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Copper(II) incorporated functionalized polystyrene catalyzed N-arylation of amides under solvent free condition with broad substrate scope

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Abstract

We demonstrate here, a new polystyrene supported Cu(II) catalyzed proficient synthetic methodology for the facile N-arylation of aromatic, aliphatic, cyclic and heterocyclic amides with aryl halides under neat condition. The catalyst, PS-Cu(II)-ala, was prepared through the grafting of copper metal on polystyrene-β-alanine imine network. The catalyst shows wide range of substrate scope, excellent functional group tolerance, and produces the desired anilides in mostly high yields. The material is thoroughly characterized by DRS-UV, FT-IR, AAS, FE-SEM, TGA analysis and energy dispersive X-ray (EDX). The catalyst can be easily recovered from the reaction medium and reused without significant loss of its catalytic activity suggesting future potential of this catalyst.

Keywords: Polymer supported Cu(II) catalyst, One-pot synthesis, Cross coupling, C-N bond formation, Neat condition.

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1 Introduction

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The transition metal catalyzed cross-coupling of amides and aryl halides is one of the most proficient and powerful method for the synthesis of N-aryl amides, as it plays a significant role in the synthesis of several biologically, medicinally and materially potent molecules.¹ Arguably, aryl amides are one of the most important part in the synthesis of natural as well as synthetic products.² In particular, N-arylation involving heterocyclic entities generate highly significant biologically active molecules and drugs³ as outlined in Figure 1.



Figure 1. Potent molecules bearing amide skeleton.

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As a result, amide skeleton synthesis has become one of the most challenging topics towards the synthetic organic chemists. More than a century ago, after the pioneer work performed by Goldberg,⁴ metal catalyzed C-N cross-coupling has obtained a significant attention. However, the traditional methodologies, involving harsh reaction condition, longer reaction time and low functional group tolerance, require to be developed further. Notably, a lot of alternative methods for the synthesis of amide bond have been developed. Most of these reaction pathways are catalyzed by a variety of transition metal catalysts like Fe,⁵ Co,⁶ Ni,⁷ and Pd⁸ etc. But easy availability, cheap and environmentally benign nature of copper metal have attracted our concentration to it. However, a number of copper catalyzed cross-coupling of amides with aryl halides are reported in literature.⁹ But, homogeneous nature of the catalyst, lack of recyclability, possibility of metal contamination in end product, utilization of additives, use of hazardous solvents and obviously use of expensive ligand system etc. insist to develop a greener alternative, so that, the catalyst become economically cheap and can be reused further. To avoid these drawbacks, a variety of heterogeneous catalysts were developed through immobilization of copper metal on various kind of solid supports.¹⁰ In recent times, polymer supported ligands have been developed to immobilize Cu metal onto Besides, application of hazardous solvents in the catalytic system makes the it ¹¹ methodology expensive and harmful to the nature. Our group has already explored a number



Scheme 1. Polymeric PS-Cu(II)-ala catalyzed C-N cross coupling reactions.

of heterogeneous polymer supported metal catalyst for C–N, C-O and C–C cross coupling reactions.¹² Herein, for the first time we report, polymeric β -alanine incorporated Cu(II) catalyzed C-N bond formation through the mild and efficient coupling of aromatic, aliphatic, cyclic and heterocyclic amides with aryl halides under solvent free condition (Scheme 1). This synthetic protocol may offer potential route for the progress of carbon-heteroatom bond forming reactions employing catalytic amount of PS-Cu(II)-ala.

2 Results and Discussion

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To evaluate the optimal reaction conditions, a series of reactions were performed with the variation of reaction parameters like base, solvent, temperature and the catalyst amount etc. for the representative reaction of benzamide (1a) with iodobenzene (2a). The results are summarized in Table 1.

