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Facile Preparation of a New BINAP-Based Building Block, 5,5′-DiiodoBINAP, and Its Synthetic Application

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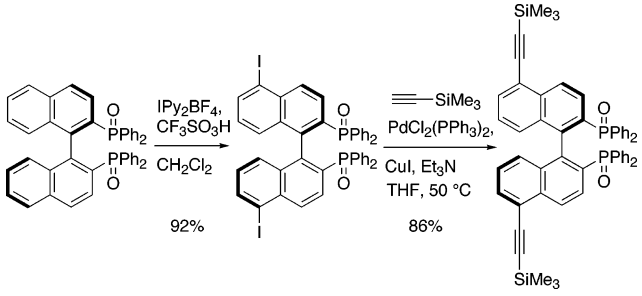

Bis(pyridine)iodonium tetrafluoroborate was successfully used for regioselective iodination of BINAP dioxide to give 5,5′-diiodoBINAP dioxide in an excellent yield of 92%, with no observed formation of 4,4′-diiodoBINAP dioxide. A Sonogashira cross-coupling reaction with 5,5′-diiodoBINAP dioxide gave the desired bis(trimethylsilylethynyl) product in 86% yield. The resulting 5,5′-disubstituted BINAP dioxides were reduced to the corresponding phosphines, which were used as chiral ligands for rhodium-catalyzed asymmetric 1,4-addition of phenylboronic acid to 2-cyclohexenone to give 3-phenylcyclohexanone in excellent yield with high enantioselectivity.

One of the most useful chiral phosphine ligands is 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP),[1] which exhibits high enantioselectivity in several types of asymmetric reactions including ruthenium-catalyzed hydrogenation[2] and rhodium-catalyzed 1,4-addition and its related reactions.[3] Over the past decade, there have been major efforts to prepare BINAP derivatives for recycling catalytic systems and achieving higher selectivity in asymmetric synthesis.[4] Most of these BINAP derivatives have been prepared in several steps starting from 6- or 6,6′-substituted 1,1′-bi-2-naphthol.[4,5] However, these derivatizations are inferior to direct functionalization of BINAP due to their low yields and associated handling losses. Direct nitration at the 5,5′-positions of BINAP dioxide,[6] followed by reduction to 5,5′-diamino-BINAP, was reported in 1987.[7] The 5,5′-diamino-BINAP was for the first time used by Chan et al. for preparation of soluble polymer-supported catalysts for asymmetric hydrogenation.[8] Recently, Köckritz et al. have reported regioselective bromination at the 4,4′-positions of BINAP dioxide and Lemaire et al. have reported bromination at the 5,5′-positions of BINAP dioxide in the presence of iron.[9] Although Lemaire et al. transformed bromo atoms at the 5,5′-positions of BINAP dioxide to perfluoroalkyl or cyano groups, transition metal-catalyzed cross-coupling reactions at the 5,5′-positions have not been reported. It is well-known that arylbromide is less reactive than aryliodide toward transition metal-catalyzed cross-coupling.[10] To our knowledge, the preparation of 4,4′-diphenyl-BINAP by Suzuki coupling is the only cross-coupling reaction of this type that has been reported in the literature.[11] Here we report a new facile regioselective iodination at the 5,5′-position of BINAP and subsequent Sonogashira coupling reaction leading to the ethynyl-BINAP, which is useful as a chiral ligand for a rhodium-catalyzed asymmetric 1,4-additon.

First, we attempted to direct iodination of BINAP dioxide[6] with iodine monochloride[12] and with *N*-iodosuccinimide in the presence of trifluoroacetic acid.[13] However, in both cases no iodination reaction occurred and the starting materials were recovered unchanged. More

