

## Ligand-Accelerated Catalysis of the Ullmann Condensation: Application to Hole Conducting Triarylaminines

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High-purity triarylaminines find employment in xerographic photoreceptors where, as concentrated solid solutions in polymeric transport layers, they function as efficient hole conductors.<sup>1,2</sup> Under the influence of an applied electric field, injected positive charge migrates through such layers by a hopping mechanism to create latent electrostatic images.<sup>3</sup> This process occurs readily since triarylaminines possess an easily accessible oxidation potential and on hole injection give up a nonbonding electron to generate amine cation radicals, the stable spin centers responsible for transport. Triarylaminines are also important to a number of emerging technologies. Transport layers are equally fundamental to electroluminescent devices where, in essentially the reverse of electrophotography, electrons and holes are separately injected and transported to an emitting species where their recombination produces singlet excitons whose radiative decay results in visible light.<sup>4</sup> They are also constituents of nonlinear optical chromophores useful in the design of integrated electrooptic switches and modulators.<sup>5</sup> In each of these applications, achievement of an electronic grade purity level is required for optimal device performance. Thus, clean and efficient syntheses which can be readily scaled to multi-kilogram lot sizes are desirable. Despite their structural simplicity, synthetic protocols which satisfy these criteria are uncommon and the heightened importance of triarylaminines has led to extensive recent research attention.

The classic technique for the construction of triarylaminines has been the venerable Ullmann condensation.<sup>6</sup> As usually practiced, the reaction entails the condensation of a diphenylamine and an unactivated aryl halide with catalysis by some form of copper (metal, alloy, copper(I) or -(II) salt) in the presence of added base. The reaction is noted for its capricious nature and sensitivity to catalyst type. Strongly aggressive conditions involving

high temperature and extended reaction times are generally needed to secure at best moderate yields. Although halide reduction and homocoupling often negatively impact yields, control of the substitution pattern of all three rings is afforded. In a variant, bis(arylation) of a substituted aniline with 2 equiv of an aromatic halide allows access, depending on reactants, to products in which two or perhaps all three of the aromatic ring are identically substituted. Yields tend to be substantially poorer in these cases.

Attempts have been made to moderate the harshness of the reaction conditions. Fréchet and Gauthier reported that crown ethers induce rate accelerations and improve yields in certain Ullmann condensations.<sup>7</sup> The procedure, however, does not obviate the requirement for high temperature, and the long reaction times (15 h in the best case) make it unattractive for large scale industrial applications. Catalyst effects still persist, as is common when potassium carbonate is used as base, and the high cost of the crown would necessitate its recovery and reuse.

An area of research showing rapid progress is the application of transition metal catalysis to the formation of the aromatic carbon–nitrogen bond. Palladium-catalyzed aromatic amination reactions, as described by both Buchwald and Hartwig,<sup>8</sup> have created interesting new possibilities. Aromatic amines with a wide structural variation have been successfully synthesized under exceptionally mild reaction conditions. It is as yet premature to judge whether this chemistry will supplant the Ullmann condensation as the robustness and economics of a method requiring noble metal catalysis in a large scale industrial application requires demonstration, particularly in the commodity chemicals arena.<sup>9</sup>

**Background.** Important information on the kinetics of amine Ullmann condensations is available. The reaction is zero order in amine with the rate-determining step being the loss of halide from the substrate with the reactivity order being  $I > Br > Cl \gg F$ .<sup>6a,10</sup> Detailed kinetics have proven difficult to extract under the heterogeneous conditions normally employed. Paine, by studying a homogeneous but synthetically nonviable reaction surrogate, concluded that only copper(I) states actively participate as catalysts regardless of the oxidation level of the added copper. Additionally, despite the apparent heterogeneity of the reaction, the nucleophilic species is posited to be a soluble amine cuprate.<sup>11</sup>

Rate accelerations have been reported in the related, industrially important Ullmann condensation of phenols leading to diphenyl ethers. Careful work by Weingarten clearly demonstrated that impurities present in his reaction solvent, diglyme, imparted enhanced catalytic activity. Such activity was destroyed by LAH treatment

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(1) Borsenberger, P. M.; Weiss, D. S. *Organic Photoreceptors for Imaging Systems*; Marcel Dekker: New York, 1993.

(2) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449.

(3) (a) Facci, J. S.; Stolka, M. *Philos. Mag. B* **1986**, *54*, 1. (b) Abkowitz, M.; Bassler, H.; Stolka, M. *Philos. Mag. B* **1991**, *63*, 201.

