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ORIGINAL ARTICLE

Cu(II) complex of pyridine-based polydentate as a novel, efficient, and highly reusable catalyst in C–N bond-forming reaction

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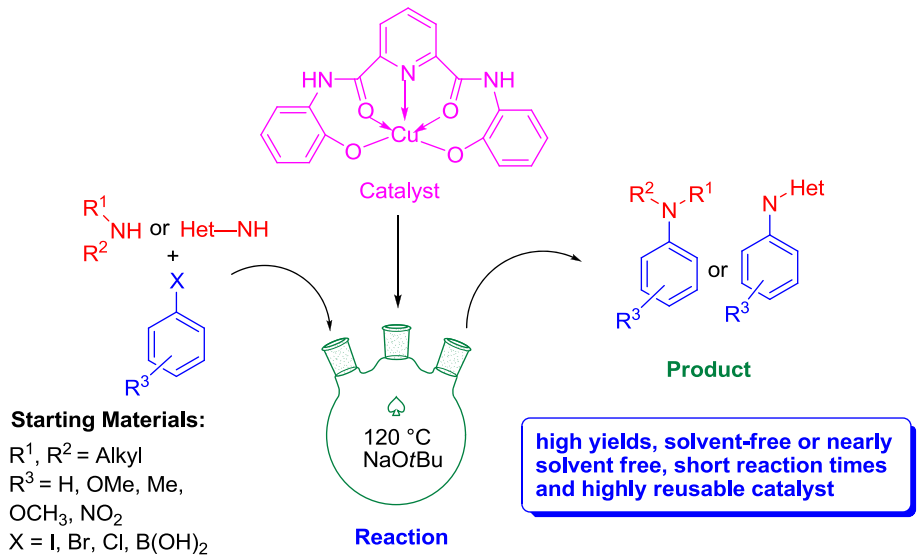
Abstract In this paper, a highly reusable copper(II) complex of pyridine-based polydentate is able to efficiently catalyze a C–N bond-forming reaction under mild conditions. A variety of *N*-heterocyclic and amine compounds arylated with different aryl iodides, bromides, and chlorides produced *N*-substituted compounds in good to excellent yields. This methodology can be also used for the arylation of *N*-unsubstituted compounds using arylboronic acids under solvent-free conditions. All reactions are performed in short times under air, and the catalyst can be reused up to seven times.

Graphical Abstract



Keywords Cu(II)complex · Pyridine-based polydentate ligand · C–N bond-forming reaction · Solvent free · Reusable catalyst · Boronic acids

Electronic supplementary material The online version of this article (doi:10.1007/s11030-017-9759-2) contains supplementary material, which is available to authorized users.

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Introduction

N-containing organic moieties have considerably attracted attention owing to their wide applications in medicinal [1] and natural products [2], and some of them (e.g., imidazoles, benzimidazoles) are also utilized for the preparation of *N*-heterocyclic carbenes and ionic liquids [3,4]. One of the most important synthetic methodologies for the C–N bond formation is transition-metal-catalyzed cross-coupling reactions [2]. Palladium-catalyzed C–N cross-coupling reactions have been described as a popular method for C–N bond formation. A variety of ligands, especially phosphine-based ligands, have been reported to promote the rate of C–N cross-coupling reactions [5,6]. However, because of high costs of palladium catalysts and toxic phosphine-based ligands, other metal catalysts have been used for this type of reactions [7]. Ni-based [8] and Fe-based [9] catalysts have been reported for cross-coupling reactions. Although these catalysts have some significant advantages (i.e., Pd to use mild conditions and Fe to reduce costs), they also show some disadvantages including low selectivity, low tolerance of functional groups, and high toxicity. During the last five decades, a series of copper catalysts with good to excellent catalytic performance for C–N cross-coupling reactions have also been developed. Among them the Buchwald–Hartwig and Chan–Lam protocols have been proven very successful [10–13]. Synthesis and investigation of various suitable ligands containing different functional groups are a popular topic for Cu(I)-catalyzed C–N bond formation [14,15]. Cu(I) was largely reported as copper source in cross-coupling reactions in the literature; however, because of their poor thermodynamic stability and formation of undesired products, other sources of copper had been used [16]. In this aspect, our research group has been studying the catalytic effect of Cu(II) sources in organic reactions. Copper(II) is inexpensive, air-stable and cheaper compared with copper(I); however, there are some restrictions in the choice of appropriate ligands [17].

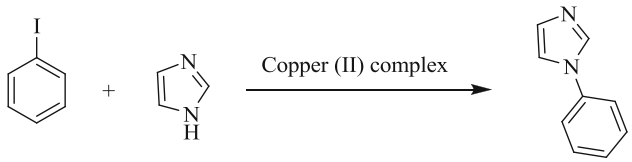
Pyridine and pyridine derivatives can coordinate with different metals [18,19], and a series of experimental, theoretical, and catalytic investigations have been established for metal–pyridine complexes [20–23].

Herein, we report our work to develop C–N bond-forming reactions using pyridine-based polydentate copper complex as an inexpensive, efficient, and versatile catalyst.

