Synthesis of Optically Active *N,N,N′,N′*-Tetraphenyl-1,1′-binaphthyl-2,2′-diamine Derivatives as Analogues of BINAP

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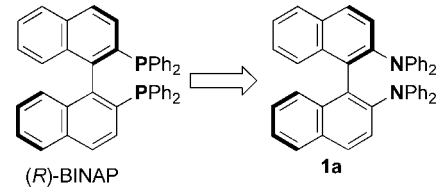
Summary: As analogues of BINAP, optically active N,N,N′,N′-tetraaryl-1,1′-binaphthyl-2,2′-diamines have been prepared by palladium-catalyzed coupling reactions of optically active 1,1′-binaphthyl-2,2′-diamine with an excess amount of aryl bromides. A novel diamine-bridged dirhodium π-arene complex has been produced and characterized by X-ray analysis.

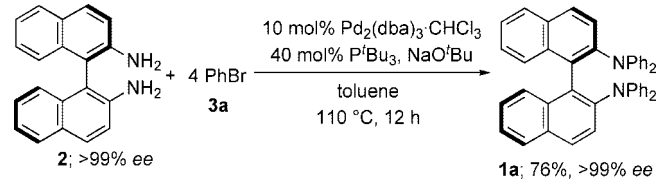
The development of asymmetric reactions catalyzed by transition-metal complexes is a field attracting great interest in current organic synthesis.[1] The design and preparation of optically active ligands which coordinate to transition metals are important key factors in obtaining high to excellent enantioselectivity.[1] In particular, a variety of optically active diphosphine ligands such as BINAP[2] (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) and its derivatives have been studied extensively and many excellent catalytic systems have been obtained. Especially, BINAP has been reported to serve as the most reliable chiral ligand in various transition-metal-catalyzed asymmetric reactions such as ruthenium-catalyzed asymmetric hydrogenation,[3] rhodium-catalyzed asymmetric hydroboration,[4] and rhodium-catalyzed asymmetric 1,4-addition of aryboronic acids to enones.[5]

Quite recently, we have found the copper-catalyzed asymmetric propargylic amination of propargylic acetates with amines by use of optically active diphosphines such as BINAP and Cl-MeO-BIPHEP (5,5′-dichloro-6,6′-dimethoxy-2,2′-bis(diphenylphosphino)-1,1′-biphenyl) as chiral ligands to give the corresponding propargylic amines in good to high yields with a high enantioselectivity (up to 89% enantiomeric excess (ee)).[6,7] This reaction provides a novel synthetic method for the preparation of chiral propargylic amines, although available nucleophiles are limited to secondary amines such as *N*-methylanilines. These results prompted us to develop a more effective reaction system for propargylic amination, including the design and preparation of novel chiral ligands. As an extension of our study, we have now envisaged *N,N,N′,N′*-tetraphenyl-1,1′-binaphthyl-2,2′-diamine (**1a**), which has two nitrogen atoms instead of the two phosphorus atoms of BINAP (Chart 1), as a new type of chiral ligand for copper-catalyzed propargylic amination, because a variety of optically active diamines have recently been prepared and used as chiral ligands in various transition-metal-catalyzed asymmetric reactions.[8] Herein, we describe the preparative method of optically active *N,N,N′,N′*-tetraaryl-1,1′-binaphthyl-2,2′-diamines (**1**) by palladium-catalyzed coupling reactions[9] of 1,1′-binaphthyl-2,2′-diamine (**2**) with aryl bromides (**3**) together with copper-catalyzed asymmetric propargylic amination and rhodium-catalyzed asymmetric hydroboration of styrene by use of compounds **1** as chiral ligands.

Chart 1



Scheme 1



Heating of (*R*)-1,1′-binaphthyl-2,2′-diamine (**2**) with 10 equiv of bromobenzene (**3a**) in the presence of 10 mol % of $Pd_2(dba)_3 \cdot CHCl_3$ and 40 mol % of P^tBu_3 in toluene at 110 °C for 12 h gave **1a** in 76% isolated yield with >99% ee (Scheme 1).[10] This result indicates that the coupling reaction proceeded without any loss of optical purity. A slightly lower yield (64% yield) of **1a** was obtained when a reaction with 5 equiv of **3a** was carried out under the same reaction conditions. The reaction with 10 equiv of **3a** in the presence of 5 mol % of

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(5) For a review, see: Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829.

