Preparation of Enantiomerically Pure 2′-Substituted 2-Diphenylphosphino-1,1′-binaphthyls by Reductive Cleavage of the Carbon−Phosphorus Bond in a Borane Complex of 2-Diphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthyl

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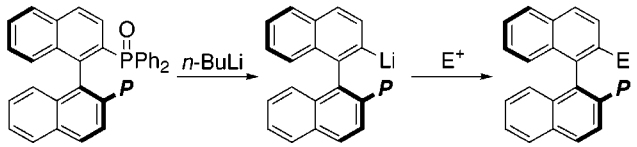
Reaction of (*S*)-2′-boranatodiphenylphosphino-2-diphenylphosphinyl-1,1′-binaphthyl (**3**, borane complex of BINAP monoxide) with an excess of *n*-butyllithium in THF at −78 °C brought about a selective cleavage of the carbon−phosphorus bond between the binaphthyl and diphenylphosphinyl groups to generate the binaphthyllithium **14**, the treatment of which with electrophiles MeOD, I_2, and $ClSnMe_3$ gave, after removal of the borane, the corresponding 2′-substituted 2-diphenylphosphino-1,1′-binaphthyls (E-MOP **9**: E = D, I, $SnMe_3$), without loss of the enantiomeric purity.

Introduction

It has been well documented that enantiomerically pure phosphines whose chirality is due to an axially chiral 1,1′-binaphthyl backbone are useful as chiral ligands for transition metal-catalyzed asymmetric reactions.[1,2] One of the most useful chiral phosphine ligands is 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP),[3] which exhibits high enantioselectivity in several types of asymmetric reactions, including ruthenium-catalyzed hydrogenation[4] and rhodium-catalyzed 1,4-addition of organoboronic acids.[5] We have developed axially chiral monodentate phosphine ligands, represented by 2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl (MeO-MOP),[6,7] for the catalytic asymmetric reactions where bisphosphine−metal catalysts cannot be used because of their low catalytic activity and/or low selectivity toward a desired reaction pathway. The high efficiency of the MOP ligands has been demonstrated in palladium-catalyzed asymmetric hydrosilylation of olefins,[8] rhodium-catalyzed arylation of imines,[9] and so on.[6,10] The MOP ligands have an advantage over others in that fine-tuning can be performed by introducing a desired group at the 2′ position of the 1,1′-binaphthyl skeleton according to the reaction type. The substituents at the 2′ position have been introduced in most cases by alkylation of the 2′-hydroxyl group or by nickel-catalyzed cross-coupling-type reactions of the 2′-trifluoromethanesulfonyloxy group.[7,11] For an extension of the utility of the MOP ligands, we have made a search for new methods of introducing 2′-substituents on the 1,1′-binaphthyl. The report by Seyferth[12] that the carbon−phosphorus bond in triphenylphosphine oxide is cleaved by treatment with an alkyllithium to generate phenyllithium and alkyldiphenylphosphine oxide attracted our attention. We studied the selectivity of this lithiation in phosphine oxide derivatives of BINAP **1**−**3** and found that the carbon−phosphorus bond cleavage takes place selectively between the binaphthyl and diphenylphosphinyl groups generating 2-lithio-1,1′-binaphthyl derivatives, and addition of electrophiles to the lithiated binaphthyls leads to the preparation of 2′-substituted 2-diphenylphosphino-1,1′-binaphthyls (MOP) (Scheme 1). The retention or loss of the enantiomeric purity during the lithiation was dependent on the substituents at 2 position. Thus, the racemization

Scheme 1



P = $P(O)Ph_2$ (**1**)
PPh_2 (**2**)
$PPh_2{\cdot}BH_3$ (**3**)

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(1) For a pertinent review, see: McCarthy, M.; Guiry, P. J. *Tetrahedron* **2001**, *57*, 3809.

(2) For reviews on catalytic asymmetric reactions, see: (a) Jacobsen, E.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999; Vols. 1−3. (b) Takaya, H.; Ohta, T.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH Publishers: New York, 1993; Chapter 1. (c) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40.

(3) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932.

(4) Okuma, T.; Noyori, R. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. 1, Chapter 6.1.

(5) (a) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579. (b) Hayashi, T.; Senda, T.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **1999**, *121*, 11591. (c) Hayashi, T.; Senda, T.; Ogasawara, M. *J. Am. Chem. Soc.* **2000**, *122*, 10716 and references therein.

(6) For a review, see: Hayashi, T. *Acc. Chem. Res.* **2000**, *33*, 354.

(7) (a) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887. (b) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945. (c) Uozumi, Y.; Suzuki, N.; Ogiwara, A.; Hayashi, T. *Tetrahedron* **1994**, *50*, 4293.

(8) Hayashi, T.; Hirate, S.; Kitayama, K.; Tsuji, H.; Torii, A.; Uozumi, Y. *J. Org. Chem.* **2001**, *66*, 1441 and references therein.

(9) Hayashi, T.; Ishigedani, M. *J. Am. Chem. Soc.* **2000**, *122*, 976.

(10) (a) Hayashi, T.; Iwamura, H.; Uozumi, Y.; Matsumoto, Y.; Ozawa, F. *Synthesis* **1994**, 526. (b) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775. (c) RajanBabu, T. V.; Nomura, N.; Jin, J.; Radetich, B.; Park, H.; Nandi, M. *Chem. Eur. J.* **1999**, 1963. (d) Lloyd-Jones, G. C.; Stephen, S. C.; Murray, M.; Butts, C. P.; Vyskocil, S.; Kocovsky, P. *Chem. Eur. J.* **2000**, 4348.

(11) Hayashi, T.; Han, J.-W.; Takeda, A.; Tang, J.; Nohmi, K.; Mukaide, K.; Tsuji, H.; Uozumi, Y. *Adv. Synth. Catal.* **2001**, *343*, 279.

