JOC*Note*

Acid-Catalyzed Rearrangement of Diaryl Hydrazides for the Efficient Synthesis of Functionalized 2,2′-Diamino-1,1′-biaryls

Young-Kwan Lim, Jin-Woo Jung, Haiwon Lee, and Cheon-Gyu Cho*

Department of Chemistry, Hanyang University, Seoul 131-791, Korea, and Center for Bioactive Molecular Hybrids, Yonsei University, Seoul 120-747, Korea

ccho@hanyang.ac.kr

Received April 30, 2004

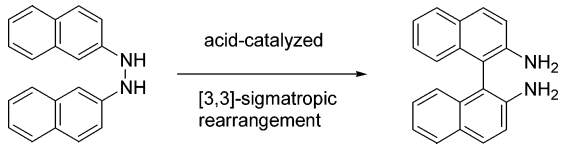
Abstract: Diaryl hydrazides prepared from the Pd(0)- or Cu(I)-catalyzed coupling reactions of aryl hydrazides and aryl halides underwent the acid-catalyzed rearrangements to a series of previously unknown 2,2′-diaminobiaryls in good overall yields. The mildness of the reaction conditions allows the presence of various functional groups.

Axially chiral binaphthyl based diols, diamines, and diphosphines are among the most remarkable classes of asymmetric chiral ligands, proven to be effective in a wide variety of important enantioselective transformations including Diels−Alder, Mukaiyama aldol, and hydrogenation reactions.[1] Various other C_1 as well as C_2-symmetrical biaryl ligands differ in the molecular shape and electronic properties have also been developed for higher asymmetric inductions. The biaryl cores are primarily synthesized through the Cu(II), Fe(III), Mn(III), or V(IV)/O_2 mediated oxidative couplings of aryl alcohols.[2] The resulting biaryl diols serve as platforms for many other analogues that include BINAP and BINAM. More recently, arylamines were directly taken for Cu(II)-mediated oxidative couplings to the C_2-symmetric 2,2′-diamino-1,1′-biaryls, under rather harsh reaction conditions.[3] Alternatively, they can be prepared through the acid-catalyzed rearrangements of diaryl hydrazines (Scheme 1). Despite their potential in the synthesis of the 2,2′-diamino-1,1′-biaryls, however, the acid-catalyzed rearrangements of diaryl hydrazines have only scarcely been used as the starting diaryl hydrazines cannot be readily prepared, especially the ones with different aryl groups.[4]

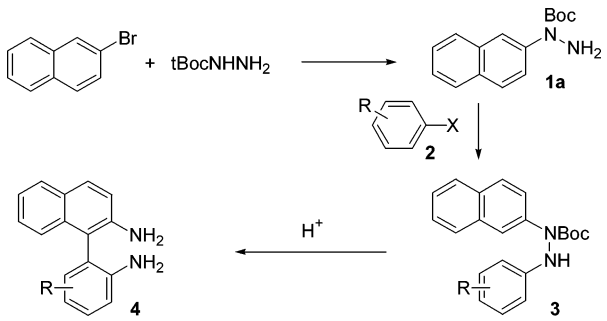
As an extension of our research on the synthetic applications of aryl hydrazides,[5] we envisaged that the diaryl hydrazide (**3**), easily prepared from the coupling of **1a** with aryl halide (**2**), could undergo an acid-catalyzed rearrangement to the corresponding 2,2′-diamino-1,1′-biaryl (**4**), analogous to diaryl hydrazine (Scheme 2). The synthetic generality for **3** would allow the presence of various functional groups, securing structural and functional diversity in **4**. The required starting diaryl hydrazides **3** were prepared according to the protocol we reported earlier[5b] (Table 1). The coupling reaction of *tert*-butyl hydrazate with 2-bromonaphthalene needed an optimization as the reaction did not proceed as smoothly as expected under the literature conditions,[5] affording **1a** in less than 30% yield. A systematic screening of various catalysts and ligands showed that the coupling would be best conducted with Pd_2dba_3/xantphos (66% yield). The Pd-catalyzed coupling reactions proceeded well with both electron rich (entries 2, 3, 4, and 5) and electron poor aryl halides (entries 7, 8, 9, 10, and 11) as shown in Table 1.

The resulting aryl hydrazides **3** underwent the acid-catalyzed rearrangements within an hour to afford the corresponding C_1-symmetric 2,2′-amino-1,1′-biaryls **4**, mostly previously unknown, in good yields, along with some carbazole byproducts **5**,[4a] when heated with a catalytic amount of HCl (aq) in EtOH at 80 °C (Table 2). The much milder reaction conditions, compared to those for oxidative coupling approaches,[3] allowed the presence of a variety of functionalities, except the NO_2 group (entry 7). Use of other acids or solvents provided similar results.

SCHEME 1. Acid-Catalyzed Rearrangement of Diaryl Hydrazine



SCHEME 2. Acid-Catalyzed Rearrangement of Diaryl Hydrazides



* Address correspondence to this author at The Hanyang University. Phone: +82+2-2290-0936.

