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Preparation and Use of Chiral Ferrocenylphosphines Containing New Alkyl Substituents on the Ferrocenylmethyl Position

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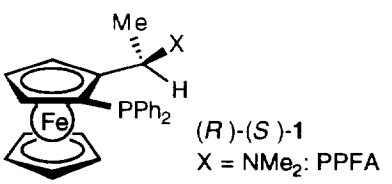
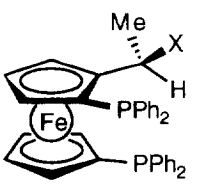
Abstract: New homochiral ferrocenylphosphines, (Et-PPFA **5a**), (Et-BPPFA **6a**), and (Bu-BPPFA **6b**), containing an ethyl or butyl group on the ferrocenylmethyl position were prepared by way of stereoselective ortho lithiation of (*R*)-*N*,*N*-dimethyl-1-ferrocenylpropylamine (**4a**) or its pentylamine analogue **4b**, the lithiation proceeding with high (>99%) diastereoselectivity. Ethyl-substituted ferrocenylmonophosphine (Et-PPFA **5a**) and ferrocenylbisphosphine (Et-BPPFA **6a**) were found to be more effective as chiral ligands than the methyl-substituted ferrocenylphosphines, PPFA **1** and BPPFA **2**, respectively, for some catalytic asymmetric reactions including nickel-catalyzed cross-coupling and palladium-catalyzed allylic silylation.

Homochiral ferrocenylphosphines, whose chirality is due to the ferrocene planar chirality, have been demonstrated to be very useful as chiral ligands for several types of asymmetric reactions catalyzed by transition metal complexes.[1,2,3] Most of the ferrocenylphosphines, both monophosphines and bisphosphines, have been prepared through the diastereoselective ortho lithiation of resolved *N*,*N*-dimethyl-1-ferrocenylethylamine[4] and hence they have methyl group on the stereogenic carbon center at the ferrocenylmethyl position. The representatives are PPFA (**1**) and BPPFA (**2**) for ferrocenylmonophosphines and -bisphosphines, respectively.[5] Although steric fine tuning of the ferrocenylphosphines by replacement of the methyl group by other alkyl groups is expected to bring about higher enantioselectivities in the catalytic asymmetric reactions, only a few attempts have been reported on this type of modification.[6,7,8] Here we report the preparation of new chiral ferrocenylphosphines which contain ethyl and butyl groups on the side chain and their use for nickel-catalyzed cross-coupling and palladium-catalyzed allylic substitution reactions where the ethyl-substituted ferrocenylphosphines were found to be more enantioselective ligands than their methyl analogues.



(*R*)-(*S*)-**1**
X = NMe_2: PPFA



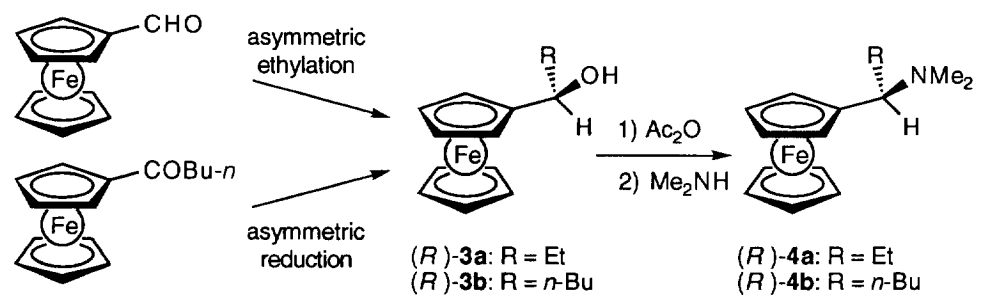
(*R*)-(*S*)-**2**
X = NMe_2: BPPFA

Dedicated to the memory of Professor Hidemasa Takaya, deceased on 5 October 1995

Results and Discussion:

Preparation of Chiral Ferrocenylphosphines. The homochiral ferrocenylphosphines containing an ethyl or butyl group are expected to be prepared by the stereoselective ortho lithiation of the corresponding homochiral *N*,*N*-dimethyl-1-ferrocenylalkylamines in a similar manner to the preparation of PPFA (**1**) and BPPFA (**2**). We have previously reported[9] that (*R*)-*N*,*N*-dimethyl-1-ferrocenylpropylamine (**4a**) (>96% ee), which is key intermediate for the ethyl-substituted phosphines, is readily obtained in a high yield by enantioselective alkylation[10] of ferrocenecarboxaldehyde with diethylzinc in the presence of (*R*)-3,3-dimethyl-1-piperidino-2-butanol as a catalyst[11] followed by acetylation of the resulting (*R*)-1-ferrocenylpropanol (**3a**) with acetic anhydride and amination with dimethylamine[12] (Scheme 1). Optically active *N*,*N*-dimethyl-1-ferrocenylpentylamine (**4b**) was prepared by asymmetric reduction of 1-ferrocenyl-1-pentanone. Catalytic asymmetric reduction of 1-ferrocenyl-1-pentanone with chiral oxazaborolidine-borane,[13] which is derived from (*S*)-α,α-diphenyl-2-pyrrolidinemethanol, at –20 °C gave (*R*)-1-ferrocenylpentanol (**3b**) in 80% yield, which was then subjected to the acetylation-amination to give (*R*)-*N*,*N*-dimethyl-1-ferrocenylpentylamine (**4b**) in 77% yield. Its enantiomeric purity was determined to be 90% ee by HPLC analysis with a chiral stationary phase column, and the absolute configuration was tentatively assigned by an empirical rule for the asymmetric reduction of aromatic ketones with the oxazaborolidine-borane reagent.[13]

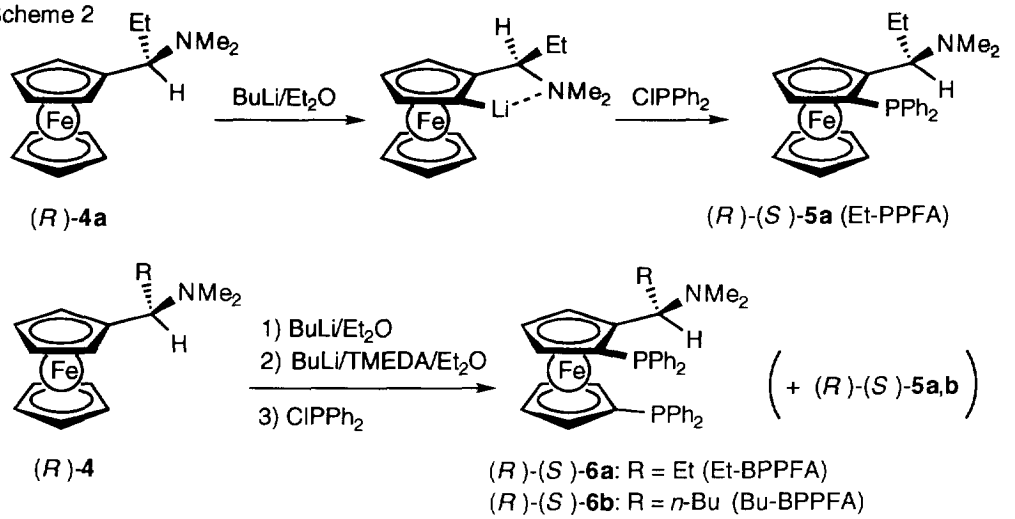
Scheme 1



Lithiation of (*R*)-**4a** with 1.2 equiv of butyllithium in ether at room temperature followed by addition of chlorodiphenylphosphine to the lithiated ferrocene gave 59% yield of ferrocenylmonophosphine, (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]propylamine (Et-PPFA, **5a**) (Scheme 2). The ferrocene planar chirality (*S*) was assigned by assuming that ortho lithiation of (*R*)-**4a** takes place in the same stereochemistry as that of its ethylamine analogue, *N*,*N*-dimethyl-1-ferrocenylethylamine.[4] The diastereomeric isomer containing (*R*) planar chirality was not detected by NMR studies of the crude reaction mixture. It is interesting that the diastereoselectivity in the lithiation of (*R*)-**4a** observed here is higher than the reaction of its ethylamine analogue.[4]

