Transition Met Chem (2011) 36:447–458
DOI 10.1007/s11243-011-9489-8

An efficient polymer-supported copper(II) catalyst for the *N*-arylation reaction of N(H)-heterocycles with aryl halides as well as arylboronic acids

Manirul Islam · Sanchita Mondal · Paramita Mondal · Anupam Singha Roy · Kazi Tuhina · Noor Salam · Sumantra Paul · Dildar Hossain · Manir Mobarok

Received: 3 January 2011 / Accepted: 23 March 2011 / Published online: 7 April 2011

Abstract Immobilization of copper onto polystyrene provided a polymer-supported copper(II) catalyst, which was effective in cross-coupling reactions between *N*-containing substrates and arylboronic acids using methanol as a solvent in air under base-free conditions. This catalyst was also effective in *N*-arylation of imidazole with aryl halides in DMSO using K_2CO_3 as a base under nitrogen atmosphere. The catalyst was characterized by physico-chemical and spectroscopic techniques. The product *N*-arylimidazoles and *N*-arylbenzimidazoles were isolated in good to excellent yields. This copper catalyst was air stable and could be recycled with minimal loss of activity.

Introduction

Recently, copper-catalyzed Ullmann-type C(aryl)–N bond formation under mild conditions has become a focus of research to include a wide range of subsrates [1–3]. The synthesis of *N*-arylimidazoles and *N*-arylbenzimidazoles has attracted significant interest because of the frequent occurrence of these structural units in biologically active inhibitors [4]. *N*-arylimidazoles and *N*-arylbenzimidazoles are prevalent in compounds that are of biological, pharmaceutical, and material interest [5]. The most straightforward route to *N*-arylimidazoles involves the direct formation of the aryl-nitrogen bond. However, the standard practice for carrying out such reactions involves nucleophilic aromatic substitution [6] and traditional Ullmann reactions [7] as well as the coupling of imidazoles with aryllead, arylbismuth, arylborane, and arylsilane reagents [8]. These reactions have been carried out at high temperatures and many functional groups are not tolerated, and therefore their use is greatly limited [9]. In addition, these reactions often require the use of stoichiometric amounts of copper reagents, which, on scaleup, leads to problems of waste disposal [10]. To overcome these drawbacks, several Pd-catalyzed C–N bond formation methods have been developed, which, together with sterically hindered phosphine ligands, allow many coupling reactions of aryl halides with *N*-containing compounds to proceed under relatively mild conditions and at low temperature [11]. However, industrial use of these methods is problematic in many cases due to their air and moisture sensitivity, as well as the higher costs of Pd catalysts and the ligands [12]. However, copper-mediated couplings are still the reaction of choice for large- and industrial-scale formation of C–N bonds. Chan and Lam established an efficient approach to *N*-arylimidazoles via $Cu(OAc)_2$- mediated coupling of imidazoles with readily available arylboronic acids [13]. Xie and coworkers have shown the simple copper salt-catalyzed coupling of imidazoles with arylboronic acids in protic solvent without any base [14]. Recently, Buchwald used diimine as ligand for effective copper-mediated cross-coupling reactions under mild conditions [15]. Very recently, Buchwald et al. and others have reported a copper-based protocol for the formation of *N*-aryl bonds [16–18]. Immobilization of the soluble catalysts onto an insoluble matrix using a simplified protocol will allow easy separation and recyclability of the catalyst with minimal amount of product. In this direction, we have already

---

M. Islam (✉) · S. Mondal · P. Mondal ·
A. S. Roy · N. Salam · S. Paul · D. Hossain · M. Mobarok
Department of Chemistry, University of Kalyani, Kalyani,
Nadia, West Bengal 741235, India
e-mail: manir65@rediffmail.com

K. Tuhina
Department of Chemistry, B. S. College, S-24 PGS, Canning,
West Bengal, India

reported reusable palladium catalysts for C–C cross-coupling reaction [19, 20]. Homogeneous catalysts have some disadvantages, such as they may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse. These disadvantages can be overcomed by anchoring the metal on a polymer [21]. There are many examples of heterogeneous catalysts for C–N coupling reactions, and they are prepared by different approaches like encapsulation or immobilization of a catalytically active metal complex on solid supports [22].

In this present work, *N*-arylation reactions of imidazole and benzimidazole with various arylboronic acids were carried out in methanol with polymer-supported copper(II) catalyst, without the need of any organic cosolvent, base, or additives such as phase-transfer catalysts. This catalyst was also effective in *N*-arylation reactions of imidazole with various aryl halides using K_2CO_3 in DMSO medium. The experimental results reveal that the anchoring of the complex on a solid support not only exhibits improved catalyst activity, stability and selectivity of the product but also enables easy recovery and reuse of the catalyst.

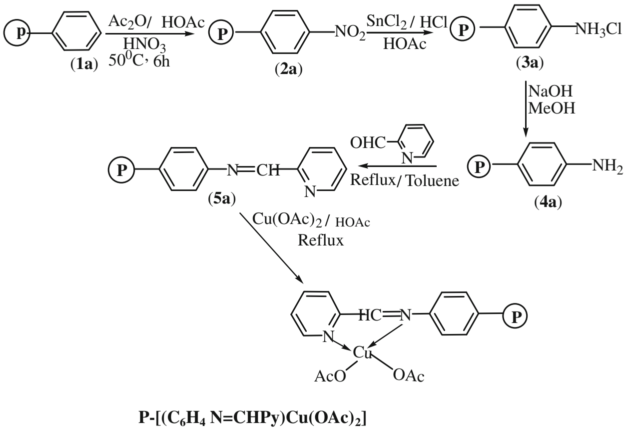
Results and discussion

Preparation of catalysts

The synthesis of the polymer-anchored Cu(II) Schiff base catalyst is shown in Scheme 1.

Characterization of the polymer-anchored Cu(II) Schiff base catalyst

Due to insolubilities of the polymer-supported Cu(II) catalyst in all common organic solvents, its structural investigation was limited to the physicochemical properties, chemical analysis, SEM, EDAX, IR, TGA-DTA, and UV–Vis spectral data. Table 1 provides the data of elemental analysis of different functionalized polymers and the copper(II) catalyst. Copper content in the catalyst determined by AAS suggests 1.98 wt% Cu in the catalyst. The morphology of the copper catalyst was studied using scanning electron microscopy. The micrographs of the polymer-supported Schiff base ligand and the catalyst obtained from the scanning electron microscope are presented in Fig. 1a and b, respectively. The morphological change in the polymer-supported Schiff base ligand and the immobilized copper catalyst is quite evident from these images, suggesting the loading of copper metal on the surface of the polymer matrix. Energy dispersive spectroscopy analysis of X-rays (EDAX) data for the polymer-supported Schiff base ligand and the catalyst is given in Fig. 2a and b, respectively. The EDX data also inform the attachment of copper metal on the surface of the polymer matrix.



