Synthesis of Optically Active 2-(Diarylphosphino)-1,1'-binaphthyls, Efficient Chiral Monodentate Phosphine Ligands

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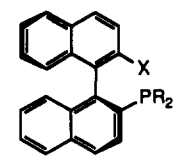
Introduction

Asymmetric reactions catalyzed by transition metal complexes containing optically active phosphine ligands have attracted significant interest for their synthetic utility.[1] One of the most exciting and challenging subjects in research on the catalytic asymmetric synthesis is development of the chiral ligand which will realize high enantioselectivity in a given reaction. Most of the chiral phosphine ligands so far prepared and used for the catalytic asymmetric reactions are the chelating bisphosphines[2] which are expected to construct an effective chiral environment by bidentate coordination to metal and have been demonstrated to be effective for a variety of asymmetric reactions.[1] On the other hand, there exist transition metal-catalyzed reactions where the bisphosphine–metal complexes can not be used because of their low catalytic activity and/or low selectivity toward a desired reaction pathway, and therefore chiral monodentate phosphine ligands are required for the realization of catalytic asymmetric synthesis.[3] Unfortunately, there have been reported only a limited number of monodentate chiral phosphine ligands, which are not so useful as bisphosphine ligands with few exceptions.[1,2,4] We have continued our efforts to develop new chiral monodentate phosphine ligands and found that 2-(diphenylphosphino)-2'-alkoxy-1,1'-binaphthyls (MOPs, 1) are very effective for several types of catalytic asymmetric reactions including palladium-catalyzed asymmetric hydrosilylation of olefins.[5] Here we describe in detail the preparation of the axially chiral monodentate phosphine ligands.



(*S*)-MOPs (1)

1a : R = Ph, X = OH
1b : R = Ph, X = OMe
1c : R = Ph, X = OCH_2Ph
1d : R = Ph, X = OPr-*i*
1e : R = Ph, X = OCH_2OCH_3
1f : R = Ph, X = $OSiMe_2Bu$-*t*
1g : R = Ph, X = Et
1h : R = *p*-$MeOC_6H_4$, X = OMe

Results and Discussion

Since axially chiral binaphthyl compounds have been well-documented to construct an effective chiral template for asymmetric reactions,[6] we chose the chiral binaphthyl skeleton as a basic structure of monodentate phosphine ligand. We have also attached importance to introduction of a functional group into the chiral ligand which is expected to increase the stereoselectivity by an attractive interaction with a functional group in the substrate.[7] Morgans and co-workers[8] have reported the selective monophosphinylation of 2,2'-bis((trifluoromethanesulfonyl)oxy)-1,1'-binaphthyl (2) with diphenylphosphine oxide in the presence of palladium catalyst giving a high yield (77%) of 2-(diphenylphosphinyl)-2'-((trifluoromethanesulfonyl)oxy)-1,1'-binaphthyl (3), which attracted our attention as a versatile starting compound for the preparation of chiral monophosphine ligands. The (trifluoromethanesulfonyl)oxy group on 3 must be useful for the introduction of various types of functional groups onto the binaphthyl.

We have carried out the monophosphinylation of ditriflate (*S*)-2, under the slightly modified Morgans' conditions,[8] with 5 mol % of palladium diacetate and 5 mol % of 1,4-bis(diphenylphosphino)butane (dppb) in dimethyl sulfoxide at 100 °C for 12 h, which gave 95% yield of (*S*)-3 without racemization. Hydrolysis of the remaining triflate with aqueous sodium hydroxide in 1,4-dioxane and methanol (2/1) gave (*S*)-4a in 99% yield. The phenolic hydroxy moiety of (*S*)-4a was easily alkylated by treatment with alkyl halide (MeI, $PhCH_2Br$, i-PrI, and CH_3OCH_2Cl) in the presence of base (potassium carbonate in acetone or sodium hydride in THF) to give the corresponding (*S*)-2-(diphenylphosphinyl)-2'-alkoxy-1,1'-binaphthyl ((*S*)-4b (R = Me, 99%), (*S*)-4c (R = CH_2Ph, 91%), (*S*)-4d (R = i-Pr, 92%), (*S*)-4e (R = CH_2OCH_3,

(1) For recent reviews on catalytic asymmetric reactions: (a) Brunner, H. *Synthesis* **1988**, 645. (b) Brunner, H. *Top. Stereochem.* **1988**, *18*, 129. (c) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257. (d) Noyori, R.; Kitamura, M. *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: New York, 1989; Vol. 5, p 115. (e) Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901. (f) Noels, A. F., Graziani, M., Hubert, A. J., Eds. *Metal Promoted Selectivity in Organic Synthesis*; Kluwer Academic Publishers: Dordrecht, 1991. (g) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron Asymmetry* **1992**, *3*, 1089.

(2) For reviews: (a) Kagan, H. B. *Asymmetric Synthesis*; Morrison, J. D. Ed.; Academic Press: London, 1985; vol. 5, p 1. (b) Kagan, H. B.; Sasaki, M. *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: Chichester, 1990; Vol. 1, p 51.