la	NH ₂ +	PS-Cu base, ter	u(II)-ala solvent np.	A Sa	
Entry	Amount of	Solvent	Base	Temperature	Yield
	Catalyst (mg)			(°C)	(%) ^b
1	-	DMF	K ₂ CO ₃	140	-
2	15	DMF	K ₂ CO ₃	140	60
3	15	<i>p</i> -xylene	K ₂ CO ₃	120	00
4	15	H ₂ O	K ₂ CO ₃	110	00
5	15	neat	K ₂ CO ₃	120	92
6	15	CH ₃ CN	K ₂ CO ₃	70	5
7	15	NMP	K ₂ CO ₃	70	00
8	15	neat	Cs ₂ CO ₃	120	62
9	15	neat	NaHCO ₃	120	85
10	15	neat	K ₃ PO ₄	120	17
11	15	neat	KF	120	10
12	10	neat	K ₂ CO ₃	120	79
13	25	neat	K ₂ CO ₃	120	90
14	15	neat	K ₂ CO ₃	rt	-
15 ^c	1.8	neat	K ₂ CO ₃	120	67
16 ^d	-	neat	K ₂ CO ₃	120	78
17 ^e	15	neat	K ₂ CO ₃	120	00

^aReaction condition: **1a** (1.0 mmol), **2a** (1.1 mmol), base (1.0 mmol), solvent (2.5 mL), 15 h. ^bIsolated yield. ^creaction using copper(II) acetate (0.9 mol%). ^dreaction using copper(II) acetate and β -alanine (1:1). ^ereaction using polymeric ligand (**3**).

The best result in terms of yield was obtained using 15 mg (0.9 mol%) of the Cu(II) catalyst in solvent free condition for 15 h at 120 °C (Table 1, Entry 5). Various bases *viz*. K₂CO₃, Cs₂CO₃, NaHCO₃, K₃PO₄ and KF were used for this reaction. But K₂CO₃ was found the best. Though, NaHCO₃ gave comparable product yield. No product was formed at room temperature. Various solvents *viz*. DMF, *p*-xylene, H₂O, NMP, CH₃CN were used for this reaction, but no one can produce better yield. Polar, low coordinating solvents like DMF and CH₃CN gave low yields whereas water did not initiate the reaction. Water may form a boundary between the amide and catalyst which disturbs their interaction. Because the binding of the catalyst to the amide is the initial step of the reaction.^{9d} The catalyst showed best activity in neat condition at 120 °C. Low yield of the desired N-arylated product was obtained when homogeneous copper(II) acetate was used as catalyst (Table 1, Entry 15). The yield slightly increases from the previous one when the mixture of copper salt and β-alanine was used as catalytic system (Table 1, Entry 16). But the yield in the above two cases was low compared to the polymer supported copper catalyst. No product was obtained when polymeric ligand (**3**) was used (Table 1, Entry 17).

After getting the optimal condition, a series of reactions were carried out using aromatic amide with various aryl halides to explore the catalytic scope. The results are concise in Table 2. It is quite evident that, besides iodo-, bromobenzene also gives good yield (**3a** and **3b**, Table 2). However, both electron withdrawing and donating groups attached to the phenyl ring of the aryl halide partner are equally compatible for this reaction.

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^aConditions:**1** (1.0 mmol), **2** (1.1 mmol), catalyst (15 mg, 0.9 mol%), K₂CO₃ (1.0 mmol), neat, 120 °C, 15 h, under air. ^bIsolated yield. TOF given in parentheses.

Next, we investigate our synthetic protocol for the cross-coupling of the aryl halides with aliphatic amide (Table 3). Acetamide undergoes this C-N coupling reaction very smoothly with iodobenzene as well as bromobenzene resulting good yield.

Table 3 N-arylation of acetamide with aryl halides.^a



^aConditions: **4** (1.0 mmol), **2** (1.1 mmol), catalyst (15 mg, 0.9 mol%), K₂CO₃ (1.0 mmol), neat, 120 °C, 15 h, under air. ^b Isolated yield. TOF given in parentheses

Next, we have studied that cyclic amides also undergo C-N cross-coupling reaction to their corresponding products. The results are concise in Table 4. 2-oxazolidinone reacts with iodobenzene without any difficulty to give the product in 82% yield (7d, Table 4). We are pleased to state that along with six membered cyclic amide, seven and eight membered cyclic amides also go through this coupling reaction to furnish their product in good to moderate yields (7a, 7b and 7c, Table 4).

