

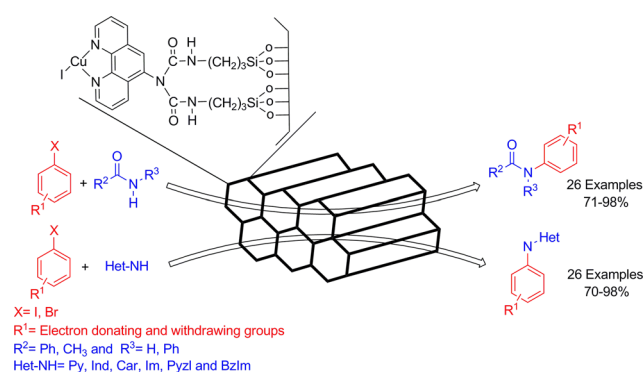
SBA-15 Immobilized Phenanthroline–Copper(I) Complex as a Recyclable Efficient Catalyst for *N*-Arylation of Amides and *N*–*H* Heterocycles with Aryl Halides

Rahman Hosseinzadeh¹ · Nora Aghili¹ · Mahmood Tajbakhsh¹

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Abstract 5-(*N,N*-bis-3-(triethoxysilyl) propyl) ureyl-1,10-phenanthroline was prepared and successively grafted onto mesoporous silica of SBA-15 to get SBA-15 anchored ligand which was then reacted with Cu(I) to get SBA-15 anchored complex as the heterogeneous copper catalyst. This catalyst was characterized by FT-IR, XRD, CHN, AAS, TGA, EDAX, BET, SEM and TEM. The activities of the catalyst were tested in C–N cross-coupling of amides and *N*–*H* heterocycle compounds with aryl halides. The catalyst showed high catalytic activities for these cross-coupling reactions providing good to excellent yields of desired products. Moreover, the catalyst can be easily recovered by simple filtration and reused several times without significant loss of its catalytic activity.

Graphical Abstract



Keywords Supported copper catalyst · Functionalized of SBA-15 · *N*-Arylation reaction · Aryl halides · Coupling reaction

1 Introduction

N-Aryl amides and *N*-aryl heterocycles are valuable compounds that are prevalent in numerous compounds of biological, pharmaceutical, and materials interest [1–4]. Copper-catalyzed Goldberg-type coupling reaction [5–7] (*N*-arylation of amide) and Ullmann-type coupling reaction [8–10] (*N*-arylation of *N*–*H* heterocycles) are a traditional choice for formation of C(aryl)–N bond. However, both of these methods have limitation in some of following area: use of stoichiometric amount of copper, strong bases, highly polar solvents, high reaction temperatures, long reaction times and showing poor substrate generality [11, 12]. To overcome these drawbacks, researchers have employed several organic ligands and copper salts to facilitate the *N*-arylation of amides [13–17] and *N*–*H* heterocycles [18–23].

Despite the remarkable efficiency of these homogenous catalyst systems, they suffer from some drawbacks, such as product contamination with catalyst and require cumbersome catalyst separation procedure. These disadvantages can be overcome by anchoring metal on suitable supports which will allow easy separation and recyclability of the catalyst with minimal amount of product contamination with metal.

Several heterogeneous catalysts such as hydroxyapatite supported copper [24], zeolite supported Cu(II) [25], cellulose supported Cu(0) [26], silica supported Cu(II) [27], carbon nanotube supported Cu(II) [28], CuO nanoparticle [29–31], polyaniline supported Cu(I) [32], Cu₂O [33, 34],

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Cu–Al hydrotalcite [35], Cu₂O nanoparticle [36, 37], polymer supported Cu(II) [38, 39], MCM-41 supported Cu(I) [40], porous zinc-base metal–organic framework supported copper [41] and CuI nanoparticle [42] have been reported for copper catalysed C–N cross coupling reactions.

The modified mesoporous materials with various active sites have been extensively investigated in recent decade [43]. Among the various types of mesoporous silica, SBA-15 with tunable uniform hexagonal channels ranging from 5 to 30 nm and thick framework walls (3–6 nm), is a better support due to its high hydrothermal stability and substantial larger pore sizes.

1,10-Phenanthroline and its derivatives are well-established ligands for transition-metal coordination chemistry [44] and are widely used in transition-metal-catalyzed reactions [13, 18–21]. The rigid framework of 1,10-phenanthroline and its high affinity toward various cations, which can provide sufficient protecting shield for the transition metal center, are attractive features for the construction of highly effective catalyst.

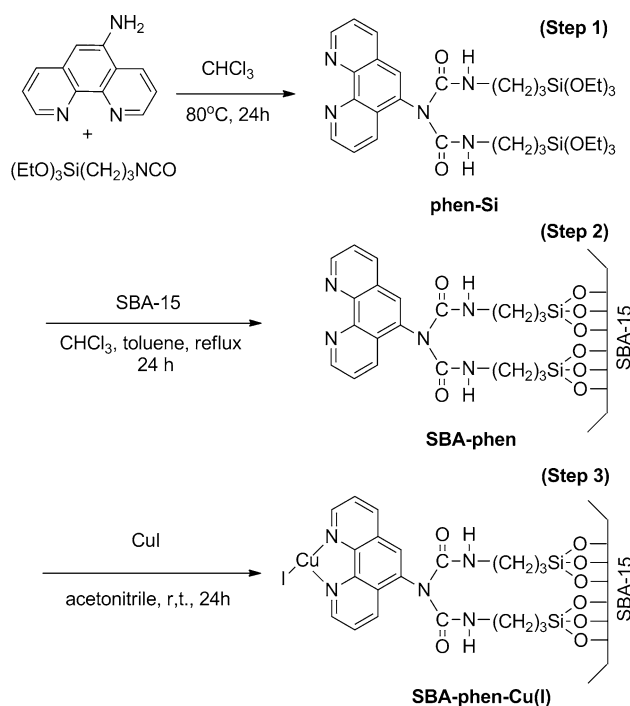
We have recently reported copper(I) *N*-arylation of amides [13] and *N*-*H* heterocyclic compounds [18–20] using phenanthroline as ligand. Herein, in a greener synthetic pathway, we report the synthesis of SBA-15 supported phenanthroline copper(I) catalyst as the reusable catalyst for *N*-arylation of amides and *N*-*H* heterocyclic compounds with aryl halides.