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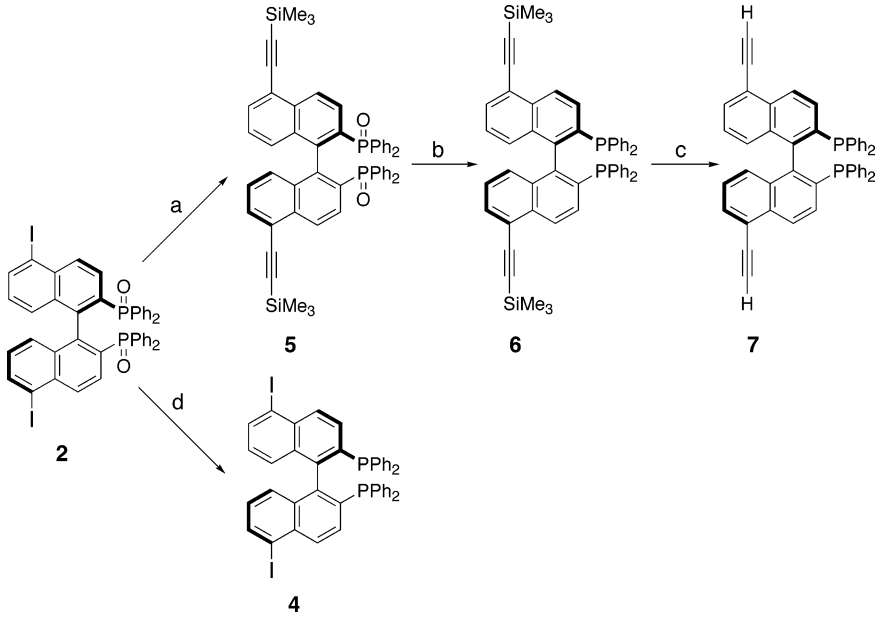
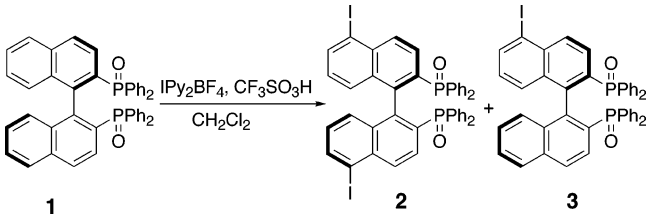
SCHEME 1[a]



[a] Reaction conditions: (a) trimethylsilylacetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 50 °C, 86%; (b) MeOTf, $LiAlH_4$, cyclopentylmethyl ether, room temperature, 82%; (c) TBAF, THF, room temperature, 98%; (d) trichlorosilane, toluene, reflux, 92%.

reactive iodination reagents were required to obtain iodinated BINAP dioxide. We found that the use of bis(pyridine)iodonium tetrafluoroborate (IPy_2BF_4)[14] gives the corresponding diiodoBINAP dioxide in excellent yield. IPy_2BF_4, which was developed by Barluenga,[14] is a powerful and highly selective iodination reagent under mild conditions. Iodination of (*R*)-2,2′-bis(diphenylphosphinyl)-1,1′-binaphthyl (**1**) with 3 equiv of IPy_2BF_4 in CH_2Cl_2 at 25 °C for 20 h gave (*R*)-2,2′-bis(diphenylphosphinyl)-5,5′-diiodo-1,1′-binaphthyl (**2**), with high regioselectivity, in 92% yield, with no observed formation of the 4,4′-diiodo product (entry 2).[15] The use of 2 equiv of IPy_2BF_4 under the same reaction conditions afforded a reaction mixture consisting of (*R*)-2,2′-bis(diphenylphosphinyl)-5-iodo-1,1′-binaphthyl (**3**) and **2** in a ratio of 35/64 together with **1** (1%) (entry 1). Although a decrease to 1 equiv of IPy_2BF_4 produced **3** preferentially (46%), a halved amount of starting material was unreactive (entry 3). Carrying out the reaction at −30 °C for 40 h in the presence of 2 equiv of IPy_2BF_4 increased selectivity, resulting in a ratio of 49/7 for **3** and **2**, and increasing the reaction time to 80 h afforded **3** and **2** in a ratio of 56/37 (entry 4 and 5). After purification by silica gel chromatography, monoiodoBINAP dioxide was isolated, albeit in 15% yield because of difficulty in separating the monoiodo product from starting material **1**. In this work, iodination of BINAP dioxide with use of IPy_2BF_4 is shown to be a simple method for obtaining the diiodo product **2**

TABLE 1. Direct Iodination of BINAP Dioxide 1



entry	IPy_2BF_4 (equiv)	temp (°C)	time (h)	recovery or yields (%)[a] 1	2	3	yield (%)
1	2.0	25	20	1	64	35	
2	3.0	25	20	0	100	0	92[b]
3	1.0	25	20	49	5	46	
4	2.0	−30	40	44	7	49	
5	2.0	−30	80	7	37	56	15[c]

[a] Determined by NMR analysis. [b] Isolated yield of **2**. [c] Isolated yield of **3**.

in excellent yield,[16] compared to the corresponding bromination procedure, which generates a mixture of mono- and dibromo products.[9] Furthermore, the higher reactivity of aryl iodide in transition metal-catalyzed coupling reactions, which is known as the order of PhI ≫ PhOTf > PhBr,[10] is to expected to facilitate preparation for new functionalized BINAPs starting from **2**.

