Note

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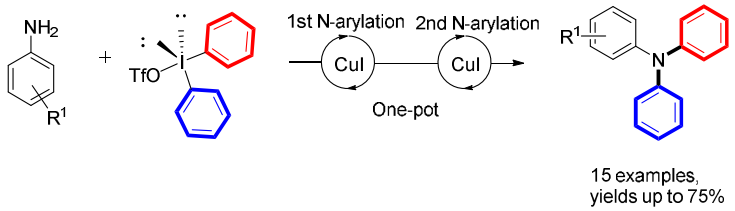
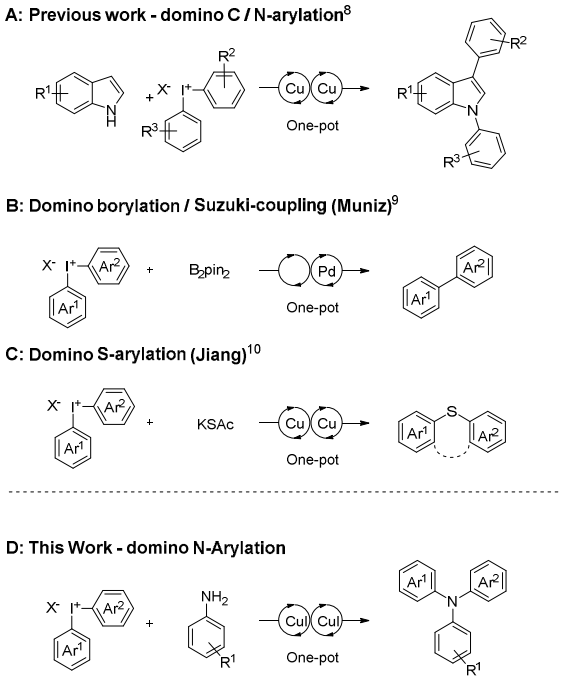


ABSTRACT: A one-pot domino N-arylation protocol is described using diaryliodonium reagents under copper catalysis. The reaction uses both aryl groups of the diaryliodonium reagent to generate triarylamines starting from simple anilines, representing an atom-economical preparation of an important class of organic material building blocks.

Diaryliodonium reagents, discovered in 1894,[1] have seen extensive development as electrophilic arylating agents for carbon and heteroatom nucleophiles.[2] They exhibit an appealing combination of stability, being crystalline solids that are easy to handle and store, and reactivity: Recent applications encompass aryl radical generation and utilization under photoredox catalysis,[3] metal-free arylation,[4] stereo-controlled arylation of double bonds,[5] aryne generation,[6] and extensive metal-catalyzed arylation processes.[7] Despite this extremely versatile portfolio of reactivity, almost all of these applications share the common drawback of generating at least one equivalent of an iodobenzene as a waste product – *ca.* 50% of the atomic mass of the iodonium reagent, depending on the counterion. Whilst the iodobenzene can in principle be separated from the product mixture and recycled, this poor atom economy is clearly an obstacle to wider application of these reagents on scale.

Scheme 1. Atom economical use of diaryliodonium reagents



We have addressed this atom economy issue by designing domino processes that can capture the aryl iodide side product in a second arylation step *in situ* (Scheme1A).[8] Copper-catalyzed C-H

arylation of indole with a diaryliodonium salt, for example, can be followed by N-arylation with the liberated aryl iodide to yield di-arylated products. This concept of domino arylation was subsequently demonstrated by Muñiz and co-workers who reported borylation / Suzuki-Miyaura coupling of diaryliodoniums and diboron reagents, [9] and further developed by Jiang and co-workers, who described double arylation of a sulfur salt under copper catalysis to produce diarylsulfides from diaryliodoniums (Scheme 1B and C).[10] Similar double-functionalization ideas have been explored with $ArI(OAc)_2$ by Dauban and co-workers, and alkynyl iodine(III) derivatives by the Yoshikai and Waser groups.[11] Collectively, these reports demonstrate that aryliodine(III) reagents can be used as powerful arene synthons in a variety of contexts, without having to sacrifice atom-economy. Indeed, by offering the possibility of two transformations from a single reagent, they create new opportunities for streamlined reaction design.