(3) For example, nickel-catalyzed cross-coupling reaction generating biaryl compounds is one of the typicals: (a) Tamao, K.; Minato, A.; Miyake, N.; Matsuda, T.; Kiso, Y.; Kumada, M. *Chem. Lett.* **1975**, 133. (b) Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153.

(4) Examples of optically active monophosphine ligands so far reported: (a) (*S*)-(*o*-methoxyphenyl)cyclohexylmethylphosphine ((*S*)-CAMP): Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *J. Chem. Soc., Chem. Commun.* **1972**, 10. (b) Neomentyldiphenylphosphine: Morrison, J. D.; Burnett, R. E.; Aguiar, A. M.; Morrow, C. J.; Phillips, C. *J. Am. Chem. Soc.* **1971**, *93*, 1301. (c) (*S*)-1-[(*R*)-2-(diphenylphosphino)-ferrocenyl]ethyl methyl ether ((*S*)-(*R*)-PPFOMe): Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.

(5) Very recently, we have reported that the palladium–MOP complex is one of the most effective catalyst for both enantioface and enantioposition selective asymmetric hydrosilylation: (a) Enantioface selective reaction: Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887. (b) Enantioposition selective reaction: Uozumi, Y.; Lee, S.-Y.; Hayashi, T. *Tetrahedron Lett.* **1992**, *33*, 7185.

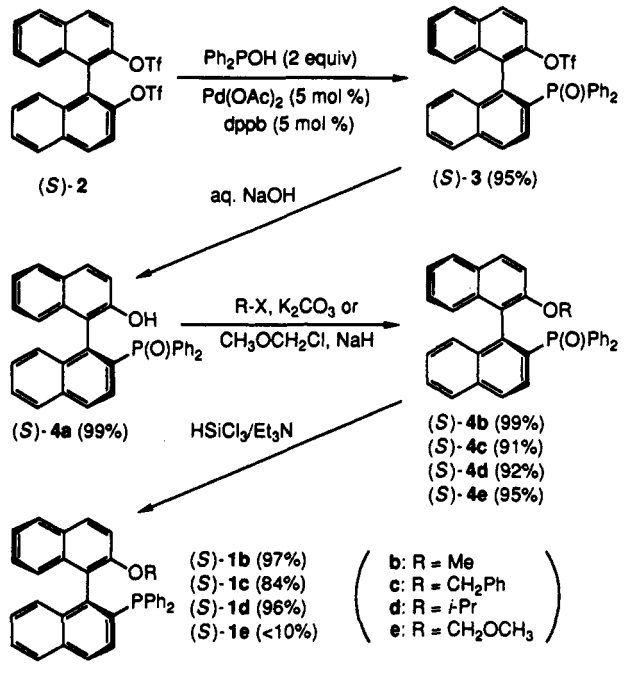
(6) For reviews: (a) Morrison, J. D., Ed. *Asymmetric Synthesis*; Academic Press: London, 1983–1985; Vols. 1–5. (b) Nógrádi, M. *Stereoselective Synthesis*; Weinheim: New York, 1987. (c) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581. (d) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvaori, P. *Synthesis* **1992**, 503.

(7) A variety of tailor-made phosphines having chiral ferrocene skeleton have been prepared by introduction of functionalized side chains. For examples: (a) Hayashi, T. *Pure Appl. Chem.* **1988**, *60*, 7. (b) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301. (c) Hayashi, T.; Matsumoto, Y.; Morikawa, I.; Ito, Y. *Tetrahedron Asymmetry* **1990**, *1*, 151. (d) Hayashi, T.; Sawamura, M.; Ito, Y. *Tetrahedron* **1992**, *48*, 1999 and references cited therein.

(8) Kurz, L.; Lee, G.; Morgans, Jr., D.; Waldyke, M. J.; Wars, T. *Tetrahedron Lett.* **1990**, *31*, 6321.

0022-3263/93/1958-1945$04.00/0

Scheme I



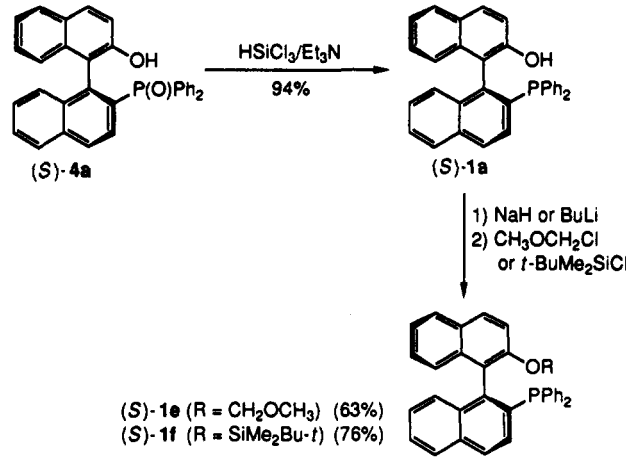
(dppb = 1,4-bis(diphenylphosphino)butane)

95%)). Reduction of phosphine oxide (*S*)-**4b–d** was achieved with trichlorosilane and triethylamine[9] in xylene upon heating to give corresponding phosphines (*S*)-**1b**, (*S*)-**1c**, and (*S*)-**1d** in 97%, 84%, and 96% yields, respectively (Scheme I). Miyano has reported the multistep preparation of **1b** starting with (−)-menthyl 1-(−)-menthoxy-2-naphthoate.[10] The present method provides a more practical route to **1b** which is obtained in 90% total yield from 2,2′-binaphthol.

