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Synthesis of 3,3′-Diaryl-Substituted 2,2′-Diamino-1,1′-binaphthyl and Its Derivatives

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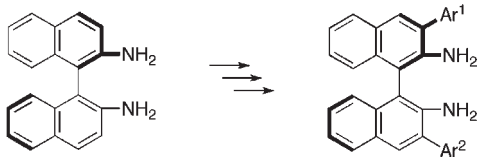

Substitution at the 3 and/or 3′ position of a binaphthyl skeleton sometimes enhances stereoselectivity during asymmetric reactions. High-yield and stepwise introduction of aryl groups into the 2,2′-diamino derivative has been established for the first time via an *ortho*-lithiation/iodization/Suzuki−Miyaura coupling protocol. The results described herein will facilitate the synthesis of a variety of 3,3′-substituted 2,2′-diamino-1,1′-binaphthyl compounds, which are key intermediates for obtaining valuable related ligands and organocatalysts.

The binaphthyl skeleton is recognized as a privileged structure for chiral ligands in organometallic complex catalysts, for organocatalysts, and for asymmetric reagents.[1] Various elements including phosphorus,[2] sulfur,[3] oxygen,[4] nitrogen,[5] and carbon[6] can be introduced into the 2 and 2′ positions, endowing the primary structure with neutral, acidic, monoanionic, dianionic, or onium character that has its own peculiar function. Introduction of substituents at the 3 and/or 3′ position (Figure 1) is known to exert a considerable effect on the reactivity and stereoselectivity of the binaphthyl. This is illustrated by BINOL (X = O),[7] its phosphates (X = O),[8] and 3,3′-carbon-substituted derivatives (X = C) such as dihydroazepinium salts,[9] dihydroguanidiums,[10] bisoxazolines,[11] bisesters,[12] and dihydrostannepine.[13] In particular, Ar substitution has a major influence on enantioselectivity. Such a phenomenon should also be observed in reactions using BINAN (2,2′-diamino-1,1′-binaphthyl) (X = N)[14] or its *N*-substituted derivatives.[15]

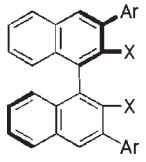

FIGURE 1. 3,3′-Diaryl-substituted 2,2′-X-1,1′-binaphthyl.

Indeed, several synthetic methods to generate 3,3′-substituted BINAN have been reported.[16] These are efficient routes to symmetric 3,3′-substituted BINAN, but there are

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(14) In this paper, 3-R-3′-R′-substituted 2,2′-diamino-1,1′-binaphthyl is abbreviated as follows. R ≠ R′ ≠ H: R,R′-BINAN. R = R′ ≠ H: diR-BINAN. R or R′ = H: monoR-BINAN. diBoc-monoR-BINAN means *N*,*N*′-diBoc-protected monoR-BINAN.

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no reports concerning the preparation of the corresponding nonsymmetric compound. This communication describes the first example of the stepwise, but selective, introduction of aryl groups into C(3) and C(3′) of BINAN.

The synthetic strategy for diAr-BINAN is simple. Among the many possibilities, we focused on the most direct route starting from the readily available optically pure BINAN. The key issue is the realization of *ortho*-arylation that can be applied to the synthesis not only of C_2 symmetric diAr-BINAN but also of the corresponding nonsymmetrical substituted compound. For the stepwise introduction of the same or different aryl groups into the 3 and 3′ positions, a conventional *ortho*-lithiation/iodization/Suzuki−Miyaura coupling protocol was used rather than a Pd-catalyzed direct arylation.[16d,17]

