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A reusable polymer supported copper(I) complex for the C–N bond cross-coupling reaction

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ABSTRACT

The Ullmann coupling of amines with aryl iodide as well as arylboronic acids and N(H)-heterocycles with arylboronic acids has been carried out efficiently using PS-LCu(I) catalyst. The copper complex has been prepared and characterized by using scanning electron microscope (SEM), elemental analysis, atomic absorption spectroscopy (AAS), Thermo gravimetric analysis and spectrometric methods like Fourier transform infrared spectroscopy (FTIR). The effects of various parameters such as temperature, solvent and base on the reaction system were studied. The reusability experiments show that the catalyst can be used five times without much loss in the catalytic activity.

The synthesis of N-aryl amines and N-aryl heterocycles is an active area in organic synthesis due to their occurrence in biologically important natural products, pharmaceuticals and their applications in materials research [1,2]. Among the various strategies developed to date, the copper-catalyzed Ullmann reaction has proven to be the most convenient synthetic route for installing an N-aryl functionality [3,4]. In addition, Buchwald [5] and Hartwig [6,7] have reported on Pd mediated C–N bond formation. However, the cost of reagents and removal trace palladium from late stage synthetic intermediate are the major drawbacks of this method. Copper mediated amination and N-arylation is another choice of reaction for the production of these compounds due to cheap price and environmental friendly nature. However, copper-mediated couplings are still the reaction of choice for large and industrial scale formation of C–N bonds. The reaction system mostly employs an in situ generated catalyst from a copper source and highly efficient N/P-containing ligands such as amino acids, [8] diamines, [9] diimines, [10] pyridine, [11] oximephosphine oxides [12] and phosphoramidite [13]. In spite of the significant advances in this area, very few reports employing a structurally well defined and stable copper complex as a catalyst have been reported [14–16]. Chan and Lam established an efficient approach to *N*-arylimidazoles via $Cu(OAc)_2$-mediated coupling of imidazoles with readily available arylboronic acids [17]. Later, Collman and coworkers reported using Cu(II) complexes with nitrogen-chelating bidentate ligands in the coupling of imidazoles at room temperature [18]. Very recently, Xie and coworkers have shown the simple copper salt catalyzed coupling of imidazoles with arylboronic acids in protic solvent without any base [19]. Recently, calcium hydroxyapatite has been used as a heterogeneous support for transition metals, and the supported hydroxyapatite is used for organic transformations [20].

Nowadays solid-phase technique has gained much importance in this cross-coupling reaction. 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 overcome by anchoring metal on suitable supports. 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 [21].

In this present work, *N*-arylation reactions of various N(H)-heterocycles with arylboronic acids were carried out in methanol with PS-LCu(I) catalyst, without the need of any organic co-solvent, base or additives such as phase transfer catalysts. This catalyst was also effective in amination reactions of primary amines with various aryl halides as well as arylboronic acids. 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.

The synthesis of the immobilized PS-LCu(I) catalyst illustrated in Scheme 1. It was readily prepared through a two-step procedure. Firstly the 0.2 g of chloromethylated polystyrene copolymer (2) treated with 0.979 g of β-alanine (1) to produce the corresponding polymer supported ligand (PS-L) in the presence of sodium carbonate (0.490 g) in *N,N*-dimethylformamide (DMF) to obtained a light brown polymer. The polymer was washed thoroughly with DMF to remove excess β-alanine and then with 1 M HCl to remove excess base. Finally, it

