A highly efficient heterogeneous copper-catalysed cascade reaction of aryl iodides with acetamidine hydrochloride leading to primary arylamines

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A highly efficient heterogeneous copper-catalysed cascade reaction of aryl iodides with acetamidine hydrochloride was achieved in DMF in the presence of 10 mol% of an MCM-41-immobilised L-proline-copper(I) complex (MCM-41-L-proline-CuI) with Cs_2CO_3 as base, yielding a variety of primary arylamines in good to excellent yields. The new heterogeneous copper complex can be easily prepared from commercially readily available and inexpensive reagents, recovered by a simple filtration of the reaction solution and used at least seven more times without any decrease in activity.

Keywords: supported copper catalyst, cascade reaction, acetamidine hydrochloride, primary arylamine, heterogeneous catalysis, MCM-41

Primary aromatic amines are important subunits and precursors of natural products, agrochemicals, dyes, polymers and pharmaceuticals.[1–3] The traditional methods for the preparation of arylamines are based on the hydrogenation of nitro compounds catalysed by copper-, nickel- or platinum-group metals[4] and nucleophilic amination of haloarenes or phenols.[5] Although transition-metal-catalysed C–N coupling of aryl halides with ammonia has been used for the synthesis of primary arylamines, in most cases, high pressure, high temperature and sealed reaction vessels were required.[6–8] Therefore, the procedures might not be operationally simple and safe from the perspective of application. The palladium-catalysed amination of aryl halides/triflates has emerged as a powerful tool for the construction of arylamines in the past decades,[9–14] but the use of ammonia as the nitrogen source does not furnish the corresponding primary anilines due to competition between the more reactive aniline product and remaining ammonia, which results in the formation of diaryl and triaryl amines.[15–18] Various copper-catalysed aminations of aryl halides have also been developed for the preparation of primary arylamines.[19–28] However, the direct utilisation of ammonia as the amino source of primary arylamines is still ineffective in the absence of pressure thus far. Recently, proline-derived copper complexes have been reported to catalyse the aminations of aryl iodides with NH_4Cl or amidine hydrochlorides for efficient synthesis of primary arylamines.[29,30]

Although these copper-catalysed aminations of aryl halides are highly efficient for the construction of primary arylamines, about 10 mol% of copper catalysts are usually used to obtain high yields. Moreover, the majority of reported systems, in particular the systems that use homogeneous copper catalysts, have been susceptible to contamination by the cytotoxic copper ions due to the formation of copper complexes with the arylamine products, which restricts the application of such systems in electronics and biomedicine. These problems are of particular environmental and economic concern in large-scale syntheses and in industry. To overcome these drawbacks the development of highly efficient and recyclable heterogeneous catalysts, for example by immobilisation of catalytically active species onto a solid support to generate a molecular heterogeneous catalyst, is essential.[31,32]

The discovery of mesoporous MCM-41 has provided a new possible candidate for an ideal solid support for immobilising homogeneous catalysts and given an enormous stimulus to research in heterogeneous catalysis.[33,34] MCM-41 has ultrahigh surface area, large and defined pore size, big pore volume and many silanol groups in the inner walls. So far, some functionalised MCM-41-immobilised palladium,[35–39] rhodium,[40] molybdenum,[41] gold[42] and copper[43-45] complexes have been successfully used as potentially green and sustainable catalysts in organic synthesis. In continuation of our efforts to develop economical and eco-friendly synthetic pathways for organic transformations,[37–39,43–45] we report here the synthesis of the L-proline-functionalised MCM-41-immobilised copper(I) complex (MCM-41-L-proline-CuI) and its successful application to the cascade reaction of aryl iodides with acetamidine hydrochloride leading to primary arylamines. The new heterogeneous copper catalyst exhibits high catalytic activity in the reaction and can easily be recovered by a simple filtration of the reaction solution; its catalytic efficiency remains unaltered even after recycling eight times.

