

Silica immobilized copper complexes: Efficient and reusable catalysts for *N*-arylation of N(H)-heterocycles and benzyl amines with aryl halides and arylboronic acids[☆]

Pravin R. Likhar^{a,*}, Sarabindu Roy^a, Moumita Roy^a, M. Lakshmi Kantam^a, Rajib Lal De^b

^a *Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India*

^b *Department of Chemistry, Jadavpur University, Kolkata 700032, India*

Received 22 December 2006; received in revised form 20 February 2007; accepted 21 February 2007

Available online 25 February 2007

Abstract

Silica tethered copper complexes are effectively used as reusable catalysts in the *N*-arylation of N(H)-heterocycles and benzyl amines with aryl halides and arylboronic acids. *N*-Arylated products were isolated in good to excellent yields, demonstrating the versatility of the protocol. Moreover the Cat2 was easily recovered by simple filtration and reused for several cycles with consistent activity.

© 2007 Published by Elsevier B.V.

Keywords: Silica; Copper; *N*-Arylation; Heterogeneous catalyst

1. Introduction

N-Arylheterocycles and benzyl amines are common motifs in pharmaceutical research [1]. Usually these compounds were synthesized via S_NAr substitution with aryl halides bearing electron-withdrawing substituent or via the Ullmann type coupling at high temperatures [2]. After the initial reports of Chan and Lam, the Cu-catalyzed cross coupling between *N*-heterocycles and arylboronic acids has become an important synthetic methodology in modern organic synthesis [3]. Later the discovery and development of the catalytic path for *N*-arylation of heterocycles by Buchwald with bromo- and iodoarenes using copper in the presence of basic ligands generated greater interest in industry. Initially Buchwald used 1,10-phenanthroline as ligand and subsequently shown that 1,2-diamines were better ligand to promote this *N*-arylation [4]. Afterwards Taillefer et al. reported oxime type and Schiff base ligands [5] and Ma et al. reported α - and β -amino acids as ligands for effective *N*-arylation of *N*-heterocycles with aryl halides [6]. 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 contamination with metal.

In this direction, we have already reported reusable copper catalysts such as Cu-exchanged fluoroapatite, [7] Cu-exchanged Y-zeolite [8] and cellulose supported Cu(0) [9], Son et al. reported [10] nano Cu₂O coated Cu particle catalyst for *N*-arylation of N(H)-heterocycles with aryl halides and arylboronic acids and Lipshutz et al. reported [11] Ni/charcoal catalyzed aromatic amination reactions.

Silica modified with different functionalities such as $-NH_2$, $-SH$, diamines, amino acids etc. is reported to be a good support for various metals like Pd, Cu, Sc, Ru, Pt, V, etc. in different organic transformations [12]. But to our knowledge there is no report with silica supported copper catalyzed *N*-arylation reactions. Herein we wish to report the *N*-arylation of N(H)-heterocycles and benzyl amines with aryl halides and arylboronic acids using silica immobilized copper complexes.

2. Experimental

2.1. Materials and methods

IR spectra were recorded on BIORAD 175C FTIR spectrometer for samples as KBr pellets. ¹H NMR spectra were recorded on a Varian Gemini 200 MHz and Avance 300 MHz

[☆] IICT Communication No. 070212.

* Corresponding author. Tel.: +91 40 27160921; fax: +91 40 27160921.

E-mail address: plikhar@iict.res.in (P.R. Likhar).

spectrometers. Chemical shifts (δ) are reported in ppm, using TMS as internal standard for ^1H NMR. SEM–EDX (scanning electron microscopy–energy dispersive X-ray analysis) was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. X-ray photoemission spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg $K\alpha$ anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species were first determined by using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible within ± 0.1 eV. ACME silica gel (100–200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F₂₅₄ plates. ICP-AES analyses were performed on IRIS Intrepid II XDL ICP-AES (Thermo Electron Corporation). 3-Aminopropyl functionalized silica gel (AFS), iodoarenes, and bromoarenes were purchased from Aldrich. All other chemicals were procured from commercial sources and used as such without further purification.