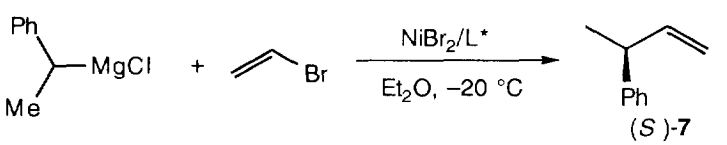
Two diphenylphosphino groups were introduced onto (*R*)-**4a** according to the procedures used for the preparation of BPPFA (**2**). Thus, treatment of (*R*)-**4a** with 2.5 equiv of butyllithium in the presence of 1,2-bis(dimethylamino)ethane (TMEDA) in ether followed by diphenylphosphination of the dilithiated ferrocene gave 32% yield of ferrocenylbisphosphine, (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1',2-bis(diphenylphosphino)ferrocenyl]-propylamine (Et-BPPFA, **6a**), and a minor amount (8%) of monophosphine (*R*)-(*S*)-**5a**. Similarly, dilithiation of (*R*)-**4b** in the presence of TMEDA followed by the phosphination gave 44% yield of the ferrocenylbisphosphine, (*R*)-(*S*)-**6b** (Bu-BPPFA), that has *n*-butyl group at the ferrocenylmethyl position.

Scheme 2

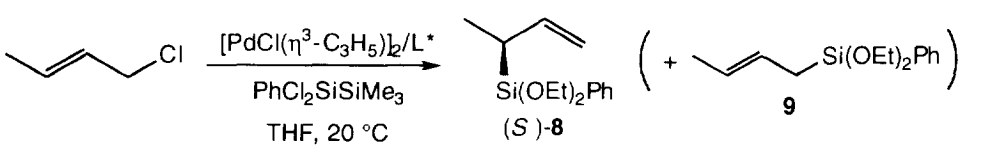


Catalytic Asymmetric Reactions. The ethyl-substituted ferrocenylmonophosphine (Et-PPFA, **5a**) and -bisphosphine (Et-BPPFA, **6a**) prepared here were examined for their enantioselectivity in three asymmetric reactions which are catalyzed by nickel or palladium complexes.[14] The results obtained are summarized in Scheme 3, which also contains data reported with the methyl-substituted analogues, PPFA (**1**) and BPPFA (**2**).

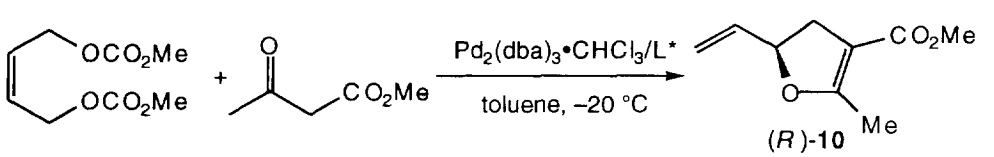
Scheme 3



L* = (*R*)-(*S*)-**5a** (Et-PPFA): 82% ee
L* = (*R*)-(*S*)-**1** (PPFA): 68% ee



L* = (*R*)-(*S*)-**6a** (Et-BPPFA): 81% ee (**8**/**9** = 30/70)
L* = (*R*)-(*S*)-**2** (BPPFA): 61% ee (**8**/**9** = 21/79)



L* = (*R*)-(*S*)-**6a** (Et-BPPFA): 70% ee
L* = (*R*)-(*S*)-**2** (BPPFA): 55% ee

The reaction of 1-phenylethylmagnesium chloride with vinyl bromide in ether at –20 °C in the presence of 0.5 mol % of nickel catalyst generated in situ by mixing nickel bromide with 2 equiv of Et-PPFA (**5a**) gave (*S*)-3-phenyl-1-butene (**7**) in 82% ee. The enantioselectivity observed here is one of the highest in the nickel-catalyzed cross-coupling of 1-phenylethyl Grignard reagents and is higher than the enantioselectivity (68% ee) reported with PPFA (**1**).[1,15]