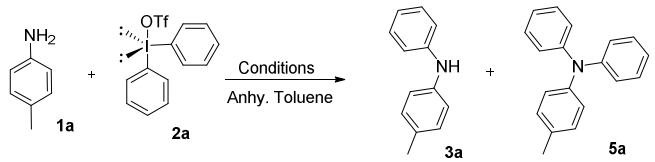
We were interested in further exploring the scope of domino applications of iodonium reagents, and chose to investigate the synthesis of triarylamines (Scheme 1D). Triarylamines are important building blocks in organic electronics, where their electron donor properties and characteristic propeller shapes have seen extensive application in the field of photovoltaics.[12] They are commonly accessed through variants of the Ullman coupling, using excess aryl halide and high temperatures to drive reaction to completion. Synthesis using a single equivalent of iodonium reagent would present an alternative, and very direct route, to their preparation. The groups of Nachtsheim and Wen have described the domino assembly of N-aryl carbazoles through reaction of anilines with cyclic iodonium salts, but the synthesis of triarylamines remains unexplored.[13]

Our initial trial reactions examined the coupling of *p*-toluidine, **1a**, with one equivalent of diphenyliodonium triflate, **2a**, to give either the mono or di-phenylated products **3a** and **5a** (Table 1), using toluene as the solvent of choice. It was apparent that monophenylation was straightforward under both copper-catalysis at room temperature and metal-free conditions at 130 ºC,[14] but there was no trace of the diphenylated product in either case (Entries 1 and 2). Despite the good yields of **3a**, a small amount of starting *p*-toluidine remained in each case, which would potentially complicate the second N-arylation. Switching to the organic base 2,6-di-*tert*-butylpyridine (DTBPY) gave complete conversion and improved the yield up to 86% (entry 3), and catalyst loading could be decreased to 2 mol% without loss of yield or conversion (entry 4).

With conditions established for high conversions of one equivalent of iodonium reagent in the first N-arylation, we turned to the two-step one-pot sequence. Copper-catalyzed N-arylation of weakly nucleophilic diarylamines usually requires a strong base and ligand system – we initially trialed an addition of CuI (10 mol%), bis(2,6-diisopropylphenyl)diaza-butadiene (DAB) [15] (12 mol%) and KO*t*Bu (2.2 equiv) to the reaction following initial N-phenylation, and stirring at 120 ^{o}C for 24 h. The desired *N*,*N*-diphenyl-4-methylaniline (**5a**) could be isolated in 35% yield, but significant amounts of unreacted **3a** (42%) were present (entry 5). Increased ligand loading did not improve the yield (entry 6), and a switch to Pd-catalysis for the second step was completely ineffective (entry 7). Using phenanthroline as ligand was initially unsuccessful when paired with K_3PO_4 (entry 8), but changing back to KO*t*Bu in the presence of 10% CuI, gave good conversions to the product **5a** (59% yield over two steps) along with a small amount of **3a** (Table 1, entry 10).

Having optimized conditions in hand for the one-pot double N-arylation sequence, we examined the diphenylation of various aniline substrates. A variety of substituents (*o*, *m*, *p*-methyl, *o*, *p*-fluoro, *p*-chloro, *p*-methoxy and *m*-phenyl) were well-tolerated to give substituted triarylamines in good yields over two steps (Table 2). As for *p*-toluidine, small amounts of the mono-arylated product were isolated as side products in some cases (Table 2, entries 1, 5-7, 9). Variously substituted diaryliodonium triflates were employed next, to study the scope of the reagent with aniline. Iodonium reagents containing *tert*-butyl, fluoro, chloro, methoxy, and methyl reacted smoothly to give the desired triarylamines in good yields (Table 3), with a single equivalent of iodonium reagent being employed in each case. In terms of limitations, anilines containing strong electron withdrawing groups (*e.g.* *p*-NO_2) were ineffective, being too deactivated to undergo the second arylation step. Attempts at selective aryl transfer using unsymmetrical diaryliodoniums were also unsuccessful under the current protocol, giving low yields of mixtures of N-arylated material in the first step.

