 20 μmol) were dissolved in diethylamine (2 mL). After 30 min of stirring at 50 °C the solvent was evaporated under reduced pressure.

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Table 3. Yield, Melting Point, R_f, IR, Elemental Analysis, and ESI-MS Data for 5, 9, 12, 15, 17, 18, and 19

	yield	mp (°C)	R_f (eluent); appearance	IR (cm^{-1})	elemental analysis	ESI-MS, m/z (%)
5a	0.316 g (80%) (by S_N^H reaction); 0.085 g (40%) (by cross-coupling reaction)	104	0.2 (hexane/EtOAc, 8:2); orange crystals	2920, 2850, 1597, 1041, 1004	Anal. Calcd for $C_{26}H_{21}FeNOS$: C, 69.18; H, 4.69; N, 3.10. Found: C, 69.52; H, 4.98; N, 2.99.	$[M + H]^+$ = 452 (100)
5b	0.339 g (75%) (by S_N^H reaction); 0.144 g (60%) (by cross-coupling reaction)	107	0.1 (hexane/EtOAc, 4:6); red crystals	3020, 2916, 2867, 1732, 1715, 1037, 808, 761	Anal. Calcd for $C_{25}H_{20}FeN_2OS$: C, 66.37; H, 4.42; N, 6.19. Found: C, 66.36; H, 4.34; N, 6.04.	$[M + H]^+$ = 453 (100)
9a	0.368 g (72%)	142	0.4 (hexane/EtOAc, 8:2); orange crystals	2963, 2380, 2343, 1099, 1056, 1016, 797	Anal. Calcd for $C_{31}H_{27}BFeNP$: C, 72.80; H, 5.28; N, 2.74. Found: C, 72.47; H, 5.60; N, 2.49.	$[M + H]^+$ = 512 (25), $[M + H - BH_3]^+$ = 498 (100)
9b	0.348 g (68%)	103	0.4 (hexane/EtOAc, 6:4); dark red crystals	3052, 2920, 2850, 2419, 2376, 739, 692	Anal. Calcd for $C_{30}H_{26}BFeN_2P$: C, 70.35; H, 5.12; N, 5.47. Found: C, 70.46; H, 5.05; N, 5.43.	$[M + H]^+$ = 513 (100), $[M + H - BH_3]^+$ = 499 (85)
12	0.625 g (100%)		0.4 (hexane/EtOAc, 9:1); dark orange oil	2975.78, 1106.92, 1085.56, 816.12	Anal. Calcd for $C_{13}H_{16}FeO$: C, 63.99; H, 6.56. Found: C, 63.90; H, 6.45.	$[M + H]^+$ = 244 (27.03), $[M + H - CH_3OH]$ = 212 (8.93)
15a	0.382 g (50%)		0.2 (hexane/EtOAc, 8:2); orange oil	2974.09, 2930.76, 1599.24, 1506.40, 1083.22, 823.45, 757.23	Anal. Calcd for $C_{22}H_{21}FeNO$: C, 71.20; H, 5.66; N, 3.77. Found: C, 71.11; H, 5.55; N, 3.97.	$[M + H]^+$ = 371 (100), $[M + H - CH_3OH]$ = 339 (5.7)
15b	0.022 g (45%)		0.2 (hexane/EtOAc, 9:1); red oil	2926.39, 1549.85, 1492.54, 1984.86, 817.02, 762.05	Anal. Calcd for $C_{21}H_{20}FeN_2O$: C, 67.78; H, 5.37; N, 7.53. Found: C, 67.68; H, 5.48; N, 7.65.	$[M + H]^+$ = 372 (87.33), $[M + H - CH_3OH]$ = 340 (7.7)