(1) For recent reviews on binaphthyls, see: (a) Kočovský, P.; Vyskočil, Š.; Smrčina, M. *Chem. Rev.* **2003**, *103*, 3213. (b) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008. (c) Shibasaki, M.; Kanai, M.; Funabashi, K. *Chem. Commun.* **2002**, 1989. (d) Ojima, I. *Catalytic Asymmetric Synthesis*, 2nd ed.; J. Wiley & Sons: New York, 2000. (e) Hayashi, T. *Acc. Chem. Res.* **2000**, *33*, 354. (f) Pu, L. *Chem. Rev.* **1998**, *98*, 2405.

(2) (a) Hon, S.-W.; Li, C.-H.; Kuo, J.-H.; Barhate, N. B.; Liu, Y.-H.; Wang, Y.; Chen, C.-T. *Org. Lett.* **2001**, *3*, 869. (b) Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S.; Noji, M.; Koga, K. *J. Org. Chem.* **1999**, *64*, 2264. (c) Ding, K.; Xu, Q.; Wang, Y.; Liu, J.; Yu, Z.; Du, B.; Wu, Y.; Koshima, H.; Matsuura, T. *Chem. Commun.* **1997**, 693.

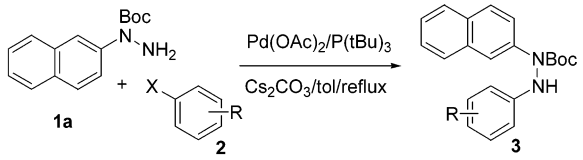
(3) Vyskočil, Š.; Smrčina, M.; Lorenc, M.; Tišlerová, I.; Brooks, R. D.; Kulagowski, J. J.; Langer, V.; Farrugia, L. J.; Kočovský, P. *J. Org. Chem.* **2001**, *66*, 1359.

(4) (a) Shine, H. J.; Kupczyk-Subotkowska, L.; Subotkowski, W. *J. Am. Chem. Soc.* **1985**, *107*, 6674. (b) Shine, H. J.; Gruszecka, E.; Subotkowski, W.; Brownawell, M.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 3218. (c) Brown, K. J.; Berry, M. S.; Murdoch, *J. Org. Chem.* **1985**, *50*, 4345. (d) Sannicolö, F. *Tetrahedron Lett.* **1985**, *26*, 119.

(5) (a) Kim, K.-Y.; Shin, J.-T.; Lee, K.-S.; Cho, C.-G. *Tetrahedron Lett.* **2004**, *45*, 117. (b) Chae, J.; Buchwald, S. *J. Org. Chem.* **2004**, *69*, 3336. (c) Lim, Y.-K.; Lee, K.-S.; Cho, C.-G. *Org. Lett.* **2003**, *5*, 979. (d) Lim, Y.-K.; Pang, S.-J.; Paek, S.-U.; Lee, H.; Cho, C.-G. *Bull. Korean Chem. Soc.* **2003**, *24*, 543. (e) Lee, K.-S.; Lim, Y.-K.; Cho, C.-G. *Tetrahedron Lett.* **2002**, *43*, 7463. (f) Wolter, M.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 3803.

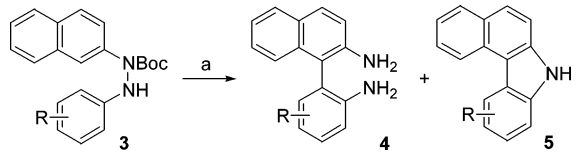
10.1021/jo049270g CCC: $27.50
Published on Web 07/21/2004

TABLE 1. Syntheses of Diaryl Hydrazides



entry	R	X	time, h	3	yield, %
1	H	I	2	**3a**	68
2	*p*-Me	I	1.5	**3b**	83
3	*p*-oMe	I	1.5	**3c**	63
4	*o*-oMe	I	1.5	**3d**	94
5	*p*-*t*-Bu	Br	1.5	**3e**	66
6	*p*-Ph	Br	1.5	**3f**	81
7	*p*-NO_2	I	1.5	**3g**	96
8	*p*-CO_2Me	I	1.5	**3h**	93
9	*p*-COMe	Br	1.5	**2i**	81
10	*p*-CN	Br	1.5	**3j**	88
11	*p*-COPh	Br	1.5	**3k**	88

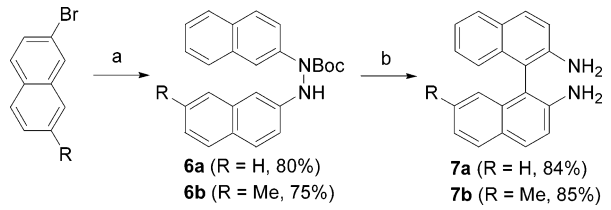
TABLE 2. Acid-Catalyzed Rearrangements of Diaryl Hydrazides