2 Results and Discussion

2.1 Preparation and Characterization of the Catalyst

SBA-15 immobilized phenanthroline–copper(I) catalyst was prepared using the three-step procedure summarized in scheme 1. The 5-(*N,N*-bis-3-(triethoxysilyl) propyl) ureyl-1,10-phenanthroline (phen-Si) was first synthesized through the reaction of 5-amino-1,10-phenanthroline with 3-(triethoxysilyl)propyl isocyanate in CHCl₃ at 80 °C for 24 h (Step 1), as reported perviously [45]. Next, the mesoporous SBA-15 reacted with phen-Si in reflux of toluene for 24 h (Step 2). The latter was subsequently treated with CuI in acetonitrile at room temperature for 24 h to generate the SBA-15 immobilized phenanthroline–copper(I) (SBA–phen–CuI) in a form of green powder.

Figure 1 shows the FT-IR of the phen-Si (a), SBA–phen (b), SBA–phen–Cu(I) (c) and SBA-15 (e). From the IR spectra presented in Fig. 1a–c, the stretching vibration of C=O, C=N and C=C band appeared as follows: 1,704, 1,652 and 1,537 cm⁻¹ for phen-Si (Fig. 1a), 1,701, 1,651 and 1,548 for SBA–phen (Fig. 1b) and 1,701, 1,635 and



Scheme 1 Preparation of SBA-15 immobilized phenanthroline-copper (I) catalyst (SBA–phen–Cu(I))

1,551 cm⁻¹ for SBA–phen–Cu(I) (Fig. 1c). The lowering in frequencies of C=N peak in SBA–phen–Cu(I) (Fig. 1c) is indicative of formation of metal–ligand bonds [27]. Also the presence of vibration bands at about 1,080 cm⁻¹ which is due to Si–O–Si framework (Fig. 1e), demonstrates the existence of SBA-15 in SBA–phen and SBA–phen–Cu(I) (Fig. 1b, c).

The low angle XRD pattern of SBA-15 and SBA–phen–Cu(I) are presented in Fig. 2. The XRD pattern of the SBA–phen–Cu(I) shows a strong peak at 2θ smaller than 2 degree along with some small peaks similar to XRD pattern of the mesoporous SBA-15 that confirm the presence of SBA-15 in the prepared SBA–phen–Cu(I) sample [46, 47].

Figure 3 shows The TGA analysis for SBA-15 (Fig. 3a) and SBA–phen–Cu(I) (Fig. 3b). For SBA-15, the weight loss below 150 °C is not significant, while for SBA–phen–Cu(I) the weight loss within 100–200 °C is ~1.0 % could be due to the desorption of physisorbed water on the surface of the catalyst. The weight loss (20 %, 0.36 mmol g⁻¹) at 200–600 °C could be attributed to the decomposition of phenanthroline–copper complex on the SBA-15.

Elemental analysis for SBA–phen–Cu(I) was carried out and the data were tabulated in Table 1. The phen–Cu(I) was found to be 0.38 mmol g⁻¹ based on the percentage of nitrogen obtained from elemental analysis. Clearly, the organic moiety contents measured by CHN were in accord with those obtained by TGA (Fig. 3). On the other hand,

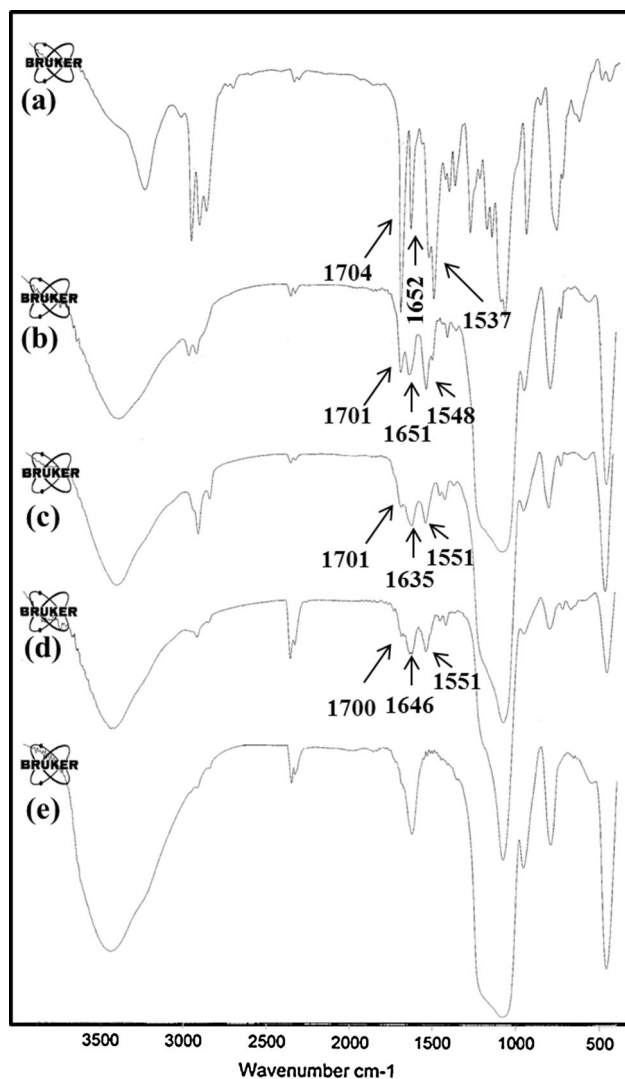


Fig. 1 FT-IR spectra of phen-Si (a), SBA-phen (b), fresh SBA-phen-Cu(I) (c), reused SBA-phen-Cu(I) (d), and SBA-15 (e)

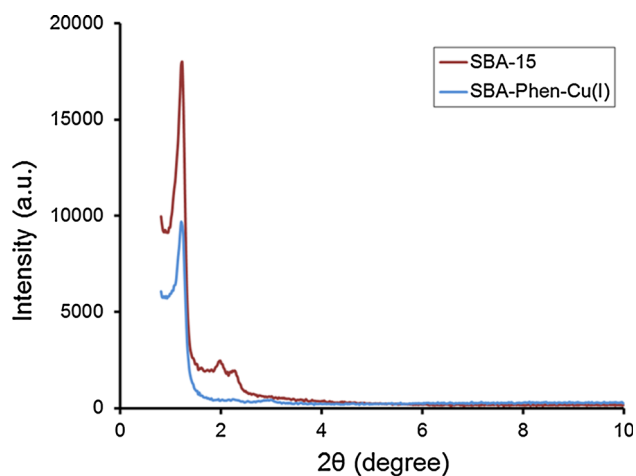


Fig. 2 XRD patterns of the SBA-15 and SBA-phen-Cu(I)