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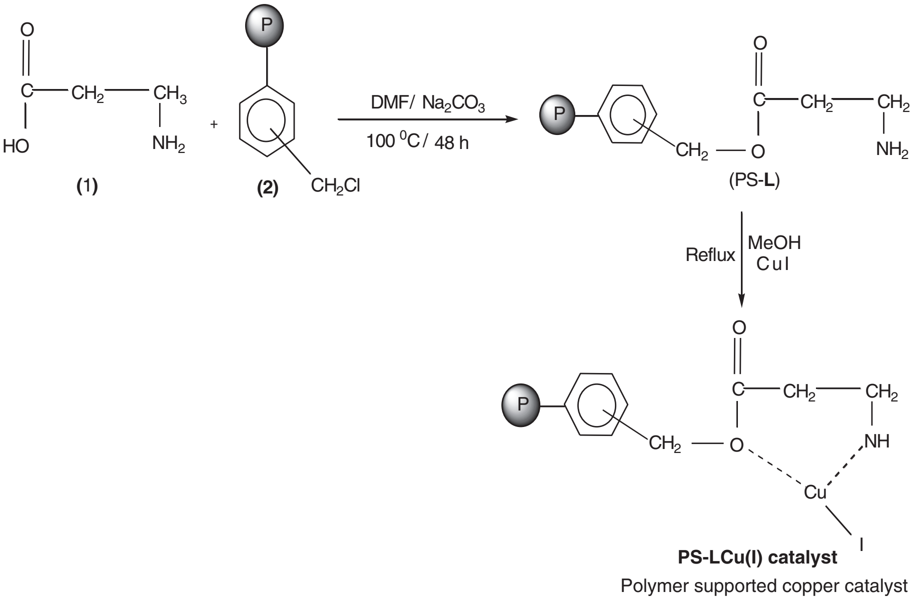


Scheme 1. Synthesis of the PS-LCu(I) catalyst.

was washed with double distilled water, dried and stored at room temperature for further use. Then the polymer anchored β-alanine ligand (1 g) in methanol (20 mL) was treated with 5 mL 1% (w/v) methanolic solution of copper iodide over a period of nearly 30 min under constant stirring. Then the reaction mixture was refluxed for 24 h. The green color copper complex thus formed was filtered and washed thoroughly with ethanol and dried in room temperature under vacuum.

The outline for the preparation of PS-LCu(I) catalyst is given in Scheme 1.

Table 1
Chemical composition of various compounds and PS-LCu(I) catalyst.

Compound	Color	C %	H %	Cl %	N %	Cu %
(1)	White	40.45	7.87	–	15.73	–
(2)	White	70.82	5.90	23.28	–	–
(PS-L)	White	70.24	7.32	–	6.83	–
PS-LCu(I)	Green	47.29	4.60	–	4.60	0.83 0.82[a]

[a] Used catalyst.

Due to insolubilities of the PS-LCu(I) catalyst in all common organic solvents, its structural investigation was limited to its physicochemical properties, chemical analysis, SEM, TGA and IR spectroscopic data. Table 1 provides the data of elemental analysis of different functionalized polymer and the complexes. Copper content in the catalysts determined by AAS suggests 0.83 wt.% Cu in the catalyst. The band at 676 cm^{-1} for –C–Cl stretching had disappeared in the polymer anchored ligand. A few new bands appeared, e.g. those at 3422 cm^{-1} along with bands at 1641 cm^{-1} showed the presence of free $-NH_2$ groups in the ligand. On complexation with copper, the frequency of free $-NH_2$ groups is reduced in intensity. In addition, the bands at 528 cm^{-1} may be assigned to the Cu–N [22] stretching vibration. The scanning electron micrographs of the PS-L and PS-LCu(I) catalyst clearly show the morphological change which occurred on the surface of polystyrene after loading of metal on it (Fig. 1A and B). Energy dispersive spectroscopy analysis of X-rays (EDAX) data for the PS-L and PS-LCu(I) catalyst is given in Fig. 2A and B. The EDX data also inform that the attachment of copper metal on the surface of the polymer matrix. Thermal stability of the complex was investigated using TGA-DTA at a heating rate of 10 °C /min in air over a temperature range of 30–600 °C.