Furthermore, our catalytic system equally works proficiently for the cross-coupling of heterocyclic amides with iodobenzene (Table 5). Thiophene-2-carboxamide and Furan-2-carboxamide both go through this C-N coupling reaction effortlessly. 2-iodo pyridine reacts with Furan-2-carboxamide to gives the corresponding heterocyclic product in very good yield (**9e**, Table 5).

Table 4 N-arylation of cyclic amides with aryl halides.^a

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^aConditions: **6** (1.0 mmol), **2** (1.2 mmol), catalyst (15 mg, 0.9 mol%), K_2CO_3 (1.0 mmol), neat, 120 °C, 20 h, under air. ^b Isolated yield. TOF given in parentheses.





^a Conditions: **8** (1.0 mmol), **2** (1.1 mmol), catalyst (15 mg, 0.9 mol%), K_2CO_3 (1.0 mmol), neat, 120 °C, 16 h, under air. ^b Isolated yield. TOF given in parentheses.

The most possible reaction mechanism for this PS-Cu(II)-ala catalyzed one pot synthesis of N-arylated products follows the well recognized mechanisms reported in literature.^{9d,13}

3 Experimental

3.1. Chemicals: Chloromethylated polystyrene (5.5 mmol Cl/gm of resin) was purchased from Sigma-Aldrich. All other chemicals used for these investigation purposes were purchased from commercial sources and were used without purification. Before use, all solvents were distilled and dried following the standard process.

3.2. Synthetic pathway of the PS-Cu(II)-ala

Synthetic procedure of functionalized polymer supported ligand: The ligand (**3**) was prepared from the organically modified chloromethylated polystyrene beads (**1**) according to literature

procedure. In first step, polystyrene beads (1) were functionalized to –CHO groups to form (2)¹⁴ and then react with β -alanine to give ligand (3)^{12a, b} as the final product.

Loading of metal ions on to the functionalized ligand (3): Copper acetate (30 mg) in acetic acid solution (8 mL) and 0.5 gm of functionalized polymeric ligand (3) were heated at reflux condition for 22 h. The ensuing solid (metal-loaded functionalized polymer 4) was filtered and washed with water followed by methanol, repetitively. Finally it was dried in oven at 90 °C for 5 h under vacuum.

3.4. Characterization techniques: A PerkinElmer 2400 C elemental analyzer was used to collect micro-analytical data (C, H and N). The FT-IR spectra of the samples were recorded from 400 to 4000 cm⁻¹ on a PerkinElmer FT-IR 783 spectrophotometer. A Mettler Toledo TGA/SDTA 851 instrument was used for TGA. The morphology of the functionalized polystyrene and complex was analyzed using a scanning electron microscope (Zeiss EVO40, UK) equipped with EDX facility. The copper content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer. The X-ray photoluminescence spectroscopic analysis has been performed on a Omicron Nanotechnology GmbH. The EPR spectra were recorded using a JES-FA200ESR spectrometer (JEOL). NMR spectra were monitored on a Bruker AMX- 400 NMR spectrophotometer (400 MHz for 1H NMR) using tetramethylsilane as internal standard.

3.5. General procedure for the N-arylation of amides: A mixture of benzamide (121 mg, 1.0 mmol), iodobenzene (~0.2 mL, 1.1 mmol), K_2CO_3 (138 mg, 1.0 mmol), and PS-Cu(II)-ala (0.9 mol%) were heated at 120 °C (oil bath temperature) for 15 h under air. The reaction mixture was allowed to cool and extracted with ethyl acetate (3 × 20 mL). The organic part was washed with brine, dried over Na₂SO₄ (anhy.), and evaporated to leave the crude product, which was purified by column chromatography over silica gel with pet ether/ethyl acetate (85:15) as eluent to furnish pure *N*-phenyl benzamide (**3a**, 181 mg, 92 %) as a white

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crystalline solid. ¹H NMR (400 MHz, CDCl₃) δ 7.82 - 7.80 (m, 2H), 7.73 (bs, 1H), 7.59 - 7.57 (m, 2H), 7.51 - 7.41 (m, 3H), 7.33 - 7.29 (m, 2H), 7.11 - 7.07 (m, 1H).