Results and discussion

The new MCM-41-immobilised L-proline-copper(I) complex (MCM-41-L-proline- CuI) was prepared from commercially available and inexpensive reagents according to the procedure summarised in Scheme 1. Firstly, the chloromethyl-functionalised MCM-41 material (MCM-41-CH_2Cl) was obtained by the condensation reaction of MCM-41 with 4-(chloromethyl)phenyltrichlorosilane in toluene at 100 °C for 24 h, followed by treatment with anhydrous ethanol at 80 °C for 24 h and then silylation with Me_3SiCl in toluene at room temperature for 24 h. The MCM-41-CH_2Cl was then treated with *N*-Boc-*trans*-4-hydroxy-L-proline in THF in the presence of NaH, followed by deprotection with TFA in CH_2Cl_2 to afford the L-proline-functionalised MCM-41 material (MCM-41-L-proline). Finally, the reaction of MCM-41-L-proline with CuI in acetone at room temperature for 12 h generated the MCM-41-immobilised L-proline copper(I) iodide complex (MCM-41-L-proline-CuI) as a light blue powder. The copper content of the catalyst was found to be 0.83 mmol g^{-1} according to inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements.

Small angle X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the modified material MCM-41-L-proline-CuI are presented in Fig. 1. The parent MCM-41 is a well-ordered mesoporous phase, which can be indexed according to a hexagonal lattice characteristic of MCM-41.[33] For the MCM-41-L-proline-CuI complex, the (100) reflection of MCM-41 with decreased intensity remained, while the (110) and (200)

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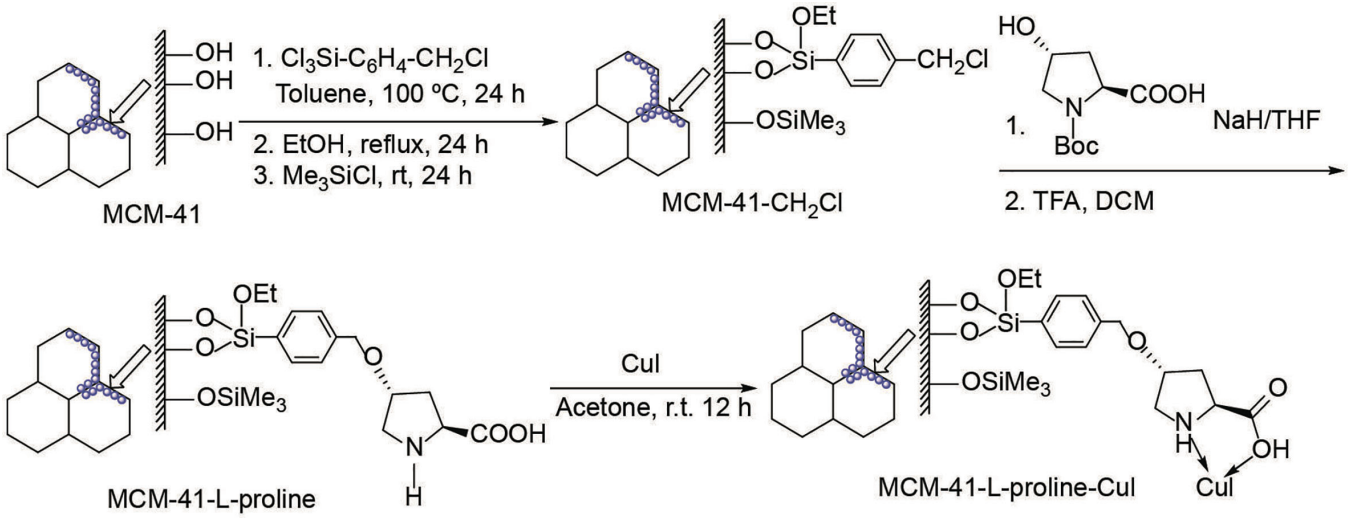


Scheme 1

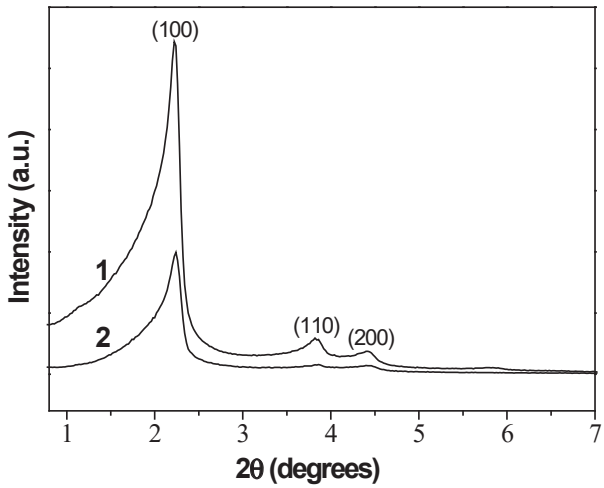


Fig. 1 XRD patterns of the parent MCM-41 (**1**) and MCM-41-L-proline-CuI (**2**).