2.2. Preparation of silica immobilized copper complexes

3-Aminopropyl functionalized silica gel (AFS, 9% functionalization) was derivatized (to imine) with carbonyl compounds according to a reported procedure [12b]. In a typical experiment, AFS (1 g) and salisaldehyde (2 mmol) were taken in a 100 mL round bottom flask fitted with a reflux condenser and 50 mL absolute ethanol was added and refluxed for 18 h. Then it was filtered and washed with copious amount of ethanol followed by water and finally with acetone. Then the imine-modified silica gel was dried in an oven at 60 °C. Then the imine modified silica gel (1 g) was stirred with a solution of $\text{Cu}(\text{OAc})_2$ (1 mmol) in acetone (25 mL) for 24 h to get the silica immobilized copper catalyst (Cat4; Cu: 0.41 mmol/g).

Similarly AFS modified imine silica gel derived from 2-pyridine carboxaldehyde, 2-thiophene carboxaldehyde, and 2-bipyridyl ketone were prepared and then subsequently complexed with $\text{Cu}(\text{OAc})_2$ to afford the final silica immobilized copper catalysts Cat2, Cat3, Cat5, respectively.

2.3. N-Arylation of amines with aryl halides

In an oven dried 10 mL round-bottom flask, catalyst (5 mol% with respect to aryl halide), aryl halide (1 mmol), amine (1.2 mmol), Cs_2CO_3 (2 mmol), toluene (3 mL) were stirred under nitrogen atmosphere at 100 °C and the reaction was monitored by TLC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried at 60 °C in oven. The filtrate was diluted with ethyl acetate and washed with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and con-

centrated to get the crude product. The crude product was column chromatographed using hexane: ethyl acetate (7:3) as eluent. All the products were characterized by using NMR and mass spectroscopy and compared with the literature data [4,5,7].

2.4. N-Arylation of amines with arylboronic acids

In an oven dried 10 mL round-bottom flask, amine (1 mmol), arylboronic acid (1.2 mmol), catalyst (2 mol%) and methanol (2 mL) were taken and stirred at 60 °C under air. After the completion of the reaction as monitored by TLC, the catalyst was filtered off. The filtrate was diluted with ethyl acetate and washed with 10% NaOH solution followed by saturated aqueous NaCl solution. The organic layer was dried with Na_2SO_4 and concentrated to get the crude product. The crude product was column chromatographed using hexane:ethyl acetate (7:3) as eluent. All the products were characterized by using NMR and mass spectroscopy and compared with the literature data [4,5,7].

Spectroscopic data of some of the representative products:

1-Phenyl-1*H*-imidazole (Table 5, entry 1) ^1H NMR (300 MHz, CDCl_3): δ 7.83 (s, 1H), 7.50–7.30 (m, 5H), 7.25 (bs, 1H), 7.18 (bs, 1H); EI-MS: 144 (M^+), 142, 92 and 57.

1-[4-(1*H*-Imidazol-1-yl)phenyl]-1*H*-imidazole (Table 5, entry 8) ^1H NMR (300 MHz, CDCl_3): δ 8.01 (br s, 2H), 7.63 (s, 4H), 7.42 (br s, 2H), 7.17 (br s, 2H); EI-MS: 210 (M^+), 209, 182, 156, 141, 129, 116, 89, 76, 63 and 41.

1-(4-Methoxyphenyl)-1*H*-benzimidazole (Table 5, entry 10) ^1H NMR (300 MHz, CDCl_3): δ 8.06 (br s, 1H), 7.82 (bs, 1H), 7.45–7.31 (m, 3H), 7.30–7.33 (m, 2H), 7.06 (d, 2H, $J=9.0$ Hz), 3.88 (s, 3H); EI-MS: 224 (M^+), 209, 182, 77 and 63.

N-Phenylbenzylamine (Table 5, entry 13) ^1H NMR (300 MHz, CDCl_3): δ 7.38–7.29 (m, 3H), 7.28–7.18 (m, 2H), 7.15–7.06 (m, 2H), 6.65 (t, 1H, $J=7.55$ Hz), 6.57 (d, 2H, $J=8.03$ Hz), 4.30 (s, 2H), 3.93 (br s, 1H); EI-MS: 183 (M^+), 155, 141, 91, 77, 55 and 43.