entry	3	time, h	4 (yield, %)	5 (yield, %)
1	**3a** (R = H)	1	**4a** (77)	**5a** (22)
2	**3b** (R = *p*-Me)	1	**4b** (76)	**5b** (23)
3	**3c** (R = *p*-oMe	1	**4c** (75)	**5c** (22)
4	**3d** (R = *o*-OMe)	1	**4d** (80)	**5d** (19)
5	**3e** (R = *p*-*t*-Bu)	1	**4e** (80)	**5e** (18)
6	**3f** (R = *p*-Ph)	1	**4f** (69)	**5f** (24)
7	**3g** (R = *p*-NO_2)	1	**4g** (trace)	**5g** (15)
8	**3h** (R = *p*-CO_2Me)	1	**4h** (79)	**5h** (19)
9	**3i** (R = *p*-COMe)	1	**4i** (81)	**5i** (9)
10	**3j** (R = *p*-CN)	1	**4j** (80)	**5j** (13)
11	**3k** (R = *p*-COPh)	1	**4k** (86)	**5k** (11)

[a] Conditions: cat. HCl(aq)/EtOH/80 °C.

SCHEME 3. Synthesis of 2,2′-Diamino-1,1′-binaphthyls[a]

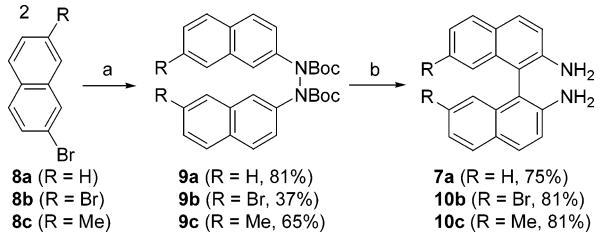


[a] Reagents and conditions: (a) **1a**, $Pd(OAc)_2/P(t\text{-}Bu)_3/Cs_2CO_3$/tol/reflux; (b) HCl/EtOH/reflux.

The binaphthyl hydrazides **6a** and **6b** prepared from the coupling reactions with 2-bromonaphthalene and 2-bromo-7-methylnaphthalene, respectively, also underwent the acid-catalyzed rearrangement reactions to the 2,2′-diamino-1,1′-binaphthyl (BINAM) derivatives **7a** and **7b**, with carbazoles in 11% and 12% yield, respectively (Scheme 3).

The C_2-symmetric 2,2′-diamino-1,1′-binaphthyls can be prepared more conveniently in two steps by using the coupling reaction of di-*tert*-butyl hydrazodiformate with 2 equiv of 2-bromonaphthalene as exemplified in Scheme 4. The coupling products prepared from **8a**, **8b**, and **8c** were nicely rearranged into the diamines **7a**, **10b**, and **10c**, with the corresponding carbazoles in 20%, 7%, and 18% yield, respectively. The low yield for **9b** is due to the double couplings. The bromine and/or methyl groups in **9b** and **9c** can be further manipulated into other functional groups, leading to various other 7,7′-disubstituted 2,2′-diamino-1,1′-binaphthalanes, worthy of further study as the binaphthalene systems with substituents at 7 and/or 7′ positions are rare in the literature.

SCHEME 4. Pd-Catalyzed Couplings of BocNHNHBoc with Aryl Halides and Rearrangements[a]



[a] Reagents and conditions: (a) BocNHNHBoc/$Pd_2(dba)_3$/xantphos/Cs_2CO_3/48 h; (b) cat. HCl(aq)/EtOH/80 °C/1 h.

In summary, we have found that the diaryl hydrazides prepared from the Pd(0)-catalyzed coupling reactions of aryl hydrazides with aryl halides undergo facile acid-catalyzed rearrangement reactions into the functionalized 2,2′-diamino-1,1′-biaryls, mostly previously unknown, in good overall yields. This new protocol would be a powerful alternative to the present methods, further enabling the development of C_1- and C_2-symmetric biaryl chiral ligands for higher efficiency in asymmetric induction. We are currently exploring the effect of substituents at the 7 and/or 7′ position on the geometry around the chiral pocket.

Experimental Section

***N*-Naphthalen-2-yl-hydrazine Carboxylic Acid *tert*-Butyl Ester (1a).** A mixture of **3** (50 mg, 0.24 mmol), Boc-$NHNH_2$ (96 mg, 0.72 mmol), Pd_2dba_3 (5 mol %), xantphos (15 mol %), Cs_2CO_3 (111 mg, 0.34 mmol), and 0.5 mL of toluene was heated to 80 °C under Ar. After 48 h, the reaction mixture was concentrated and chromatographed (hexanes:EtOAc 7:1) to afford 41 mg of **1a** (solid, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.76−7.73 (m, 3H), 7.43−7.36 (m, 2H), 4.52 (br s, 2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 140.4, 133.1, 130.6, 127.5, 127.4, 127.2, 125.9, 125.0, 122.9, 120.4, 81.8, 28.3; FT-IR ($CHCl_3$) 3347, 3026, 2976, 1691, 1632, 1598, 1509 cm^{-1}; HRMS (FAB) *m*/*z* $(M + 1)^+$ calcd for $C_{15}H_{19}N_2O_2$ 259.1447, found 259.1441.

