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Synthesis of Novel 1,3,5-Tris(arylazo)benzenes via Pd-Catalyzed Couplings and Cu(I)-Mediated Direct Oxidations

Young-Kwan Lim, Sunju Choi,† Kyung Bae Park,† and Cheon-Gyu Cho*

Department of Chemistry, Hanyang University,
Seoul 131-791, Korea, and Radioisotope & Radiation
Application Team, HANARO Center,
KAERI, Daejon 305-301, Korea

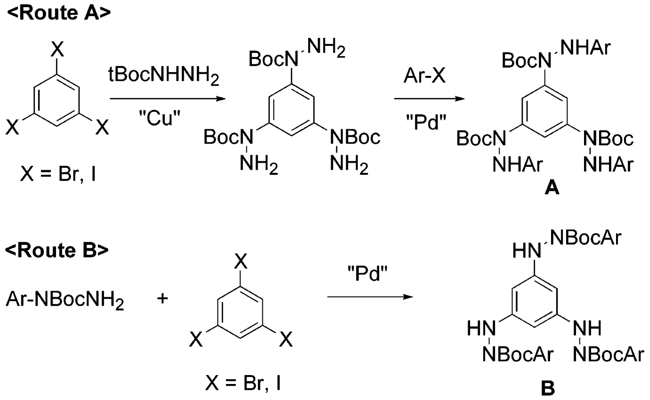
ccho@hanyang.ac.kr

Received November 22, 2003

Abstract: A series of novel 1,3,5-tris-azobenzenes were prepared from 1,3,5-trihalobenzene via Pd-catalyzed couplings of *N*-Boc aryl hydrazines and subsequent Cu(I)-mediated direct oxidations. The oxidation of tris-arylhydrazide provided the azobenzene as a mixture of all four of the possible *E*/*Z*-isomers; [*E*,*E*,*E*]-, [*E*,*E*,*Z*]-, [*E*,*Z*,*Z*]-, and [*Z*,*Z*,*Z*]-1,3,5-tris-azobenzenes. A slow removal of the solvent in the dark transformed the isomers into the all-trans, [*E*,*E*,*E*]-isomer.

Azobenzenes have received a great deal of interest for their potential applications in the area of nonlinear optics, optical storage media, chemosensors, and photochemical switches, due to the characteristic reversible cis−trans isomerization of the diazo linkage, causing changes of molecular geometry under visible light.[1] In recent years, various dendritic,[2] peptidic,[3] and polymeric polyazobenzenes[4] have emerged as new promising photochemical material in those fields. Dendritic or starburst-shaped azobenzenes are of particular interest for their characteristic properties not present in nondendritic azobenzenes.[2] A brief literature survey revealed many examples bearing photochromic azobenzene units positioned in various places within the dendritic skeletons. Their photochemical and mechanical behaviors would be governed by the types of substituents present, location of diazo-linkages as well as the shape of the molecules. Conventional synthetic methods, primarily based on the couplings of functionalized azobenzene moieties, exert much restriction on the type of chemical ligation methods due to the lability of the diazo group, hence limiting their molecular structures and functional groups.[5] We have previously reported a new synthetic approach to various linear azobenzenes from aryl hydrazides and aryl halides via Pd-catalyzed couplings and subsequent direct oxidations.[6] Our coupling−oxidation protocol would be a powerful alternative to the conventional methods, as the labile diazo-linkages are realized at the final stage of the synthesis. Prompted by the immediate applicability of our coupling−oxidation protocol toward starburst-shaped azobenzenes, we have studied the couplings of aryl hydrazides with 1,3,5-trihalobenzene and subsequent direct oxidations into the 1,3,5-tris(arylazo)benzenes. In this account, we wish to present the details of our study on the synthesis of various functionalized 1,3,5-tris(arylazo)benzenes.

SCHEME 1. Synthesis of Tris-arylhydrazide



The required tris(arylhydrazido)benzenes can be prepared through the two possible routes as depicted in Scheme 1, where the hydrazides **A** and **B** are isomeric each other with respect to the location of the Boc group.