(4) (a) Thelekkat, M.; Fink, R.; Haubner, F.; Schmidt, H.-W. *Macromol. Symp.* **1997**, *125*, 157–164. (b) Tamato, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077–1085. (c) Tanaka, H.; Tokito, S.; Taga, Y.; Okada A. *Chem. Commun.* **1996**, 2175–2176. (d) Chen, C.; Shi, J.; Tang, C. W. *Macromol. Symp.* **1997**, *125*, 1–48. (e) Tsutsui, T. *MRS Bull.* **1997**, *39*. (f) Bellmann, E.; Shaheen, S.; Thayumanavan, S.; Barlow, S.; Grubbs, R.; Marder, S.; Kippelen, B.; Peyghambarian, N. *Chem. Mater.* **1998**, *10*, 1668–1676.

(5) Miller, R. D.; Lee, V. Y.; Twieg, R. J. *Chem. Commun.* **1995**, 245–246.

(6) For general reviews of Ullmann condensation chemistry, see: (a) Lindley, J. *Tetrahedron* **1984**, *40*, 1433–1456. (b) Fanta, P. E. *Synthesis* **1974**, 1–21. (c) Bacon, R. G. R.; Hill, H. A. O. *Q. Rev.* **1965**, *19*, 95–125.

(7) Gauthier, S.; Fréchet, J. M. J. *Synthesis* **1987**, 383–385.

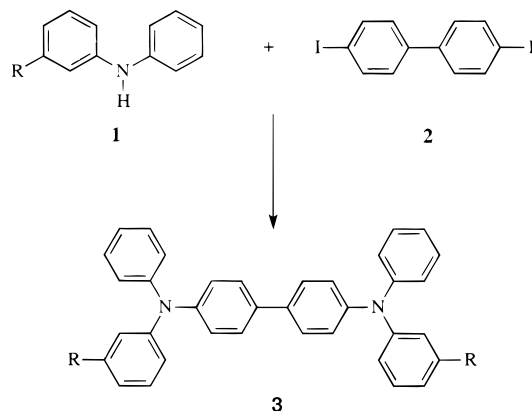
(8) For leading references, see: (a) Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2046–2067.

(9) (a) Beller, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1316–1317.

(b) Reaction modifications with a view to accommodating large scale work have recently been described, see: Wüllner, G.; Jänsch, H.; Kannenberg, S.; Schubert, F.; Boche, G. *Chem. Commun.* **1998**, 1509–1510.

(10) Weingarten, H. *J. Org. Chem.* **1964**, *29*, 977–978.

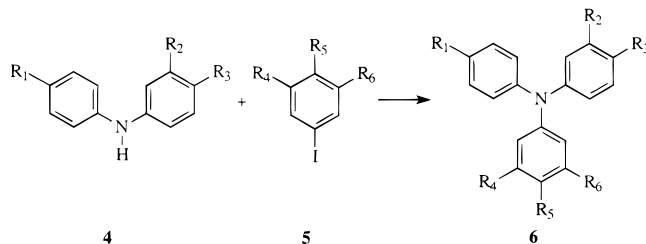
(11) Paine, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1496–1502.

**Table 1. Ligated Catalysis of the Ullmann Condensation. Double Arylation**

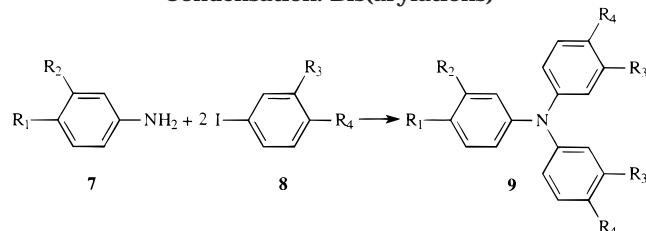
entry	R	T (°C)	time (h)	% yield
<b>3a</b>	Me	125	5	85
<b>3b</b>	OMe	130	5	75