Scheme 2. Outline for the synthesis of PS-Cu(II)-ala.

3.6. Characterization of supported copper(II) complex.

The overall synthetic route for the preparation of functionalized polymer-supported copper(II) catalyst is shown in Scheme 2. The catalyst (PS-Cu(II)-ala) was characterized by elemental analysis (CHN), AAS, UV-Vis spectra, IR, SEM, TGA, XPS and EPR.

The elemental analysis data for the functionalized polymeric ligand (**3**) and PS-Cu(II)-ala (**4**) are shown in Table 6. The quantity of the Cu metal in the catalyst was determined using AAS technique. It is found that the catalyst contains just 4.01 wt% of Cu metal.

Table 6. Chemical composition of functionalized polymer supported ligand (3) and PS-Cu(II)-ala catalyst (4)

Compound	C%	Н%	N%	Cu%
Ligand 3	74.95	6.37	4.60	-
PS-Cu(II)-ala (4)	72.00	6.04	4.44	4.01 (3.98) ^a

^aCopper content of recycled catalyst after 8th cycles.

FT-IR Study: The link of relationship of β -alanine and copper metal onto the support were established by IR spectra (Figure 2). In the FT-IR spectrum (Figure 2a), a new peak arose at

1705 cm⁻¹ which was confirmed to carbonyl C=O bond stretching vibration of the aldehyde group while the peak nearly at 1264 cm⁻¹ (due to C-Cl bond stretching of -CH₂Cl) was absent.¹⁵ A new peak at 1632 cm⁻¹ was observed which is assigned for the formation of a C=N bond in Figure 2b. Due to the complexation of Cu metal with the ligand system, this band moved to lower wave numbers (Figure 2c). In Figure 2c, two peaks at 1574 cm⁻¹ and 1421 cm⁻¹ were exhibited,¹⁶ which assigned to the asymmetric and symmetric vibrations of the bridging acetate ions (v COO bridged).

DRS-UV study: The DRS UV-Vis absorption spectra (Figure 3) of the functionalized polymeric ligand and copper catalyst (PS-Cu(II)-ala) have been recorded as MgCO₃/BaSO₄ disc. Both of them exhibited broad band around 265 to 330 nm, which may be ascribed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ shift in the phenyl ring moiety. LMCT caused the generation of the band at around 355 to 375 nm in PS-Cu(II)-ala catalyst.

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Figure 2. FT-IR spectra of (a) aldehyde functionalized polymer, (b) polymer supported Schiff base ligand and (c) polymer supported Cu(II) catalyst, PS-Cu(II)-ala.



Figure 3. DRS-UV-vis spectra of polymeric ligand (3) and PS-Cu(II)-ala Catalyst.

Scanning Electron Micrographs (SEM) and Energy Dispersive X-ray Analyses (EDX):

The SEM image of the functionalized polymeric ligand (**3**) and PS-Cu(II)-ala catalyst are given in Figure 4a and 4b. It is reflected that, reasonably homogeneous but insignificant variation in the particle size is seen all over the specimens. The existence of the copper metal in the final copper catalyst is also established by EDAX data (Figure 4c).



Figure 4. SEM images of polymeric ligand (**3**) (a), PS-Cu(II)-ala Catalyst (b) and EDX plot of PS-Cu(II)-ala Catalyst (c).

TGA analysis: To investigate the thermal stability of the catalyst, the catalyst sample was heated at a rate of 10 $^{\circ}$ C min⁻¹ under air over the range of temperature of 30–600 $^{\circ}$ C. The thermograph is given in Figure 5. The Materials, ligand (**3**) and copper catalyst (**4**) are stable to higher temperature around 400 $^{\circ}$ C. From the curve we can observed that the heterogeneous copper catalyst is more stable than the corresponding polymer supported ligand (**3**).



Figure 5. Thermograph of polymeric ligand (3), PS-Cu(II)-ala Catalyst (4).