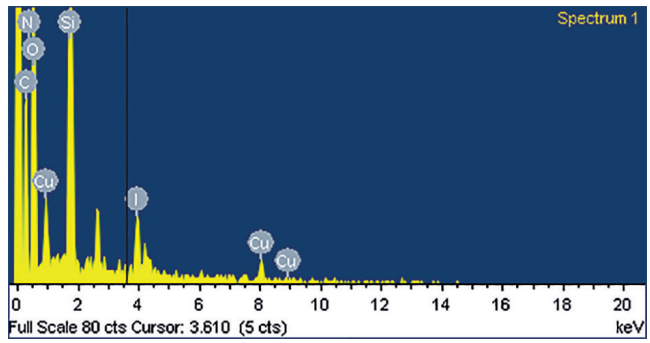
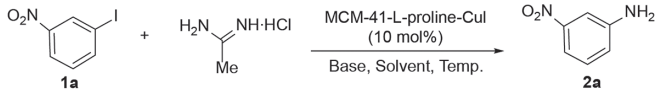


Fig. 2 Energy dispersive spectra of MCM-41-L-proline-CuI.

reflections became weak and diffuse after introduction of the copper complex, which may be mainly due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results indicate that the structure of the parent MCM-41 remains intact through the functionalisation procedure. Energy dispersive X-ray spectroscopy (EDS) shows the elements present in the material. EDS analysis of fresh MCM-41-L-proline-CuI complex shows the presence of Si, O, C, N, I, and Cu elements (Fig. 2).

The MCM-41-immobilised L-proline-copper(I) complex (MCM-41-L-proline-CuI) was then used as a catalyst for the cascade reaction of aryl iodides with acetamidine hydrochloride. Initially, 3-iodonitrobenzene (**1a**) was selected as the model substrate to optimise the reaction conditions and the results are summarised in Table 1. Firstly, the effect of temperature was examined by using 10 mol% of MCM-41-L-proline-CuI as catalyst and Cs_2CO_3 as base in dimethylformamide (DMF) under Ar (Table 1, entries 1–4). It is evident that the yield of the desired product **2a** increased with the increase in reaction temperature (110–130 °C) and that 130 ºC gave the best result (Table 1, entry 3), further raising the temperature to 140 ºC did not improve the yield (Table 1, entry 4). The effects of base and solvent on the reaction were also investigated. Among several inorganic bases tested K_2CO_3 gave a good yield, both Na_2CO_3 and K_3PO_4 were substantially less effective (Table 1,

Table 1 Optimisation of reaction conditions for the synthesis of 3-nitroaniline[a]



Entry	Base	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	Cs_2CO_3	DMF	110	24	26
2	Cs_2CO_3	DMF	120	20	79
3	Cs_2CO_3	DMF	130	20	94
4	Cs_2CO_3	DMF	140	20	93
5	K_2CO_3	DMF	130	20	87
6	Na_2CO_3	DMF	130	20	75
7	K_3PO_4	DMF	130	20	67
8	Cs_2CO_3	DMAc	130	20	81
9	Cs_2CO_3	NMP	130	20	76
10	Cs_2CO_3	DMSO	130	24	52
11	Cs_2CO_3	DMF	130	40	77[c]
12	Cs_2CO_3	DMF	130	12	94[d]

[a] Reaction conditions: 3-iodonitrobenzene (**1a**) (1 mmol), acetamidine hydrochloride (1.2 mmol), base (2 mmol), solvent (3 mL) under Ar.

[b] Isolated yield.

[c] 5 mol% MCM-41-L-proline-CuI was used.

[d] 20 mol% MCM-41-L-proline-CuI was used.

entries 5–7) and Cs_2CO_3 proved to be the best base (Table 1, entry 3). When other strong dipolar aprotic solvents such as dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP) and dimethylsulfoxide (DMSO) were used, no improvement of yield was observed and DMF gave the best result (Table 1, entries 3 and 8–10). Finally, the amount of the copper catalyst was also screened. Reducing the amount of the catalyst to 5 mol% resulted in a significant decrease in yield and a longer reaction time was required (Table 1, entry 11). Increasing the amount of the catalyst could shorten the reaction time, but did not improve the yield (Table 1, entry 12). Thus, the optimised reaction conditions for this transformation were taken as MCM-41-L-proline-CuI (10 mol%) and acetamidine hydrochloride (1.2 equiv.) in DMF with Cs_2CO_3 (2 equiv.) as base at 130 ºC under Ar for 20 h (Table 1, entry 3).