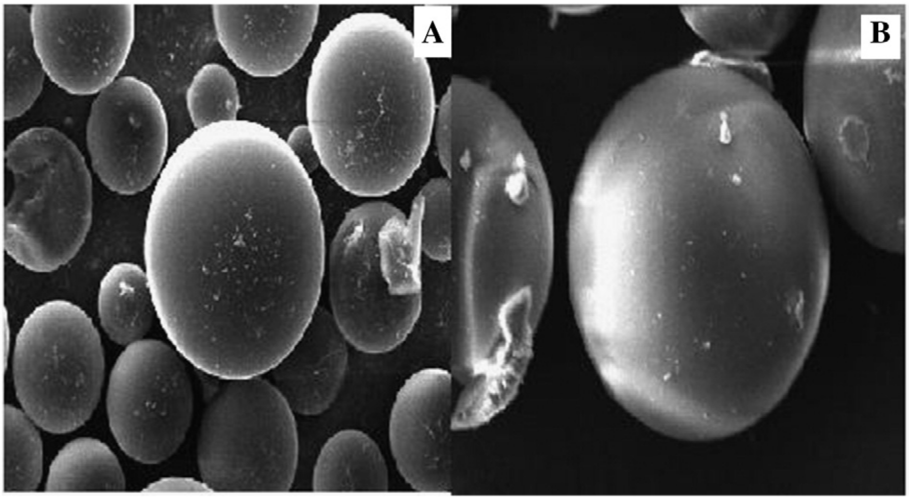


Fig. 1. FE SEM image of PS-L (1A) and PS-LCu(I) catalyst (1B).

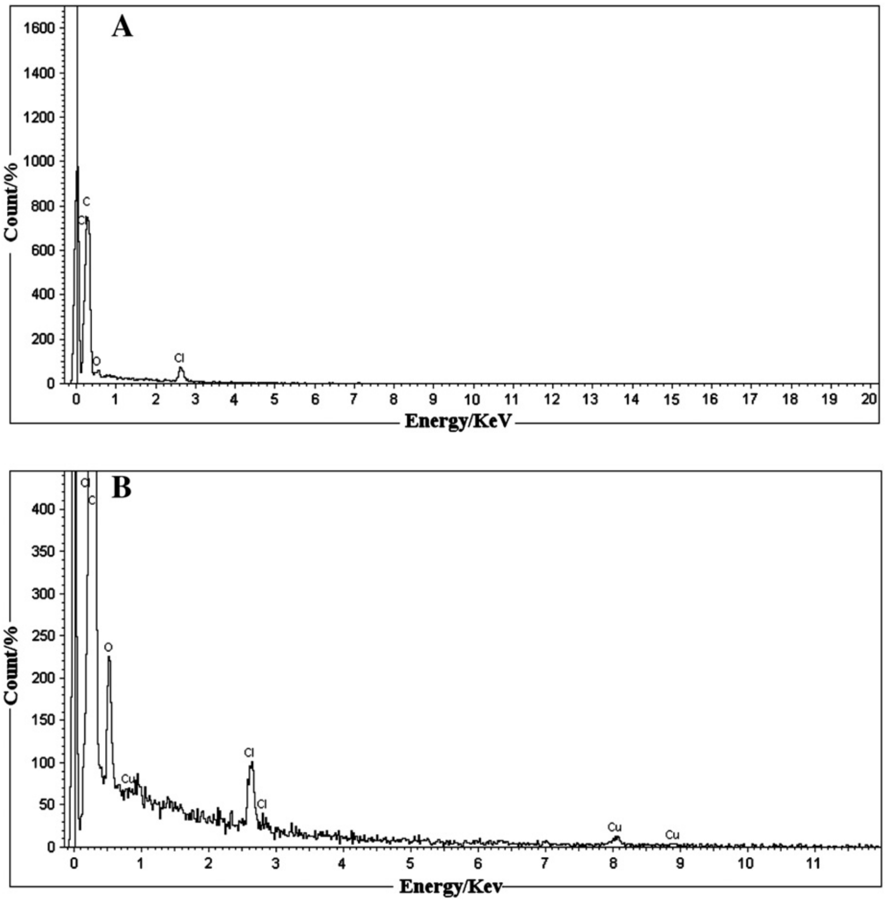


Fig. 2. EDAX data of PS-L (2A) and PS-LCu(I) catalyst (2B).

TGA–DTA curves of the PS-L and PS-LCu(I) catalyst are shown in Fig. 3. The complex is stable up to 200 °C and above this temperature it decomposes. Thermo gravimetric study suggests that the PS-LCu(I) catalyst degrades at considerably higher temperature.