(6) Hattori, G.; Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 3781.

(7) The first example of the copper-catalyzed asymmetric propargylic substitution reactions with amines has quite recently been reported, where optically active 2,6-bis(oxazolinyl)pyridines (Pybox) are used as chiral ligands: Detz, R. J.; Delville, M. M. E.; Hiemstra, H.; van Maarseveen, J. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 3777.

(8) For a recent review, see: Kizirian, J.-C. *Chem. Rev.* **2008**, *108*, 140.

(9) For reviews, see: (a) Hartwig, J. F. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002; Vol. 1, p 1051. (b) Jiang, L.; Buchwald, S. L. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; De Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004; p 699.

(10) Nozaki and co-workers reported the first example of double *N*-arylation: Nozaki, K.; Takahashi, K.; Nakano, K.; Hiyama, T.; Tang, H.-Z.; Fujiki, M.; Yamaguchi, S.; Tamao, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2051.

10.1021/om800485s CCC: $40.75
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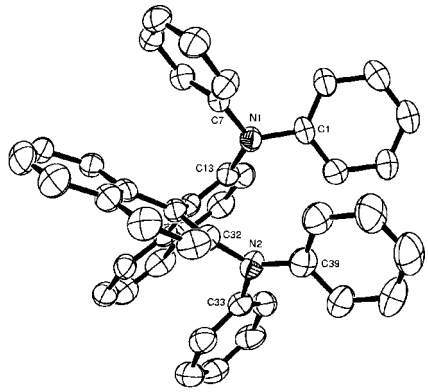


Figure 1. ORTEP drawing of **1a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): N(1)---N(2) = 3.496(4), N(1)−C(1) = 1.431(4), N(1)−C(7) = 1.434(5), N(1)−C(13) = 1.428(5), N(2)−C(32) = 1.444(5), N(2)−C(33) = 1.433(5), N(2)−C(39)=1.417(4);C(1)−N(1)−C(7)=118.6(3),C(1)−N(1)−C(13) = 119.8(3), C(7)−N(1)−C(13) = 118.1(2), C(32)−N(2)−C(33) = 115.8(2), C(32)−N(2)−C(39) = 120.5(3), C(33)−N(2)−C(39) = 121.0(3).

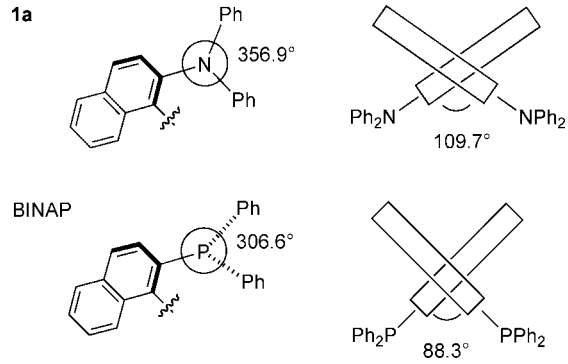
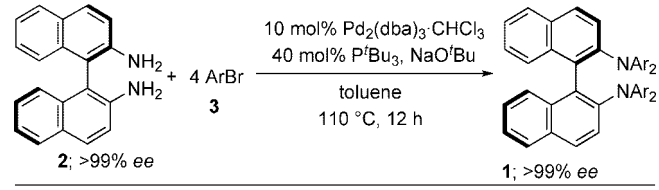


Figure 2. Selected angles (deg) of **1a** and BINAP.

$Pd_2(dba)_3 \cdot CHCl_3$ and 20 mol % of P^tBu_3 proceeded slowly to afford **1a** in only 52% yield. Interestingly, no formation of **1a** was observed in the reaction of (*R*)-1,1′-binaphthyl-2,2′-bis(nonaflate) (nonaflate = $CF_3(CF_2)_3S(O_2)O$) with 4 equiv of diphenylamine in the presence of 5 mol % of $Pd_2(dba)_3 \cdot CHCl_3$ and 10 mol % of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) at 110 °C for 24 h.[11] Thus, the method described in this paper provides a reliable route to **1a** as an analogue of BINAP.