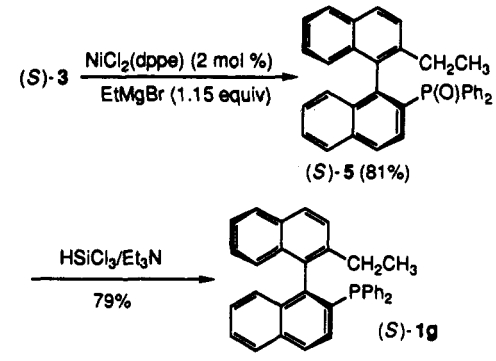
The reduction of **4e** (R = CH_2OCH_3) was not successful; the desired phosphine, 2-(diphenylphosphino)-2′-(methoxymethoxy)-1,1′-binaphthyl (**1e**) was obtained in less than 10% yield. The main product was hydroxy phosphine **1a**, suggesting cleavage of the acid-sensitive etheric carbon–oxygen bond under the reduction conditions. This problem was overcome by reduction of **4a** and subsequent alkylation (Scheme II). Hydroxy phosphine oxide (*S*)-**4a** was reduced to phosphine (*S*)-**1a** in 94% yield, treatment of which with sodium hydride followed by addition of chloromethyl methyl ether gave (*S*)-**1e** in 63% yield. The silyloxy moiety was also introduced through the similar sequence. The sodium alkoxide of (*S*)-**1a** was allowed to react with *tert*-butyldimethylsilyl chloride to give silyl ether (*S*)-**1f** in 76% yield.

Alkyl substituents were also introduced at the 2′-position of the (diphenylphosphino)binaphthyl skeleton by a nickel-catalyzed cross-coupling reaction.[5a,11] For example, triflate (*S*)-**3** was treated with ethylmagnesium bromide in the presence of a catalytic amount of dichloro[1,2-bis(diphenylphosphino)ethane]nickel ($NiCl_2$(dppe), 2 mol %) in Et_2O to give 2′-ethylated compound (*S*)-**5** in 81% yield.

Scheme II



Scheme III



(dppe = 1,2-bis(diphenylphosphino)ethane)

Phosphine oxide (*S*)-**5** was reduced by trichlorosilane/triethylamine to give (*S*)-**1g** in 79% yield.

A bis(substituted phenyl)phosphino group was readily introduced on the binaphthyl by the palladium-catalyzed reaction with the corresponding diarylphosphine oxide. The same procedure as employed for preparation of **3** was followed with bis(*p*-methoxyphenyl)phosphine oxide and (*S*)-**2** to give bis(*p*-methoxyphenyl)phosphinyl derivative (*S*)-**6** in 93% yield. Compound (*S*)-**6** was converted to 2-methoxy-2′-(bis(*p*-methoxyphenyl)phosphino)-1,1′-binaphthyl ((*S*)-**1h**) through hydrolysis, alkylation, and reduction processes in 95% overall yield (Scheme IV).

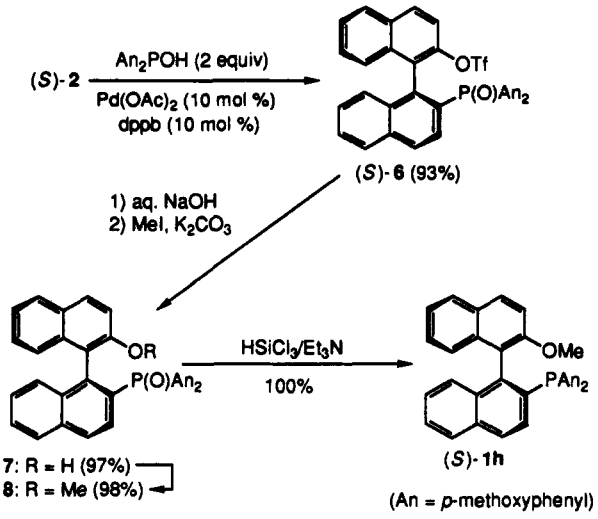
In summary, a new class of optically active monodentate phosphine ligands, MOPs, were synthesized in high total yields. The flexibility of the synthetic route realizes the fine tuning of the phosphine ligand by the introduction of several types of side chain and control of the steric and electronic effects of the phosphino group. Needless to say, the synthetic procedures shown here can be used for the preparation of MOPs having *R* absolute configuration by using (*R*)-binaphthol as a starting material.