and distillation of the solvent.<sup>12</sup> Subsequently, this impurity was identified as a diester and several related simple diesters were found to invoke this efficacious effect. Paradoxically, other structurally similar diesters produced no such effect. A mechanistic rationale for this phenomenon was not identified but increased catalyst solubility was suspected and catalyst competency appeared to be related to the ligating ability of the ligand. Bryant<sup>13</sup> and Capdevielle<sup>14</sup> have extended the usefulness of the effect to the copper(I)-catalyzed methanolysis of aryl bromides to form methyl aryl ethers. In these instances, the most effective additives were found to be simple alkyl formates or esters. Here the effect was explained as being a stabilization and solubilization of the copper(I) catalyst. Unfortunately, the direct transfer of such approaches to the amine Ullmann condensation is not possible since the presence of large excesses of hydroxide together with the production of water of reaction would ensure the rapid hydrolytic destruction of these ligands. A subsequent patent reported that the copper(I) ligand, 8-hydroxyquinoline, produced a similar effect in aromatic ether formation, but in our hands, when tested under typical conditions no rate accelerations in triarylamine formation were produced.<sup>15</sup> This approach did suggest that other such ligands should be examined. We report herein reaction conditions which permit the amine Ullmann condensation to be conducted under substantially milder conditions than heretofore possible while suffering no rate or yield penalties.<sup>16</sup>

**Results and Discussion.** A group of hydrolytically stable ligands known to coordinate copper(I) salts was selected for study, and their effect on reaction rate was examined in a standard double Ullmann condensation to produce the archetypal hole transporting small molecule TPD (Table 1, entry 3a). The ligands comprised alkyl and aryl monodentate and bidentate nitrogen-

**Table 2. Ligated Catalysis of Ullmann Condensations. Monoarylation**

entry	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	T (°C)	time (h)	yield (%)
<b>6a</b>	H	H	H	Me	H	Me	125	6	85
<b>6b</b>	H	OMe	H	H	Me	H	125	6	61
<b>6c</b>	Ph	Me	Me	OMe	H	H	125	5	80
<b>6d</b>	Ph	Me	Me	H	Ph	H	125	5	78
<b>6e</b>	Ph	Me	Me	Me	Me	H	125	5	80
<b>6f</b>	Ph	Me	Me	H	H	H	125	5	80
<b>6g</b>	H	Me	H	H	<i>p</i> -BrPh	H	125	5	80

**Table 3. Ligated Catalysis of the Ullmann Condensation. Bis(arylations)**

entry	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	T (°C)	time (h)	% yield
<b>9a</b>	H	H	H	Me	125	5	73
<b>9b</b>	Br	H	H	Me	125	5	85
<b>9c</b>	Br	H	Me	Me	125	5	83
<b>9d</b>	Me	Me	Me	Me	127	22	70
<b>9e</b>	Ph	H	Me	Me	130	4	83
<b>9f</b>	Br	H	H	Br	130	5	73

containing compounds added in an equimolar amount with respect to cuprous chloride (3.5 mol % catalyst based on the limiting reagent) and encompassed a broad structural range (1,10-phenanthroline, pyridine, 2,2'-dipyridyl, racemic sparteine, 1,8-bis(dimethylamino)naphthalene, 8-hydroxyquinoline, and *N,N,N,N*-tetramethylethylenediamine). Of the seven ligands investigated, 1,10-phenanthroline produced significant rate accelerations. That the rate acceleration is real and large is demonstrated by the fact that the modified reaction reaches completion in 3 h in refluxing toluene at 125 °C. This is a temperature significantly lower and a reaction time shorter than the 6 h at 160 °C normally required. At this lowered temperature, reactions containing no copper ligating reagent or any of the nonactive ligands produce a complex mixture of starting materials, mono-substituted intermediate, and product. Extending the reaction time was ineffective in improving conversion to product in these cases.

Having observed rate accelerations with the addition of 1,10-phenanthroline, we wished to establish the scope and limitations of the new catalyst. This was done for three distinct types of Ullmann condensation: sequential double arylations, monoarylation, and bis(arylations). These results are shown in Tables 1, 2, and 3, respectively. Yields are good and reaction times rapid for almost all of the entries. Of particular interest are the yields reported in Table 3 for bis(arylations). This type of reaction generally affords indifferent yields with tradi-

(12) Weingarten, H. *J. Org. Chem.* **1964**, *29*, 3624–3627.

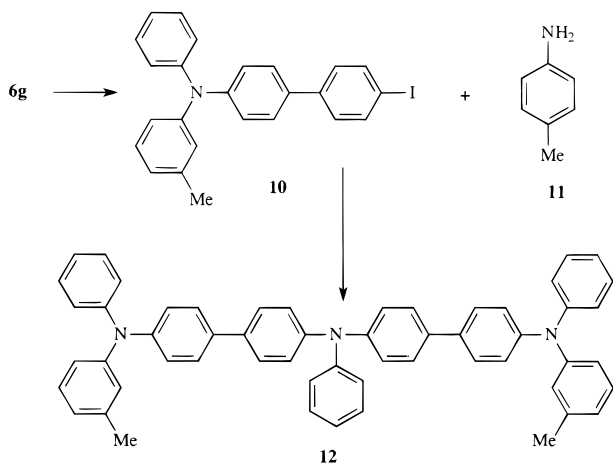
(13) Bryant, R. J. Brit. UK Pat. Appl. GB 2,089,672, 1982 (*Chem. Abstr.* **1982**, *97*, 215738).