General Procedure for the Preparation of *N*-Naphthalen-2-yl-*N*′-phenyhydrazinecarboxylic Acid *tert*-Butyl Ester (3a). A mixture of **1a** (100 mg, 0.39 mmol), iodobenzene (66 mg, 0.32 mmol), $Pd(OAc)_2$ (5 mol %), $P(t\text{-}Bu)_3$ (5 mol %), Cs_2CO_3 (156 mg, 0.48 mmol), and 3 mL of anhydrous toluene was heated at 110 °C for 1.5 h. The reaction mixture was cooled, concentrated, and chromatographed (hexanes/EtOAc 30/1) to afford 74 mg of **3a** in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.79−7.74 (m, 4H), 7.43−7.35 (m, 2H), 7.23−7.18 (m, 2H), 6.90−6.81 (m, 3H), 6.44 (s, 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 148.1, 140.2, 133.3, 130.6, 129.0, 127.9, 127.6,

127.2, 126.0, 125.0, 121.0, 118.4, 113.0, 82.4, 28.2; FT-IR ($CHCl_3$) 3336, 3057, 2977, 1699, 1602, 1496 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{21}H_{23}N_2O_2$ 335.1760, found 335.1760.

***N*-Naphthalen-2-yl-*N′*-*p*-tolylhydrazinecarboxylic Acid *tert*-Butyl Ester (3b, solid).** ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.79−7.74 (m, 4H), 7.43−7.35 (m, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.70 (d, $J = 8.4$ Hz, 2H), 6.40 (s, 1H), 2.26 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 145.7, 140.3, 133.4, 130.6, 130.3, 129.6, 127.9, 127.7, 127.2, 126.0, 125.0, 121.3, 118.4, 113.1, 82.3, 28.2, 20.7; FT-IR ($CHCl_3$) 3337, 2975, 1713, 1513 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{22}H_{25}N_2O_2$ 339.1916, found 349.1903.

***N′*-(4-Methoxyphenyl)-*N*-naphthalen-2-ylhydrazinecarboxylic Acid *tert*-Butyl Ester (3c, solid).** The same method as for **3a** was used. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.78−7.74 (m, 4H), 7.43−7.35 (m, 2H), 6.78 (s, 4H), 6.35 (s, 1H), 3.73 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 153.9, 145.7, 141.8, 140.3, 133.3, 130.6, 127.9, 127.6, 127.2, 126.0, 125.0, 121.3, 118.5, 114.5, 82.3, 55.6, 28.2; FT-IR ($CHCl_3$) 3327, 2978, 1711, 1510, 1312, 1239, 1153 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{22}H_{25}N_2O_3$ 365.1865, found 365.1873.

***N′*-(2-Methoxyphenyl)-*N*-naphthalen-2-ylhydrazinecarboxylic Acid *tert*-Butyl Ester (3d, solid).** ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, $J = 1.6$ Hz, 1H), 7.82 (dd, $J = 2.0$, 2.4 Hz, 1H), 7.77−7.75 (m, 3H), 7.04 (s, 1H), 6.86−6.80 (m, 4H), 3.89 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 146.8, 140.4, 137.6, 133.4, 130.5, 127.9, 127.6, 127.2, 126.0, 124.9, 121.2, 120.9, 120.5, 118.2, 112.1, 109.9, 82.0, 55.5, 28.1; FT-IR ($CHCl_3$) 3356, 3056, 2976, 1714, 1600, 1504, 1368, 1310, 1249, 1153 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{22}H_{25}N_2O_3$ 365.1865, found 365.1873.

***N′*-(4-*tert*-Butylphenyl)-*N*-naphthalen-2-ylhydrazinecarboxylic Acid *tert*-Butyl Ester (3e, solid).** ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.78−7.23 (m, 4H), 7.42−7.34 (m, 2H), 7.23−7.18 (m, 2H), 6.78−6.74 (m, 2H), 6.43 (s, 1H), 1.39 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 145.6, 143.7, 140.3, 133.3, 130.6, 127.8, 127.6, 127.2, 126.0, 125.8, 125.0, 121.4, 118.6, 112.8, 82.3, 34.1, 31.6, 28.2; FT-IR ($CHCl_3$) 3341, 1964, 1714, 1515 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{25}H_{31}N_2O_2$ 391.2386, found 391.2373.

***N′*-Biphenyl-4-yl-*N*-naphthalen-2-ylhydrazinecarboxylic Acid *tert*-Butyl Ester (3f, solid).** ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.80−7.74 (m, 4H), 7.52−7.34 (m, 8H), 7.24 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 2H), 6.52 (s, 1H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 147.5, 140.7, 140.1, 133.9, 133.3, 130.6, 128.5, 128.0, 127.8, 127.6, 127.3, 126.4, 126.1, 125.1, 121.2, 118.5, 113.3, 82.5, 28.2; FT-IR ($CHCl_3$) 3344, 2978, 1713, 1612, 1488, 1308, 1152 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{27}H_{27}N_2O_2$ 411.2073, found 411.2074.