Catalytic activity of the PS-LCu(I) catalyst

Although the current catalyst is performed in the N-arylation reaction of N(H)-heterocycles with phenylboronic acid using methanol as solvent in absence of any base and with a limited range of substrates, it is likely that our catalyst should be applicable to other substituted arylboronic acid systems. To check the generality and scope of the catalyst, we tried the *N*-arylation of N–H heterocycles with several other arylboronic acids in MeOH without using any base under this experimental condition [23] and the results are summarized in Table 2. The reaction of imidazole with phenylboronic acid is completed within 12 h at lower temperature (40 °C). Imidazole is successfully applied to couple electron rich arylboronic acids with in high yields (Table 2, entries 2–5). Electron withdrawing arylboronic acids reacted at a slower rate with moderate to good yields (entries 6–9). The coupling of 3-nitroboronic acid which is a difficult substrate also proceeded smoothly under the present conditions (Table 2, entry 7). A similar observation is made when benzimidazole is used in place of imidazole to obtain the corresponding *N*-arylbenzimidazoles, but the reactions took longer time compared to that in the reactions of imidazole (Table 2, entries 10–12). In an endeavor to expand the scope of the above methodology, the catalytic system was also applied to amides and sulfonamides. Such coupling of benzamide was found to give the desired *N*-arylation products in good yields, as shown in Table 2, entry 13, but for sulfonamide, which afforded the corresponding products in lower yield (Table 2, entry 14). Phenylboronic acid and 4-methylphenylboronic acid (Table 2, entries 15 and 16) were coupled with phthalimide under the generalized reaction conditions to afford the corresponding products in excellent yields.

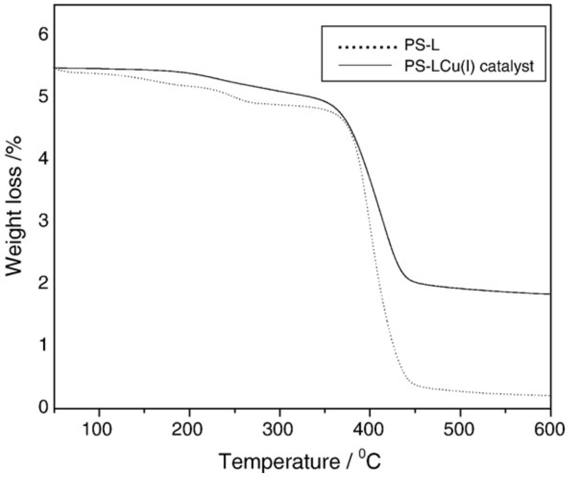
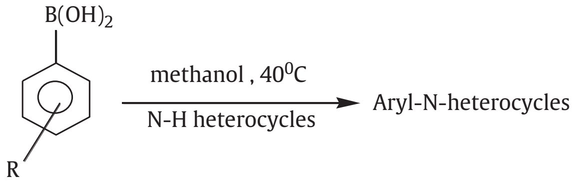


Fig. 3. Thermogravimetric weight loss plots for the PS-L and PS-LCu(I) catalyst.

After achieving excellent results with N(H)-heterocycles, we further applied this catalytic system for the amination of aromatic amines. Preliminary experiments are carried out by taking phenylboronic acid as a test molecule for the amination of aniline. In order to determine the best reaction medium, we tested different solvents

Table 2
N-arylation of N–H heterocycle with various arylboronic acids[a].