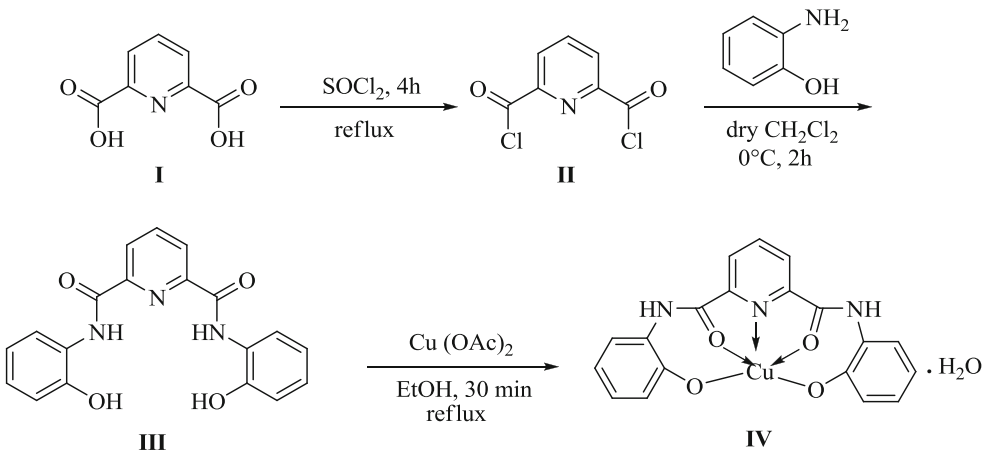
Results and discussion

The catalyst that used in this method was prepared in three steps as shown in Scheme 1 [24].

Our study was initiated by optimizing the Buchwald–Hartwig C–N cross-coupling reaction between imidazole and aryl iodide under different conditions (Scheme 2). For this purpose, different parameters were varied, such as metal complexes, solvent, base, temperature, and catalyst loadings. The catalytic activity of metal complexes with pyridine-based polydentate was investigated, and a Cu(II) complex was found to be more effective based on isolated yield and reaction time (Table 1, entries 1–4). The impact of the solvent was determined, and it was found that lower yields were obtained for arylated imidazole **1c** when using EtOH, PEG



Scheme 2 Model reaction for the synthesis of 1-phenyl-1*H*-imidazole (**1c**)



Scheme 1 Synthesis of Cu(II) complex of pyridine-based polydentate catalyst

Table 1 Results of the Buchwald–Hartwig reaction under different reaction conditions[a]

Entry	Catalyst (mol%)	Solvent	Base	Temp (°C)	Time (h)	Yield (%)[b]
1[c]	10	DMSO (2.0 mL)	NaO^{t}Bu	120	24	56
2[d]	10	DMSO (2.0 mL)	NaO^{t}Bu	120	24	45
3[e]	10	DMSO (2.0 mL)	NaO^{t}Bu	120	24	5
4[f]	10	DMSO (2.0 mL)	NaO^{t}Bu	120	24	5
5	10	DMSO (2.0 mL)	NaO^{t}Bu	120	1.5	96
6	10	DMF (2.0 mL)	NaO^{t}Bu	120	4.5	80
7	10	EtOH (2.0 mL)	NaO^{t}Bu	120	24	20
8	10	PEG (200) (2.0 mL)	NaO^{t}Bu	120	24	7
9	10	H_2O (2.0 mL)	NaO^{t}Bu	Reflux	24	5
10	10	i-PrOH (2.0 mL)	NaO^{t}Bu	Reflux	24	47
11	10	–	NaO^{t}Bu	120	24	76
12[g]	**10**	**DMSO (0.3 mL)**	**NaO^{t}Bu**	**120**	**1.5**	**97**
13	10	DMSO (0.3 mL)	K_2CO_3	120	24	50
14	10	DMSO (0.3 mL)	K_3PO_4	120	24	65
15	10	DMSO (0.3 mL)	Et_3N	120	24	60
16	10	DMSO (0.3 mL)	NaOH	120	9	85
17	15	DMSO (0.3 mL)	NaO^{t}Bu	120	1.5	96
18	5	DMSO (0.3 mL)	NaO^{t}Bu	120	24	75
19	10	DMSO (0.3 mL)	NaO^{t}Bu	110	4.5	65
20	10	DMSO (0.3 mL)	NaO^{t}Bu	130	1.5	97

[a] Reaction conditions: imidazole (1.0 mmol), iodobenzene (1.0 mmol), base (1.0 eq) in the presence of Cu(II) complex
[b] Isolated yield
[c] The reaction was performed in the presence of Zn(II)-pyridine-based polydentate
[d] The reaction was performed in the presence of Co(II)-pyridine-based polydentate
[e] The reaction was performed in the presence of Mn(II)-pyridine-based polydentate
[f] The reaction was performed in the presence of Fe(II)-pyridine-based polydentate
[g] The best conditions

200, H_2O and *i*PrOH, whereas higher yield was obtained in DMF and DMSO or under solvent-free conditions. Although the reaction performed well under solvent-free conditions, a low amount of DMSO was needed in order to increase the yield (from 76 to 97%) and accelerate the reaction. Next, the effect of various inorganic and organic bases including sodium *tert*-butoxide, potassium carbonate, tripotassium phosphate, triethylamine, and sodium hydroxide was investigated and determined that sodium *tert*-butoxide was the best option. Then, the amount of Cu(II) catalyst was varied and found that 10 mol% was optimal for the synthesis of **1c**.

We investigated the impact of different temperatures on the reaction (Table 1, entries 12, 19, and 20). As shown in Table 1, the best results were obtained when using sodium *tert*-butoxide (1.0 eq) as base and 10 mol% Cu(II) catalyst at 120 °C under nearly solvent-free conditions.