With this promising result in hand, we started to examine the scope and limitation of this heterogeneous copper-catalysed cascade reaction between aryl iodides and acetamidine hydrochloride under the optimised reaction conditions (Scheme 2) and the results are summarised in Table 2. The amination reaction of aryl iodides having strong electron-withdrawing groups **1a–g** with acetamidine hydrochloride proceeded smoothly under the optimised reaction conditions to afford the corresponding electron-deficient primary arylamines **2a–g** in good to excellent yields (Table 2, entries 1–7). However, aryl iodides having weak electron-withdrawing groups **1h–l** exhibited lower reactivity and the amination reaction was carried out with 2 equiv. of acetamidine hydrochloride to obtain good yields of the desired products **2h–l** (Table 2, entries 8–12). The reactivity of electron-rich aryl iodides was lower than that of electron-deficient ones. For example, the amination reactions of electron-rich aryl iodides **1m–r** with acetamidine hydrochloride could not proceed until the temperature was raised to 140 ºC and the use of 2 equiv. of acetamidine hydrochloride was also required to produce the corresponding electron-rich primary arylamines **2m–r** in good yields (Table 2, entries 13–18). The amination of sterically congested aryl iodides **1s–x** with acetamidine hydrochloride (1.2 or 2 equiv.) could also proceed effectively at 130 or 140 ºC to give the corresponding *ortho*-substituted primary arylamines **2s–x** in good yields (Table 2, entries 19–24). For instance, the reactions of 2-iodonitrobenzene (**1s**) and 4-iodo-1,3-dinitrobenzene (**1t**) with 1.2 equiv. of acetamidine hydrochloride at 130 ºC gave the desired **2s** and **2t** in 82 and 78% yield respectively. The amination of 2-chloroiodobenzene (**1u**) and methyl 2-iodobenzoate (**1v**) required the use of 2 equiv. of acetamidine hydrochloride and the amination of electron-rich aryl iodides **1w** and **1x** needed not only the use of 2 equiv. of acetamidine hydrochloride, but also higher temperature (140 ºC). It is noteworthy that bulky 1-iodonaphthalene (**1y**) and a hetero-aryl iodide **1z** were good substrates and afforded the expected products **2y** and **2z** in good yields (Table 2, entries 25 and 26). A range of functional groups such as methyl, methoxy, amino, fluoro, chloro, bromo, cyano, nitro, ester and ketone were tolerated well. The present method provides a simple, general and practical route to a wide variety of functionalised primary arylamines.

To determine whether the observed catalysis was due to the heterogeneous catalyst MCM-41-L-proline-CuI or to a leached copper species in solution, the amination of 4-iodonitrobenzene (**1b**) was carried out until an approximately 50% conversion of **1b** was reached. Then the MCM-41-L-proline-CuI was removed from the reaction mixture by hot filtration[46] and the filtrate was again stirred at 130 ºC under an Ar atmosphere for 14 h. In this case, no significant increase in conversion of **1b** was observed, indicating that leached copper species from the MCM-41-L-proline-CuI (if any) are not responsible for the observed catalysis. ICP-AES analysis showed that no copper species could be detected in the filtrate. These results demonstrated that the heterogeneous MCM-41-L-proline-CuI complex was stable during the reaction and the amination reaction catalysed by copper was intrinsically heterogeneous.

A plausible mechanism for heterogeneous copper-catalysed formation of primary arylamines is proposed in Scheme 3. Firstly, reaction of acetamidine hydrochloride with Cs_2CO_3 produces free acetamidine and water. Oxidative addition of

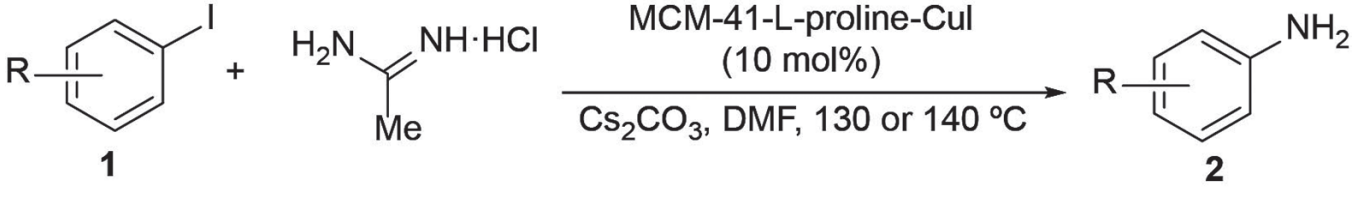
Table 2 Heterogeneous copper-catalysed synthesis of primary arylamines by the cascade reaction of aryl iodides with acetamidine hydrochloride[a]