XPS Analysis: The XPS binding energies of Cu $2p_{1/2}$ and Cu $2p_{3/2}$ are found to be 954 and 934 eV, which is agrees well with +2 oxidation state of Cu in PS-Cu(II)-ala.¹⁷ A satellite peak between these two is characteristic feature of $2p \rightarrow 3d$ transition of Cu in +2 oxidation state.^{17,18} The amount of Cu atoms present on the surface of PS-Cu(II)-ala is found to be 0.40 atomic per cent. The C1s, O1s, N1s peaks are found at 284 eV, 532 eV and 399 eV respectively confirms the presence of C, O, N.¹⁸ The full range scan is shown in Figure 6e and the narrow range scan is shown in Figure 6a-d.



Figure 6. XPS data of PS-Cu(II)-ala, narrow range XPS spectrum for (a) Cu 2p, (b) O 1s, (c) N 1s, (d) C 1s and (e) full range spectrum.

EPR Analysis: The EPR (Electron Paramagnetic Resonance) spectroscopic studies have been carried out with fresh as well as used catalyst in solid state at room temperature. Both the EPR spectra show (Figure 7) four hyperfine lines which appear due to the coupling of unpaired electron of copper with its nucleus.¹⁹ This indicates +2 oxidation states of copper for both the fresh and reused catalysts. This implies the oxidation state of the Cu remained unchanged after the catalytic reaction.



Figure 7. EPR spectrum of (a) fresh catalyst and (b) used catalyst

4 Recyclability and Reusability of Cu(II) catalyst:

To evaluate the recyclability and reusability of Cu(II)-catalyst we performed the *N*-arylation reaction of benzamide with iodobenzene under optimized conditions. After completion of the reaction, the crude reaction mixture was centrifuged. The recovered catalyst was washed thoroughly using water and methanol respectively. Finally the catalyst was dried in oven at 70 °C for 5 h under vacuum for reactivation. It is quite evident that the catalyst can be recycled for 8th successful runs without prior loss in its catalytic activity (Figure 8). The possibility of copper metal leaching was examined by IR spectrum and AAS analysis. The SEM image also indicates the parallel observation (Figure 9a). The IR spectrum of the reused catalyst was found to be quite similar with the fresh one (Figure 9b). Finally, the AAS analysis of the reused catalyst also confirms that the copper content in the reused catalyst remains almost unchanged after 8th successful catalytic runs (Table 6).



Figure 8. Recycling experiment of PS-Cu(II)-ala.



Figure 9. SEM image (a) and FT-IR spectrum (b) of the reused catalyst

Conclusions

In this context, functionalized polystyrene supported copper(II) catalyst was synthesized and characterized. C-N cross coupling reaction was selected to understand the catalytic activity of this copper(II) catalyst. The reactions were carried out under neat condition. The scope and utility of this reaction were broad and environment friendly due to the wide span of the substrates. Aromatic, aliphatic, cyclic and heterocyclic amides successfully coupled with the aryl iodide as well as aryl bromide in presence of this copper(II) catalyst. The catalyst exhibited excellent recyclability. As a result, the trouble-free mode of operation, broad

substrates scope and good recycling of the catalyst allowed us to go ahead for a good future of this course in academic in addition to in production industry.

Associated Content

Notes

The authors declare no competing financial interest.

[†]Electronic Supplementary Information (ESI) available. ¹H NMR spectral data of all products listed in Table 2, 3, 4, 5.

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Reference

1. (a) M. Negwer, In Organic-Chemical Drugs and their Synonyms: (An International Survey), 7th edn., Akademie Verlag, Berlin, 1994; (b) C. L. Allen and J. M. J. Williams, Chem. Soc. Rev., 2011, 40, 3405-3415; (c) T. Cupido, J. Tulla-Puche, J. Spengler and F. Albericio, Curr. Opin. Drug Discovery Dev., 2007, 10, 768-783; (d) E. Valeur and M.

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RSC Advances

Bradley, *Chem. Soc. Rev.*, 2009, **38**, 606–631; (e) J. M. Humphrey and A. R. Chamberlin, *Chem. Rev.*, 1997, **97**, 2243-2266; (f) M. A. Mintzer and E. E. Simanek, *Chem. Rev.*, 2009, **109**, 259-302; (g) J. S. Carey, D. Laffan, C. Thomson and M. T. Williams, *Org. Biomol. Chem.*, 2006, **4**, 2337-2347; (h) P. Anastas and N. Eghbali, *Chem. Soc. Rev.*, 2010, **39**, 301-312; (i) J. B. Buckingham, *Dictionary of Natural Products*, Chapman and Hall, London, UK, 1994, vol. **1**.