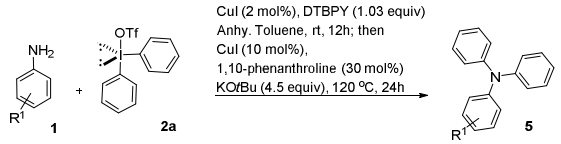
Table 1. Reaction optimization[a]

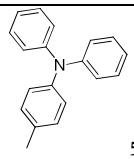
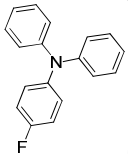
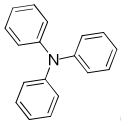
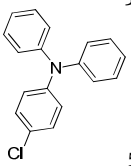
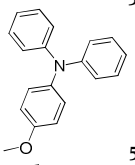
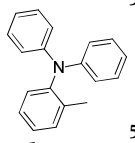
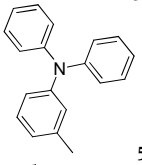
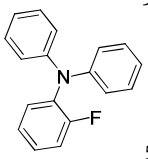
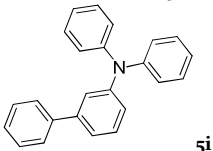


entry	catalyst (mol%)/ligand (mol%)	base (equiv)	temp (°C)	time (h)	yield (%) (**3a**:**5a**)
1	CuI (10)	K_2CO_3 (1.5)	rt	24	72:0[b]
2	-	-	130	24	68:0[b]
3	CuI (10)	DTBPY (1.1)	rt	24	86:0
4	CuI (2)	DTBPY (1.03)	rt	12	87:0
5	CuI (2); then CuI (10) and DAB (12)	DTBPY (1.03); then KO*t*Bu (2.2)	rt; then 120	12; then 24	42:35
6	CuI (2); then CuI (10) and DAB (30)	DTBPY (1.03); then KO*t*Bu (4)	rt; then 120	12; then 24	35:32
7	CuI (2); then $Pd(OAc)_2$ (4) and BINAP (8)	DTBPY (1.03); then KO*t*Bu (2.2)	rt; then 120	12; then 24	62:traces
8	CuI (2); then CuI (5) and 1,10-phenanthroline (6)	DTBPY (1.03); then K_3PO_4 (2.5)	rt; then 120	12; then 24	56:traces
9	CuI (2); then CuI (5) and 1,10-phenanthroline (6)	DTBPY (1.03); then KO*t*Bu (2.5)	rt; then 120	12; then 24	52:15
10	CuI (2); then CuI (10) and 1,10-phenanthroline (30)	DTBPY (1.03); then KO*t*Bu (4.5)	rt; then 120	12; then 24	15:59

[a]Unless otherwise noted, all reaction were run with **1a** (0.3 mmol) and **2a** (1.02 equiv) in a crimped cap glass vial under an inert atmosphere. [b] Incomplete conversion.

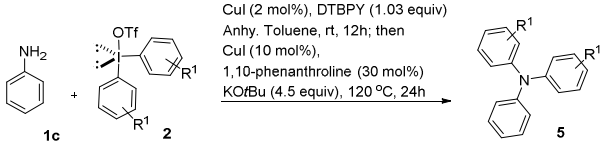
Table 2. Scope of aniline substrate[a]