R= H, Me, OMe, Cl, F, CF_3, NO_2

Entry	N–H heterocycle	Aryl halides	Products	Time (h)	Isolated yield[b](%)
1.	Imidazole	$C_6H_5–B(OH)_2$	N-Phenylimidazole	10 h	96
2.	Imidazole	$4-Me–C_6H_4B(OH)_2$	N-(4-Methylphenyl)imidazole	10 h	95
3.	Imidazole	$4-MeO–C_6H_4B(OH)_2$	N-(4-Methoxyphenyl)imidazole	10 h	92
4.	Imidazole	$2-Me–C_6H_4B(OH)_2$	N-(2-Methylphenyl)imidazole	15 h	80
5.	Imidazole	$3,4-MeO–C_6H_3B(OH)_2$	N-(3,4-dimethoxyphenyl)imidazole	15 h	73
6.	Imidazole	$4-Cl–C_6H_4B(OH)_2$	N-(4-Chlorophenyl)imidazole	18 h	82
7.	Imidazole	$4-F–C_6H_4B(OH)_2$	N-(4-Fluorophenyl)imidazole	18 h	83
8.	Imidazole	$3-NO_2–C_6H_4B(OH)_2$	N-(3-nitrophenyl)imidazole	18 h	79
9.	Imidazole	$4-CF_3–C_6H_4B(OH)_2$	N-(4-Trifluoromethylphenyl)imidazole	18 h	60
10.	Benzimidazole	$C_6H_5–B(OH)_2$	N-phenylbenzimidazole	14 h	94
11	Benzimidazole	$4-Me–C_6H_4B(OH)_2$	N-(4-Methylphenyl)benzimidazole	16 h	91
12	Benzimidazole	$4-MeO–C_6H_4B(OH)_2$	N-(4-Methoxyphenyl)benzimidazole	16 h	90
13	Benzamide	$C_6H_5–B(OH)_2$	N-Phenylbenzamide	14 h	90
14	Sulfonamide	$C_6H_5–B(OH)_2$	N-phenylbenzenesulfonamide	14 h	38
15	Phalimide	$C_6H_5–B(OH)_2$	N-phenylphalimide	14 h	94
16	Phalimide	$4-Me–C_6H_4B(OH)_2$	N-(4-Methylphenyl)phalimide	14 h	92

[a] Reaction conditions: PS-LCu(I) catalyst (0.05 g, 0.0065 mmol), 1 mmol of arylboronic acid, 1.2 mmol of N–H heterocycle, MeOH (10 ml), 40 °C, N_2 atm.
[b] Isolated yield after column chromatography.

such as MeOH, ACN, toluene, DMF and DMSO for the amination reaction of aniline with phenylboronic acid (Table 3). MeOH is found to be the best solvent for the amination of aniline (Table 3, entry 1). On the other hand, reaction in other solvents gives low to moderate coupled product (Table 3, entries 2–5). Further experiments with different arylboronic acids are carried out under these optimized conditions [24] and results are summarized in Table 4. It is clear from Table 4 that amination proceeds very effectively and affords the corresponding products in good to excellent yields under our reaction conditions. No spectacular electronic effects are observed in the amination of aniline; only a slight decrease in the reaction rate is noted with the 3-nitrophenylboronic acid. Benzyl amine gives 85% yield of the desired product when reacted with phenylboronic acid.

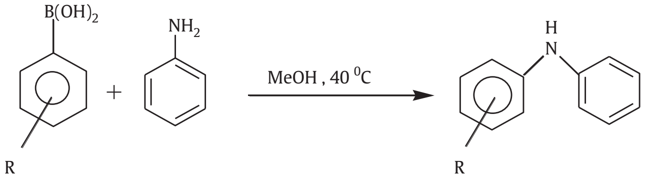
Table 3
Effect of solvent on the amination reaction of aniline with phenylboronic acids[a].

Entry	Solvent	Temperature	Time (h)	Yield[b] (%)
1.	MeOH	40 °C	14	90
2.	ACN	40 °C	14	76
3.	DMSO	130 °C	16	81
4.	DMF	140 °C	20	77
5.	Toluene	90 °C	16	64

[a] Reaction conditions: PS-LCu(I) catalyst (0.05 g, 0.0065 mmol), 1.5 mmol of phenylboronic acid, 1.2 mmol of aniline, solvent (10 ml), 140 °C, N_2 atm.
[b] Yield determined by GC and GCMS analysis.

After achieving excellent results with arylboronic acids, we further applied this catalytic system for the amination reaction of aromatic amines with aryl halides. To optimize the conditions for the amination reaction, we have chosen the reaction between iodobenzene and aniline as a model reaction and various solvents and bases were screened. The results are shown in Table 5. The amount of copper catalyst (0.05 g) was the same for all experiments and was not further optimized. The solvents also play an important role in the amination reaction and best results were obtained with toluene as a solvent

Table 4
Amination reaction of aniline with various arylboronic acids[a].