(4-Methoxy-benzyl)-phenylamine (Table 5, entry 15) ^1H NMR (300 MHz, CDCl_3): δ 7.17 (d, 2H, $J=9.065$ Hz), 7.03 (t, 2H, $J=7.55$ Hz), 6.74 (d, 2H, $J=8.3$ Hz), 6.56 (t, 1H, $J=7.55$ Hz), 6.48 (d, 2H, $J=8.3$ Hz), 4.14 (s, 2H), 3.70 (s, 3H); EI-MS: 213 (M^+), 121, 77 and 53.

1-(2-Methylphenyl)-1*H*-benzimidazole (Table 6, entry 10) ^1H NMR (300 MHz, CDCl_3): δ 7.91 (br s, 1H), 7.82 (m, 1H), 7.37–7.33 (m, 2H), 7.32–7.16 (m, 4H), 7.10–7.13 (m, 1H), 2.02 (s, 3H); EI-MS: 208 (M^+), 207, 180, 155, 142, 104, 65 and 51.

3. Results and discussion

3.1. Preparation of silica tethered copper catalysts

3-Aminopropyl functionalized silica and imine modified silica supported copper catalysts were prepared by stirring the appropriate silica support with an acetone solution of the $\text{Cu}(\text{OAc})_2$ at room temperature and the tentative structure [12d] of the catalysts are shown in Scheme 1.

Table 1
Characterization of silica supported copper catalysts

Entry	Catalyst	Stretching frequency of C=N (cm ⁻¹) before complexation	Change in C=N bands (cm ⁻¹) after complexation	Loading of Cu (mmol/g)
1	Cat1	–	–	0.38
2	Cat2	1640	1631	0.43
3	Cat3	1641	1338	0.41
4	Cat4	1645	1631	0.41
5	Cat5	1643	Almost no shift	0.39

3.2. Characterization of the silica immobilized copper catalysts

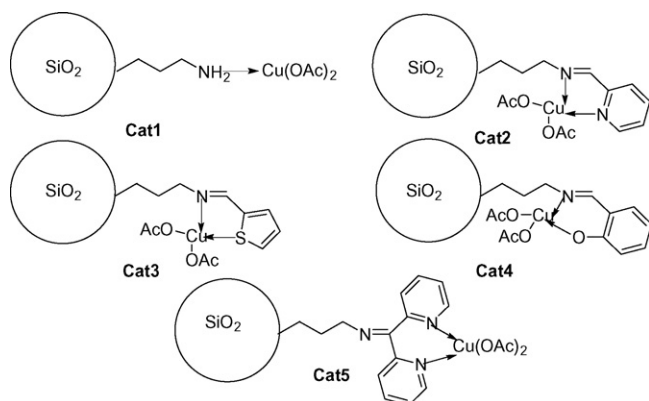
All the prepared catalysts were fully characterized by using FTIR, ICP-AES, XPS and EDAX.

The FTIR of chemically modified silica (imine) shows peak due to C=N around 1640 cm⁻¹, which on complexation with copper shifts to lower value [12b]. The lowering in frequencies of the C=N peak is indicative of the formation of metal–ligand bond. The difference in the values of C=N stretching band before and after complexation for all the catalysts is shown in Table 1.

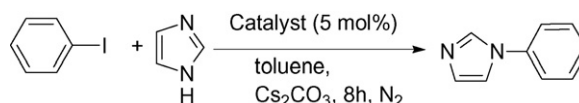
XPS analysis of the catalysts shows that in the entire catalysts, two intense peaks appear at 933–934.6 eV and 952–954 eV. The peaks are attributable to Cu 2p_{3/2} and Cu 2p_{1/2} levels of Cu^{0-δ+} species, which may be due to the formation of the mono/bi/multidentate copper complexes with nitrogen ligands [12f,d]. But for the sake of simplicity, we have shown the structure of the catalysts as mono (amine) and bidentate (imine) in Scheme 1. The copper content of the catalysts was estimated by using ICP-AES and the results are shown in Table 1.

3.3. Catalytic activity of silica immobilized copper catalysts in *N*-arylation using aryl halides

To find the best catalyst for the *N*-arylation reaction, all the catalysts (5 mol% Cu) were screened in the reaction of iodobenzene with imidazole in toluene using Cs₂CO₃ at 100 °C under nitrogen atmosphere (Scheme 2) and the results are summarized in Table 2. From Table 2 it can be seen that the catalysts derived from pyridine-2-carboxaldehyde (Cat2) and 2-bipyridyl ketone (Cat5) were equally good, Cat3 showed moderate activi-



Scheme 1. Structure of silica tethered copper catalysts.