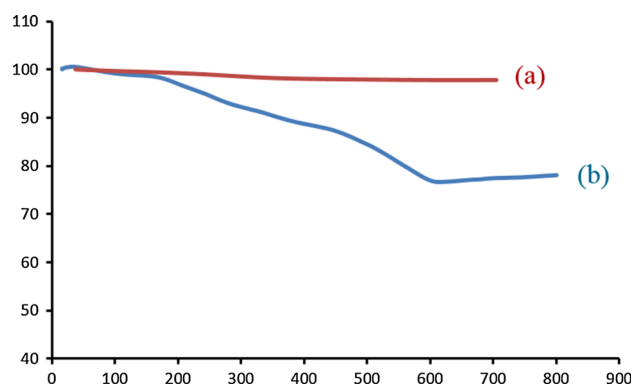


Fig. 3 TGA patterns of SBA-15 (a) and SBA-phen-Cu(I) (b)

Table 1 Elemental analysis for SBA-phen-Cu(I)

Sample	C %	H %	N %	Cu % ^a
SBA-phen-Cu(I)	10.71	1.46	2.63	1.46 ^b , 1.40 ^c

^a The amount of copper was determined using AAS

^b Fresh catalyst

^c Used catalyst after ten times

according to AAS results, copper content in the SBA-phen-Cu(I) was 0.23 mmol/gr (1.46 Wt %) that represents mole fraction of ligand is ca. 38 % obtained from the following calculation:

$$(0.23/0.23 + 0.38) \times 100 = 38\%$$

Further to support the above observation, the EDAX analysis of SBA-phen-Cu(I) was done and indicated that CuI was chelated on the surface of the SBA-15 (Fig. 4).

N₂ adsorption-desorption isotherms and BJH pore size distribution of the SBA-15 and SBA-phen-Cu(I) are depicted in Fig. 5. The nitrogen adsorption-desorption isotherms of the samples were obtained at 77 K and specific surface area was determined by applying the BET equation to the isotherm [48]. The pore size distribution was calculated using the desorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula [49].

The nitrogen adsorption-desorption isotherms of the SBA-15 and SBA-phen-Cu(I) showed a typical profile of type IV, which consisted of a step condensation behavior due to the formation of mesopores in the SBA-15 and the presence of mesoporous SBA-15 in the SBA-phen-Cu(I) [46].

Table 2, shows the specific surface area, pore volume, and pore size of the SBA-15 and SBA-phen-Cu(I) samples. The BET surface area of the SBA-phen-Cu(I) sample was 275 m² g⁻¹, which is less than the surface area of the SBA-15 (816 m² g⁻¹). This may be a result of blocking of

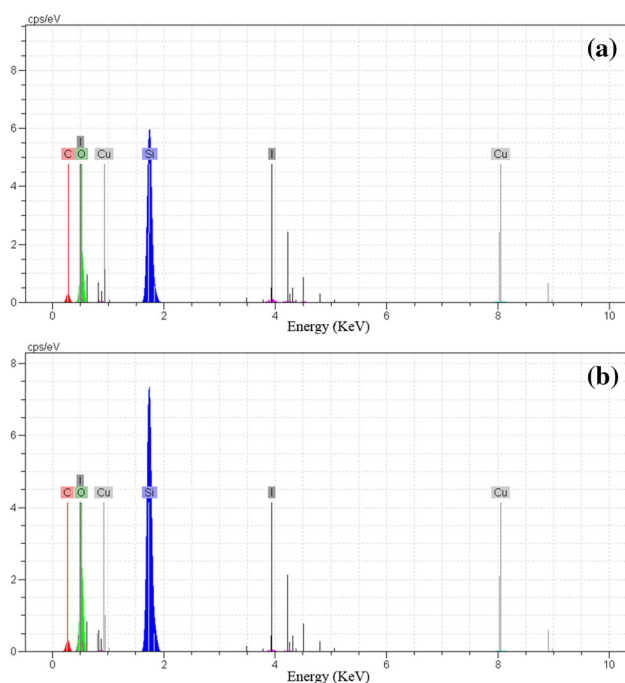


Fig. 4 EDAX image of fresh catalyst (a), and EDAX image of catalyst after 10th run

some pores of mesoporous SBA-15 by the entry of phenanthroline–Cu(I) complex.

The SEM image of mesoporous SBA–phen–Cu(I) was taken using 2 min gold coat for high magnification and is shown in Fig. 6. The formation of SBA-15 with fibrous morphology and the presence of SBA-15 in the prepared SBA–phen–Cu(I) sample were confirmed by scanning electron microscopy.

The TEM images of fresh catalyst is shown in Fig. 7. As can be seen, the TEM micrographs clearly reveal the presence of ordered array of mesopores with uniform pore size which is also confirmed by XRD in Fig. 2. The pore size of SBA–phen–Cu(I) is ~ 3.5 nm which is in good agreement with N_2 adsorption–desorption results (Fig. 5).

2.2 Catalytic Activity of the Catalyst in *N*-Arylation of Amides with Aryl halides

To determine the most suitable reaction conditions, the *N*-arylation of benzamide with 4-iodoanisole was chosen as a model reaction, and the influence of various reaction parameters such as base, solvent, temperature, catalyst and amounts of catalyst on the reaction yield were tested. The results are summarized in Table 3. First of all, the influence of bases on the reaction was investigated (entries 1–7). Among the bases examined, K_3PO_4 was the most effective base (entry 3), while Et_3N and K_2CO_3 were less effective (entries 1 and 2) and KF and DBU were ineffective (entries 4 and 5). Using strong base such as, KO^tBu resulted in no