17a	0.278 g (78%)	132	0.2 (hexane/EtOAc, 9:1); red crystals	3278, 2962, 1615, 1506, 1365, 1118, 1065, 755	Anal. Calcd for $C_{21}H_{19}FeNO$: C, 70.59; H, 5.32; N, 3.92. Found: C, 70.52; H, 5.48; N, 3.86.	$[M + H]^+$ = 358 (40%), $[M + H - H_2O]^+$ = 340 (100%)
17b	0.268 g (75%)	74	0.2 (hexane/EtOAc, 9:1); dark red crystals	3318, 3082, 2974, 2870, 1549, 1123, 1005, 819	Anal. Calcd for $C_{20}H_{18}FeN_2O$: C, 67.04; H, 5.03; N, 7.82. Found: C, 66.96; H, 5.27; N, 7.72.	$[M + H]^+$ = 359 (40%), $[M + H - H_2O]^+$ = 341 (100%)
18a	0.399 g (100%) (by S_N^H reaction)	20	0.3 (hexane/EtOAc, 10:1); dark orange crystals	3057, 2959, 2925, 2853, 1721, 1254, 1017, 818	Anal. Calcd for $C_{23}H_{21}FeNO_2$: C, 69.17; H, 5.26; N, 3.51. Found: C, 69.08; H, 5.11; N, 3.86.	$[M + H]^+$ = 400 (20%), $[M + H - CH_3COOH]^+$ = 340 (100%)
18b	0.400 g (100%) (by S_N^H reaction)	136	0.2 (hexane/EtOAc, 9:1); dark red crystals	2925, 1716, 1550, 1365, 1244	Anal. Calcd for $C_{22}H_{20}FeN_2O_2$: C, 66.00; H, 5.00; N, 7.00. Found: C, 66.05; H, 5.08; N, 7.01.	$[M + H]^+$ = 401 (20%), $[M + H - CH_3COOH]^+$ = 341 (100%)
19a	0.539 g (100%)	137	0.2 (hexane/EtOAc, 9:1); orange crystals	3077, 2954, 2923, 1597, 1504, 1435, 1104, 1057, 818, 751, 738, 688	Anal. Calcd for $C_{33}H_{31}BFeNP$: C, 73.47; H, 5.75; N, 2.60. Found: C, 73.20; H, 6.05; N, 2.52.	$[M + H]^+$ = 540 (100%), $[M + H - BH_3]^+$ = 526 (40%)
19b	0.540 g (100%)	137	0.4 (hexane/EtOAc, 6:4); dark red crystals	3053, 2956, 2924, 2853, 2378, 2352, 1030, 689, 643	Anal. Calcd for $C_{32}H_{30}BFeN_2P$: C, 71.11; H, 5.56; N, 5.19. Found: C, 71.06; H, 5.48; N, 5.14.	$[M + H]^+$ = 541 (100%), $[M + H - BH_3]^+$ = 527 (40%)

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Table 4. ^{1}H, ^{13}C, and ^{31}P NMR Data for 5, 9, 12, 15, 17, 18, 19, 10a, and 20a

	$[\alpha]^{20}_{D}$	^{1}H NMR data	^{13}C NMR data	^{31}P NMR data
