



Spherical CuO Nanoparticles as Catalyst for Chan–Lam Cross-Coupling Reaction under Base Free Condition

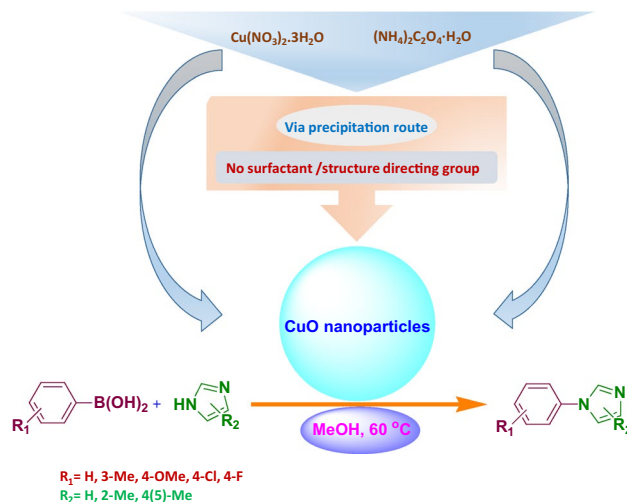
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Abstract

An easy methodology has been developed for the *N*-arylation of imidazole with arylboronic acid in absence of base and ligand with the aid of as-synthesized CuO nanoparticles. The CuO nanoparticles have been synthesized via precipitation route. The as-synthesized copper oxide nanoparticles are well characterized by various analytical and spectroscopic techniques, such as powder XRD, Raman spectroscopy, TEM and BET surface area analyses. The CuO nanoparticles appear as spherical in shape with a surface area of 15.4 m²/g. The mentioned reaction successfully proceeds at moderate temperature in presence of the as-synthesized nanoparticles. The protocol is applicable to a wide variety of electronically diverse precursor moieties signifying its well applicability.

Graphical Abstract



Keywords N-arylation · CuO nanoparticles · Imidazole · Phenylboronic acid · MeOH

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1 Introduction

In modern synthetic organic chemistry, the construction of *N*-arylated products from *N*-containing heterocycles have found immense consideration in recent days. The *N*-arylated products find importance because of their wide applications as structural and functional units in natural products as well as in biological compounds [1–15]. A wide number

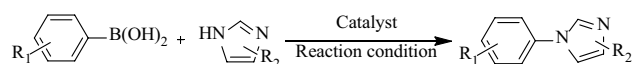
of biologically active compounds such as cyclic AMP phosphodiesterase inhibitors [16, 17], AMPA receptor antagonists [17], cardiotoxic agents [18–20], thromboxane synthase inhibitors [21, 22] and topical antiglaucoma agents [23] etc. have been prepared from N-arylated products. Traditionally, N-arylated products are obtained by two methods viz. nucleophilic aromatic substitution, which requires activated substrates bearing electron withdrawing groups [13, 17, 19, 20, 24, 25] and classical Ullmann-type coupling, which extensively needs higher temperature and longer reaction time along with the use of stoichiometric amount of copper salt [26–31]. In recent years, Buchwald and Hartwig as well as many others developed palladium based protocols for the construction of C–N bond [32–41]. Considering the issue of high cost of palladium, copper is given more importance for this type of conversion. This continual process of finding new routes with copper catalysts was successfully further enhanced by Chan–Lam for the C–N bond formation reaction using arylboronic acids as aryl source [42–44]. Many other literatures demonstrated the use of copper salts as catalyst for C–N bond formation reaction in later time [45–48]. Collman has developed an efficient catalytic methodology for C–N bond formation using Cu(II) complex with nitrogen chelating bidentate ligands at room temperature [49]. Thus, continuous efforts have been devoted towards the development of mild and efficient routes for this type of reaction. In recent times, arylboronic acid has attained immense attraction as a cross-coupling partner due to its stability, structural diversity and less toxic nature as compared to other aryl halides [50]. Consequently, arylboronic acid has been used as an alternative arylating agent in C–N cross-coupling reaction.

In this era, nanoparticles have found keen attention of the researchers as catalysts for synthetic organic reactions because of their unique property like high surface to volume ratio. And as such, they provide more reaction sites so

that higher activity and selectivity can be achieved easily as compared to the bulk materials thereby minimising the formation of undesired products [51–58]. Looking towards the aspects of nanoparticles for organic transformations, we have synthesized CuO nanoparticles to implicate on the Chan–Lam cross coupling reaction. Recent literatures advocated the use of commercial as well as synthesized Cu and CuO nanoparticles for different organic transformations including C–N bond formation reactions [59–64]. Suramwar et al. synthesized CuO nanoparticles via a thermal-assisted strategy at reflux temperature using stabilising agent for the N-arylation of indoles [59]. Punniyamurthy and co-workers successfully utilised commercially available CuO nanoparticles for the C–N, C–O and C–S cross coupling reaction [62, 63].