The superiority of the ethyl-substituted ferrocenylphosphine over the methyl-substituted one was also observed in two types of allylic substitution reactions catalyzed by palladium-bisphosphine complexes.[16] In the silylation of crotyl chloride with 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane carried out in THF at 20 °C, palladium catalyst (1 mol %) coordinated with Et-BPPFA (**6a**) gave (*S*)-3-silyl-1-butene (**8**) in 81% ee together with its regioisomeric allylsilane, 1-silyl-2-butene (**9**) (**8**/**9** = 30/70), the enantioselectivity being 20% higher than that with palladium-BPPFA (**2**) catalyst.[17] Reaction of 2-butenylene dicarbonate with methyl acetylacetate in the presence of 2 mol % of palladium-Et-BPPFA (**6a**) catalyst in toluene at –20 °C for 43 h gave 87% yield of vinyldihydrofuran **10** which is 70% enantiomerically pure. Under the same reaction conditions, palladium-BPPFA (**2**) catalyst gave **10** of 55% ee.[18]

Conclusion. Most of the ferrocenylphosphines so far used for catalytic asymmetric reactions have a methyl group at the ferrocenylmethyl position and were prepared from optically active *N*,*N*-dimethyl-1-ferrocenylethylamine which is obtained by resolution of the racemic amine.[1] On the other hand, the new ferrocenylphosphines shown here, which contain an ethyl group in place of methyl, were prepared from *N*,*N*-dimethyl-1-ferrocenylpropylamine which is readily accessible in a homochiral form by a catalytic asymmetric alkylation. The ethyl-substituted ferrocenylphosphines were demonstrated to be better enantioselective ligands than the methyl-substituted ones for some catalytic asymmetric reactions. The enhancement of enantioselectivity by the substitution of methyl with ethyl has also been observed in the asymmetric reactions with analogous ruthenocenylbisphosphine ligands.[19] It is well-known that structural modification on ferrocenylphosphine ligands can be readily made by introduction of a desired functional group on the side chain according to the demand of the reaction type.[1] The new ferrocenylphosphines are expected to be modified by the functionalization in a similar manner to take the place of the old ones as better enantioselective chiral ligands in some transition metal-catalyzed asymmetric reactions.

Experimental:

(*R*)-1-Ferrocenylpentanol (3b). To a solution of 14.5 mg (0.05 mmol) of (*S*)-tetrahydro-1-methyl-3,3-diphenyl-1*H*,3*H*-pyrrolo[1,2-*c*][1,3,2]oxazaborole-borane complex[13] in 1.0 mL of dichloromethane, was added 0.10 mL (1.0 mmol) of neat borane-dimethyl sulfide complex at –20 °C. At the same temperature, a solution of 272 mg (1.01 mmol) of 1-ferrocenyl-1-pentanone in 2.0 mL of dichloromethane was added over a period of 1 h. After the mixture was stirred at –20 °C for 0.5 h, the reaction was quenched with methanol. Evaporation of the solvent followed by silica gel column chromatography (ethyl acetate/hexane = 1/20) gave 219 mg (80%) of 1-ferrocenylpentanol (**3b**). The absolute configuration is assigned to be (*R*) by an empirical rule for the asymmetric reduction of aromatic ketones with the chiral borane reagent.[13] ^{1}H NMR ($CDCl_3$) δ 0.96 (t, *J* = 6.9 Hz, 3 H), 1.20-1.52 (m, 4 H), 1.58-1.78 (m, 2 H), 1.81 (bs, 1 H), 4.19 (s, 5 H), 4.12-4.28 (m, 4 H), 4.29-4.35 (m, 1 H). $[\alpha]_D^{20}$ –42.3 (*c* 1.1, benzene). Anal. Calcd for $C_{15}H_{20}OFe$: C, 66.20; H, 7.41. Found: C, 66.17; H, 7.22.