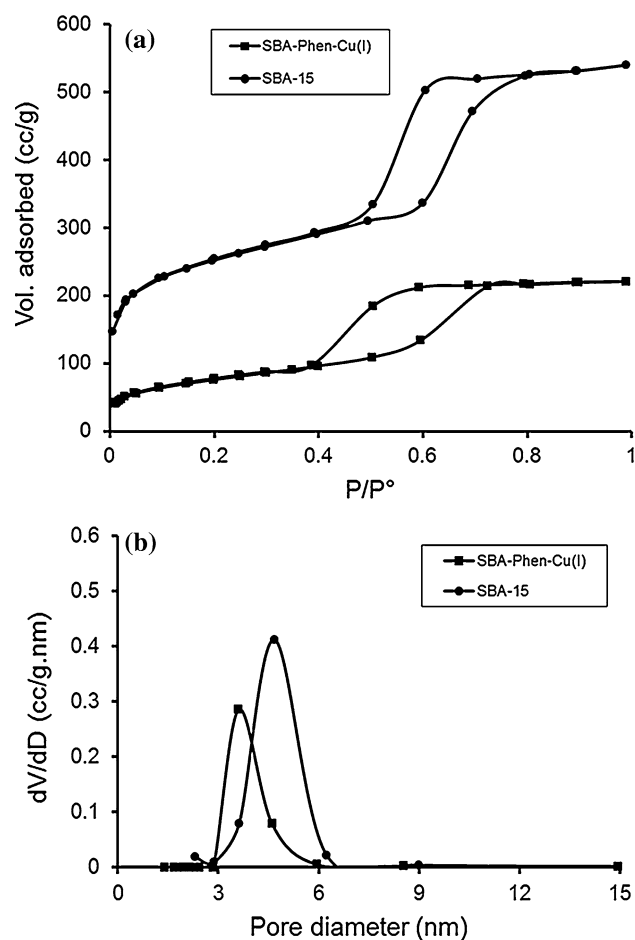
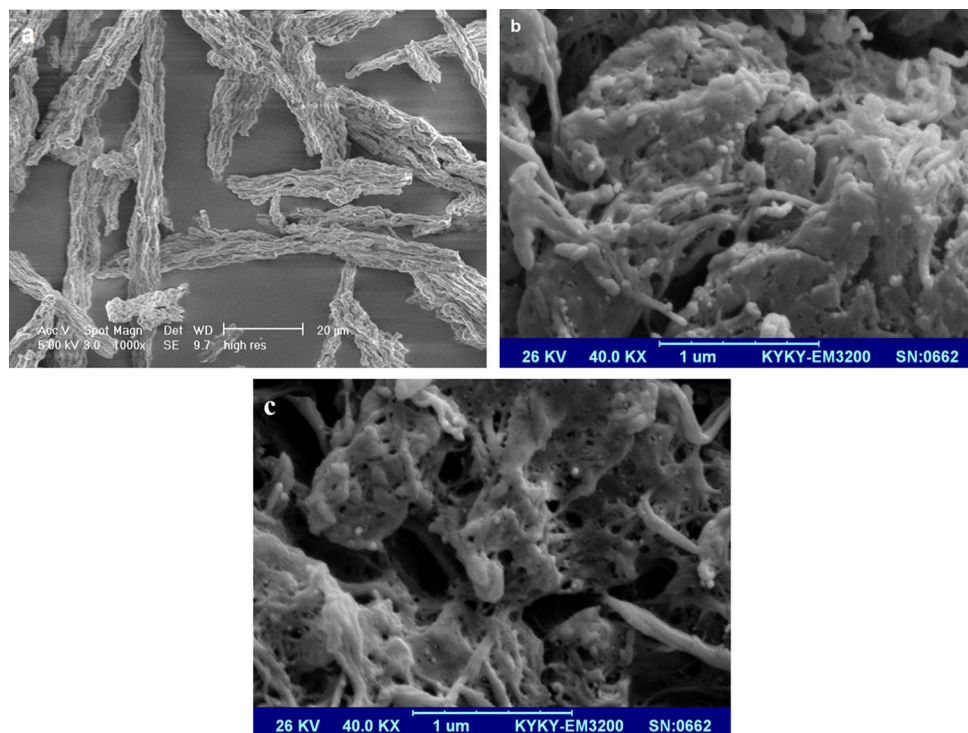


Fig. 5 Nitrogen adsorption–desorption isotherms (a) and pore size distribution curves (b) of the SBA-15 and SBA–phen–Cu(I)

reaction (entry 6). Due to the acidic character of amide proton, it is believed that using strong base could generate an excess of the deprotonated amide leading to formation of a non-reactive cuprate complex, which hinders desired catalytic cycle of amidation [50]. The coupling reaction did not proceed in the absence of the base, showing the role of the base in this reaction (entry 7). Next, the effect of solvent on model reaction was examined (entries 3 and 8–12). The use of nonpolar solvents, such as toluene and xylene, resulted in excellent yields of the product (entries 3 and 8), while the reactions in aprotic polar solvents, such as DMF, DMSO, THF and dioxane, gave moderate yield of the product (entries 9–12). The effect of reaction temperature was also investigated (entries 3 and 13–14). At the lower temperature (r.t. and $65^\circ C$) only very low to moderate yields were obtained (entries 13 and 14). In order to investigate the role of SBA–phen–Cu(I) for the *N*-arylation reaction, we have carried out the reaction with SBA-15 (entry 15) and ligand grafted SBA-15 (entry 16) under the similar conditions. But in these cases no reaction takes place. The reaction was also carried out by using of

Table 2 Physical properties of the prepared SBA–phen–Cu(I)

Sample	BET surface area (m ² g ⁻¹)	BJH Pore diameter (nm)	Total pore volume (cc g ⁻¹)
SBA-15	816	4.09	0.84
SBA–phen–Cu(I)	275	3.61	0.34

Fig. 6 SEM image of the SBA-15 (a), SBA–phen–Cu(I) (b) and reused catalyst (c)