The molecular structure of **1a** was confirmed by X-ray analysis. An ORTEP drawing of **1a** is shown in Figure 1. Two important findings on the molecular structure of **1a** are as follows (Figure 2): (1) the stereochemistry of **1a** around the nitrogen atoms is nearly planar (average sum of the valence angles around the nitrogen atoms is 356.9°), as opposed to the pyramidal structure found in the phosphorus atoms of (*R*)-BINAP (306.6°),[12] but is comparable to the value found in triphenylamine (358.9°),[13] which may contribute to the poorer basicity of the nitrogen atom as a consequence of resonance of the lone pair of each nitrogen atom with its neighboring three aryl groups; (2) the dihedral angle between the two naphthyl moieties in **1a** is extended up to 109.7°, compared with that of (*R*)-BINAP (88.3°).[12] As a result, the ability of **1a** to coordinate to transition metals is considered to be relatively low,[14] in contrast to that of BINAP.

Table 1. Palladium-Catalyzed Coupling Reactions of 2 with Aryl Bromides (3)[a]

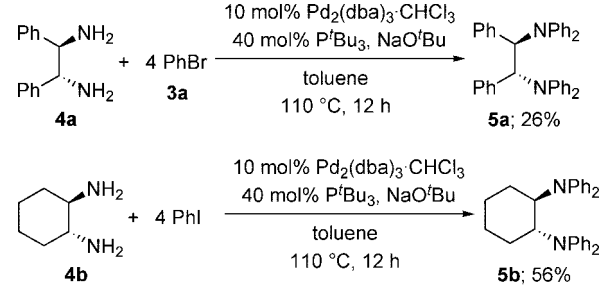


2; >99% *ee* — **1**; >99% *ee*

run	Ar of **3**	yield of **1** (%)[b]
1	Ph (**3a**)	76 (**1a**)
2	*p*-$CH_3C_6H_4$ (**3b**)	76 (**1b**)
3	*p*-$CH_3OC_6H_4$ (**3c**)	77 (**1c**)
4	*p*-FC_6H_4 (**3d**)	75 (**1d**)
5	*p*-ClC_6H_4 (**3e**)	81 (**1e**)
6	*p*-PhC_6H_4 (**3f**)	75 (**1f**)
7	*o*-MeC_6H_4 (**3g**)	0 (**1g**)[c]
8	3,5-$(CH_3)_2C_6H_3$ (**3h**)	72 (**1h**)

[a] All reactions of **2** (0.20 mmol) with **3** (2.0 mmol) were carried out in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (0.020 mmol), P^tBu_3 (0.080 mmol), and NaO^tBu (2.0 mmol) in toluene (1 mL) at 110 °C for 12 h. [b] Isolated yield of **1**. [c] *N,N′*-Di-*o*-tolyl-1,1′-binaphthyl-2,2′-diamine was obtained in 83% yield.

Scheme 2



Other analogues of BINAP were also prepared by coupling reactions of **2** with 10 equiv of other aryl bromides (**3**). Typical results are shown in Table 1. The presence of a substituent such as a methyl, methoxy, fluoro, chloro, or phenyl group at the *para* position in the benzene ring of **3** did not have much effect on the yield of the produced **1** (Table 1, runs 1−6),[15] while only *N,N′*-diaryl diamine was obtained when a methyl group was present at the *ortho* position of the benzene ring of **3g** (Table 1, run 7). The coupling reaction with 3,5-dimethylphenyl bromide (**3h**) proceeded smoothly to give **1h** in 72% isolated yield (Table 1, run 8).