Scheme 1 Synthesis of the polymer-anchored copper(II) Schiff base catalyst. *P* polystyrene framework

The IR data of the various functionalized polystyrenes and the corresponding metal complex are presented in Table 2. The presence of the Schiff base moiety in the ligand is indicated by the absorption band at 1,639 cm^{-1} due to C=N-stretching vibration of azomethine group. This on complexation with Cu shifted to 1,614 cm^{-1}, while the bands at 1,583 and 1,453 cm^{-1} have been assigned to the aromatic skeletal vibration [23, 24]. The lowering in frequency of C=N is indicative of the formation of the metal–ligand bonding. The absorption signal at 1,594 cm^{-1} can be assigned to the stretching frequency of C=N (ν C=N) of pyridine in the Schiff base ligand which on complexation with Cu shifted to 1,600 cm^{-1} [25]. In the metal complex, a medium or weak band is observed at 545 cm^{-1} which can be attributed to the metal with pyridine nitrogen mode [26] and a band at 462 cm^{-1} can be attributed to the metal with azomethine nitrogen mode [27]. In this catalyst, a medium intensity band observed at 1,318 cm^{-1} suggests the monodentate coordination of the acetate groups [28]. Monodentate acetate usually shows two bands at 1,630 and 1,310 cm^{-1} due to antisymmetric and symmetric stretching, respectively [29]. Since the absorption of the Schiff base moiety (ν C=N) also appeared in this region, the band at 1,630 cm^{-1} could not be located. The acetate oxygen involved in the complexation with copper in copper catalyst which is clearly evident from the presence of a new medium intensity band at 430 cm^{-1} assignable to ν Cu–O in the IR spectra [29].

The electronic spectrum of the polymer-supported Cu(II) Schiff base catalyst was recorded in diffuse reflectance mode as a $MgCO_3/BaSO_4$ disk due to its solubility limitations in common organic solvents. In Fig. 3, the electronic spectrum for the copper catalyst is shown. The spectrum exhibits five bands at *ca.* 218, 265, 295, 322, and 380 nm. The first two peaks in the UV region can be

Table 1 Chemical analysis of different compounds

Compound	Color	Cl %	C %	H %	N %	Cu %
(**1a**)	Colorless	–	92.50	7.60	–	–
(**2a**)	Light yellow	–	74.10	5.69	6.01	–
(**3a**)	Yellow	13.25	72.01	6.72	5.81	–
(**4a**)	Pale yellow	–	84.12	7.34	6.72	–
(**5a**)	Brown		83.23	6.28	9.07	
P-[(C_6H_4 N=CHPy)Cu$(OAc)_2$]	Deep brown	–	67.80	5.46	6.62	1.98 (1.97)[a]

P polystyrene framework

[a] Used catalyst

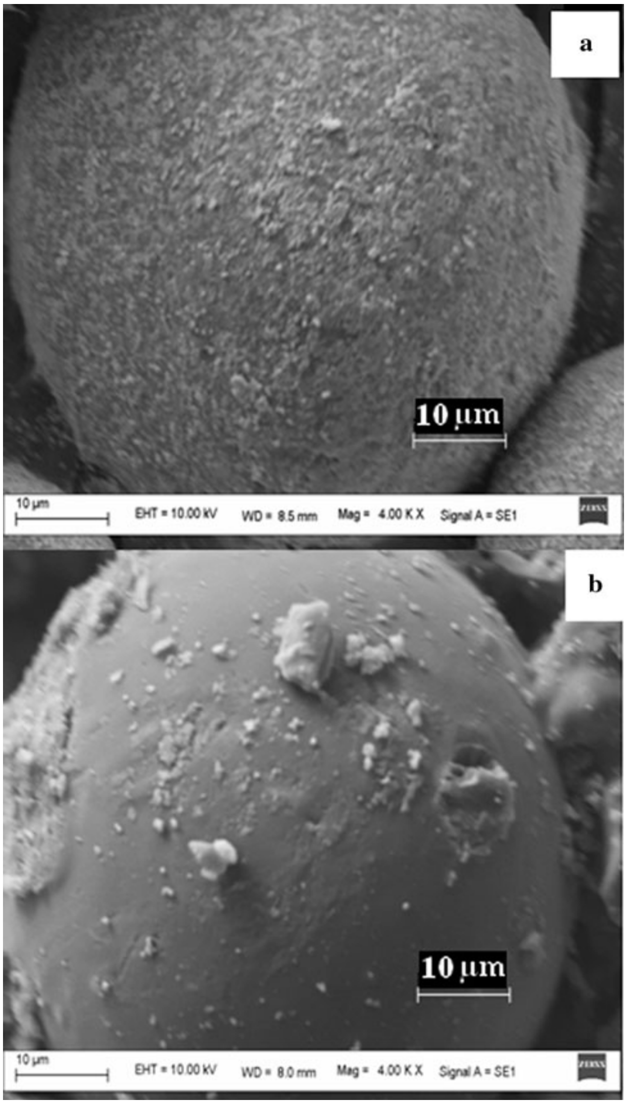


Fig. 1 FE SEM image of polymer-supported Schiff base ligand (**1a**) and polymer-supported copper(II) Schiff base catalyst (**1b**)

assigned to intraligand π–π* transitions. The two bands at 295 nm and 322 nm arise due to n–π* [30] and π–π* [26] transitions of pyridine. The peak at 380 nm may be due to ligand-to-metal charge transfer [31]. The expected d–d bands are not observed in the polymer-supported copper catalyst. Possibly poor loading of the complex on the polymer matrix has prevented the observation of the d–d band, which are a low energy and eventually less intense band [32].

Thermal stability of the catalyst was investigated using TGA-DTA at a heating rate of 10 °C/min in air over a temperature range of 30–600 °C. The catalyst is stable up to 300 °C, and above this temperature, it decomposed. Thermogravimetric study suggests that the polymer-supported copper(II) catalyst degrades at a slightly higher temperature.

Catalytic activity

The *N*-arylation reaction is a convenient method for the C–N bond formation between N–H heterocycles with aryl halides and arylboronic acids. To test the applicability of the polymer-anchored copper(II) catalyst, we examined the *N*-arylation reaction between N–H heterocycles with various aryl halides and arylboronic acids.