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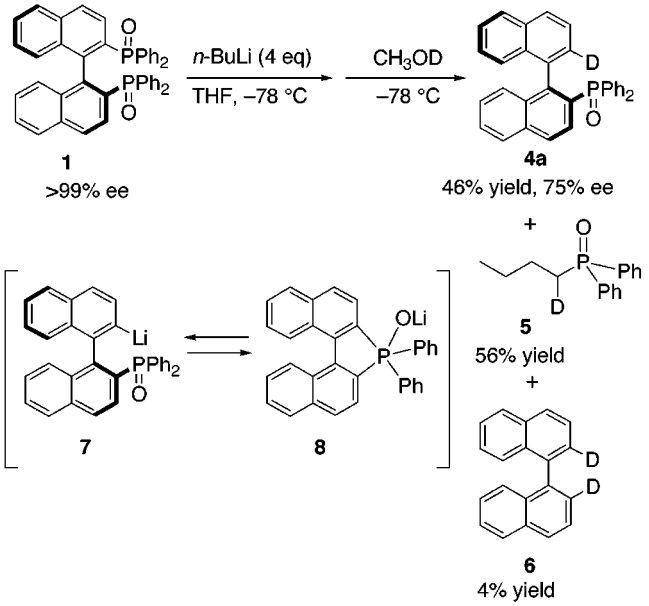
Scheme 2

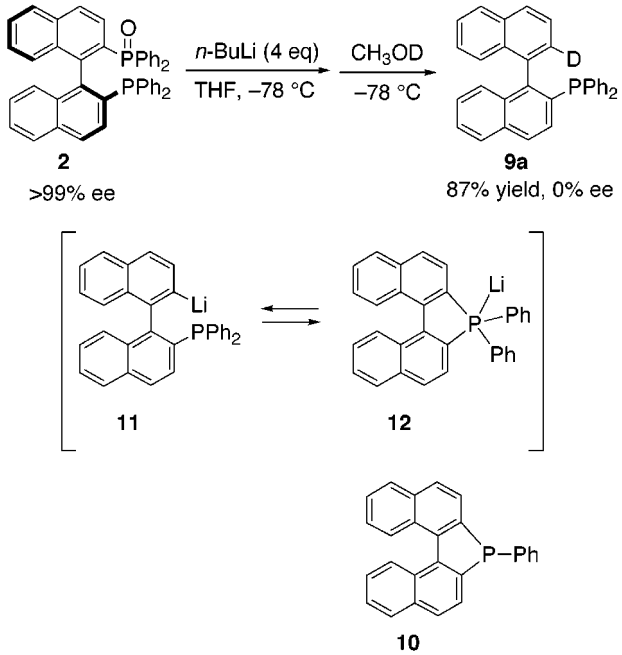


was fast with the diphenylphosphino group while the enantiomeric purity was retained with its borane complex. Here we report the preparation of new MOP ligands through the selective lithiation of the phosphine oxide derivatives of BINAP.

Results and Discussion

First, the dioxide of BINAP (**1**)[13] was allowed to react with *n*-butyllithium under several reaction conditions and the reaction was quenched with methanol-*d* to see the lithiated position in the products by the deuterium incorporation (Scheme 2). It was found that the carbon−phosphorus bond cleavage with *n*-butyllithium takes place at −78 °C and the selectivity of the cleavage between the binaphthyl moiety and the diphenylphosphinyl group is very high. Thus, the reaction of enantiomerically pure (*S*)-**1** with 4 equiv of *n*-butyllithium in THF at −78 °C for 3 h followed by addition of excess methanol-*d* at the same temperature gave 46% yield of 2′-deuterio-2-diphenylphosphinyl-1,1′-binaphthyl (**4a**), 56% yield of 1-deuteriobutyldiphenylphosphine oxide (**5**), and 4% yield of 2,2′-dideuterio-1,1′-binaphthyl (**6**). These results indicate the selective cleavage of the carbon−phosphorus bond between the binaphthyl moiety and the diphenylphosphinyl group generating 2′-lithio-2-diphenylphosphinyl-1,1′-binaphthyl (**7**) together with butyldiphenylphosphine oxide. Other carbon−phosphorus bonds did not undergo cleavage by *n*-butyllithium, which is demonstrated by the absence of 2-diphenylphosphinyl-2′-butyl(phenyl)phosphinyl-1,1′-binaphthyl in the reaction products. The deuteration on the carbon bonded to the phosphinyl group in the phosphine oxide **5** has been reported by Seyferth.[12] Unfortunately, the enantiomeric purity of **4a** obtained under the conditions described above was 75% enantiomeric excess (ee), indicating that the reaction was accompanied by racemization of the axially chiral binaphthyl skeleton. The racemization is ascribed probably to the equilibrium between **7** and an

Scheme 3



achiral dinaphthophosphole-type intermediate **8**. A quite similar racemization mechanism has been reported by Cereghetti in the reaction that proceeds through 6,6′-dimethyl-2′-lithio-2-diphenylphosphinyl-1,1′-biphenyl.[14]

Second, the carbon−phosphorus bond cleavage with *n*-butyllithium was examined for BINAP monoxide **2**[15] (Scheme 3). Under the same conditions used for BINAP dioxide **1** (in THF at −78 °C for 3 h), the lithiation proceeded with higher selectivity to give, after quenching with methanol-*d*, 2′-deuterio-2-diphenylphosphino-1,1′-binaphthyl (D-MOP, **9a**) in 87% yield together with the corresponding amount of butylphosphine oxide **5**. However, complete loss of the enantiomeric purity was observed in **9a**. Similar to the racemization during the lithiation of dioxide **1**, the formation of phosphole-type intermediate is considered to be responsible for this racemization. Thus, the racemization is caused by reversible transformation of lithiated binaphthyl **11** to lithium phosphoranide **12**.[16,17] An attempt to quench the reaction of the lithiated mixture with chlorotrimethylsilane resulted in the formation of dinaphthophosphole **10**[18] (75%) and phenyltrimethylsilane. Interestingly, hydrolysis of the lithiated reaction mixture after it was allowed to stand at room temperature for 1 h did not give any detectable amount of phosphole **10**, leaving a complex mixture of unidentified compounds. It follows that lithiated binaphthyl **11** is in an equilibrium with phosphole **10** and phenyllithium by way of phosphoranide **12** and that the addition of chlorotrimethylsilane shifts the equilibrium by removing the phenyllithium.

