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C–N Bond Formation Catalysed by CuI Bonded to Polyaniline Nanofiber

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Polyaniline nanofiber as a macroligand for the supported cuprous iodide catalyst (CuI-PANInf) has been developed for the coupling of aryl halides (including aryl chlorides) with aliphatic, aromatic, and N(H)-heterocyclic amines under ambient conditions (80 °C for aryl chlorides) has been developed. This simple and efficient method for coupling reactions is highly versatile, convenient, and also the catalyst can be used for several cycles with good-to-excellent yields.

Introduction

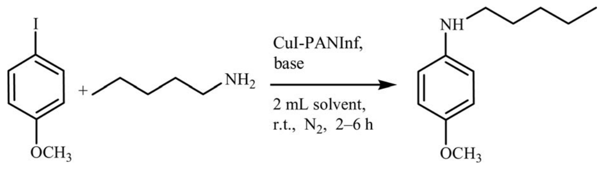
Transition-metal-catalyzed C–N bond formation is a powerful strategy for the synthesis of key intermediates in the biological, pharmaceutical, and material sciences. The most frequently used classical pathway for coupling reactions is copper-mediated Ullmann condensation of aryl halides with amines.[1] The contributions of Buchwald and Taillefer[2,3] and their co-workers to *N*-arylation reactions using copper in the presence of different ligands has generated huge interest in this area of research. The *N*-arylation of aliphatic amines has been reported in the presence of *N*-methylglycine or proline,[4] amino acids,[5] amino alcohols,[6] phosphoramidite,[7] oxime phosphane oxide,[8] and copper and CuI/*rac*-BINOL[9] at elevated temperatures.

Buchwald,[10] Fu, and Ding[11] and their co-workers have recently developed highly selective copper-catalyzed C–N coupling reactions at room temperature in the presence of ligands. Despite their synthetic elegance these coupling protocols suffer from serious limitations: (1) The nonreusability of the catalysts, (2) possible contamination of the product with metal, and (3) the use of toxic and/or expensive ancillary ligands. Therefore a simple, mild, and general procedure for the copper-catalyzed coupling of aliphatic, aromatic, and N(H)-heterocyclic amines with aryl halides (including aryl chlorides) under mild conditions would undeniably be a major advance.

One of the most promising solutions to this problem seems to be the immobilization of soluble catalysts on to an insoluble matrix by using a simplified protocol; this should allow easy separation and recyclability of the catalyst with a minimal amount of product contamination with the metal and and the matrix would also serve as a ligand. Herein we disclose an improved method for the preparation, characterization, and evaluation of CuI-supported polyaniline nanofibers (CuI-PANInf; for their synthesis and characterization see the Supporting Information) as a catalyst for the *N*-arylation of aliphatic, aromatic, and (*N*)H-heterocyclic amines with aryl iodides at ambient temperature (25 °C) and aryl chlorides at 80 °C. This catalytic system circumvents the use of high temperatures, ancillary ligands, and high catalyst loading owing to the enhanced activity of the catalyst compared with other copper catalysts,[4–21] which can be explained by the high basicity and size of the polyaniline nanofibers.

Results and Discussion

To identify the ideal reaction conditions, a diverse range of bases and solvents were screened using 4-iodoanisole and pentylamine as model substrates in the presence of CuI-PANInf (Scheme 1). The results are summarized in Table 1.



Scheme 1. CuI-PANInf-catalyzed synthesis of *N*-arylated amines via coupling of aliphatic amines with aryl iodides.

Different nonpolar solvents such as toluene, 1,4-dioxane, and xylene and the polar protic solvent methanol gave the coupling product in low yields in the presence of K_2CO_3 (Table 1, entries 1–4). Among the polar aprotic solvents screened, acetonitrile, DMSO, and NMP gave the product in good yields (Table 1, entries 5–7) whereas the reaction in DMF afforded the product in high yield and in a shorter reaction time with K_2CO_3 as the base (Table 1, entry 8). Other bases, such as Cs_2CO_3 and NaOAc, were ineffective

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Table 1. Screening of various copper catalysts in the amination of *p*-iodoanisole with pentylamine.[a]

Entry	Solvent	Bases	Time (h) [b]	Isolated yield (%)[c]
1	toluene	K_2CO_3	21	15
2	dioxane	K_2CO_3	19	17
3	xylene	K_2CO_3	24	5
4	MeOH	K_2CO_3	17	12
5	CH_3CN	K_2CO_3	18	49
6	DMSO	K_2CO_3	6	81
7	NMP	K_2CO_3	9	79
8	DMF	K_2CO_3	6	99,98[d]
9	CH_3CN	Cs_2CO_3	24	7
10	NMP	Cs_2CO_3	12	10
11	DMSO	Cs_2CO_3	9	12
12	DMF	Cs_2CO_3	24	–
13	DMF	NaOAc	9	12
14	DMF	NaOH	10	55
15	DMF	K_3PO_4	3	65
16	DMF	Na_2CO_3	6	60

[a] Reagents and conditions: 4-iodoanisole (1.0 mmol), pentylamine (1.2 mmol), base (1.2 mmol), CuI-PANInf (5.0 mol-%), and solvent (2.0 mL) at room temperature (25 °C) under N_2. [b] Time required for the formation of *N*-arylated amine. [c] Isolated yields of *N*-arylated amine. [d] Isolated yield after the 5th cycle.

for the coupling reaction (Table 1, entries 9–13) whereas NaOH, K_3PO_4, and Na_2CO_3 gave the product in moderate yields (Table 1, entries 14–16).

To investigate the superiority of CuI-PANInf, the results obtained with different supported copper catalysts reported in the literature were compared with those of the synthesized CuI-PANInf for the formation of the C–N bond between iodobenzene and imidazole. The results are presented in Table 2.

The use of heterogeneous catalysts reported in the literature gave the product in good-to-excellent yields at high temperatures and catalyst loading and also required longer reaction times (Table 2, entries 1–7) than the reaction with CuI-PANInf, which gave the product in high yield in a shorter reaction time at ambient temperature (Table 2, entry 8). Lowering the amount of copper to 2.5 mol-% (in CuI-PANInf) afforded the desired *N*-arylated product in 47% yield after 18 h. Note also that the reaction with homogeneous CuI (5.0 mol-%) resulted in the *N*-arylated product in low yield (Table 2, entry 10). However, there was no reaction when undoped PANInf was used as catalyst even after 18 h (Table 2, entry 11). Thus, 5.0 mol-% of CuI in CuI-PANInf in the presence of K_2CO_3 with DMF as solvent are the ideal conditions for the coupling reaction at ambient temperature.

