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

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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.

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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_NAr) 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

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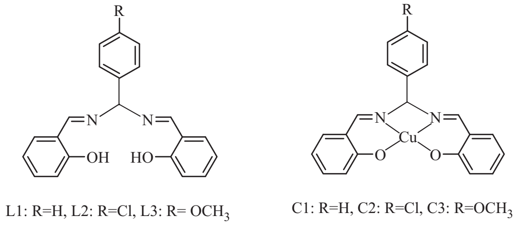
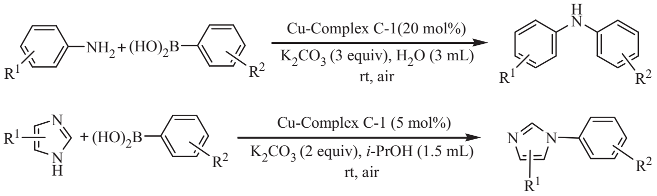


Figure 1. Screened ligands and complex.

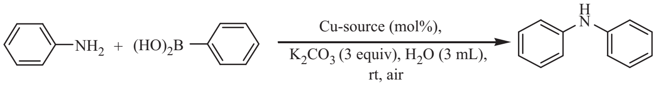


Scheme 1. Chan–Lam coupling reaction.

(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.

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.

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

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