5a	+188.08 (*c* 0.1, $CHCl_3$)	2.37 (s, 3H, CH_3); 4.18 (s, 5H, Cp); 4.39 (m, 1H, C_5H_3); 4.57 (m, 1H, C_5H_3); 5.25 (m, 1H, C_5H_3); 7.24–7.26 (m, 2H, ^3J = 8.00 Hz, C_6H_4); 7.50–7.52 (t, 1H, ^3J = 8.00 Hz, 7′-H); 7.68 (d, 1H, ^3J = 8.00 Hz, 8′-H); 7.71 (d, 1H, ^3J = 4.00 Hz, 5′-H); 7.78 (d, 1H, ^3J = 8.00 Hz, 4′-H); 8.09 (m, 2H, C_6H_4); 8.12 (d, 1H, ^3J = 8.00 Hz, 3′-H)	21.5 (CH_3); 70.3 (C_5H_3); 71.4 (Cp); 71.8 (C_5H_3); 72.6 (C_5H_3); 85.3 (C-Cp); 94.5 (C-Cp); 121.5 (C_6H_4); 125.6 (C8); 125.7 (C7); 126.9 (C4); 127.5 (C6); 129.3, 129.4 (C_6H_4); 129.5 (C5); 135.1 (C3); 140.9 (C8a); 141.4 (C_6H_4); 148.0 (C4a); 157.2 (C2)	
5b	+15.84 (*c* 0.148, $CHCl_3$)	2.35 (s, 3H, CH_3); 4.22 (s, 5H, Cp); 4.48 (m, 1H, C_5H_3); 4.64 (m, 1H, C_5H_3); 5.25 (m, 1H, C_5H_3); 7.26 (m, 2H, C_6H_4); 7.70 (m, 2H, C_6H_4); 7.72 (t, 2H, ^3J = 8.00 Hz, 5′-H, 8′-H); 8.07 (m, 2H, 7′-H, 6′-H); 9.42 (s, 1H, 3′-H)	21.3 (CH_3); 70.9 (C_5H_3); 71.5 (Cp); 71.6 (C_5H_3); 72.9 (C_5H_3); 81.7 (C-Cp); 95.0 (C-Cp); 125.4 (C_6H_4); 129.09 (C7); 129.1 (C6); 129.2 (C5); 129.3 (C_6H_4); 130.0 (C8); 140.9 (C_6H_4); 141.0 (C_6H_4); 142.07 (C4a); 142.08 (C8a); 145.5 (C3); 153.0 (C2)	
9a	+305.00 (*c* 0.1, $CHCl_3$)	1.26 (s, 3H, BH_3); 3.94 (m, 1H, C_5H_3); 4.38 (s, 5H, CpH); 4.60 (m, 1H, C_5H_3); 5.12 (m, 1H, C_5H_3); 7.28–7.32 (m, 2H, Ph); 7.38–7.44 (m, 5H, Ph); 7.49–7.53 (m, 1H, 8′-H); 7.56–7.60 (m, 2H, 5′-H, 7′-H); 7.63–7.66 (m, 3H, Ph); 7.69 (s, 1H, 4′-H); 7.73–7.77 (t, 1H, ^3J = 4.00 Hz, 6′-H); 7.92–7.95 (d, 1H, ^3J = 8.00 Hz, 3′-H)	71.4 (C_5H_3); 71.5 (Cp); 73.7 (C_5H_3); 76.8 (C_5H_3); 89.8 (C-Cp); 89.9 (C-Cp); 120.7 (C4); 125.9, 126.6, 127.3, 128.0, 128.1, 128.2 (Ph); 128.3 (C8); 128.9 (C8a); 129.3 (C7); 131.4 (C5); 132.8, 132.9, 133.3 (Ph) 133.4 (C6); 135.3 (C3); 147.1 (C4a); 156.1 (C2)	29.85 (PPh_2)
9b	−16.97 (*c* 0.055, $CHCl_3$)	1.26 (s, 3H, BH_3); 4.02 (m, 1H, C_5H_3); 4.43 (s, 5H, CpH); 4.69 (m, 1H, C_5H_3); 5.19 (m, 1H, C_5H_3); 7.30–7.34 (m, 2H, Ph); 7.35–7.49 (m, 6H, Ph); 7.55–7.68 (m, 3H, 6′-H, Ph); 7.73–7.77 (m, 2H, 5′-H, 7′-H); 7.94 (d, 1H, ^3J = 8.00 Hz, 8′-H); 9.01 (s, 1H, 3′-H)	70.7 (C_5H_3); 71.1 (C_5H_3); 71.7 (CpH); 72.0 (C_5H_3); 86.1 (C-Cp); 86.2 (C-Cp); 124.9 (C6); 128.1 (C5); 128.3 (C8); 128.4 (Ph); 128.9 (C7); 129.0, 129.4, 130.0, 130.4, 130.8, 131.7, 131.9, 132.6, 132.7, 133.6, 133.7 (Ph); 140.6 (C4a); 141.3 (C8a); 144.7 (C3); 152.1 (C2)	−18.00 (PPh_2)