(14) Capdevielle, P.; Maumy, M. *Tetrahedron Lett.* **1993**, *34*, 1007–1010.

(15) Jpn. Kokai Tokkyo Koho, JP 59,134,743 (to Toray Industries Inc.) (*Chem. Abstr.* **1984**, *101*, 191333x).

(16) Rights to the commercial uses of this catalyst are held by Xerox Corporation under U.S. patents 5,648,539; 5,648,542; 5,654,482; 5,705,697; 5,723,669; and 5,723,671 and pending European and Japanese equivalents.

### Scheme 1. Synthesis of the Polyarylamine Derivative



tional catalysis. Catalyst ligation thus provides a superior method for the direct synthesis of triarylamines from monoaryl precursors. Comparison of the yields for the identical compounds **6e** and **9e** illustrates this point.

The ligated catalyst with its attendant mild reaction conditions permits one to exploit the reactivity differences exhibited by the leaving group halides. Under high-temperature Ullmann condensation conditions with conventional catalysis, both bromides and iodides possess sufficient reactivity to be preparatively useful. It is therefore difficult to use reaction partners which contain both halides if a regioselective reaction is required. At the low temperatures enabled by the ligated catalyst, bromides are no longer reactive and only iodides are effective leaving groups. This principle is illustrated in the tables where brominated triarylamines can be conveniently prepared from precursors which contain bromine in the nucleophilic species (**9b**, **9c**), the nucleofugic partner (**6g**), or both (**9f**). This protocol can be utilized to advantage in the synthesis of more complex molecular architectures, an example of which is shown in Scheme 1. Here two different types of Ullmann condensation are used in conjunction to rapidly assemble in good overall yield a complex starburst type triarylamine. Compound **6g** is prepared by monoarylation of 4-bromo-4'-iodobiphenyl by 3-methyldiphenylamine via selective displacement of iodide. Butyllithium-mediated exchange of bromine affords the substrate **10** for the final bis(arylation) reaction. Ullmann condensation with half an equivalent of *p*-toluidine then secures the desired triarylamine **12** possessing two biphenyl residues.

It has been subsequently demonstrated that copper(II) salts may also be used as catalysts. In all cases examined, cuprous chloride may be replaced with cupric acetate monohydrate with comparable results. This is useful in large-scale work where the corrosive effect of chloride on stainless steel is a concern and the utilization of the more benign acetate counterion is advantageous. For copper catalysts which are not complexed by 1,10-phenanthroline, such as cuprous oxide, no rate acceleration is observed.

It is also possible to carry out Ullmann condensations at even lower temperatures than reported above. Reactions were examined in Isopar C, a commercially available branched chain hydrocarbon solvent which boils over the range 98–106 °C. At this significantly lower temperature, rates become slower but reactions still reach

completion within 24 h in the cases examined. This is a remarkable result since this temperature is lower than the liquefaction point of KOH ( $\approx 120$  °C) and the base remains in a solid flake form as opposed to a viscous lower layer. When reaction times are not an issue, this represents the mildest conditions yet reported for an Ullmann amine condensation on an unactivated substrate.

The finding of this telling effect engendered by 1,10-phenanthroline is at first puzzling. It is reminiscent of the work of Weingarten on aromatic ethers in that only certain ligands of a particular class show these special effects.<sup>12</sup> Both that and the current work are probably best described as instances of ligand-accelerated catalysis. As defined by Sharpless, the phenomenon arises when the addition of a ligand increases the rate of an already existing catalytic transformation.<sup>17</sup> Both the basic and ligand-assisted process operate simultaneously and in competition with one another. The distinguishing features of ligand-accelerated catalysis are (1) such effects are relatively uncommon and (2) no design rules for evoking the phenomenon exist. The fact that only one of the ligands examined produced substantial acceleration affirms the first point. The rationalization of this result is made difficult since the exact structure of the catalytically active species is not known with certitude. The rate accelerations observed on phenanthroline ligation most likely result from the synergistic interplay of such variables as ligand solubility, metal binding affinity, ligand  $\pi/\sigma$  acceptor capability, the hybridization state and geometry of the coordinating orbitals, enhanced electron density on the metal, and the bite angle of coordination. All contribute to a successful outcome. It has also been suggested that in systems showing such effects, van der Waals attraction between substrate and catalyst may reduce the entropic cost of the reaction.<sup>18</sup>