This enhanced catalytic activity of CuI-PANInf in comparison with other screened supported copper catalysts as well as its homogeneous analogue can be explained by the high basicity and dual role of the PANI nanofibers as sup-

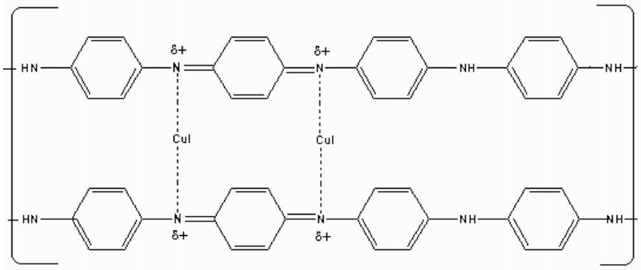
Table 2. Comparative study of different catalysts in the C–N coupling reaction of iodobenzene and imidazole.[a]

Entry	Catalyst	Cu (mol-%)	Solvent	Temp. (°C)	Time (h)	Yield (%)	Ref.
1	NanoCuO	2.5	DMSO	110	24	91	12
2	Cu_2O	10	DMSO	110	24	90	13
3	Cu-FAP	12.5	DMSO	110	6	92	15
4	Cu-Y Zeolite	10.8	DMF	120	24	99	17
5	Cellulose Cu(0)	0.92	DMSO	130	12	95	18
6	SiO_2-Py-$Cu(OAc)_2$	5.0	toluene	100	8	89	19
7	PANICu	2.5	CH_3CN	80	12	92	22
8	CuI-PANInf	5.0	DMF	25	2-10	99	present work
9	CuI-PANInf	2.5	DMF	25	18	47	
10	CuI	5.0	DMF	25	2-10	33	
11	PANInf	–	DMF	25	18	–	

[a] Reaction conditions are as exemplified in the reaction procedure.

port and macroligand, which facilitates the reaction similarly to other nitrogen-containing ligands with Cu reported in the literature.[4–6] Earlier similar observations have prompted for designing a novel catalytic system in which polyaniline serves as a ligand with redox functionality in transition-metal-catalyzed reactions.[23]

The incorporation of CuI into the PANI nanofiber resulted in no appreciable shifts in the quinoid or benzenoid ring IR band positions. The most important bands in the FTIR spectrum of PANI are located at 1565, 1494, 1388, 1306, 1194, and 778 cm^{-1} (Figure S1 of the Supporting Information) and are a result of the stretching vibrations of the amine (quinoid, $\nu_{C=N} + \nu_{C=C}$) and imine (benzenoid, $\nu_{C=C}$) units in the polymer, deformations of the C–N bond, stretching vibrations of the C–N bond, in-plane deformations of CH bonds in the aromatic rings of the undoped polymer, and out-of-plane deformations of CH bonds in the 1,4-substituted aromatic ring, respectively.[24] A high-resolution XPS narrow scan of CuI-PANInf showed the Cu $2p_{3/2}$ line at 932.5 eV and the Cu $2p_{1/2}$ line at 925.7 eV, which can be attributed to the +1 oxidation state of copper in CuI-PANInf.[25] We analyzed the PANI nanofiber by XPS for N 1s and it showed three types of N, namely N (398.7 eV, share 45%), NH (399.7 eV, share 45%), and N^+ (401.3 eV, share 10%). Similarly, CuI-PANInf showed the presence of N (398.7 eV, share 13%), NH (400 eV, share 65%), and N^+ (401. 4 eV, share 22%). The decrease in the proportion of the imine nitrogen indicates that most of the copper is bound to the PANInf through an imine nitrogen rather than an amine nitrogen and the possible structure of CuI-PANInf is shown in Scheme 2. Moreover, the enhanced activity that is observed with the *o*-nitro, *o*-formyl, *o*-carboxylic, and *o*-cyano substituents compared with the *para* substituents (see below) can be explained by the chelating effect of the substituents on coordination to the Cu^I atom of CuI-PANInf, which further stabilizes the Cu^I atom. Thus, the coordinatively unsaturated Cu^+ ions readily accept incoming nucleophilic reagents with chelating character for further stabilization.



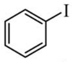
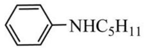
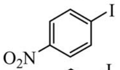
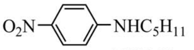
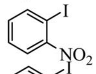
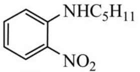
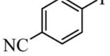
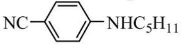
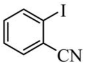
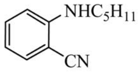
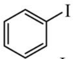
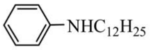
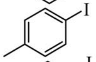
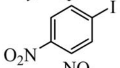
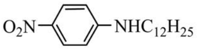
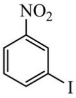
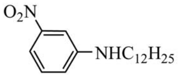
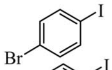
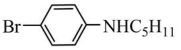
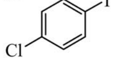
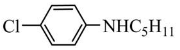
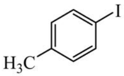
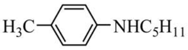
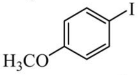
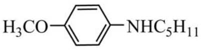
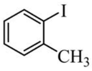
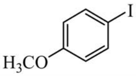
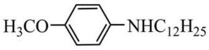
Scheme 2. Structure of CuI-PANInf.

Under the optimized conditions, a number of different haloarenes were subjected to coupling reactions with amines to produce the corresponding secondary and tertiary *N*-arylated amines in good-to-excellent yields. Initially, we studied the coupling reactions of various aryl iodides with aliphatic amines such as pentylamine and dodecylamine and the results are presented in Table 3. Interestingly, structurally diverse aryl iodides with electron-withdrawing groups such as NO_2 and CN at the *ortho* position showed higher reactivity than the *para*-substituted aryl iodides and gave the desired *N*-arylated products with pentylamine in excellent yields (Table 3, entries 1–5). This may be because the *ortho*-substituted electron-withdrawing groups serve as chelating groups for the Cu atom thereby providing an activating effect. As the number of carbon atoms in the aliphatic amine increases, the yields of the coupling products also increase and in a shorter time (Table 3, entries 6–8) in accordance with the literature.[26] The presence of the NO_2 electron-withdrawing substituent at the *meta* position gave the expected *N*-arylated product in only a moderate yield with longer reaction time due to the non-availability of the NO_2 group for chelation (Table 3, entry 9). The coupling reactions of 4-bromo- and 4-chloro-1-iodotoluene with pentylamine took place preferentially with the activation of the C–I bond (Table 3, entries 10 and 11) over the C–Br or C–Cl bond, thus revealing the selectivity of the catalyst in bond activation. The activity of the catalyst was also tested in the coupling reactions of aryl halides with electron-rich substituents such as 4-iodotoluene and 4-iodoanisole with pentylamine; the reaction afforded the corresponding *N*-arylated products in good yields and with slightly longer reaction times (Table 3, entries 12 and 13). In contrast, the presence of an electron-donating substituent at the *ortho* position exerted an inhibitive influence with no product being formed (Table 3, entry 14). This can be attributed to the steric hindrance caused by the substituent at the *ortho* position.

