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Unique copper–salen complex: an efficient catalyst for N-arylations of anilines and imidazoles at room temperature

Ankur Gogoi [a,†], Gayatri Sarmah [a,†], Anindita Dewan [a], Utpal Bora [a,b,*]

[a] Department of Chemistry, Dibrugarh University, Dibrugarh 786004, Assam, India
[b] Department of Chemical Sciences, Tezpur University, Tezpur 784028, Assam, India

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ABSTRACT

We have reported here the catalytic activity of a unique Cu–salen type complex in N-arylation of anilines with arylboronic acids in water. The protocol is found to be applicable for a wide range of electronically diversified arylboronic acids and anilines with excellent yields of the isolated product. Further the scope of this protocol has been extended to the synthesis of various *N*-aryl imidazoles in iso-propanol.

The *N*-containing organic moiety possesses indispensable importance in the modern field of synthetic organic chemistry.[1] Among them diarylamines and *N*-arylimidazoles draw considerable attention owing to their wide applications in different medicinal and natural products.[2] In addition, imidazoles are also utilized for the preparation of *N*-heterocyclic carbenes[3] and ionic liquids.[4] Consequently their synthetic methods have been reviewed from time to time.[5] Traditional strategy of accessing these moieties was either by the aromatic nucleophilic substitution reaction (S_{N}-Ar) of nitrogen nucleophiles with activating aryl halides or the classical Ullmann[6] coupling using stoichiometric amounts of Cu salt at higher temperatures.[7] Besides these procedures, Buchwald and Hartwig established the wide applicability of Pd-source in the C–N coupling reactions.[8] Subsequent research efforts in the past decades have resulted in significant improvements in the copper and palladium catalyzed C–N bond formation reactions. Most of the catalytic systems developed for these transformations composed of copper or palladium derivatives associated with appropriate ligands in conventional organic or biphasic media.[9] Another copper mediated protocol for the C–N bond formation reaction was developed by Chan and Lam using arylboronic acid as coupling partner.[10] Arylboronic acids are well-known organometallic species which find wide applicability in contemporary organic synthesis because of their stability, structural diversity, and lower toxicity.[11] However requirement of 1–2 equiv of $Cu(OAc)_2$, large excess of arylboronic acid and long reaction times[12] are the few limitations associated with this cross coupling method. Further work on the Chan–Lam coupling reaction resulted in its catalytic version[13] along with its application to couple with other nucleophilic derivatives such as amide,[14] oxime,[15] sulfoximines,[16] thiols,[17] etc. Moreover, there are some reports available where the copper mediated Chan–Lam cross coupling was carried out in the presence of additives such as TEMPO, molecular oxygen, pyridine-*N*-oxide etc.[18] From the green chemistry points of view, the use of water as an environmentally benign and economically favorable alternative to organic solvents in organic synthesis has received tremendous interest.[19] In this respect, the development of catalyst in pure water seems particularly suitable for the Chan–Lam reaction due to the excellent stability of arylboronic acids in aqueous media. Moreover the ability to dissolve bases in water for activating arylboronic acid has made water an interesting candidate for these types of reactions. To the best of our knowledge precedent of the Cu-catalyzed Chan–Lam coupling reaction in water is very limited.[20] In this communication we wish to report the use of quadridentate Cu–Schiff base complex C1–C3 (Fig. 1) in Chan–Lam cross-coupling reactions of (i) arylboronic acids with anilines in water; (ii) arylboronic acids with imidazoles in *iso*-propanol at room temperature (Scheme 1).

We began our experiment with the hope of finding an efficient Cu-source which could catalyze the reaction between aniline and arylboronic acid in water. For that purpose different Cu-sources were investigated with aniline (0.5 mmol) and phenyl boronic acid

* Corresponding author. Tel.: +91 373 2370210; fax: +91 373 2370323.
E-mail addresses: utbora@yahoo.co.in, ubora@tezu.ernet.in (U. Bora).
† Equal contribution.