12	+1.5 (c 0.12, $CHCl_3$)	1.55 (d, 3H, ^3J = 8.00 Hz, CH(OCH_3)$\underline{CH_3}$); 3.27(s, 3H, CH($O\underline{CH_3}$)CH_3); 4.14 (s, 5H, CpH); 4.15–4.16 (m, 2H, C_5H_3); 4.20–4.21 (m, 1H, C_5H_3); 4.21 (m, 1H, C_5H_3); 4.22 (m, 1H, $\underline{CH}(OCH_3)CH_3$)	20.1 (CH(OCH_3)$\underline{CH_3}$); 55.6 (CH($O\underline{CH_3}$)CH_3); 65.8 (C_5H_3); 67.6 (C_5H_3); 67.9 (C_5H_3); 68.6 (C_5H_3); 68.6 (Cp); 74.9 ($\underline{CH}(OCH_3)CH_3$); 89.2 (C-Cp)	
15a	+28.39 (*c* 0.056, $CHCl_3$)	1.74 (d, 3H, ^3J = 4.00 Hz, CH(OCH_3)$\underline{CH_3}$); 3.24 (s, 3H, CH($O\underline{CH_3}$)CH_3); 4.04 (s, 5H, CpH); 4.41 (m, 1H, C_5H_3); 4.56–4.57 (m, 1H, C_5H_3); 4.85–4.86 (m, 1H, C_5H_3); 5.40–5.45 (m, 1H, $\underline{CH}(OCH_3)CH_3$); 7.43–7.47 (m, 1H, 6′-H); 7.60–7.66 (m, 2H, 3′-H, 7′-H); 7.72–7.74 (m, 1H, 5′-H), 8.00 (d, 1H, ^3J = 8.00 Hz, 4′-H), 7.99–8.01 (d, 1H, ^3J = 8.00 Hz, 4′-H) 8.04–8.06 (d, 1H, ^3J = 8.00 Hz, 8′-H)	20.2 (CH(OCH_3)$\underline{CH_3}$); 55.8 (CH($O\underline{CH_3}$)CH_3); 68.7 (C_5H_3); 69.0 (C_5H_3); 69.6 (C_5H_3); 70.4 (Cp); 72.6 ($\underline{CH}(OCH_3)CH_3$) 83.2 (C-Cp); 89.8 (C-Cp); 121.3 (C3); 125.4 (C6); 125.6 (C5); 126.4 (C4a); 129.2 (C8); 129.3 (C7); 135.1 (C4); 148.0 (C8a); 160.0 (C2)	
15b	+9.5 (*c* 0.04, $CHCl_3$)	1.67 (d, 3H, ^3J = 8.00 Hz, CH(OCH_3)$\underline{CH_3}$); 3.22 (s, 3H, CH($O\underline{CH_3}$)CH_3); 4.03 (s, 5H, CpH); 4.44–4.46 (m, 1H, C_5H_3); 4.59–4.60 (m, 1H, C_5H_3); 4.89–4.90 (m, 1H, C_5H_3); 5.23–5.28 (m, 1H, $\underline{CH}(OCH_3)CH_3$); 7.59–7.67 (m, 2H, 6′-H, 7′-H); 7.95–7.98 (m, 2H, 5′-H, 8′-H); 8.98 (s, 1H, 3′-H)	19.6 (CH(OCH_3)$\underline{CH_3}$); 55.7 (CH($O\underline{CH_3}$)CH_3); 69.5 (C_5H_3); 69.62 (C_5H_3); 69.68 (C_5H_3); 70.5 (Cp); 72.6 ($\underline{CH}(OCH_3)CH_3$); 79.6 (C-Cp); 90.2 (C-Cp); 128.6 (C6); 128.9 (C8); 129.1 (C5); 129.9 (C7); 140.4 (C4a); 142.2 (C8a); 145.2 (C3); 155.9 (C2)	
17a	+19.34 (*c* 0.303, $CHCl_3$)	1.66 (d, 3H, ^3J = 8.00 Hz, CH(OH)$\underline{CH_3}$); 4.07 (s, 5H, CpH); 4.40–4.41 (m, 1H, C_5H_3); 4.57 (m, 1H, C_5H_3); 4.82 (m, 1H, C_5H_3); 5.11–5.16 (m, 1H, $\underline{CH}(OH)CH_3$); 7.50–7.53 (t, 1H, 6′-H); 7.64–7.70 (m, 3H, 5′-H, CH($\underline{OH}$)CH_3, 7′-H); 7.78 (d, 1H, ^3J = 8.00 Hz, 4′-H); 7.99 (d, 1H, ^3J = 8.00 Hz, 8′-H); 8.11 (d, 1H, ^3J = 8.00 Hz, 3′-H)	20.1 (CH(OH)$\underline{CH_3}$); 64.4 ($\underline{CH}(OH)CH_3$); 68.7 (C_5H_3); 69.1 (C_5H_3); 70.4 (Cp); 71.7 (C_5H_3); 80.9 (C-Cp); 91.8 (C-Cp); 121.2 (C7); 126.1 (C6); 126.6 (C8a); 127.6 (C4); 128.3 (C8); 130.1 (C5); 136.3 (C3); 146.8 (C4a); 160.3 (C2)	