(*R*)-*N*, *N*-Dimethyl-1-ferrocenylpentylamine (4b). To a solution of 1.19 g (4.36 mmol) of (*R*)-1-ferrocenylpentanol (**3b**), which was obtained by the asymmetric reduction, in 7.0 mL of dichloromethane

was added 0.9 mL (6.5 mmol) of triethylamine, 0.5 mL (5.3 mmol) of acetic anhydride, and a catalytic amount of 4-dimethylaminopyridine. After the mixture was stirred at room temperature for 14 h, it was washed with water, dried over anhydrous sodium sulfate, and stripped of the solvent. To the residue was added 2.8 mL (31 mmol) of aqueous 50% dimethylamine and 16 mL of ethanol, and the mixture was stirred at room temperature for 23 h. After ethanol and excess dimethylamine was evaporated under reduced pressure, ether was added and the product was extracted with 10% phosphoric acid. The aqueous layer was made alkaline (pH 9) by the addition of 3 M sodium hydroxide and extracted with ether. The organic layer was dried over anhydrous sodium sulfate and stripped of the solvent. Distillation of the residue (bp 180 °C/0.2 mmHg) gave 1.01 g (77%) of (*R*)-**4b**: The enantiomeric purity was determined to be 90% ee by HPLC analysis with chiral stationary phase column (Sumichiral OA-4100, hexane/1,2-dichloroethane/ethanol = 50/15/1). ^{1}H NMR ($CDCl_3$) δ 0.99 (t, *J* = 6.9 Hz, 3 H), 1.41-1.50 (m, 4 H), 1.50-1.60 (m, 1 H), 1.61-1.65 (m, 1 H), 1.99 (s, 6 H), 3.32-3.37 (m, 1 H), 4.02-4.12 (m, 4 H), 4.10 (s, 5 H). $[\alpha]_D^{20}$ –18.0 (*c* 1.3, benzene). Anal. Calcd for $C_{17}H_{25}NFe$: C, 68.24; H, 8.42; N, 4.68. Found: C, 68.34; H, 8.53; N, 4.64.

(*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]propylamine (5a). To a solution of 2.24 g (8.27 mmol) of (*R*)-*N*,*N*-dimethyl-1-ferrocenylpropylamine (**4a**) (>96% ee) in 20.0 mL of dry diethyl ether was added dropwise 7.24 mL (9.92 mmol) of 1.37 M butyllithium in hexane at room temperature. The mixture was stirred at room temperature for 12 h, and then 1.93 mL (10.8 mmol) of chlorodiphenylphosphine was added at 0 °C. The mixture was stirred at room temperature for 1 h, and then it was hydrolyzed with aqueous sodium bicarbonate. The resulting organic layer and extracts from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated under a reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexane = 1/2) to give 2.23 g (59%) of (*R*)-(*S*)-**5a** and 0.59 g (26%) of starting (*R*)-**4a** was recovered. (*R*)-(*S*)-**5a**: mp 133-136 °C. ^{1}H NMR ($CDCl_3$) δ 1.17 (t, *J* = 7.3 Hz, 3 H), 1.78 (s, 6 H), 1.82-1.85 (m, 2 H), 3.80-3.90 (m, 1 H), 3.90 (s, 5 H), 4.05-4.14 (m, 1 H), 4.25-4.26 (m, 1 H), 4.29-4.30 (m, 1 H), 7.16-7.19 (m, 6 H), 7.22-7.32 (m, 2 H), 7.57-7.61 (m, 2 H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ –22.8 (s). $[\alpha]_D^{20}$ –330 (*c* 0.9, benzene). Anal. Calcd for $C_{27}H_{30}NPFe$: C, 71.22; H, 6.64; N, 3.08. Found: C, 71.54; H, 6.54; N, 3.10.