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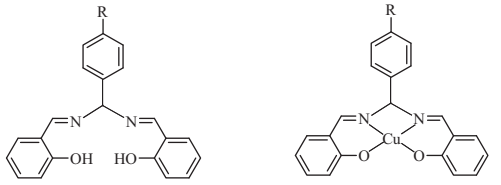
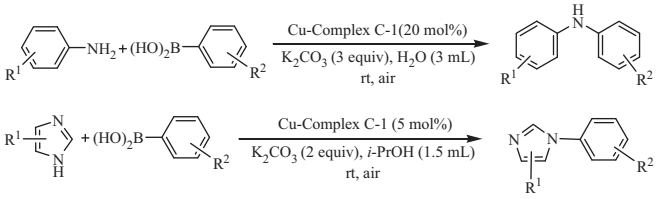


Figure 1. Screened ligands and complex.



Scheme 1. Chan–Lam coupling reaction.

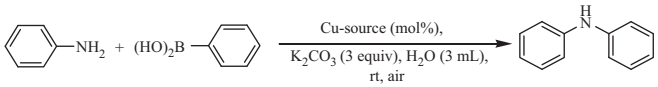
(1 mmol) as model substrates. The results obtained are summarized in Table 1.

Initially we probed some common Cu(II)-salt such as $Cu(OAc)_2{\cdot}H_2O$, $CuSO_4{\cdot}5H_2O$, $CuCl_2{\cdot}2H_2O$ for the N-arylation reaction which gave only 15–36% of diphenylamine (Table 1, entries 1–3). However Cu(I) salts were found to be completely inactive for this coupling reaction and gave only trace amounts of coupling products (Table 1, entries 4 & 5). It has been well documented in the literature that various Cu(II)–Schiff base complexes, particularly Cu(II)–salen type complexes were very effective for different organic transformations in organic solvents.[21] However only sulfonated Cu(II)–salen type complexes were found to be effective in water.[20,22] Among the various types of salens, *N*,*N*′-bis(salicylidene)arylmethanediamines are very simple, easily accessible, and form water soluble Cu(II) complexes (Fig. 1).[23–25] During our experiment we found that the Cu(II) complex (C-1) of the salen ligand (L-1) showed significantly improved isolated yields of diphenylamine under the reaction conditions (Table 1, entry 6). On the other hand, the Cu(II) complex (C-2), of the salen ligand (L-2) with an electron withdrawing group was found comparatively less effective and exhibited lower conversion (Table 1, entry 7). However the Cu(II) complex (C-3) of the salen ligand (L-3) with the electron donating group afforded 73% of the cross coupling product (Table 1, entry 8). As expected it was noticed that the reaction did not proceed in the absence of Cu-source (Table 1, entry 9). To optimize the amounts of catalyst we performed some test reactions using various amounts of the complex (C-1). The isolated yield decreased to 65% with 10 mol % of catalyst loading (Table 1, entry 10). When the catalyst loading was increased to 25 mol % no significant improvement in the yield of diphenylamine was observed (Table 1, entry 11). We also optimized the minimum amount of phenyl boronic acid required for the effective coupling. In most of the reported Chan–Lam type arylation, 2–3 equiv of phenyl boronic acid was used.[26,18c] But in our methodology 1.5 equiv of phenyl boronic acid was found to be sufficient for an effective cross coupling between aniline and phenyl boronic acid (Table 1, entry 12). However, the yield was dramatically decreased when 1.2 equiv of phenyl boronic acid was used (Table 1, entry 13). A controlled experiment with $Cu(OAc)_2{\cdot}H_2O$ and salen ligand (L-1, 20 mol %) resulted in only 55% of the yield (Table 1, entry 14). It has been observed that the use of the pre-formed complexes C1–C3 as a catalyst gave higher yields of the desired product compared to that of the in situ catalyst (Table 1, entries 12 vs 14). Although the reason for these differences in activities is not clear, one possible explanation could be the slow rate of formation of the in situ complex.