To clarify the availability of diiodoBINAP dioxide as a building block, we examined the Sonogashira coupling reaction of **2** with trimethylsilylacetylene. As expected, the reaction proceeded smoothly under the general Sonogashira reaction conditions[17] to give the corresponding (*R*)-2,2′-bis(diphenylphosphinyl)-5,5′-bis(trimethylsilylethynyl)-1,1′-binaphthyl (**5**) in 86% yield (Scheme 1). Reduction of diphenylphosphinyl groups in **5** was carried

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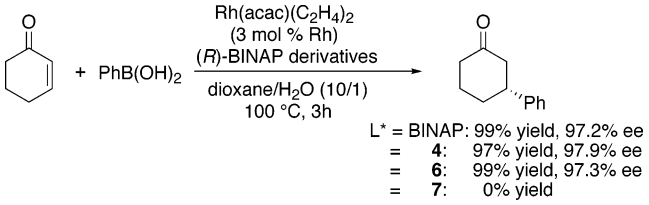
(15) The position of the diiodo in BINAP dioxide was determined by the 2D ^1H NMR spectrum of **2** and previously reported ^1H NMR data of both BINAP dioxide[6] and brominated BINAP dioxides[9] (see the Supporting Information).

(16) Direct iodination of BINAP with 10 equiv of IPy_2BF_4 at 25 °C for 20 h gave 5,5′-diiodoBINAP dioxide **2** with several unidentified byproducts.

SCHEME 2



out under reduction condition of **2** with trichlorosilane to (*R*)-2,2′-bis(diphenylphosphino)-5,5′-diiodo-1,1′-binaphthyl (**4**) in 92% yield. However, the reduction of **5** by trichlorosilane gave many reduction products, which displayed a large number of ^{31}P NMR signals ranging throughout the phosphine region. Instead of trichlorosilane, the use of lithium aluminum hydride with methyl trifluoromethanesulfonate, as previously reported by Imamoto,[18] successfully reduced the phosphine oxide **5** to give (*R*)-2,2′-bis(diphenylphosphino)-5,5′-bis(trimethylsilylethynyl)-1,1′-binaphthyl (**6**), which was transformed to **7** by deprotection of the trimethylsilyl group with TBAF (Scheme 1).

Next we attempted the rhodium-catalyzed asymmetric 1,4-addition of phenyl boronic acid to 2-cyclohexenone (Scheme 2).[19] As shown in Scheme 2, both **4** and **6** showed high enantioselectivities, as did BINAP, although the reaction with **7** did not proceed, probably due to unfavorable interaction between the catalyst and its terminal alkyne groups. We concluded that derivatization at the 5,5′-positions of BINAP does not influence enantioselectivities or yields in rhodium-catalyzed asymmetric 1,4-additions.

In summary, we have achieved facile preparation of a new BINAP-based building block, 2,2′-bis(diphenylphosphinyl)-5,5′-diiodo-1,1′-binaphthyl, using IPy_2BF_4 as an iodination reagent. Efficient iodination of BINAP dioxide with IPy_2BF_4 followed by Sonogashira coupling proceeded smoothly to afford diethynyl BINAP dioxide in 79% overall yield. Since functionalization at the 5,5′-positions of BINAP does not influence enantioselectivity, 5,5′-substituted BINAP and BINAP dioxide are useful as BINAP building blocks. Several functionalizations of BINAP are currently in progress.

Experimental Section

General. All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. NMR spectra were recorded at 270 MHz for ^{1}H, 67.5 MHz for ^{13}C, and 109 MHz for ^{31}P. Chemical shifts are reported in δ ppm, referenced to an internal tetramethylsilane standard for ^{1}H NMR, chloroform-*d* (δ 77.0) for ^{13}C NMR, and external 85% H_3PO_4 standard for ^{31}P NMR.

Materials. IPy_2BF_4[14] and $[Rh(acac)(C_2H_4)_2]$[20] were prepared according to the reported procedures.