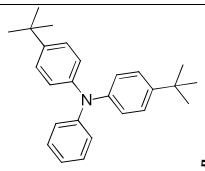
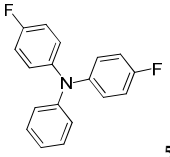
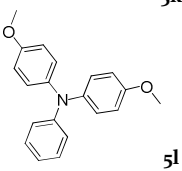
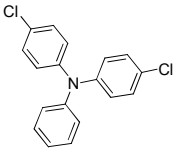
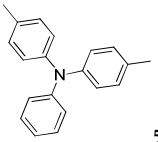
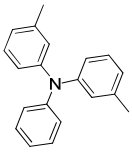


entry	R^1	product	% yield **5** (% yield **3**)
1	4-Me	 **5a**	59 (15)
2	4-F	 **5b**	53
3	H	 **5c**	66
4	4-Cl	 **5d**	59
5	4-OMe	 **5e**	44 (5)
6	2-Me	 **5f**	47 (17)
7	3-Me	 **5g**	68 (18)
8	2-F	 **5h**	40
9	3-Ph	 **5i**	47 (8)

[a]All reactions were run with **1** (0.98 mmol), **2a** (1 mmol) under optimized condition in a Schlenk flask under inert atmosphere.

Table 3. Scope of diaryliodonium reagents[a]

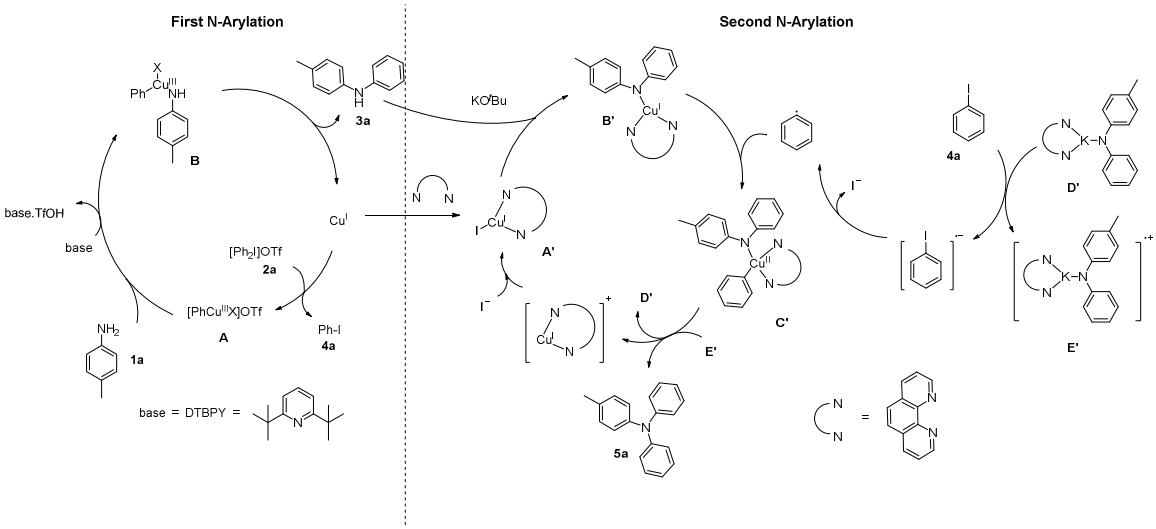


entry	R^1	product	% yield **5**
1	4-*t*Bu	 **5j**	69
2	4-F	 **5k**	65
3	4-OMe	 **5l**	75
4	4-Cl	 **5m**	48
5	4-Me	 **5n**	50
6	3-Me	 **5o**	54

[a]All reactions were run with **1c** (1 mmol), **2** (1.02 mmol) under optimized condition in a Schlenk flask under inert atmosphere.

A mechanistic pathway for the two step process is set out in Scheme 2, and likely involves a switch in mechanism between the first and second arylation steps. Whilst initial aniline arylation with the reactive diaryliodonium salt **2** proceeds through familiar Cu(I) / Cu(III) oxidative addition / reductive elimination processes,[16] Shyu and co-workers have implicated an electron transfer pathway for the second arylation of N-arylaniline **3** under KO*t*Bu and CuI / phenanthroline conditions.[17] Electron transfer from the potassium complex of phenanthroline and diarylamine **D'** to aryl iodide **4a** generates an aryl radical which can be trapped with the Cu(I)-phenanthroline diarylamine species **B'**. One electron oxidation by radical cation **E'** then enables reductive elimination to furnish the triarylamine **5a** and regenerate a Cu(I)-phenanthroline species to continue the catalytic cycle.