Interestingly, the reaction did not proceed under nitrogen atmosphere (Table 1, entry 15). However excellent yields of diphenylamine were obtained under oxygen atmosphere (Table 1, entry 16), which indicates the requirement of air/oxygen as oxidant for this transformation under the present reaction conditions. But due to operational simplicity we have decided to investigate the reaction parameter under aerial conditions. All these observations are consistent with the earlier report made by Evans and co-workers.[10c,18b] On the other hand, bases also play a significant role in the reactions of arylboronic acids, because bases are used to activate the arylboronic acids during the course of reactions. A typical experiment without bases gave only 24% of the isolated product (Table 2, entry 1). Considering its importance we then investigated the effect of different inorganic and organic bases on the C–N cross coupling reaction under the present reaction conditions using the Cu(II) complex C-1 as catalyst. Among the different bases used, carbonate bases such as Na_2CO_3, Cs_2CO_3, $NaHCO_3$ gave nearly comparable yields (Table 2, entries 2–4) with superior results in case of K_2CO_3 (Table 2, entry 5). Other bases $Na_3PO_4{\cdot}12H_2O$ and NaOH gave only trace amounts of the cross coupling product (Table 2, entries 6 & 7). On the other hand organic base triethylamine afforded very poor yields (Table 2, entry 8). Further screening with different amounts of K_2CO_3 established that maximum yield was obtained with three equivalents of K_2CO_3 (Table 2, entry 5). The reaction did not complete with 2 equiv of the base (Table 2, entry 9). On the other hand, use of four equivalents of K_2CO_3 resulted only in 56% of the desired product (Table 2, entry 10) along with the formation of significant amounts of phenol as side product (detected by GCMS).

The catalytic activity of this protocol under optimized reaction conditions was evaluated with respect to electronically diverse anilines and arylboronic acids.[28] It is clear from Table 3 that cross coupling of arylboronic acids with different aromatics gives better to excellent yields of the cross coupling product. Both

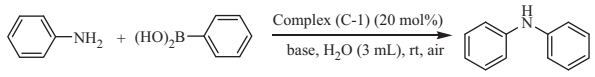
Table 1
Optimization of reaction conditions in water[a]



Entry	Cu-source (mol %)	Time (h)	Yield[b] (%)
1	$Cu(OAc)_2{\cdot}H_2O$ (20)	24	30
2	$CuSO_4{\cdot}5H_2O$ (20)	24	15
3	$CuCl_2{\cdot}2H_2O$ (20)	24	36
4	CuCl (20)	24	Trace
5	CuI (20)	24	Trace
6	C-1 (20)	18	75
7	C-2 (20)	21	65
8	C-3 (20)	20	73
9	—	24	—
10	C-1 (10)	24	65
11	C-1 (25)	20	72
12[c]	C-1 (20)	15	91
13[d]	C-1 (20)	22	61
14[e]	$Cu(OAc)_2{\cdot}H_2O$ (20) + L-1 (20)	24	55
15[f]	C-1 (20)	15	Trace
16[g]	C-1 (20)	14	93

[a] Reaction conditions: aniline (0.5 mmol), phenyl boronic acid (1 mmol), K_2CO_3 (1.5 mmol), water (3 mL), ca. 28 °C in air unless otherwise noted.
[b] Isolated yields.
[c] 0.75 mmol of phenyl boronic acid was used.
[d] 0.6 mmol of phenyl boronic acid was used.
[e] In situ $Cu(OAc)_2{\cdot}H_2O$ and Schiff base ligand (L-1) were used.
[f] Nitrogen atmosphere was used.
[g] Oxygen atmosphere was used.