Whatever the cause, the present work clearly demonstrates the subtlety of this effect. Even closely related ligands such as 2,2'-bipyridyl and 1,10-phenanthroline produce dramatically different results. One might reasonably expect some degree of rate acceleration from 2,2'-bipyridyl even though rotation about the aryl-aryl bond would be expected to reduce binding efficiency. A major difference however is the increased central bond length of the bipyridine which manifests itself as a widened ligand bite angle, and this apparently negates the effect.

**Conclusion.** We have demonstrated that the addition of the copper-binding ligand 1,10-phenanthroline to traditional Ullmann condensation catalysts dramatically moderates the severity of the conditions required to effect these reactions. Reactions are rapid and clean at temperatures of 50–100 °C lower than was heretofore required. The new catalyst system is particularly well suited to bis(arylation) reactions, which have been viewed as being more difficult, as well as for large scale work.

### Experimental Section

**General Methods.** All reactions were carried out under an argon atmosphere in oven-dried glassware. Aryl iodide, aromatic amines, and copper compounds were purchased from commercial sources except where noted and were utilized without further

(17) Berrisford, D. J.; Bolm, C.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1059–1070.

(18) Corey, E. J.; Noe, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 11038–11053.

purification. Yields in the tables refer to isolated yields of compounds estimated to be greater than 99% pure as determined by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) as well as reversed phase HPLC. Elemental analyses were conducted in-house on samples purified by hot column chromatography using the technique described by Kauffman.<sup>19</sup> Melting points were recorded on a TA Instruments Model 2910 differential scanning calorimeter and are reported as peak maximum values. Experimental procedures are illustrated by the following typical reactions.

**Method A. General Procedure for Monoarylation Ullmann Condensations.** To a 500 mL round-bottomed flask containing 70 mL of toluene equipped with a mechanical stirrer, an argon gas purge, and a Dean–Stark trap under a reflux condenser were added in the following order while maintaining good stirring 110 mmol of the diarylamine, 110 mmol of the aryl iodide, 4 mmol of 1,10-phenanthroline, 4 mmol of cuprous chloride, and 860 mmol of potassium hydroxide flakes.<sup>20</sup> The reaction mixture was rapidly heated over the course of 30 min to the reflux temperature of 125 °C and maintained at that temperature until qualitative HPLC analysis revealed the conversion to be substantially complete. Usually 4–5 h are sufficient. The reaction mixture was cooled to 75 °C and partitioned between 200 mL of toluene and 150 mL of deionized water. After washing with an additional amount of water, the organic phase was decolorized by slurry treating it over 3 h at 75 °C with 36 g of Filtrol-24,<sup>21</sup> an acid leached bentonite clay, and 24 g of Alcoa CG-20 alumina. The adsorbents were then removed by hot filtration, and the solvent was removed by rotary evaporation. The product was subjected to further purification by hot column chromatography with heptane elution.

**Method B. General Procedure for Double Arylation Ullmann Condensations.** These reactions were run in an identical manner as described in method A with the exception that a 10% excess of 2 equiv of the amine component with respect to the iodide was employed. A reaction temperature of 125 °C was maintained until HPLC analysis showed qualitative completion. Workup proceeded as before.

**Method C. General Procedure for Bis(arylation) Ullmann Condensations.** These reactions were run in an identical manner as described in method A with the exception that a 10% excess of 2 equiv of the iodide component with respect to the amine was utilized. Again, a reaction temperature of 125 °C was maintained until HPLC analysis indicated substantial qualitative completion. Workup proceeded as before.

***N,N*-Diphenyl-*N,N*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (3a):** method B, white solid; mp 169.1 °C;  $^1\text{H}$  NMR 2.30 (s, Me), 6.87–7.26 (m, aromatic);  $^{13}\text{C}$  NMR 21.83, 122.05, 123.02, 124.22, 124.42, 124.60, 125.50, 127.63, 129.46, 129.59, 134.99, 139.52, 147.20, 148.05, 148.21. Anal. Calcd for  $\text{C}_{38}\text{H}_{32}\text{N}_2$ : C, 88.63; H, 6.24; N, 5.42. Found: C, 88.49; H, 6.32; N, 5.57.