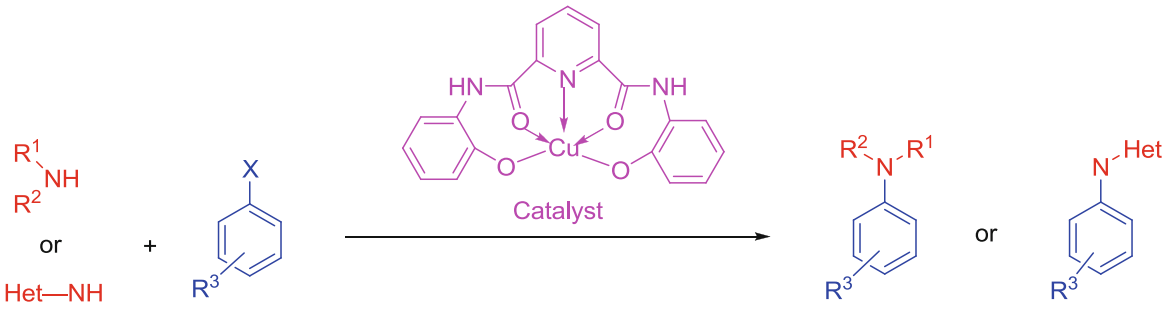
To explore the generality and versatility of this procedure, the reaction was used to construct a library of *N*-arylated products using different aryl iodides and *N*-heterocycles (Table 2).

As it is shown in Table 2, our optimized conditions were quite efficient for the C–N cross-coupling reaction of aryl iodides bearing different substituted groups such as Me, NO_2, OMe, and Cl with diverse *N*-heterocyclic compounds. Aryl iodides with electron-withdrawing groups afforded better yields under shorter reaction times than electron-donating groups. Aryl bromides were also used and produced the corresponding products in moderate to excellent yields also in short reaction times (1.5–4.5 h).

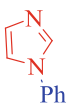
During our investigations, it was found that the substituent effects on aryl iodide are less significant than on aryl bromides (Table 2). We also studied the reactivity of the catalyst for C–N bond-forming reactions using aryl chlorides as inexpensive source of aryl halides, and the results are shown in Table 3 (products **1c**, **23c**, and **28c**). Moreover, strictly aryl halides produced products (**23c** (X = Br, Cl) and **28c**) in 85, 71, and 78% yields, respectively.

It is noteworthy to observe that numerous azoles including 1*H*-imidazole, 1*H*-benzimidazole, 2-methyl-1*H*-imidazole, 2-methyl-4-nitro-1*H*-imidazole, 1*H*-indole, 5-bromo-1*H*-indole, 1*H*-pyrrole, 3,5-dimethyl-1*H*-pyrazole, 9*H*-carbazole, 2-methyl-1*H*-indole, 1*H*-benzotriazole, and 10*H*-phenothiazine can be successfully coupled to aryl iodides to give *N*-arylated products **1c–22c** in good to

Table 2 Synthesis of arylated products from various HN-compounds and aryl halides catalyzed by a Cu(II) complex in the presence of NaO*t*Bu as base

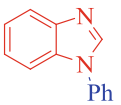


R^1, R^2 = Alkyl
R^3 = H, OMe, Me, OCH_3, NO_2
X = I, Br, Cl



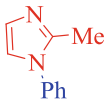
1c

X = I, 1.5h, 97%
X = Br, 4.5h, 97%
X = Cl, 24h, 30%
X = I, 5h, 75%[a]