Preparation of (*R*)-2,2′-Bis(diphenylphosphinyl)-5,5′-diiodo-1,1′-binaphthyl (2). To a solution of bis(pyridine)-iodonium tetrafluoroborate (395 mg, 1.06 mmol) and (*R*)-2,2′-bis(diphenylphosphinyl)-1,1′-binaphthyl (**1**) (229 mg, 0.35 mmol) in dichloromethane (6 mL) was added dropwise trifluoromethanesulfonic acid (0.19 mL, 2.12 mmol) and the mixture was stirred at room temperature for 20 h. The reaction was quenched with saturated sodium thiosulfate solution and extracted with dichloromethane. The organic phase was washed with brine and then with water, dried over sodium sulfate, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc = 1/2) to give 304.0 mg (92%) of (*R*)-2,2′-bis(diphenylphosphinyl)-5,5′-diiodo-1,1′-binaphthyl: mp 325−327 °C; $[\alpha]^{20}_D$ +299.6 (*c* 0.50, benzene); ^{1}H NMR ($CDCl_3$) δ 8.14 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.93 (dd, *J* = 7.3, 0.8 Hz, 2H), 7.68 (ddd, *J* = 12.1, 7.0, 1.9 Hz, 4H), 7.51 (dd, *J* = 11.3, 8.9 Hz, 2H), 7.21−7.41 (m, 16H), 6.73 (d, *J* = 8.6 Hz, 2H), 6.46 (dd, *J* = 8.6, 7.3, 0.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 99.5 (*C*-I); ^{31}P NMR ($CDCl_3$) δ 28.34. HRMS-FAB (*m/z*) M^+ calcd for $C_{44}H_{30}I_2O_2P_2$ 905.9810, found 905.9797. Anal. Calcd for $C_{44}H_{30}I_2O_2P_2$: C, 58.24; H, 3.34. Found: C, 58.24; H, 3.20.

(*R*)-2,2′-Bis(diphenylphosphinyl)-5-iodo-1,1′-binaphthyl (3). To a solution of bis(pyridine)iodonium tetrafluoroborate (151 mg, 0.406 mmol) and (*R*)-2,2′-bis(diphenylphosphinyl)-1,1′-binaphthyl (**1**) (133 mg, 0.203 mmol) in dichloromethane (4 mL) was added dropwise trifluoromethanesulfonic acid (72 μL, 0.812 mmol) at −30 °C and the mixture was stirred for 80 h. The reaction was quenched with saturated sodium thiosulfate solution and extracted with dichloromethane. The organic phase was washed with brine and then with water, dried over sodium sulfate, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc = 1/1) to give 75.3 mg (15%) of (*R*)-2,2′-bis(diphenylphosphinyl)-5-iodo-1,1′-binaphthyl: ^{1}H NMR ($CDCl_3$) δ 8.11 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.86 (dd, *J* = 8.1, 2.2 Hz, 2H), 7.80 (d, *J* = 8.9 Hz, 2H), 7.64−7.72 (m, 4H), 7.22−7.52 (m, 17H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.75 (d, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 1H), 6.49 (t, *J* = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 99.5 (*C*-I); ^{31}P NMR ($CDCl_3$) δ 28.88, 28.24. HRMS-FAB (*m/z*) M^+ calcd for $C_{44}H_{31}IO_2P_2$ 780.0844, found 780.0819.

(*R*)-2,2′-Bis(diphenylphosphino)-5,5′-diiodo-1,1′-binaphthyl (4). To a solution of (*R*)-2,2′-bis(diphenylphosphinyl)-5,5′-diiodo-1,1′-binaphthyl (**2**) (1.93 g, 2.12 mmol) in toluene (120 mL) was added dropwise trichlorosilane (7.0 mL, 69.4 mmol) and the mixture was refluxed for 3 h. Excess trichlorosilane and toluene were removed under reduced pressure and the residue was chromatographed on silica gel (hexane/EtOAc = 5/1) to give 1.71 g (92%) of (*R*)-2,2′-bis(diphenylphosphino)-5,5′-diiodo-1,1′-binaphthyl: mp 259−261 °C; $[\alpha]^{20}_D$ +163.1 (*c* 0.50, benzene); ^{1}H NMR ($CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.19−6.98 (m, 20H), 6.68 (d, *J* = 8.6 Hz, 2H), 6.51 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 99.4 (*C*-I); ^{31}P NMR ($CDCl_3$) δ −14.98. HRMS-FAB (*m/z*) M^+ calcd for $C_{44}H_{30}I_2P_2$ 874.9912, found 874.9891