First, the ideal conditions for mono *ortho*-lithiation of diBoc-BINAN (**1**)[15] were established through the total amount of D incorporation into the C(3) and C(3′) of **1** obtained after treatment with alkyllithium followed by deuteration on a 100-mg scale.[18] The starting conditions were adjusted to those reported for *N*-Boc-aniline[19] (50 mM, 3 equiv of *t*-BuLi, ether, −20 °C, 2 h),[19c] and D_2O (99.9%) was used as the D source. Under these conditions, D incorporation was determined to be 77% by ^{1}H NMR analysis of a decrease in signal intensity of C(3)H and C(3′)H (δ 8.55) by reference to that of C(4)H and C(4′)H (δ 8.06). Assuming the minimum formation of dideuterated compound **1**-3*d*,3′*d*, a 23:77:0 mixture of nondeuterated **1**, monodeuterated **1**-3*h*,3′*d* and **1**-3*d*,3′*d* was anticipated.[20] Treatment of the same lithiation mixture with 3.5 equiv of I_2 (sublimed from CaO under 10^{-1} mbar at 60 °C)[21] instead of D_2O afforded **1** in 28% isolated yield and a 93:7 mixture of monoI-BINAN and diI-BINAN in 72% isolated yield.[22] The conditions of the type and amount of alkyllithium, addition temperature, and reaction time were finally optimized as follows.[18] Compound **1** was treated with 2 equiv of *n*-BuLi at −78 °C, and the mixture was warmed to 27 °C for 1 h. Addition of 1.2 equiv of *t*-BuLi to the solution at −78 °C followed by raising the temperature to 27 °C for 0.5 h gave, after addition of D_2O, deuterated-**1** with 101% D incorporation. The reaction with I_2 followed by removal of Boc afforded **1**, monoI-BINAN, and diI-BINAN in a ratio of 4:93:3. Without raising the temperature to 27 °C after addition of *n*-BuLi at −78 °C, the degree of lithiation decreased to ca. 40%. At the second lithiation stage, prolonged reaction time (3 h) resulted in overdeuteration (117%), while D incorporation decreased to 82% with *n*-BuLi instead of *t*-BuLi.

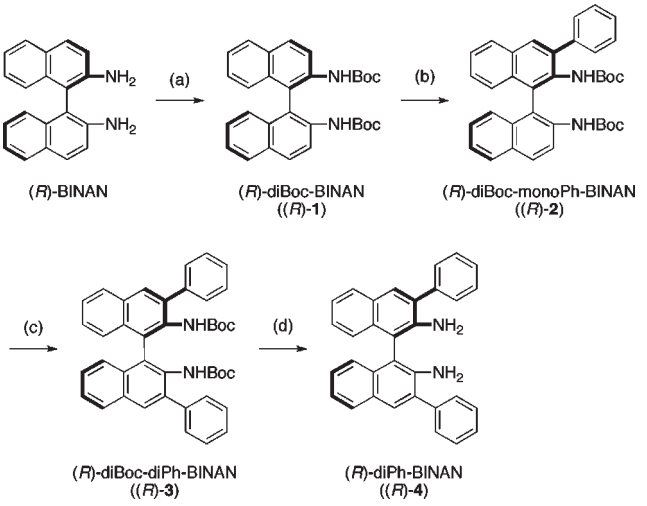

FIGURE 2. Synthetic scheme for (*R*)-diPh-BINAN. Conditions: (a) (i) (*R*)-BINAN (10 g, 35 mmol), 4.5 equiv of NaHMDS, THF, 27 °C, 1 h, (ii) 2.2 equiv of Boc_2O, THF, 0−27 °C, 3 h, 94% yield; (b) (i) 2 equiv of *n*-C_4H_9Li, 1.2 equiv of *t*-C_4H_9Li, 3.5 equiv of I_2, ether, −78 to +27 °C, 1 h, (ii) 0.03 equiv of $Pd(P(C_6H_5)_3)_4$, 1.7 equiv of $C_6H_5B(OH)_2$, 6.0 equiv of $NaHCO_3$, H_2O−DME, 100 °C, 12 h, 96% yield; (c) repeat of (b) (i) and (ii), 93% yield (1.5 equiv of *t*-C_4H_9Li was used instead of 1.2 equiv of *t*-C_4H_9Li); (d) 30 equiv of CF_3COOH, CH_2C1_2, 27 °C, 5 h, quant.