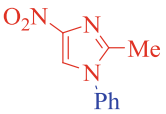
2c

X = I, 1.5h, 96%
X = Br, 3.5h, 98%



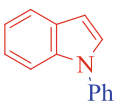
3c

X = I, 2h, 85%
X = Br, 4h, 85%



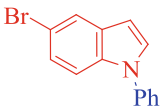
4c

X = I, 2.5h, 90%



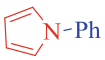
5c

X=I, 1.5h, 92%



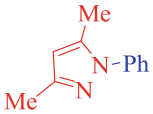
6c

X = I, 3h, 85%



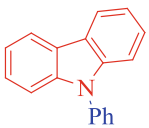
7c

X = I, 1.5h, 96%



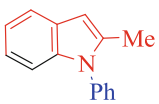
8c

X = I, 1.5h, 92%



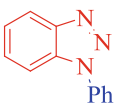
9c

X=I, 2h, 97%



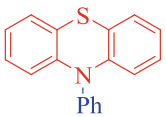
10c

X = I, 3h, 72%



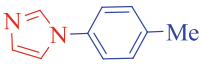
11c

X = I, 4h, 82%



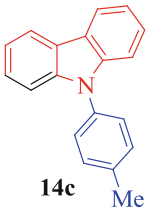
12c

X = I, 3h, 65%



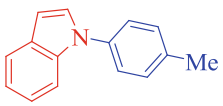
13c

X=I, 2.5h, 92%
X=Br, 4.5h, 95%



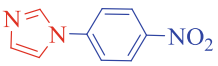
14c

X = I, 3h, 97%



15c

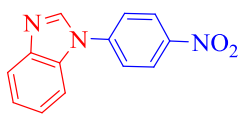
X = I, 3h, 92%



16c

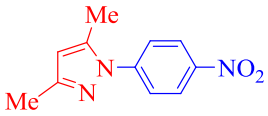
X = I, 2h, 98%
X = Br, 3h, 95%

Table 2 continued



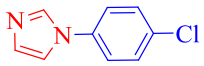
17c

X = I, 2h, 98%
X = Br, 3h, 95%



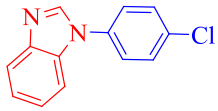
18c

X = I, 2h, 98%
X = Br, 3h, 90%



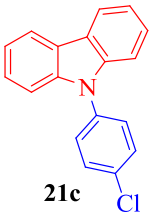
19c

X = I, 3h, 95%
X = Br, 4.5h, 87%



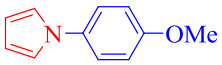
20c

X = I, 3h, 95%
X = Br, 4.5h, 85%



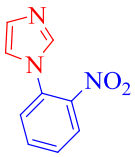
21c

X = I, 2.5h, 97%



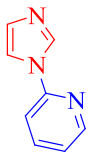
22c

X = I, 6h, 80%



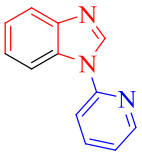
23c

X = Br, 4h, 85%
X = Cl, 12h, 71%



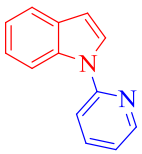
24c

X = Br, 1.5h, 96%



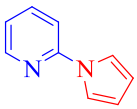
25c

X = Br, 1.5h, 95%



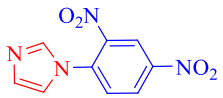
26c

X = Br, 1.5h, 95%



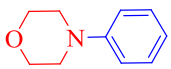
27c

X = Br, 1.5h, 96%



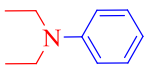
28c

X=Cl, 12h, 78%



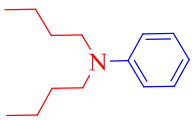
29c

X = I, 3h, 75%



30c

X = I, 3.5h, 45%

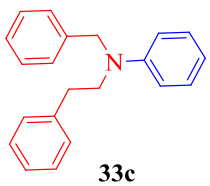


31c

X = I, 3.5h, 65%

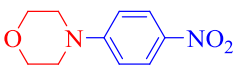
32c

X = I, 3h, 75%



33c

X = I, 3h, 72%



34c

X = I, 2.5h, 85%

35c

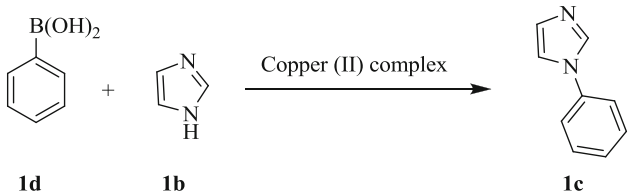
X = Br, 2.5h, 85%

[a] Reaction carried out on a 10 mmol scale

Table 3 Results of the Chan–Lam coupling reaction under different conditions[a]

Entry	Catalyst (mol%)	Solvent	Base	Temp (°C)	Time (h)	Yield (%)[b]
1	10	DMSO (2.0 mL)	NaO^{t}Bu	120	7.0	80
2	10	DMF (2.0 mL)	NaO^{t}Bu	120	5.0	40
3	10	EtOH (2.0 mL)	NaO^{t}Bu	120	5.0	40
4	10	PEG (200) (2.0 mL)	NaO^{t}Bu	120	24.0	15
5	10	H_2O (2.0 mL)	NaO^{t}Bu	Reflux	24.0	10
6	10	*i*-PrOH (2.0 mL)	NaO^{t}Bu	Reflux	7.0	65
7[c]	**10**	–	**NaO^{t}Bu**	**120**	**1.5**	**95**
8	10	–	K_2CO_3	120	20.0	90
9	10	–	K_3PO_4	120	20.0	92
10	10	–	Et_3N	120	20.0	95
11	10	–	NaOH	120	20.0	95
12	15	–	NaO^{t}Bu	120	1.5	95
13	5	–	NaO^{t}Bu	120	16	78
14	10	–	NaO^{t}Bu	130	1.0	94
15	10	–	NaO^{t}Bu	110	5.5	90

[a] Reaction conditions: imidazole (1.0 mmol), phenyl boronic acid (1.0 mmol), base (1.0 eq) in the presence of Cu(II) complex
[b] Isolated yield
[c] The best conditions



Scheme 3 Model reaction for synthesis of 1-phenyl-1*H*-imidazole (**1c**)

excellent yields. *N*-Heterocycles such as 2-methyl-1*H*-imidazole, 2-methyl-4-nitro-1*H*-imidazole, and 2-methyl-1*H*-indole were also successfully reacted with corresponding aryl halides to give *N*-arylated products **3c**, **4c**, and **10c**. The coupling of nitro-substituted 1*H*-imidazole took place with iodobenzene to give the corresponding product **4c** in good yield. We also applied these optimized conditions for the *N*-arylation of the secondary amines and iodobenzene and observed good yields at the suitable time.

We next investigated a larger-scale (10 mmol) synthesis of 1-phenyl-1*H*-imidazole (**1c**) from iodobenzene (**1a**, 10 mmol) and 1*H*-imidazole (**1b**, 10 mmol) in the presence of 10 mol% catalyst in DMSO (3.0 mL) at 120 °C (Table 2). To the best of our knowledge, the present study is the first report that investigates the arylation of diverse *N*-heterocycles and secondary amines using a general procedure.