N-arylation reaction of imidazole with aryl halides using polymer-supported copper(II) Schiff base catalyst

To optimize the conditions for the *N*-arylation reaction, we have chosen the reaction between iodobenzene and imidazole as a model reaction (Scheme 2) and various catalysts, solvents, and bases were screened. In an effort to evolve a better catalytic system, various catalysts were screened for *N*-arylation of imidazole and iodobenzene in DMSO using K_2CO_3 at 120 °C. The results are summarized in Table 3. Homogeneous copper catalyst, CuI, $CuCl_2$, and $Cu(OAc)_2$, gave very low yield (entries 2–4). As can be seen from Table 3, polymer-supported copper catalysts were superior. Among polymer-supported copper(II) catalysts, polymer-supported copper(II) Schiff base catalyst from copper(II) acetate was found to be the most effective one (entry 7).

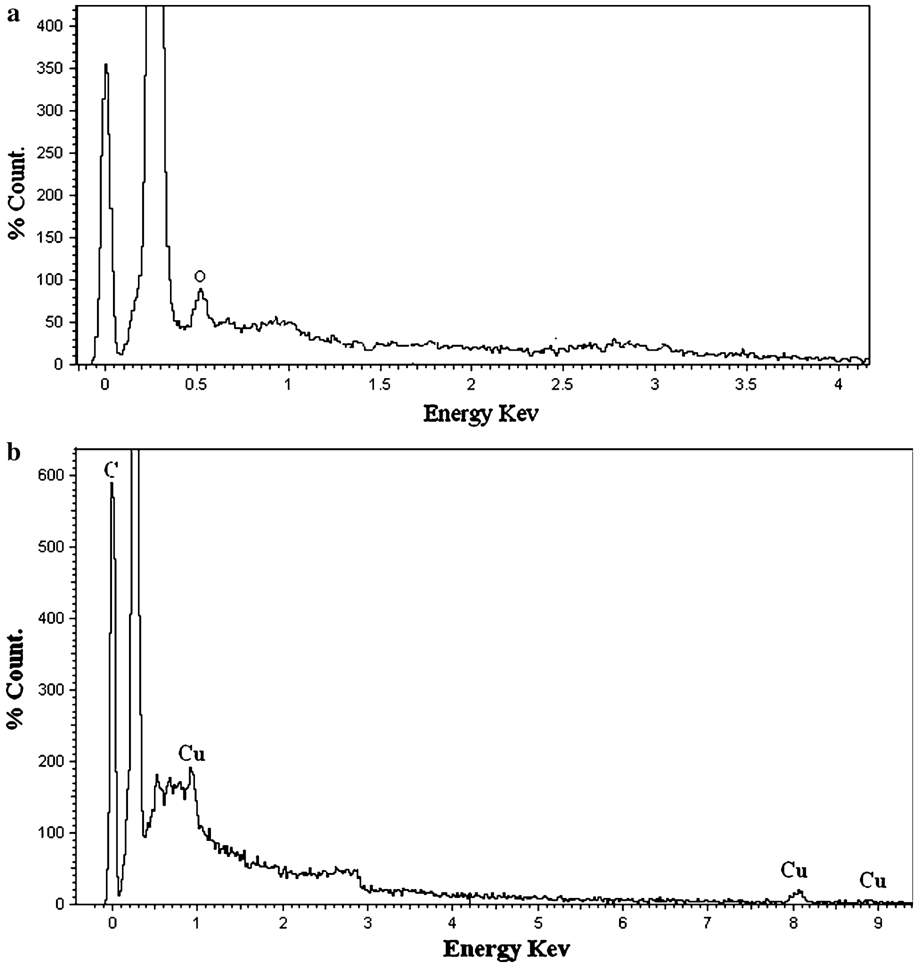


Fig. 2 EDAX data of polymer-supported Schiff base ligand (**2a**) and polymer-supported copper(II) Schiff base catalyst (**2b**)

Table 2 IR spectral data (cm^{-1}) of the compounds

Compound	δNH_2	νNH_3Cl	νNO_2	$\nu C{=}N^a$	$\nu C{=}N^b$	$\nu Cu{-}N^c$	$\nu Cu{-}N^d$	$\nu Cu{-}O$
(**2a**)			1,520(s) 1,350(s)					
(**3a**)		2,550	1,520(w) 1,350(w)					
(**4a**)	1,625		1,520(w) 1,350(w)					
(**5a**)			1,520(w) 1,350(w)	1,639	1,594			
$P\text{-}[(C_6H_4\ N{=}CHPy)Cu(OAc)_2]$			1,520(w) 1,350(w)	1,614	1,600	462	545	430

P Polystyrene, *s* strong, *w* weak

[a] Azomethine group

[b] Pyridine moiety

[c] Azomethine nitrogen

[d] Nitrogen in the pyridine moiety

The comparison of heterogeneous Schiff base copper catalyst and corresponding homogeneous Schiff base copper catalyst in the *N*-arylation reaction was carried out under the same reaction conditions. The results (entries 7, 8) clearly show that the polymer-supported copper(II) Schiff base catalyst was more active than its homogeneous

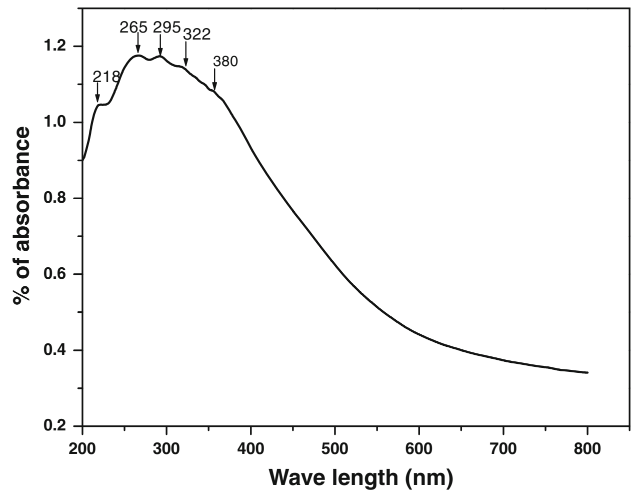
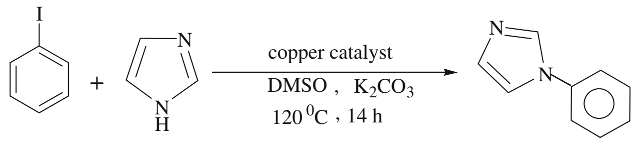
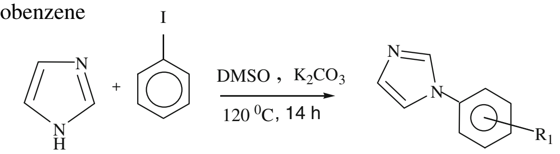