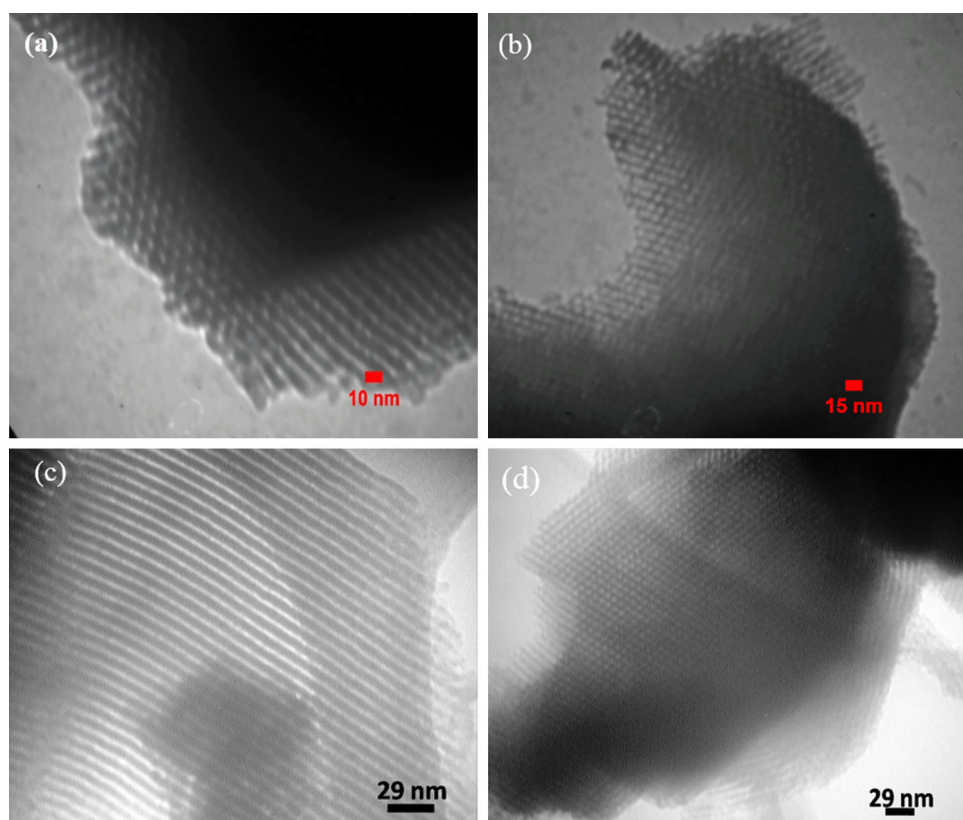
homogeneous condition, CuI as catalyst and 1,10-phenanthroline as ligand (entry 17). The yield of this reaction was relatively good in comparison with that carried out with SBA–phen–Cu(I) (83 % vs. 95 %). As the main goal of the present work is to develop a suitable catalyst system which allows easy separation and recyclability of the catalyst with minimal amount of product contamination, phenanthroline–copper supported on SBA-15 is selected as heterogeneous catalyst for *N*-arylation reaction. Finally, the reaction was carried out with different amounts of SBA–phen–Cu(I) over the range of 0.01–0.07 g (entries 3 and 18–20) and it was found that 0.05 g (entry 3) of catalyst was enough to proceed the reaction smoothly. It was apparent that increasing the amount of the catalyst could shorten the reaction time, but did not improve the yield of desired product (entry 20).

In order to examine the scope and limitations of the protocol a wide variety of amides reacted with aryl halides under the optimized reaction conditions and the results are summarized in Table 4. The reactions of benzamide and acetamide with iodobenzene under optimum reaction conditions gave excellent yields of the corresponding *N*-aryl compounds (entries 1 and 7). Aryl iodides possessing

electron-releasing groups such as methoxy (entries 2, 3 and 8) and methyl groups (entries 4 and 9) in the ortho- and para-positions of the aromatic ring also gave good to excellent yields of the corresponding C–N coupling products. Aryl iodides with electron-withdrawing groups such as –NO₂ in para-position on the reaction with benzamide also gave satisfactory yields of the corresponding *N*-aryl compounds (entries 5). 1-Iodonaphthalene was also proceeded smoothly and gave a high yield of amidation product (entry 6). When acetanilide as a secondary amide reacted with aryl iodides under the same reaction conditions, the corresponding products were obtained in lower yields at longer reaction times (entries 10–12). This could be due to the steric hindrance of the substituted amide (e.g. comparing entry 12 with entries 4 and 9).

As shown in Table 4, the present catalytic system was also effective for the coupling reaction of aryl bromides and amides (entries 13–24). Similar to aryl iodides, both electron-rich and electron-deficient aryl bromides were suitable substrates, and afforded the desired products in good yields (entries 14–17, 20, 21, 23 and 24). It is interesting to mention that the coupling reaction with *p*-chloro and *p*-bromo iodobenzene with benzamide selectively gave

Fig. 7 TEM images of the fresh SBA-phen-Cu(I) (a–b) and used catalyst (c–d)



the corresponding coupling products without displacing bromine or chlorine (entries 25 and 26).

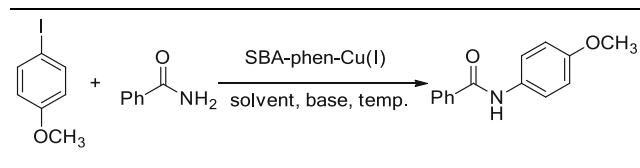
2.3 Catalytic Activity of the Catalyst in *N*-Arylation of *N*-*H* Heterocycles with Aryl halides

The promising results described above, prompted us to test the present copper catalyst on another important C–N bond forming, *N*-arylation of *N*-*H* heterocycles. Screening the reaction conditions for coupling reaction of 4-iodoanisole with indole, similar to those in Table 3, resulted in using 0.07 g (0.016 mmol) copper catalyst and K_2CO_3 as a base in toluene to achieve the best yield of the desired coupling product (Scheme 2).

With the optimized conditions in hand, we chose a variety of structurally divergent *N*-*H* heterocyclic compounds to investigate the scope and generality of this catalytic system. As can be seen in Table 5, pyrrole, indole, carbazole, imidazole, benzimidazole, and pyrazole were successfully transformed to the corresponding *N*-aryl compounds. The reaction between these mono and diazole with iodo and bromobenzene gives excellent yields after specified times (entries 1–10). Substrates possessing electron-releasing groups such as *-OMe* (entries 11–16, 19 and 20), and *-Me* (entries 17, 18, 21 and 22) in the ortho-, and para- positions of the aromatic ring also gave good to

excellent yields of the corresponding *N*-aryl compounds. Fused compounds such as 1-iodo and bromonaphthalene on reaction with imidazole gave a satisfactory yield of the corresponding *N*-aryl compound (entries 23 and 24). It is interesting to mention that the coupling reaction of *p*-bromiodobenzene with imidazole selectively gave the corresponding coupling products without displacing bromine (entry 25). 2-Bromopyridine reacted with imidazole to give an excellent yield of the corresponding *N*-pyrid-2-yl compound (entry 26).