R= H, Me, OMe, Cl, NO_2.

Entry	Arylboronic acids	Aryl amines	Products	Time (h)	Isolated yield[b] (%)
1.	$C_6H_5–B(OH)_2$	$C_6H_5NH_2$	N-(Phenyl)aniline	14	90
2.	$4-Me–C_6H_4B(OH)_2$	$C_6H_5NH_2$	N-(4-Methylphenyl)aniline	15	94
3.	$4-MeO–C_6H_4B(OH)_2$	$C_6H_5NH_2$	N-(4-Methoxyphenyl)aniline	15	91
4.	$4-Cl–C_6H_4B(OH)_2$	$C_6H_5NH_2$	N-(4-Chlorophenyl)aniline	16	70
5.	$3-NO_2–C_6H_4B(OH)_2$	$C_6H_5NH_2$	N-(3-nitrophenyl) aniline	20	65
6.	$C_6H_5–B(OH)_2$	$C_6H_5CH_2NH_2$	N-Phenylbenzylamine	17	85

[a] Reaction conditions: PS-LCu(I) catalyst (0.05 g, 0.0065 mmol), 1.5 mmol of arylboronic acid, 1.2 mmol of aniline, MeOH (10 ml), 40 °C, N_2 atm.
[b] Isolated yield after column chromatography.

Table 5
Effect of solvent, base, temperature, reaction time on the amination reaction of aniline with iodobenzene[a].

Entry	Base	Solvent	Temperature	Time (h)	Yield[b](%)
1.	KOt-Bu	Toluene	120 °C	12	95
2.	KOt-Bu	1, 4 dioxane	80 °C	14	89
3.	KOt-Bu	ACN	40 °C	12	90
4.	KOt-Bu	DMSO	130 °C	16	71
5.	KOt-Bu	DMF	120 °C	12	65
6.	KOt-Bu	NMP	140 °C	14	79
7.	KOH	Toluene	120 °C	12	65
8.	NaOMe	Toluene	120 °C	12	51
9.	K_3PO_4	Toluene	120 °C	14	75
10.	K_2CO_3	Toluene	120 °C	14	72
11.	Cs_2CO_3	Toluene	120 °C	16	69

[a] Reaction conditions: PS-LCu(I) catalyst (0.05 g, 0.0065 mmol), 2 mmol of iodobenzene, 1 mmol of aniline, 1 mmol base, solvent (10 ml), N_2 atm.

[b] Yield determined by GC and GCMS analysis.

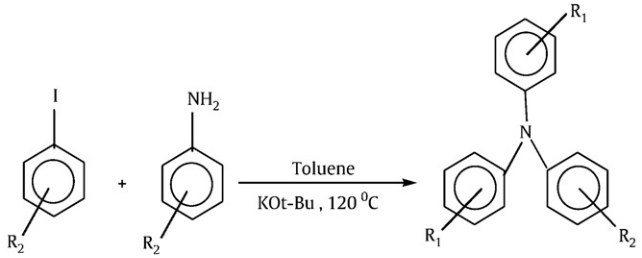
(Table 5, entry 1). Low yields of triphenylamine (TPA) were obtained with polar solvents like DMF and THF (Table 5, entries 2–3). Moderate to good yields were obtained for the solvents like 1,4-dioxane and acetonitrile (Table 5, entries 4–5). Very poor yields were obtained using polar solvent like NMP (Table 5, entry 6). The influence of bases on the yields of TPA in the presence of copper catalyst was investigated to find that potassium tertiary butoxide (KOt-Bu) was the most effective base (Table 5, entry 1). With KOH and NaOMe as a base very poor activity was obtained (Table 5, entries 7–8). Using milder bases such as K_3PO_4, K_2CO_3, and Cs_2CO_3 significantly resulted in lower yields (Table 5, entries 9–11). This reaction using polymer supported Cu(I) catalyst was also performed at higher temperature (120 °C) and higher reaction time (12 h). From the above discussions, it can be seen that the best yield was obtained in the amination reaction of aniline with iodobenzene by using KOt-Bu in toluene solvent at 120 °C for 12 h. The scope of this methodology was further extended for coupling of primary amines with aryl iodides under this experimental condition [25] (Table 6, entries 1–6). Substrates with varying degrees of substitution on both the reagents were examined and were found to provide triarylamines in good to excellent yields. Usually, primary amines give a mixture of secondary and tertiary amines, however, in the present case the coupling of aniline with iodobenzene gave triphenylamine selectively in 94% yield (entry 1). A variety of functional groups including methyl, methoxy and bromo were well tolerated.