Thus, considering the efficient catalytic properties of Cu based nanoparticles, herein we report the synthesis of CuO nanoparticles via a precipitation route without use of any surfactant or structure directing agent. The as-synthesized CuO nanoparticles are characterized by X-ray diffraction, transmission electron microscopy (TEM), Raman spectroscopy and BET surface area analyses. Further a facile protocol for N-arylation of imidazole with arylboronic acid using the as-synthesized CuO nanoparticles is reported. To minimise the use of harsh reaction conditions as well as costly procedures are seemed to be main concerned area of current research. Consequently, the uses of excess base, higher temperature and complicated catalytic system have been avoided in our report. The newly synthesized CuO nanoparticles have effectively catalyzed the current reaction with greater activity in absence of base and other ligands at a moderate temperature. Below some of the previously reported procedures for C–N coupling [64–69] are enlisted in comparison to our report (Table 1).

Table 1 A comparison with the reported literature with the current protocol



Entry	Reaction conditions	Catalyst	Yield (%)
1 [64]	MeOH–H ₂ O(1:1), K ₂ CO ₃ , rt, 8–13 h	CuO nanoparticles	81–88
2 [65]	MeOH, TEA, Reflux, 2.5–5 h	CELL-Cu(0)	80–98
3 [66]	H ₂ O, 100 °C, air, 6 h	Sulfonatocopper(II)(salen) complex	43–93
4 [67]	MeOH, 40 °C, N ₂ atm, 10–18 h	Polymer supported copper(I) complex	38–96
5 [68]	MeOH, K ₂ CO ₃ , 65 °C, air, 3–5 h	Copper(I) 3-methylsalicylate (CuMeSal)	24–84
6 [69]	EtOH, TEA, rt, 12–18 h	Cu(tpa) MOF	87–99
7 [This work]	MeOH, 60 °C, air, 5–18 h	CuO nanoparticles	42–96

2 Experimental Section

2.1 Materials Used

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), diammonium oxalate monohydrate ($(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$), Imidazole ($\text{C}_3\text{H}_4\text{N}_2$), Methanol (CH_3OH) and silica gel were supplied by Merck, India. Phenylboronic acid was purchased from SRL Chemical, India. All of the chemicals were of analytical grade and used without any purification. Again, all the experiments were performed with distilled water.

2.2 Characterization Techniques

The powder X-ray diffraction (PXRD) pattern was recorded using a nickel-filtered $\text{CuK}\alpha$ (0.15418 nm) radiation source on a Rigaku instrument. Raman spectrum was recorded using a laser micro-Raman system (make: Horiba Jobin Vyon, model: LabRam HR) at room temperature on 488 nm excitation wavelength. Transmission electron microscopic (TEM) investigations were carried out on a FEI-Technai (G2 F20S-TWIN) instrument operating at an accelerating voltage of 200 kV that equipped with a slow-scan CCD camera. The surface areas were determined by Brunauer–Emmett–Teller (BET) method measured by N_2 physisorption using a quantachrome instrument (Model: NOVA 1000e). The pore size and pore volume were determined following Barrett–Joyner–Halenda (BJH) method in the same instrument. The ^1H NMR spectra were recorded on 400 MHz JEOL, JNM ECS NMR spectrometer using CDCl_3 as solvent and TMS (0 ppm) as internal reference. The ^{13}C NMR spectra were recorded at 100 MHz using CDCl_3 (77.0 ppm) as standard. The thin layer chromatography observation was carried out on Merck silica gel 60F254 plates using short wavelength (254 nm) of UV light. Silica gel (60–120 mesh) was used for the column chromatography technique for the purification of the crude products.

2.3 Synthesis of Copper Oxide (CuO) Nanoparticles

For the synthesis of copper oxides, 4.832 g of copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and 2.842 g of diammonium oxalate monohydrate ($(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) were dissolved in 100 mL of distilled water separately to form homogeneous solutions, respectively. The molar ratio of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was kept as 1:1. The $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ solution was then added dropwise to the $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution with vigorous stirring. Subsequently, the mixed solution was then aged for 24 h at room temperature without any disturbance. The resulting precipitate was separated by centrifugation, washed several times with distilled water and

dried in an oven at 80 °C for 12 h. Finally, the dried product was sintered at 350 °C for 3 h in air atmosphere.