The major advantage of a heterogeneous catalyst is the possibility of recovering and reusing it in the next runs. This was investigated in the reaction of benzamide and indole with iodobenzene for ten consecutive reaction cycles using SBA-phen-Cu(I) catalyst. After completion of the reaction, the catalyst was separated by simple filtration and washed several times with water (2×5 mL), ethanol (2×5 mL) and diethyl ether (2×5 mL) and then dried under vacuum for direct reuse in the next run. The results depicted in Fig. 8 demonstrate that there was almost no change in catalytic activity even after the ten run. SBA-phen-Cu(I) also maintained its structure during the reactions; this was confirmed by examining the IR spectra (Fig. 1d) and SEM images (Fig. 6c) of the reused catalyst showed no significant change in its structure and morphology. Furthermore, comparison of TEM images of the

Table 3 Reaction condition screening for *N*-arylation of benzamide with 4-iodoanisole


Entry	Base	Solvent	Temperature (°C)	Yield ^a (%)
1	Et ₃ N	Toluene	110	72
2	K ₂ CO ₃	Toluene	110	85
3	K ₃ PO ₄	Toluene	110	95
4	KF	Toluene	110	Trace
5	DBU	Toluene	110	Trace
6	KO ^t Bu	Toluene	110	–
7	None	Toluene	110	–
8	K ₃ PO ₄	Xylene	110	93
9	K ₃ PO ₄	DMF	110	65
10	K ₃ PO ₄	DMSO	110	63
11	K ₃ PO ₄	Dioxane	100	70
12	K ₃ PO ₄	THF	70	72
13	K ₃ PO ₄	Toluene	r.t.	Trace
14	K ₃ PO ₄	Toluene	65	73
15 ^b	K ₃ PO ₄	Toluene	110	–
16 ^c	K ₃ PO ₄	Toluene	110	–
17 ^d	K ₃ PO ₄	Toluene	110	83
18 ^e	K ₃ PO ₄	Toluene	110	52
19 ^f	K ₃ PO ₄	Toluene	110	72
20 ^g	K ₃ PO ₄	Toluene	110	95

Reaction conditions: benzamide (1 mmol), 4-iodoanisole (2 mmol), copper catalyst (0.05 g, 0.011 mmol), base (2 mmol), solvent (5 mL), 10 h

^a Isolated yield

^b SBA-15 as catalyst was used

^c SBA-phen as catalyst was used

^d CuI as catalyst and 1,10-phenanthroline as ligand was used

^e Copper catalyst (0.01 g, 0.002 mmol) was used

^f Copper catalyst (0.03 g, 0.007 mmol) was used

^g Copper catalyst (0.07 g, 0.016 mmol) was used

fresh and used catalyst show that catalyst pores have not been destroyed (Fig. 7c, d).

In order to determine the heterogeneity of the catalyst, hot-filtration test [58] was performed in the *N*-arylation reaction of indole with iodobenzene. The hot reaction mixture was filtered out, after the reaction proceeded for 4 h and the conversion was 55 %. After addition of K₂CO₃ to the filtrate, it was continually stirred under the reaction conditions. After 6 h the conversion was determined to be 55 %. Time conversion curve of this test reaction is shown in Fig. 9. It was found that the catalytic reaction was occurred by the solid catalyst. However, Cu was also not detected in the liquid phase of the reaction using atomic

absorption spectrometric (AAS) analysis. These results suggest that the Cu⁺ was not being leached out from the catalyst during *N*-arylation reactions after first run. The amount of Cu⁺ leaching after 10 repeated recycling was analyzed with AAS to be only 4.1 % (Table 1). The EDAX spectrum further authenticates the presence of copper in the catalyst after ten runs (Fig. 4b). These observations confirmed the heterogeneous character of the catalytically active species.

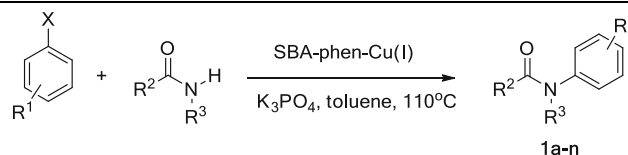
3 Conclusions

SBA-15 supported phenanthroline–copper (I) complex was prepared, characterized and effectively used as a heterogeneous catalyst for *N*-arylation of amides and *N*-*H* heterocycles with aryl halides. A wide range of primary and secondary amides such as benzamide, acetamide and acetanilide were found to react with aryl iodides and bromides to afford the corresponding coupled product in good to excellent yields. The same catalyst has been successfully employed in the *N*-arylation of divergent *N*-*H* heterocycles such as pyrrole, indole, carbazole, imidazole, benzimidazole, and pyrazole with aryl iodides and bromides. The catalyst shows not only high catalytic activity, but also offers many practical advantages such as thermal stability, and recyclability of the catalyst with minimal amount of product contamination with metal. The catalyst could be recovered by simple filtration and reused for at least ten consecutive cycles with consistent activity.

4 Experimental Section

1,10-Phenanthroline monohydrate, fuming sulfuric acid, 10 % Pd/C catalyst and 3-(triethoxysilyl)propyl isocyanate were purchased from Merck. Other commercially available chemicals were laboratory grade reagents obtained from local suppliers. All the solvents were distilled, dried and purified by standard procedures.

Melting points were measured on an Electrothermal 9,100 apparatus. ¹H NMR spectra were recorded in CDCl₃ on a Bruker avance III 400 and 500 MHz spectrometer. C, H and N analyses were performed with a Vario EL III elemental. Thermo gravimetric analysis (TGA) was performed using a Rheometric Scientific model STA-1500 analyzer. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Bruker vector 22 spectrometer using KBr pellets. Small-angle X-ray diffraction (XRD) patterns were recorded in the 2θ range of 0.8–10 using a X'Pert Pro MPDX-ray diffractometer using CuKα radiation. Nitrogen (N₂) adsorption/desorption isotherms (BET) were measured using a NOVA 2200e analyzer. The

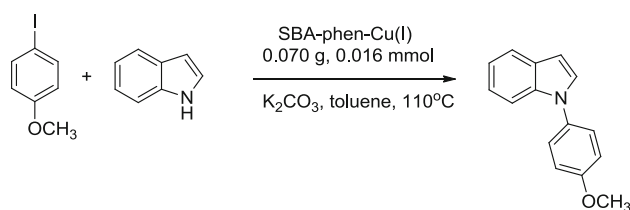
Table 4 Coupling reaction of amides with aryl halides catalyzed by SBA-phen-Cu(I)