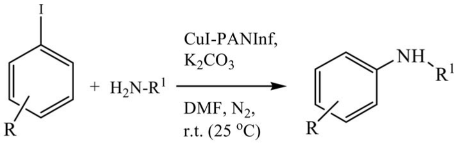
Next we explored the efficacy of the catalytic system for the coupling of secondary amines with aryl iodides (Scheme 3). The results are presented in Table 4. It was observed that simple linear aliphatic secondary amines were less effective substrates for the coupling reaction than aliphatic heterocyclic amines (Table 4, entries 1–12). The lower yields and longer reaction times for the linear aliphatic secondary amines can be explained by the steric hindrance caused by the free alkyl groups at the reaction center of the amines, whereas such affects were not observed with aliphatic heterocyclic amines. The shorter reaction times in the reactions of *ortho*-substituted iodobenzene with cyclic secondary amines in comparison with *para*-substituted iodobenzene clearly proves the chelating effect (Table 4, entry 11). Reactions of the aromatic cyclic amine pyrrole with substituted iodobenzenes afforded the corresponding *N*-arylated products in good-to-excellent yields at 25 °C (Table 4, entries 13–16). However, there was no coupling reaction observed in the case of the sterically hindered dibenzylamine (Table 4, entry 21).

Next we extended the applicability of the catalyst to the *N*-arylation of primary alkylamines, namely benzyl-, cyclohexyl-, and cyclopentylamines, with aryl iodides: The results are summarized in Table 5. Iodobenzene on reaction with benzylamine gave the *N*-arylated product in a moderate yield at ambient temperature (Table 5, entry 1). The

Table 3. *N*-Arylation of aliphatic amines with iodoarenes using CuI-PANInf.[a]

Entry	Aryl iodide	Amine	Product	Reaction[b] Time (h)	Isolated yield (%) [c]
1		$NH_2C_5H_{11}$		8	61
2		$NH_2C_5H_{11}$		4	85
3		$NH_2C_5H_{11}$		2	99, 98 [d]
4		$NH_2C_5H_{11}$		6	63
5		$NH_2C_5H_{11}$		4	75
6		$NH_2C_{12}H_{25}$		4	99
7		$NH_2C_{12}H_{25}$		13	68
8		$NH_2C_{12}H_{25}$		3	98
9		$NH_2C_{12}H_{25}$		7	76
10		$NH_2C_5H_{11}$		5	92
11		$NH_2C_5H_{11}$		6	99
12		$NH_2C_5H_{11}$		9	56
13		$NH_2C_5H_{11}$		6	99
14		$NH_2C_5H_{11}$	n.r.	6	–
15		$NH_2C_{12}H_{25}$		8	68

[a] Reagents and conditions: Iodobenzene (1.0 mmol), amine (1.2 mmol), K_2CO_3 (1.2 mmol), catalyst (5.0 mol-%), and DMF (2 mL) at room temperature under N_2. n.r.: no reaction. [b] Time required for the formation of the product. [c] Isolated yield. [d] Isolated yield after the 5th cycle.



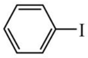
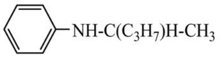
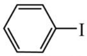
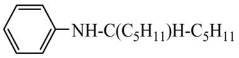
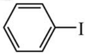
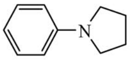
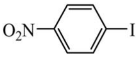
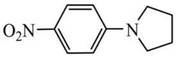
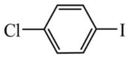
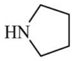
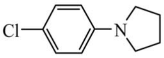
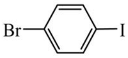
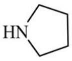
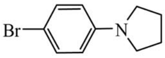
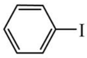
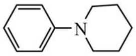
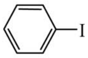
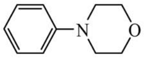
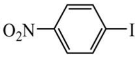
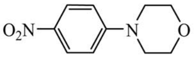
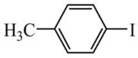
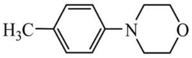
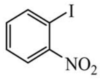
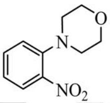
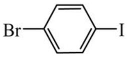
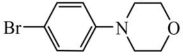
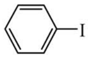
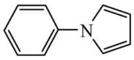
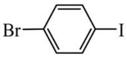
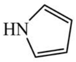
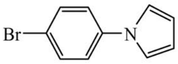
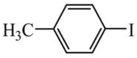
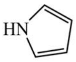
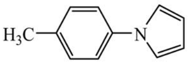
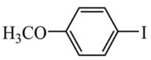
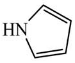
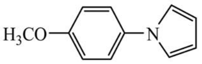
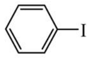
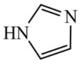
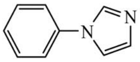
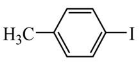
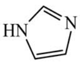
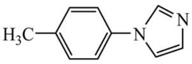
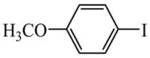
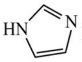
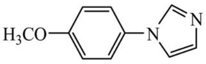
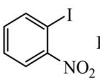
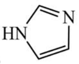
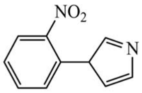
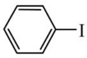
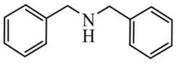
R = NO_2, Br, Cl
R^1 = secondary and N(H)-heterocyclic amine

Scheme 3. *N*-Arylation of secondary aliphatic and N(H) heterocyclic amines with iodoarenes using CuI-PANInf.

CuI-PANInf catalyst showed enhanced catalytic activity in the *N*-arylation of benzylamine with iodobenzene at 50 °C (99%) in comparison with the conventional PANI-supported catalyst, which required Cs_2CO_3 as base, a temperature of 80 °C, and 15 h (90%).[26] Moreover, with the present catalyst system, no oxidation of benzylamine to *N*-benzylidenebenzylamine was observed as the reaction was performed under N_2 at room temperature.[27] This may be due to the fact that the nano-sized materials provide unique chemical and physical properties different to those of the bulk material.