2.4 General Procedure for the N-Arylation of Imidazole

A 50 mL round bottomed flask was charged with a mixture of imidazole (0.5 mmol) and phenylboronic acid (0.6 mmol) followed by the addition of 15 wt% CuO nanoparticles in 3 mL of MeOH at 60 °C. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was extracted with ethyl acetate (3×10 mL). Then, the extracted part was dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. The concentrated product was purified by column chromatography over silica gel (eluent:ethyl acetate–hexane) to obtain the pure product. The N-arylated products of imidazole thus obtained were confirmed by ^1H and ^{13}C NMR.

3 Results and Discussion

3.1 Catalyst Characterization

After the thermal treatment in air atmosphere at 350 °C for 3 h, the as-obtained product was subjected to PXRD analysis. The X-ray diffraction pattern (Fig. 1a) confirms the formation of the product as monoclinic phase of CuO with lattice constants $a = 4.686 \text{ \AA}$, $b = 3.423 \text{ \AA}$, and $c = 5.132 \text{ \AA}$ (JCPDS Card No. 41–0254). The peaks at 32.5°, 35.5°, 38.9°, 48.7°, 52.6°, 58.5°, 61.4°, 66.0° and 68.1° are assigned to the (110), (11-1), (200), (20-2), (020), (202), (11-3), (220) and (22-1) lattice planes of monoclinic CuO, respectively. The high intensity diffraction peaks of the sample confirm its crystallinity and no other impurities are detected. The Raman spectrum of the as-synthesized CuO shows three intense Raman peaks around 287 (A_g), 334 (B_g^1) and 615 (B_g^2) cm^{-1} (Fig. 1b). The Raman spectroscopic study indicates that the as-synthesized CuO belongs to the C_{2h}^6 space group with only three Raman active ($A_g + 2B_g$) modes. This is in accordance with our previous reports [70–73]. Figure 1c shows the TEM images of the as-synthesized CuO, suggesting that the particles of CuO are spherical in shape with irregular sizes (a maximum of 80 nm in range). A clear lattice fringe with spacing of 0.25 nm, corresponding to the (11-1) planes of monoclinic CuO is also observed (Fig. 1d). The selected area electron diffraction (SAED) measurement of the respective CuO nanoparticles (inset of Fig. 1c) shows a highly crystalline nature with three diffraction rings. These three rings can