Experimental Section

General. ^1H NMR spectra were measured on a JEOL JNM-EX90 spectrometer (90 MHz) or JEOL JNM-EX270 spectrometer (270 MHz) in $CDCl_3$. Chemical shifts of protons are reported in δ ppm referred to tetramethylsilane as an internal standard. ^{31}P NMR spectra were measured on a JEOL JNM-EX90 spectrometer (36 MHz) or JEOL JNM-EX270 spectrometer (109 MHz) in $CDCl_3$ using H_3PO_4 as an external standard. Optical rotations were measured on a JASCO DIP-370 polarimeter. IR spectra were recorded on a Perkin-Elmer 1720X FT-IR spec-

(9) Gilheany, D. G.; Mitchell, C. M. *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: Chichester, 1990; Vol. 1, p 151 and references cited therein.
(10) Hattori, T.; Shijo, M.; Kumagai, S.; Miyano, S. *Chem. Express* **1991**, *6*, 335.
(11) Sengupta, S.; Leite, M.; Raslan, D. S.; Quesnelle, C.; Sniecus, V. *J. Org. Chem.* **1992**, *57*, 4066.

Scheme IV



trometer. EI-mass spectra and high-resolution mass spectra were measured on a JEOL JMS-DX-303 spectrometer at an ionization voltage of 70 eV. Silica gel column chromatography was carried out using Merck silica gel 60 (70–325 mesh ASTM). Air- and moisture-sensitive reactions were performed under usual inert atmosphere techniques. All dry solvents were distilled under N_2. THF and Et_2O were distilled from sodium/benzophenone ketyl. Xylene, DMSO, and CH_2Cl_2 were distilled from CaH_2. The purity of compounds **1d**, **1f**, and **5** was judged to be ≥95% by ^1H NMR spectral determination. Satisfactory results in combustion analysis were obtained for all other title compounds.

(*S*)-2,2′-Bis((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl (2). To a solution of (*S*)-binaphthol (14.3 g, 50 mmol) and pyridine (12 mL, 148 mmol) in CH_2Cl_2 was added trifluoromethanesulfonic anhydride (20.0 mL, 33.5 g, 119 mmol) at 0 °C, and the mixture was stirred for 6 h. After removal of the solvent, the residue was diluted with 200 mL of EtOAc and then washed with 5% HCl, saturated $NaHCO_3$, and brine (once for each). The organic phase was dried over Na_2SO_4, concentrated under reduced pressure, and chromatographed on silica gel (elution with CH_2Cl_2) to give **2** as a white powder (27.5 g, 100%): $[\alpha]^{22}_D$ +143.4° (*c* 1.1, $CHCl_3$) (literature rotation for (*S*)-**2**:[12] $[\alpha]^{22}_D$ +142° (*c* 1.035, $CHCl_3$)).

(*S*)-(−)-2-(Diphenylphosphinyl)-2′-((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl (3). To a mixture of **2** (12.5 g, 22.7 mmol), diphenylphosphine oxide (9.18 g 45.4 mmol), palladium diacetate (255 mg, 1.14 mmol), and 1,4-bis(diphenylphosphino)butane (dppb, 484 mg, 1.14 mmol) were added 100 mL of dimethyl sulfoxide and diisopropylethylamine (11.7 g, 90.8 mmol), and the mixture was heated with stirring at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure (0.1–0.2 mmHg) to give a dark brown residue. The residue was diluted with EtOAc, washed twice with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (elution with *n*-hexane/EtOAc, 1/1) to give **3** as a white solid (13.0 g, 95%): $[\alpha]^{20}_D$ −44.45° (*c* 0.50, $CHCl_3$), $[\alpha]^{20}_D$ −6.61° (*c* 1.40, CH_2Cl_2) (literature rotation for (*R*)-**3**:[8] $[\alpha]_D$ +6.29° (*c* 1.00, CH_2Cl_2)); IR (KBr) ν 1410, 1205, 1140, and 945 cm^{-1}; ^1H NMR δ 6.9–8.1 (m, aromatic); ^{31}P NMR δ 28.1 (s); EIMS *m/z* 603 (M + 1), 454, 201 (base peak). Anal. Calcd for $C_{33}H_{22}O_4SF_3P$: C, 65.78; H, 3.68. Found: C, 65.65; H, 3.79.

(*S*)-(+)-2-(Diphenylphosphinyl)-2′-hydroxybinaphthyl (4a). To a solution of **3** (13.0 g, 21.6 mmol) in 2/1 mixture of 1,4-dioxane and MeOH (100 mL) was added 3 N aqueous NaOH solution at ambient temperature. The reaction mixture was stirred for 12 h, acidified (pH = 1) by addition of concd HCl, and then extracted twice with EtOAc. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to give pale yellow solid material, which was chromatographed on silica gel (elution with *n*-hexane/EtOAc, 1/1) to give **4a** as a white solid (10.0 g, 99%): $[\alpha]^{20}_D$ +105.0° (*c* 0.52, $CHCl_3$), $[\alpha]^{20}_D$ +110.6° (*c* 0.85, CH_2Cl_2) (literature rotation for (*R*)-**4a**:[8] $[\alpha]_D$ −108.3° (*c* 1.00, CH_2Cl_2)); ^1H NMR δ 6.35–8.10 (m, 22 H), 9.01 (br s, 1 H); ^{31}P NMR δ 30.80 (s); EIMS *m/z* 470 (M^+), 268 (base peak); HRMS calcd for $C_{32}H_{23}PO_2$ 470.1436, found 470.1415. Anal. Calcd for $C_{32}H_{23}PO_2$: C, 81.69; H, 4.93. Found: C, 81.66; H, 4.96.