17b	+52.98 (*c* 0.025, $CHCl_3$)	1.68 (d, 3H, ^3J = 8.00 Hz, CH(OH)$\underline{CH_3}$); 4.11 (s, 5H, CpH); 4.51–4.52 (m, 1H, C_5H_3); 4.65 (m, 1H, C_5H_3); 4.95 (m, 1H, C_5H_3); 5.06–5.11 (m, 1H, $\underline{CH}(OH)CH_3$); 6.53 (d, 1H, ^3J = 4.00 Hz, CH($\underline{OH}$)CH_3); 7.69–7.75 (m, 2H, 6′-H, 7′-H); 7.95–7.97 (m, 1H, 8′-H); 8.05–8.07 (m, 1H, 5′-H); 9.10 (s, 1H, 3′-H)	20.1 (CH(OH)$\underline{CH_3}$); 64.3 ($\underline{CH}(OH)CH_3$); 69.7 (C_5H_3); 69.7 (C_5H_3); 70.5 (Cp); 71.7 (C_5H_3); 79.7 (C-Cp); 92.0 (C-Cp); 128.2 (C8); 129.0 (C5); 129.3 (C7); 130.7 (C6); 140.6 (C8a); 140.8 (C4a); 145.8 (C3); 155.8 (C2)	
18a	+4.19 (c 0.031, $CHCl_3$)	1.79 (d, 3H, ^3J = 8.00 Hz, CH($OOCCH_3$)$\underline{CH_3}$); 1.98 (s, 3H, CH($OOC\underline{CH_3}$)CH_3); 4.06 (s, 5H, CpH); 4.48 (m, 1H, C_5H_3); 4.64 (m, 1H, C_5H_3); 4.92 (m, 1H, C_5H_3); 6.79–6.84 (m, 1H, $\underline{CH}(OOCCH_3)CH_3$); 7.46 (t, 1H, ^3J = 8.00 Hz, 4′-H); 7.58 (d, 1H, ^3J = 8.00 Hz, 5′-H); 7.65 (t, 1H, ^3J = 8.00 Hz, 8′-H); 7.72 (d, 1H, ^3J = 8.00 Hz, 7′-H); 8.01 (t, 2H, ^3J = 8.00 Hz, 3′-H, 6′-H)	18.8 (CH($OOCCH_3$)$\underline{CH_3}$); 21.8 (CH($OOC\underline{CH_3}$)CH_3); 69.1 (C_5H_3); 69.4 (C_5H_3); 69.5 ($\underline{CH}(OOCCH_3)CH_3$); 70.6 (Cp); 70.9 ($C_5H_3$); 82.8 (C-Cp); 86.5 (C-Cp); 120.3 (C5); 125.7 (C4); 126.4 (C4a); 127.3 (C7); 129.5 (C6); 129.6 (C8); 135.3 (C3); 148.3 (C8a); 159.3 (C2); 170.9 (CH($OO\underline{C}CH_3$)CH_3)	
18b	+38.72 (*c* 0.053, $CHCl_3$)	1.78 (d, 3H, ^3J = 8.00 Hz, CH($OOCH_3$)$\underline{CH_3}$); 1.98 (s, 3H, CH($OOC\underline{CH_3}$)CH_3); 4.11 (s, 5H, CpH); 4.58 (m, 1H, C_5H_3); 4.72 (m, 1H, C_5H_3); 5.04 (m, 1H, C_5H_3); 6.66–6.70 (m, 1H, $\underline{CH}(OOCCH_3)CH_3$); 7.67–7.71 (m, 2H, 6′-H, 7′-H); 8.00 (t, 2H, ^3J = 8.00 Hz, 5′-H, 8′-H); 9.00 (s, 1H, 3′-H)	18.7 (CH($OOCH_3$)$\underline{CH_3}$); 21.8 (CH($OO\underline{CH_3}$)CH_3); 69.0 ($\underline{CH}(OOCCH_3)CH_3$); 69.9 ($C_5H_3$); 69.9 ($C_5H_3$); 70.6 ($C_5H_3$); 70.7 (Cp); 79.6 (C-Cp); 86.9 (C-Cp); 128.8 (C7); 129.0 (C5); 129.2 (C8); 130.3 (C6); 140.3 (C4a); 142.3 (C8a); 144.6 (C3); 155.2 (C2); 170.7 (CH($OO\underline{C}CH_3$)CH_3)	