We investigated coupling reactions of other types of diamines with **3a** or iodobenzene by use of the methodology given in Scheme 2. The reaction of (*R,R*)-1,2-diphenylethylenediamine (**4a**) with **3a** in the presence of 10 mol % of $Pd_2(dba)_3 \cdot CHCl_3$ and 40 mol % of P^tBu_3 in toluene at 110 °C for 12 h gave *N,N,N′,N′*-tetraphenyl-1,2-diphenylethylenediamine (**5a**) in 26% isolated yield together with the formation of *N,N,N′*-triphenyl-1,2-diphenylethylenediamine as a byproduct. Similarly, the reaction of (*R,R*)-1,2-cyclohexanediamine (**4b**) with iodobenzene gave *N,N,N′,N′*-tetraphenyl-1,2-cyclohexanediamine (**5b**) in 56% isolated yield. These results indicate that this methodology might become a general synthetic approach to the formation of the corresponding *N,N,N′,N′*-tetraaryl diamines.

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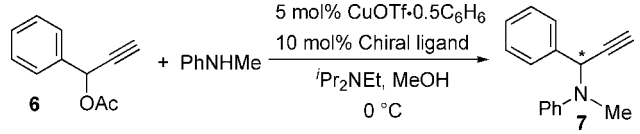
(14) As examples of the *N*-coordination of triarylamines to the metal ions, see: (a) Michalczyk, L.; de Gala, S.; Bruno, J. W. *Organometallics* **2001**, *20*, 5547. (b) Wörl, S.; Hellwinkel, D.; Printzkow, H.; Hofmann, M.; Krämer, R. *Dalton Trans.* **2004**, 2750.

(15) The molecular structure of **1c**·MeCN obtained by recrystallization from MeCN/diethyl ether was also confirmed by X-ray analysis. See the Supporting Information for experimental details.

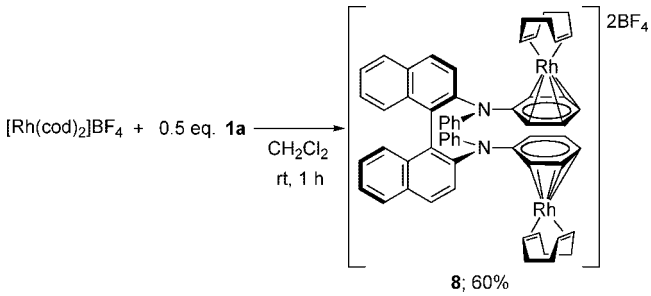
Table 2. Copper-Catalyzed Propargylic Amination of Propargylic Acetate (6) with *N*-Methylaniline[a]



run	ligand	time (h)	yield of **7** (%)[b]	ee of **7** (%)[c]
1	(*R*)-BINAP	12	82	85 (*S*)
2	**1a**	24	7	0
3	**5a**	17	15	0
4	**5b**	17	16	0

[a] All reactions of **6** (0.20 mmol) with *N*-methylaniline (0.40 mmol) and *N*,*N*-diisopropylethylamine (0.80 mmol) were carried out in the presence of copper trifluoromethanesulfonate benzene complex (0.010 mmol) and chiral ligands (0.020 mmol) in MeOH (2.0 mL) at 0 °C. [b] Isolated yield of **7**. [c] Determined by HPLC.

Scheme 3



Catalytic propargylic amination[6] by use of **1a** as a chiral ligand was investigated because we expected **1a** to work as a chiral ligand. Typical results are shown in Table 2. Unfortunately, the reaction of 1-phenyl-2-propynyl acetate (**6**) with *N*-methylaniline and *N*,*N*-diisopropylethylamine in the presence of 5 mol % of CuOTf·0.5C_6H_6 and 10 mol % of **1a** in methanol at 0 °C for 24 h gave *N*-methyl-*N*-(1-phenyl-2-propynyl)aniline (**7**) in only 7% isolated yield as a racemate (Table 2, run 2), in sharp contrast to that of BINAP[6] (Table 2, run 1). Similarly, **7** was obtained in low yields without any enantioselectivity when other arylated diamines were used as chiral ligands (Table 2, runs 3 and 4). These results indicate that the arylated diamines, including **1a** presented in this paper, did not work as chiral ligands effectively.