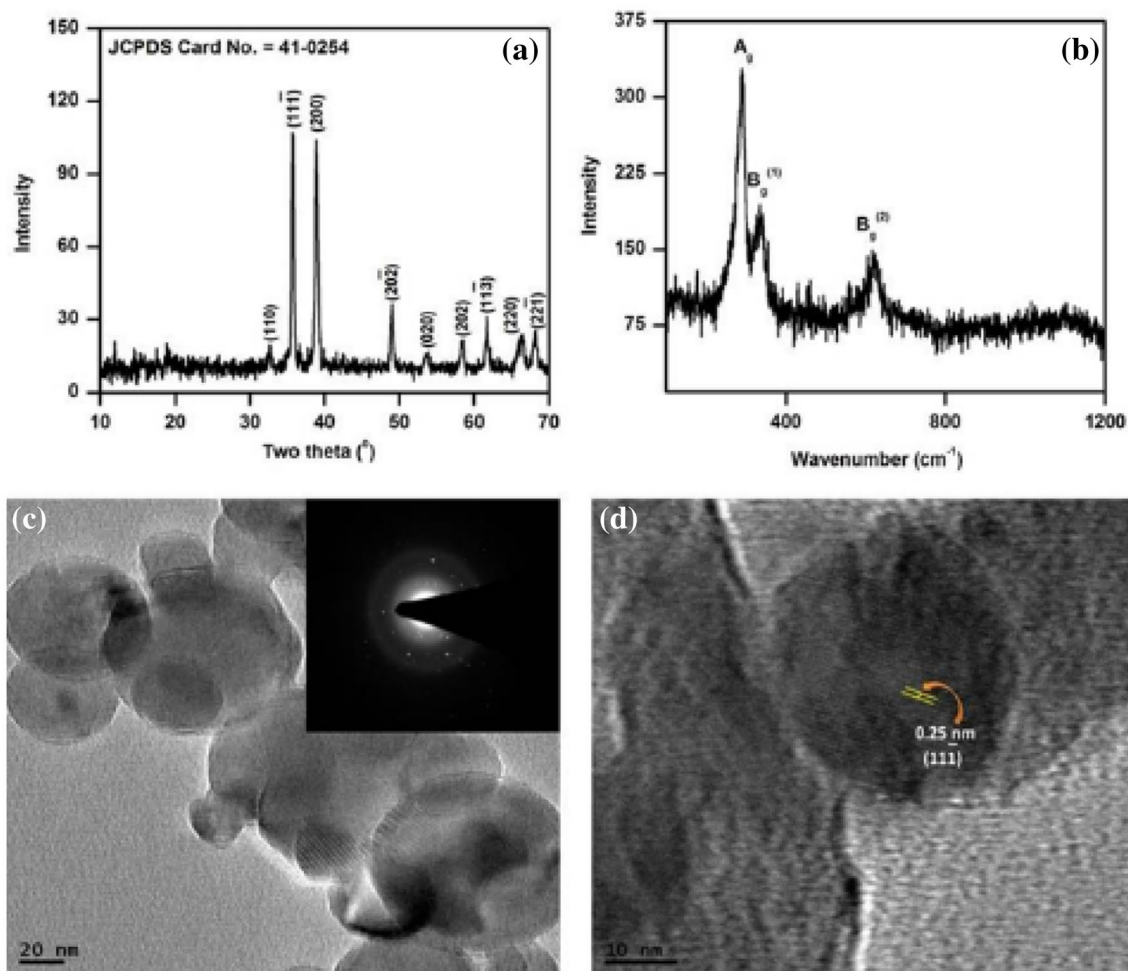


Fig. 1 X-ray diffraction pattern (a) Raman spectrum (b) TEM images (c, d) of the as-synthesized CuO nanoparticles; inset of (c) corresponding SAED pattern of the CuO nanoparticles

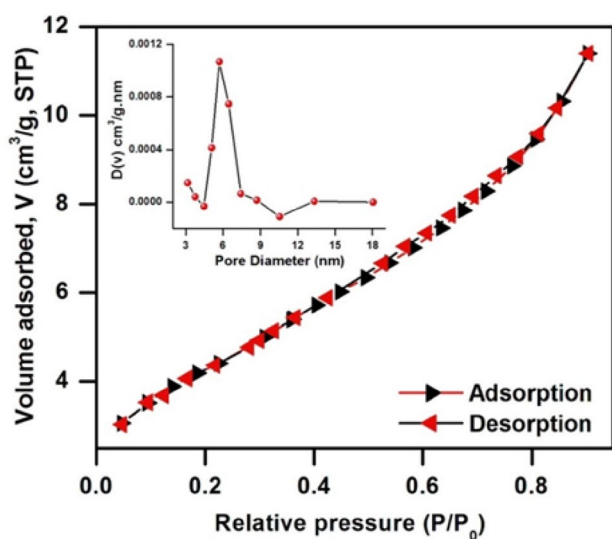


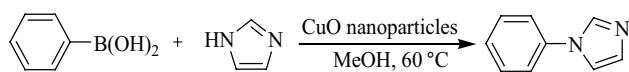
Fig. 2 N₂ adsorption/desorption isotherm of CuO nanoparticles; inset pore size distribution of CuO nanoparticles

be attributed to the (200), (020) and (110) lattice planes of monoclinic CuO, respectively.

Further, the textural property of CuO nanoparticles was assessed by N₂ adsorption/desorption analysis at liquid N₂ temperature. The corresponding adsorption/desorption isotherm and pore size distribution curve (inset) are shown in Fig. 2. The N₂ adsorption/desorption isotherm represents the CuO nanoparticles as a mesoporous material. Moreover, a typical surface area of 15.4 m²/g with a pore volume and diameter of 0.013 cm³/g and 5.7 nm, respectively is observed for the as-synthesized CuO nanoparticles. This value of surface area is quite larger than that of usually used commercial CuO powder (*ca.* 0.1 m²/g) and quite reasonable for the CuO nanomaterials [70, 73, 74].