With the optimized conditions for mono *ortho*-lithiation in hand, (*R*)-diPh-BINAN was prepared on a 10-g scale in six steps as shown in Figure 2. The process was attained in 84% total yield starting from (*R*)-BINAN. BINAN was first protected as **1** in 94% yield by slow addition of Boc_2O into the corresponding disodium diamide.[15] *Ortho*-lithiation of **1** under the conditions established above followed by treatment with iodine installed I onto C(3), giving diBoc-monoI-BINAN and diBoc-diI-BINAN in a 97:3 ratio together with a small amount of **1** (ca. 4%).[22]

General Suzuki−Miyaura coupling conditions replaced I with a phenyl group to give diBoc-monoPh-BINAN **2**.[22] The isolated yield of a 97:3 mixture of monoPh-BINAN and diPh-BINAN was 96% after two steps of iodization/coupling. Repetition of the *ortho*-lithiation/iodization/phenylation followed by removal of Boc groups quantitatively yielded a 96:4 mixture of (*R*)-diPh-BINAN **4** and (*R*)-monoPh-BINAN.[23] The six-step process could be attained without purification of the intermediates, and at the final stage, the products were separated by silica gel column chromatography to give (*R*)-**4** in 93% isolated yield together with (*R*)-monoPh-BINAN (< 4% yield). Use of 4-methoxyphenylboronic acid or 3,5-dimethylphenylboronic acid at the second Suzuki−Miyaura coupling gave, after Boc deprotection, unsymmetrical Ph,4-CH_3OPh-BINAN or Ph,3,5-Xylyl-BINAN in 85% or 87% isolated yield, respectively. (*S*)-diPh-BINAN was also prepared in the same way. The NMR signals of the aromatic rings for the full assignment were complex. The structure was confirmed by X-ray crystallographic analysis of racemic diPh-BINAN, which was prepared by mixing (*R*)- and

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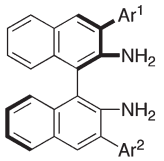
(20) The ratio ranged from 61.5:0:38.5 to 23:77:0 only with the deuteration percentage. For determining an accurate ratio, detailed analysis of the ^{1}H, ^{2}H, and ^{13}C NMR signal patterns of the 3,3′ and 4,4′ positions of **1** is required.

(21) Dryness of I_2 is essential for obtaining high yield.

(22) The NMR spectra of Boc-protected compounds are unclear, probably due to the existence of rotamers. The ratio was determined after conversion to the diamines (CF_3COOH, CH_2Cl_2, 27 °C, 5 h).

(23) A slightly greater excess of *t*-BuLi than that for the first stage of *ortho*-lithiation (1.5 vs 1.2 mol amount) was used.

(*S*)- diPh-BINAN in a 1:1 ratio to generate a colorless prism single crystal (mp 121−126 °C).[24]



(*R*)-Ph,4-CH_3OPh-BINAN: $Ar^1 = C_6H_5$; $Ar^2 = 4\text{-}CH_3OC_6H_4$ ((*R*)-**5a**)
(*R*)-Ph,3,5-Xylyl-BINAN: $Ar^1 = C_6H_5$; $Ar^2 = 3,5\text{-}(CH_3)_2C_6H_3$ ((*R*)-**5b**)

In summary, we have established a simple and direct route to 3,3′-diaryl-substituted BINAN derivatives. These derivatives, as well as being important in their own right, have the potential to act as key intermediates in the synthesis of a variety of chiral ligands for organometallic complex catalysts and organocatalysts. Deuterium-labeling experiments have determined the optimized conditions for *ortho*-lithiation, making the present method highly reproducible on a 10-g scale. The iodide intermediate should be usable for the introduction of a variety of substituents other than aryl groups.