(*S*)-(−)-2-(Diphenylphosphinyl)-2′-alkoxy-1,1′-binaphthyl (4b–e). A typical procedure is given for the preparation of **(*S*)-(−)-2-(diphenylphosphinyl)-2′-methoxy-1,1′-binaphthyl (4b):**[10] To a mixture of (*S*)-2-(diphenylphosphinyl)-2′-hydroxy-1,1′-binaphthyl (**4a**) (235 mg, 0.5 mmol) and K_2CO_3 (276 mg, 2.0 mmol) in acetone (3 mL) was added MeI (285 mg, 2.0 mmol), and the reaction mixture was refluxed for 3 h. After being cooled to room temperature, the mixture was filtered through Celite, and the solid was washed with Et_2O. The combined organic layer was concentrated under reduced pressure. The residue was chromatographed on silica gel using EtOAc as eluent to give 240 mg (99%) of **4b**: $[\alpha]^{20}_D$ −126.9° (*c* 0.52, $CHCl_3$); ^1H NMR δ 3.58 (s, 3 H), 6.75–8.01 (m, 22 H); ^{31}P NMR δ 28.67 (s); EIMS *m/z* 484 (M^+), 453, 282 (base peak); HRMS calcd for $C_{33}H_{25}PO_2$ 484.1592, found 484.1574. Anal. Calcd for $C_{33}H_{25}PO_2$: C, 81.80; H, 5.20. Found: C, 81.77; H, 5.38. **(*S*)-(−)-2-(Diphenylphosphinyl)-2′-(benzyloxy)-1,1′-binaphthyl (4c):** 87% yield; $[\alpha]^{20}_D$ −116.5° (*c* 0.11, $CHCl_3$); ^1H NMR δ 4.94 (s, 2 H), 7.80–8.12 (m, 27 H); ^{31}P NMR δ 28.96 (s); EIMS *m/z* 560 (M^+), 469, 201 (base peak); HRMS calcd for $C_{39}H_{29}PO_2$ 560.1905, found 560.1925. Anal. Calcd for $C_{33}H_{25}PO_2$: C, 83.55; H, 5.21. Found: C, 83.80; H, 5.33. **(*S*)-(−)-2-(Diphenylphosphinyl)-2′-isopropoxy-1,1′-binaphthyl (4d):** 92% yield; $[\alpha]^{20}_D$ −315.2° (*c* 0.13, $CHCl_3$); ^1H NMR δ 0.88 (d, *J* = 6.0 Hz, 3 H), 1.13 (d, *J* = 6.0 Hz, 3 H), 4.46 (m, 1 H), 6.75–8.15 (m, 22 H); ^{31}P NMR δ 29.88 (s); MS *m/z* 512 (M^+), 453, 268 (base peak); HRMS calcd for $C_{35}H_{29}PO_2$ 512.1905, found 512.1913. Anal. Calcd for $C_{33}H_{25}PO_2$: C, 82.01; H, 5.70. Found: C, 81.79; H, 5.55. **(*S*)-(−)-2-(Diphenylphosphinyl)-2′-(methoxymethoxy)-1,1′-binaphthyl (4e):** 95% yield; ^1H NMR δ 3.12 (s, 3 H), 4.80 (d, *J* = 7 Hz, 1 H), 5.09 (d, *J* = 7 Hz, 1 H), 6.72–8.04 (m, 22 H); MS *m/z* 514 (M^+), 499, 268, 201 (base peak); HRMS calcd for $C_{34}H_{27}PO_3$ 514.1698, found 514.1673. Anal. Calcd for $C_{34}H_{27}PO_3$: C, 79.36; H, 5.29. Found: C, 79.33; H, 5.45.