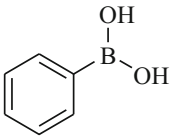
In continuation of our study, we screened the construction of C–N bond via the Cu(II)-catalyzed Chan–Lam coupling reaction of HN-compounds with boronic acids. Initially, we chose the reaction between imidazole and phenylboronic acid as our model reaction (Scheme 3) and studied the effects of different solvents, bases, temperatures, and catalyst loadings (Table 3). Since performing reactions under green media is of high interest, we tested the performance of the reaction using different solvents as well as in the absence of solvents (solvent-free conditions) and found that the reaction performed well without the use of a solvent (Table 3).

We then evaluated various organic and inorganic bases. Although all bases including sodium *tert*-butoxide, potassium carbonate, tripotassium phosphate, triethylamine, and sodium hydroxide resulted in products with good yields, it was sodium *tert*-butoxide that was chosen according to the reaction time (Table 3, entry 7). The reaction gave high yield of the desired product in 90 min by using this base, whereas using other bases, the reaction time increased to 24 h.

The amount of the catalyst was then optimized, and 10 mol% catalyst was optimal for the Chan–Lam coupling reaction. Finally, the effect of temperature was checked and it was found that reaction was carried out in the presence of phenyl boronic acid (1.0 mmol), imidazole (1.0 mmol), sodium *tert*-butoxide (1.0 mmol), and Cu(II) complex (10 mol%) at 120 °C under solvent-free conditions. In most reported Chan–Lam C–N cross-coupling reactions, in addition to using solvent, 2.0 or more equivalents of phenyl boronic acid were used, whereas in our methodology, only 1.0 equivalent of phenyl boronic acid was needed and without the use of a solvent (Table 3, entry 7).

The scope of this ligated Cu(II) catalyst was further examined by the cross-coupling reactions between various HN-compounds as a substrate and phenyl boronic acid under our optimized conditions (Table 4). It is noteworthy that

Table 4 Chan–Lam cross-coupling reaction of various *N*-heterocycles (1.0 mmol) and phenyl boronic acid (1.0 mmol) in the presence of *t*BuONa (1.0 mmol) as base and copper(II)-pyridine-based polydentate complex (10 mol%) as catalyst under solvent-free conditions

Entry	Aryl boronic acid	Product	Time (h)	Yield (%)[a]
				
1		**1c**	1.5	95
2	**1d**	**2c**	1.5	90
3	**1d**	**3c**	4.0	85
4	**1d**	**4c**	4.0	80
5	**1d**	**5c**	1.5	90
6	**1d**	**6c**	3.0	80
7	**1d**	**7c**	1.5	95
8	**1d**	**8c**	3.0	90
9	**1d**	**9c**	2.5	95
10	**1d**	**10c**	3.5	65
11	**1d**	**11c**	4.0	80
12	**1d**	**12c**	4.0	70
13	**1d**	**1c**	10	70[b]

[a] Isolated yield
[b] Reaction carried out on a 10-mmol scale

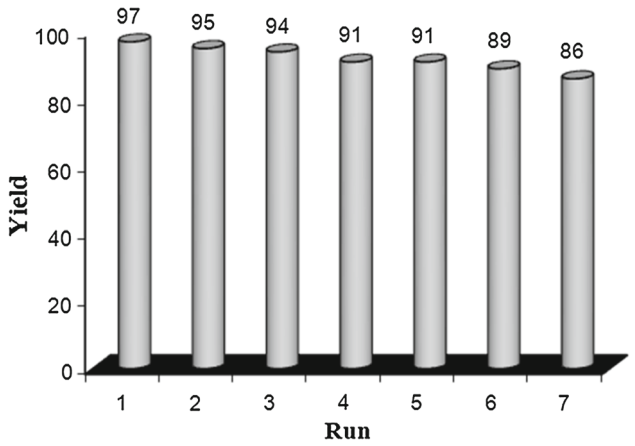


Fig. 1 Catalytic activity of Cu(II)-pyridine-based polydentate complex in seven cycles for the reaction of iodobenzene (**1a**) and imidazole (**1b**) under our optimized conditions

strictly HN-compounds were also employed in this study (Table 4, entries 3, 4, 8, 10).

The possibility of recycling this Cu(II)-polydentate complex was examined using the reaction of iodobenzene (**1a**) and imidazole (**1b**) under our optimized conditions. After the completion of the reaction, ethyl acetate (30 mL) was added to the reaction mixture and was then recovered by filtration. The resulting solid was washed with ethyl acetate (30 mL) and dried under vacuum. As shown in Fig. 1, the catalyst could be reused up to seven times to achieve to yields >85%.

Conclusion

In conclusion, a novel, efficient, and practical procedure for the preparation of N-arylated products via the C–N bond-forming reaction of HN-compounds with aryl halides or aryl boronic acid using heterogeneous Cu(II)-pyridine-based polydentate complex was developed. Fast reaction times, easy isolation of products, and excellent yields are the advantages of this procedure. Also, the heterogeneous Cu(II)-based catalyst can be separated from the reaction mixture by simple filtration and reused up to seven consecutive times without significant decrease in efficiency.

Experimental section

Chemical materials were purchased from Fluka, Aldrich, and Merck without any purification. NMR spectra were recorded on a Bruker Avance DPX-250 (^{1}H-NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard. The abbreviations used for NMR spectra are: s = single, d = doublet, t = triplet, dd = doublet of doublet, and m = multiple. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Mass spectra were obtained on a Shimadzu GCMS-QP 1000 EX instruments at 70 or 20 ev. Melting points were obtained in open capillary tubes in a Buchi-535 circulating oil melting point apparatus and are uncorrected. The purity of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates.