Route A turned out to be ineffective as the Cu(I)-catalyzed coupling of *tert*-butyl carbazate with 1,3,5-tribromobenzene did not proceed as smoothly as we hoped.[7] Attempted couplings provided a complex mixture

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* Corresponding author. Phone: +82+2-2290-0936.

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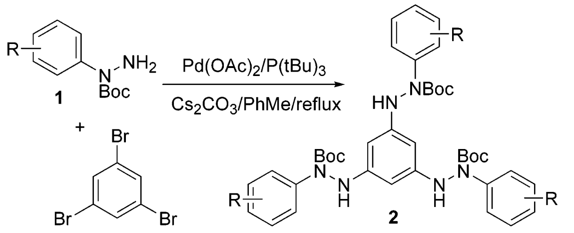
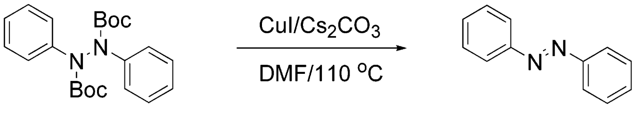
10.1021/jo035720d CCC: $27.50

TABLE 1. Couplings of Various *N*-Boc Aryl Hydrazines with Tribromobenzene



entry	**1**	time (h)	product	yield (%)
1	R = H	2	**2a**	98
2	R = p-Me	2	**2b**	98
3	R = p-OMe	2	**2c**	91
4	R = p-tBu	3	**2d**	86
5	R = p-Ph	3	**2e**	99
6	R = p-NO$_2$	2	**2f**	77
7	R = p-CO$_2$Me	3	**2g**	93
8	R = p-COMe	2	**2h**	90
9	R = p-CN	2	**2i**	99
10	R = p-COPh	3	**2j**	99
11	R = o-OMe	2	**2k**	99
12	R = p-n-hexyl	2	**2l**	99
13	R = p-n-dodecyl	2	**2m**	94

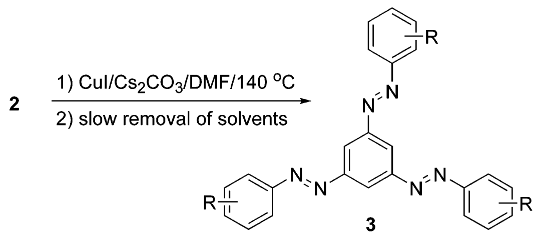
SCHEME 2. Cu(I)-Mediated Direct Oxidations of Bis-Boc-diaryl Hydrazines to Azobenzenes



of products, some of which resulted from the couplings at $-NH_2$ rather than the desired $-NHBoc$ site. No significant improvement was observed with more reactive 1,3,5-triiodobenzene.[8] Meanwhile, *N*-Boc aryl hydrazines were well coupled with 1,3,5-triiodobenzene as well as 1,3,5-tribromobenzene under the Pd(OAc)$_2$/P(t-Bu)$_3$ catalyst system to provide the corresponding tris(arylhydrazido)benzenes in good to excellent yields (route B). In this case, the aryl substituent would exert a steric hindrance to prevent the coupling reactions from taking place at the $-NH_2$ side. Table 1 summarizes the results on the coupling reactions of various substituted aryl hydrazides with 1,3,5-tribromobenzene.

The resulting tris(arylhydrazido)benzenes (**2a**−**m**), however, did not give the desired 1,3,5-tris(arylazo)benzenes under the conditions that were successfully employed for the oxidation of monodiaryl hydrazides.[6] We isolated instead several products including the ones resulted from the brominations at the nitrogen and/or aryl groups. Unlike the cases with diaryl hydrazides, the *tert*-butyl groups in this trisubstituted system might be too hindered for the oxidations to proceed. While we were studying the Cu(I)-catalyzed coupling reactions of aryl hydrazides with aryl halides, we have learned that bis-Boc diaryl hydrazines can be directly oxidized into the azobenzenes when heated at 110 °C in the presence of Cu(I) and a base (Scheme 2).[9]