The reactions of iodoanisole and iodotoluene with benzylamine resulted in the formation of the *N*-arylated products after longer reaction times (Table 5, entries 2 and 3). In the case of 4-chloro-1-iodobenzene, coupling took place at the C–I bond (Table 5, entry 4) showing higher selectivity in the activation of C–I bond even in presence of the C–Cl bond. The presence of electron-withdrawing substituents such as NO_2, CHO, and CN at the *ortho* and/or *para* positions of iodobenzene led to facile coupling reactions with benzyl-, cyclohexyl-, and cyclopentylamines to give the corresponding *N*-arylated products in good-to-excellent yields

Table 4. *N*-Arylation of secondary aliphatic and N(H) heterocyclic amines with iodoarenes using CuI-PANInf.[a]

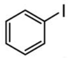
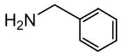
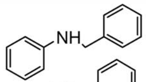
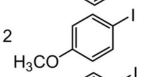
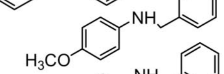
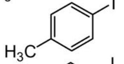
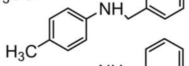
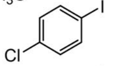
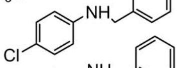
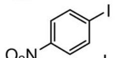
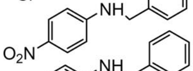
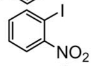
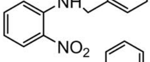
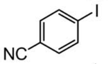
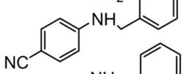
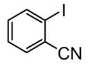
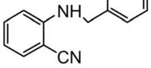
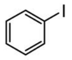
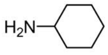
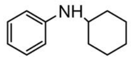
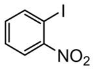
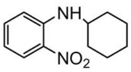
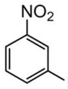
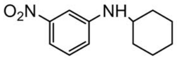
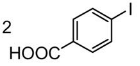
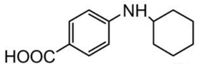
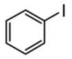
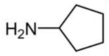
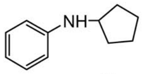
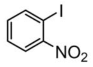
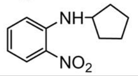
Entry	Aryl iodide	Amine	Product	Reaction time (h)[b]	Isolated yield [c]
1		$CH_3CH(NH_2)C_3H_7$		10	71
2		$C_5H_{11}CH(NH_2)C_5H_{11}$		10	79
3				6	67
4				5	71
5				6	82
6				6	75
7				6	67
8				5	83
9				4	85
10				12	65
11				3	96, 95[d]
12				6	85
13				8	80
14				8	75
15				12	63
16				12	55
17				6	99
18				14	55
19				12	65
20				4	99
21			n.r.	10	-

[a] Reagents and conditions: iodobenzene (1.0 mmol), amine (1.2 mmol), K_2CO_3 (1.2 mmol), catalyst (5.0 mol-%), and DMF (2 mL) at room temperature (25 °C) under N_2. [b] Time required for the formation of the product. [c] Isolated yield. [d] Isolated yield after the 5th cycle.

(Table 5, entries 5–14). Interestingly, it can also be seen that *ortho*-nitroiodobenzene showed enhanced rates of reaction and higher yields than *para*/*meta*-substituted iodobenzene (Table 5, entries 5, 6, 10, and 11).

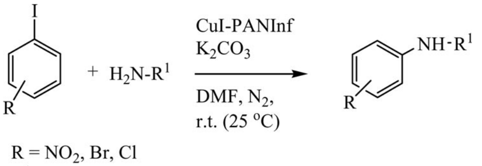
Encouraged by these promising results, we broadened the scope of our catalytic system to the *N*-arylation of aliphatic and N(H)-heterocyclic amines using aryl chlorides, less reactive but more desirable substrates than their bromide and

Table 5. *N*-Arylation of benzyl- and cycloalkylamines with iodoarenes using CuI-PANInf.[a]

Entry	Aryl iodide	Amine	Product	Reaction time (h)[b]	Isolated yield (%)[c]
1				6	61, 99[d], 90[e]
2				11	23
3				14	37
4				3	85
5				4	98
6				2	99
7				5	41
8				3	59
9				5	98
10				1	99, 99[f]
11				6	56
12				4	75
13				5	73
14				3	62

[a] Reagents and conditions: aryl iodide (1.0 mmol), amine (1.2 mmol), K_2CO_3 (1.2 mmol), catalyst (5.0 mol-%), and DMF (2 mL) at room temperature under N_2. [b] Time required for the formation of the product. [c] Isolated yield. [d] At 50 °C. [e] See ref.[22]. [f] Isolated yield after the 5th cycle.

iodide counterparts in terms of cost and availability[24] (Scheme 4, Table 6). The reactions proceeded smoothly although lower yields were obtained than with their iodide analogues under ambient reaction conditions. However, at an elevated temperature of 80 °C, the desired *N*-arylated products were obtained in good-to-moderate yields.

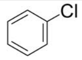
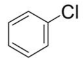
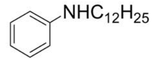
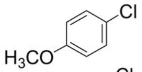
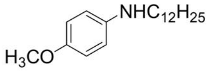
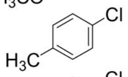
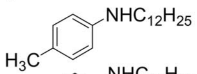
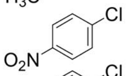
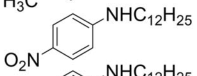
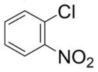
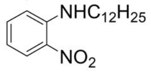
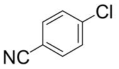
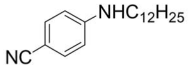
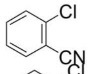
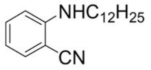
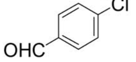
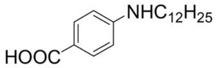
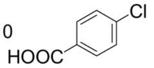
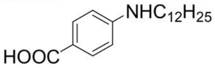
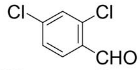
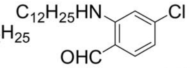
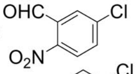
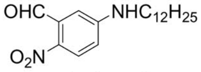
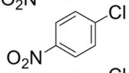
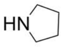
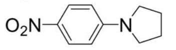
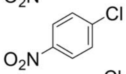
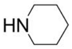
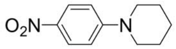
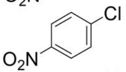
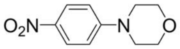
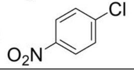
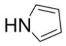
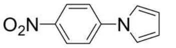


Scheme 4. *N*-Arylation of alkyl and N(H)-heterocyclic amines with chloroarenes using Cu-PANInf.