Fig. 3 DRS-UV–Visible absorption spectra of polymer-supported Cu(II) catalyst



Scheme 2 *N*-arylation of imidazole with iodobenzene using polymer-supported copper(II) catalyst

Table 3 Effect of copper source on the coupling of imidazole with iodobenzene



Entry	Copper source	Yield[a] (%)
1.	None	No reaction
2.	CuI (0.05 g)	30
3.	$CuCl_2$ (0.05 g)	56
4.	$Cu(OAc)_2$ (0.05 g)	64
5.	Polymer-supported copper(I)[b] catalyst (0.05 g)	72
6.	Polymer-supported copper(II)[c] catalyst (0.05 g)	79
7.	Polymer-supported copper(II)[d] catalyst (0.05 g)	93
8.	Homogeneous copper(II)[d] catalyst (0.05 g)	83

Reaction conditions: Polymer-supported copper(II) catalyst (0.05 g, 0.0156 mmol), 1 mmol of iodobenzene, 1.2 mmol of imidazole, 2 mmol K_2CO_3, DMSO (10 mL), 120 °C, N_2 atm

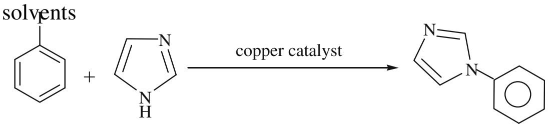
[a] Yield determined by GC and GCMS analysis

[b] Catalyst prepared from CuI

[c] Catalyst prepared from $CuCl_2$

[d] Catalyst prepared from $Cu(OAc)_2$

Table 4 *N*-arylation reaction using copper catalyst at various bases and solvents



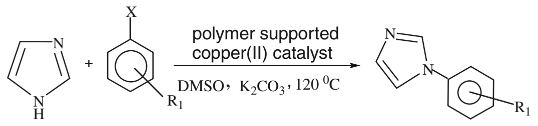
Entry	Base	Solvent	Temperature (°C)	Time (h)	Yield (%)[a]
1.	K_2CO_3	DMSO	120	14	93
2.	K_3PO_4	DMSO	120	18	78
3.	Et_3N	DMSO	120	12	45
4.	Cs_2CO_3	DMSO	120	18	47
5.	K_2CO_3	DMF	140	20	90
6	K_2CO_3	NMP	130	20	89
7.	K_2CO_3	ACN	100	20	90
8.	K_2CO_3	THF	100	20	67
9.	K_2CO_3	DME	100	18	62

Reaction conditions: Polymer-supported copper(II) catalyst (0.05 g, 0.0156 mmol), 1 mmol of iodobenzene, 1.2 mmol of imidazole, 2 mmol base, solvent (10 mL), N_2 atm

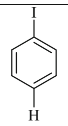
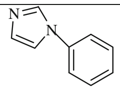
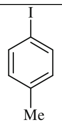
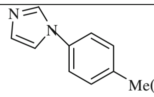
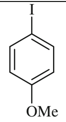
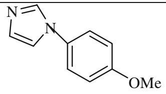
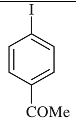
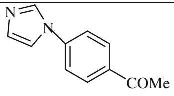
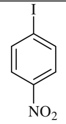
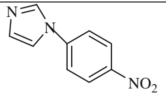
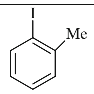
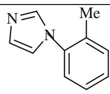
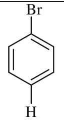
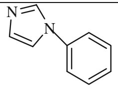
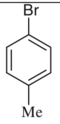
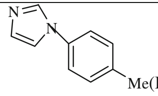
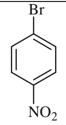
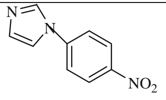
[a] Yield determined by GC and GCMS analysis

analogue copper(II) Schiff base analogue. Additionally, the supported catalyst is expected to have several advantages over the homogenous one. The immobilized catalyst can be removed easily from the reaction mixture by a simple filtration, and it is more easily handled. Several bases were screened using the polymer-supported copper(II) catalyst for the *N*-arylation of imidazole with iodobenzene in DMSO solvent at 120 °C, and the results are summarized in Table 4. It was observed that K_2CO_3 gave the best result (Table 4, entry 1). K_3PO_4 was also found to be fairly active (entry 2). But the organic bases like Et_3N and Cs_2CO_3 were almost inactive (entries 3, 4). Next, to check the solvent effects in the *N*-arylation of imidazole with iodobenzene, several solvents were screened and results are summarized in Table 4. It was observed that the polar solvents like DMSO, DMF, NMP, and acetonitrile were effective (Table 4, entries 1, 5–7). THF and dimethoxyethane (DME) were less effective (entries 8, 9). Consequently, DMSO was used as a solvent for the rest of the studies. With optimized conditions now in hand, we explored the scope of this process with respect to aryl iodide structure, and the results are summarized in Table 5. To our delight, the *N*-arylation of imidazole is smoothly performed with the extensive pool of aryl iodides to afford the corresponding products in good to excellent yields. It was observed that iodoarenes with electron-withdrawing groups (Table 5, entries 4, 5) reacted at a faster rate than iodoarenes with electron-donating groups (Table 5, entries 2, 3). Sterically hindered 2-iodotoluene took longer duration to afford a good yield (Table 5, entry 6). Extension of this arylation process with aryl bromides yielded interesting results: The use of bromobenzene in place of iodobenzene afforded lower conversion with 74% yield (entry 7) with longer reaction time and longer reaction temperature. Bromobenzene with an electron-donating group

Table 5 *N*-Arylation of imidazoles with different aryl halides



X=I, Br; R_1= H, Me, OMe, COMe, NO_2.

Entry	Aryl halides	Products	Time (h)	Isolated Yield (%) [a]
1.		 (A)	14	92
2.		 (B)	15	83
3.		 (C)	18	82
4.		 (D)	10	93
5.		 (E)	12	92
6.		 (F)	20	62
7.[c]		 (A)	24	74
8.[c]		 (B)	24	37
9.[c]		 (E)	18	88

Reaction conditions: Polymer supported copper(II) catalyst (0.05 g, 0.0156 mmol), 1 mmol of aryl halide, 1.2 mmol of imidazole, 2 mmol K_2CO_3, DMSO (10 mL), 120 °C, N_2 atm

[a] Isolated yield after column chromatography

[b] Yield after consecutive cycles

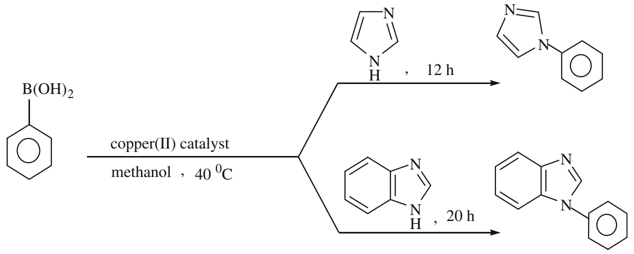
[c] Reaction teamparature = 150 °C

gave lower yield (entry 8), whereas bromobenzene with an electron-withdrawing group gave excellent yield of product (entry 9).