Next, we checked the ability of **1a** to complex with transition-metal complexes. No complexation was observed in the reaction of CuOTf·0.5C_6H_6 with **1a**. On the other hand, we have newly obtained a dirhodium π-arene complex (**8**) in 60% yield from the reaction of $[Rh(cod)_2]BF_4$ with **1a** (Scheme 3). An ORTEP drawing of **8** is shown in Figure 3. In sharp contrast to the formation of $[Rh(BINAP)(cod)]^+$, where bidentate phosphorus atoms in BINAP coordinate to the rhodium center via phosphorus atoms,[16] nitrogen atoms in **1a** do not coordinate to rhodium atom, but one of the phenyl rings attached to each nitrogen atom in **1a** coordinates to a rhodium atom of each Rh(cod) moiety to form a unique diamine-bridged dirhodium π-arene complex. Two coordinated phenyl groups stack almost in parallel (0.8°) to each other at a distance of 3.34 Å. It is noteworthy that the interatomic distance between the rhodium atom and the ipso carbon atom is elongated (2.429(5) Å) in comparison with the other five bond distances (2.28−2.38 Å), while the bond distance between the nitrogen atom and the ipso carbon atom of each coordinated phenyl group is significantly shortened (1.383(7) Å) in comparison with those of the other two

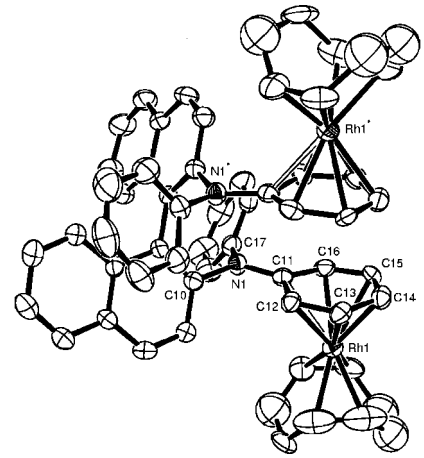
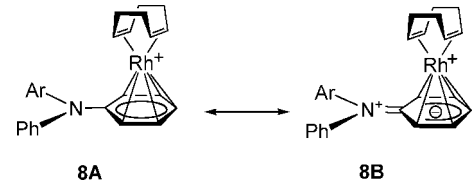


Figure 3. ORTEP drawing of **8**. Hydrogen atoms and BF_4 anions are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Rh(1)---Rh(1)* = 7.1589(6), Rh(1)---C(11) = 2.429(5), Rh(1)−C(12) = 2.375(5), Rh(1)−C(13) = 2.277(6), Rh(1)−C(14) = 2.304(5), Rh(1)−C(15) = 2.297(5), Rh(1)−C(16) = 2.252(5), N(1)---N(1)* = 3.610(6), N(1)−C(10) = 1.443(6), N(1)−C(11) = 1.383(7), N(1)−C(17) = 1.442(7); C(10)−N(1)−C(11) = 121.0(4), C(10)−N(1)−C(17) = 116.2(4), C(11)−N(1)−C(17) = 120.7(4).

Scheme 4



C−N bond distances (1.442−1.443 Å). These metric features agree with the assignment of an η^5 coordination mode of each phenyl group, presumably as a result of the lower basicity of nitrogen atoms contributing an essential resonance structure (**8B**) as shown in Scheme 4, where an electron on the nitrogen atom is transferred to the coordinated rhodium center. The related π-arene complexation of arylamine has been confirmed for an iridium π-arylamine complex, where the η^5 coordination mode is observed.[17] Finally, we attempted the hydroboration of styrene catalyzed by **8**. Unfortunately, no reaction took place between styrene and catecholborane in the presence of 1 mol % of **8** in DME at −78 °C for 6 h, in contrast to the case for BINAP.[4]

In summary, we have newly prepared optically active *N*,*N*,*N*′,*N*′-tetraaryl-1,1′-binaphthyl-2,2′-diamines as analogues of BINAP by palladium-catalyzed coupling reactions of optically active 1,1′-binaphthyl-2,2′-diamine with an excess amount of aryl bromides. These novel diamines did not work as chiral ligands in the copper-catalyzed propargylic amination and rhodium-catalyzed hydroboration of styrene. The novel diamine-bridged dirhodium π-arene complex **8** was formed and characterized by X-ray analysis. Further work to investigate the electronic and optical properties of compounds **1** as organic materials[10,11,18] is currently in progress.