Simple chlorobenzene and *p*-methoxy- and *p*-methylchlorobenzene underwent coupling reactions (Table 6, entries 1–4) at 100 °C whereas aryl chlorides with electron-withdrawing substituents reacted more readily (Table 6, entries 5–16) at 80 °C. The presence of NO_2 at the *ortho* position led to an enhanced rate of reaction and a higher yield of the *N*-arylated product in comparison with *p*-nitrochlorobenzene due to the chelation effect (Table 6, entries 5 and 6). It was observed that the formyl functionality of 4-chlorobenzaldehyde could not be preserved at this temperature (Table 6, entry 9) whereas with disubstituted chlorobenzaldehydes (Table 6, entries 11 and 12) selectivity towards *ortho* substituents rather than *para* substituents was observed in the *N*-arylation reaction with preservation of the formyl substitution. This methodology was further extended to secondary aliphatic and aromatic amines (Table 6, entries 13–16), which afforded the *N*-arylated products in good-to-excellent yields.

The reusability of the CuI-PANInf catalytic system was studied for five consecutive cycles with 2-nitroiodobenzene and pentylamine as the coupling partners. After each cycle the catalyst was filtered, washed with organic solvent, and air-dried. The recovered catalyst showed almost consis-

Table 6. *N*-Alkylation of chloroarenes with alkyl and N(H)-heterocyclic amines using CuI-PANInf.[a]

Entry	Aryl chloride	Amine	Product[b]	Time [h][b]	Yield [%][c]
1		$NH_2C_5H_{11}$	n.r.	24	-
2		$NH_2C_{12}H_{25}$		18	7
3		$NH_2C_{12}H_{25}$		10	65
4		$NH_2C_{12}H_{25}$		12	47
5		$NH_2C_{12}H_{25}$		5	93
6		$NH_2C_{12}H_{25}$		2	95,94[d]
7		$NH_2C_{12}H_{25}$		6	64
8		$NH_2C_{12}H_{25}$		4	78
9		$NH_2C_{12}H_{25}$		4	72
10		$NH_2C_{12}H_{25}$		2	85
11		$NH_2C_{12}H_{25}$		4	86
12		$NH_2C_{12}H_{25}$		1.5	98
13				9	95
14				7	96
15				4	98
16				6	93

[a] Reagents and conditions: aryl chloride (1.0 mmol), amine (1.2 mmol), K_2CO_3 (1.2 mmol), catalyst (5.0 mol-%), and DMF (2 mL) stirred at 80 °C (100 °C for entries 1–4) for an appropriate time under N_2. n.r.: no reaction. [b] Time required for the formation of the *N*-alkylated product. [c] Isolated yield of the *N*-alkylated product. [d] Isolated yield after 5th cycle.

tent activity for five cycles. From the seventh cycle, the activity of the catalyst diminished slightly in the case of the 2-nitrochlorobenzene due to the partial solubility of the catalyst in DMF at elevated temperatures and almost 1.1% of the charged copper leached into the solution. To check the activity of the leached copper, we terminated the reaction between 2-nitrochlorobenzene and pentylamine after 2 h with 27% conversion. The catalyst was removed by filtration and then we continued the reaction with the filtrate for an additional 11 h; the conversion increased to 29%. In the presence of the fresh catalyst, the conversion reached almost 99%. These studies showed that the leached copper is catalytically active but less effective than CuI-PANInf. At elevated temperatures, polyaniline nanofiber is also soluble in DMF to some extent so the leached copper is not pure CuI but a combination of the polyaniline nanofiber and CuI.

Conclusions

We have reported a novel copper iodide–polyaniline nanofiber (CuI-PANInf) catalyzed *N*-arylation of aliphatic, aromatic, and N(H)-heterocyclic amines using aryl iodides and chlorides as the arylating agents. The cross-coupling reactions are facile and provide easy access to a wide range of *N*-arylated products in the absence of any additives. Considering the substrate scope of this reaction, we foresee that this new catalyst will find widespread application in the synthesis of a wide variety of pharmaceutically and industrially important secondary and tertiary amines with a wide variety of functionalities in a one-pot coupling of aryl halides and amines. The catalyst shows consistent activity for five cycles and is cost effective for industrial use.

Experimental Section

General: All chemicals were purchased from Aldrich and were used as received. All solvents were of analytical grade and were used as received from Merck India Pvt. Ltd. X-ray powder diffraction (XRD) data were collected with a Simens/D-5000 diffractometer using Cu-K_α radiation. XPS spectra were recorded with a Kratos AXIS 165 instrument with a dual anode (Mg and Al) using the Mg-K_α anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration we used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. The spectra were deconvoluted by using the Sun Solaris based Vision 2 curve resolver. The location and full-width at half-maximum (FWHM) for a species were first determined by using the spectrum of a pure sample; the location and FWHM of the products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetrical Gaussian shapes were used in all cases. The Cu/Al ratio was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). GC analysis was performed using a Shimadzu GC-2010 instrument and a ZB-5 capillary column. ^{1}H and ^{13}C spectra were recorded with a Bruker Avance 300 (300 MHz ^{1}H and ^{13}C) spectrometer at room temperature with respect to TMS and $CDCl_3$ for ^{1}H and ^{13}C NMR, respectively. Chemical shifts are reported in ppm relative to the residual $CDCl_3$ (^{1}H: δ = 7.28 ppm; ^{13}C: δ = 77.0 ppm) Coupling constants (J) are reported in Hz. All the heterogeneous catalysts used were synthesized following literature[13–24] and Cu-PANInf was prepared according to the procedure reported (see Supporting Information for details).

General Procedure for the Amination of Alcohols with Amines: The haloarene (1.0 mmol), amine (1.2 mmol), K_2CO_3(1.2 mmol), CuI-PANInf (Cu: 5.0 mol-%), and DMF (2.0 mL) were stirred in an oven-dried 25 mL two-necked round-bottomed flask at room temperature under nitrogen for an appropriate time. After completion of the reaction as judged by TLC, the reaction mixture was centrifuged to remove the solid catalyst. The reaction mixture was then diluted with water (20 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to yield the crude product and purified by flash chromatography on silica gel (60–120 mesh) using ethyl acetate/hexane (2:100 v/v) as eluent. All the products were characterized by ^{1}H NMR and mass spectroscopic data and compared with literature values.[9,10] Unknown compounds were characterized by ^{1}H and ^{13}C NMR, CHNS, and mass spectrometry.

***N*-Pentylaniline:** (Table 3, entry 1) Yellow oil, isolated yield 61%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18–8.10 (d, J = 8.08 Hz, 2 H), 8.02 (br. s, 1 H), 7.38 (t, J = 7.35 Hz, 1 H), 6.80 (d, J = 8.16 Hz, 2 H), 3.34–3.20 (m, 2 H), 1.82–1.66 (m, 2 H), 1.54–1.28 (m, 4 H), 0.92 (t, J = 6.61 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.703, 126.501, 118.097, 113.547, 53.926, 31.454, 29.009, 21.815, 14.495 ppm. MS (EI): m/z = 164 [M + H]$^+$. $C_{11}H_{17}N$ (163.26): calcd. C 80.93, H 10.50, N 8.58; found C 79.29, H 10.55, N 8.20.