***N*-Naphthalen-2-yl-*N′*-(4-nitrophenyl)hydrazinecarboxylic Acid *tert*-Butyl Ester (3g, solid).** ^1H NMR (400 MHz, $CDCl_3$) δ 8.16−8.12 (m, 2H), 7.93 (d, $J = 2.4$ Hz, 1H), 7.81−7.75 (m, 3H), 7.66 (dd, $J = 2.4$, 2.0 Hz, 1H), 7.48−7.40 (m, 2H), 6.89−6.86 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 153.3, 140.8, 139.1, 133.2, 130.9, 128.3, 127.6, 127.3, 126.4, 125.8, 125.5, 121.0, 118.9, 111.6, 83.2, 28.1; FT-IR ($CHCl_3$) 3323, 3062, 2978, 1716, 1598 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{21}H_{22}N_3O_4$ 380.1610, found 380.1607.

4-(*N′*-*tert*-Butoxycarbonyl-*N′*-naphthalen-2-ylhydrazino)-benzoic Acid Methyl Ester (3h, solid). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99−7.72 (m, 4H), 7.47−7.40 (m, 2H), 6.88−6.85 (m, 2H), 6.70 (s, 1H), 3.87 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 153.4, 152.0, 139.6, 133.3, 131.3, 130.7, 128.2, 127.6, 127.3, 126.2, 125.3, 122.5, 121.0, 118.6, 112.0, 82.8, 51.9, 28.2; FT-IR ($CHCl_3$) 3323, 2979, 1715, 1608 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{23}H_{25}N_2O_4$ 393.1814, found 393.1809.

***N*-(4-Acetylphenyl)-*N*-naphthalen-2-ylhydrazinecarboxylic Acid *tert*-Butyl Ester (3i, solid).** ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, $J = 1.6$ Hz, 1H), 7.85−7.83 (m, 4H), 7.77−7.67 (m, 4H), 7.44−7.37 (m, 2H), 6.87 (s, 1H), 6.84−6.81 (m, 2H), 2.50 (1s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 153.4, 152.1, 139.5, 133.2, 130.7, 130.3, 130.1, 128.1, 127.6, 127.3, 126.2, 125.3, 121.0, 118.6, 111.8, 82.8, 28.1, 26.3; FT-IR ($CHCl_3$) 3314, 3057, 2979, 1716, 1600, 1367, 1311, 1153 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{23}H_{25}N_2O_3$ 377.1865, found 377.1865.

***N*-(4-Cyanophenyl)-*N*-naphthalen-2-ylhydrazinecarboxylic Acid *tert*-Butyl Ester (3j, solid).** ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, $J = 1.6$ Hz, 1H), 7.82−7.77 (m, 4H), 7.69 (dd, $J = 2.0$, 2.4 Hz, 1H), 7.55−7.52 (m, 2H), 7.49−7.42 (m, 2H), 6.92−6.88 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 151.5, 139.3, 133.5, 133.2, 130.8, 128.2, 127.6, 127.3, 126.3, 125.4, 121.0, 119.4, 118.8, 112.6, 103.1, 84.0, 28.1; FT-IR ($CHCl_3$) 3316, 3065, 2978, 2220, 1718, 1608 cm^{-1}; HRMS decomposition.

***N′*-(4-Benzoylphenyl)-*N*-naphthalen-2-ylhydrazinecarboxylic Acid *tert*-Butyl Ester (3k, solid).** ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.85−7.72 (m, 8H), 7.56−7.52 (m, 1H), 7.48−7.37 (m, 4H), 6.90 (d, $J = 8.4$ Hz, 2H), 6.85 (s, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 153.5, 151.9, 139.6, 138.2, 133.2, 132.4, 131.5, 130.7, 129.8, 128.1, 128.0, 127.6, 127.3, 126.2, 125.3, 121.2, 118.7, 111.7, 82.8, 28.2; FT-IR ($CHCl_3$) 3313, 3058, 2979, 2932, 1716, 1650, 1598, 1368, 1315, 1150 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{28}H_{27}N_2O_3$ 439.2022, found 439.2021.

General Procedure for the Preparation of 1-(2-Aminophenyl)naphthalen-2-ylamine (4a). A mixture of **3a** (50 mg, 0.15 mmol), 3 mL of ethanol, and three drops of concentrated HCl (35%) was heated under reflux for 1 h. Upon being cooledg and neutralized with $NaHCO_3$, the reaction mixture was filtered, concentrated, and chromatographed (2:1 hexanes:CH_2Cl_2 to 9:1 EtOAc:MeOH) to afford 27 mg (77% yield) of **4a** as a solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.67 (m, 2H), 7.27−7.19 (m, 4H), 7.10 (dd, $J = 1.6$, 1.2 Hz, 1H), 7.03 (d, $J = 8.8$ Hz, 1H), 6.90−6.84 (m, 2H), 3.64 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.7, 133.3, 131.7, 130.7, 129.0, 128.9, 128.0, 127.9, 126.5, 123.8, 122.2, 121.2, 118.9, 118.1, 115.6, 115.3; FT-IR ($CHCl_3$) 3381, 3052, 1620, 1497, 1392, 1291, 1150 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{16}H_{15}N_2$ 235.1235, found 235.1227.