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Experimental Section

General Methods. ^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were measured on a JEOL Excalibur 270 spectrometer using $CDCl_3$, CD_2Cl_2, and C_6D_6 as solvents. HPLC analyses were performed on a Hitachi L-7100 apparatus equipped with a UV detector using a 25 cm × 4.6 mm DAICEL Chiralpak AD column. Elemental analyses were performed at the Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer.

All reactions were carried out under a dry nitrogen atmosphere. (*R*)-1,1′-Binaphthyl-2,2′-diamine (**2**) was commercially available (Wako Pure Chemical Industries, Ltd.). All solvents were distilled under N_2 over appropriate drying reagents and degassed before use.

Palladium-Catalyzed Coupling Reaction of (*R*)-1,1′-Binaphthyl-2,2′-diamine with Aryl Bromide. A typical experimental procedure for **1a** is described below. In a 20 mL Schlenk tube were placed $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.020 mmol), **2** (56.9 mg, 0.200 mmol, >99% ee), sodium *tert*-butoxide (0.192 g, 2.00 mmol), **3a** (0.21 mL, 2.00 mmol), and tri-*tert*-butylphosphine (19.4 μL, 0.080 mmol) under N_2. Anhydrous toluene (1 mL) was added, and the mixture was magnetically stirred at 110 °C for 12 h. After the complete consumption of **2**, as monitored by TLC, the reaction mixture was diluted with ethyl acetate and filtered through Celite. The solvent was concentrated under reduced pressure by an aspirator, and the residue was purified by flash column chromatography (SiO_2) with hexane and ethyl acetate and recrystallization from ethanol to give **1a** as a white solid (89.5 mg, 0.152 mmol, 76% isolated yield). $[\alpha]_D^{24} = +1093.6°$ (c = 1.06, $CHCl_3$). The optical purity of **1a** was determined by HPLC analysis: DAICEL Chiralpak AD, hexane/^{i}PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm, retention time 9.0 min (minor) and 10.4 min (major), >99% ee. Mp: 222.6−223.2 °C. ^{1}H NMR ($CDCl_3$): δ 6.44 (d, J = 8.1 Hz, 2H), 6.45−6.58 (m, 12H), 6.61−6.77 (m, 10H), 7.12 (td, J = 1.2, 7.6 Hz, 2H), 7.62 (m, 4H), 7.78 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 121.7, 123.2, 124.4, 125.2, 126.6, 126.7, 127.1, 128.3, 128.7, 131.2, 131.7, 134.0, 144.4, 147.2. Anal. Calcd for $C_{44}H_{32}N_2$: C, 89.76; H, 5.48; N, 4.76. Found: C, 89.83; H, 5.47; N, 4.61. A larger scale reaction of **2** (1.200 mmol) gave a similar yield of **1a** (73% yield).

Spectroscopic data and isolated yields of other products at the same scale as for **1a** are as follows.

(*R*)-*N*,*N*,*N*′,*N*′-Tetrakis(4-methylphenyl)-1,1′-binaphthyl-2,2′-diamine (1b). Isolated yield 76%. Pale yellow solid. Mp: 223.8 °C dec. ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 12H), 6.40−6.53 (m, 18H), 6.68 (td, J = 1.1, 7.6 Hz, 2H), 7.11 (dt, J = 1.1, 7.6 Hz, 2H), 7.58 (m, 4H), 7.73 (d, J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.4, 123.1, 123.6, 124.9, 126.5, 126.9, 127.0, 128.5, 128.8, 130.7, 131.1, 131.2, 134.2, 144.8, 145.0. Anal. Calcd for $C_{48}H_{40}N_2$: C, 89.40; H, 6.25; N, 4.34. Found: C, 89.30; H, 6.31; N, 4.16.