Scheme 2.

Table 2
Screening of different copper catalysts for *N*-arylation of imidazole with iodobenzene^a

Entry	Catalyst	Yield (%)	Leaching of Cu (%) ^b
1	Cat1	23	25
2	Cat2	92	2.5
3	Cat3	69	7
4	Cat4	31	9
5	Cat5	91	6.5
6	Cu(OAc) ₂	3	–

^a Reaction conditions: iodobenzene (1 mmol), imidazole (1.2 mmol), Cs₂CO₃ (2 mmol), toluene (3 mL), catalyst (5 mol%), 100 °C, N₂ atmosphere. GC yields.

^b Determined by ICP-AES and expressed as percentage of the total copper charged.

ties whereas Cat1 and Cat4 gave poor yield. Most interestingly, it was observed that with neat Cu(OAc)₂ there was no reaction (Table 2, entry 6). Cat2 showed negligible leaching of Cu after the reaction when compared with other catalyst. So we have chosen Cat2 for rest of the studies.

Similarly several bases were screened using Cat2 for the *N*-arylation of imidazole with iodobenzene in toluene solvent at 100 °C and the results are summarized in Table 3. It was observed that Cs₂CO₃ gave the best result (Table 3, entry 2). K₃PO₄ was also found to be fairly active. But the organic bases like Et₃N and Bu₃N were almost inactive. 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

Table 3
Screening of bases for *N*-arylation of imidazole with iodobenzene^a

Entry	Base	Yield (%)
1	K ₂ CO ₃	78
2	Cs ₂ CO ₃	92
3	K ₃ PO ₄	89
4	NaOAc	23
5	Et ₃ N	15
6	Bu ₃ N	18

^a Reaction conditions: iodobenzene (1 mmol), imidazole (1.2 mmol), base (2 mmol), toluene (3 mL), Cat2 (5 mol%), 100 °C, N₂ atmosphere, 8 h. GC yields.

Table 4
Screening of different solvents in *N*-arylation of imidazole using Cat2^a

Entry	Solvent	Yield (%)	Leaching of Cu (%) ^b
1	Toluene	92	2.5
2	Xylene	90	2.4
3	DMF	78	9
4	NMP	67	13
5	THF	N. R.	n. d.
6	CH ₃ CN	53	7
7	DME	10	n. d.

^a Reaction conditions: iodobenzene (1 mmol), imidazole (1.2 mmol), Cs₂CO₃ (2 mmol), solvent (3 mL), Cat2 (5 mol%), 100 °C, N₂ atmosphere, 8 h. GC yields.

^b Determined by ICP-AES and expressed as percentage of the total copper charged.

observed that though the polar solvents like DMF, NMP and acetonitrile were effective but high amounts of leaching were observed after the reaction. THF and dimethoxyethane (DME) were less effective. Only toluene and xylene were found to be effective with negligible amount of Cu leaching. As toluene has lower boiling point it was used as a solvent for the rest of the studies due to easy work up procedure.

To explore the scope and limitations of the current catalyst (Cat2), several haloarenes were used for the arylation of the imidazole under the optimized conditions (Scheme 3) and the results are summarized in Table 5. It was observed that iodoarenes with electron-withdrawing group (Table 5, entries 4 and 5) reacted at a faster rate than iodoarenes with electron donating group (Table 5, entries 2 and 3). Sterically hindered 2-iodotoluene took longer duration to give a good yield (Table 5, entry 6). When

Table 5
N-Arylation of N(H)-heterocycles and benzyl amines with aryl halides using Cat2^a