Scheme 2. Mechanistic pathway for one-pot double *N*-arylation.



In summary, we have developed a copper-catalyzed, one-pot, domino *N*-arylation sequence to generate triarylamines starting from simple anilines. The protocol uses both aryl groups of diaryliodonium reagents, from a single equivalent of reagent, and a common CuI catalyst. Further atom-economical transformations of aryliodine (III) reagents are under investigation in our laboratory.

EXPERIMENTAL

General Information. Nuclear Magnetic Resonance (NMR) spectra were recorded on 500 or 400 MHz Bruker NMR spectrometers in $CDCl_3$ at 298 K (unless stated otherwise). All chemical shift values are reported in parts per million (ppm) relative to the solvent signal (1H NMR: δ = 7.26 ppm. 13C NMR: δ = 77.16 ppm) with coupling constant (*J*) values reported in Hz. The notation of signals is: Proton: δ chemical shift in ppm (number of protons, multiplicity, *J* value(s), proton assignment). Carbon: δ chemical shift in ppm. Fluorine: δ chemical shift in ppm (Fluorine assignment). Splitting patterns are assigned s = singlet, b = broad, d = doublet, td = triplet of doublet, dt = doublet of triplet, t = triplet, q = quartet, bs = broad singlet. Reactions were carried out under N_2 using pre-dried glassware. All reaction were carried out in Schlenk flask and heated in oil baths with a thermocouple temperature control. Toluene, THF and dichloromethane were freshly distilled over sodium or calcium hydride and stored under N_2. Other solvents, unless otherwise stated, were purchased in reagent grade or anhydrous quality and used as received. Reagents were either purchased directly from commercial suppliers or

prepared according to literature procedures. TLC: Macherey-Nagel, TLC plates Alugram® Sil G/UV254. Detection under UV light at 254 nm. Chromatography: Separations were carried out on Biotage® Isolera Four flash chromatography instrument, with dryloading on Biotage SNAP Ultra columns using ethyl acetate / hexane (5 / 95 - 20 / 80 for triaryl amines, rising to 70 / 30 for elution of diarylamines when they were present). High Resolution Mass Spectrometry (HRMS) were recorded on Thermo Finnigan MAT95XP (ion trap). Melting points were determined using a Buchi M565 melting point apparatus. Iodonium salts **2a-g** were prepared according to literature procedures.[18]

