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Preparation of Optically Active Binaphthylmonophosphines (MOP's) Containing Various Functional Groups

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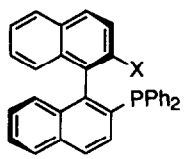
Abstract: Optically active 2'-diphenylphosphino-1,1'-binaphthyls (MOP's) having various functional groups, cyano, aminomethyl, methoxycarbonyl, carboxy, and hydroxymethyl, at the C2-position were prepared. A cyano group was introduced on the MOP skeleton by nickel-catalyzed cyanation of 2-diphenylphosphinyl-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl which is readily prepared from optically active binaphthol. Preparation of the MOP derivatives bearing carboxylic groups were achieved by palladium-catalyzed monocarbonylation of binaphthyl 2,2'-bis(triflate) followed by phosphinylation of the remaining triflate group.

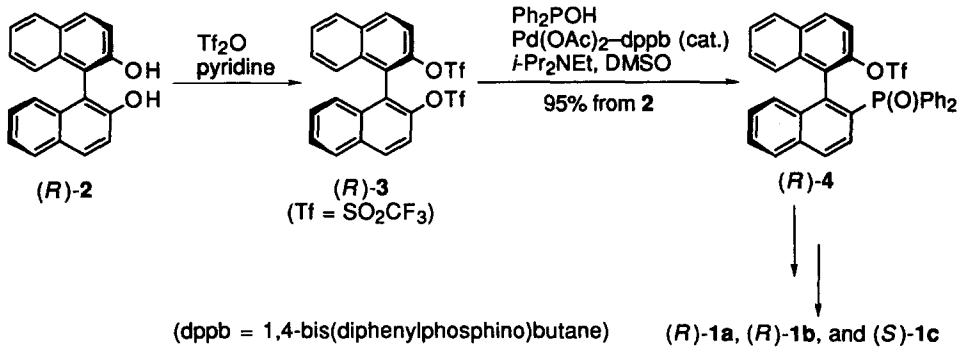
A great deal of attention has been focused on optically active 2,2'-difunctionalized-1,1'-binaphthyls because they exhibit high enantioselectivity in asymmetric synthesis,[1] the typical examples being 2,2'-diol (BINOL) in asymmetric reduction of ketones by the aluminum hydride reagent[2a] and 2,2'-bisphosphine (BINAP) in asymmetric catalysis by use of transition metals.[2b] However, few works have been concerned with the design and preparation of optically active monodentate ligands[3] whose chirality is based on the 1,1'-binaphthyl skeleton.[4] Recently we have reported the preparation of monodentate, optically active phosphine ligands, 2-alkoxy-2'-(diarylphosphino)-1,1'-binaphthyls (RO-MOP's) (**1a**),[4,5] and their successful use for several types of transition metal-catalyzed asymmetric reactions[6] including palladium-catalyzed hydrosilylation of olefins,[6a-d] where a monodentate phosphine ligand is required for the generation of a catalytically active species. On the other hand, we have continued our efforts to design chiral ferrocenylphosphine ligands bearing a variety of functional groups on the side chain which can induce high enantioselectivity by attractive interactions between functional groups on the ligands and reaction substrates.[7] In order to increase the applicability of the chiral binaphthylmonophosphines, we introduced several functional groups on the binaphthyl skeleton.



1 (*R*)-X-MOP

1a: X = OR (R = alkyl or silyl)
1b: X = OH
1c: X = Et (*S*)
1d: X = CN
1e: X = CH_2NH_2
1f: X = CH_2NMe_2
1g: X = COOMe
1h: X = COOH
1i: X = CH_2OH
1j: X = H (*S*)