(*R*)-*N*,*N*,*N*′,*N*′-Tetrakis(4-methoxyphenyl)-1,1′-binaphthyl-2,2′-diamine (1c). Isolated yield 77%. Pale yellow solid. Mp: 223.6 °C dec. ^{1}H NMR (C_6D_6): δ 2.83 (s, 12H), 5.98 (d, J = 8.6 Hz, 8H), 6.19−6.20 (m, 4H), 6.39 (d, J = 8.6 Hz, 8H), 6.60 (td, J = 3.0, 6.6 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 55.3, 113.8, 123.8, 124.4, 124.9, 125.9, 126.6, 127.0, 128.5, 130.9, 134.3, 141.3, 145.3, 154.5. Anal. Calcd for $C_{48}H_{40}N_2O_4$: C, 81.33; H, 5.69; N, 3.95. Found: C, 81.19; H, 5.76; N, 3.88.

(*R*)-*N*,*N*,*N*′,*N*′-Tetrakis(4-fluorophenyl)-1,1′-binaphthyl-2,2′-diamine (1d). Isolated yield 75%. White solid. Mp: >300 °C. ^{1}H NMR ($CDCl_3$): δ 6.40−6.48 (m, 18H), 6.78 (td, J = 1.1, 7.8 Hz, 2H), 7.20 (td, J = 1.1, 7.8 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 115.1 (d, J_{F-C} = 22.8 Hz), 124.3, 124.7, 125.7 (d, J_{F-C} = 17.3 Hz), 126.3, 127.3, 129.2, 131.3 (d, J_{F-C} = 8.4 Hz), 134.0, 143.4, 144.3, 158.2 (d, J_{F-C} = 241.4 Hz). HRMS (EI): m/z calcd for $C_{44}H_{28}F_4N_2$ [M] 660.2189, found 660.2186.

(*R*)-*N*,*N*,*N*′,*N*′-Tetrakis(4-chlorophenyl)-1,1′-binaphthyl-2,2′-diamine (1e). Isolated yield 81%. White solid. Mp: >300 °C. ^{1}H NMR ($CDCl_3$): δ 6.41 (m, 10H), 6.69 (d, J = 8.4 Hz, 8H), 6.80 (td, J = 1.2, 7.6 Hz, 2H), 7.27 (td, J = 1.2, 7.6 Hz, 2H), 7.59 (d, J = 8.9 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.83 (d, J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 125.0, 125.9, 126.0, 126.4, 127.3, 128.5, 129.4, 131.4, 131.7, 133.9, 143.1, 145.1. Anal. Calcd for $C_{44}H_{28}Cl_4N_2$: C, 72.74; H, 3.88; N, 3.86. Found: C, 72.64; H, 4.08; N, 3.66.

(*R*)-*N*,*N*,*N*′,*N*′-Tetrakis(4-biphenyl)-1,1′-binaphthyl-2,2′-diamine (1f). Isolated yield 75%. White solid. Mp: 261.4−262.8 °C. ^{1}H NMR ($CDCl_3$): δ 6.51 (d, J = 8.4 Hz, 2H), 6.69 (m, 10H), 6.97 (m, 8H), 7.06 (t, J = 6.8 Hz, 2H), 7.26 (m, 20H), 7.62 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 124.6, 125.3, 126.4, 126.7, 126.8, 127.1, 128.4, 129.0, 131.4, 132.0, 134.2, 140.8, 143.8, 146.0. Anal. Calcd for $C_{68}H_{48}N_2$: C, 91.45; H, 5.42; N, 3.14. Found: C, 91.47; H, 5.58; N, 3.08.