Table 2
Optimization of base for the coupling reaction of phenyl boronic acid and aniline[a]



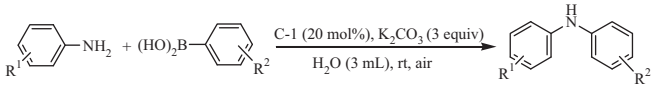
Entry	Base	Time (h)	Yield[b] (%)
1	–	36	24
2	Na_2CO_3	24	62
3	Cs_2CO_3	24	60
4	$NaHCO_3$	24	47
5	K_2CO_3	15	91
6	$Na_3PO_4{\cdot}12H_2O$	24	13
7	NaOH	24	12
8	Et_3N	24	30
9[c]	K_2CO_3	30	50
10[d]	K_2CO_3	15	56

[a] Reaction conditions: aniline (0.5 mmol), phenyl boronic acid (0.75 mmol), base (1.5 mmol), C-1 complex (20 mol %), water (3 mL), ca. 28 °C in air unless otherwise noted.
[b] Isolated yields.
[c] 2 equiv of base was used
[d] 4 equiv of base was used.

electron-deficient and electron-rich aromatics coupled efficiently under the condition resulting in good yields of diaryl amines (Table 3, entries 2–5). Notably, *meta*-substituted aromatics also produces significant amounts of the desired product (Table 3, entry 6). A series of electron-rich arylboronic acids were tested, bearing good yields of the desired cross coupling product (Table 3, entries 8–12). However, the presence of electron withdrawing groups at the *para*-position of arylboronic acid decreased the reaction rate and rendered modest yields of diarylamine (Table 3, entries 13–15). It was noticed that the majority of the catalytic systems developed for C–N cross coupling reactions were not selective as they successively combine with –OH functionality to give the C–O coupling product along with C–N coupling. We were pleased to find that our catalytic system was selective for –NH functionality in the presence of –OH group as 3-hydroxy aniline gave only the C–N cross coupling product (Table 3, entry 7).

Our next endeavor was to extend the scope of this protocol for the N-arylation of imidazoles. But unfortunately we were able to isolate only 51% the *N*-phenyl imidazole with complex C-1 in water

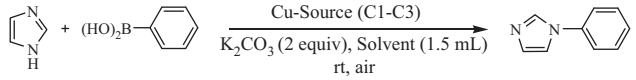
Table 3
Reaction of different arylboronic acids with anilines[a]



Entry	R^1	R^2	Time (h)	Yield[b] (%)
1	H	H	15	91
2	4-OCH_3	H	16	94
3	4-CH_3	H	12	95
4	4-Cl	H	24	74
5	4-COOH	H	24	81
6	3-CH_3	H	22	85
7	3-OH	H	24	75
8	H	4-OCH_3	16	82
9	H	3-CH_3	19	75
10	H	4-*t*-Butyl	18	76
11	4-OCH_3	4-OCH_3	21	84
12	4-CH_3	4-OCH_3	20	80
13	H	4-F	24	71
14	H	4-Cl	24	79
15	4-CH_3	4-F	24	76

[a] Reaction conditions: aryl amine (0.5 mmol), arylboronic acid (0.75 mmol), water (3 mL), ca. 28 °C in air unless otherwise noted.
[b] Yields are given for isolated products.

Table 4
Optimization of reaction condition for N-arylation of imidazole by phenyl boronic acid[a]