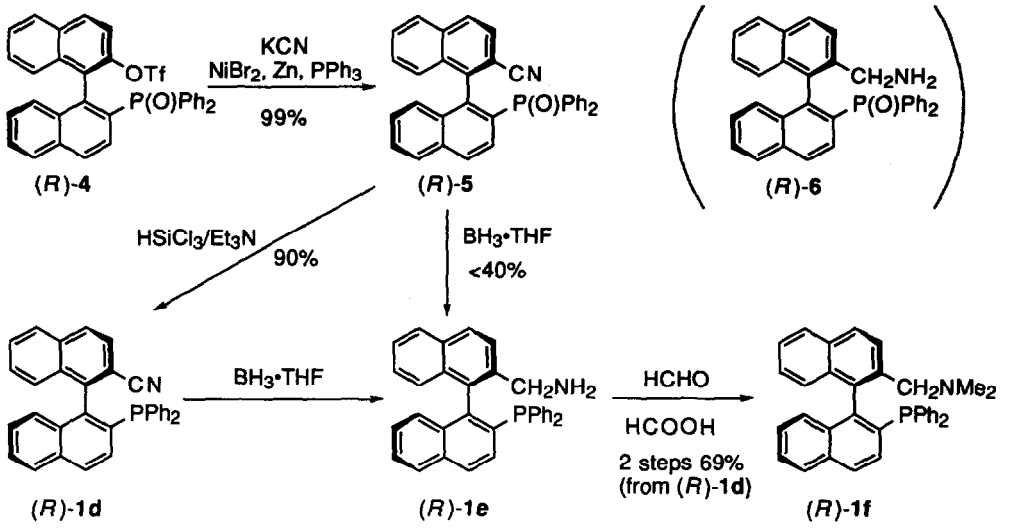
We report here the preparation of functionalized binaphthylmonophosphines, 2-functionalized-2'-diphenylphosphino-1,1'-binaphthyls, that contain cyano, aminomethyl, methoxycarbonyl, carboxy, and hydroxymethyl groups at C2-position. Those functional groups are expected to interact with transition metals or reacting substrates.[8,9,10,11] In our previous report[4] we described the preparation of optically active 2-alkoxy, 2-hydroxy and 2-alkyl-2'-diphenylphosphino-1,1'-binaphthyls (**1a**, **1b**, and **1c**) (Scheme 1), by way of 2-diphenylphosphinyl-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl (**4**) as a key intermediate, whose preparation has been reported by Morgans, Jr. and coworkers.[12] The introduction of the functional groups at C2-position of **4** looks easy because there have been reported many examples of transition metal-catalyzed substitution reactions of aryl triflates,[13] but it turned out that the substitution of triflate on **4** is not always successful because of the steric bulk of the diphenylphosphinyl group present at close proximity.