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Table 4. continued

	$[\alpha]^{20}_D$	^{1}H NMR data	^{13}C NMR data	^{31}P NMR data
19a	+5.89 (*c* 0.322, $CHCl_3$)	0.89 (s, 3H, BH_3); 1.77−1.83 (m, 3H, CH(PPh_2)$\underline{CH_3}$); 4.05 (s, 5H, CpH); 4.43 (m, 1H, C_5H_3); 4.52 (m, 1H, C_5H_3); 4.79 (m, 1H, C_5H_3); 5.96−6.02 (m, 1H, $\underline{CH}(PPh_2)CH_3$); 6.56 (d, 2H, ^3J = 4.00 Hz, 5′-H, Ph); 6.79 (t, 2H, ^3J = 8.00 Hz, Ph); 6.86−6.89 (m, 2H, 4′-H, Ph); 7.47−7.51 (m, 4H, 6′-H, Ph); 7.68−7.74 (m, 3H, 3′-H, 4′-H, 8′-H); 8.04−8.09 (m, 3H, Ph)	16.8 (CH(PPh_2)$\underline{CH_3}$); 27.5 ($\underline{CH}(PPh_2)CH_3$); 67.1 ($C_5H_3$); 68.5 ($C_5H_3$); 70.3 (Cp); 71.1 ($C_5H_3$); 81.9 (C-Cp); 89.3 (C-Cp); 120.2 (C4); 125.4 (C6); 126.2 (C4a); 126.7 (Ph); 126.8 (C5); 127.6 (C7); 128.6, 128.7, 128.8, 129.3, 132.8, 133.3 (Ph); 133.4 (C3); 134.9 (C8); 147.5 (C8a); 160.9 (C2)	26.07 (PPh_2)
19b	+7.17 (*c* 0.046, $CHCl_3$)	1.26 (s, 3H, BH_3); 1.76−1.82 (m, 3H, CH(PPh_2)$\underline{CH_3}$); 4.08 (s, 5H, CpH); 4.54−4.56 (t, 1H, ^3J = 4.00 Hz, C_5H_3); 4.64 (m, 1H, C_5H_3); 4.88 (m, 1H, C_5H_3); 5.59−5.69 (m, 1H, $\underline{CH}(PPh_2)CH_3$); 6.53−6.57 (m, 1H, 6′-H, 7′-H); 6.76 (t, 2H, ^3J = 8.00 Hz, Ph); 6.90 (t, 1H, ^3J = 8.00 Hz, Ph); 7.52−7.53 (m, 3H, Ph); 7.68 (t, 1H, ^3J = 8.00 Hz, 5′-H); 7.77 (t, 1H, ^3J = 8.00 Hz, 8′-H); 7.99−8.05 (m, 4H, Ph); 8.26 (s, 1H, 3′-H)	16.6 (CH(PPh_2)$\underline{CH_3}$); 27.5 ($\underline{CH}(PPh_2)CH_3$); 66.8 ($C_5H_3$); 69.4 ($C_5H_3$); 70.4 (Cp); 71.9 ($C_5H_3$); 78.9 (C-Cp); 89.7 (C-Cp); 126.7 (C6); 127.4, 128.0 (Ph); 128.3 (C5); 128.5 (C7); 128.8, 128.9, 129.3 (Ph); 130.1 (C8); 130.4, 131.4, 132.7, 132.8, 133.3, 133.4 (Ph); 140.2 (C4a); 141.6 (C8a); 144.1 (C3); 156.5 (C2)	26.38 (PPh_2)
10a		3.83 (m, 1H, C_5H_3); 4.10 (s, 5H, CpH); 4.53 (m, 1H, C_5H_3); 5.20 (m, 1H, C_5H_3); 7.23−7.41 (m, 6H, Ph); 7.51−7.71 (m, 7H, 4′-H, 5′-H, 7′-H, Ph); 7.80 (d, 1H, ^3J = 8.00 Hz, 6′-H); 7.92 (d, 1H, ^3J = 8.00 Hz, 8′-H); 8.03 (d, 1H, ^3J = 8.00 Hz, 3′-H)		−17.59 (PPh_2)