Experimental Section

(*R*)-*N*2,*N*2′-Bis(*tert*-butoxycarbonyl)-3-iodo-1,1′-binaphthyl-2,2′-diamine. To a solution of (*R*)-*N*2,*N*2′-bis(*tert*-butoxycarbonyl)-1,1′-binaphthyl-2,2′-diamine ((*R*)-**1**) (dried over phosphorus pentoxide (10^{-2} mbar, 100 °C, 8 h), 10.1 g, 20.8 mmol) in ether (400 mL) was added dropwise 1.71 M *n*-C_4H_9Li (25.0 mL of *n*-hexane solution, 42.8 mmol) at −78 °C, and the mixture was stirred at 27 °C for 1 h. The reddish brown solution was cooled again to −78 °C, and then 1.68 M *t*-C_4H_9Li (15.0 mL *n*-hexane solution, 25.2 mmol) was added dropwise. After 1 h of stirring at 27 °C followed by recooling to −78 °C, a solution of I_2 (18.2 g, 71.7 mmol)[18,21] in ether (140 mL) was added. The resulting reddish brown solution was warmed to 27 °C and stirred for 1 h. The whole mixture was poured into saturated Na_2SO_3 aq (200 mL) and stirred at 27 °C for 1 h. The organic layer was separated and the aqueous layer extracted two times with ethyl acetate (300 mL). The combined organic layers were then washed with brine (200 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure afforded a pale yellow solid (13.2 g), which was used for the next reaction without further purification. A small part of the crude product (503 mg, 0.819 mmol as diBoc-monoI-BINAN) was subjected to Boc removal conditions (CF_3COOH (1.9 mL, 2.6 mmol), CH_2Cl_2 (10 mL), 27 °C, 5 h), and then the product was separated using a chromatographic procedure on a silica gel (50 g, eluent: 4:1 hexane−ethyl acetate mixture) to give (*R*)-monoI-BINAN (313 mg, 93% yield), (*R*)-diI-BINAN (13.2 mg, 3% yield), and (*R*)-BINAN (9.3 mg, 4% yield). (*R*)-monoI-BINAN: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.68 (brs, 2H), 4.12 (brs, 2H), 7.02 (dd, J = 2.1, 8.3 Hz. 2H), 7.14 (d, J = 8.2 Hz. 1H), 7.18−7.26 (m, 4H), 7.69 (dd, J = 2.1, 8.3 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.9 Hz, 1H), 8.42 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 88.13, 112.52, 112.82, 118.29, 122.56, 123.00, 123.64, 124.09, 127.07, 127.12, 127.35, 128.19, 128.41, 129.49, 129.86, 133.27, 133.41, 139.15, 142.11, 142.57; $[\alpha]^{24}_D$ +112.4 (*c* 0.5, $CHCl_3$); IR 3458, 3372, 1608, 1506, 1426, 1380, 1269, 1106, 816, 784, 755 cm^{-1}; HRMS calcd for $C_{20}H_{15}N_2I$ 410.0280, found 410.0274.

(24) Space group = *Ibca* (#73); *a* = 6.790(14) Å; *b* = 20.97(5) Å; *c* = 35.56(9) Å; $\alpha = \beta = \gamma = 90°$; vol = 5063(21) $Å^3$; *Z* = 8; *R* = 0.079; R_w = 0.062.

(*R*)-diI-BINAN:[16b] ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.11 (brs,4H), 6.96 (dd, J = 2.0, 7.6 Hz, 2H), 7.21−7.25 (m, 4H), 7.69 (dd, J = 2.0, 7.6 Hz, 2H), 8.43 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 87.99, 112.71, 123.18, 123.80, 127.12, 127.62, 129.48, 133.06, 139.57, 141.96; $[\alpha]^{21}_D$ +54.06 (*c* 0.25, $CHCl_3$); IR 3432, 1605, 1497, 1423, 1384, 1358, 1271, 1204, 1115, 987, 884, 780, 747 cm^{-1}; HRMS calcd for $C_{20}H_{14}N_2I_2$ 535.9246, found 535.9208.