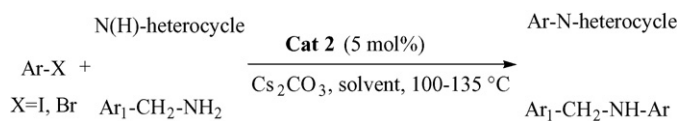
Entry	Aryl halide	N(H)-heterocycle/amine	Time (h)	Yield (%)
1	C ₆ H ₅ -I	Imidazole	8	89, 72 ^b
2	4-Me-C ₆ H ₄ -I	Imidazole	14	90
3	4-MeO-C ₆ H ₄ -I	Imidazole	16 (24) ^c	94 (96) ^c
4	44-MeCO-C ₆ H ₄ -I	Imidazole	4	92
5	4-NO ₂ -C ₆ H ₄ -I	Imidazole	3	90
6	2-Me-C ₆ H ₄ -I	Imidazole	24	79
7	4-Cl-C ₆ H ₄ -I	Imidazole	10	90
8 ^d	4-I-C ₆ H ₄ -I	Imidazole	16	85
9	C ₆ H ₅ -I	Benzimidazole	14	88
10	4-MeO-C ₆ H ₄ -I	Benzimidazole	24	82
11	C ₆ H ₅ -I	Pyrazole	12	90
12	C ₆ H ₅ -I	Pyrrole	10	82
13	C ₆ H ₅ -I	Benzyl amine	12	90
14	C ₆ H ₅ -I	4-Methyl benzyl amine	10	94
15	C ₆ H ₅ -I	4-Methoxy benzyl amine	10	94
16	C ₆ H ₅ -I	Dibenzyl amine	16	N. R.
17	4-MeO-C ₆ H ₄ -I	Benzyl amine	18	72
18	C ₆ H ₅ -Br	Imidazole	24	78
19	4-MeCO-C ₆ H ₄ -Br	Imidazole	18	90
20	4-NO ₂ -C ₆ H ₄ -Br	Imidazole	12	90
21	4-Me-C ₆ H ₄ -Br	Imidazole	24	20

^a Reaction conditions: aryl halide (1 mmol), amine (1.2 mmol), Cat2 (5 mol%), Cs₂CO₃ (2 mmol), toluene or xylene (2 mL), 100 or 135 °C, N₂ atmosphere, isolated yield.

^b Cat2 (2 mol%), reaction time 24 h.

^c (CuOTf)₂·PhH (10 mol% Cu), dba (5 mol%), 1,10-phenanthroline 100 mol%, 110 °C, cited from Ref. [4a].

^d 3 mmol imidazole used.



Scheme 3.

we decreased amount of catalyst from 5 mol% to 2 mol%, it gave good yield only after 24 h (Table 5, entry 1). When we compared our catalytic protocol with Buchwalds' CuOTf-1,10-phenanthroline system [4a] for *N*-arylation of imidazole with 4-iodoanisole almost similar yields were observed (Table 5, entry 3). To expand the scope of the catalyst, a variety of other nitrogen containing heterocycles such as benzimidazole, pyrrole, and pyrazole were successfully coupled with iodoarenes to give the corresponding *N*-arylated products in good yields. Next benzyl amine was reacted with iodobenzene and good yield was obtained after 14 h. Benzyl amine with electron donating moieties found to be more active than simple benzyl amine (Table 5, entries 13–15). When dibenzyl amine was employed in the reaction, no product formation was observed (Table 5, entry 16). This may be due to the steric hindrance of the benzyl amine. Bromoarenes were found to be unreactive but an increase in temperature from 100 to 135 °C and a change in solvent from toluene to xylene gave excellent yield of product for bromoarenes with electron-withdrawing group (Table 5, entries 19 and 20). Bromobenzene gave a satisfactory yield after 24 h (Table 5, entry 18) whereas bromoarenes with electron-donating group gave moderate yield (Table 5, entry 21). This is in agreement with the findings of earlier researchers who noticed that unactivated aryl halides work better than activated aryl halides in

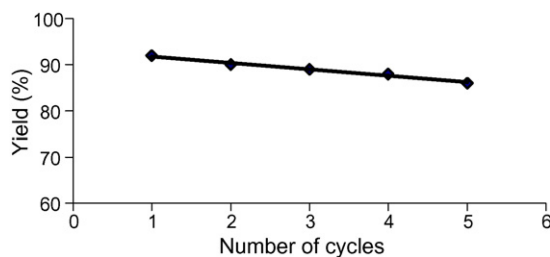


Fig. 1. Reusability study of Cat2 in *N*-arylation of imidazole with iodobenzene.

N-arylation reaction [5a,7a,b]. When chlorobenzene was reacted with imidazole almost no product formation was observed.