(*S*)-(−)-2-(Diphenylphosphino)-2′-alkoxy-1,1′-binaphthyl (1b–d). A typical procedure is given for the preparation of **(*S*)-(−)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (1b):** To a mixture of **4b** (600 mg, 1.24 mmol) and Et_3N (2.50 g, 24.8 mmol) in xylene (30 mL) was added Cl_3SiH (840 mg, 6.20 mmol) at 0 °C. The reaction mixture was stirred at 120 °C for 5 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite, and the solid was washed with Et_2O. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude phosphine was purified by silica gel column chromatography with Et_2O as eluent, giving 559 mg (96%) of **1b**: $[\alpha]^{20}_D$ −94.5° (*c* 0.27, $CHCl_3$), $[\alpha]^{16}_D$ −59.7° (*c* 1.40, benzene) (literature rotation for (*S*)-**1b**:[10] $[\alpha]^{16}_D$ −59.3° (*c* 1.0, benzene)); mp 174–176 °C (recrystallization from CH_2Cl_2/*n*-hexane); ^1H NMR δ 3.34 (s, 3 H), 6.95–8.05 (m, 22 H); ^{31}P NMR δ −13.64 (s); EIMS *m/z* 468 (M^+), 437 (base peak); HRMS calcd for $C_{33}H_{25}PO_2$ 468.1643, found 468.1672. Anal. Calcd for $C_{33}H_{25}PO$: C, 84.60; H, 5.38. Found: C, 84.35; H, 5.44. **(*S*)-(−)-2-(Diphenylphosphino)-2′-(benzyloxy)-1,1′-binaphthyl (1c):** 96% yield; $[\alpha]^{20}_D$ −96.1° (*c* 0.12, $CHCl_3$); ^1H NMR δ 4.71 (d, *J* = 12.9 Hz, 1 H, AB type), 4.94 (d, *J* = 12.9 Hz, 1 H, AB type), 6.80–8.02 (m, 27 H); ^{31}P NMR δ −13.35 (s); EIMS *m/z* 544 (M^+), 437 (base peak); HRMS calcd for $C_{39}H_{29}PO$ 544.1956, found 544.1942. Anal. Calcd for $C_{39}H_{29}PO$: C, 86.00; H, 5.36. Found: C, 85.65; H, 5.71. **(*S*)-(−)-2-(Diphenylphosphino)-2′-isopropoxy-1,1′-binaphthyl (1d):** 84% yield; $[\alpha]^{20}_D$ −90.0° (*c* 0.13, $CHCl_3$); ^1H NMR δ 0.88 (d, *J* = 6.0 Hz, 6 H), 4.48 (septet, *J* = 6.0 Hz, 1 H), 6.75–8.05 (m, 22 H); ^{31}P NMR δ −13.69 (s); EIMS *m/z* 496 (M^+), 437 (base peak); HRMS calcd for $C_{35}H_{29}PO$ 496.1956, found 496.1942.

(*S*)-(−)-2-(Diphenylphosphino)-2′-hydroxy-1,1′-binaphthyl (1a). The same procedure as employed for the preparation of **1b** was followed with **4a** (470 mg, 1.00 mmol), Et_3N (730 mg, 7.20 mmol), and Cl_3SiH (670 mg, 5.00 mmol) in 10 mL of toluene,

(12) Vondenhof, M.; Mattay, J. *Tetrahedron Lett.* **1990**, *31*, 985.

and the reaction mixture was heated upon 100 °C for 16 h. After the workup, the residue was chromatographed on silica gel (elution with *n*-hexane/EtOAc, 3/1) to give 427 mg (94%) of **1a**: $[\alpha]^{20}_D$ −5.01° (*c* 0.45, $CHCl_3$); ^1H NMR δ 4.58 (br s, 1 H), 6.65–8.02 (m, 22 H); ^{31}P NMR δ −13.67 (s); EIMS *m/z* 454 (M^+), 453, 358, 268, 201, 108, 79 (base peak); HRMS calcd for $C_{32}H_{23}PO$ 454.1487, found 454.1474. Anal. Calcd for $C_{32}H_{23}PO$: C, 84.56; H, 5.10. Found: C, 84.75; H, 5.27.

(*S*)-(−)-2-(Diphenylphosphino)-2′-(methoxymethoxy)-1,1′-binaphthyl (1e). Sodium hydride (60% oil suspension, 11 mg, 0.275 mmol) was washed with pentane, and **1a** (113.5 mg, 0.25 mmol) was added. To the mixture was added 2.5 mL of THF at 0 °C, and the mixture was stirred for 5 min at ambient temperature. Chloromethyl methyl ether (19 μL, 0.25 mmol) was added at 0 °C, and the reaction mixture was stirred at ambient temperature for 5 h. The mixture was diluted with Et_2O and quenched with small amount of water. The organic phase was washed with 1 N NaOH, H_2O, and brine and dried over $MgSO_4$. After removal of solvent, the residue was chromatographed on silica gel (elution with *n*-hexane/EtOAc, 5/1) to give **1e** (78 mg, 63%): $[\alpha]^{20}_D$ −126.9° (*c* 0.71, $CHCl_3$); ^1H NMR δ 3.03 (s, 3 H), 4.57 (d, *J* = 7.0 Hz, 1 H), 4.80 (d, *J* = 7.0 Hz, 1 H), 6.80–8.11 (m, 22 H); EIMS *m/z* 498 (M^+), 483, 453, 437 (base peak); HRMS calcd for $C_{34}H_{27}PO_2$ 498.1748, found 498.1767. Anal. Calcd for $C_{34}H_{27}PO_2$: C, 81.91; H, 5.46. Found: C, 81.65; H, 5.85.