3.2 Catalytic Activity

To examine the catalytic activity of our as-synthesized CuO nanoparticles, we have selected the N-arylation

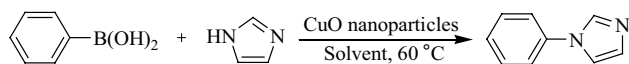
Table 2 Optimization condition for the amount of CuO nanoparticles as catalyst

Entry	Amount of catalyst (wt%)	Time (h)	Yield ^a (%)
1	10	9	56
2	15	5	94
3	20	4	94

Reaction conditions: phenylboronic acid (0.6 mmol), imidazole (0.5 mmol), MeOH (3 mL)

^aIsolated yield

reaction of imidazole with arylboronic acid. So, we tried to obtain an optimized condition for this reaction. For that purpose, we have chosen phenylboronic acid and imidazole as the model substrates and the reaction was performed by taking MeOH as the solvent at 60 °C. We performed a set of reactions to investigate the amount of catalyst necessary for the reaction. For that, we used different amounts of catalyst loadings (Table 2, entries 1–3). From Table 2, it is observed that 15 wt% of the catalyst loading gave an excellent yield of 94% (Table 2, entry 2). However, 10 wt% loading of the catalyst led to comparatively lower yield than that of the as mentioned earlier

Table 3 Effect of different solvents on N-arylation of imidazole with phenylboronic acid

Entry	Solvent	Time (h)	Yield ^a (%)
1	H ₂ O	7	56
2	EtOH	6	80
3	MeOH	5	94
4	THF	10	40
5	2-Me THF	9	–
6 ^b	H ₂ O:THF	15	78
7 ^b	H ₂ O:2-Me THF	7	84
8 ^b	H ₂ O:MeOH	6	75
9 ^c	MeOH	10	–

Reaction conditions: phenylboronic acid (0.6 mmol), imidazole (0.5 mmol), CuO nanoparticles (15 wt%), solvent (3 mL)

^aIsolated yield

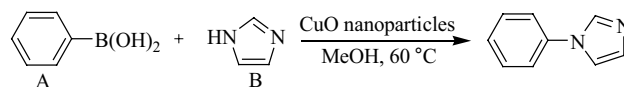
^bSolvents were used in 1:1 (v/v) ratio

^cReaction was performed at room temperature

(Table 2, entry 1 vs. entry 2). On the other hand, increase in the amount of catalyst to 20 wt%, exhibited similar yield as that of 15 wt% catalyst loading (Table 2, entry 2 vs. entry 3). Thus, by analyzing the results, we took 15 wt% catalyst for the current reaction.

Then we studied the effect of different solvents on our current reaction protocol. For that purpose, we conducted several test reactions by choosing different solvents viz H₂O, MeOH, EtOH, THF and 2-Me THF. Lower yield was observed in case of H₂O and THF (Table 3, entry 1 & entry 4). Again, no product formation was evident with 2-Me THF (Table 3, entry 5). On the other hand, a relatively good yield (80%) was observed by considering EtOH as solvent (Table 3, entry 2). However, MeOH, on taking as solvent afford excellent yield of desired product with 94% isolated yield (Table 3, entry 3). We also investigated the role of aqueous mixtures of solvents such as H₂O:MeOH, H₂O:THF and H₂O:2-Me THF (Table 3, entries 6–8) for the current reaction. Although some acceptable yields were obtained with the aqueous solvents, they were lower than that of MeOH (Table 3, entry 3 vs. entries 6–8). From these studies, MeOH was considered as the best solvent for our present reaction protocol. Further, we wished to know what happens to the reaction at room temperature. But no product formation was observed (Table 3, entry 9) even after a long time. That suggests the requirement of moderate temperature (60 °C) for this protocol.

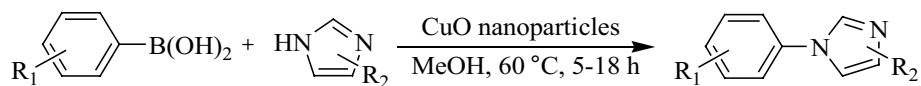
Further we investigated the amount of substrates in so far optimized reaction conditions. Test reactions were carried out by choosing different proportions of substrates in order to evaluate their appropriate ratio (Table 4, entries 1–3). Use of 1 equivalent of the imidazole and 1.2 equivalent of the phenylboronic acid exhibited the best result (Table 4, entry 3). The increase in the amount of imidazole or the decrease in the amount of phenylboronic acid did not exhibit good results (Table 4, entries 1 and 2). Therefore, we decided to

Table 4 Effect of amount of substrates on N-arylation of imidazole with phenylboronic acid