(*R*)-*N*2,*N*2′-Bis(*tert*-butoxycarbonyl)-3-phenyl-1,1′-binaphthyl-2,2′-diamine ((*R*)-2). The crude product of (*R*)-3-iodo-*N*2,*N*2′-bis(*tert*-butoxycarbonyl)-1,1′-binaphthyl-2,2′-diamine (8.91 g, equivalent to 14.6 mmol) and $Pd(P(C_6H_5)_3)_4$ (508 mg, 0.44 mmol) was dissolved in dimethoxyethane (150 mL). To this reddish brown solution were added $C_6H_5B(OH)_2$ (3.02 g, 24.8 mmol), $NaHCO_3$ (7.35 g, 87.5 mmol), and water (75 mL), successively. The whole mixture was degassed by one freeze−vacuum−thaw process and refluxed for 19 h. After the mixture was cooled to 27 °C, saturated $NaHCO_3$ aq (100 mL) was added. The organic layer was separated and the aqueous layer extracted two times with ethyl acetate (100 mL). The combined organic layers were then washed with saturated $NaHCO_3$ aq (100 mL) and brine (100 mL). The solution was dried over anhydrous Na_2SO_4 and filtered and solvent removed under reduced pressure to afford a yellowish solid (10.2 g), which was used directly for the next step.[22] Boc deprotection (crude product (459 mg), CF_3COOH (1.9 mL, 2.6 mmol), CH_2Cl_2 (10 mL), 27 °C, 5 h) followed by silica gel chromatography (50 g, 4:1 hexane−ethyl acetate mixture) gave monoPh-BINAN (275 mg, 93% yield), diPh-BINAN (10.7 mg, 3% yield), and BINAN (9.3 mg, 4% yield). (*R*)-monoPh-BINAN: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.76 (brs, 2H), 3.80 (brs, 2H), 7.06 (d, J = 8.2 Hz, 1H), 7.16 (d, J = 8.2 Hz, 2H), 7.19−7.24 (m, 4H), 7.40 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.76 (s, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 112.64, 112.92, 118.36, 122.45, 122.59, 123.81, 123.95, 126.75, 126.87, 127.66, 128.14, 128.18, 128.20, 128.52, 128.85, 128.90, 129.34, 129.36, 129.51, 129.74, 130.68, 133.13, 133.64, 139.23, 140.72, 142.72; $[\alpha]^{21}_D$ +123.24 (*c* 0.5, $CHCl_3$); IR 3432, 1622, 1507, 1429, 1380, 1276, 820, 801, 749 cm^{-1}; HRMS calcd for $C_{26}H_{20}N_2$ 360.1626, found 360.1634.

(*R*)-*N*2,*N*2′-Bis(*tert*-butoxycarbonyl)-3-iodo-3′-phenyl-1,1′-binaphthyl-2,2′-diamine. Repetition of the above *ortho*-lithiation process (conditions: crude substrate (8.9 g), 1.71 M *n*-C_4H_9Li (18.5 mL *n*-hexane solution, 31.7 mmol), 1.68 M *t*-C_4H_9Li (18.9 mL *n*-hexane solution, 31.7 mmol), I_2 (14.1 g, 55.6 mmol), ether (350 mL)) afforded a yellowish solid (10.1 g). ^{1}H NMR analysis of the product indicated that it contained 4% of diBoc-monoI-BINAN and 3% of diBoc-diPh-BINAN. The mixture was used directly for the next step. Boc deprotection (crude product (562 mg), CF_3COOH (1.9 mL, 2.6 mmol), CH_2Cl_2 (10 mL), 27 °C, 5 h) followed by silica gel chromatography (50 g, 4:1 hexane−ethyl acetate mixture) gave Ph,I-BINAN (370 mg, 93% yield), monoI-BINAN (13.4 mg, 4% yield), and diPh-BINAN (10.7 mg, 3% yield). (*R*)-Ph,I-BINAN: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.79 (brs, 2H), 4.20 (brs, 2H), 7.01 (d, J = 8.2 Hz, 1H), 7.10 (dd, J = 4.1, 6.8 Hz, 1H), 7.21−7.25 (m, 4H), 7.41 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.70 (dd, J = 4.1, 6.8 Hz, 1H), 7.77 (s, 1H), 7.80 (d, J = 8.5 Hz, 1H), 8.43 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 88.17, 112.61, 113.17, 122.74, 123.04, 123.50, 124.11, 126.98, 127.06, 127.39, 127.74, 128.14, 128.18, 128.87, 128.88, 129.29, 129.30, 129.55, 130.08, 130.68, 132.72, 133.37, 138.98, 139.18, 140.61, 142.15; $[\alpha]^{24}_D$ +81.71 (*c* 0.5, $CHCl_3$); IR 3462, 3378, 1600, 1495, 1425, 1360, 1275, 1202, 1099, 887, 780, 748 cm^{-1}; HRMS calcd for $C_{26}H_{19}N_2I$ 486.0593, found 486.0607.