4-Nitro-*N*-pentylaniline: (Table 3, entry 2) Yellow gummy oil, isolated yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.71 Hz, 2 H), 6.50 (d, J = 7.71 Hz, 2 H), 3.25–3.15 (m, 2 H), 1.50–1.15 (m, 6 H), 0.90 (t, J = 6.51 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.234, 137.431, 126.926, 113.972, 52.629, 31.880, 29.434, 23.007, 13.826 ppm. GC–MS: m/z = 208 [M + H]$^+$. $C_{11}H_{16}N_2O_2$ (208.26): calcd. C 63.44, H 7.74, N 13.45; found C 63.45, H 7.45, N 13.42.

2-Nitro-*N*-pentylaniline: (Table 3, entry 3) Yellow oil, isolated yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (br. s, 1 H), 7.85 (d, J = 9.25 Hz, 1 H), 7.42–7.40 (m, 1 H), 6.80 (d, J = 8.68 Hz, 1 H), 6.60 (d, J = 6.68 Hz, 1 H), 3.32–3.24 (m, 2 H), 1.52–1.24 (m, 6 H), 0.89 (t, J = 6.87 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.940, 136.005, 134.001, 124.738, 118.596, 113.972, 50.350, 31.880, 29.743, 23.094, 14.921 ppm. GC–MS: m/z = 209 [M + H]$^+$. $C_{11}H_{16}N_2O_2$ (208.26): calcd. C 63.44, H 7.74, N 13.45; found C 64.05, H 7.75, N 14.02.

4-Cyano-*N*-pentylaniline: (Table 3, entry 4) Yellow oil, isolated yield 63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, J = 7.57 Hz, 2 H), 8.00 (br. s, 1 H), 6.80 (d, J = 7.56 Hz, 2 H), 3.35–3.20 (m, 2 H), 1.80–1.65 (m, 2 H), 1.40–1.20 (m, 4 H), 0.90 (t, J = 6.56 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.025, 131.817, 117.020, 113.009, 100.130, 52.054, 31.748, 29.469, 22.522, 13.951 ppm. MS (EI): m/z = 189 [M + H]$^+$. $C_{12}H_{16}N_2$ (188.27): calcd. C 76.55, H 8.57, N 14.88; found C 76.45, H 7845, N 14.42.

2-Cyano-*N*-pentylaniline: (Table 3, entry 5) Yellow oil, isolated yield 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.0 (br. s, 1 H), 7.85 (d, J = 8.85 Hz, 2 H), 6.80 (d, J = 7.73 Hz, 1 H), 6.60 (t, J = 6.89 Hz, 1 H), 3.32–3.20 (m, 2 H), 1.80–1.65 (m, 2 H), 1.50–1.20 (m, 4 H), 0.90 (t, J = 6.51 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.621, 133.871, 131.355, 117.978, 116.181, 96.787, 51.002, 31.721, 29.976, 22.522, 14.069 ppm. MS (EI): m/z = 189 [M + H]$^+$. $C_{12}H_{16}N_2$ (188.27): calcd. C 76.55, H 8.57, N 14.88; found C 77.05, H 8.55, N 14.82.

***N*-Dodecylaniline:** (Table 3, entry 6) A white oily liquid, isolated yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (br. s, 1 H), 7.50–7.35 (m, 2 H), 6.80 (d, J = 7.91 Hz, 1 H), 6.60 (t, J = 7.3 Hz, 1 H), 3.43–3.20 (m, 2 H), 1.81–1.70 (m, 2 H), 1.50–1.21 (m, 18 H), 0.90 (t, J = 6.51 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.234, 126.926, 117.089, 112.940, 44.979, 32.114, 30.486, 30.016, 29.916, 27.140, 22.962, 13.917 ppm. MS (EI): m/z = 262 [M + H]$^+$. $C_{18}H_{31}N$ (261.45): calcd. C 82.69, H 11.95, N 5.36; found C 82.60, H 11.89, N 5.85.

***N*-Dodecyl-4-nitroaniline:** (Table 3, entry 8) Yellow oil, isolated yield 98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.03 Hz, 2 H), 8.09 (br. s, 1 H), 6.80 (d, J = 8.03 Hz, 2 H), 3.35–3.20 (m, 2 H), 1.50–1.20 (m, 20 H), 0.90 (t, J = 6.59 Hz, 3 H) ppm. ^{13}C NMR (75 MHz,$CDCl_3$): δ = 153.814, 137.875, 122.636, 114.507, 44.979, 31.880, 30.486, 30.016, 29.434, 27.245, 22.962, 13.917 ppm. MS (EI): m/z. = 306 [M]$^+$. $C_{18}H_{30}N_2O_2$ (306.45): calcd. C 70.55, H 9.87, N 9.14; found C 71.09, H 9.90, N 9.38.

***N*-Dodecyl-3-nitroaniline:** (Table 3, entry 9) Yellow oil, isolated yield 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (br. s, 1 H), 7.85 (d, J = 6.9 Hz, 2 H), 7.50–7.30 (m, 2 H), 6.60 (t, J = 6.87 Hz, 1 H), 3.32–3.20 (m, 2 H), 1.81–1.68 (m, 2 H), 1.55–1.20 (m, 18 H), 0.90 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.090, 148.234, 130.992, 120.059, 109.530, 107.431, 44.979, 32.712, 31.880, 30.486, 29.743, 26.871, 22.240, 13.826 ppm. MS (EI): m/z = 307 [M + H]$^+$. $C_{18}H_{30}N_2O_2$ (306.45): calcd. C 70.55, H 9.87, N 9.14; found C 70.19, H 9.20, N 9.14.

4-Bromo-*N*-pentylaniline: (Table 3, entry 10) Yellow oil, isolated yield 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.43 Hz, 2 H), 6.50 (d, J = 8.43 Hz, 2 H), 3.25–3.15 (m, 2 H), 1.50–1.51

(m, 6 H), 0.90 (t, J = 6.07 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.651, 133.693, 115.638, 111.716, 45.349, 30.043, 29.398, 22.811, 14.398 ppm. MS (EI): m/z = 242 [M + H]$^+$. $C_{11}H_{16}BrN$ (242.16): calcd. C 54.56, H 6.66, N 5.78; found C 55.06, H 6.55, N 5.82.