Finally, we succeeded in the selective cleavage of the phosphorus−carbon bond without loss of the enantio-

(12) Seyferth, D.; Welch, D. E.; Heeren, J. K. *J. Am. Chem. Soc.* **1964**, *86*, 1100.

(13) Takaya, H.; Akutagawa, S.; Noyori, R. *Org. Synth.* **1989**, *67*, 20.

(14) Cereghetti, M.; Arnold, W.; Broger, E. A.; Rageot, A. *Tetrahedron Lett.* **1996**, *37*, 5347.

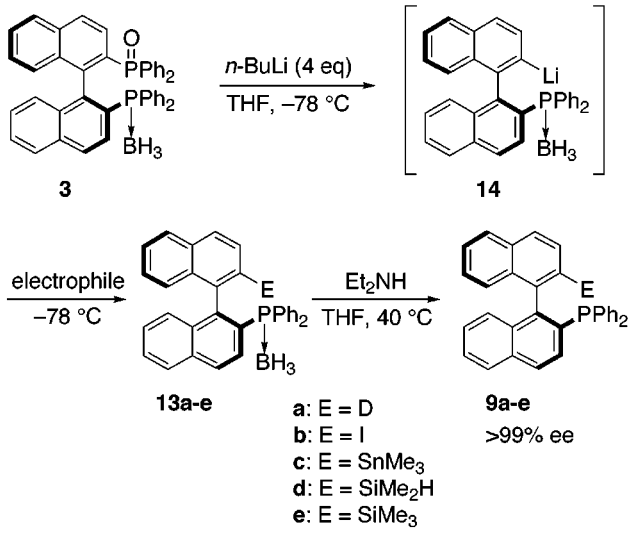
(15) (a) Ozawa, F.; Kubo, A.; Hayashi, T. *Chem. Lett.* **1992**, 2177. (b) Gladiali, S.; Pulacchini, S.; Fabbri, D.; Manassero, M.; Sansoni, M. *Tetrahedron: Asymmetry* **1998**, *9*, 391. (c) Grushin, V. V. *J. Am. Chem. Soc.* **1999**, *121*, 5831.

(16) Hellwinkel, D. *Chem. Ber.* **1965**, *98*, 576.

(17) Desponds, O.; Schlosser, M. *J. Organomet. Chem.* **1996**, *507*, 257.

(18) (a) Dore, A.; Fabbri, D.; Gladiali, S.; Lucchi, O. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1124. (b) Gladiali, S.; Dore, A.; Fabbri, D. *J. Org. Chem.* **1994**, *59*, 6363.

Scheme 4



meric purity by using the borane complex of BINAP monoxide **3**, which is readily accessible by treatment of BINAP monoxide **2** with borane in THF.[19] Thus, the reaction of (*S*)-**3** (>99% ee) with butyllithium at −78 °C followed by treatment of the resulting lithiated binaphthyl with methanol-*d* gave 89% yield of the borane complex of D-MOP **13a** whose enantiomeric purity is >99% ee (Scheme 4). The retention of the axial chirality of the binaphthyl skeleton is ascribed to the coordination of the diphenylphosphino group to borane, which retards the intramolecular attack of the naphthyllithium on the neighboring phosphorus atom in **14** forming a phosphacyclopentadiene derivative. The borane in **13a** was readily removed[19] by treatment with diethylamine to give enantiomerically pure D-MOP (**9a**).

The present reaction of borane complex **3** opens a new route to the preparation of 2′-substituted MOP ligands starting from BINAP. The reaction of the lithiated binaphthyl **14**, generated by the lithiation of **3**, with iodine and chlorotrimethylstannane gave, after removal of borane, enantiomerically pure (>99% ee) 2-diphenylphosphino-1,1′-binaphthyls **9b** and **9c**, which contain an iodo and a trimethylstannyl group, respectively, at the 2′-position (entries 2 and 3 in Table 1). Unfortunately, less reactive electrophiles cannot be used in the present reaction. For example, the reaction with chlorotrimethylsilane is very slow at −78 °C giving only a low yield of 2′-trimethylsilyl binaphthyl **9e** (entry 5), though the reaction with chlorodimethylhydrosilane gave a higher yield of the corresponding silylation product **9d** (entry 4). The reaction with chlorotrimethylsilane at higher temperatures was accompanied by racemization to some extent (entry 6), indicating that the retention of the enantiomeric purity is realized only at the low temperature even with the borane complex **3**.

In summary, we have found that the carbon−phosphorus bond cleavage takes place selectively between the binaphthyl and diphenylphosphinyl group in the reaction of phosphine monoxide and dioxide of BINAP with *n*-butyllithium and the enantiomeric purity of the binaphthyl axial chirality is retained in the reaction of the borane complex of BINAP monoxide. The reaction of the lithiated binaphthyl with electrophiles provides a new method for the introduction of new substituents at the 2′-position of MOP ligands. The MOP derivatives substituted with an iodo and a stannyl group obtained here are useful intermediates for further transformation into new MOP ligands, for example, by palladium- or nickel-catalyzed cross-coupling-type reactions.[20]

Table 1. Preparation of New MOP Derivatives from a Borane Complex of BINAP Monoxide[a]

entry	electrophile	yield[b] (%) of **13**	% ee[c]	$[\alpha]_D^{20}$ of **9** (*c* in $CHCl_3$)
1[d]	MeOD	89 (**13a**)	>99	−100.0 (0.76)
2	I_2	57 (**13b**)	>99	−52.5 (0.96)
3	$ClSnMe_3$	69 (**13c**)	>99	−21.0 (1.01)
4	$ClSiMe_2H$	59 (**13d**)	>99	−39.8 (1.00)
5	$ClSiMe_3$	14 (**13e**)	96	−25.2 (0.66)
6[e]	$ClSiMe_3$	43 (**13e**)	77	