N-arylation reaction of N(H)-heterocycles with arylboronic acids using polymer-supported copper(II) Schiff base catalyst

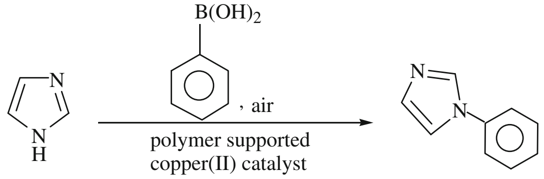
N-arylation of N(H)-heterocycles with arylboronic acids is complementary to the *N*-arylation with aryl halides as it requires very mild conditions and less time but uses expensive arylboronic acids (Scheme 3). *N*-arylation reaction of imidazole with phenylboronic acid using the polymer-supported copper(II) catalyst was carried out in absence of any base. Table 6 illustrates the effect of solvent in the *N*-arylation reaction of imidazole with phenyl boronic acid using copper(II) catalyst. Methanol (MeOH), Acetonitrile (ACN), dimethylformamide (DMF), toluene, and dimethylsulfoxide (DMSO) were used as a solvent without any base. It was observed that MeOH was effective providing higher yield than the other solvents. The solvent (MeOH) and temperature (40 °C) parameters were kept constant for further arylation reaction of substituted phenylboronic acid with N(H)-heterocycles using this copper(II) catalyst under base-free conditions. Our method was successfully amenable to a wide range of arylboronic acids, allowing preparation of *N*-arylimidazoles and *N*-arylbenzimidazoles in high yield, and the results are shown in Table 7. It was observed that arylboronic acids with electron-donating groups reacted at a faster rate and afforded better yields than arylboronic acids with electron-withdrawing groups (entries 2–6). Similar observations were made when benzimidazole was used in place of imidazole to obtain the corresponding *N*-arylbenzimidazoles but the reactions took longer time compared with the reactions of imidazole (entries 9–11). *o*- and *p*-substituted arylboronic acids were equally effective for the coupling with imidazole (entries 2, 7).

We compared the activity of the copper catalyst in the *N*-arylation reaction with other reported copper catalysts [33–35] (Table 8). From Table 8, it can be seen that the activity of the copper catalyst is more than the other reported systems.



Scheme 3 *N*-arylation of imidazole and benzimidazole with phenylboronic acid using polymer-supported copper(II) catalyst

Table 6 Effect of solvent on the coupling of imidazole with phenylboronic acid



Entry	Solvent	Temperature	Time	Yield[a] (%)
1.	MeOH	40 °C	12 h	96
2.	ACN	70 °C	12 h	87
3.	DMF	120 °C	16 h	79
4.	DMSO	115 °C	16 h	75
5.	Toluene	100 °C	20 h	67

Reaction conditions: Polymer-supported copper(II) catalyst (0.05 g, 0.0156 mmol), phenylboronic acid (0.0182 g, 1.5 mmol), imidazole (0.082 g, 1.2 mmol), solvent (10 mL), air

[a] Yield determined by GC and GCMS analysis

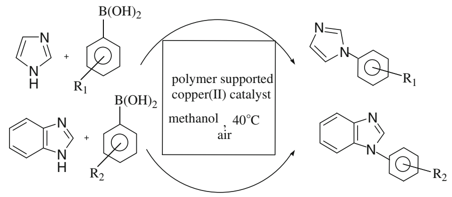
Heterogeneity tests

To determine whether the catalyst was actually functioning in a heterogeneous manner, a hot-filtration test [36] was performed in the *N*-arylation reaction of imidazole with phenyl boronic acid. The solid catalyst was filtered out after the reaction had proceeded for 6 h and the yield determined by GC and GCMS analysis was 72%, and the liquid phase of the reaction mixture was collected at the reaction temperature. Atomic absorption spectrometric analysis of the liquid phase of the reaction mixtures collected by filtration confirmed that Cu was absent from the reaction mixture. The obtained filtrate was stirred under the reaction conditions. After 12 h, the yield was determined to be still 72%. This result indicated that the catalytic reaction was caused by the solid catalyst. Cu was also not detected in the liquid phase of the reaction mixture after the completion of the reaction. It is noteworthy that the MeOH remains completely colorless on addition of copper(II) catalyst. These results also suggested that the Cu was not being leached out from the catalyst during the *N*-arylation reactions.

Catalyst recycling

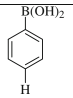
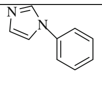
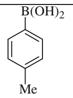
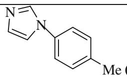
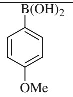
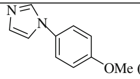
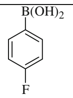
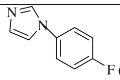
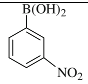
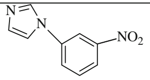
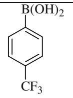
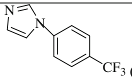
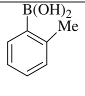
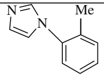
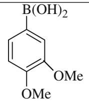
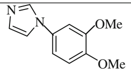
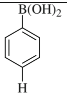
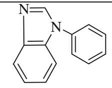
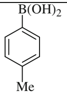
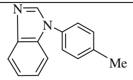
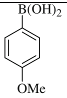
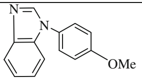
The best advantage of the heterogeneous catalysis was the possibility of recovering and reusing the catalyst during the reaction. The capability of recycling of the catalyst was confirmed after five consecutive *N*-arylation reactions of

Table 7 *N*-Arylation of imidazole/benzimidazole with various arylboronic acids



R_1= H, Me, OMe, F, CF_3, NO_2.

R_2= H, Me, OMe.