4-Chloro-*N*-pentylaniline: (Table 3, entry 11) Yellow oil, isolated yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.31 Hz, 2 H), 6.50 (d, J = 8.31 Hz, 2 H), 4.15 (br. s, 1 H), 3.25–3.15 (m, 2 H), 1.50–1.25 (m, 6 H), 0.89 (t, J = 6.51 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.129, 130.404, 123.627, 115.096, 45.122, 30.486, 29.434, 22.934, 13.917 ppm. MS (EI): m/z = 198 [M + H]$^+$. $C_{11}H_{16}ClN$ (197.71): calcd. C 66.83, H 8.16, N 7.08; found C 66.86, H 8.15, N 7.12.

4-Methoxy-*N*-pentylaniline: (Table 3, entry 13) Yellow gummy solid, isolated yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.0 (br. s, 1 H), 6.80 (d, J = 8.71 Hz, 2 H), 6.60 (d, J = 8.71 Hz, 2 H), 4.40–3.85 (m, 2 H), 3.70 (s, 3 H), 1.60–1.20 (m, 7 H), 0.88 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.128, 139.285, 115.312, 114.636, 55.933, 45.104, 31.880, 30.185, 22.958, 13.951 ppm. MS (EI): m/z = 194 [M + H]$^+$. $C_{12}H_{19}NO$ (193.29): calcd. C 74.57, H 9.91, N 7.25; found C 75.21, H 9.89, N 7.28.

1-Phenylpyrrolidine: (Table 4, entry 3) Yellow oil, isolated yield 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05 (d, J = 8.30 Hz, 2 H), 6.60–6.49 (m, 3 H), 2.75 (d, J = 7.01 Hz, 4 H), 1.85 (d, J = 7.01 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.877, 130.577, 118.523, 113.972, 51.507, 25.429 ppm. MS (EI): m/z = 147 [M]$^+$. $C_{10}H_{13}N$ (147.22): calcd. C 81.59, H 8.90, N 9.51; found C 82.07, H 8.91, N 9.55.

1-(4-Nitrophenyl)pyrrolidine: (Table 4, entry 4) A pale-yellow solid, isolated yield 71%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.86 Hz, 2 H), 7.50 (d, J = 8.86 Hz, 2 H), 2.90 (d, J = 7.79 Hz, 4 H), 1.85 (d, J = 7.79 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.050, 137.807, 121.487, 116.532, 51.507, 25.429 ppm. GC–MS: m/z = 193 [M + H]$^+$. $C_{10}H_{12}N_2O_2$ (192.22): calcd. C 62.49, H 6.29, N 14.57; found C 62.51, H 6.25, N 14.59.

1-(4-Chlorophenyl)pyrrolidine: (Table 4, entry 5) A white solid, isolated yield 82%, m.p. 77–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05 (d, J = 8.75 Hz, 2 H), 6.65 (d, J = 8.75 Hz, 2 H), 3.00 (d, J = 7.02 Hz, 4 H), 1.6 (d, J = 7.02 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.234, 130.577, 123.627, 116.240, 51.507, 25.429 ppm. GC–MS: m/z = 181 [M]$^+$. $C_{10}H_{12}ClN$ (181.66): calcd. C 66.12, H 6.66, N 7.71; found C 66.19, H 6.65, N 7.70.

1-Phenylpiperidine: (Table 4, entry **7**) A pale-yellow thick oil, isolated yield 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05 (d, J = 7.01 Hz, 2 H), 6.70–6.50 (m, 3 H), 3.01 (d, J = 7.01 Hz, 4 H), 1.65–1.51 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.239, 130.644, 118.523, 113.972, 51.507, 26.668, 25.878 ppm. MS (EI): m/z = 162 [M + H]$^+$. $C_{11}H_{15}N$ (161.25): calcd. C 81.94, H 9.38, N 8.69; found C 81.90, H 9.35, N 8.72.

4-Phenylmorpholine: (Table 4, entry 8) White solid, isolated yield 83%, m.p. 52–54 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85 (d, J = 7.20 Hz, 2 H), 6.50–6.71 (m, 3 H), 3.63 (t, J = 4.47 Hz, 4 H), 3.17 (t, J = 4.47 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.174, 131.039, 119.302, 113.972, 66.570, 46.493 ppm. GC–MS: m/z = 164 [M + H]$^+$. $C_{10}H_{13}NO$ (163.22): calcd. C 73.59, H 8.03, N 8.58; found C 73.62, H 8.05, N 8.61.

4-(4-Nitrophenyl)morpholine: (Table 4, entry 9) Yellow solid, isolated yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.01 Hz, 2 H), 6.85 (d, J = 8.01 Hz, 2 H), 3.75 (t, J = 5.02 Hz, 2 H), 3.05 (t, J = 5.02 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.744, 137.875, 121.487, 116.240, 66.150, 46.493 ppm. GC–MS: m/z = 208 [M]$^+$. $C_{10}H_{12}N_2O_3$ (208.22): calcd. C 57.68, H 5.81, N 13.45; found C 57.72, H 5.85, N 14.20.

4-(2-Nitrophenyl)morpholine: (Table 4, entry 11) Yellow solid, isolated yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85–8.80 (m, 1 H), 8.25–8.10 (m, 1 H), 6.85 (d, J = 7.93 Hz, 2 H), 3.65 (t, J = 5.01 Hz, 2 H), 3.01 (t, J = 5.01 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.971, 134.067, 132.512, 122.092, 119.936, 116.532, 67.626, 46.493 ppm. GC–MS: m/z = 208 [M]$^+$. $C_{10}H_{12}N_2O_3$ (208.22): calcd. C 57.68, H 5.81, N 13.45; found C 57.65, H 5.79, N 13.50.

4-(4-Bromophenyl)morpholine: (Table 4, entry 12) A white solid, isolated yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.35 (m, 2 H), 6.70–6.50 (m, 2 H), 3.72 (t, J = 5.09 Hz 2 H), 2.98 (t, J = 5.09 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.234, 133.531, 116.342, 111.798, 67.626, 46.493 ppm. GC–MS: m/z = 242 [M]$^+$. $C_{10}H_{12}BrNO$ (242.11): calcd. C 49.61, H 5.00, N 5.79; found C 49.65, H 5.09, N 5.80.

1-Phenyl-1*H*-pyrrole: (Table 4, entry 13) Yellow oil, isolated yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.32 (m, 5 H), 6.85 (d, J = 2.55 Hz, 2 H), 6.60 (d, J = 2.55 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.566, 130.769, 126.926, 123.627, 121.487, 111.323 ppm. GC–MS: m/z = 144 [M + H]$^+$. $C_{10}H_9N$ (143.19): calcd. C 83.88, H 6.34, N 9.78; found C 83.80, H 6.25, N 9.75.