TABLE 2. Cu(I)-Mediated Direct Oxidations of Tris-aryl Hydrazides into Tris-azobenzenes



entry	R	time (h)	product	yield (%)
1	H	3	**3a**	64
2	p-Me	2	**3b**	80
3	p-OMe	3	**3c**	52
4	p-tBu	2	**3d**	64
5	p-Ph	3	**3e**	74
6	p-NO$_2$	0.5	**3f**	trace
7	p-CO$_2$Me	2	**3g**	74
8	p-COMe	2	**3h**	trace
9	p-CN	1.5	**3i**	42
10	p-COPh	2	**3j**	71
11	o-OMe	3	**3k**	63
12	p-n-hexyl	2	**3l**	74
13	p-n-dodecyl	2	**3m**	68

A set of subsequent control experiments yielded the optimized conditions, allowing the generation of various 1,3,5-tris(arylazo)benzenes from tris(arylhydrazido)benzenes (Table 2).[10] In all cases, the oxidations provided all possible cis/trans isomers; [*E*,*E*,*E*]-, [*E*,*E*,*Z*]-, [*E*,*Z*,*Z*]-, and [*Z*,*Z*,*Z*]-1,3,5-tris(arylazo)benzenes. The ratio of four *E*/*Z* isomers were determined to be 70:20:7:3 by isolation with silica gel chromatography in the case of **3a**. We also found that the *E*/*Z* isomers converse into the [*E*,*E*,*E*]-isomer upon slow removal of the solvents in the dark. The yields reported are the values after the isomerization. Incompatible were the ones bearing NO$_2$ or COMe groups (entries 6 and 8) due to the their thermal instability. Running the oxidations at lower temperatures indeed provided the corresponding 1,3,5-tris(arylazo)benzenes, but at much slower rates (20−30% conversion after 7 days). The isolated pure [*E*,*E*,*E*] isomers are photochemically stable when they are in the solid phase but rapidly undergo cis−trans photoisomerization in solution to provide a mixture of all four *E*/*Z* isomers when exposed to the lights. A slow removal of the solvent in the dark again transformed the isomers back into the all-trans, [*E*,*E*,*E*]-isomer.

In summary, we have shown that various functionalized 1,3,5-tris(arylazo)benzenes can be readily prepared from 1,3,5-trihalobenzene via Pd-catalyzed couplings with *N*-Boc aryl hydrazines and subsequent Cu(I)-mediated direct oxidations. Our new protocol would allow a precise integration of azobenzene units into the target molecules for the generation of new functional poly-azobenzenes with various intentions. We are currently investigating the applications of 1,3,5-tris-azobenzenes, **3l** or **3m**, in particular, as new holographic grating materials. A further extension of our method to the synthesis of

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(10) Compounds **3a** and **3f** have been prepared from 1,3,5-(NO$_2$)$_3$-benzene in three steps with overall yields of less than 2% through the formation of 1,3,5-tris(*aci*-nitro)benzene followed by the diazo-couplings with the corresponding aryl diarzonium salts and denitrations. Severin, T.; Hufnagel, J.; Temme, H.-L. *Chem. Ber.* **1968**, *101*, 2468.

multigeneration dendrimers and cyclic polyazobenzenes is also underway.