Scheme 1

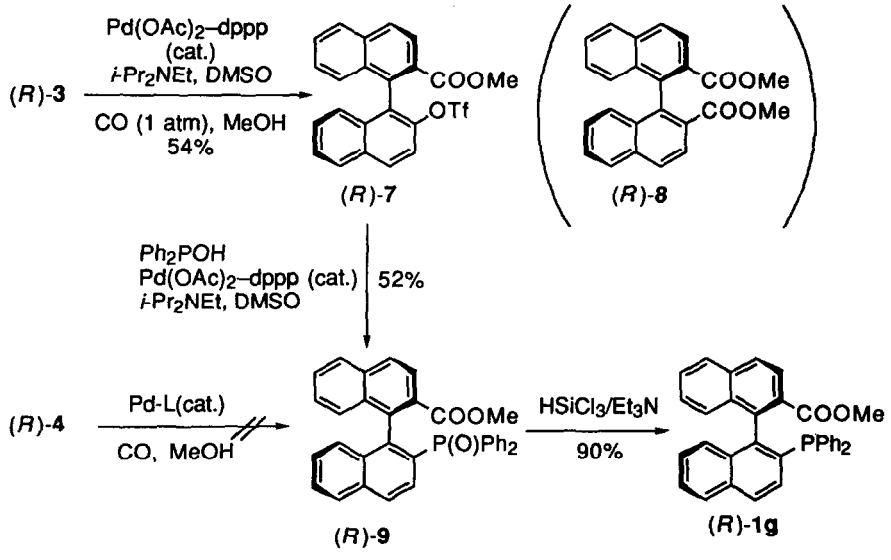
First, we examined the introduction of a cyano group at C2-position of the binaphthyl skeleton. Although attempts to introduce a cyano group on triflate **4** by palladium-catalyzed cyanation were unsuccessful, the cyanation was found to proceed quantitatively by use of a nickel catalyst[14] (Scheme 2). Thus, reaction of (*R*)-**4** with potassium cyanide in the presence of nickel bromide as a catalyst and activated zinc powder in acetonitrile under reflux gave quantitative yield of 2-cyano-2'-diphenylphosphinyl-1,1'-binaphthyl ((*R*)-**5**). The phosphine oxide of (*R*)-**5** was reduced selectively with trichlorosilane/triethylamine in toluene[15] to give (*R*)-2-cyano-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-**1d**) in 90% yield, the cyano group remaining intact. The reduction of the cyano group in (*R*)-**1d** with borane[16] in refluxing THF followed by decomposition of the resulting amino-borane complex (and phosphine-borane complex) by treatment with diluted HCl gave 2-aminomethyl-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-**1e**). Methylation of the primary amine in (*R*)-**1e** with formaldehyde /formic acid[17] gave (*R*)-2-dimethylaminomethyl-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-**1f**) in 69% yield from (*R*)-**1d**. Treatment of phosphine oxide (*R*)-**5** with an excess of borane resulted in a low yield of the desired amino-phosphine (*R*)-**1e** together with a considerable amount of phosphine oxide **6**[18] where only the cyano group is reduced to aminomethyl. Thus, amino-phosphine **1e** is obtained in higher yield by way of cyano-phosphine **1d** rather than the simultaneous reduction of both cyano and phosphine oxide with borane in **5**.

Scheme 2



Since the cyano group of **5** or **1d** resisted acid or alkaline hydrolysis to a carboxy group, the introduction of a carboxy group was examined by the use of palladium-catalyzed carbonylation of triflate.[19] However, the carbonylation reaction did not take place with the triflate **4** containing diphenylphosphinyl group. The low reactivity of triflate **4** towards the palladium-catalyzed carbonylation is ascribed to the steric hindrance of diphenylphosphinyl group, suggesting that the carboxylic function should be introduced into the binaphthyl skeleton at an earlier stage of the synthesis. According to the procedures reported by Miyano et al.,[20]

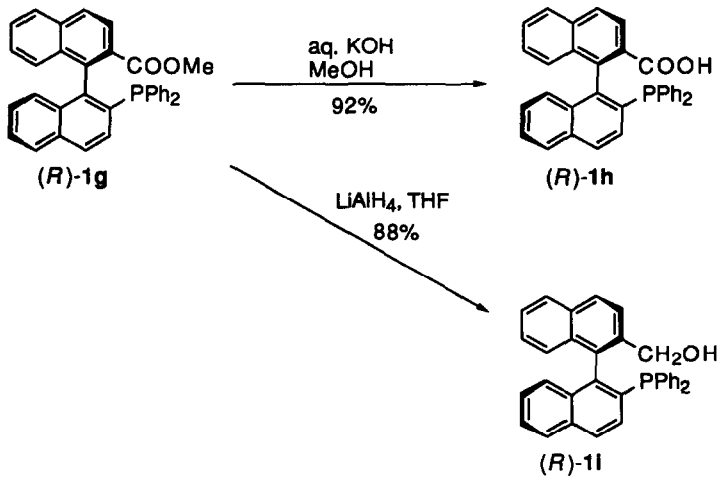
Scheme 3



(dppp = 1,3-bis(diphenylphosphino)propane)