(*S*)-(+)-2-(Diphenylphosphino)-2′-((*tert*-butyldimethylsilyl)oxy)-1,1′-binaphthyl (1f). Sodium hydride (60% oil suspension, 11 mg, 0.275 mmol) was washed with pentane, and then **1a** (113.5 mg, 0.25 mmol) was added. To the mixture was added 2.5 mL of THF at 0 °C, and then the resulting mixture was stirred for 5 min at ambient temperature. *tert*-Butylchlorodimethylsilane (38 mg, 0.25 mmol) was added at 0 °C, and the reaction mixture was stirred at ambient temperature for 8 h. The mixture was diluted with Et_2O and quenched with a small amount of water. The organic phase was washed with 1 N NaOH, H_2O, and brine and dried over $MgSO_4$. After removal of solvent, the residue was chromatographed on silica gel (elution with *n*-hexane/EtOAc, 5/1) to give **1f** (108 mg, 76%): $[\alpha]^{20}_D$ +29.3° (*c* 0.71, $CHCl_3$); ^1H NMR δ −0.33 (s, 3 H), 0.11 (s, 3 H), 0.45 (s, 9 H), 6.74–7.89 (m, 22 H); EIMS *m/z* 568 (M^+, base peak), 437, 326; HRMS calcd for $C_{38}H_{37}OPSi$ 568.2351, found 568.2362.

(*S*)-2-(Diphenylphosphinyl)-2′-ethyl-1,1′-binaphthyl (5). To a mixture of 2-(diphenylphosphinyl)-2′-((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl (**3**) (120 mg, 0.2 mmol) and $NiCl_2$(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) in Et_2O (1 mL) was added EtMgBr (0.9 M Et_2O solution, 0.25 mL, 0.23 mmol), and the reaction mixture was refluxed for 24 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with small amount of saturated NH_4Cl. The organic layer was washed with H_2O and dried over $MgSO_4$. Evaporation of the solvents under reduced pressure followed by column chromatography on silica gel using EtOAc as eluent gave 78 mg (81%) of **5**: ^1H NMR δ 0.89 (t, *J* = 6.8 Hz, 3 H), 2.30 (dq, *J* = 7.26 and 7.59 Hz, 1 H), 2.54 (dq, *J* = 7.26 and 7.59 Hz, 1 H), 6.62–8.02 (m, 22 H); EIMS *m/z* 482 (M^+), 453, 377 (base peak); HRMS calcd for $C_{34}H_{27}OP$ 482.1800, found 482.1790.

(*S*)-(−)-2-(Diphenylphosphino)-2′-ethyl-1,1′-binaphthyl (1g). The same procedure as employed for the preparation of **1b** was followed with **5** (38 mg, 0.08 mmol), Et_3N (73 mg, 0.72 mmol), and Cl_3SiH (67 mg, 0.50 mmol) in 1 mL of xylene, and the reaction mixture was heated upon 120 °C for 3 h. After workup, the residue was chromatographed on silica gel (elution with *n*-hexane/EtOAc, 5/1) to give 29 mg (79%) of **1g**: $[\alpha]^{20}_D$ −85.1° (*c* 0.20, $CHCl_3$); ^1H NMR δ 0.82 (t, *J* = 6.4 Hz, 3 H), 2.12 (q, *J* = 6.4 Hz, 2 H), 6.65–7.96 (m, 22 H); EIMS *m/z* 466 (M^+), 437, 280 (base peak); HRMS calcd for $C_{34}H_{27}P$ 466.1851, found 466.1833. Anal. Calcd for $C_{34}H_{27}P$: C, 87.53; H, 5.83. Found: C, 87.81; H, 6.19.

Preparation of Bis(*p*-methoxyphenyl)phosphine Oxide. To a solution of diethyl phosphite (5.52 g, 40.0 mmol) in 15 mL of THF was added sodium metal (920 mg, 40 mmol), and the mixture was stirred under reflux for 20 h. The resulting solution was added to a 1.425 M solution (THF/Et_2O, 1/2) of (*p*-methoxyphenyl)magnesium bromide (60 mL, 85.5 mmol) at 0 °C and then refluxed for 6 h. After being quenched with small amount of water, the reaction mixture was diluted EtOAc and washed once with 5% HCl and twice with water. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give crude bis(*p*-methoxyphenyl)phosphine oxide. The crude solid was purified by recrystallization from EtOAc to give bis(*p*-methoxyphenyl)phosphine oxide (6.25 g, 59.6%).