[a] Lithiation was carried out on a 0.10 mmol reaction scale with 4 equiv of *n*-butyllithium in THF at −78 °C for 3 h. An electrophile (11 equiv) was added at −78 °C, and the mixture was kept stirring at −78 °C for 1 h. After the reaction was quenched with methanol at −78 °C, the mixture was warmed to room temperature. [b] Isolated yield. [c] Determined by HPLC analysis of phosphine oxide, obtained by removal of borane in **13** followed by oxidation (see Experimental Section), with chiral stationary phase columns: Daicel Chiralcel OD-H (hexane/2-propanol = 90/10 (entries 1−3) and hexane/2-propanol = 98/2 (entry 4)), and AD (hexane/2-propanol = 90/10 (entries 5 and 6)). [d] As an electrophile, methanol-*d* (25 equiv) was added at −78 °C, and the mixture was warmed to room temperature after it was stirred at −78 °C for 1 h. [e] After the addition of chlorotrimethylsilane as an electrophile at −78 °C, the mixture was immediately warmed to room temperature.

Experimental Section

General. All moisture sensitive manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. Optical rotations were recorded with a JASCO DIP-370 polarimeter. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (500 MHz for ^1H, 76.5 MHz for ^2H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P in $CDCl_3$). Chemical shifts are reported in δ parts per million referenced to an internal $SiMe_4$ standard for ^1H NMR, chloroform-*d* (δ 7.26) for ^2H NMR, chloroform-*d* (δ 77.0) for ^{13}C NMR, and an external 85% H_3PO_4 for ^{31}P NMR. High-resolution mass spectroscopy (HRMS) was recorded with a JEOL JMS−HX110 spectrometer.

Materials. Tetrahydrofuran was distilled from benzophenone-ketyl under nitrogen prior to use. BINAP[21] and BINAP monoxide[15c] were prepared according to the reported procedures.

Preparation of (*S*)-2,2′-Bis(diphenylphosphinyl)-1,1′-binaphthyl (BINAP Dioxide, 1). To a solution of BINAP (3.11 g, 5.00 mmol) in 150 mL of acetone was added 35% H_2O_2*aq* (10 mL, 103 mmol) at room temperature. The mixture was stirred at room temperature for 11 h, and a small amount of manganese(IV) oxide was added. The suspension was stirred at room temperature for 15 min, before it was filtered and evaporated. The residue was dissolved in chloroform and washed with saturated $NaHCO_3$ solution. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The crude product was purified by silica gel column chromatography

(19) (a) Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301. (b) Oba, G.; Phok, S.; Manuel, G.; Koenig, M. *Tetrahedron*. **2000**, *56*, 121.

(20) (a) Klunder, J. M.; Posner, G. In *Catalytic Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, Part 1.5, p 227. (b) Farina, V. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12, p 161. (c) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (d) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (e) Ogasawara, M.; Hayashi, T. In *Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; VCH Publishers: New York, 2000; Chapter 8F.

(21) Cai, D.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *J. Org. Chem.* **1994**, *59*, 7180.

(acetone) to give BINAP dioxide[13] (3.02 g, 92%): $[\alpha]^{25}_D$ −388 (*c* 0.53, benzene).

Preparation of (*S*)-2′-Boranatodiphenylphosphino-2-diphenylphosphinyl-1,1′-binaphthyl (3). To a solution of BINAP monoxide (919 mg, 1.44 mmol) in 20 mL of THF was added borane-THF (2.16 mmol) at room temperature. After the mixture was stirred at room temperature for 2 h, it was diluted with ethyl acetate and washed with brine. The organic phase was dried over anhydrous $MgSO_4$ and evaporated to give BINAP monoxide borane (917 mg, 98%): $[\alpha]^{20}_D$ −141.9 (*c* 1.00, chloroform); ^{1}H NMR ($CDCl_3$) δ 6.38 (d, J = 8.5 Hz, 1H), 6.45 (t, J = 7.6 Hz, 1H), 6.81−6.85 (m, 2H), 7.12 (dt, J = 7.6, 2.9 Hz, 2H), 7.16−7.30 (m, 9H), 7.36−7.47 (m, 6H), 7.55−7.63 (m, 5H), 7.73−7.77 (m, 3H), 7.82 (d, J = 8.3 Hz, 1H), 7.85 (dd, J = 8.7, 2.4, 1H), 7.88 (d, J = 9.4, 1H); ^{31}P{^{1}H} NMR δ 22.8 (br s), 27.8 (s); HRMS (FAB) calcd for $C_{44}H_{34}OP_2B$ $(M - H)^+$ 651.2186, found 651.2180.