Representative procedure for domino C-N bond formation: 4-Methyl-*N*,*N*-diphenylaniline (**5a**). To an oven dried 25 mL Schlenk flask containing a stir bar was added the 4-methylaniline (**1a**) (105 mg, 0.98 mmol, 1.00 equiv), CuI (3.8 mg, 0.02 mmol, 2 mol %) and diphenyliodonium triflate (**2a**) (430 mg, 1 mmol, 1.02 equiv). The Schlenk flask was sealed with a glass stopper. A vacuum / N_2 cycle was applied three times to the flask in order to ensure the removal of air. To this flask was added 2,6-di-*tert*-butylpyridine (227 µL, 1.0094 mmol, 1.03 equiv) via glass syringe (250 µL capacity) and dry Toluene (10 mL) via disposable syringe. The reaction mixture was allowed to stir at room temperature for 12 h. After confirming completion of the reaction by TLC (Hexane/diethyl ether – 8/2); CuI (18.7 mg, 0.098 mmol, 10 mol %), 1, 10-phenanthroline (53 mg, 0.294 mmol, 30 mol %) and KO^{t}Bu (495 mg, 4.41 mmol, 4.5 equiv) were added to the flask followed by N_2 flush to ensure the inert atmosphere and sealed again with the glass stopper. The flask-stopper joint was sealed by taflon tape and secured with a clip. The reaction mixture was then allowed to stir at 120 ^{o}C for 24 h. After confirming the product formation by TLC (Hexane/diethyl ether – 9/1) the reaction mixture was diluted with EtOAc (100 mL) and washed with water (50 mL) (In case of emulsion, it was passed through a celite plug). The organic layer was further washed with brine (50 mL) dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude was purified by Biotage flash chromatography instrument to yield 4-methyl-*N*,*N*-diphenylaniline **5a** (156 mg, 59% yield) as a white solid; MP 72-73 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.24 – 7.20 (m, 4H), 7.08 – 7.05 (m, 6H), 7.02 – 6.99 (m, 2H), 6.97 (tt, J = 7.3, 1.1 Hz, 2H), 2.32 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 148.0, 145.2, 132.7, 129.9, 129.1, 124.9, 123.6, 122.2, 20.8; HR-MS (EI) *m/z* calcd for $C_{19}H_{18}N$ $[M+H]^+$ 260.1439, found 260.1433; and 4-methyl-*N*-phenylaniline **3a** (27 mg, 15%) as a white solid; MP 88-90 ^{o}C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.24 (m, 2H), 7.12 – 7.10 (m, 2H), 7.04 – 7.02 (m, 4H), 6.90 (bt, J = 7.3, 1.0 Hz, 1H), 5.62 (bs, 1H), 2.33 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 143.9, 140.3, 130.9, 129.8, 129.3, 120.3, 118.9, 116.8, 20.7; HR-MS (EI) *m/z* calcd for $C_{13}H_{14}N$ $[M+H]^+$ 184.1126, found 184.1128.

4-Fluoro-*N*,*N*-diphenylaniline (**5b**). White solid (137 mg, 53%). MP 98-100 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.23 (m, 4H), 7.11 – 7.04 (m, 6H), 7.03 – 6.96 (m, 4H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 158.90 (d, J = 243 Hz), 147.8, 143.8 (d, J = 2.8 Hz), 129.2, 126.5 (d, J = 8.0 Hz), 123.5, 122.5, 116.0 (d, J = 22.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): -119.7 (s, 1F); HR-MS (EI) *m/z* calcd for $C_{18}H_{15}FN$ $[M+H]^+$ 264.1189, found 264.1180.

T**riphenylamine** (**5c**). White solid (158 mg, 66%). MP 127-129 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.24 (m, 6H), 7.13 – 7.09 (m, 6H), 7.05 – 7.0 (m, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 147.8, 129.2, 124.1, 122.6; HR-MS (EI) *m/z* calcd for $C_{18}H_{16}N$ $[M+H]^+$ 246.1283, found 246.1277.

4-Chloro-*N*,*N*-diphenylaniline (**5d**). White solid (162 mg, 59%). MP 108-109 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.24 (m, 4H), 7.20 – 7.17 (m, 2H), 7.08 – 7.06 (m, 4H), 7.03 – 6.99 (m, 4H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 147.4, 146.5, 129.3, 129.2, 127.3, 124.9, 124.3, 123.1; HR-MS (EI) *m/z* calcd for $C_{18}H_{15}ClN$ $[M+H]^+$ 280.0893, found 280.0885.

4-Methoxy-*N*,*N*-diphenylaniline (**5e**). White solid (120 mg, 44%). MP 102-103 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.23 – 7.19 (m, 4H), 7.08 – 7.06 (m, 2H), 7.05 – 7.03 (m, 4H), 6.94 (tt, J = 7.3, 1.1 Hz, 2H) 6.86 – 6.83 (m, 2H), 3.80 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 156.1, 148.1, 140.7, 129.0, 127.3, 122.8, 121.8, 114.7, 55.5; HR-MS (EI) *m/z* calcd for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1388, found 276.1380; and **4-Methoxy-*N*-phenylaniline** (**3e**). White solid (9 mg, 5%) Data of this compound were in accordance with those reported in literature.[14b]