(*R*)-*N*,*N*,*N*′,*N*′-Tetrakis(3,5-dimethylphenyl)-1,1′-binaphthyl-2,2′-diamine (1h). Isolated yield 72%. Pale yellow solid. Mp: >300 °C. ^{1}H NMR ($CDCl_3$): δ 1.85 (s, 24H), 6.20 (m, 12H), 6.45 (d, J = 8.6 Hz, 2H), 6.76 (td, J = 1.1, 7.6 Hz, 2H), 7.10 (td, J = 1.1, 7.6 Hz, 2H), 7.63 (m, 4H), 7.73 (d, J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.0, 118.6, 121.5, 123.0, 123.1, 126.0, 126.6, 127.0, 128.3, 131.0, 131.3, 134.0, 137.5, 144.9, 147.2. Anal. Calcd for $C_{52}H_{48}N_2$: C, 89.10; H, 6.90; N, 4.00. Found: C, 88.99; H, 7.06; N, 3.86.

(*R*,*R*)-*N*,*N*,*N*′,*N*′-Tetraphenyl-1,2-diphenylethylenediamine (5a). Isolated yield 26%. Yellow solid. Mp: 197.9 °C dec. ^{1}H NMR ($CDCl_3$): δ 5.76 (s, 2H), 6.83 (d, J = 7.6 Hz, 8H), 6.94−6.99 (m, 14H), 7.10−7.17 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 62.4, 122.1, 124.2, 126.8, 127.4, 128.9, 129.4, 138.4, 146.5. Anal. Calcd for $C_{38}H_{32}N_2$: C, 88.34; H, 6.26; N, 5.42. Found: C, 88.07; H, 6.38; N, 5.39.

(*R*,*R*)-*N*,*N*,*N*′,*N*′-Tetraphenyl-1,2-cyclohexanediamine (5b). Isolated yield 56%. White solid. Mp: 210.7−211.1 °C. ^{1}H NMR ($CDCl_3$): δ 1.10−1.19 (m, 2H), 1.45 (m, 2H), 1.72 (m, 2H), 2.17 (m, 2H), 3.60−3.71 (m, 2H), 6.74−7.00 (m, 12H), 7.06−7.15 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 25.2, 29.2, 58.2, 121.7, 129.0, 146.2. Anal. Calcd for $C_{30}H_{30}N_2$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.05; H, 7.40; N, 6.50.

Preparation of Dirhodium π-Arene Complex 8. In a 20 mL Schlenk tube were placed $[Rh(cod)_2]BF_4$ (81.2 mg, 0.200 mmol) and **1a** (58.9 mg, 0.100 mmol) under N_2. Anhydrous dichloromethane (4 mL) was added, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through Celite under N_2, and the filtrate was concentrated in vacuo. The residue was recrystallized from CH_2Cl_2−diethyl ether to give orange crystals of **8** (71.1 mg, 0.060 mmol, 60% yield). ^{1}H NMR (CD_2Cl_2): δ 2.15−2.19 (m, 8H), 2.47−2.50 (m, 8H), 4.60 (br s, 4H), 4.67 (br s, 4H), 5.14 (dd, J = 1.9, 6.9 Hz, 2H), 5.72 (t, J = 6.8 Hz, 2H), 6.12 (d, J = 8.4 Hz, 2H), 6.45−6.75 (m, 16H), 7.02 (t, J = 6.5 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 8.35 (d, J = 8.6 Hz, 2H), 8.75 (d, J = 8.6 Hz, 2H). ^{13}C NMR (CD_2Cl_2): δ 31.6, 32.1, 77.3 (d, J_{Rh-C} = 12.8 Hz), 78.6 (d, J_{Rh-C} = 12.3 Hz), 92.6, 99.5 (d, J_{Rh-C} = 2.2 Hz), 99.7 (m), 108.2 (d, J_{Rh-C} = 2.8 Hz), 123.7, 126.1, 127.0, 127.3, 127.8, 127.9, 130.1, 131.3, 132.6, 132.8, 134.2, 138.6, 139.0, 140.1. Anal. Calcd for $C_{60}H_{56}B_2F_8N_2Rh_2 \cdot 4H_2O$: C, 57.35; H, 5.13; N, 2.23. Found: C, 57.68; H, 5.11; N, 1.98.

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Supporting Information Available: Text, tables, figures, and CIF files giving experimental procedures for X-ray analysis and crystallographic data for **1a**, **1c**·CH_3CN, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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