Experimental Section

***N′*-[3,5-Bis(*N*-*tert*-butoxycarbonyl-*N′*-phenylhydrazino)phenyl]-*N*-phenylhydrazinecarboxylic Acid *tert*-Butyl Ester (2a).** To a flask were charged 2.150 g (10.3 mmol) of phenyl hydrazide (**1a**), 0.325 g (1.0 mmol) of 1,3,5-tri-bromobenzene, 0.035 g (15 mol %) of Pd(OAc)$_2$, 0.095 mL of P(t-Bu)$_3$ (15 mol %) dissolved in hexane, 3.360 g of Cs$_2$CO$_3$, and 10 mL of anhydrous toluene at rt. The resulting mixture was stirred for 30 min at rt and heated at 110 °C. After 2 h, the reaction mixture was cooled, concentrated, and chromatographed (hexanes/EtOAc = 7:1) to afford 0.708 g of the product **2a** in 98% yield: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, $J = 8.4$ Hz, 6H), 7.21 (dd, $J = 8.4, 7.2$ Hz, 6H), 7.03 (t, $J = 7.2$ Hz, 3H), 6.43 (bs, 3H), 5.81 (s, 3H), 1.32 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.6, 150.1, 142.5, 128.1, 124.2, 121.8, 90.7, 82.0, 28.1; FT-IR (CHCl$_3$) 3350, 2980, 1714, 1620, 1495, 1347, 1308, 1156 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{39}$H$_{49}$N$_6$O$_6$ 697.3714, found 697.3687.

The following compounds **2b**−**m** were prepared by using the same procedure as described for **2a**.

***N′*-[3,5-Bis(*N′*-*tert*-butoxycarbonyl-*N*-*p*-tolylhydrazino)phenyl]-*N*-*p*-tolylhydrazinecarboxylic acid *tert*-butyl ester (2b):** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, $J = 8.4$ Hz, 6H), 7.01 (d, $J = 8.4$ Hz, 6H), 6.39 (bs, 3H), 5.79 (s, 3H), 2.28 (s, 9H), 1.33 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.8, 150.2, 140.1, 133.8, 128.8, 122.0, 90.8, 91.8, 28.2, 21.0; FT-IR (CHCl$_3$) 3343, 2980, 1713, 1616, 1510, 1336, 1160 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{42}$H$_{55}$N$_6$O$_6$ 739.4183, found 739.4199.

***N′*-[3,5-Bis(*N′*-*tert*-butoxycarbonyl-*N′*-(4-methoxyphenyl)hydrazino)phenyl]-*N*-(4-methoxyphenyl)hydrazinecarboxylic acid *tert*-butyl ester (2c):** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, $J = 8.4$ Hz, 6H), 6.78−6.74 (m, 6H), 6.29 (bs, 3H), 5.82 (s, 3H), 3.79 (s, 9H), 1.35 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.2, 153.9, 150.0, 135.8, 123.7, 113.3, 90.7, 81.6, 55.3, 28.2; FT-IR (CHCl$_3$) 3340, 2976, 1710, 1620, 1507, 1339, 1251, 1156 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{42}$H$_{55}$N$_6$O$_9$ 787.4031, found 787.4001.

***N′*-{3,5-Bis[*N*-*tert*-butoxycarbonyl-*N*-(4-*tert*-butylphenyl)hydrazino]phenyl}-*N*-(4-*tert*-butylphenyl)hydrazinecarboxylic acid *tert*-butyl ester (2d):** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, $J = 8.8$ Hz, 6H), 7.27−7.24 (m, 6H), 6.26 (bs, 3H), 5.83 (s, 3H), 1.34 (s, 27H), 1.29 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.8, 150.2, 147.0, 139.9, 125.1, 121.4, 90.9, 81.9, 34.4, 31.5, 28.2; FT-IR (CHCl$_3$) 3343, 2965, 1718, 1616, 1515, 1371, 1335, 1160 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{51}$H$_{73}$N$_6$O$_6$ 865.5592, found 865.5578.

***N*-Biphenyl-4-yl-*N′*-[3,5-bis(*N′*-biphenyl-4-yl-*N′*-*tert*-butoxycarbonylhydrazino)phenyl]hydrazinecarboxylic acid *tert*-butyl ester (2e):** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53−7.42 (m, 18H), 7.37−7.33 (m, 6H), 7.29−7.25 (m, 3H), 6.53 (bs, 3H), 5.87 (s, 3H), 1.36 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.6, 150.1, 141.8, 140.3, 136.9, 128.5, 126.8, 126.74, 126.65, 122.0, 90.7, 82.2, 28.2; FT-IR (CHCl$_3$) 3347, 2980, 1721, 1612, 1487, 1336, 1156 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{57}$H$_{61}$N$_6$O$_6$ 925.4653, found 925.4620.