(*S*)-(−)-2-(Bis(*p*-methoxyphenyl)phosphino)-2′-methoxy-1,1′-binaphthyl (1h). The preparation of **1h** was carried out by following the procedures used for the preparation of **1b** from **2**. The amounts of starting materials and reagents are given below: **(*S*)-2-(Bis(*p*-methoxyphenyl)phosphinyl)-2′-((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl (6).** **2** (2.20 g, 40 mmol), bis(*p*-methoxyphenyl)phosphine oxide (2.52 g, 9.6 mmol), palladium diacetate (90 mg, 0.4 mmol), dppb (170 mg, 0.4 mmol), diisopropylethylamine (2.8 mL, 16.0 mmol), and 20 mL of dimethyl sulfoxide, 90 °C, 22 h. **6**: 2.45 g (93% yield); ^1H NMR δ 3.78 (s, 6 H), 6.61–8.11 (m, 20 H); ^{31}P NMR δ 28.08 (s); EIMS *m/z* 662 (M^+), 513 (base peak); HRMS calcd for $C_{35}H_{26}O_6SF_3P$ 662.1140, found 662.1143. Anal. Calcd for $C_{35}H_{26}O_6SF_3P$: C, 63.44; H, 3.96. Found: C, 63.36; H, 3.66. **(*S*)-(+)-2-(Bis(*p*-methoxyphenyl)phosphinyl)-2′-hydroxy-1,1′-binaphthyl (7).** **6** (2.27 g, 3.43 mmol) and 14 mL of 3 N aqueous NaOH solution in 1,4-dioxane–MeOH (2/1, 20 mL). **7**: 1.76 g (97% yield); $[\alpha]^{20}_D$ +126.3° (*c* 0.67, $CHCl_3$); ^1H NMR δ 3.50 (s, 3 H), 3.84 (s, 3 H), 6.19 (dd, *J* = 1.0 and 8.8 Hz, 2 H), 6.41 (br d, *J* = 8.1 Hz, 1 H), 6.82–8.02 (m, 17 H); ^{31}P NMR δ 31.24 (s); EIMS *m/z* 530 (M^+), 421, 268, 262 (base peak); HRMS calcd for $C_{34}H_{27}O_4P$ 530.1647, found 530.1655. Anal. Calcd for $C_{34}H_{27}O_4P$: C, 76.97; H, 5.13. Found: C, 76.81; H, 5.13. **(*S*)-(−)-2-(Bis(*p*-methoxyphenyl)phosphinyl)-2′-methoxy-1,1′-binaphthyl (8).** **7** (1.70 g, 3.2 mmol), MeI (906 mg, 6.4 mmol), K_2CO_3 (460 mg, 3.33 mmol), and 35 mL of acetone. **8**: 1.71 g (98% yield); $[\alpha]^{20}_D$ −167.7° (*c* 0.63, $CHCl_3$); ^1H NMR δ 3.53 (s, 3 H), 3.65 (s, 3 H), 3.72 (s, 3 H), 6.33 (dd, *J* = 1.0 and 8.8 Hz, 2 H), 6.57–8.02 (m, 18 H); ^{31}P NMR δ 29.23 (s); EIMS *m/z* 544 (M^+), 407, 282, 262 (base peak); HRMS calcd for $C_{35}H_{29}PO_4$ 544.1803, found 544.1815. Anal. Calcd for $C_{35}H_{29}PO_4$: C, 77.19; H, 5.37. Found: C, 77.27; H, 5.69. **(*S*)-(−)-(Bis(*p*-methoxyphenyl)phosphino)-2′-methoxy-1,1′-binaphthyl (1h).** **8** (1.48 g, 2.72 mmol), Et_3N (5.49 g, 54.4 mmol), Cl_3SiH (1.84 g, 13.6 mmol), and 70 mL of xylene. **1h**: 1.44 g (100% yield); $[\alpha]^{20}_D$ −100.0° (*c* 1.04, CH_2Cl_2); ^1H NMR δ 3.39 (s, 3 H), 3.75 (s, 3 H), 3.79 (s, 3 H), 6.77 (dd, *J* = 0.98 and 8.79 Hz, 2 H), 6.85 (br d, *J* = 8.79 Hz, 2 H), 6.92 (d, *J* = 7.82 Hz, 1 H), 7.02 (dd, *J* = 6.84 and 8.79 Hz, 2 H), 7.14 (dd, *J* = 6.84 and 8.79 Hz, 2 H), 7.12–7.18 (m, 1 H), 7.15 (d, *J* = 7.82 Hz, 1 H), 7.24 (ddd, *J* = 1.47, 7.82, and 7.84 Hz, 1 H), 7.30 (ddd, *J* = 0.98, 6.84, and 7.84 Hz, 1 H), 7.32 (d, *J* = 8.79 Hz, 1 H), 7.38 (dd, *J* = 2.93 and 8.79 Hz, 1 H), 7.47 (ddd, *J* = 1.47, 6.83, and 7.84 Hz, 1 H), 7.87 (d, *J* = 8.79 Hz, 1 H), 7.88 (br d, *J* = 6.83 Hz, 1 H), 7.88 (br d, *J* = 6.83 Hz, 1 H), 8.01 (d, *J* = 8.79 Hz, 1 H); ^{31}P NMR δ −16.58 (s); EIMS *m/z* 528 (M^+), 497 (base peak); HRMS calcd for $C_{35}H_{29}O_3P$ 528.1856, found 528.1862. Anal. Calcd for $C_{35}H_{29}O_3P$: C, 79.53; H, 5.53. Found: C, 79.91; H, 5.40.

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Supplementary Material Available: ^1H NMR spectra for **1d**, **1f**, and **5** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.