Reaction of (*S*)-2,2′-Bis(diphenylphosphinyl)-1,1′-binaphthyl (1) with *n*-Butyllithium. To a solution of BINAP dioxide (**1**) (66 mg, 0.10 mmol) in 1.0 mL of THF was added dropwise a solution of *n*-butyllithium in hexane (0.25 mL, 0.40 mmol) at −78 °C. The mixture was stirred at −78 °C for 3 h, and MeOD (0.10 mL, 2.5 mmol) was added. The mixture was kept stirring at −78 °C for 1 h, allowed to reach room temperature, diluted with ether, and washed with brine. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The residue was chromatographed on silica gel (benzene/ethyl acetate = 1/1) to give 21 mg (46%) of (*R*)-2′-deuterio-2-diphenylphosphinyl-1,1′-binaphthyl (**4a**), 14 mg (56%) of 1-deuteriobutyldiphenylphoshine oxide (**5**), and 1 mg (4%) of 2,2′-dideuterio-1,1′-binaphthyl[22] (**6**). **(*R*)-2′-Deuterio-2-diphenylphosphinyl-1,1′-binaphthyl (4a):** ^{1}H NMR ($CDCl_3$) δ 6.89 (d, J = 8.4 Hz, 1H), 6.93 (dt, J = 7.6, 2.9 Hz, 2H), 7.04−7.07 (m, 2H), 7.12 (d, J = 8.5 Hz, 1H), 7.17−7.35 (m, 8H), 7.50−7.54 (m, 3H), 7.59 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.84 (dd, J = 11.7, 8.6 Hz, 1H), 7.93 (d, J = 8.2, 1H), 7.98 (dd, J = 8.6, 1.9 Hz, 1H); ^{2}H NMR ($CHCl_3$) δ 7.50; ^{31}P-{^{1}H} NMR δ 28.5 (s); HRMS (FAB) calcd for $C_{32}DH_{23}OP$ $(M + H)^+$ 456.1628, found 456.1628. The enantiomeric purity of **4a** was determined to be 75% by HPLC analysis with Chiralcel OD-H (hexane/2-propanol = 90/10). **1-Deuteriobutyl(diphenyl)phosphine Oxide (5):** ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H), 1.42 (sextet, J = 7.4 Hz, 2H), 1.60 (dq, J = 9.5, 7.4 Hz, 1H), 2.25 (dd, J = 10.9, 8.6 Hz, 1H), 7.45−7.52 (m, 6H), 7.74 (dd, J = 11.8, 11.4 Hz, 4H); ^{2}H NMR ($CHCl_3$) δ 2.25; ^{31}P-{^{1}H} NMR δ 33.2 (s). **2,2′-Dideuterio-1,1′-binaphthyl (6):** ^{1}H NMR ($CDCl_3$) δ 7.29 (d, J = 7.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.48 (m, 4H), 7.60 (t, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.1 Hz, 2H); ^{2}H NMR ($CHCl_3$) δ 7.54.

Reaction of (*S*)-2′-Diphenylphosphino-2-diphenylphosphinyl-1,1′-binaphthyl (2) with *n*-Butyllithium: (a) Methanol-*d* as an Electrophile. To a solution of BINAP monoxide (**2**) (64 mg, 0.10 mmol) in 1.0 mL of THF was added dropwise a solution of *n*-butyllithium in hexane (0.27 mL, 0.41 mmol) at −78 °C. The mixture was stirred at −78 °C for 3 h, and MeOD (50 μL, 1.2 mmol) was added. The mixture was brought to room temperature, diluted with ether, and washed with brine. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The residue was chromatographed on silica gel (benzene/ethyl acetate = 1/1) to give 39 mg (87%) of 2′-deuterio-2-diphenylphosphino-1,1′-binaphthyl (**9a**). This sample was determined to be racemic by HPLC analysis of oxide **4a** with Chiralcel OD-H (hexane/2-propanol = 90/10). **2′-Deuterio-2-diphenylphosphino-1,1′-binaphthyl (9a):** ^{1}H NMR ($CDCl_3$) δ 7.10−7.25 (m, 11H), 7.26−7.31 (m, 3H), 7.34 (dd, J = 8.5, 2.8 Hz, 1H), 7.39−7.48 (m, 3H), 7.85 (d, J = 8.6 Hz, 1H), 7.88 (t, J = 8.3 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H); ^{2}H NMR ($CHCl_3$) δ 7.24; ^{31}P{^{1}H} NMR δ −13.4 (s); HRMS (FAB) calcd for $C_{32}DH_{22}P$ $(M)^+$ 439.1600, found 439.1595. Anal. Calcd for $C_{32}DH_{22}P$: C, 87.45; H + D, 5.50. Found: C, 87.25; H + D, 5.78.

(b) Chlorotrimethylsilane as an Electrophile: The same procedure described above for treatment of **2** with *n*-butyllithium was carried out to generate 2′-lithiated MOP **11**. To the reaction mixture containing **11** was added chlorotrimethylsilane (81 mg, 0.75 mmol) at −78 °C, and the mixture was allowed to reach room temperature. The mixture was stirred for 1 h before it was diluted with ether and washed with brine. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The residue was chromatographed on silica gel (benzene/hexane = 1/1) to give 21 mg (57% yield) of 7-phenyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole[18] (**10**): ^{1}H NMR ($CDCl_3$) δ 7.21 (t, J = 7.2 Hz, 2H), 7.26−7.34 (m, 3H), 7.50 (t, J = 8.2 Hz, 2H), 7.55 (t, J = 7.8 Hz, 2H), 7.78−7.83 (m, 2H), 7.87 (dd, J = 8.1, 2.6 Hz, 2H), 7.96 (d, J = 7.9 Hz, 2H), 8.47 (d, J = 8.4 Hz, 2H); ^{31}P{^{1}H} NMR δ −4.17 (s).