Entry	A (equivalent)	B (equivalent)	Time (h)	Yield ^a (%)
1	1	1	5	65
2	1	1.2	5	53
3	1.2	1	5	94

Reaction conditions: phenylboronic acid (1.2 mmol), imidazole (1 mmol), CuO nanoparticles (15 wt%), MeOH (3 mL)

^aIsolated yield

Table 5 Study of different substrates

Entry	R ₁	R ₂	Time (h)	Yield ^a (%)
1	4-F	H	6	96
2	4-F	2-Me	7	60
3	4-Cl	H	8	83
4	4-Cl	4(5)-Me	7	65
5	4-Cl	2-Me	5	42
6	H	H	5	94
7	H	2-Me	8	78
8	H	4(5)-Me	7	79
9	4-OMe	H	4	86
10	4-OMe	4(5)-Me	16	49
11	4-OMe	2-Me	18	44
12	3-Me	H	4	87
13	3-Me	2-Me	7	72
14	H	4,5-Dicyano	12	–

Reaction conditions: phenylboronic acid (0.6 mmol), imidazole (0.5 mmol), CuO nano (15 wt%), MeOH (3 mL)

^aIsolated yield

consider the condition of substrate ratio 1.2:1 of phenylboronic acid and imidazole respectively (Table 4, entry 3).

After these screenings, we obtained an optimized condition for the current reaction protocol. Further, we expanded the scope and limitations of this method to various electronically diverse imidazole and phenylboronic acid moieties (Table 5, entries 1–14). Both the electron withdrawing and the electron donating group containing phenylboronic acid as well as imidazole were seemed to be compatible with our current methodology. Phenylboronic acid with the electron withdrawing –F group at the 4-position showed excellent yield (Table 5, entry 1). But a moderate yield was observed with 4-fluorophenylboronic acid with imidazole containing electron donating –CH₃ group at 2-position (Table 5, entry 2).

Similarly, –Cl group containing phenylboronic acid at the 4-position gave good yield with imidazole, but moderate yields were achieved with 4(5)-methyl imidazole and 2-methylimidazole (Table 5, entries 3–5). Similar trends were observed for phenylboronic acid with –OCH₃ group at the 4-position. A very good yield was observed for the coupling of 4-methoxyphenylboronic acid with imidazole, but with 4(5)-methylimidazole and 2-methylimidazole, it gave relatively lower yields (Table 5, entry 9 and entries 10 and 11). The electron donating –CH₃ group at the 3-position of phenylboronic acid also enhanced the reaction with imidazole and 2-methylimidazole (Table 5, entries 12 and

13). Again, phenylboronic acid with imidazole, 4(5)-methylimidazole and 2-methylimidazole gave good to excellent yield (Table 5, entries 6–8). However, no product formation was observed for electron withdrawing –CN group containing imidazole with phenylboronic acid even after a long time (Table 5, entry 14).

The current methodology provides a base free reaction conditions for the N-arylation of imidazole with arylboronic acid. The basic characteristic of imidazole moiety may provide the required basic conditions to catalyze the reaction. As a result, the reaction mixture after addition of imidazole may lead to the activation of the phenylboronic acid moiety which subsequently leads to the formation of the product [75, 76]. Moreover, CuO surface is also known to be basic in nature which may further enhance the activity under base free condition.

3.3 Recyclability of the CuO Nanoparticles

We performed the recyclability test to check the activity and stability of the CuO nanoparticles. After the 1st cycle, we recovered the catalyst by centrifugation and the catalyst was dried and used for the 2nd cycle. But a decrease in activity of the catalyst was observed and we obtained 60% yield of the cross coupling product in the 2nd catalytic cycle. The reason for this decrease in the activity of the CuO nanoparticles

may be due to the change of surface morphology by aggregation of the nanoparticles [77, 78].

4 Conclusions

In summary, we have developed an easy method for the synthesis of CuO nanoparticles. The activity of these as-synthesized CuO nanoparticles have been well explained for the N-arylation reaction of imidazole and phenylboronic acid. One of the main key features of the reaction is that it proceeds under base and ligand free condition. Moreover, the reaction proceeds at moderate temperature which avoids the necessity of harsh temperature for the N-arylation reaction of imidazole with phenylboronic acid. Furthermore, the application of the CuO nanoparticles for this reaction protocol seems to be beneficial because a comparatively lower amount of catalyst loading is necessary to enhance the reaction along with a wide range of substrate tolerance. Thus, it might be an efficient and facile protocol for the synthesis of N-arylated products of imidazole with arylboronic acid.

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