General procedure for the preparation of *N*-substituted compounds with aryl halides

A mixture of *N*-unsubstituted heterocycles or secondary amines (1.0 mmol), aryl halide (1.0 mmol), and *t*BuONa (1.0 mmol) was stirred in DMSO (0.3 mL) in the presence of Cu(II) complex (10 mol%) at 120 °C for an appropriate time. When the reaction was finished (monitored by TLC), the catalyst was filtered, the filtrate evaporated, and the residue purified by column chromatography over silica gel using petroleum ether–ethyl acetate (7:3) to afford desired product.

General procedure for the synthesis of *N*-substituted compounds with phenyl boronic acid

A mixture of *N*-unsubstituted heterocycles (1.0 mmol), phenyl boronic acid (1.0 mmol), and *t*BuONa (1.0 mmol) was stirred in solvent-free condition in the presence of Cu(II) complex (10 mol%) at 120 °C for an appropriate time. When the reaction was complete (monitored by TLC), the catalyst

was filtered, the filtrate evaporated, and the residue purified by column chromatography over silica gel using petroleum ether–ethyl acetate (7:3) to afford desired product.

*1-Phenyl-1H-imidazole (**1c**) [25]*

Dark brown oil; yield 97%. IR (KBr): 516 (m), 663 (s), 694 (s), 763 (s), 817 (m), 910 (m), 1056 (s), 1110 (m), 1257 (s), 1303 (s), 1512 (s), 1596 (s), 1681 (w), 1867 (w), 1951 (w), 2923 (w), 3062 (w), 3116 (m), 3394 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.13–7.43 (m, 7 H), 7.78 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 118.2, 121.4, 127.5, 129.9, 130.4, 135.5, 137.3.

*1-Phenyl-1H-benzimidazole (**2c**) [26]*

Brown oil; yield 96%. IR (KBr): 694 (s), 748 (s), 887 (w), 972 (w), 1010 (w), 1080 (w), 1149 (w), 1223 (s), 1288 (s), 1373 (w), 1458 (s), 1496 (s), 1596 (s), 1712 (m), 2954 (w), 3062 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.29–7.33 (m, 2 H), 7.42–7.57 (m, 6 H), 7.86–7.89 (m, 1 H), 8.08 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 110.5, 120.6, 122.8, 123.7, 124.0, 128.0, 130.0, 133.6, 136.3, 142.3, 144.1.

*2-Methyl-1-phenyl-1H-imidazole (**3c**) [26]*

Light brown oil; yield 85%. IR (KBr): 694 (m), 763 (m), 1134 (w), 1172 (w), 1303 (m), 1419 (m), 1504 (s), 1596 (w), 1712 (w), 2360 (s), 2923 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 2.29 (s, 3 H), 6.93 (s, 1 H), 6.96 (s, 1 H), 7.19–7.23 (m, 2 H), 7.38–7.41 (m, 3 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 13.7, 120.7, 120.7, 125.5, 127.6, 128.1, 129.4, 137.9. MS: m/z (%) = 159 (M^+ + 1, 12.2), 158 (M^+, 76.2), 130 (50.7), 77 (100.0), 51 (90.5).

*2-Methyl-4-nitro-1-phenyl-1H-imidazole (**4c**)*

Light brown oil; yield 90%. IR (KBr): 509 (w), 586 (w), 686 (m), 763 (m), 825 (m), 987 (w), 1072 (w), 1141 (w), 1211 (w), 1296 (s), 1380 (s), 1496 (s), 1596 (s), 1743 (w), 2360 (s), 2854 (w), 2923 (w), 3132 (w),3602 (w),3726 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 2.32 (s, 1 H), 7.26–7.29 (m, 2 H), 7.48–7.51 (m, 3 H), 7.76 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 13.7, 120.4, 125.5, 129.9, 130.1, 135.8, 144.9. MS: m/z (%) = 205 (M^+ + 2, 1.6), 204 (M^+ + 1, 4.9), 203 (M^+, 12.7), 131 (46.0), 104 (28.7), 77 (100.0), 51 (30.3).

*5-Bromo-1-phenyl-1H-indole (**6c**)*

Light brown oil; yield 85%. IR (KBr): 717 (m), 748 (m), 786 (m), 1064 (w), 1226 (w), 1458 (s), 1504 (s), 1596 (m), 1720 (w), 2923 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 6.55 (s, 1 H), 7.25–7.49 (m, 8 H), 7.73 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 103.0, 111.9, 113.5, 123.5, 124.3, 125.1, 126.8, 129.1, 129.7, 130.7, 139.8.

*9-Phenyl-9H-carbazole (**9c**) [27]*

Light brown solid; mp: 94–96 °C. yield 97%. IR (KBr): 486 (w), 524 (w), 563 (w), 624 (m), 694 (s), 748 (s), 840 (w), 925 (m), 1026 (m), 1110 (m), 1172 (m), 1234 (s), 1326 (s), 1357 (s), 1450 (s), 1504 (s), 1596 (s), 2360 (s), 2846 (w), 2931 (w), 3055 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.36–7.42 (m, 2 H), 7.50–7.62 (m, 5 H), 7.65–7.67 (m, 4 H), 8.24–8.28 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 109.9, 120.0, 120.4, 123.4, 126.0, 127.2, 127.5, 129.9, 137.8, 141.0. MS: m/z (%) = 245 (M^+ + 2, 6.6), 244 (M^+ + 1, 55.6), 243 (M^+, 100.0).