(*R*)-*N*,*N*-Dimethyl-1-[(*S*)-1',2-bis(diphenylphosphino)ferrocenyl]propylamine (6a). To a solution of 2.44 g (9.00 mmol) of (*R*)-*N*,*N*-dimethyl-1-ferrocenylpropylamine (**4a**) (>96% ee) in 12.0 mL of dry diethyl ether was added dropwise 6.70 mL (10.9 mmol) of 1.62 M butyllithium in hexane at room temperature. The mixture was stirred at room temperature for 3 h, and then 1.80 mL (11.9 mmol) of TMEDA and 7.20 mL (11.7 mmol) of 1.62 M butyllithium in hexane were added successively. After 19 h of stirring at room temperature, a solution of 4.40 mL (24.5 mmol) of chlorodiphenylphosphine in 7.0 mL of ether was added at –78 °C. The mixture was slowly warmed up to room temperature, refluxed for 1 h, and then it was hydrolyzed with aqueous sodium bicarbonate. The resulting organic layer and extracts from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated under a reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexane = 1/5) to give 1.82 g (32%) of (*R*)-(*S*)-**6a** and 0.34 g (8%) of (*R*)-(*S*)-**5a**. (*R*)-(*S*)-**6a**: mp 144-146 °C. ^{1}H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.3 Hz, 3 H), 1.53-1.77 (m, 2 H), 1.77 (s, 6 H), 3.44-3.46 (m, 1 H), 3.68-3.69 (m, 1 H), 3.78-3.82 (m, 1 H), 3.88-3.89 (m, 1 H), 4.06-4.07 (m, 2 H), 4.27-4.28 (m, 1 H), 4.34-4.35 (m, 1 H), 7.16-7.29 (m, 20 H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ –23.3 (s), –16.8 (s). $[\alpha]_D^{20}$ –375 (*c* 0.8, benzene). Anal. Calcd for $C_{39}H_{39}NP_2Fe$: C, 73.24; H, 6.15; N, 2.19. Found: C, 73.14; H, 6.17; N, 2.18.

(*R*)-*N*, *N*-Dimethyl-1-[(*S*)-1',2-bis(diphenylphosphino)ferrocenyl]pentylamine (6b). To a solution of 977 mg (3.26 mmol) of (*R*)-*N*, *N*-dimethyl-1-ferrocenylpentylamine (**4b**) (90% ee) in 2.0 mL of dry diethyl ether was added dropwise 3.00 mL (3.93 mmol) of 1.31 M butyllithium in hexane at room temperature. The mixture was stirred at room temperature for 1.5 h and then 0.60 mL (3.93 mmol) of TMEDA and 3.00 mL (3.93 mmol) of 1.31 M butyllithium in hexane were added successively. After 17 h at room temperature, 1.50 mL (8.36 mmol) of chlorodiphenylphosphine was added at –78 °C. The mixture was refluxed for 0.5 h, and then it was hydrolyzed with aqueous sodium bicarbonate. The resulting organic layer and extracts from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated under a reduced pressure. The residue was chromatographed on silica gel with ethyl acetate and benzene (1:20) as the eluent to give 961 mg (44%) of crude (*R*)-(*S*)-**6b**, which was recrystallized from ethanol to give 736 mg (34%) of enantiomerically pure as orange crystals: mp 127-128 °C. ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 6.9 Hz, 3 H), 1.47-1.66 (m, 4 H), 1.76-1.85 (m, 2 H), 1.85 (s, 6 H), 3.53-3.55 (m, 1 H), 3.79-3.81 (m, 1 H), 3.98-4.02 (m, 2 H), 4.17-4.19 (m, 2 H), 4.35-4.36 (m, 1 H), 4.41-4.43 (m, 1 H), 7.25-7.30 (m, 4 H), 7.32-7.45 (m, 14 H), 7.57-7.64 (m, 2 H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ –22.5 (s), –16.1 (s). $[\alpha]_D^{20}$ –318 (*c* 0.9, benzene). Anal. Calcd for $C_{41}H_{43}NP_2Fe$: C, 73.77; H, 6.49; N, 2.10. Found: C, 73.76; H, 6.59; N, 2.00. Ferrocenylmonophosphine, (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]pentylamine ((*R*)-(*S*)-**5b**) (112 mg, 7%), was also isolated by the chromatography: ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J = 6.9 Hz, 3 H), 1.40-1.73 (m, 5 H), 1.76 (s, 6 H), 3.90 (s, 5 H), 3.89-3.97 (m, 2 H), 4.24-4.26 (m, 1 H), 4.26-4.28 (m, 1 H), 7.16-7.25 (m, 5 H), 7.32-7.35 (m, 3 H), 7.57-7.63 (m, 2 H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ –22.8 (s). $[\alpha]_D^{20}$ –235 (*c* 0.2, benzene). Anal. Calcd for $C_{29}H_{34}NPFe$: C, 72.05; H, 7.09; N, 2.90. Found: C, 71.75; H, 7.01; N, 2.86.