20a		1.48−1.53 (m, 3H, CH(PPh_2)$\underline{CH_3}$); 3.96 (s, 5H, CpH); 4.21 (m, 1H, C_5H_3); 4.27 (m, 1H, C_5H_3); 4.59 (m, 1H, C_5H_3); 5.06−5.11 (m, 1H, $\underline{CH}(PPh_2)CH_3$); 6.75−6.78 (m, 2H, 6′-H, Ph); 6.85−6.93 (m, 4H, Ph); 7.18 (t, 1H, ^3J = 4.00 Hz, 4′-H); 7.31−7.50 (m, 5H, Ph); 7.58−7.70 (m, 3H, 6′-H, 7′-H, 8′-H); 7.76 (d, 1H, ^3J = 4.00 Hz, 3′-H)		9.06 (PPh_2)

The procedure was carried out five times. The deprotection was monitored by using the ^{31}P NMR spectroscopy. The ligand obtained was ready for use in metal catalysis after the final evaporation.

Allylic Alkylation. The freshly deprotected ligands **10a**, **20a** (4 mol %), and an allylpalladium(II) chloride (dimer, 0.004 g, 10 μmol, 2 mol %) were dissolved in an appropriate solvent (toluene, THF, CH_2Cl_2) (3 mL) and stirred for 15 min at room temperature under an argon atmosphere. 3-Acetoxy-1,3-diphenylpropene **23** (0.126 g, 0.50 mmol) in the same solvent (1 mL), *N*,*O*-bis(trimethylsilyl)-acetamide (0.38 mL, 0.312 g, 1.54 mmol), diethyl malonate (0.23 mL, 0.246 g, 1.54 mmol), and potassium acetate (0.002 g, 24 μmol, 4 mol %) were subsequently added. In the case of either THF or toluene, saturated 1 M HCl (50 mL) and a solution of NH_4Cl (50 mL) were added after 24 h, and the reaction mixture was extracted with diethyl ether (60 mL). The organic layers were washed with water and dried over Na_2SO_4. The crude product was purified by a column chromatography (hexane/EtOAc, 9:1) to obtain the product **24**. In the case of CH_2Cl_2, the reaction mixture was purified on silica gel immediately. An enantiomeric excess was determined by HPLC (Chiralcel, OD-H, *n*-hexane/*i*-PrOH/MeOH, 100:1.5:1.5); t_R (min): 5.2 (*S*), 5.8 (*R*). The spectral properties obtained proved to be in accordance with the literature data (see Tables 3 and 4).[34]

■ ASSOCIATED CONTENT

Supporting Information

Details of the experimental procedures and characterization of compounds along with copies of all ^{1}H, ^{13}C, and ^{31}P NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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