1-(2-Amino-5-methylphenyl)naphthalen-2-ylamine (4b, solid). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, $J = 7.6$ Hz, 1H), 7.66 (d, $J = 8.88$ Hz, 1H), 7.29−7.17 (m, 3H), 7.04 (dd, $J = 2.0$, 2.4 Hz, 1H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.91 (d, $J = 2.0$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 3.57 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 141.7, 133.3, 132.0, 129.5, 128.8, 128.1, 128.0, 127.8, 126.4, 123.8, 122.1, 121.3, 118.1, 115.8, 115.5, 20.6; FT-IR ($CHCl_3$) 3453, 3361, 3050, 2861, 1621, 1504, 1351, 1281, 1147 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{17}H_{17}N_2$ 249.1392, found 249.1397.

1-(2-Amino-5-methoxyphenyl)naphthalen-2-ylamine (4c, solid). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.68 (m, 2H), 7.31−7.28 (m, 2H), 7.24−7.20 (m, 1H), 7.04 (d, $J = 8.4$ Hz, 1H), 6.88−6.82 (m, 2H), 6.71 (d, $J = 2.4$ Hz, 1H), 3.81−3.76 (br s, 2H), 3.74 (s, 3H), 3.28 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 141.6, 138.5, 133.2, 129.1, 128.0, 127.9, 126.6, 123.8, 122.4, 122.2, 118.1, 117.1, 116.2, 115.3, 55.7; FT-IR ($CHCl_3$) 3444, 3360, 3208, 3049, 1620, 1501, 1420, 1278, 1204, 1038 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{17}H_{17}N_2O$ 265.1241, found 265.1347.

1-(2-Amino-3-methoxyphenyl)naphthalen-2-ylamine (4d, solid). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.8$ Hz, 1H), 7.32−7.28 (m, 1H), 7.26−7.20 (m, 2H), 7.05 (d, $J = 8.8$ Hz, 1H), 6.91−6.84 (m, 2H), 6.77 (dd, $J = 2.4$, 1.6 Hz, 1H), 3.93 (s, 3H), 3.80 (br s, 2H), 3.70 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 141.7, 134.8, 133.2, 128.9, 128.0, 127.8,126.4, 123.9, 123.5, 122.1, 121.2, 118.1, 118.0, 115.2, 109.4, 55.6; FT-IR ($CHCl_3$) 3465, 3372, 3053, 2934, 2836, 1602, 1473, 1279, 1198, 1052 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{17}H_{17}N_2O$ 265.1241, found 265.1321.

6-*tert*-Butyl-[1,1′]binaphthalenyl-2,2′-diamine (4e, solid). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 8.8$ Hz, 1H), 7.30−7.19 (m, 4H), 6.81 (d, $J = 8.4$ Hz, 1H), 3.62 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 141.8, 141.7, 133.4, 128.9, 128.5, 128.0, 127.9, 126.4, 125.7, 124.0, 122.1, 120.9, 118.1, 116.0, 115.4, 34.2, 31.7; FT-IR ($CHCl_3$) 3489, 3369, 3203, 3052, 2961, 2868, 1620, 1501, 1285, 1258, 1210 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{20}H_{23}N_2$ 291.1861, found 291.1857.

6-Phenyl-[1,1′]binaphthalenyl-2,2′-diamine (4f, solid). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74−7.70 (m, 2H), 7.56−7.52 (m, 3H),

7.41 (d, J = 2.4 Hz, 1H), 7.37−7.33 (m, 3H), 7.31−7.26 (m, 1H), 7.25−7.20 (m, 2H), 7.05 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 3.83 (br s, 2H), 3.60 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.3, 141.8, 140.6, 133.3, 131.6, 130.2, 129.1, 128.5, 128.0, 127.9, 127.5, 126.6, 126.14, 126.10, 123.8, 122.2, 121.6, 118.1, 116.0, 115.1; FT-IR ($CHCl_3$) 3465, 3374, 3201, 3053, 1615, 1512, 1484, 1303, 1263, 1147 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for $C_{22}H_{19}N_2$ 311.1548, found 311.1546.

2,2′-Diamino-[1,1′]binaphthalenyl-6-carboxylic Acid Methyl Ester (4h, solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 2.0, 2.0 Hz, 1H), 7.84 (d, J = 2.0 Hz, 1H), 7.73−7.70 (m, 2H), 7.30−7.20 (m, 3H), 7.03 (d, J = 8.8 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 3.96 (br s, 2H), 3.82 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 149.3, 141.9, 134.0, 133.1, 131.2, 129.5, 128.00, 127.97, 126.7, 123.5, 122.3, 120.14, 120.12, 118.1, 114.4, 113.8, 51.7; FT-IR ($CHCl_3$) 3472, 3368, 3213, 3054, 1703, 1617, 1304, 1254, 1147 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for $C_{18}H_{17}N_2O_2$ 293.1290, found 293.1299.