Nickel-Catalyzed Asymmetric Cross-Coupling of 1-Phenylethylmagnesium Chloride with Vinyl Bromide. The asymmetric cross-coupling was carried out in a similar manner to that we have previously reported.[15] Thus, to a mixture of 4.1 mg (0.019 mmol) of anhydrous nickel bromide, 18.1 mg (0.040 mmol) of (*R*)-(*S*)-Et-PPFA, and 0.28 mL (3.97 mmol) of vinyl bromide was added at –78 °C 26.7 mL (16.0 mmol) of 0.6 M 1-phenylethylmagnesium chloride in ether. The mixture was kept stirring at –20 °C for 24 h, and hydrolyzed with 10% hydrochloric acid. The organic layer and ether extracts from the aqueous layer were combined, washed with saturated sodium carbonate solution and water, and dried over anhydrous sodium sulfate. After evaporation of solvent, distillation (<100 °C/ 20 mmHg) gave 399 mg (76%) of 3-phenyl-1-butene. The olefin was oxidized with sodium periodate and potassium permanganate according to the reported procedure[20] to give 80% yield of (*R*)-2-phenylpropionic acid[21] ($[\alpha]_D^{20}$ –42 (*c* 1.1, chloroform)). The enantiomeric purity was determined to be 82% ee by HPLC analysis of its anilide with a chiral stationary phase column, Sumichiral OA-1000 (hexane/1,2-dichloroethane/ethanol = 250/20/1).

Palladium-Catalyzed Asymmetric Silylation of Allylic Chlorides. The silylation was carried out in essentially the same manner as reported previously.[17] A mixture of 0.100 mL (1.01 mmol) of crotyl chloride, 293 mg (1.18 mmol) of 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane, and a palladium catalyst, generated from 1.9 mg (0.005 mmol) of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 7.0 mg (0.011 mmol) of (*R*)-(*S*)-Et-BPPFA, in 2.0 mL of THF was stirred at 20 °C for 41 h. Ethanol (0.3 mL, 5.1 mmol) and triethylamine (0.5 mL, 3.6 mmol) were added. The mixture was stirred for 2 h and filtered through a Celite pad. Removal of solvent followed by bulb-to-bulb distillation (<150 °C/0.2 mmHg) gave 213 mg (84%) of a 30 to 70 mixture of 3-(phenyldiethoxy)silyl-1-butene (**8**) and 1-(phenyldiethoxy)silyl-2-butene (**9**). The absolute configuration of **8** was determined by oxidation into known (*S*)-1-buten-3-ol[22] by treatment with hydrogen peroxide in the

presence of potassium fluoride and potassium hydrogen carbonate,[2,3] and the enantiomeric purity of the alcohol was determined by HPLC analysis of its (3,5-dinitrophenyl)carbamate ester with a chiral stationary phase column, Sumichiral OA-4100 (hexane/1,2-dichloroethane/ethanol = 50/15/1).

Palladium-Catalyzed Asymmetric Cyclization of 2-Butenylene Dicarbonate with Methyl Acetylacetate.[18,19] A mixture of 6.2 mg (0.006 mmol) of $Pd_2(dba)_3$•$CHCl_3$ and 8.3 mg (0.013 mmol) of (*R*)-(*S*)-Et-BPPFA in 9.0 mL of toluene was stirred at room temperature for 30 min. At –20 °C, 182 mg (0.89 mmol) of dimethyl (*Z*)-2-butenylene dicarbonate and 640 μL (0.59 mmol) of methyl acetylacetate was added and the mixture was stirred at the same temperature for 43 h. The reaction mixture was passed through a short silica-gel column to remove the catalyst, and purified by a silica-gel column (hexane/ethyl acetate = 3/1) to give 87 mg (88%) of methyl 2-methyl-5-vinyl-4,5-dihydrofuran-3-carboxylate (**10**). The enantiomeric purity was determined to be 70% ee by GLC analysis with a chiral stationary phase column, CP Cyclodex β326M.

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