***N′*-{3,5-Bis[*N*-*tert*-butoxycarbonyl-*N′*-(4-nitrophenyl)hydrazino]phenyl}-*N*-(4-nitrophenyl)hydrazinecarboxylic acid *tert*-butyl ester (2f):** ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12−8.03 (m, 6H), 7.72−7.68 (m, 6H), 6.36 (bs, 3H), 5.70 (s, 3H), 1.36 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.5, 149.5, 147.9, 143.0, 124.1, 120.0, 90.8, 83.8, 27.9; FT-IR (CHCl$_3$) 3351, 2984, 1725, 1593, 1519, 1942, 1916, 1156 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{39}$H$_{46}$N$_9$O$_{12}$ 832.3266, found 832.3280.

2g: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, $J = 8.8$ Hz, 6H), 7.52 (d, $J = 8.8$ Hz, 6H), 6.58 (bs, 3H), 5.73 (s, 3H), 3.88 (s, 9H), 1.32 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.3, 153.0, 149.8, 146.4, 129.8, 125.3, 120.3, 90.7, 82.9, 51.9, 28.0; FT-IR (CHCl$_3$) 3339, 2979, 1720, 1605, 1320, 1279, 1155, 1112 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{45}$H$_{55}$N$_6$O$_{12}$ 871.3878, found 871.3845.

2h: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J = 8.8$ Hz, 6H), 7.56 (d, $J = 8.8$ Hz, 6H), 6.48 (bs, 3H), 5.73 (s, 3H), 2.55 (s, 9H), 1.34 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.6, 152.9, 149.8, 146.5, 132.5, 128.8, 120.3, 90.8, 83.1, 28.0, 26.5; FT-IR (CHCl$_3$) 3335, 2984, 1725, 1682, 1604, 1328, 1273, 1156 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{45}$H$_{55}$N$_6$O$_9$ 823.4031, found 823.4061.

2i: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, $J = 8.8$ Hz, 6H), 7.52−7.49 (m, 6H), 6.50 (bs, 3H), 5.69 (s, 3H), 1.33 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.6, 149.6, 146.2, 132.3, 120.6, 118.6, 106.8, 90.7, 83.5, 27.9; FT-IR (CHCl$_3$) 3334, 2980, 2228, 1720, 1602, 1499, 1322, 1302, 1152 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{42}$H$_{46}$N$_9$O$_6$ 772.3571, found 772.3569.

2j: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75−7.72 (m, 12H), 7.64 (d, $J = 8.8$ Hz, 6H), 7.57−7.53 (m, 3H), 7.46−7.42 (m, 6H), 6.43 (bs, 3H), 5.80 (s, 3H), 1.36 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.0, 153.0, 149.8, 146.2, 137.4, 132.5, 131.9, 130.5, 129.5, 127.5, 120.1, 90.4, 82.8, 27.9; FT-IR (CHCl$_3$) 3335, 2980, 1725, 1659, 1601, 1328, 1281, 1156 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{60}$H$_{61}$N$_6$O$_9$ 1009.4500, found 1009.4489.

2k: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35−7.32 (m, 3H), 7.19−7.15 (m, 3H), 6.87−6.81 (m, 6H), 6.36 (bs, 3H), 6.03 (s, 3H), 3.84 (s 9H), 1.35 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.7, 154.1, 149.5, 131.4, 128.7, 129.2, 120.3, 111.3, 91.2, 81.0, 55.5, 28.2; FT-IR (CHCl$_3$) 3347, 2980, 1721, 1616, 1503, 1343, 1160 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{42}$H$_{55}$N$_6$O$_9$ 787.4031, found 787.4033.