Reaction of (*S*)-2-Boranatodiphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthyl (3) with *n*-Butyllithium. The results are summarized in Table 1. Procedures are given for the preparation of **(*R*)-2-boranatodiphenylphosphino-2′-deuterio-1,1′-binaphthyl (13a)** and **(*S*)-2′-boranatodiphenylphosphino-2-trimethylstannyl-1,1′-binaphthyl (13c)** (entries 1 and 3 in Table 1). To a solution of BINAP monoxide−borane (**3**) (65 mg, 0.10 mmol) in 2.5 mL of THF was added dropwise a solution of *n*-butyllithium in hexane (0.25 mL, 0.40 mmol) at −78 °C. The mixture was stirred at −78 °C for 3 h, and MeOD (0.10 mL, 2.5 mmol) was added. The mixture was kept stirring at −78 °C for 1 h and allowed to reach room temperature, diluted with ether, and washed with brine. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The residue was chromatographed on silica gel (benzene/hexane = 1/1) to give 40 mg (89% yield) of (*R*)-2-boranatodiphenylphosphino-2′-deuterio-1,1′-binaphthyl (**13a**). **(*R*)-2-Boranatodiphenylphosphino-2′-deuterio-1,1′-binaphthyl (13a):** $[\alpha]^{20}_D$ −41.9 (*c* 1.00, chloroform); ^{1}H NMR ($CDCl_3$) δ 6.97 (d, J = 8.1 Hz, 1H), 7.02−7.26 (m, 10H), 7.28−7.33 (m, 3H), 7.39 (d, J = 10.7 Hz, 1H), 7.41 (d, J = 10.9 Hz, 1H), 7.52 (t, J = 7.0 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H), 7.66 (t, J = 8.2 Hz, 1H), 7.74 (dd, J = 10.7, 8.7 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H); ^{2}H NMR ($CHCl_3$) δ 7.20; ^{31}P{^{1}H} NMR δ 23.0 (br s). Anal. Calcd for $C_{32}DH_{25}PB$: C, 84.78; H + D, 6.00. Found: C, 84.54; H + D, 6.00. **(*S*)-2′-Boranatodiphenylphosphino-2-trimethylstannyl-1,1′-binaphthyl (13c).** A procedure identical to that described above for treatment of **3** with *n*-butyllithium was carried out to generate 2′-lithiated borane complex **14**. To the reaction mixture containing **14** was added chlorotrimethylstannane (221 mg, 1.1 mmol) as an electrophile at −78 °C, and the mixture was kept stirring at −78 °C for 1 h. After the reaction was quenched with methanol (0.10 mL, 2.5 mmol) at −78 °C, the mixture was warmed to room temperature, diluted with ether, and washed with brine. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The residue was chromatographed on silica gel (benzene/hexane = 1/1) to give 42 mg (69% yield) of (*S*)-2′-boranatodiphenylphosphino-2-trimethylstannyl-1,1′-binaphthyl (**13c**). In a similar manner, borane complexes **13b**, **d**, and **e** were prepared from **3**. **(*S*)-2′-Boranatodiphenylphosphino-2-trimethylstannyl-1,1′-binaphthyl (13c):** $[\alpha]_D^{20}$ +15.0 (*c* 0.84, chloroform); ^{1}H NMR ($CDCl_3$) δ −0.24 (s, 9H, J (Sn−CH_3 = 54.8 Hz)), 6.60 (d, J = 8.3 Hz, 1H), 6.67 (dd, J = 8.3, 7.8 Hz, 1H), 6.92 (dt, J = 7.8, 2.2 Hz, 2H), 7.07−7.16 (m, 4H), 7.19 (d, J = 8.5 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.35 (dt, J = 7.4 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.49−7.59 (m, 5H), 7.63 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H); ^{31}P{^{1}H} NMR δ 21.7 (br s); ^{13}C NMR ($CDCl_3$) δ −8.39 (J (^{119}Sn−CH_3) = 348.8 Hz, J (^{117}Sn−CH_3) = 333.3 Hz); HRMS (FAB) calcd for $C_{32}H_{23}PB$ $(M - SnMe_3 - 2H)^+$ 449.1636, found 449.1634. **(*S*)-2′-Boranatodiphenylphosphino-2-iodo-1,1′-binaphthyl (13b):** $[\alpha]^{20}_D$ −175.3 (*c* 1.00, chloroform); ^{1}H NMR ($CDCl_3$) δ 6.93 (d, J = 8.5 Hz, 1H), 7.02−7.07 (m, 2H), 7.09 (dt, J = 7.8, 2.4 Hz, 2H), 7.22−7.25 (m, 3H), 7.28−7.32 (m, 3H), 7.35−7.41 (m, 3H), 7.51−7.56 (m, 3H), 7.67 (dd, J = 10.1, 9.0 Hz, 1H), 7.70−7.73 (m, 2H), 7.93 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H); ^{31}P{^{1}H} NMR δ 23.7 (br s); HRMS (FAB) calcd for $C_{32}H_{23}PI$ $(M - BH_3 + H)^+$ 565.0582, found 565.0586.

(22) (a) Forrest, J. *J. Chem. Soc.* **1960**, 566. (b) Hennings, D. D.; Iwama, T.; Rawal, V. H. *Org. Lett.* **1999**, *1*, 1205.

(*S*)-2′-Boranatodiphenylphosphino-2-dimethylsilyl-1,1′-binaphthyl (13d): $[\alpha]^{20}_D$ −47.4 (*c* 0.70, chloroform); ^{1}H NMR ($CDCl_3$) δ −0.34 (d, J = 3.7, 3H), 0.20 (d, J = 3.7 Hz, 3H), 3.80 (septet, J = 3.7 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 6.84 (dd, J = 8.0, 7.2 Hz, 1H), 7.05−7.09 (m, 3H), 7.21−7.29 (m, 7H), 7.33−7.39 (m, 3H), 7.51 (dd, J = 7.7, 7.2 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.61 (t, J = 9.2 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H); ^{31}P{^{1}H} NMR δ 22.8 (br s); ^{13}C NMR ($CDCl_3$) δ −3.73 (Si−*C*H$_3$), −2.67 (Si−*C*H$_3$); HRMS (FAB) calcd for $C_{32}H_{23}PB$ (M − $SiMe_2H$ − 2H)$^+$ 449.1636, found 449.1634. **(*S*)-2-Boranatodiphenylphosphino-2′-trimethylsilyl-1,1′-binaphthyl (13e):** $[\alpha]^{20}_D$ −8.2 (*c* 1.00, chloroform) for **(*S*)-13e** of 96% ee; ^{1}H NMR ($CDCl_3$) δ −0.18 (s, 9H), 6.58 (d, J = 8.4 Hz, 1H), 6.64 (t, J = 7.6 Hz, 1H), 6.95 (dt, J = 7.5, 2.2 Hz, 2H), 7.09 (dd, J = 10.8, 8.3 Hz, 2H), 7.14−7.19 (m, 3H), 7.26 (m, 1H), 7.36 (m, 2H), 7.43 (t, J = 7.3 Hz, 1H), 7.47−7.54 (m, 3H), 7.58 (t, J = 9.4 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.92 (t, J = 8.7 Hz, 2H); ^{31}P{^{1}H} NMR δ 22.6 (br s); ^{13}C NMR ($CDCl_3$) δ +0.01 (Si−*C*H$_3$); HRMS (FAB) calcd for $C_{32}H_{23}PB$ (M − $SiMe_3$ − 2H)$^+$ 449.1636, found 449.1634.