(a) Z. -T. Li, J. -L. Hou and C. Li, *Acc. Chem. Res.*, 2008, **41**, 1343-1353; (b) S. K. Meegalla, M. J. Wall, J. Chen, K. J. Wilson, S. K. Ballentine, R. L. DesJarlais, C. Schubert, C. S. Crysler, Y. Chen, C. J. Molloy, M. A. Chaikin, C. L. Manthey, M. R. Player, B. E. Tomczuk and C. R. Illig, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 3632-3637; (c) T. Nuijens, C. Cusan, J. A. W. Kruijtzer, D. T. S. Rijkers, R. M. J. Liskamp and P. J. L. M. Quaedflieg, *J. Org. Chem.*, **2009**, **74**, 5145-5150; (d) D. Liu, S. Choi, B. Chen, R. J. Doerksen, D. J. Clements, J. D. Winkler, M. L. Klein and W. F. DeGrado, *Angew. Chem., Int. Ed.*, 2004, **43**, 1158-1162; (e) H. Yin, K. K. Frederick, D. Liu, A. J. Wand and W. F. DeGrado, *Org. Lett.*, 2006, **8**, 223-225; (f) J. Dalton, C. Barrett, Y. He, S. Hong, D. D. Miller, M. L. Mohler, R. Narayanan and Z. Wu, *WO 2007/ 062230 A2*, 2007.

(a) B. Clarke, E. Demont, C. Dingwal, R. Dunsdon, A. Faller, J. Hawkins, I. Hussain, D. MacPherson, G. Maile and R. Matico, *Bioorg. Med. Chem. Lett.*, 2008, 18, 1011; (b) A. Bebbington, R. W. Brimblecombe and D. Shakeshaft, *Br. J. Pharmacol. Chemother.*, 1966, 26, 56-67; (c) P. J. M. B. Raboisson, L. Hu, S. Vendeville and O. Nyanguile, *PCT Int. Appl. WO 2009080836A2 20090702*, 2009; (d) H. E. Demont, A. Faller, D. T. MacPherson, P. H. Milner, A. Naylor, S. Redshaw, S. J. Stanway, R. D. Vesey and D. S. Walter, *PCT Int. Appl.* WO 2004050619A1 20040617, 2004.

4. I. Goldberg, Ber. dtsch. chem. Ges., 1906, 39, 1691.

RSC Advances Accepted Manuscript

RSC Advances

5. (a) M. Taillefer, N. Xia and A. Ouali, *Angew. Chem., Int. Ed.*, 2007, 46, 934-936; (b) A.
Correa and C. Bolm, *Angew. Chem., Int. Ed.*, 2007, 46, 8862-8865; (c) V. H. Jadhav, D. K.
Dumbre, V. B. Phapale, H. B. Borate and R. D. Wakharkar, *Catal. Commun.*, 2007, 8, 65-68.

6. (a) P. Saha, M. A. Ali, P. Ghosh and T. Punniyamurthy, Org. Biomol. Chem., 2010, 8,

5692-5699; (b) B. Y.-H. Tan and Y.-C. Teo, Org. Biomol. Chem., 2014, 12, 7478-7481; (c)

N. Mukherjee, T. Chatterjee and B. C. Ranu, Euro. J. Org. Chem., 2015, 4018-4023.

7. Y. J. Wu, H. He and A. L. Heureux, Tetrahedron Lett., 2003, 44, 4217-4218.

Published on 09 November 2016. Downloaded by UNIVERSITY OF OTAGO on 10/11/2016 02:19:29.