*1-Phenyl-1H-benzo[d][1–3] triazole (**11c**)*

Light brown solid; mp: 88–90 °C. yield 82%. IR (KBr): 432.0 (w), 474.5 (w), 516.9 (w), 572.7 (w), 621.0 (w), 659.6 (m), 698.2 (s), 748.3 (s), 783.0 (m), 921.9 (w), 1010.6 (w), 1060.8 (s), 1091.6 (s), 1122.5 (w), 1145.6 (w), 1188.1 (w), 1245.9 (w), 1276.8 (m), 1326.9 (w), 1392.5 (w), 1458.1 (s), 1500.5 (s), 1596.9 (s), 2854.4 (w), 2923.9 (w), 3058.9 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.51–7.65 (m, 5 H), 7.74-7.81 (m, 3 H), 8.14–8.17 (m, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 110.3, 120.3, 122.9, 124.3, 128.2, 128.7, 129.8.

*1-p-Tolyl-1H-imidazole (**13c**) [25]*

Light brown oil; yield 92%. IR (KBr): 528.5 (w), 613.3 (w), 659.6 (w), 732.9 (w), 833.2 (m), 906.5 (w), 960.5 (w), 1056.9 (m), 1114.8 (w), 1180.3 (w), 1249.8 (s), 1307.6 (m), 1461.9 (m), 1519.8 (s), 1616.2 (w), 1681.8 (w), 2835.2 (w), 2931.6 (w), 3105.2 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 3.76 (s, 3 H), 6.87–6.91 (m, 2 H), 7.10–7.11 (d, J = 3.75 Hz, 2 H), 7.19–7.20 (d, J = 2.75 Hz, 1 H), 7.22–7.23 (d, J = 2 Hz, 1 H), 7.68 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 55.5, 114.8, 118.7, 123.1, 130.0, 130.6, 135.8, 158.8. MS: m/z (%) = 159 (M^+ + 1, 23.2), 158 (M^+, 3.8), 132 (67.2), 77 (57.9), 51 (31.1).

*9-p-Tolyl-9H-carbazole (**14c**) [27]*

Light brown solid; mp: 112–113 °C. yield: 97%. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 2.63 (s, 3 H), 7.50–7.62 (m, 10 H), 8.38 (d, J = 7.5 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 21.5, 110.1, 120.1, 120.6, 12.3.6, 126.2, 127.2, 130.8.

*1-(4-Nitrophenyl)-1H-imidazole (**16c**) [25]*

Yellow solid; mp: 198–200 °C. yield 98%. IR (KBr): 501.5 (m), 648.0 (s), 682.8 (m), 725.5 (s), 744.5 (s), 848.6 (s), 969.6 (w), 1049.2 (s), 1107.1 (m), 1195.8 (w), 1261.4 (s), 1299.9 (s), 1338.5 (s), 1369.4 (w), 1473.5 (w), 1508.2 (s), 1593.1 (m), 1654.8 (w), 1701.1 (w), 2221.8 (w), 2333.7 (w), 2360.7 (w), 2850.6 (w), 2920.0 (w), 3105.2 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.19 (s, 1 H), 7.32(d, J = 7.5 Hz, 1 H), 7.50–7.55 (m, 2 H), 7.92 (s, 1 H), 8.28–8.32 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 117.6, 121.0, 125.7, 131.7, 135.4, 142.0, 146.2. MS: m/z (%) = 190 (M^+ + 1, 36.4), 189 (M^+, 89.1), 132 (23.9), 116 (100.0), 89 (72.3), 50 (52.2).

*1-(4-Nitrophenyl)-1H-benzo[d]imidazole (**17c**) [25]*

Yellow solid; mp > 300 °C. yield 98%. IR (KBr): 516.9 (w), 574.7 (w), 613.3 (w), 690.5 (m), 732.9 (s), 852.5 (s), 983.6 (w), 1103.2 (s), 1230.5 (w), 1299.9 (w), 1338.5 (m), 1504.4 (s), 1589.2 (s), 1904.4 (w), 2329.8 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.37–7.41 (m, 2 H), 7.58–7.61 (m, 1 H), 7.70–7.75 (m, 2 H), 7.88–7.90 (m, 1 H), 8.17 (s, 1 H), 8.42–8.47 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 110.3, 121.1, 123.6, 123.7, 124.6, 125.8, 132.7, 141.5, 141.6, 144.4, 146.4. MS: m/z (%) = 241 (M^+ + 2, 9.0), 240 (M^+ + 1, 56.9), 239 (M^+, 100.0), 209 (17.8), 192 (44.8), 166 (24.4), 139 (17.2), 83 (16.8), 65 (24.1).

*3,5-Dimethyl-1-(4-nitrophenyl)-1H-pyrazole (**18c**)*

Yellow solid; mp: 96–98 °C. yield 98%. IR (KBr): 493 (w), 632 (w), 686 (m), 748 (m), 802 (m), 856 (s), 979 (m), 1033 (m), 1103 (s), 1172 (w), 1334 (s), 1411 (w), 1512 (s), 1596 (s), 1921 (w), 2360 (w), 2923 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 2.28 (s, 3 H), 2.41 (s, 3 H), 6.06 (s, 1 H), 7.67 (d, J = 10 Hz, 2 H), 8.31 (d, J = 10 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 13.1, 13.5, 109.3, 123.4, 124.7, 139.8, 145.5, 150.8.