Entry	N(H)-heterocycles	arylboronic acid	Products	Time	Isolated Yield[a] (%)
1.	Imidazole		 **(A)**	12	95
2.	Imidazole		 **(B)**	14	93
3.	Imidazole		 **(C)**	14	92
4.	Imidazole		 **(G)**	18	85
5.	Imidazole		 **(H)**	18	74
6.	Imidazole		 **(I)**	18	71
7.	Imidazole		 **(F)**	16	88
8.	Imidazole		 **(J)**	18	79
9.	Benzimidazole		 **(K)**	20	91
10.	Benzimidazole		 **(L)**	20	85
11.	Benzimidazole			20	86

Reaction conditions: polymer supported copper(II) catalyst (0.05 g, 0.0156 mmol), 1.5 mmol of arylboronic acid, 1.2 mmol of imidazole/benzimidazole, MeOH (10 mL), 40 °C, air

[a] Isolated yield after column chromatography

Table 8 Comparison of activity of different copper catalysts in the *N*-arylation reaction

Reaction	Catalyst	Reaction conditions	Yield (%)	Reference
N-Arylation (imidazole + iodobenzene)	P-[(C_6H_4N=CHPy)Cu($OAc)_2$]	DMSO, 120 °C, 14 h	92	This study
	Cu_2O	DMSO, 110 °C, 24 h	90	38
	Nano-CuO[a]	DMSO, 110 °C, 24 h	91	39
N-Arylation (imidazole + phenylboronic acid)	P-[(C_6H_4N=CHPy)Cu($OAc)_2$]	MeOH, 40 °C, 12 h	95	This study
	PANI-Cu[b]	MeOH, 5 h, rt.	88	40
	CuFAP[c]	MeOH, 80 °C, 1.5 h	94	21

[a] CuO nanoparticles

[b] Polyaniline-supported copper catalyst

[c] Copper-exchanged fluorapatite

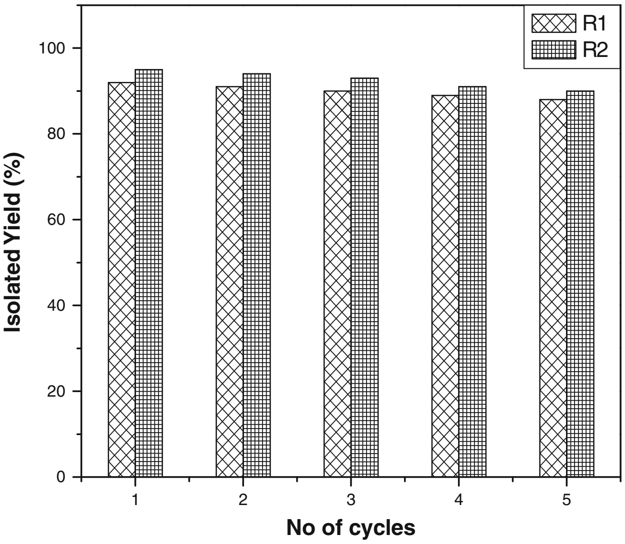


Fig. 4 Recycling activity of the Cu(II) catalyst toward the *N*-arylation reaction. Reaction condition: R1 → Polymer-supported copper(II) catalyst (0.05 g, 0.0156 mmol), 1 mmol of iodobenzene, 1.2 mmol of imidazole, 2 mmol K_2CO_3, DMSO (10 mL), 120 °C, 14 h, N_2 atm. R2 → polymer-supported copper(II) catalyst (0.05 g, 0.0156 mmol), 1.5 mmol of phenylboronic acid, 1.2 mmol of imidazole, MeOH (10 mL), 40 °C, 12 h, air

imidazole with phenylboronic acid in MeOH medium and imidazole with iodobenzene in DMSO medium. After the first run, the catalyst was separated by filtration, washed, dried under vacuum, and then subjected to the second run under the optimized reaction conditions. The catalytic run was repeated with further addition of substrates in appropriate amounts under optimum reaction conditions, and the nature and yield of the final products were comparable with that of the original one. The results summarized in Fig. 4 demonstrate that there was almost no change in catalytic activity even after the fifth recycle. Metal content of the recycled catalyst remained unaltered, indicating no leaching of the metal from the polymer support (Table 1). The nature of the recovered catalyst has been followed by IR and UV–Vis spectra. The results indicated that the catalyst after reusing several times showed no change in its IR and UV–vis spectra.

Conclusion

In summary, this paper describes a simple method for the preparation of *N*-arylated imidazoles and benzimidazoles. The catalytic system adopted is simple and cheap, starting from commercially available compounds and employing only a catalytic amount (0.05 g, 0.0156 mmol) of the Cu(II) Schiff base catalyst. We have developed a heterogeneous polymer-supported copper-catalyzed *N*-arylation of imidazoles and benzimidazoles under base-free condition with various arylboronic acids. This catalyst was also effective in *N*-arylation of imidazole with various aryl halides. Moreover, the catalyst can easily be separated by simple filtration and reused for several cycles with consistent activity.

Experimental

Surface morphology and particle size of the samples were analyzed using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. Thermogravimetric analysis (TGA) of the immobilized catalyst was determined using a Mettler Toledo TGA/SDTA 851. The FTIR spectra were recorded on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. Diffuse reflectance UV–Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. A Perkin-Elmer 2400C elemental analyzer was used to collect microanalytical data (C, H and N). Copper content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS). Analytical grade reagents and freshly distilled solvents were used throughout. All reagents and substrates were purchased from Merck. Liquid substrates were predistilled and dried by appropriate molecular sieve, and solid substrates were recrystallized before use. Distillation, purification of the solvents and substrates were done by standard procedures. Macroporous polystyrene beads cross-linked with 2% divinylbenzene and 2-pyridinecarboxaldehyde were purchased from Aldrich Chemical Company, USA. Copper salts were purchased from Merck and used without further purification.

Preparation of p-nitro-polystyrene (**2a**)

A suspension of macroporous polystyrene beads (**1a**) (5.0 g) in a mixture of acetic anhydride (20 mL), nitric acid (~70%, 2 mL), and glacial acetic acid (4 mL) was stirred for 30 min at 5 °C followed by 5 h at 50 °C [37]. The corresponding p-nitro polystyrene (**2a**) was washed successively with acetic acid, water, and methanol and finally dried under vacuum.

Preparation of p-amino-polystyrene (**4a**)

A mixture of acetic acid (20 mL), stannous chloride (5.0 g), concentrated hydrochloric acid (6 mL), and p-nitropolystyrene (**2**) (5.0 g) was stirred for 72 h at room temperature to reduce the nitro-compound to the corresponding aminehydrochloride (**3a**) [37]. The residue was washed several times with hydrochloric acid (12 M) and glacial acetic acid (1:4) mixture and then with methanol. The product on repeated treatment with dilute alcoholic NaOH (5%) produced the corresponding free amine (**4**). This was washed with alcohol and dried under vacuum.