(*R*)-2,2′-Bis(diphenylphosphinyl)-5,5′-bis(trimethylsilylethynyl)-1,1′-binaphthyl (5). To a mixture of **2** (4.80 g, 5.26 mmol), $PdCl_2(PPh_3)_2$ (369 mg, 0.526 mmol), and CuI (100 mg, 0.526 mmol) in THF (120 mL) was added triethylamine (5.8 mL, 41.4 mmol) and the mixture was stirred at room temperature for 30 min. After the mixture was cooled to 0 °C, trimethylsilylacetylene (1.30 g, 13.2 mmol) was added and the solution was stirred at 50 °C for 48 h. It was then diluted with water and extracted with Et_2O. The combined organic phases were washed with saturated ammonium chloride, brine, and water, dried over magnesium sulfate, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc = 1/2) to give 3.82 g (86%) of (*R*)-2,2′-bis(diphenylphosphinyl)-5,5′-bis(trimethylsilylethynyl)-1,1′-binaphthyl: mp 274−277 °C; $[\alpha]^{20}_D$ +377.5 (*c* 0.50, benzene); ^{1}H NMR ($CDCl_3$) δ 8.40 (dd, *J* = 8.6, 2.2 Hz, 2H), 7.74 (dd, *J* = 12.2, 7.6 Hz, 4H), 7.55−7.47 (m, 4H), 7.41−7.23 (m, 16H), 6.63 (m, 4H), 0.32 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 102.7, 99.8 (ethynyl *C*); ^{31}P NMR ($CDCl_3$) δ 28.48. Anal. Calcd for $C_{54}H_{48}O_2P_2Si_2$: C, 76.57; H, 5.71. Found: C, 76.27; H, 5.59.

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(*R*)-2,2′-Bis(diphenylphosphino)-5,5′-bis(trimethylsilylethynyl)-1,1′-binaphthyl (6). To a solution of **5** (6.34 g, 7.48 mmol) in cyclopentylmethyl ether (90 mL) was added methyl trifluoromethanesulfonate (2.1 mL, 18.6 mmol) at 0 °C and the mixture was stirred at room temperature for 2 h. After the mixture was cooled to 0 °C, lithium aluminum hydride (1.42 g, 37.4 mmol) was added and the solution was stirred at room temperature for 5 h. The reaction mixture was treated by successive dropwise addition of 1.4 mL of water, 1.4 mL of 15% sodium hydroxide solution, and 4.2 mL of water and was then extracted with benzene (three times). The combined organic phases were dried over sodium sulfate and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc = 3/1) to give 4.92 g (82%) of (*R*)-2,2′-bis(diphenylphosphino)-5,5′-bis(trimethylsilylethynyl)-1,1′-binaphthyl: mp 134−136 °C; $[\alpha]^{20}_{D}$ +199.0 (*c* 0.50, benzene); ^{1}H NMR ($CDCl_3$) δ 8.42 (d, J = 8.6 Hz, 2H), 7.55−7.50 (m, 4H), 7.39−6.99 (m, 20H), 6.77−6.59 (m, 4H), 0.38 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 82.1, 81.7 (ethynyl *C*); ^{31}P NMR ($CDCl_3$) δ −15.22. HRMS-FAB (*m/z*) M^+ calcd for $C_{54}H_{48}P_2Si_2$ 814.2770, found 814.2742.

(*R*)-2,2′-Bis(diphenylphosphino)-5,5′-diethynyl-1,1′-binaphthyl (7). To a solution of **6** (558.3 mg, 0.685 mmol) in THF (3.4 mL) was added tetrabutylammonium fluoride (4.1 mL, 4.11 mmol) and the mixture was stirred at room temperature for 2 h. It was then diluted with water and extracted with Et_2O. The combined organic phases were washed with brine and water, dried over magnesium sulfate, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc = 3/1) to give 448.9 mg (98%) of (*R*)-2,2′-bis(diphenylphosphino)-5,5′-diethynyl-1,1′-binaphthyl: mp 138−140 °C; $[\alpha]^{20}_{D}$ +170.7 (*c* 0.50, benzene); ^{1}H NMR ($CDCl_3$) δ 8.43 (d, J = 8.9 Hz, 2H), 7.57−7.51 (m, 4H), 7.35−7.00 (m, 20H), 6.81−6.69 (m, 4H), 3.41 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 82.1, 81.7; ^{31}P NMR ($CDCl_3$) δ −15.04. HRMS-FAB (*m/z*) $[M + H]^+$ calcd for $C_{48}H_{32}P_2$ 671.1979, found 671.2056.

Acknowledgment. We thank Central Glass Co. for a generous gift of trifluoromethanesulfonic anhydride, which is essential for preparing BINAP.

Supporting Information Available: ^{1}H NMR, ^{31}P NMR, and ^{13}C NMR spectra of compounds **2** and **5** and 2D ^{1}H NMR spectrum of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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