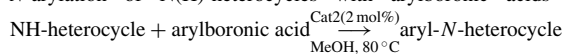
For any heterogeneous system, it is important to know its ease of separation and possible reuse. The catalyst (Cat2) can easily be separated by filtration. The recovered catalyst after washing with acetone followed by drying at 60 °C was used in the next run and minimal decrease in activity was observed (1st cycle: 92%; 5th cycle: 86%) (Fig. 1). This decrease in activity may be due to the leaching or deactivation of the metal center. Next to see whether the reaction was occurring mainly due to the leached metal or supported catalyst, a reaction between imidazole and iodobenzene was terminated after a small conversion (45 min, 18% conversion) and the catalyst was filtered off by hot filtration and the reaction was continued with the filtrate for 10 h. Almost no change in the conversion of iodobenzene was observed. These studies and the non-activity of Cu(OAc)₂ in *N*-arylation of imidazole clearly proves that the reaction occurred heterogeneously. Lipshutz et al. also reported that significant amount of supported metal can be dissolved during the reaction and would redeposit quickly on the solid during the filtration as a result of unavoidable minor temperature difference during the filtration. It may be assumed in this case also, during filtration the solid matrix (silica) may trap the copper species leached from the catalyst during the reaction.

3.4. Catalytic activity of silica tethered copper catalysts in *N*-arylation using arylboronic acids

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. To check the generality and scope of the Cat2, we tried the *N*-arylation of imidazole with phenylboronic acids in methanol using 2 mol% catalyst. It took almost 40 h to complete the reaction at room temperature whereas at 80 °C it gave almost 98% yields within 2 h and 1.7% leaching of copper was observed. Several boronic acids were reacted with imidazole using Cat2 and the results are summarized in Table 6. It was observed that boronic acids with electron-withdrawing group took longer time compared to boronic acids with electro-donating group. Further it was observed that benzimidazole was reacted sluggishly than imidazole. The catalyst was used for five cycles with consistent activity (Table 6, entry 2).

Table 6

N-arylation of N(H)-heterocycles with arylboronic acids using Cat2^a



Entry	NH-heterocycle	Arylboronic acid	Time (h)	Yield (%)
1	Imidazole	C ₆ H ₅ -B(OH) ₂	40	92 ^b
2	Imidazole	C ₆ H ₅ -B(OH) ₂	2	91, 88 ^c
3	Imidazole	4-Me-C ₆ H ₄ -B(OH) ₂	1	90
4	Imidazole	2-Me-C ₆ H ₄ -B(OH) ₂	1.5	88
5	Imidazole	4-F-C ₆ H ₄ -B(OH) ₂	2.5	90
6	Imidazole	3-NO ₂ -C ₆ H ₄ -B(OH) ₂	5	92
7	Imidazole	4-MeO-C ₆ H ₄ -B(OH) ₂	1	93
8	Benzimidazole	C ₆ H ₅ -B(OH) ₂	2.5	90
9	Benzimidazole	4-Me-C ₆ H ₄ -B(OH) ₂	2	94
10	Benzimidazole	2-Me-C ₆ H ₄ -B(OH) ₂	3	90

^a Reaction conditions: N(H)-heterocycle (1 mmol), arylboronic acid (1.2 mmol), Cat2 (2 mol%), MeOH (2 mL), 80 °C, air.

^b Room temperature.

^c Yields after fifth cycle.

4. Conclusion

In conclusion, we have prepared a silica tethered copper catalyst for effective *N*-arylation of N(H)-heterocycles and benzyl amines with aryl halides as well as arylboronic acids. Moreover the catalyst can easily be separated by simple filtration and reused for several cycles with consistent activities.