Entry	X	R ¹	R ²	R ³	Product ^a	Time (h)	Yield ^b (%)	M. P (°C) [Ref.]	TON/TOF
1	I	H	Ph	H	1a	10	98	160–162 [14]	89/0.15
2	I	4-OCH ₃	Ph	H	1b	10	95	154 [14]	86/0.14
3	I	2-OCH ₃	Ph	H	1c	10	91	59–61 [14]	83/0.14
4	I	2-CH ₃	Ph	H	1d	10	91	143–145 [14]	83/0.14
5	I	4-NO ₂	Ph	H	1e	10	86	190 [14]	78/0.13
6	I	1-naphtyl	Ph	H	1f	10	96	160–162 [51]	87/0.15
7	I	H	CH ₃	H	1g	10	96	114–116 [14]	87/0.15
8	I	4-OCH ₃	CH ₃	H	1h	10	90	130–132 [14]	82/0.14
9	I	2-CH ₃	CH ₃	H	1i	10	87	111–113 [14]	79/0.13
10	I	H	CH ₃	Ph	1j	12	86	103 [14]	78/0.11
11	I	4-OCH ₃	CH ₃	Ph	1k	12	82	110 [14]	75/0.10
12	I	2-CH ₃	CH ₃	Ph	1l	12	80	74 [14]	73/0.10
13	Br	H	Ph	H	1a	10	84	160–162 [14]	76/0.13
14	Br	4-OCH ₃	Ph	H	1b	10	82	154 [14]	75/0.12
15	Br	2-OCH ₃	Ph	H	1c	10	79	59–61 [14]	72/0.12
16	Br	2-CH ₃	Ph	H	1d	10	80	143–145 [14]	73/0.12
17	Br	4-NO ₂	Ph	H	1e	10	78	190 [14]	71/0.12
18	Br	1-naphtyl	Ph	H	1f	10	81	160–162 [51]	74/0.12
19	Br	H	CH ₃	H	1g	10	79	114–116 [14]	72/0.12
20	Br	4-OCH ₃	CH ₃	H	1h	10	86	130–132 [14]	78/0.13
21	Br	2-CH ₃	CH ₃	H	1i	10	80	111–113 [14]	73/0.12
22	Br	H	CH ₃	Ph	1j	12	72	103 [14]	65/0.10
23	Br	4-OCH ₃	CH ₃	Ph	1k	12	71	110 [14]	65/0.09
24	Br	2-CH ₃	CH ₃	Ph	1l	12	76	74 [14]	69/0.10
25	I	4-Br	Ph	H	1m	10	88	199–202 [52]	80/0.13
26	I	4-Cl	Ph	H	1n	10	84	189–191 [51]	76/0.13

^a Reaction condition: SBA supported phenanthroline copper (I) catalyst (0.05 g, 0.011 mmol), aryl halides (2 mmol), amides (1 mmol), K₃PO₄ (424 g, 2 mmol), toluene (5 mL), 110 °C

^b Isolated yields

TON turn over number (mol of product/mol of catalyst), TOF turn over frequency [mol of product/(mol of catalyst × reaction time)]

**Scheme 2** N-arylation of indole catalysed by SBA-phen-Cu(I)

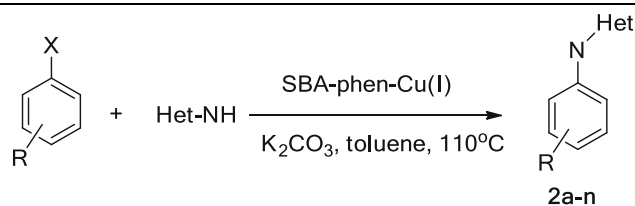
samples were out-gassed for 14 h at 60 °C under vacuum before measurement. Scanning electron microscopy (SEM) was performed using a KYKY-EM3200 analyzer. Transmission electron microscopy (TEM) experiments were

conducted on a Philips EM 208 electron microscope. Energy Dispersive X ray (EDAX) pattern was performed using a Rontec analyzer. Copper content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

4.1 General Procedure

4.1.1 Synthesis of Mesoporous SBA-15

Mesoporous silica SBA-15 was prepared under nonthermal conditions using tetraethylorthosilicate (TEOS) as the silica precursor, pluronic P123 as the template and HCl to

Table 5 Coupling reaction of *N*–*H* heterocycles with aryl halides catalyzed by SBA–phen–Cu(I)

Entry	X	R	Het-NH	Product ^a	Time (h)	Yield ^b (%)	M. P (°C) [Ref.]	TON/TOF
1	I	H	Py	2a	10	86	59–61 [20]	54/0.09
2	Br	H	Py	2a	12	80	59–61 [20]	50/0.07
3	I	H	Ind	2b	10	89	Liquid [20]	56/0.09
4	Br	H	Ind	2b	12	84	Liquid [20]	53/0.07
5	I	H	Car	2c	10	91	88–92 [20]	57/0.09
6	Br	H	Car	2c	12	82	88–92 [20]	52/0.07
7	I	H	Im	2d	15	98	Oil [53]	61/0.07
8	Br	H	Im	2d	17	95	Oil [53]	59/0.06
9	I	H	Pyzl	2e	15	94	Oil [53]	56/0.07
10	Br	H	Pyzl	2e	17	92	Oil [53]	58/0.06
11	I	4-OCH ₃	Ind	2f	10	84	58–60 [20]	53/0.09
12	Br	4-OCH ₃	Ind	2f	12	81	58–60 [20]	51/0.07
13	I	4-OCH ₃	Car	2g	10	90	154–157 [20]	56/0.09
14	Br	4-OCH ₃	Car	2g	12	83	154–157 [20]	52/0.07
15	I	4-OCH ₃	BzIm	2h	17	88	90–92 [54]	55/0.05
16	Br	4-OCH ₃	BzIm	2h	20	79	90–92 [54]	49/0.04
17	I	4-CH ₃	Pyzl	2i	15	89	Oil [55]	56/0.06
18	Br	4-CH ₃	Pyzl	2i	17	84	Oil [55]	53/0.05
19	I	2-OCH ₃	BzIm	2j	18	76	Oil [54]	48/0.04
20	Br	2-OCH ₃	BzIm	2j	20	70	Oil [54]	44/0.04
21	I	2-CH ₃	Ind	2k	12	82	Liquid [20]	51/0.07
22	Br	2-CH ₃	Ind	2k	14	77	Liquid [20]	48/0.06
23	I	naphtyl	Im	2l	15	79	Oil [20]	49/0.05
24	Br	naphtyl	Im	2l	17	71	Oil [20]	44/0.04
25	I	4-Br	Im	2m	14	70	119–121 [56]	44/0.05
26	Br	2-pyridyle	Im	2n	17	89	Oil [57]	56/0.05

^a Reaction condition: SBA supported phenanthroline copper (I) catalyst (0.07 g, 0.016 mmol), aryl halides (2 mmol), *N*–*H* heterocycles (1 mmol), K₂CO₃ (276 g, 2 mmol), toluene (5 mL), 110 °C

^b Isolated yields

TON turn over number (mol of product/mol of catalyst), TOF turn over frequency [mol of product/(mol of catalyst × reaction time)], *Py* pyrrole, *Ind* indole, *Car* carbazole, *Im* imidazole, *BzIm* Benzimidazole, *Pyzl* Pyrazole

make the media acidic [59]. 4 g of pluronic P123 triblock copolymer surfactant (EO20PO70EO20) was dissolved in water/HCl 2 M solution. Subsequently, TEOS was added. The resulting mixture was stirred for 8 h and then aged for 24 h at room temperature. The mole fraction of each component was 1 TEOS: 0.0168 P123: 5.854 HCl: 162.681 H₂O. The white product was filtered, washed and dried. Calcination was performed in an oven at 550 °C for 6 h in air atmosphere to remove the triblock copolymer organic component.