1-(2,2′-Diamino-[1,1′]binaphthalenyl-6-yl)ethanone (4i, solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 2.0, 2.0 Hz, 1H), 7.78−7.72 (m, 3H), 7.32−7.22 (m, 3H), 7.05 (d, J = 8.8 Hz, 1H), 6.85 (d, J = 8.8 Hz, 1H), 4.04 (br s, 2H), 3.79 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 149.6, 141.9, 133.5, 133.2, 130.1, 129.6, 128.3, 128.0, 126.8, 123.4, 122.4, 119.9, 118.1, 114.5, 113.7, 26.3; FT-IR ($CHCl_3$) 3471, 3351, 3213, 2928, 1620, 1510, 1298, 1261 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for $C_{18}H_{17}N_2O$ 277.1341, found 277.1354.

2,2′-Diamino-[1,1′]binaphthalenyl-6-carbonitrile (4j, solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.70 (m, 2H), 7.49 (dd, J = 2.0, 2.0 Hz, 1H), 7.39 (d, J = 6.0 Hz, 1H), 7.31−7.20 (m, 2H), 7.13 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 8.8 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 4.05 (br s, 2H), 3.75 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 141.9, 136.2, 133.2, 132.8, 129.9, 128.1, 127.9, 126.9, 123.0, 122.5, 121.2, 119.8, 118.0, 115.0, 112.1, 100.6; FT-IR ($CHCl_3$) 3471, 3366, 3206, 3055, 2215, 1620, 1503 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for $C_{17}H_{14}N_3$ 260.1188, found 260.1191.

(2,2′-Diamino-[1,1′]binaphthalenyl-6-yl)phenylmethanone (4k, solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 2.0, 2.0 Hz, 1H), 7.75−7.68 (m, 5H), 7.50−7.45 (m, 1H), 7.42−7.38 (m, 2H), 7.34−7.22 (m, 4H), 7.04 (d, J = 8.8 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 4.05 (br s, 2H), 3.80 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 149.5, 141.9, 138.5, 135.4, 133.1, 132.3, 131.2, 129.4, 129.4, 129.3, 128.0, 127.9, 127.6, 126.7, 123.4, 122.3, 120.0, 118.0, 114.3, 113.5; FT-IR ($CHCl_3$) 3471, 3361, 3210, 3054, 2655, 1639, 1511, 1320, 1144 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for $C_{23}H_{19}N_2O$ 339.1497, found 339.1493.

***N,N′*-Dinaphthalen-2-ylhydrazinecarboxylic Acid *tert*-Butyl Ester (6a, solid).** The procedure for **3a** was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 1.6 Hz, 1H), 7.83−7.70 (m, 7H), 7.60 (d, J = 4.0 Hz, 1H), 7.44−7.34 (m, 4H), 7.29−7.74 (m, 1H), 7.12 (d, J = 2.0 Hz, 1H), 7.06 (dd, J = 2.4, 2.4 Hz, 1H), 6.63 (s, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 145.7, 140.1, 134.3, 133.4, 130.7, 129.3, 129.1, 126.0, 127.7, 127.5, 127.3, 126.5, 126.3, 126.1, 125.1, 123.3, 121.1, 118.4, 115.5, 107.2, 82.5, 28.2; FT-IR ($CHCl_3$) 3330, 3052, 2978, 1713, 1637, 1365, 1315, 1154 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for $C_{25}H_{25}N_2O_2$ 385.1916, found 385.1916.

***N′*-(7-Methylnaphthalen-2-yl)-*N*-naphthalen-2-ylhydrazinecarboxylic Acid *tert*-Butyl Ester (6b, solid).** A similar procedure as that for **3a** was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.82−7.73 (m, 4H), 7.62 (dd, J = 8.8, 8.4 Hz, 2H), 7.41−7.34 (m, 3H), 7.09−6.95 (m, 3H), 5.59 (s, 1H), 2.41 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 145.7, 140.2, 135.9, 134.5, 133.4, 130.6, 128.8, 128.0, 127.7, 127.5, 127.3, 127.2, 126.1, 125.6, 125.5, 125.0, 121.1, 118.3, 114.5, 106.7, 82.4, 28.2, 21.8; FT-IR ($CHCl_3$) 3338, 2978, 1713, 1636, 1510, 1309, 1153 cm^{-1}; HRMS (FAB in NBA + Na with PEG 400) m/z (M + 23)$^+$ calcd for $C_{26}H_{26}N_2NaO_2$ 421.1892, found 421.1896.

General Procedure for the Preparation of *N,N′*-Dinaphthalenyldi-*tert*-butylhydrazodiformate (9a). A mixture of 100 mg of **8a**, 51 mg of BocNHNHBoc, 11 mg (5 mol %) of $Pd_2(dba)_3$, 19 mg (15 mol %) of xantphos, 205 mg of Cs_2CO_3, and 0.5 mL of toluene was heated to 80 °C under Ar for 48 h. The reaction mixture was chromatographed (hexanes:EtOAc 15:1) to give 190 mg of **9a** as a solid in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 2.0, 2.0 Hz, 1H), 7.75−7.68 (m, 5H), 7.50−7.45 (m, 1H), 7.42−7.38 (m, 2H), 7.34−7.22 (m, 4H), 7.04 (d, J = 8.8 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 4.05 (br s, 2H), 3.80 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 149.5, 141.9, 138.5, 135.4, 133.1, 132.3, 131.2, 129.4, 129.4, 129.3, 128.0, 127.9, 127.6, 126.7, 123.4, 122.3, 120.0, 118.0, 114.3, 113.5; FT-IR ($CHCl_3$) 3471, 3361, 3210, 3054, 2655, 1639, 1511, 1320, 1144 cm^{-1}; HRMS (FAB in NBA + Na with PEG 400) m/z (M + 23)$^+$ m/z (M + 23)$^+$ calcd for $C_{30}H_{32}N_2NaO_4$ 507.2260, found 507.2268.