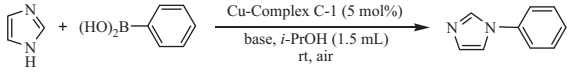
Entry	Cu-source (mol %)	Solvent (1.5 mL)	Time (h)	Yield[b] (%)
1	C-1 (20)	H_2O	24	51
2	C-1 (20)	*i*-PrOH	10	94
3	C-1 (10)	*i*-PrOH	10	94
4	C-1 (5)	*i*-PrOH	10	94
5	C-1 (3)	*i*-PrOH	18	62
6	–	*i*-PrOH	24	–
7	C-1 (5)	EtOH	24	78
8	C-1 (5)	MeOH	24	79
9	C-1 (5)	*i*-PrOH–H_2O	15	69
10	C-1 (5)	CH_3CN	24	41
11	C-1 (5)	DMSO	24	Trace
12	C-1 (5)	DCM	24	60
13	C-1 (5)	Toluene	24	45
14	C-1 (5)	DMF	24	21
15	C-1 (5)	THF	24	30
16	C-1 (5)	DMSO-H_2O	24	18
17	C-1 (5)	DMF-H_2O	24	35
18	C-2 (5)	*i*-PrOH	12	78
19	C-3 (5)	*i*-PrOH	10	73
20[c]	C-1 (5)	*i*-PrOH	15	78
21[d]	$Cu(OAc)_2{\cdot}H_2O$ + L1	*i*-PrOH	24	75
22[e]	$Cu(OAc)_2{\cdot}H_2O$	*i*-PrOH	24	41

[a] Reaction conditions: imidazole (0.5 mmol), phenyl boronic acid (1 mmol), K_2CO_3 (2 equiv), solvent (3 mL), ca. 28 °C in air unless otherwise noted.
[b] Yields are of isolated products.
[c] 1.5 equiv of phenyl boronic acid was used.
[d] 5 mol % of $Cu(OAc)_2{\cdot}H_2O$ and ligand L-1 were used.
[e] 5 mol % of $Cu(OAc)_2{\cdot}H_2O$ was used.

(Table 4, entry 1). So we planned to investigate the different reaction parameters for this transformation. Thus N-arylation of imidazole (0.5 mmol) with phenyl boronic acid (1 mmol) was studied as a model reaction to identify a suitable solvent in the presence of K_2CO_3 (1 mmol) at room temperature. After a series of experiments we found that 5 mol % of complex (**C-1**) shows maximum activity affording 94% of *N*-phenyl imidazole in *iso*-propanol (Table 4, entries 2–6).

However, a lower yield was detected with 1:1 aqueous *iso*-propanol solvent (Table 4 entry 9). Surprisingly, other organic solvents such as CH_3CN, DMSO, DCM, toluene, DMF, and THF provided very

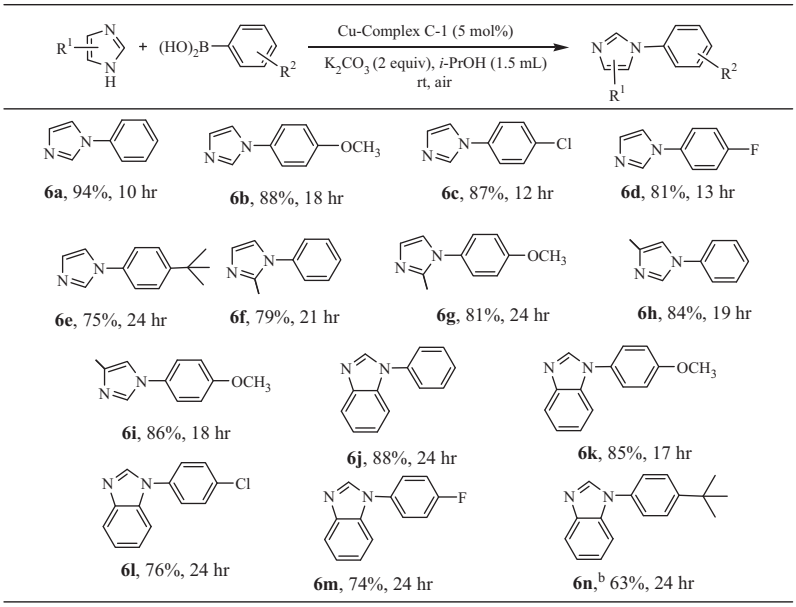
Table 5
Optimization of base for N-arylation of imodazoles[a]