Preparation of the polymer-supported Schiff base ligand (5a), P-[C_6H_4 N=CHPy]

A suspension of macroporous amino polystyrene (**4a**) (2.0 g) in toluene (25 mL) was taken in a 100 mL round bottom flask and stirred for 30 min. 2-Pyridinecarboxaldehyde (5 mL) was added dropwise to the reaction mixture. The suspension changed its color from pale yellow to yellowish brown. The reaction mixture was refluxed for 48 h at 120 °C. After cooling it to room temperature, the brown polymer-anchored Schiff base ligand (**5a**) was filtered out, washed thoroughly with methanol, and dried under vacuum.

Preparation of the polymer-supported copper(II) Schiff base catalyst, P-[(C_6H_4 N=CHPy)Cu$(OAc)_2$]

Polymer-supported Schiff base ligand (**5a**) (2.0 g) was added to acetic acid (20 mL) placed in a round bottom flask. Copper acetate (0.05 g) in acetic acid (5 mL) was added to the above suspension with constant stirring and then refluxed on an oil bath for 24 h. After cooling the reaction mixture to room temperature, the separated deep brown color solid was filtered out, washed thoroughly with methanol and dried under vacuum.

Preparation of homogeneous copper(II) Schiff base complex

The corresponding Schiff base ligand was prepared according to the published protocol [38]. The copper complex was prepared by mixing equal volumes (50 mL) of methanol solution of $CuCl_2$ (0.170 g, 1.0 mmol) with Schiff base ligand (0.182 g, 1.0 mmol). The mixtures were refluxed at about 75 °C for 2–3 h on a water bath. On cooling immediately, precipitate which settled out was filtered off, washed several times with a minimum of methanol, and dried under vacuum over anhydrous $CaCl_2$.

General procedure for the *N*-arylation of imidazole with iodobenzene catalyzed by homogeneous copper(II) Schiff base catalyst

In a 100 mL RB flask, homogeneous copper catalyst (0.0156 mmol), iodobenzene (1 mmol), imidazole (1.2 mmol), K_2CO_3 (2 mmol), and DMSO (10 mL) were stirred under nitrogen atmosphere at 120 °C. After the completion of the reaction, the filtrate was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were dried with anhydrous Na_2SO_4. The filtrate was concentrated by vacuum, then the reaction mixture was identified by GC–MS and quantified by GC analysis.

General procedure for the *N*-arylation of imidazole with aryl halides catalyzed by heterogeneous copper(II) Schiff base catalyst

In an oven dried 100 mL RB flask, copper catalyst (0.05 g, 0.0156 mmol), aryl halide (1 mmol), imidazole (1.2 mmol), K_2CO_3 (2 mmol), and DMSO (10 mL) were stirred under nitrogen atmosphere at 120 °C. The reaction mixtures were collected at different time intervals and identified by GC–MS and quantified by GC analysis. After the completion of the reaction, the catalyst was filtered off, washed with water followed by acetone, and oven dried. The filtrate was extracted with ethyl acetate (3 × 20 mL), and the combined organic layers were dried with anhydrous Na_2SO_4. The filtrate was concentrated by vacuum, and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

General procedure for the *N*-arylation of N(H)-heterocycles with arylboronic acids catalyzed by heterogeneous copper(II) Schiff base catalyst

In a 100 mL RB flask, copper(II) catalyst (0.05 g, 0.0156 mmol), aryl boronic acid (1.5 mmol), N(H)-heterocycles (1.2 mmol), and MeOH (10 mL) were stirred under open air, at 40 °C. To study the progress of the reaction, the reaction mixtures were collected at different time intervals and quantified by GC analysis. After the completion of the reaction, the catalyst was filtered off, washed with water followed by acetone, and oven dried. Then, it was extracted with ethyl acetate (3 × 20 mL), and the combined organic layers were dried with anhydrous Na_2SO_4. The filtrate was concentrated by vacuum, and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

Characterization of the products

Melting points were recorded on a melting point apparatus. All ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. The characterizations of the products were carried out by ^{1}H NMR spectroscopy using Bruker DPX-400 in $CDCl_3$ with TMS as internal standard. Chemical shifts are given as δ value with reference to tetramethylsilane (TMS) as the internal standard. The reaction products were quantified (GC data) using a Varian 3400 gas chromatograph equipped with a 30-m CP-SIL8CB capillary column and a flame ionization detector and identified (GC–MS) by Trace DSQ II GC–MS equipped with a 60-m TR-50MS capillary column. ^{1}H and ^{13}C NMR data of all the products are given below:

Spectroscopic data are as follows:

1-Phenyl-1H-imidazole (A) [39]. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.82$ (s, 1H), 7.54–7.42 (m, 2H), 7.41–7.40 (m, 3H), 7.27 (bs, 1H), 7.24 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 136.4$, 134.5, 130.5, 129.0, 126.9, 121.1, 118.2.

1-(4-Methylphenyl)-1H-imidazole (B) [39]. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.78$ (s, 1H), 7.22 (m, 4H), 7.17 (bs, 1H), 7.13 (bs, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 137.2, 135.7, 134.4, 130.1, 130.3, 121.6, 118.0, 20.90.

1-(4-Methoxyphenyl)-1H-imidazole (C) [40]. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.70$ (s, 1H), 7.25 (d, 2H, J = 9.0 Hz), 7.15 (bs, 1H), 7.13 (bs, 1H), 6.97 (d, 2H, J = 9.0 Hz), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 158.8$, 135.6, 131.2, 130.6, 120 (2C), 118.4, 114.7 (2C), 55.

1-(4-(1H-Imidazol-1-yl)phenyl)ethanone (D) [39]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, 2H), 7.95 (bs, 1H), 7.49 (d,2H), 7.35 (bs, 1H), 7.24 (bs, 1H), 2.63 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.4, 140.7, 135.7, 135.4, 131.0,130.3, 120.6, 117.7, 26.5.

1-(4-Nitrophenyl)-1H-imidazole (E) [39]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, 2H), 7.99 (bs, 1H), 7.58 (d, 2H), 7.38 (bs, 1H), 7.28 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.3, 141.9, 135.4, 131.7, 125.7, 121.0, 117.6.

1-o-Tolyl-1H-imidazole (F) [39]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (br s, 1H), 7.40–7.17 (m, 5H), 7.03 (br s, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 136.5, 133.8, 131.2, 129.2,128.7, 126.8, 126.4, 120.4, 17.5.

1-(4-Fluorophenyl)-1H-imidazole (G) [21]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (br s, 1H), 7.33–7.37 (m, 2H), 7.15–7.20 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.2, 162, 133.6, 130.1, 123.0 (2C), 118.0, 116.4 (2C).