(*R*)-3,3′-Diphenyl-1,1′-binaphthyl-2,2′-diamine ((*R*)-4). Repetition of the above Suzuki−Miyaura coupling process (conditions: crude substrate (12.4 g), $Pd(P(C_6H_5)_3)_4$ (628 mg,

0.543 mmol), $C_6H_5B(OH)_2$ (3.76 g, 30.8 mmol), $NaHCO_3$ (9.12 g, 109 mmol), dimethoxyethane (150 mL), water (75 mL)) afforded (*R*)-**3** as a yellowish solid (11.8 g). The crude product was dissolved in CH_2Cl_2 (120 mL), and CF_3COOH (40 mL, 539 mmol) was added at 0 °C. After 5 h of stirring at 27 °C, 3 M aqueous KOH solution (180 mL) was added slowly at 0 °C. The aqueous layer was extracted two times with CH_2Cl_2 (200 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was evaporated. The residue was purified by flash column chromatography (silica gel, 250 g; 10:1 to 5:1 hexane−ethyl acetate mixture as eluent) to obtain (*R*)-3,3′-diphenyl-1,1′-binaphthyl-2,2′-diamine ((*R*)-diPh-BINAN) (6.82 g) as a yellow solid and (*R*)-3-phenyl-1,1′-binaphthyl-2,2′-diamine ((*R*)-monoPh-BINAN) (242 mg) as an orange solid. (*R*)-diPh-BINAN:[15,16b,16d] ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.87 (brs, 4H), 7.14 (d, J = 7.6 Hz, 2H), 7.22−7.26 (m, 4H), 7.40 (t, J = 6.8 Hz, 2H), 7.49 (t, J = 8.2 Hz, 4H), 7.62 (d, J = 7.6 Hz, 4H), 7.77 (s, 2H), 7.79−7.81 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 112.99, 122.62, 123.85, 126.79, 127.66, 128.14, 128.25, 128.85, 129.36, 129.76, 130.75, 133.09, 139.23, 140.77; $[\alpha]^{20}_D$ +101.40 (*c* 0.33, $CHCl_3$); IR 3471, 3379, 3052, 1619, 1427, 749, 703 cm^{-1}; HRMS calcd for $C_{32}H_{24}N_2$ 436.1939, found 436.1916. (*S*)-**4** was also prepared in the same way ($[\alpha]^{20}_D$ −101.94 (*c* 0.29, $CHCl_3$). HPLC analysis:[18] Column, Daicel Chiralcel OD; eluent, 99:1 hexane−*i*-C_3H_7OH; flow rate, 0.5 mL/min; t_R, 27.5 min (*R*) and 36.5 min (*S*).

(*R*)-3-(4-Methoxyphenyl)-3′-phenyl-1,1′-binaphthyl-2,2′-diamine ((*R*)-5a). The compound (*R*)-**5a** was prepared by a procedure similar to that described for (*R*)-**4**. Suzuki−Miyaura coupling process (conditions: substrate contained 93% of (*R*)-*N*2,*N*2′-bis(*tert*-butoxycarbonyl)-3-iodo-3′-phenyl-1,1′-binaphthyl-2,2′-diamine (1.17 g, equivalent to 1.58 mmol), $Pd(P(C_6H_5)_3)_4$ (56 mg, 0.048 mmol), 4-$CH_3OC_6H_4B(OH)_2$ (413 mg, 2.72 mmol), $NaHCO_3$ (0.81 g, 9.6 mmol), dimethoxyethane (16 mL), water (8 mL)) afforded (*R*)-*N*2,*N*2′-bis(*tert*-butoxycarbonyl)-3-(4-methoxyphenyl)-3′-phenyl-1,1′-binaphthyl-2,2′-diamine as a yellowish solid (1.40 g). Boc deprotection (crude product (1.40 g), CF_3COOH (3.7 mL, 48 mmol), CH_2Cl_2 (12 mL), 27 °C, 5 h) followed by silica gel chromatography (50 g, 20:1 to 5:1 hexane−ethyl acetate mixture) gave (*R*)-Ph-4-CH_3OPh-BINAN ((*R*)-**5a**) (630 mg, 85% yield) as a white solid. (*R*)-Ph-4-CH_3OPh-BINAN: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.87 (brs, 7H), 7.03 (m, 2H), 7.14 (m, 2H), 7.21−7.26 (m, 4H), 7.41 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.56 (m, 2H), 7.63 (d, J = 6.9 Hz, 2H), 7.74 (s, 1H), 7.77 (s, 1H), 7.79 (d, J = 6.9 Hz, 1H), 7.81 (d, J = 6.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.33, 112.85, 113.08, 114.22, 114.25, 122.55, 122.59, 123.80, 123.86, 126.62, 126.76, 127.64, 128.05, 128.13, 128.23, 128.27, 128.83, 128.85, 129.34, 129.36, 129.66, 129.72, 130.42, 130.48, 130.49, 130.73, 131.45, 132.95, 133.09, 139.24, 140.75, 141.04, 159.14; $[\alpha]^{21}_D$ +75.14 (*c* 0.5, $CHCl_3$); IR 3466, 3375, 3050, 1608, 1508, 1429, 1363, 1283, 1244, 1177, 1030, 832, 748 cm^{-1}; HRMS calcd for $C_{33}H_{26}N_2O$ 466.2045, found 466.2059.