bis(triflate) (*R*)-**3** was exposed to an atmospheric pressure of carbon monoxide and an excess of methanol in the presence of palladium diacetate and 1,3-bis(diphenylphosphino)propane (dppp) as a catalyst to give 54% yield of monocarbonylation product (*R*)-**7** (Scheme 3). The aryl triflate of (*R*)-**7** which is less-hindered than that of (*R*)-**4** showed much higher reactivity towards the palladium-catalyzed reactions. Thus, the reaction of (*R*)-**7** with diphenylphosphine oxide in the presence of a catalytic amount of palladium diacetate-dppp in dimethyl sulfoxide gave (*R*)-2-methoxycarbonyl-2'-diphenylphosphinyl-1,1'-binaphthyl ((*R*)-**9**) in 52% yield. Selective reduction of the phosphine oxide in **9** with trichlorosilane/triethylamine gave a 90% yield of phosphine (*R*)-**1g**. Carboxylic acid (*R*)-**1h** was prepared by alkaline hydrolysis of ester (*R*)-**1g** with aqueous KOH in methanol upon heating in 92% yield (Scheme 4). The MOP bearing hydroxymethyl group at the C2-position (*R*)-**1i** was obtained in 88% yield by the lithium aluminum hydride reduction of (*R*)-**1g** at low temperature (–78-0 °C) in THF.

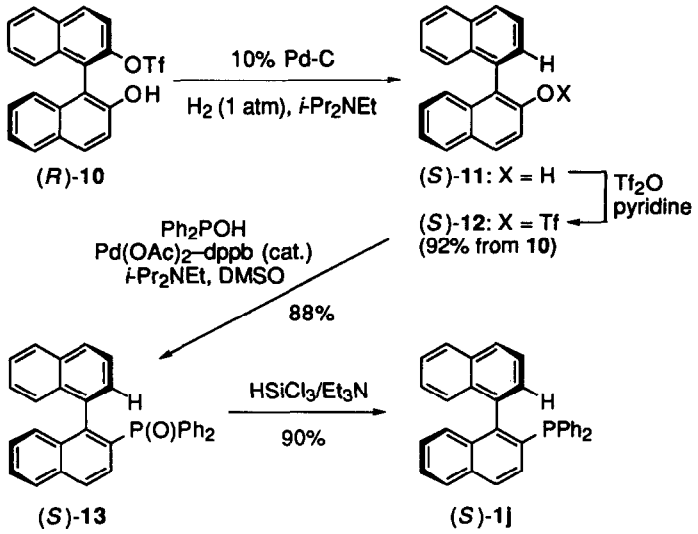
Scheme 4



The MOP derivative (*S*)-**1j** bearing no substituent at C2-position, which is important to evaluate the steric and/or electronic effects of various functional groups in other MOP derivatives, was prepared. Palladium-catalyzed reduction of triflate (*R*)-**4** with several types of hydride reagents, (e.g. formic acid/base and alkylmagnesium halides,[21]) was unsuccessful, as we expected from the low reactivity of (*R*)-**4** towards palladium-catalyzed reactions (*vide supra*). Hydroxybinaphthyl (*S*)-**11**[12] was chosen as a starting substrate, which is readily prepared in an optically active form by Katsuki's method,[22] that is, mono-sulfonylation of diol (*R*)-**2** followed by hydrogenolysis of the aryl sulfonate in (*R*)-**10**. The phenol (*S*)-**11** was converted into non-substituted MOP (*S*)-**1j** by a sequence of reactions similar to those described.[4] Namely, sulfonylation ((*S*)-**12**, 92% from (*R*)-**10**), palladium-catalyzed phosphinylation ((*S*)-**13**, 88%), and reduction (90%) gave 2-diphenylphosphino-1,1'-binaphthyl ((*S*)-**1j**) (Scheme 5).

In summary, we synthesized optically active MOP derivatives with functional groups at C2-position which may play an important role on asymmetric induction in transition metal-catalyzed asymmetric reactions. Since these functional groups have great potential to be transformed into a variety of side chains, the synthesis mentioned above paves the way for preparation of various tailor-made MOP derivatives.