*1-(4-Chlorophenyl)-1H-imidazole (**19c**) [26]*

Light brown solid; mp: 85–87 °C .yield 95%. IR (KBr): 516 (s), 655 (s), 732 (s), 825 (s), 902 (w), 964 (m), 1010 (w), 1056 (s), 1103 (s), 1257 (s), 1303 (s), 1504 (s), 1596 (m), 3109 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.17–7.32 (m, 4 H), 7.38–7.42 (m, 2 H), 7.78 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 118.1, 122.6, 130.0, 131.0, 133.1, 135.5, 135.8. MS: m/z (%) = 180 (M^+ + 2, 1.3), 179 (M^+ + 1, 0.7), 178 (M^+, 1.0), 167 (3.7), 123 (10.4), 97 (32.0), 81 (44.4), 57 (100.0).

*1-(4-Chlorophenyl)-1H-benzimidazole (**20c**)*

Light brown solid; mp: 82–84 °C. yield: 95%. IR (KBr): 424.3 (w), 524.6 (m), 578.6 (m), 617.2 (w), 640.3 (w), 663.5 (w), 740.6 (s), 833.2 (s), 894.4 (w), 975.9 (m), 1014.5 (m), 1091.6 (s), 1141.8 (w), 1230.5 (m), 1288.4 (s), 1311.5 (w), 1373.2 (w), 1411.8 (w), 1454.2 (s), 1500.5 (s), 1596.9 (m), 1608.5 (m), 1716.5 (m), 1894.0 (w), 2950.9 (w), 3058.9 (m), 3398.3 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.31–7.34 (m, 2 H), 7.42–7.55 (m, 5 H), 7.87–7.89 (m, 1 H), 8.07 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 110.2, 120.8, 123.0, 125.3, 130.3, 133.8, 134.8, 142.0.

*9-(4-Chlorophenyl)-9H-carbazole (**21c**) [27]*

Light brown solid; mp: 118–120 °C. yield: 97%. IR (KBr): 420.5 (m), 493.7 (m), 528.5 (w), 567.0 (w), 617.2 (w), 694.3 (w), 729.0 (s), 752.2 (s), 829.3 (m), 848.6 (w), 914.2 (w), 1014.5 (m), 1095.5 (s), 1180.4 (s), 1234.4 (s), 1315.4 (s), 1450.4 (s), 1593.4 (s), 1782.9 (w), 1828.4 (w), 1905.5 (w), 1940.2 (w), 2360.7 (w), 2561.3 (w), 2661.6 (w), 2854.4 (w), 2931.6 (w), 3055.0 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.26–7.64 (m, 10 H), 8.22 (dd, J_2 = 1 Hz, J_1 = 7.75 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 109.6, 120.3, 120.5, 123.5, 126.2, 128.4, 130.2, 133.1, 136.4, 140.7.

*1-(2-Nitrophenyl)-1H-imidazole (**23c**)*

Yellow solid; mp: 97–98 °C. yield 85%. IR (KBr): 540 (m), 655 (s), 709 (m), 740 (s), 786 (s), 848 (s), 1056 (m), 1110 (m), 1249 (w), 1303 (s), 1357 (s), 1604 (m), 1681 (w), 3093 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.00 (d, J = 1.25 Hz, 1 H), 7.11 (s, 1 H), 7.37–7.58 (m, 3 H), 7.63–7.67 (m, 1 H), 7.90–7.93 (m, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 120.3, 125.3, 128.7, 129.7, 130.2, 130.5, 133.8, 137.2.

*1-(2,4-Dinitrophenyl)-1H-imidazole (**28c**)*

Yellow solid; mp: 143 °C. yield 78%. IR (KBr): 513.0 (w), 655.8 (m), 748.3 (s), 821.6 (w), 867.9 (w), 902.6 (w), 960.5 (w), 987.5 (w), 1056.9 (s), 1103.2 (w), 1245.9 (w), 1303.8 (s), 1350.1 (s), 1458.1 (w), 1512.1 (s), 1535.2 (w), 1593.1 (w), 2337.6 (w), 2360.7 (w), 2854.5 (w), 2923.9 (w), 3112.9 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250MHz) δ (ppm): 6.73–6.81 (m, 1 H), 7.18–7.26 (m, 2 H), 7.44–7.47 (m, 1 H), 7.67–7.70 (m, 1 H), 8.38 (s, 1 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 118.7, 119.1, 122.8, 124.5, 127.5, 131.6, 131.7, 136.2, 136.4. MS: m/z (%) = 234 (M^+, 0.7), 207 (7.1), 191 (0.7), 149 (2.5), 133 (1.8), 98 (28.8), 73 (31.3), 55 (100.0).

*4-(4-Nitrophenyl)morpholine (**34c**)*

Yellow oil; yield 85%. IR (KBr): 667.3 (w), 752.2 (w), 848.6 (w), 929.6 (w), 1026.1 (w), 1072.3 (w), 1110.9 (m), 1242.1 (w), 1323.1 (m), 1384.8 (w), 1450.4 (w), 150.4 (w), 1596.9 (m), 1643.2 (w), 2341.4 (w), 2360.7 (m), 2854.5 (w), 2923.9 (w), 2962.4 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 3.35–3.37(m, 4 H), 3.79–3.86 (m, 4 H), 6.79–6.83 (m, 2 H), 8.10–8.14 (m, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 47.1, 66.3, 112.6, 125.9, 139.0, 155.0.

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