Acknowledgements

S. R. thanks CSIR and M. R. thanks UGC for providing fellowship.

References

- [1] P. Cozzi, G. Carganico, D. Fusar, M. Grossoni, M. Menichincheri, V. Pinciroli, R. Tonani, F. Vaghi, P. Salvati, J. Med. Chem. 36 (1993) 2964.
- [2] (a) M.C. Venuti, R.A. Stephenson, R. Alvarez, J.J. Bruno, A.M. Strosberg, J. Med. Chem. 31 (1988) 2136;
(b) R. Bambal, R.B. Haznlik, J. Org. Chem. 59 (1994) 729;
(c) C. Jacobs, M. Frotscher, G. Dannhardt, R.W. Hartmann, J. Med. Chem. 43 (2000) 1841.
- [3] (a) P.Y.S. Lam, C.G. Clark, S. Saubern, J. Adams, M.P. Winters, D.M.T. Chan, A. Combs, Tetrahedron Lett. 39 (1998) 2941;
(b) A.P. Combs, S. Saubern, M. Rafalski, P.Y.S. Lam, Tetrahedron Lett. 40 (1999) 1623;
(c) P.Y.S. Lam, G. Vincent, C.G. Clark, S. Deudon, P.K. Jadhav, Tetrahedron Lett. 42 (2001) 3415;
(d) J.P. Collman, M. Zhong, C. Zhang, S. Costanzo, J. Org. Chem. 66 (2001) 7892.
- [4] (a) A. Kiyomori, J.F. Marcoux, S.L. Buchwald, Tetrahedron Lett. 40 (1999) 2657;
(b) A. Klapars, J.C. Antilla, X. Huang, S.L. Buchwald, J. Am. Chem. Soc. 123 (2001) 7727;
(c) J.C. Antilla, A. Klapars, S.L. Buchwald, J. Am. Chem. Soc. 124 (2002) 11684;
(d) J.C. Antilla, J.M. Baskin, T.E. Barder, S.L. Buchwald, J. Org. Chem. 69 (2004) 5578.
- [5] (a) H.J. Cristau, P.P. Cellier, J.F. Spindler, M. Taillefer, Eur. J. Org. Chem. (2004) 695;
(b) H.J. Cristau, P.P. Cellier, J.F. Spindler, M. Taillefer, Chem. Eur. J. 10 (2004) 5607.

- [6] (a) Q. Cai, W. Zhu, H. Zhang, Y. Zhang, D. Ma, *Synthesis* (2005) 496;
(b) D. Ma, Q. Cai, *Synlett* (2004) 128.
- [7] (a) B.M. Choudary, C. Sridhar, M.L. Kantam, G.T. Venkanna, B. Sreedhar, *J. Am. Chem. Soc.* 127 (2005) 9948;
(b) M.L. Kantam, G.T. Venkanna, C. Sridhar, K.B.S. Kumar, *Tetrahedron Lett.* 47 (2006) 3897;
(c) M.L. Kantam, G.T. Venkanna, C. Sridhar, B. Sreedhar, B.M. Choudary, *J. Org. Chem.* 71 (2006) 9522.
- [8] M.L. Kantam, B.P.C. Rao, B.M. Choudary, R.S. Reddy, *Synlett* (2006) 2195.
- [9] K.R. Reddy, N.S. Kumar, B. Sreedhar, M.L. Kantam, *J. Mol. Catal. A: Chem.* 252 (2006) 136.
- [10] S.U. Son, I.K. Park, J. Park, T. Hyeon, *Chem. Commun.* (2004) 778.
- [11] B.H. Lipshutz, S. Tasler, *J. Org. Chem.* 68 (2003) 1190.
- [12] (a) R.B. Bedford, U.G. Singh, R.I. Walton, R.T. Williams, S.A. Davis, *Chem. Mater.* 17 (2005) 701;
(b) S. Paul, J.H. Clark, *J. Mol. Catal. A: Chem.* 215 (2004) 107;
(c) J. Horniakova, T. Raja, Y. Kubota, Y. Sugi, *J. Mol. Catal. A: Chem.* 217 (2004) 73;
(d) C.W. Jones, M.W. McKittrick, J.V. Nguyen, K. Yu, *Top. Catal.* 34 (2005) 67;
(e) B. Karimi, L. Ma'Mani, *Org. Lett.* 6 (2004) 4813;
(f) W. Cao, H. Zhang, Y. Yuan, *Catal. Lett.* 91 (2003) 243;
(g) J. Horniakova, H. Nakamura, R. Kawase, K. Komura, Y. Kubota, Y. Sugi, *J. Mol. Catal. A: Chem.* 233 (2005) 49;
(h) M. Al-Hashimi, E. Fisset, A.C. Sullivan, J.R.H. Wilson, *Tetrahedron Lett.* 47 (2006) 8017.