Removal of Borane from 2′-Substituted Boranatodiphenylphosphino-1,1′-binaphthyls (13). A typical procedure is given for the preparation of **(*R*)-2′-deuterio-2-diphenylphosphino-1,1′-binaphthyl (9a).** To a solution of borane complex **13a** (74 mg, 0.16 mmol) in 5.0 mL of THF was added diethylamine (0.17 mL, 1.7 mmol) at room temperature, and the mixture was kept stirring at 40 °C for 1 h. Evaporation followed by silica gel preparative thin-layer chromatography (benzene/hexane = 1/1) of the residue gave 65.1 mg (91% yield) of **9a**: $[\alpha]^{20}_D$ −100.0 (*c* 0.76, chloroform).

In a similar manner, treatment of the borane complex **13b**−**e** with 10 equiv of diethylamine in THF gave a high yield of the corresponding phosphines **9b**−**e**. **(*S*)-2′-Diphenylphosphino-2-iodo-1,1′-binaphthyl (9b):** $[\alpha]^{20}_D$ −52.5 (*c* 0.96, chloroform); ^{1}H NMR ($CDCl_3$) δ 6.70 (d, J = 8.4 Hz, 1H), 6.83 (t, J = 7.3 Hz, 1H), 7.01 (t, J = 7.4 Hz, 2H), 7.07−7.13 (m, 3H), 7.19 (t, J = 7.3 Hz, 1H), 7.27−7.33 (m, 7H), 7.47−7.51 (m, 2H), 7.68 (d, J = 8.7 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.91 (t, J = 8.6 Hz, 2H), 8.06 (d, J = 8.6 Hz, 1H); ^{31}P{^{1}H} NMR δ −13.0 (s); HRMS (FAB) calcd for $C_{32}H_{23}PI$ (M + H)$^+$ 565.0582, found 565.0583. Anal. Calcd for $C_{32}H_{22}PI$: C, 68.10; H, 3.93. Found: C, 68.21; H, 3.75. **(*S*)-2′-Diphenylphosphino-2-trimethylstannyl-1,1′-binaphthyl (9c):** $[\alpha]^{20}_D$ −21.0 (*c* 1.01, chloroform); ^{1}H NMR ($CDCl_3$) δ −0.40 (s, 9H, J (^{119}Sn−CH_3) = 55.6 Hz, J (^{117}Sn−CH_3) = 54.7 Hz)), 6.77 (d, J = 8.2 Hz, 1H), 6.84 (dd, J = 8.3, 6.7 Hz, 1H), 6.98 (t, J = 7.3 Hz, 2H), 7.06 (t, J = 7.5 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.23−7.28 (m, 8H), 7.46 (ddd, J = 8.0, 5.1, 2.5 Hz, 1H), 7.54 (dd, J = 8.5, 2.7 Hz, 1H), 7.74 (d, J = 6.7 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.87−7.93 (m, 3H); ^{31}P{^{1}H} NMR δ −14.8 (s); ^{13}C NMR ($CDCl_3$) δ −8.79 (J (^{119}Sn−*C*H$_3$) = 347.1 Hz, J (^{117}Sn−*C*H$_3$) = 330.6 Hz). Anal. Calcd for $C_{35}H_{31}PSn$: C, 69.91; H, 5.20. Found: C, 70.19; H, 5.39. **(*S*)-2-Diphenylphosphino-2′-dimethylsilyl-1,1′-binaphthyl (9d):** $[\alpha]^{20}_D$ −39.8 (*c* 1.00, chloroform); ^{1}H NMR ($CDCl_3$) δ −0.28 (d, J = 3.7, 3H), −0.03 (d, J = 3.7, 3H), 3.73 (septet, J = 3.7 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 6.87 (t, J = 8.6 Hz, 1H), 6.97 (t, J = 7.6 Hz, 2H), 7.07 (t, J = 7.3 Hz, 2H), 7.14−7.19 (m, 2H), 7.21−7.32 (m, 7H), 7.44−7.50 (m, 2H), 7.73 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H); ^{31}P{^{1}H} NMR δ −14.8 (s); ^{13}C NMR ($CDCl_3$) δ −3.86 (Si−*C*H$_3$), −3.00 (Si−*C*H$_3$); HRMS (FAB) calcd for $C_{34}H_{30}PSi$ (M + H)$^+$ 497.1854, found 497.1853. Anal. Calcd for $C_{34}H_{29}PSi$: C, 82.22; H, 5.89. Found: C, 82.03; H, 6.01. **(*S*)-2-Diphenylphosphino-2′-trimethylsilyl-1,1′-binaphthyl (9e):** $[\alpha]^{20}_D$ −25.2 (*c* 0.66, chloroform) for **(*S*)-9e** of 96% ee; ^{1}H NMR ($CDCl_3$) δ −0.30 (s, 9H), 6.65 (d, J = 8.4 Hz, 1H), 6.74 (t, J = 8.4 Hz, 1H), 6.94 (d, J = 7.7 Hz, 2H), 7.05 (t, J = 7.0 Hz, 2H), 7.03−7.06 (m, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.21−7.29 (m, 8H), 7.45−7.48 (m, 1H), 7.53 (dd, J = 8.6, 2.6 Hz, 1H), 7.78−7.80 (m, 2H), 7.88 (t, J = 8.3 Hz, 2H), 7.94 (d, J = 8.3 Hz, 1H); ^{31}P{^{1}H} NMR δ (s) −15.3 (s); ^{13}C NMR ($CDCl_3$) δ −0.02 (Si−*C*H$_3$); HRMS (FAB) calcd for $C_{35}H_{32}SiP$ (M + H)$^+$ 511.2011, found 511.2012. Anal. Calcd for $C_{35}H_{31}PSi$: C, 83.32; H, 6.12. Found: C, 81.83; H, 6.43.