Scheme 5



Experimental Section

General. Melting points were measured with a hot stage microscope (YANACO MP-S3) and are uncorrected. ^1H NMR spectra were measured on a 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. $^{31}P\{^1H\}$ NMR spectra were measured on a 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 spectrometer. 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. Acetonitrile was distilled from P_2O_5 and then CaH_2. Toluene, DMSO, and CH_2Cl_2 were distilled from CaH_2. The purity of compound **1i** was judged to be ≥ 95% by ^1H NMR spectral determination. Satisfactory results in combustion analysis were obtained for all other title compounds.

(*R*)-(+)-2-Cyano-2'-diphenylphosphinyl-1,1'-binaphthyl ((*R*)-5). A mixture of (*R*)-2-diphenylphosphinyl-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl ((*R*)-**4**)[4,12] (7.05 g, 11.7 mmol), potassium cyanide (7.55 g, 116 mmol), nickel dibromide (1.13 g, 5.2 mmol), triphenylphosphine (6.04 g, 23.0 mmol), and activated zinc powder (1.05 g, 16.1 mg atom) in 70 mL of acetonitrile was refluxed under N_2 for 2.5 h. After being cooled to room temperature, the reaction mixture was diluted by EtOAc and washed with H_2O (x 2) and brine. The organic phase was dried over $MgSO_4$, concentrated under reduced pressure to give pale yellow solid material, which was chromatographed on silica gel (elution with *n*-hexane/EtOAc = 1/3) to

give (*R*)-**5** as a white solid (5.57 g, 99%): mp 212-214 °C; $[\alpha]_D^{20}$ +132.1 (*c* 0.49, chloroform); IR (nujol) ν 2220, 1200, 1120, 835, 755, 700, 520 cm^{-1}; ^1H NMR δ 7.03 (t, *J* = 9.6 Hz, 2H), 7.14-7.68 (m, 16H), 7.84 (dd, *J* = 8.3 and 5.3 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 8.01 (dd, *J* = 8.6 and 2.0 Hz, 1H); $^{31}P\{^1H\}$ NMR δ 28.30 (s); EIMS m/z 479 (M^+, base peak), 453, 277, 252, 240, 202. Anal. Calcd for $C_{33}H_{22}NPO$: C, 82.66; H, 4.62; N, 2.92. Found: C, 82.50; H, 4.72; N, 2.84.

(*R*)-(+)-2-Cyano-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-1d). To a mixture of (*R*)-**5** (480 mg, 1.0 mmol) and triethylamine (2.8 mL, 20.1 mmol) in toluene (25 mL) was added trichlorosilane (500 μL, 5.1 mmol) at 0 °C. The reaction mixture was refluxed for 12 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with a small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite and the filter cake 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 (elution with Et_2O) giving 418 mg (90%) of **1d**: mp 143-144 °C; $[\alpha]_D^{20}$ +57.6 (*c* 0.53, chloroform); IR (nujol) ν 2210 cm^{-1}; ^1H NMR δ 6.96-7.93 (m, aromatic); $^{31}P\{^1H\}$ NMR δ −14.34 (s); EIMS m/z 463 (M^+, base peak), 437, 308, 277; Anal. Calcd for $C_{33}H_{22}NP$: C, 85.51; H, 4.78; N, 3.02. Found: C, 85.38; H, 5.00; N, 2.98.

(*R*)-(+)-2-Dimethylaminomethyl-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-1f). To a solution of (*R*)-**1d** (99.5 mg, 0.215 mmol) in 450 μL of THF was added 450 μL of BH_3•THF complex (1 M soln in THF) at 0 °C. The mixture was refluxed under N_2 for 1 h and cooled to room temperature. It was diluted with methanol and stirred for 30 min. The solvent was removed and the residue was dissolved in 5 mL of 5% HCl and refluxed for 1 h. After being cooled to room temperature, the mixture was made alkaline (pH ≅ 11) by addition of 40% aqueous KOH solution. The aqueous solution was extracted with EtOAc. The organic phase was washed twice with H_2O and with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give crude (*R*)-2-aminomethyl-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-**1e**): ^1H NMR δ 1.97 (s, 2 H), 3.65 (br d, *J* 13.5 Hz, 1 H), 3.89 (br d, *J* = 13.5 Hz, 1 H), 6.66 (d, *J* = 8.5 Hz, 1 H), 7.43 (m, 16 H), 7.74-8.07 (m, 5 H); $^{31}P\{^1H\}$ NMR δ −13.29 (s). The crude material was taken on to the next step without further purification.