2-Methyl-*N*,*N*-diphenylaniline (**5f**). White solid (120 mg, 47%). MP 57-59 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.15 (m, 8H), 7.02 – 6.98 (m, 4H), 6.97 – 6.93 (m, 2H), 2.07 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 147.4, 145.3, 136.5, 131.7, 129.6, 129.0, 127.3, 126.0, 121.5, 121.3, 18.6; HR-MS (EI) *m/z* calcd for $C_{19}H_{18}N$ $[M+H]^+$ 260.1439, found 260.1432; and **2-methyl-*N*-phenylaniline** (**3f**). White solid (30 mg, 17%). Data of this compound were in accordance with those reported in literature.[19]

3-Methyl-*N*,*N*-diphenylaniline (**5g**). White solid (173 mg, 68%). MP 67-68 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.24 (m, 4H), 7.16 (t, J = 7.7 Hz, 1H), 7.12 – 7.09 (m, 4H), 7.04 – 7.0 (m, 2H), 6.95 - 6.90 (m, 2H), 6.88 – 6.85 (m, 1H), 2.29 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 147.9, 147.7, 139.0, 129.1, 129.0, 124.9, 124.0, 123.7, 122.4, 121.5, 21.4; HR-MS (EI) *m/z* calcd for $C_{19}H_{18}N$ $[M+H]^+$ 260.1439, found 260.1434; and **3-methyl-*N*-phenylaniline** (**3g**). Oil (32 mg, 18%). Data of this compound were in acordance with those reported in literature.[20]

2-Fluoro-*N*,*N*-diphenylaniline (**5h**). White solid (105 mg, 40%). MP 70-72 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.24 (m, 4H), 7.22 – 7.19 (m, 1H), 7.17 – 7.09 (m, 3H), 7.06 – 7.0 (m, 6H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 158.4 (d, J = 250 Hz), 147.2, 134.6 (d, J = 10.3 Hz), 129.2 (d, J = 2Hz), 129.1, 126.0 (d, J = 7.9 Hz), 124.9 (d, J = 3.7 Hz), 122.4, 122.3, 117.1 (d, J = 19.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): -119.2 (m, 1F); HR-MS (EI) *m/z* calcd for $C_{18}H_{15}FN$ $[M+H]^+$ 264.1189, found 264.1184.

***N*,*N*-diphenyl-[1,1'-biphenyl]-3-amine** (**5i**). White solid (148 mg, 47%). MP 153-155 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.51 – 7.49 (m, 2H), 7.40 – 7.37 (m, 2H), 7.30 (bt, J = 1.9 Hz, 1H), 7.3 (t, J = 7.6 Hz, 2H), 7.28 – 7.23 (m, 5H), 7.15 – 7.13 (m, 4H) 7.07 – 7.01 (m, 3H); ^{13}C-NMR (101 MHz,

$CDCl_3$): δ 148.3, 147.7, 142.3, 140.9, 129.5, 129.2, 128.6, 127.3, 127.1, 124.2, 122.9, 122.8, 122.7, 121.5; HR-MS (EI) *m/z* calcd for $C_{24}H_{20}N$ $[M+H]^+$ 322.15996, found 322.1584.

***N*-phenyl-[1,1'-biphenyl]-3-amine** (**3i**). White solid (19 mg, 8%). MP 86-88 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.57 (m, 2H), 7.45 – 7.42 (m, 2H), 7.37 – 7.28 (m, 5H), 7.18 – 7.12 (m, 3H), 7.08 – 7.06 (m, 1H), 6.96 (tt, J = 7.3, 1.1 Hz, 1H), 5.78 (bs, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 143.5, 142.9, 142.5, 141.1, 129.7, 129.4, 128.7, 127.4, 127.1, 121.2, 120.0, 118.0, 116.6, 116.4; HR-MS (EI) *m/z* calcd for $C_{18}H_{16}N$ $[M+H]^+$ 246.1283, found 246.1277.