Entry	Base	Time (h)	Yield[b] (%)
1	–	24	12
2	K_2CO_3	10	94
3	Na_2CO_3	15	85
4	Cs_2CO_3	12	87
5	$NaHCO_3$	24	45
6	NaOH	24	30
7	$Na_3PO_4{\cdot}12H_2O$	24	71
8	Et_3N	24	63
9[c]	K_2CO_3	24	74
10[d]	K_2CO_3	10	94

[a] Reaction conditions: imidazole (0.5 mmol), phenyl boronic acid (1 mmol), C-1 (5 mol %), base (2 equiv), *iso*-propanol (1.5 mL), ca. 28 °C unless otherwise noted.
[b] Yields are of isolated products.
[c] 1.5 equiv of K_2CO_3 was used.
[d] 3 equiv of K_2CO_3 was used.

Table 6
Reaction scope with different arylboronic acid and aryl imidazole[a]



[a] Reaction conditions: aryl imidazole (0.5 mmol), arylboronic acid (1 mmol), K_2CO_3 (1 mmol), C-1 (5 mol %), *i*-PrOH (1.5 mL), ca. 28 °C unless otherwise noted. All the yields are of isolated product.
[b] Reaction did not complete after 24 h.

low yields of *N*-phenyl imidazole (Table 4, entries 10–17). We also examined the effectiveness of other two copper complexes C-2 and C-3 for the N-arylation of imidazoles. However poor yields of the product were detected compared to C-1 (Table 4, entries 4 vs 18 &19).

During the process of optimization we also tested the amount of arylboronic acid. Maximum yield was obtained with two equivalents of phenyl boronic acid (Table 4 entries 19 & 20). No significant yield of isolated *N*-aryl imidazole was observed in the in situ application of $Cu(OAc)_2{\cdot}H_2O$ and salen ligand L-1 (Table 4, entry 21).

In order to study the effect of different bases for this cross coupling reaction we have examined the reaction between imidazole (0.5 mmol) and phenyl boronic acid (1 mmol) in *iso*-propanol (1.5 mL) at room temperature. A wide range of inorganic and organic bases were tested. The maximum reaction efficiency was observed with two equivalents of K_2CO_3 (Table 5, entries 2 vs 1 and 3–10).

Next, the scope of this protocol with respect to substituted arylboronic acids and imidazoles was examined with 5 mol % of Cu–complex C-1, K_2CO_3 as base in *iso*-propanol at room temperature.[29] The results obtained are summarized in Table 6. Arylboronic acids having electron donating and electron withdrawing groups at the *para*-position furnished excellent yields of the isolated *N*-arylated product (Table 6, entries 6a–6e). The substitution in the imidazole ring has a slight effect in the efficiencies. For example, 2-methyl and 4-methyl imidazoles take longer reaction times (Table 6, entries 6f–6i). In addition, the protocol was also suitable for the N-arylation of benzimidazole (Table 6, entries 6j–6n).

In conclusion, we have developed a mild and efficient protocol for the Chan–Lam cross coupling reaction of anilines with arylboronic acid in water under aerobic conditions. In addition, the protocol can be utilized for the N-arylation of imidazoles in *iso*-propanol. Both the methods have versatile synthetic utility. Mild reaction conditions, use of non toxic solvent, and broad substrate scope make this protocol an attractive alternative for the existing Chan–Lam cross coupling reaction.