***N,N*-Diphenyl-*N,N*-bis(3-methoxyphenyl)-[1,1'-biphenyl]-4,4'-diamine (3b):** method B, white solid; mp 128.5 °C;  $^1\text{H}$  NMR 3.72 (s, OMe), 6.55–7.02 (m, aromatic);  $^{13}\text{C}$  NMR 55.64, 108.54, 110.31, 116.98, 123.38, 124.58, 124.96, 127.69, 129.63, 130.21, 135.29, 147.02, 147.99, 149.40, 160.89. Anal. Calcd for  $\text{C}_{38}\text{H}_{32}\text{N}_2\text{O}_2$ : C, 83.18; H, 5.88; N, 5.11; O, 5.83. Found: C, 83.65; H, 5.68; N, 5.08; O, 5.72.

***N,N*-Diphenyl-3,5-dimethylbenzenamine (6a):** method A, white solid; mp 136.5 °C (lit.<sup>22</sup> mp 130–132 °C);  $^1\text{H}$  NMR 2.24 (6H s, Me), 6.64–7.28 (aromatic);  $^{13}\text{C}$  NMR 21.68, 122.72, 122.76, 124.40, 125.23, 129.48, 139.23, 148.11, 148.45. Anal. Calcd for  $\text{C}_{20}\text{H}_{19}\text{N}$ : C, 87.87; H, 7.01; N, 5.12. Found: C, 88.23; H, 7.01; N, 5.02.

***N*-Phenyl-*N*-(3-methoxyphenyl)-4-methylbenzenamine (6b):** method A, white solid; mp 66.6 °C;  $^1\text{H}$  NMR 2.30 (s, Me), 3.68 (s, OMe), 6.48–7.28 (aromatic);  $^{13}\text{C}$  NMR 21.27, 55.61, 107.95, 109.66, 116.34, 122.89, 124.40, 125.60, 129.55, 130.13,

130.36, 133.32, 145.58, 148.35, 149.79, 160.87. Anal. Calcd for  $\text{C}_{20}\text{H}_{19}\text{NO}$ : C, 83.01; H, 6.62; N, 4.84; O, 5.53. Found: C, 82.83; H, 6.76; N, 4.69; O, 5.72.

***N*-(4-Biphenyl)-*N*-(3-methoxyphenyl)-3,4-dimethylbenzenamine (6c):** method A, white solid; mp 104.7 °C;  $^1\text{H}$  NMR 2.28 (s, Me), 2.35 (s, Me), 3.79 (s, OMe), 6.61–7.69 (aromatic);  $^{13}\text{C}$  NMR 19.65, 20.43, 55.68, 108.04, 109.87, 116.59, 123.49, 124.04, 127.17, 127.19, 128.37, 129.17, 130.18, 130.83, 130.93, 132.49, 135.13, 138.10, 141.16, 145.59, 147.73, 149.64, 160.85. Anal. Calcd for  $\text{C}_{27}\text{H}_{25}\text{NO}$ : C, 85.45; H, 6.64; N, 3.69; O, 4.22. Found: C, 85.01; H, 6.82; N, 3.84; O, 4.33.

***N,N*-Bis(4-biphenyl)-3,4-dimethylbenzenamine (6d):** method A, white solid; mp 221.9 °C;  $^1\text{H}$  NMR 2.20 (s, Me), 2.33 (s, Me), 6.93–7.33 (aromatic);  $^{13}\text{C}$  NMR (saturated solution) 19.17, 19.84, 123.02, 123.56, 126.61, 126.71, 126.72, 127.69, 128.71, 130.54, 132.09, 134.79, 137.73, 140.68, 145.13, 147.23. Anal. Calcd for  $\text{C}_{32}\text{H}_{27}\text{N}$ : C, 90.31; H, 6.39; N, 3.29. Found: C, 90.51; H, 6.46; N, 3.23.

***N,N*-Bis(3,4-dimethylphenyl)-4-biphenylamine (6e):** method A, white solid; mp 114.3 °C;  $^1\text{H}$  NMR 2.21 (s, Me), 2.26 (s, Me), 6.88–7.43 (m, aromatic);  $^{13}\text{C}$  NMR (saturated solution) 19.12, 19.84, 122.35, 122.43, 126.04, 126.49, 126.51, 127.47, 128.64, 130.33, 131.28, 133.72, 137.45, 140.76, 145.49, 147.75. Anal. Calcd for  $\text{C}_{28}\text{H}_{27}\text{N}$ : C, 89.08; H, 7.21; N, 3.71. Found: C, 88.80; H, 7.13; N, 3.82.