(a) J. Yin and S. L. Buchwald, Org. Lett., 2000, 2, 1101-1104; (b) B. H. Yang and S. L.
 Buchwald, J. Organomet. Chem., 1999, 576, 125-146; (c) J. Yin and S. L. Buchwald, J. Am.
 Chem. Soc., 2002, 124, 6043-6048; (d) D. Prim, J. M. Campagne, D. Joseph and B.
 Andrioletti, Tetrahedron, 2002, 58, 2041-2075; (e) J. F. Hartwig, Angew. Chem. Int. Ed., 1998, 37, 2046-2067.

9. (a) X. Guo, H. Rao, H. Fu, Y. Jiang and Y. Zhao, *Adv. Synth. Catal.*, 2006, 348, 2197-2202; (b) Y. -J. Chen and H. -H. Chen, *Org. Lett.*, 2006, 8, 5609-5612; (c) C. Wang, L. Liu, W. Wang, D. -S. Ma and H. Zhang, *Molecules*, 2010, 15, 1154-1160; (d) D. Kundu, S. Bhadra, N. Mukherjee, B. Sreedhar and B. C. Ranu, *Chem. Eur. J.*, 2013, 19, 15759-15768.

10. A. Y. Kim, H. J. Lee, J. C. Park, H. Kang, H. Yang, H. Song and K. H. Park, *Molecules*, 2009, **14**, 5169-5178;

11. (a) S. M. Islam, A. S. Roy, P. Mondal, M. Mubarok, S. Mondal, D. Hossain, S. Banerjee and S. C. Santra, *J. Mol. Catal. A: Chem.*, 2011, **336**, 106-114; (b) S. M. Islam, S. Mondal, P. Mondal, A. S. Roy, K. Tuhina, N. Salam and M. Mobarak, *J. Organomet. Chem.*, 2012, **696**, 4264-4274; (c) S. M. Islam, A. S. Roy, P. Mondal, K. Tuhina, M. Mobarak and J. Mondal, *Tetrahedron Lett.*, 2012, **53**, 127-131; (d) S. M. Islam, N. Salam, P. Mondal, A. S. Roy, K. Ghosh and K. Tuhina, *J. Mol. Catal. A: Chem.*, 2014, **387**, 7-19.

RSC Advances

12. (a) M. Halder, M. M. Islam, S. Ahammed and S. M. Islam, *RSC Adv.*, 2016, 6, 8282-8289; (b) M. M. Islam, A. S. Roy and S. M. Islam, *Catal. Lett.*, 2016, 146, 1128-1138; (c) A. S. Roy, J. Mondal, B. Banerjee, P. Mondal, A. Bhaumik and S. M. Islam, *Appl. Catal. A*, 2014, 469, 320-327; (d) S. M. Islam, S. Mondal, P. Mondal, A. S. Roy, K. Tuhina, M. Mobarok, S. Paul, N. Salam and D. Hossain, *Catal. Lett.*, 2011, 141, 1171-1181.

- 13. E. R. Strieter, B. Bhayana and S. L. Buchwald, J. Am. Chem. Soc., 2009, 131, 78-88.
- 14. J. M. Frechet and C. Schuerch, J. Am. Chem. Soc., 1971, 93, 492-496.
- 15. M. D. Angelino and P. E. Laibinis, Macromolecules, 1998, 31, 7581-7587.
- 16. P. A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., 1967, 29, 2122-2123.
- 17. J. Mondal, A. Modak, S. Basu, S. N. Jha, D. Bhattacharyya and A. Bhaumik, *Chem. Commun.*, 2012, **48**, 8000-8002.
- J. Mondal, P. Borah, A. Modak, Y. Zhao and A. Bhaumik, Org. Proc. Res. Dev., 2014, 18, 257-265.
- (a) S. Roy, T. Chatterjee, B. Banerjee, N. Salam, A. Bhaumik and S. M. Islam, *RSC Adv.*,
 2014, 4, 46075-46083; (b) N. Salam, S. K. Kundu, A. S. Roy, P Mondal, S. Roy, A. Bhaumik and S. M. Islam, *Catal. Sci. Technol.*, 2013, 3, 3303-3316.

Graphical Abstract

Copper(II) incorporated functionalized polystyrene catalyzed N-arylation of amides under solvent free condition with broad substrate scope

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A new polymer supported Cu(II) catalyst has been reported for N-arylation of various amides with aryl halides under neat reaction conditions.