A mixture of (*R*)-**1e** obtained above, formic acid (200 μL, 5.3 mmol), and 37% aqueous formaldehyde (200 μL, 27 mmol) was refluxed for 12 h. The reaction mixture was made alkaline by addition of saturated $NaHCO_3$ and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (elution with *n*-hexane/EtOAc = 1/3) giving 74 mg of (*R*)-**1f** (69% from **1d**): $[\alpha]_D^{20}$ +79.6 (*c* 0.52, chloroform); ^1H NMR δ 1.92 (s, 6 H), 2.77 (d, *J* = 14.2 Hz, 1 H), 3.05 (d, *J* = 14.2 Hz, 1 H), 6.77-7.49 (m, 17 H), 7.84-7.99 (m, 5 H); $^{31}P\{^1H\}$ NMR δ −15.00 (s); EIMS m/z 495 (M^+), 480, 468, 451, 437 (base peak), 294. Anal. Calcd for $C_{35}H_{30}PN$: C, 84.82; H, 6.10; N, 2.83. Found: C, 84.94; H, 6.22; N, 2.69.

(*R*)-2-Carbomethoxy-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl ((*R*)-7).[20a] To a solution of (*R*)-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl ((*R*)-**3**)[23] (6.00 g, 10.9 mmol), palladium diacetate (225 mg, 2.0 mmol), and 1,3-bis(diphenylphosphino)propane (414 mg, 1.0 mmol) in 3/2 mixture of DMSO and methanol (500 mL) was added 20 mL of triethylamine. The mixture was stirred under carbon monoxide (1 atm) at 70 °C for 16 h. After being cooled to room temperature, it was concentrated under reduced pressure. The red-brown residue was dissolved in 300 mL of Et_2O and washed with H_2O. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude material was purified

by silica gel column chromatography (elution with *n*-hexane/EtOAc = 5/1) giving 2.71 g (54%) of (*R*)-**7**: IR (film) ν 1727, 1417, 1246, 1216, 765 cm^{-1}; ^1H NMR δ 3.55 (s, 3H), 7.12-8.25 (m, 12H); EIMS m/z 460 (M^+), 311 (M-OTf), 268 (base peak), 239, 131, 69.

(*R*)-(+)-2-Carbomethoxy-2'-diphenylphosphinyl-1,1'-binaphthyl ((*R*)-9). To a solution of (*R*)-**7** (115 mg, 0.25 mmol), diphenylphosphine oxide (101 mg, 0.50 mmol), palladium diacetate (5.6 mg, 0.025 mmol), and 1,3-bis(diphenylphosphino)propane (10.3 mg, 0.025 mmol) in 1.5 mL of DMSO was added diisopropylethylamine (0.21 mL, 1.2 mmol), and the mixture was stirred at 100 °C for 60 h. After being cooled to room temperature, the reaction mixture was diluted with EtOAc, washed with H_2O and dried over $MgSO_4$. Removal of the solvent followed by column chromatography on silica gel (elution with *n*-hexane/EtOAc = 1/2) gave 65.5 mg of (*R*)-**9** (52%): mp 174-176 °C; $[\alpha]_D^{20}$ +41.5 (*c* 0.57, chloroform); IR (film) ν 1740, 1430, 1240 750 cm^{-1}; ^1H NMR δ 3.52 (s, 3H), 6.98-8.04 (m, 22H); $^{31}P\{^1H\}$ NMR δ 27.7; EIMS m/z 512 (M^+, base peak). Anal. Calcd for $C_{34}H_{25}PO_3$: C, 79.68; H, 4.92. Found: C, 79.84; H, 5.13.