***N*-Phenyl-*N*-(3,4-dimethylphenyl)-4-biphenylamine (6f):** method A, white solid; mp 116.7 °C;  $^1\text{H}$  NMR 2.22 (s, Me), 2.27 (s, Me), 6.90–7.28 (m, aromatic);  $^{13}\text{C}$  NMR 19.57, 20.27, 122.75, 123.25, 123.62, 124.23, 126.95, 127.00, 127.07, 128.03, 129.10, 129.53, 130.86, 132.29, 134.88, 138.07, 141.13, 145.68, 147.83, 148.29. Anal. Calcd for  $\text{C}_{26}\text{H}_{23}\text{N}$ : C, 89.36; H, 6.63; N, 4.01. Found: C, 89.43; H, 6.32; N, 4.01.

***N*-(3-Methylphenyl)-*N*-phenyl-4-bromo-1,1'-biphenyl-4'-amine (6g):** method C, white solid; mp 142.0 °C;  $^1\text{H}$  NMR 2.27 (s, Me), 6.88 (t,  $J = 7.2$  Hz, aromatic), 6.95 (m, aromatic), 7.02 (t,  $J = 7.2$  Hz, aromatic), 7.08–7.29 (m, aromatic), 7.41 (d,  $J = 8.7$  Hz, aromatic), 7.42 (d,  $J = 8.7$  Hz, aromatic), 7.51 (d,  $J = 8.4$  Hz, aromatic).  $^{13}\text{C}$  NMR 21.84, 121.26, 122.33, 123.37, 123.98, 124.56, 124.89, 125.77, 127.92, 128.58, 129.56, 129.69, 132.22, 133.82, 139.64, 140.00, 147.86, 148.03, 148.06. Anal. Calcd for  $\text{C}_{25}\text{H}_{20}\text{BrN}$ : C, 72.47; H, 4.87; N, 3.38. Found: C, 72.40; H, 4.90; N, 3.34.

***N,N*-Bis(4-methylphenyl)benzenamine (9a):** method C, white solid; mp 108.1 °C (lit.<sup>23</sup> mp 108 °C);  $^1\text{H}$  NMR 2.29 (s, Me), 6.88–7.15 (m, aromatic);  $^{13}\text{C}$  NMR 20.78, 121.70, 122.97, 124.46, 129.01, 129.82, 132.28, 145.48, 148.29. Anal. Calcd for  $\text{C}_{20}\text{H}_{19}\text{N}$ : C, 87.87; H, 7.01; N, 5.12. Found: C, 87.60; H, 7.18; N, 5.04.

***N,N*-Bis(4-methylphenyl)-4-bromobenzenamine (9b):** method C, white solid; mp 104.3 °C (lit.<sup>24</sup> mp 103.5–104.5 °C).

***N,N*-Bis(3,4-dimethylphenyl)-4-bromobenzenamine (9c):** method C, light tan powder; mp 125.3 °C;  $^1\text{H}$  NMR 2.16 (s, Me), 2.22 (s, Me), 6.78–7.22 (m, aromatic);  $^{13}\text{C}$  NMR 19.50, 20.22, 113.62, 122.73, 124.15, 126.43, 130.82, 132.04, 132.20, 138.00, 145.62, 148.03. Anal. Calcd for  $\text{C}_{22}\text{H}_{22}\text{BrN}$ : C, 69.48; H, 5.83; Br 21.01; N, 3.68. Found: C, 69.38; H, 5.87; Br, 20.97; N, 3.78.

***N,N,N*-Tris(3,4-dimethylphenyl)amine (9d):** method C, light yellow solid; mp 133.6 °C;  $^1\text{H}$  NMR 2.15 (s, Me), 2.25 (s, Me), 6.75–7.25 (m, aromatic);  $^{13}\text{C}$  NMR 19.07, 19.85, 121.51, 125.23, 130.16, 130.33, 137.23, 146.14. Anal. Calcd for  $\text{C}_{24}\text{H}_{27}\text{N}$ : C, 87.49; H, 8.26; N, 4.25. Found: C, 87.04; H, 7.82; N, 4.12.