Acknowledgments

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24. *General procedure for the synthesis of N,N′-bis(salicylidene)-arylmethanedi:*[23b] A 100 mL round bottomed flask was charged with salicylaldehyde (0.38 g, 3 mmol), benzaldehyde (0.16 g, 1.5 mmol), and NH_4OAc (0.25 g, 3.27 mmol) in the presence of NEt_3 (0.12 mL). The mixture was then stirred for 10 min. After completion of the reaction (vide TLC), pale yellow oily substance was obtained. The yellow oily mixture was then dissolved in 1.5 mL MeOH and cooled for one night, a yellow solid was precipitated. This solid product was filtered off and washed with cold MeOH. The crude product was purified by recrystallization from ethanol and the pure Schiff base, *N,N′*-bis(salicylidene)-phenylmethanediamine was obtained in 90% yield, mp = 118–120 °C. The Schiff base products were identified by comparing the physical and spectroscopic data with the literature report.[23b]
25. *General procedure for the synthesis of Cu–N,N′-bis(salicylidene)-arylmethanediamine complex:*[23a] A mixture of *N,N′*-bis(salicylidene)-arylmethanediamine (0.660 g, 2 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (0.398 g, 2 mmol) was refluxed in ethanol (30 mL) under nitrogen atmosphere for 8 h. Volatiles were removed in vacuo and the residue was washed with diethylether. The resulting dark green colored complex was crystallized from DMF/diethylether and the green colored crystals of the title compound **C1** (627 g, 80.2%) were obtained, Anal. Calcd for $C_{21}H_{16}N_2O_2Cu$: C, 64.36; H, 4.10; N, 7.15. Found: C, 64.41; H, 4.16; N, 7.20. MS: *m/z*: 392 (M^++1). IR (KBr, ν cm^{-1}): 1620 ($\nu_{C=N}$), 1338 (ν_{C-O}), 1444 (ν_{C-N}), 553 (ν_{Cu-O}), 445 (ν_{Cu-N}). ^{1}H NMR: (400 MHz, DMSO-d_6, δ ppm): 6.40 (s, 1H, NCHN), 6.95–7.95 (m, 13H, Ph + Ph + Ph), 8.60 (s, 2H, HC=N). The structure of Cu–Schiff base complexes were confirmed by comparing spectroscopic data with the literature report.[23a]
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28. *General procedure for the N-arylation of anilines with aryl boronic acids:* A 50 mL round bottomed flask was charged with amine (0.5 mmol), arylboronic acid (0.75 mmol), K_2CO_3 (1.5 mmol, 207 mg), C-1 complex (20 mol %, 39.15 mg) in 3 mL of water at room temperature. The reaction mixture was stirred with a magnetic stirrer for appropriate time. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with 20 mL of water and extracted with diethylether (3 × 20 mL). The combined organic layer were washed with brine and dried over by anhydrous Na_2SO_4 and evaporated in a rotary evaporator under reduced pressure. The crude was purified by column chromatography on silica gel (hexane/ethyl acetate, 9:1) to afford the desired product. The purity of the compound was confirmed by ^{1}H NMR, ^{13}CNMR, MS, and melting point data. **Diphenylamine** (Table 3, entry 1):[27] ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.26–7.24 (m, 4H, ArH), 7.70 (d, *J* = 7.32 Hz, 4H, ArH), 6.92 (t, *J* = 7.2 Hz, 2H, ArH), 5.68 (br s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.1, 129.4, 121.1, 117.8.
29. *General procedure for the N-arylation of imidazoles with aryl boronic acids:* A mixture of aryl imidazoles (0.5 mmol), arylboronic acid (1 mmol), K_2CO_3 (1 mmol), C-1 complex (5 mol %, 9.79 mg) in *iso*-propanol (1.5 mL) was stirred in a 50 mL oven dried round bottomed flask. After the completion of the reaction (monitored by TLC), the mixture was diluted with 20 mL water. The organic part was extracted with diethyl ether (3 × 20 mL) followed by drying over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to obtain the crude product. The residue was then purified with column chromatography using methanol/ethyl acetate (1:9) as eluent to afford the desired product. The purity of the compound was confirmed by ^{1}H NMR, ^{13}CNMR, MS, and melting point data. ***N*-Phenyl imidazole** (**6a**):[18c] ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 8.02 (s, 1H), 7.51–7.47 (m, 2H), 7.41–7.37 (m, 3H), 7.26 (s, 1H), 7.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):[9k] 138.1, 135.9, 130.5, 130.1, 127.6, 121.8, 118.5.