Oxidation of 2′-Substituted 2-Diphenylphosphino-1,1′-binaphthyls (9) with *m*CPBA for the Determination of Enantiomeric Purity. A typical procedure is given for the preparation of **(*S*)-2′-Diphenylphosphinyl-2-iodo-1,1′-binaphthyl (4b).** To a solution of **9b** (36 mg, 0.063 mmol) in 2.0 mL of CH_2Cl_2 were added $NaHCO_3$ (9.6 mg, 0.11 mmol) and *m*CPBA (17 mg, 0.096 mmol). The suspension was stirred at room temperature for 2 h and concentrated in vacuo. The residue was dissolved in ethyl acetate and washed with saturated $NaHCO_3$ solution. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The crude product was purified by silica gel preparative thin-layer chromatography (hexane/ethyl acetate = 1/1) to give 31 mg (85% yield) of **4b**: ^{1}H NMR ($CDCl_3$) δ 6.97 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 7.09 (d, J = 8.5 Hz, 1H), 7.15 (dt, J = 7.7, 2.9 Hz, 2H), 7.20 (dt, J = 7.7, 2.9 Hz, 2H), 7.27−7.36 (m, 4H), 7.39−7.49 (m, 5H), 7.55 (t, J = 8.0 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.77 (dd, J = 11.5, 8.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.7 Hz, 1H); ^{31}P{^{1}H} NMR δ 28.3 (s); HRMS (FAB) calcd for $C_{32}H_{23}OPI$ (M + H)$^+$ 581.0531, found 581.0533; $[\alpha]^{20}_D$ −110.1 (*c* 1.04, chloroform). The enantiomeric purity of **4b** was determined to be >99% by HPLC analysis with Chiralcel OD-H (hexane/2-propanol = 90/10).

In a similar manner, phosphines **9a**, **c**, and **e** were oxidized into the corresponding phosphine oxides **4a**, **c**, and **e**. In the reaction of **9d**, the hydrosilyl group was oxidized into hydroxysilyl during the oxidation of phosphine. The method for the determination of enantiomeric purity is shown in footnote c of Table 1. **(*R*)-4a**: (>99% ee), $[\alpha]^{20}_D$ −16.8 (*c* 1.00, chloroform). **(*S*)-2′-Diphenylphosphinyl-2-trimethylstannyl-1,1′-binaphthyl (4c):** (>99% ee), $[\alpha]^{20}_D$ +82.7 (*c* 1.00, chloroform); ^{1}H NMR ($CDCl_3$) δ −0.22 (s, 9H, J (Sn−CH_3) = 54.4 Hz)), 6.73−6.76 (m, 3H), 6.92 (t, J = 8.1 Hz, 2H), 7.06 (dd, J = 12.0, 8.1 Hz, 2H), 7.16−7.20 (m, 2H), 7.25 (t, J = 7.6 Hz, 1H), 7.37−7.40 (dt, J = 7.5, 2.1 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 7.52−7.58 (m, 4H), 7.64 (dd, 11.7, 8.7 Hz, 1H), 7.72−7.74 (m, 2H), 7.91−7.93 (m, 2H); ^{31}P{^{1}H} NMR δ 26.8 (s); ^{13}C NMR ($CDCl_3$) δ −7.96 (J (^{119}Sn−*C*H$_3$) = 351.8 Hz, J (^{117}Sn−*C*H$_3$) = 336.4 Hz). Anal. Calcd for $C_{35}H_{31}OPSn$: C, 68.10; H, 5.06. Found: C, 68.40; H, 5.36. **(*S*)-2-Diphenylphosphinyl-2′-dimethylhydroxysilyl-1,1′-binaphthyl (4d):** (>99% ee), $[\alpha]_D^{20}$ +33.5 (*c* 0.67, chloroform); ^{1}H NMR ($CDCl_3$) δ −0.85 (s, 3H), 0.46 (s, 3H), 6.63 (d, J = 8.6 Hz, 1H), 6.68 (dt, J = 7.7, 3.1 Hz, 2H), 6.85 (t, J = 8.1 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 7.03 (dd, J = 12.3, 7.1 Hz, 2H), 7.09 (d, J = 8.6 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.23 (t, J = 8.3 Hz, 1H), 7.47−7.54 (m, 6H), 7.66 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.85 (dd, J = 11.4, 7.0 Hz, 2H), 7.91 (d, J = 8.3 Hz, 1H), 7.94 (dd, J = 8.8, 2.2 Hz, 1H); ^{31}P{^{1}H} NMR δ 30.2 (s); ^{13}C NMR ($CDCl_3$) δ 0.26 (Si−*C*H$_3$), 0.92 (Si−*C*H$_3$); HRMS (FAB) calcd for $C_{34}H_{30}O_2PSi$ (M + H)$^+$ 529.1753, found 529.1747. **(*S*)-2-Diphenylphosphinyl-2′-trimethylsilyl-1,1′-binaphthyl (4e):** 96% ee; $[\alpha]^{20}_D$ +45.6 (*c* 1.00, chloroform); ^{1}H NMR ($CDCl_3$) δ −0.17 (s, 9H), 6.74−6.78 (m, 3H), 6.90 (t, J = 7.7 Hz, 1H), 6.95 (t, J = 7.7 Hz, 1H), 7.02 (dd, J = 12.1, 7.9 Hz, 2H), 7.14 (d, J = 8.7 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.40 (ddd, J = 7.9, 7.4, 2.7 Hz, 2H), 7.47 (t, J = 8.0 Hz, 1H), 7.53 (dd, J = 7.7, 7.1 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.61 (s, 2H), 7.67 (dd, J = 11.7, 8.8 Hz, 1H), 7.72 (dd, J = 11.3, 7.7 Hz, 2H), 7.91 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.7, 2.1 Hz, 1H); ^{31}P-{^{1}H} NMR δ 27.1 (s); ^{13}C NMR ($CDCl_3$) δ −0.05 (Si−*C*H$_3$); HRMS (FAB) calcd for $C_{35}H_{32}OPSi$ (M + H)$^+$ 527.1960, found 527.1964.

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