1-(3-nitrophenyl)-1H-imidazole (H) [39]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.366 (s, 1H), 8.25–8.01 (m, 2H), 7.92 (d, 1H, $J = 9.4$ Hz), 7.75 (t, $J = 8.6$ 1H), 7.51 (br s, 1H), 7.16 (br s, 1 H).

1-(4-Trifluoromethylphenyl)-1H-imidazole (I) [21]. *^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (br s, 1H), 7.67 (d, 2H, $J = 8.91$ Hz), 7.47 (d, 2H, $J = 8.91$ Hz), 7.22 (br s, 1H), 7.14(br s, 1H).*

1-(3,4-dimethoxyphenyl)-1H-imidazole (J) [21]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (s, 1H), 7.13 (br s, 1H), 7.10 (br s, 1H), 6.86 (br s, 2H), 6.85 (br s, 1H), 3.92 (s, 6H).

1-phenyl-1H-benzimidazole (K) [21]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (s, 1H), 7.82–7.85 (m, 1H), 7.44–7.61 (m, 6H), 7.5–7.3 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142, 142.4, 136.7, 133.6, 130, 127.7, 126, 123.8, 122.7 (2C), 120.3, 110.3.

1-(4-Methylphenyl)-1H-benzimidazole (L) [21]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (br s, 1H), 7.77–7.85 (m, 1H), 7.40–7.47 (m, 1H), 7.20 –7.33 (m, 6H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144, 142, 137, 135 (2C), 130.4, 124, 123.8, 122.8 (2C),120.2, 110.1(2C), 21.

1-(4-Methoxyphenyl)-1H-benzimidazole (M) [21]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (br s, 1H), 7.85–7.88 (m, 1H), 7.45–7.47 (m, 1H), 7.40 (d, 2H, J = 9.0 Hz), 7.30–7.33 (m, 2H), 7.05 (d, 2H, $J = 9.0$ Hz), 3.90 (s, 3H).

Acknowledgments We thank the Department of chemistry, University of Calcutta, for providing us the instrumental support. We gratefully acknowledge DST, New Delhi, for award of grant under its FIST program to the Department of Chemistry, University of Kalyani. SMI acknowledges the following agencies for funding: DST, CSIR, and UGC, New Delhi, India.

References

1. Beletskaya IP, Cheprakov AV (2004) Coor Chem Rev 248:2337–2364
2. Ullmann F, Ber D (1903) Chem Ges 40:2382
3. Ley SV, Thomas AW (2003) Angew Chem Int Ed 42:5400
4. Wolfe JP, Wagaw S, Marcoux JF, Buchwald SL (1998) Acc Chem Res 31:805

5. Lewis JC, Bergman RG, Ellman JA (2008) Acc Chem Res 41: 1013
6. Ohmori J, Shimizu-Sasamata M, Okada M, Sakamoto SJ (1996) J Med Chem 39:3971
7. Pavik WJJW, Connors RE, Burns DS, Kurzweil EM (1993) J Med Chem 115:7645
8. Lam PYS, Deudon S, Averill KM, Li R, He MY, Deshong P, Clark CG (2000) J Am Chem Soc 122:7600
9. Hassan J, Sevignon M, Gozzi C, Schulz E, Lemaire M (2002) Chem Rev 102:1359
10. Zhang H, Cai Q, Ma D (2005) J Org Chem 70:5164
11. Antilla JC, Baskin JM, Barder TE, Buchwald SL (2004) J Org Chem 69:5578
12. Kwong FY, Klapars A, Buchwald SL (2002) Org Lett 4:581
13. Lam PYS, Clark CG, Saubern S, Adams J, Averill KM, Chan DMT, Combs A (2000) Synlett :674
14. Lan JB, Chen L, Yu XQ, You JS, Xie RG (2004) Chem Commun 2:188
15. Surry DS, Buchwald SL (2010) Chem Sci 1:13
16. Cristau HJ, Cellier PP, Spindler JF, Taillefer M (2004) Chem Eur J 10:5607
17. Surry DS, Buchwald SL (2011) Chem Sci 2:27
18. Maiti D, Fors BP, Henerson JL, Nakamura Y, Buchwald SL (2011) Chem Sci 2:57
19. Islam SM, Mondal P, Tuhina K, Roy AS, Mondal S, Hossain D (2010) J Organomet Chem 695:2284–2295
20. Islam SM, Mondal S, Roy AS, Mondal P, Mobarak M, Hossain D, Pandit P (2010) Transit Met Chem 35:305–313
21. Islam SM, Mondal P, Roy AS, Tuhina K (2010) Transit Met Chem 35:491–499
22. Kantam ML, Venkanna GT, Sridhar C, Sreedhar B, Choudary BM (2006) J Org Chem 71:9522
23. Sharma BD, Bailar JC (1955) J Am Chem Soc 77:5476
24. Sharma BD, Ray KR, Sievers RE, Bailar JC (1964) J Am Chem Soc 86:14
25. Zhong C, Guo R, Wu Q, Zhang H (2007) React Funct Polym 67:408
26. Zhou Y, Zhong C, He Y, Xiao L, Liu Y, Zhang H (2009) J. Inorg Organomet Polym 19:328
27. Gupta KC, Sutar AK (2008) J Mol Catal 280:173
28. Krishnankutty K, Ummathur MB, Sayudevi PJ (2009) Indian Chem Soc 86:325
29. Nakamoto N (1997) Infrared spectra and Raman spectra of inorganic and coordination compounds. Wiley, New York
30. Gup R, Kırkan B (2005) Spectrochim Acta A 62:1188
31. Gupta KC, Sutar AK (2008) Polym Adv Technol 19:186
32. Maurya MR, Kumar M, Kumar A, Pessoa JC (2008) Dalton Trans 4220
33. Karimi B, Enders D (2006) Org Lett 8:1237
34. King RB, Sweet EM (1979) J Org Chem 44:385
35. Johnson D, Mayer H, Minard J, Banaticla J, Miller C (1988) Inorg Chim Acta 144:167
36. Ashton PR, Koniger R, Stoddart JF, Alker D, Harding VD (1996) J Org Chem 61:903
37. Choudary BM, Sridhar C, Kantam ML, Venkanna GT, Sreedhar B (2005) J Am Chem Soc 127:9948
38. Huang YZ, Miao H, Zhang QH, Chen C, Xu J (2008) Catal Lett 122:344
39. Rout L, Jammi S, Punniyamurthy T (2007) Org Lett 9:3397
40. Kantam ML, Roy M, Roy S, Sreedhar B, Lal De R (2008) Catal Commun 9:2226