(*R*)-(+)-2-Carbomethoxy-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-1g). To a mixture of (*R*)-**9** (990 mg, 1.93 mmol) and triethylamine (7.30 g, 10.0 mL, 72.0 mmol) in toluene (45 mL) was added trichlorosilane (2.0 mL, 20 mmol) at 0 °C, the mixture was refluxed for 41 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 filter cake 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 (elution with *n*-hexane/EtOAc = 3/1) giving 862 mg (90%) of (*R*)-**1g**: mp 105-108 °C; $[\alpha]_D^{20}$ +42.0 (*c* 0.52, chloroform); IR (film) ν 1725, 1440, 1240, 750 cm^{-1}; ^1H NMR δ 3.25 (s, 3 H), 6.97-7.28 (m, 14 H), 7.85-7.94 (m, 3 H), 8.02 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 8.6 Hz, 1H); $^{31}P\{^1H\}$ NMR δ –14.65 (s); EIMS m/z 496 (M^+, base peak); HRMS calcd for $C_{34}H_{25}PO_2$ 496.1592, found 496.1563. Anal. Calcd for $C_{34}H_{25}PO_2$: C, 82.24; H, 5.07. Found: C, 82.27; H, 5.13.

(*R*)-(+)-2'-Diphenylphosphino-1,1'-binaphthyl-2-carboxylic acid ((*R*)-1h). To a solution of (*R*)-**1g** (100 mg, 0.20 mmol) in 2.5 mL of methanol was added 500 μL of 40% KOH solution and the mixture was refluxed for 13 h. The reaction mixture was acidified (pH ≅ 2) by addition of conc. HCl at 0 °C and extracted with EtOAc. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative TLC (elution with *n*-hexane/EtOAc = 2/1) to give 89 mg of (*R*)-**1h** (92%): mp 124-126 °C; $[\alpha]_D^{20}$ +65.9 (*c* 0.54, chloroform); IR (film) ν 3200-2800, 1680, 750 cm^{-1}; ^1H NMR δ 6.96-7.25 (m, 14 H), 7.38-7.50 (m, 3H), 7.85-7.93 (m, 3 H), 8.01 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 8.6 Hz, 1H); $^{31}P\{^1H\}$ NMR δ –14.23 (s); EIMS m/z 496 (M^+, base peak); HRMS calcd for $C_{33}H_{23}PO_2$ 482.1436, found 482.1441.

(*R*)-(+)-2-Hydroxymethyl-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-1i). To a suspension of $LiAlH_4$ (11.4 mg, 0.30 mmol) in 1 mL of THF was added THF solution (1 mL) of (*R*)-**1g** (100 mg, 0.20 mmol) at –78 °C under N_2 and the mixture was stirred at 0 °C for 5 h. The reaction mixture was diluted with Et_2O and quenched by addition of $Na_2SO_4 \cdot 10H_2O$ and brine. The organic phase was separated by decantation and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (elution with *n*-hexane/EtOAc = 2/1) to give 83 mg of (*R*)-**1i** (88%): $[\alpha]_D^{20}$ +68.5 (*c* 0.79, chloroform); IR (film) ν 3500-3100, 1440, 810 cm^{-1}; ^1H NMR δ 1.43 (br s, 1 H), 4.06 (dd, *J* = 12.9 and 4.9 Hz, 1H), 4.19 (dd, *J* = 12.9 and 7.9 Hz, 1H), 6.82-7.49 (m, 17H), 7.74-8.24 (m, 5 H); $^{31}P\{^1H\}$ NMR δ –14.07 (s); EIMS m/z 468 (M^+, base peak); HRMS calcd for $C_{33}H_{25}PO$ 468.1643, found 468.1639. Anal Calcd for $C_{33}H_{25}PO$: C, 84.60; H, 5.38. Found: C, 84.30; H, 5.59.