(*R*)-3-(3,5-Dimethyphenyl)-3′-phenyl-1,1′-binaphthyl-2,2′-diamine ((*R*)-5b). The compound (*R*)-**5b** was prepared by a procedure similar to that described for (*R*)-**4**. Suzuki−Miyaura coupling process (conditions: substrate contained 93% of (*R*)-*N*2,*N*2′-bis(*tert*-butoxycarbonyl)-3-iodo-3′-phenyl-1,1′-binaphthyl-2,2′-diamine (117 mg, equivalent to 158 μmol), $Pd(P(C_6H_5)_3)_4$ (5.6 mg, 4.8 μmol), 3,5-$(CH_3)_2C_6H_3B(OH)_2$ (41.0 mg, 273 μmol), $NaHCO_3$ (81.0 mg, 964 μmol), dimethoxyethane (2 mL), water (1 mL)) afforded (*R*)-*N*2,*N*2′-bis(*tert*-butoxycarbonyl)-3-(3,5-dimethyphenyl)-3′-phenyl-1,1′-binaphthyl-2,2′-diamine as a yellowish solid (158 mg). Boc deprotection (crude product (158 mg), CF_3COOH (0.37 mL, 4.8 mmol), CH_2Cl_2 (2 mL), 27 °C, 5 h) followed by silica gel chromatography (10 g, 20:1 to 5:1 hexane−ethyl acetate mixture) gave (*R*)-Ph-3,5-Xylyl-BINAN ((*R*)-**5b**) (63.9 mg, 87% yield) as a white solid. (*R*)-Ph-3,5-Xylyl-BINAN: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.38 (s, 6H), 3.88 (brs, 4H), 7.04 (m, 1H), 7.13 (m, 2H), 7.21−7.24 (m, 6H), 7.39 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.62 (d, J = 6.9 Hz, 2H), 7.74 (s, 1H), 7.76 (s, 1H), 7.79 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.35, 112.78, 113.10, 122.51, 122.59, 123.77, 123.86, 126.65, 126.77, 127.03, 127.63, 128.11, 128.13, 128.22, 128.82, 129.28, 129.34, 129.56, 129.71, 130.72, 131.00, 133.00, 133.11, 138.41, 139.10, 139.25, 140.74, 140.85; $[\alpha]^{18}_D$ +88.82 (*c* 0.5, $CHCl_3$); IR 3475, 3377, 3050, 1608, 1497, 1428, 1364, 1276, 1216, 1099, 1022, 894, 851, 747 cm^{-1}; HRMS calcd for $C_{34}H_{28}N_2$ 464.2252, found 464.2262.

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Supporting Information Available: The details of deuterium-labeling experiments, ^{1}H and ^{13}C NMR spectra of new compounds, and crystallographic data for (±)-diPh-BINAN. This material is available free of charge via the Internet at http://pubs.acs.org.