2l: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, $J = 8.4$ Hz, 6H), 7.03 (d, $J = 8.4$ Hz, 6H), 6.29 (bs, 3H), 5.82 (s, 3H), 2.54 (t, $J = 8.0$ Hz 6H), 1.62−1.53 (m, 6H), 1.39−1.23 (m, 18H), 1.34 (s, 27H), 0.88 (t, $J = 6.8$ Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.8, 150.2, 140.2, 138.9, 128.1, 121.8, 90.9, 81.8, 35.4, 31.8, 31.5, 29.1, 28.2, 22.7, 14.2; FT-IR (CHCl$_3$) 3346, 2929, 1716, 1615, 1510, 1334, 1159 cm^{-1}; HRMS (FAB) m/z (M+1)$^+$ calcd for C$_{57}$H$_{85}$N$_6$O$_6$ 949.6531, found 949.6520.

2m: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, $J = 8.4$ Hz, 6H), 7.02 (d, $J = 8.4$ Hz, 6H), 6.32 (bs, 3H), 5.82 (s, 3H), 2.53 (t, $J = 8.0$ Hz, 6H), 1.58−1.55 (m, 6H), 1.37 − 1.25 (m, 54H), 1.33 (s, 27H), 0.87 (t, $J = 6.8$ Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.8, 150.2, 140.2, 138.9, 128.1, 121.9, 90.8, 81.8, 35.4, 32.0, 31.6, 29.8 (2C), 29.7 (2C), 29.6 (2C), 29.4, 28.2, 22.8, 14.2; FT-IR (CHCl$_3$) 3346, 2929, 2855, 1716, 1619, 1510, 1334, 1159 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{75}$H$_{121}$N$_6$O$_6$ 1201.9348, found 1201.9369.

3a: To a sealed tube were charged 50 mg (0.07 mmol) of **2a**, 55 mg (0.29 mmol) of CuI, 94 mg (0.29 mmol) of Cs$_2$CO$_3$, and 1 mL of anhydrous DMF at room temperature. After 3 h at 140 °C, the reaction mixture was cooled and chromatographed (hexanes/EtOAc = 9:1) to furnish 18 mg of tris-azobenzenes (as a mixture of four isomers, 64% of total yield), which were isomerized to **3a** upon slow removal of the solvent in the dark: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.58 (s, 3H), 8.02−7.80 (m, 6H), 7.58−7.50 (m, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.8, 152.3, 131.6, 129.2, 123.2, 118.9; FT-IR (CHCl$_3$) 2922, 1604, 1503, 1421, 1152 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{24}$H$_{19}$N$_6$ 391.1671, found 391.1622.

The following compounds **3b**−**m** were prepared by using the same procedure as described for **3a**.

3b: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.51 (s, 3H), 7.90 (d, $J = 8.4$ Hz, 6H), 7.33 (d, $J = 8.0$ Hz, 6H), 2.54 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.8, 150.4, 142.1, 129.7, 123.1, 118.3, 21.7; FT-IR (CHCl$_3$) 2965, 2922, 1600, 1269, 1094 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{27}$H$_{25}$N$_6$ 433.2145, found 433.2132.

3c: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.45 (s, 3H), 7.99 (d, $J = 8.8$ Hz, 6H), 7.03 (d, $J = 8.8$ Hz, 6H), 3.90 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.2, 153.8, 146.7, 125.0, 117.8, 114.2, 55.7; FT-IR (CHCl$_3$) 2926, 1601, 1503, 1258, 1145, 1027 cm^{-1}; HRMS (FAB) m/z (M + 1)$^+$ calcd for C$_{27}$H$_{25}$N$_6$O$_3$ 481.1988, found 481.1980.

3d: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.53 (s, 3H), 7.94 (d, $J = 8.4$ Hz, 6H), 7.56 (d, $J = 8.4$ Hz, 6H), 1.40 (s, 27H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.1, 153.8, 150.3, 126.0, 122.8, 118.3, 35.2, 31.4; FT-IR (CHCl$_3$) 2965, 2867, 1604, 1503, 1464, 1269, 1109

cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{36}H_{43}N_6$ 559.3549, found 559.3549.