4.1.2 Synthesis of 5-(*N,N*-Bis-3-(triethoxysilyl) propyl) ureyl-1,10-phenanthroline (*phen-Si*)

The starting reagent 5-amino-1,10-phenanthroline (*phen-NH₂*) and the modified phenanthroline group (*phen-Si*) were prepared according to the procedure described perviously [45]. ¹H NMR (400 Hz, CDCl₃): δ 0.50–0.60 (m, 4H), 1.15 (t, *J* = 6.8 Hz, 18H), 1.56–1.63 (m, 4H), 3.21–3.26 (m, 4H), 3.71 (q, *J* = 6.8 Hz, 12H), 7.17 (br s, 2H), 7.69–7.72 (m, 2H), 7.89 (s, 1H), 8.24–8.29 (m, 2H), 9.24–9.28 (m, 2H).

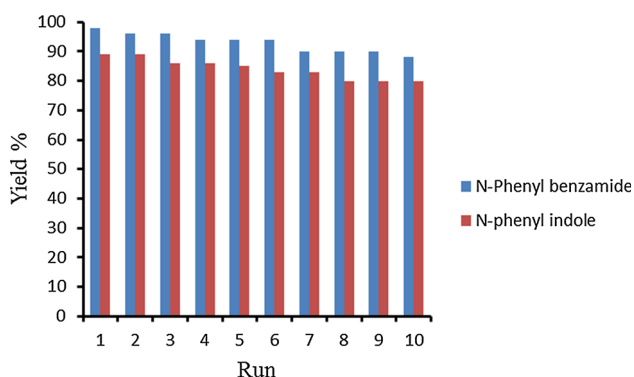
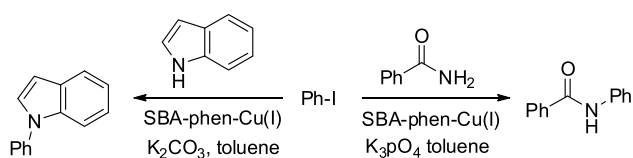


Fig. 8 Reusability of the SBA-phen-Cu(I) for *N*-arylation of benzamide and indole with iodobenzene

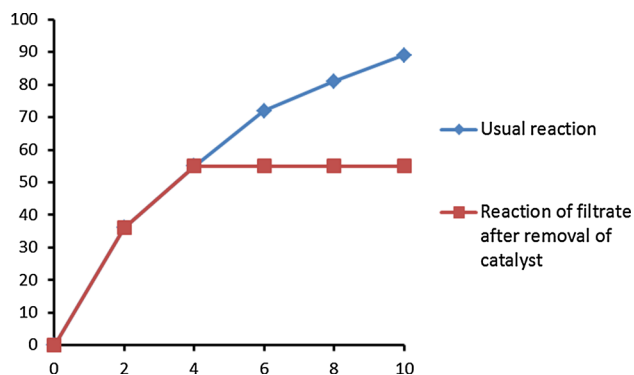


Fig. 9 Time conversion curve for the hot-filtration test

4.1.3 Modification of SBA-15 with phen-Si (SBA-phen)

0.5 g of SBA-15 was slurried in about 80 mL of anhydrous toluene. Phen-Si (0.5 mmol; 0.344 g) was dissolved in 8 mL of anhydrous CHCl_3 and added to the above mixture. The reaction mixture was stirred for 24 h under argon at reflux temperature. The reaction mixture was filtered and the collected solid was washed several times with toluene and dried overnight under vacuum.

4.1.4 Preparation of SBA-15 Immobilized Phenanthroline-Cu(I) (SBA-phen-Cu(I))

To 5.0 g of phen-SBA-15 added CuI (0.95 g, 5 mmol) in 30 mL anhydrous acetonitrile and stirred at room temperature for 24 h. A green solid was collected by filtration and washed with acetonitrile. The resulting material was transferred to a Soxhlet tube in argon. The excess CuI was

removed by Soxhlet extraction with acetonitrile for 24 h. The resulting solid is denoted as SBA-phen-Cu(I).

4.1.5 General Procedure for *N*-Arylation of Amides with Aryl Halides

To a solution of amide (1 mmol) and aryl halide (2 mmol) in toluene were added catalyst (0.05 g, 0.011 mmol) and K_3PO_4 (424 g, 2 mmol) and the mixture stirred at 110 °C for the specified time. The progress of the reaction was monitored by TLC. The reaction mixture allowed cooling to room temperature and ethyl acetate (25 mL) was added and the mixture stirred for 15 min to ensure product removal from catalyst. Then the catalyst was filtered, washed with ethyl acetate (2×25 mL). The organic layer was evaporated under vacuum on a rotary evaporator and the crude product was obtained. Further purification was achieved by column chromatography using ethyl acetate/*n*-hexane gradient. Structural assignments of the products are based on their ^1H NMR and melting point.

4.1.6 General Procedure for *N*-Arylation of *N*-*H* Heterocycle with Aryl Halides

To a solution of *N*-*H* heterocycle (1 mmol) and aryl halide (2 mmol) in toluene were added catalyst (0.07 g, 0.016 mmol) and K_2CO_3 (276 g, 2 mmol) and the mixture stirred at 110 °C for the specified time. The progress of the reaction was monitored by TLC. The reaction mixture allowed cooling to room temperature and ethyl acetate (25 mL) was added and the mixture stirred for 15 min to ensure product removal from catalyst. Then the catalyst was filtered, washed with ethyl acetate (2×25 mL). The organic layer was evaporated under vacuum on a rotary evaporator and the crude product was obtained. Further purification was achieved by column chromatography using ethyl acetate/*n*-hexane gradient. Structural assignments of the products are based on their ^1H NMR and melting point.

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