Table 7 provides a comparison of the results obtained for our present catalytic system with those reported in the literature. From Table 7, it is seen that present catalyst exhibited higher conversions and yields compared to the other reported system [11,21,26].

To determine whether the catalyst is actually functioning in a heterogeneous manner, a hot-filtration test was performed in the *N*-arylation reaction of imidazole with phenylboronic acid, the solid catalyst was filtered out after the reaction proceeded for 4 h and the determined yield was 72%. The liquid phase of the reaction mixture is collected at the reaction temperature. Atomic absorption spectrometric analysis of the liquid phase of the reaction mixtures thus collected by filtration confirms that Cu is absent in the reaction mixture. The obtained filtrate was continually stirred under the reaction conditions. After 4 h the conversion was determined to still be 72%. This result indicated that the catalytic reaction was caused by the solid catalyst. Cu is also not detected in the liquid phase of the reaction mixture after the completion of the reaction. It is noteworthy that the methanol remains completely colorless on addition of copper catalyst. These results suggest that the Cu is not being leached out from the catalyst during *N*-arylation reactions.

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 imidazole with phenylboronic acid in MeOH medium, amination reaction of aniline with phenylboronic acid in DMSO medium and amination of aniline with iodobenzene in DMSO medium. After 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 amount under optimum reaction conditions and the nature and yield of the final products were comparable to that of the original one. The results for the *N*-arylation reaction of imidazole with phenylboronic acid summarized in Fig. 4, demonstrate that there was almost no change in catalytic activity even after fifth recycle. Metal content of the recycled catalyst remained almost unaltered indicating no leaching of the metal from the polymer support.

Table 6
Amination reaction of primary amines with various arylhalides[a].



R_1 = H, Me, MeO; R_2 = H, Me, MeO, Br.

Entry	Aryl halides	Aryl amines	Products	Time (h)	Isolated yield[b] (%)
1.	C_6H_5I	$C_6H_5NH_2$	N-(Phenyl)aniline	12	95
2.	4-Me–C_6H_4I	$C_6H_5NH_2$	N-(4-Methylphenyl)aniline	14	72
3.	4-MeO–C_6H_4I	$C_6H_5NH_2$	N-(4-Methoxyphenyl)aniline	14	70
4.	C_6H_5I	4-Me–$C_6H_5NH_2$	N-(4-Methylphenyl)aniline	14	65
5.	C_6H_5I	4-MeO–$C_6H_5NH_2$	N-(4-Methoxyphenyl)aniline	14	61
6.	C_6H_5I	4-Br$C_6H_5NH_2$	N-(4-Methoxyphenyl)aniline	16	57
7.	4-Me–C_6H_4I	4-Me–$C_6H_5NH_2$	N-(4,4-Methylphenyl)aniline	12	76
8.	4-MeO–C_6H_4I	4-MeO–$C_6H_5NH_2$	N-(4,4-Methoxyphenyl)aniline	12	75
9.	2-Me–C_6H_4I	$C_6H_5NH_2$	N-(2-Methylphenyl)aniline	16	62

[a] Reaction conditions: PS-LCu(I) catalyst (0.05 g, 0.0065 mmol), 2 mmol of aryl halide, 1 mmol of aromatic amine, 1 mmol KOt-Bu, Toluene (10 ml), 120 °C, N_2 atm.

[b] Isolated yield after column chromatography.

Table 7
Comparison of activity of different catalysts in the *N*-arylation and amination reaction.