(*S*)-(–)-2-Hydroxy-1,1'-binaphthyl ((*S*)-11).[22] To a suspension of 10% palladium on charcoal (119 mg) in 5 mL of ethanol was added diisopropylethylamine (290 mg, 2.24 mmol) and (*R*)-2-hydroxy-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl ((*R*)-**10**)[22] (470 mg, 1.12 mmol) at room temperature. The mixture was stirred under hydrogen gas (1 atm) for 6 h. The mixture was filtered through Celite plug and the Celite was washed with EtOAc. The combined organic layer was concentrated under reduced pressure to give white solid. The crude material was purified by silica gel column chromatography (elution with *n*-hexane/EtOAc = 6/1) to give 284 mg (100%) of (*S*)-**11**: $[\alpha]_D^{25}$ –14.2 (*c* 1.3, tetrahydrofuran) (lit for (*R*)-**11** of 90% ee (ref 22c): $[\alpha]_D$ +13.8 (tetrahydrofuran)); ^{1}H NMR δ 5.18 (br s, 1 H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.20-7.69 (m, 8H), 7.85-8.04 (m, 4H); EIMS m/z 270 (M^+, base peak), 239, 126.

(*S*)-(–)-2-Trifluoromethanesulfonyloxy-1,1'-binaphthyl ((*S*)-12).[12] To a solution of (*S*)-**11** (270 mg, 1.0 mmol) in 4 mL of CH_2Cl_2 was added pyridine (200 μL, 2.47 mmol) and trifluoromethanesulfonic anhydride (200 μL, 1.19 mmol) at 0 °C and the mixture was stirred for 2 h. The mixture was diluted with Et_2O and washed with 5% HCl, saturated $NaHCO_3$, and brine. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel (elution with *n*-hexane/EtOAc = 10/1) giving 374 mg (92%) of (*S*)-**12**: $[\alpha]_D^{20}$ –9.2 (*c* 1.0, dichlorometane) (lit for (*S*)-**12** (ref 12): $[\alpha]_D$ –8.97 (*c* 0.50, dichloromethane)); ^{1}H NMR δ 7.22-8.12 (m, aromatic).

(*S*)-(+)-2-Diphenylphosphinyl-1,1'-binaphthyl ((*S*)-13).[12] To a mixture of (*S*)-**12** (374 mg, 0.92 mmol), diphenylphosphine oxide (372 mg 1.84 mmol), palladium diacetate (41 mg, 0.09 mmol), and 1,4-bis(diphenylphosphino)butane (dppb, 78 mg, 0.09 mmol) was added 4 mL of DMSO and diisopropylethylamine (475 mg, 3.7 mmol), and the mixture was heated with stirring at 100 °C for 8 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure (0.1–0.2 mm Hg) to give 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 (*S*)-**13** as a white solid (370 mg, 88%): $[\alpha]_D^{20}$ +15.5 (*c* 0.77, dichloromethane) (lit for (*S*)-**13** (ref 12): $[\alpha]_D$ +18.14 (*c* 1.02, dichloromethane)); ^{31}P{^{1}H} NMR δ (dichloromethane) +27.35 (s).

(*S*)-(+)-2-Diphenylphosphino-1,1'-binaphthyl ((*S*)-1j). The same procedure as employed for the preparation of (*R*)-**1d** was followed with (*S*)-**13** (370 mg, 0.81 mmol), triethylamine (1.65 g, 16.3 mmol) and trichlorosilane (542 mg, 4 mmol) in 20 mL of toluene, and the reaction mixture was heated upon 100 °C for 16 h. After the workup, the residue was chromatographed on silica gel (elution with dichloromethane) to give 322 mg (90%) of (*S*)-**1j**: $[\alpha]_D^{20}$ +102.4 (*c* 2.03, chloroform); ^{1}H NMR δ 6.84-8.12 (m, aromatic); ^{31}P{^{1}H} NMR δ (chloroform) –13.52 (s). Anal. Calcd for $C_{32}H_{23}P$: C, 87.65; H, 5.29. Found: C, 87.53; H, 5.48.

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