1-(4-Bromophenyl)-1*H*-pyrrole: (Table 4, entry 14) A white solid, isolated yield 75%, m.p. 94–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, J = 7.02 Hz, 2 H), 7.35 (d, J = 7.02 Hz, 2 H), 6.80–6.90 (m, 2 H), 6.50–6.70 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.416, 133.206, 125.207, 123.627, 119.743, 111.178 ppm. MS (EI): m/z = 221 [M + H]$^+$. $C_{10}H_8BrN$ (222.08): calcd. C 54.08, H 3.63, N 6.31; found C 54.09, H 3.65, N 6.25.

***N*-Benzylaniline:** (Table 5, entry 1) A colorless liquid, isolated yield 61%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.35 (m, 5 H), 6.85–6.70 (m, 3 H), 4.50 (d, J = 5.6 Hz, 2 H), 4.00 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.796, 140.684, 128.601, 127.732, 126.621, 126.310, 117.949, 114.820, 53.710 ppm. MS (EI): m/z = 183 [M]$^+$. $C_{13}H_{13}N$ (183.25): calcd. C 85.21, H 7.15, N 7.64; found C 85.07, H 7.19, N 7.55.

Benzyl(4-methoxyphenyl)amine: (Table 5, entry 2) A pale-yellow solid, isolated yield 23%, m.p. 48–50 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, J = 7.8 Hz, 2 H), 6.85–6.70 (m, 5 H), 6.50 (d, J = 7.8 Hz, 2 H), 4.20 (d, J = 5.6 Hz, 2 H), 4.0 (br. s, 1 H), 3.75 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.234, 141.445, 135.875, 128.425, 126.926, 126.451, 57.028, 56.621 ppm. GC–MS: m/z = 214 [M + H]$^+$. $C_{14}H_{15}NO$ (213.28): calcd. C 78.84, H 7.09, N 6.57; found C 79.19, H 7.05, N 6.60.

Benzyl(4-chlorophenyl)amine: (Table 5, entry 4) A light-yellow liquid, isolated yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (br. s, 1 H), 7.41–7.39 (m, 4 H), 6.90–6.80 (d, J = 8.3 Hz, 2 H), 6.65–6.50 (d, J = 8.3 Hz, 2 H), 3.45 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.450, 140.466, 128.445, 127.875, 126.834, 122.532, 116.181, 45.881 ppm. MS (EI): m/z = 218 [M + H]$^+$. $C_{13}H_{12}ClN$ (206.61): calcd. C 71.72, H 5.56, N 6.43; found C 71.80, H 5.55, N 6.39.

***N*-Cyclohexylaniline:** (Table 5, entry 9) A colorless oil, isolated yield 98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15–8.10 (m, 2 H), 7.17 (t, J = 7.61 Hz, 2 H), 6.67 (t, J = 8.31 Hz, 1 H), 6.57 (d, J = 8.48 Hz, 2 H), 3.31–3.27 (m, 1 H), 2.21–2.07 (m, 2 H), 1.86–1.78 (m, 2 H), 1.51–1.12 (m, 6 H) ppm. ^{13}C NMR [75 MHz, $CDCl_3$/DMSO (1:3)]: δ = 142.985, 131.061, 116.543, 113.232, 53.017, 33.329, 27.136, 22.980 ppm. GC–MS: *m*/*z* = 177 [M + 2 H]$^+$. $C_{12}H_{17}N$ (175.27): calcd. C 82.23, H 9.78, N 7.99; found C 82.02, H 9.85, N 8.01.

***N*-Cyclohexyl-2-nitroaniline:** (Table 5, entry 10) An orange crystalline solid, isolated yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35–8.10 (m, 1 H), 7.40–7.25 (m, 1 H), 6.85 (d, *J* = 7.99 Hz, 1 H), 6.66 (d, *J* = 8.7 Hz, 1 H), 3.51 (br. s, 1 H), 2.20–0.80 (m, 11 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO): δ = 138.664, 135.549, 131.061, 124.750, 116.999, 112.928, 53.017, 33.889, 28.306, 22.164 ppm. GC–MS: *m*/*z* = 220 [M]$^+$. $C_{12}H_{16}N_2O_2$ (220.27): calcd. C 65.43, H 7.32, N 12.72; found C 65.42, H 7.25, N 12.70.

***N*-Cyclohexyl-3-nitroaniline:** (Table 5, entry 11) Yellow crystalline solid, isolated yield 56%, m.p. 76–78 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.17 (m, 1 H), 6.85–6.82 (t, *J* = 8.39 Hz, 1 H), 6.55–6.45 (m, 1 H), 3.79 (br. s, 1 H), 3.35–3.25 (m, 1 H), 2.25–2.02 (m, 2 H), 1.50–1.10 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO): δ = 151.176, 146.080, 131.061, 118.165, 113.232, 107.593, 53.017, 33.385, 27.136, 22.164 ppm. GC–MS: *m*/*z* = 221 [M + H]$^+$. $C_{12}H_{16}N_2O_2$ (220.27): calcd. C 65.43, H 7.32, N 12.72; found C 64.92, H 7.30, N 12.69.

4-(Cyclohexylamino)benzoic Acid: (Table 5, entry 12) Yellow crystalline solid, isolated yield 75%, m.p. 142–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (m, 2 H), 7.65 (m, 3 H), 7.35–7.20 (m, 2 H), 3.10 (br. s, 1 H), 1.90–1.11 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO): δ = 172.221, 151.176, 131.061, 121.445, 110.700, 53.017, 32.754, 27.136, 23.633 ppm. MS (EI): *m*/*z* = 220 [M + H]$^+$. $C_{13}H_{17}NO_2$ (219.13): calcd. C 71.21, H7.81, N 6.39; found C 71.20, H75.79, N 6.40.

***N*-Cyclopentyl-2-nitroaniline:** (Table 5, entry 14) Orange thick liquid, isolated yield 62%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20–8.19 (m, 1 H), 8.05 (br. s, 1 H), 7.40 (t, *J* = 8.31 Hz, 1 H), 6.85 (d, *J* = 9.31 Hz, 1 H), 6.60 (t, *J* = 8.30 Hz, 1 H), 4.01–3.90 (m, 1 H), 2.20–2.00 (m, 2 H), 1.81–1.62 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.859, 136.019, 131.995, 124.600, 117.671, 113.340, 56.077, 31.657, 20.753 ppm. MS (EI): *m*/*z* = 207 [M + H]$^+$. $C_{11}H_{14}N_2O_2$ (206.24): calcd. C 64.06, H 6.84, N 13.58; found C 64.00, H 6.55, N 13.20.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for all of the products.

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