***N,N′*-Di-(7-bromonaphthalenyl)di-*tert*-butylhydrazodiformate (9b, solid).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 2.0 Hz, 2H), 7.72 (d, J = 8.8 Hz, 4H), 7.62 (d, J = 8.4 Hz, 4H), 7.46 (dd, J = 2.0, 1.6 Hz, 2H), 1.54(s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 139.6, 134.4, 129.7, 129.5, 128.97, 128.88, 128.3, 121.7, 120.3, 118.4, 83.0, 28.3; FT-IR ($CHCl_3$) 3059, 2978, 2931, 1731, 1627, 1503 cm^{-1}; HRMS (FAB in NBA + Na with PEG 400) m/z (M + 23)$^+$ calcd for $C_{30}H_{30}Br_2N_2NaO_4$ 535.2573, found 535.2568.

***N,N′*-Di-(7-methylnaphthalenyl)di-*tert*-butylhydrazodiformate (9c, solid).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (br s, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.56 (br s, 2H), 7.50 (s, 2H), 7.23 (d, J = 9.6 Hz, 2H), 2.45 (s, 6H), 1.55 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 138.8, 135.7, 133.4, 129.5, 127.8, 127.1, 126.8, 120.7, 118.9, 82.4, 28.3, 21.8; FT-IR ($CHCl_3$) 2978, 1928, 1724, 1637, 1513 cm^{-1}; HRMS (FAB in NBA + Na with PEG 400) m/z (M + 23)$^+$ calcd for $C_{32}H_{36}N_2NaO_4$ 535.2573, found 535.2568.

7-Methyl-[1,1′]binaphthalenyl-2,2′-diamine (7b, solid). A similar procedure as that for **4a** was used. ^{1}H NMR (400 MHz, CD_3OD) δ 7.80−7.73 (m, 3H), 7.65 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.18−7.09 (m, 3H), 7.02 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.73 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 143.6, 143.4, 137.1, 135.0, 134.8, 130.1, 129.9, 128.92, 128.88, 128.2, 119.6, 118.7, 114.5, 114.2; FT-IR ($CHCl_3$) 3468, 3376, 3200, 2921, 2532, 1908, 1731, 1513 cm^{-1}; HRMS (FAB in NBA + Na with PEG 400) m/z (M + 23)$^+$ calcd for $C_{21}H_{18}N_2Na$ 321.1368, found 321.1369.

7,7′-Dibromo-[1,1′]binaphthalenyl-2,2′-diamine (10b, solid). A similar procedure as that for **4a** was used. ^{1}H NMR (400 MHz, CD_3OD) δ 7.71 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.28 (dd, J = 2.0, 2.0 Hz, 2H), 7.14 (d, J = 1.6 Hz, 2H), 7.70 (d, J = 8.8 Ha, 2H), 3.75 (br s, 4H); ^{13}C NMR (100 MHz, CD_3OD) δ 146.3, 136.5, 131.3, 130.7, 128.1, 126.5, 126.2, 122.2, 120.1, 111.5; FT-IR ($CHCl_3$) 3470, 3376, 3206, 3048, 2928, 1731, 1617, 1498 cm^{-1}; HRMS (FAB in NBA + Na with PEG 400) m/z (M + 23)$^+$ calcd for $C_{20}H_{14}Br_2N_2Na$ 462.9402, found 462.9430.

7,7′-Dimethyl-[1,1′]binaphthalenyl-2,2′-diamine (10c, solid). A similar procedure as that for **4a** was used. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.07−7.03 (m, 4H), 6.84 (d, J = 0.8 Hz, 2H), 3.54 (br s, 4H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 136.3, 133.7, 129.0, 127.8, 126.6, 124.5, 122.8, 117.3, 112.3, 22.1; FT-IR ($CHCl_3$) 3465, 3371, 3209, 3049, 2921, 1612, 1519, 1452 cm^{-1}; HRMS (FAB in NBA + Na with PEG 400) m/z (M + 23)$^+$ calcd for $C_{22}H_{20}N_2Na$ 335.1524, found 335.1520.

Acknowledgment. This work was supported by IMT-2000 Program of Ministry of Information & Communication, Korea. L.Y.K. and J.J.W. thank the financial support from the BK 21 Program.

Supporting Information Available: Spectral data for all unknown diaryl hydrazides and 2,2′-diamino-1,1′-biaryls. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049270G