***N,N*-Bis(3,4-dimethylphenyl)-4-biphenylamine (9e):** method C, white solid; mp 114.1 °C;  $^1\text{H}$  NMR 2.21 (s, Me), 2.26 (s, Me), 6.88–7.43 (m, aromatic);  $^{13}\text{C}$  NMR (saturated solution) 19.12, 19.84, 122.35, 122.43, 126.04, 126.49, 126.51, 127.47, 128.64, 130.33, 131.28, 133.72, 137.45, 140.76, 145.49, 147.75. Anal. Calcd for  $\text{C}_{28}\text{H}_{27}\text{N}$ : C, 89.08; H, 7.21; N, 3.71. Found: C, 88.91; H, 7.15; N, 3.89.

***N,N,N*-Tris(4-bromophenyl)amine (9f):** method C, white solid; mp 143.8 °C (lit.<sup>25</sup> mp 144.5–146.5 °C).

(19) Kauffman, J. M.; Bjorkman, C. O. *J. Chem. Educ.* **1976**, *53*, 33.

(20) The flake form of KOH is preferred because, although it is slightly less pure than the pellet form, it contains less water.

(21) Available from Harshaw/Filtrol Partnership, Cleveland, OH.

(22) Haga, K.; Oohashi, M.; Kanfko, R. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1586–1590.

(23) Sato, N.; Yoshikawa, M. *Chem. Phys.* **1992**, *160*, 289–297.

(24) Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055–2065.

(25) Baker, N.; Doherty, W.; Kelley, W.; Newmeyer, W.; Rogers, J.; Spalding, R.; Walter, R. *J. Org. Chem.* **1965**, *30*, 3714–3718.

***N*-(3-Methylphenyl)-*N*-phenyl-4-iodo-1,1'-biphenyl-4'-amine (10).** This precursor was derived from iodine exchange of *N*-(3-methylphenyl)-*N*-phenyl-4-bromo-1,1'-biphenyl-4'-amine (**6g**). To an ice bath cooled suspension of compound **6g** (4.12 g, 10.0 mmol) in anhydrous ether (100 mL) was added dropwise 4.3 mL (10.75 mmol) of 2.5 M *n*-butyllithium solution in cyclohexane. After completion of the addition, the reaction mixture was warmed to room temperature and stirred for 1.0 h. The mixture was then quenched with iodine powder (2.5 g, 10.0 mmol) at 0 °C. The resultant dark solution was treated with an aqueous sodium metabisulfite solution to remove excess iodine. After distillation of the solvent, the precipitated solid was collected by filtration and washed with water and methanol. The crude product was further purified by recrystallization from toluene: light yellow solid; mp 161.8 °C; <sup>1</sup>H NMR 2.31 (s, Me), 6.92 (t, *J* = 7.56 Hz, aromatic), 6.99 (d, *J* = 5.4 Hz, aromatic), 7.07 (t, *J* = 7.2 Hz, aromatic), 7.13–7.33 (m, aromatic), 7.34 (d, *J* = 8.4 Hz, aromatic), 7.44 (d, *J* = 8.7 Hz, aromatic), 7.76 (d, *J* = 8.4 Hz, aromatic); <sup>13</sup>C NMR 21.85, 92.66, 122.36, 123.39, 123.94, 124.57, 124.91, 125.79, 127.87, 128.87, 129.56, 129.69, 133.84, 138.19, 139.64, 140.59, 147.85, 148.02, 148.12. Anal.

Calcd for C<sub>25</sub>H<sub>20</sub>IN: C, 65.09; H, 4.37; N, 3.04. Found: C, 65.58; H, 4.76; N, 2.88.

***N,N*-Bis[4'-(*N*-phenyl-*N*-(3-methylphenyl)amino)-1,1'-biphenyl-4-yl]-4-methylbenzeneamine (12):** method (C); light yellow powder; amorphous with no distinct mp; <sup>1</sup>H NMR 2.33 (s, Me), 2.39 (s, Me), 6.91 (d, *J* = 7.5 Hz, aromatic), 6.97–7.04 (m, aromatic), 7.07 (d, *J* = 7.5 Hz, aromatic), 7.11–7.23 (m, aromatic), 7.31 (t, *J* = 7.8 Hz, aromatic), 7.50 (d, *J* = 8.4 Hz, aromatic); <sup>13</sup>C NMR 20.86, 21.41, 121.63, 122.60, 123.69, 123.80, 123.99, 124.17, 125.07, 127.20, 129.04, 129.17, 129.99, 132.96, 134.44, 134.57, 139.08, 146.75, 147.62, 137.78. Anal. Calcd for C<sub>57</sub>H<sub>47</sub>N<sub>3</sub>: C, 88.45; H, 6.12; N, 5.43. Found: C, 88.22; H, 6.32; N, 5.35.

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