Reaction	Catalyst	Reaction conditions	Yield (%)	Reference
N-Arylation	PS-LCu(I)	MeOH, 40 °C, 10 h	96	This study
(imidazole + phenylboronic acid)	Cu-FAP	MeOH, 5 h, rt.	88	21
Amination (aniline+ phenylboronic acid)	PS-LCu(I)	MeOH, 40 °C, 14 h	90	This study
	Cu-FAP	MeOH, 3 h, rt.	90	21
	$Cu(OAc)_2$	DCM, Et_3N/Py, rt, 2 h	71	26
Amination (aniline+ iodobenzene)	PS-LCu(I)	Toluene, KOt-Bu, 120 °C, 12 h	95	This study
	CuI	Toluene, KOt-Bu, 2,2′-bipyridine, 115 °C, 3.5 h	95	11

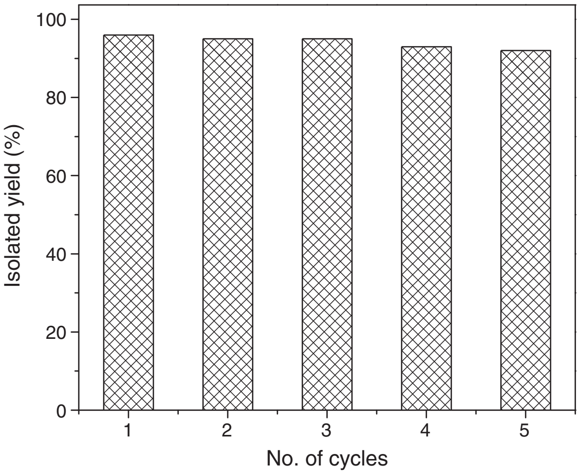


Fig. 4. Recycling activity of the PS-LCu(I) catalyst. Reaction conditions: 1 mmol of phenylboronic acid, 1.2 mmol of imidazole, MeOH (10 ml), 40 °C, 10 h, N_2 atm.

Conclusions

In conclusion, a new PS-LCu(I) catalyst have been synthesized and the structure of this catalyst was confirmed by means of elemental analysis, FTIR, SEM picture, EDAX spectra and TGA spectra. A detailed investigation of *N*-arylation reaction of N–H heterocycles with arylboronic acids and aromatic amines with aryl iodides as well as arylboronic acids were carried out using this catalyst under heterogeneous conditions. The methodology was successfully applied to a wide variety of substrates. Further work is in progress to broaden the scope of this catalytic system especially for aryl chlorides and to understand the reaction mechanism.

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[23] General procedure for N-arylation of N–H heterocycles with arylboronic acids: In a 100 mL RB flask, PS-LCu(I) catalyst (50 mg, 0.0065 mmol), aryl boronic acid (1 mmol), N–H heterocycles (1.2 mmol), and 10 ml methanol were stirred under nitrogen atmosphere, at 40 °C. The reaction mixtures were collected at different time intervals and identified by GCMS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted with ethyl acetate (3×20 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated by vacuum and the resulting residue was purified by column chromatography on silica gel to provide the desired product.
[24] General procedure for amination of aromatic amines with aryl boronic acids: In a 100 mL RB flask, PS-LCu(I) catalyst (50 mg, 0.0065 mmol), aryl boronic acid (1.5 mmol), aromatic amines (1.2 mmol) and 10 ml MeOH were stirred under nitrogen atmosphere, at 40 °C. The reaction mixtures were collected at different time intervals and identified by GCMS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted with ethyl acetate (3×20 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated by vacuum and the resulting residue was purified by column chromatography on silica gel to provide the desired product.
[25] General procedure for amination of aromatic amines with aryl halides: In a 100 mL RB flask, PS-LCu(I) catalyst (50 mg, 0.0065 mmol), aryl halide (4 mmol), aromatic amines (2 mmol), KOt-Bu (1 mmol) and 10 ml toluene were stirred under nitrogen atmosphere, at 120 °C. The reaction mixtures were collected at different time intervals and identified by GCMS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted with ethyl acetate (3×20 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated by vacuum and the resulting residue was purified by column chromatography on silica gel to provide the desired product.
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