3e: ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 3H), 8.11−8.08 (m, 6H), 7.80−7.77 (m, 6H), 7.69−7.67 (m, 6H), 7.50−7.46 (m, 6H), 7.42−7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 151.4, 144.2, 139.9, 128.8, 127.9, 127.8, 127.1, 123.7, 118.8; FT-IR ($CHCl_3$) 2926, 1601, 1408, 1265, 1156 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{42}H_{31}N_6$ 619.2610, found 619.2607.

3g: ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 3H), 8.23 (d, J = 8.4 Hz, 6H), 8.05 (d, J = 8.4 Hz, 6H), 3.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 154.5, 153.6, 132.4, 130.6, 122.9, 119.7, 52.5; FT-IR ($CHCl_3$) 2920, 1730, 1603, 1432, 1279, 1108 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{30}H_{25}N_6O_6$ 565.1836, found 565.1839.

3i: ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 3H), 8.09 (d, J = 8.4 Hz, 6H), 7.87 (d, J = 8.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 153.4, 133.3, 123.6, 120.2, 118.1, 114.9; FT-IR ($CHCl_3$) 2926, 2856, 2227.1, 1737, 1596, 1262 cm^{-1}. No mass data available due to the decomposition.

3j: ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 3H), 8.11 (d, J = 8.4 Hz, 6H), 7.99 (d, J = 8.4 Hz, 6H), 7.86−7.84 (m, 6H), 7.65−7.61 (m, 3H), 7.54−7.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 154.0, 153.7, 139.8, 137.1, 132.7, 131.0, 130.0, 128.3, 122.9, 119.7; FT-IR ($CHCl_3$) 2926, 1663, 1601, 1449, 1308, 1281 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{45}H_{31}N_6O_3$ 703.2458, found 703.2456.

3k: ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 3H), 7.66−7.64 (m, 3H), 7.42−7.38 (m, 3H), 7.04 (d, J = 8.0 Hz, 3H), 7.00−6.93 (m, 3H), 3.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 154.2, 142.0, 132.9, 120.7, 118.8, 117.0, 112.8, 56.4; FT-IR ($CHCl_3$) 2965, 2922, 1558, 1402, 1270, 1094 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{27}H_{25}N_6O_3$ 481.1988, found 481.1990.

3l: ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 3H), 7.91 (d, J = 8.4 Hz, 6H), 7.34 (d, J = 8.4 Hz, 6H), 2.70 (t, J = 7.6 Hz, 6H), 1.71−1.64 (m, 6H), 1.41−1.25 (m, 18H), 0.90 (t, J = 6.8 Hz, 9H; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.6, 147.1, 129.1, 123.1, 118.7, 36.1, 31.8, 31.4, 29.1, 22.7, 14.2; FT-IR ($CHCl_3$) 2960, 2929, 2859, 1603, 1459, 1155 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{42}H_{55}N_6$ 643.4488, found 644.4478.

3m: ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 3H), 7.92 (d, J = 8.4 Hz, 6H), 7.34 (d, J = 8.4 Hz, 6H), 2.70 (t, J = 7.6 Hz, 6H), 1.69−1.64 (m, 6H), 1.34−1.18 (m, 54H), 1.88 (t, J = 7.2 Hz, 9H; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.6, 147.1, 129.1, 123.1, 123.0, 118.3, 36.1, 32.0, 31.4, 29.81, 29.78, 29.75, 29.69, 29.6, 29.5, 29.4, 22.8, 14.3; FT-IR ($CHCl_3$) 2962, 2929, 2855, 1462, 1262 cm^{-1}; HRMS (FAB) *m/z* $(M + 1)^+$ calcd for $C_{60}H_{91}N_6$ 895.7305, found 895.7290.

Acknowledgment. This work was supported by the Nuclear R&D Program of the Ministry of Science and Technology (MOST). L.Y.K. acknowledges the financial support from the BK 21 Program.

Supporting Information Available: Spectral data of unreported *N*-Boc aryl hydrazines, 1,3,5-tris(arylhydrazido)-benzenes, and 1,3,5-tris-(arylazo)benzenes. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035720D