4-(*tert*-butyl)-*N*-(4-(*tert*-butyl)phenyl)-*N*-phenylaniline (**5j**). White solid (238 mg, 69%). MP 106-108 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.20 (m, 6H), 7.08 – 7.06 (m, 2H), 7.03 – 7.0 (m, 4H), 6.95 (tt, J = 7.3, 1.1 Hz, 1H), 1.31 (s, 18H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 148.1, 145.4, 145.1, 129.0, 125.9, 123.7, 123.3, 121.8, 34.2, 31.4; HR-MS (EI) *m/z* calcd for $C_{26}H_{32}N$ $[M+H]^+$ 358.2535, found 358.2529.

4-fluoro-*N*-(4-fluorophenyl)-*N*-phenylaniline (**5k**). White solid (183 mg, 65%). MP 92-93 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.24 (m, 2H), 7.07 – 6.96 (m, 11H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 158.8 (d, J = 243 Hz), 148.0, 143.9 (d, J = 2.8 Hz), 129.2, 125.9 (d, J = 7.8 Hz), 122.8, 122.3, 116.1 (d, J = 22.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): -119.8 (m, 2F); HR-MS (EI) *m/z* calcd for $C_{18}H_{14}F_2N$ $[M+H]^+$ 282.1094, found 282.1084.

4-methoxy-*N*-(4-methoxyphenyl)-*N*-phenylaniline (**5l**). White solid (229 mg, 75%). MP 104-106 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.19 – 7.16 (m, 2H), 7.06 – 7.03 (m, 4H), 6.95 – 6.93 (m, 2H), 6.88 – 6.85 (m, 1H), 6.84 – 6.81 (m, 4H), 3.80 (s, 6H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 155.6, 148.7, 141.1, 128.9, 126.4, 120.9, 120.5, 114.6, 55.5; HR-MS (EI) *m/z* calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$ 306.1494, found 306.1486.

4-chloro-*N*-(4-chlorophenyl)-*N*-phenylaniline (**5m**). White solid (150 mg, 48%). MP 76-78 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.25 (m, 2H), 7.21 – 7.18 (m, 4H), 7.06 – 7.03 (m, 3H), 7.0 – 6.97 (m, 4H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 147.0, 146.1, 129.5, 129.3, 127.8, 125.0, 124.4, 123.5; HR-MS (EI) *m/z* calcd for $C_{18}H_{14}Cl_2N$ $[M+H]^+$ 314.0503, found 314.0498.

4-methyl-*N*-phenyl-*N*-(*p*-tolyl)aniline (**5n**). White solid (137 mg, 50%). MP 113-114 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.22 – 7.18 (m, 2H), 7.06 – 7.02 (m, 6H), 7.0 – 6.98 (m, 4H), 6.94 (bt, J = 7.25 Hz, 1H), 2.31 (s, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 148.2, 145.4, 132.3, 129.8, 129.0, 124.4, 122.9, 121.6, 20.8; HR-MS (EI) *m/z* calcd for $C_{20}H_{20}N$ $[M+H]^+$ 274.1596, found 274.1591.

3-methyl-*N*-phenyl-*N*-(*m*-tolyl)aniline (**5o**). White solid (147 mg, 54%). MP 68-70 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.24 (m, 2H), 7.16 (t, J = 7.8 Hz, 2H) 7.10 – 7.08 (m, 2H), 7.01 (bt, J = 7.3 Hz, 1H), 6.94 (bs, 2H), 6.92 – 6.89 (m, 2H), 6.87 – 6.84 (m, 2H), 2.29 (s, 6H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 148.0, 147.8, 139.0, 129.1, 128.9, 124.9, 123.9, 123.5, 122.3, 121.4, 21.4; HR-MS (EI) *m/z* calcd for $C_{20}H_{20}N$ $[M+H]^+$ 274.1596, found 274.1588.

ASSOCIATED CONTENT

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Supporting information

Copies of ^{1}H and ^{13}C NMR spectra are available free of charge on the ACS Publications website.

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