Entry	ArI	Temp. (ºC)	Product	Yield[b] (%)
1	3-$O_2NC_6H_4I$ (**1a**)	130	3-$O_2NC_6H_4NH_2$ (**2a**)	94
2	4-$O_2NC_6H_4I$ (**1b**)	130	4-$O_2NC_6H_4NH_2$ (**2b**)	92
3	4-NCC_6H_4I (**1c**)	130	4-$NCC_6H_4NH_2$ (**2c**)	90
4	4-$MeCOC_6H_4I$ (**1d**)	130	4-$MeCOC_6H_4NH_2$ (**2d**)	88
5	4-$PhCOC_6H_4I$ (**1e**)	130	4-$PhCOC_6H_4NH_2$ (**2e**)	86
6	4-$MeOCOC_6H_4I$ (**1f**)	130	4-$MeOCOC_6H_4NH_2$ (**2f**)	85
7	3-$MeCOC_6H_4I$ (**1g**)	130	3-$MeCOC_6H_4NH_2$ (**2g**)	82
8[c]	4-FC_6H_4I (**1h**)	130	4-$FC_6H_4NH_2$ (**2h**)	78
9[c]	4-ClC_6H_4I (**1i**)	130	4-$ClC_6H_4NH_2$ (**2i**)	82
10[c]	3-ClC_6H_4I (**1j**)	130	3-$ClC_6H_4NH_2$ (**2j**)	76
11[c]	4-BrC_6H_4I (**1k**)	130	4-$BrC_6H_4NH_2$ (**2k**)	77
12[c]	3-BrC_6H_4I (**1l**)	130	3-$BrC_6H_4NH_2$ (**2l**)	72
13[c]	4-MeC_6H_4I (**1m**)	140	4-$MeC_6H_4NH_2$ (**2m**)	75
14[c]	3-MeC_6H_4I (**1n**)	140	3-$MeC_6H_4NH_2$ (**2n**)	76
15[c]	4-$MeOC_6H_4I$ (**1o**)	140	4-$MeOC_6H_4NH_2$ (**2o**)	81
16[c]	3-$MeOC_6H_4I$ (**1p**)	140	3-$MeOC_6H_4NH_2$ (**2p**)	78
17[c]	3,4-$Me_2C_6H_3I$ (**1q**)	140	3,4-$Me_2C_6H_3NH_2$ (**2q**)	73
18[c]	4-$H_2NC_6H_4I$ (**1r**)	140	4-$H_2NC_6H_4NH_2$ (**2r**)	92
19	2-$O_2NC_6H_4I$ (**1s**)	130	2-$O_2NC_6H_4NH_2$ (**2s**)	82
20	2,4-$(O_2N)_2C_6H_3I$ (**1t**)	130	2,4-$(O_2N)_2C_6H_3NH_2$ (**2t**)	78
21[c]	2-ClC_6H_4I (**1u**)	130	2-$ClC_6H_4NH_2$ (**2u**)	74
22[c]	2-$MeOCOC_6H_4I$ (**1v**)	130	2-$MeOCOC_6H_4NH_2$ (**2v**)	76
23[c]	2-$MeOC_6H_4I$ (**1w**)	140	2-$MeOC_6H_4NH_2$ (**2w**)	73
24[c]	2-MeC_6H_4I (**1x**)	140	2-$MeC_6H_4NH_2$ (**2x**)	70
25[c]	1-Naphthyl iodide(**1y**)	140	1-Naphthylamine (**2y**)	68
26[c]	2-Pyridinyl iodide (**1z**)	130	Pyridin-2-amine (**2z**)	81

[a] Reaction conditions: aryl iodide **1** (1 mmol), acetamidine hydrochloride (1.2 mmol), Cs_2CO_3 (2 mmol), MCM-41-L-proline-CuI (0.1 mmol), DMF (3 mL) under Ar for 20 h.

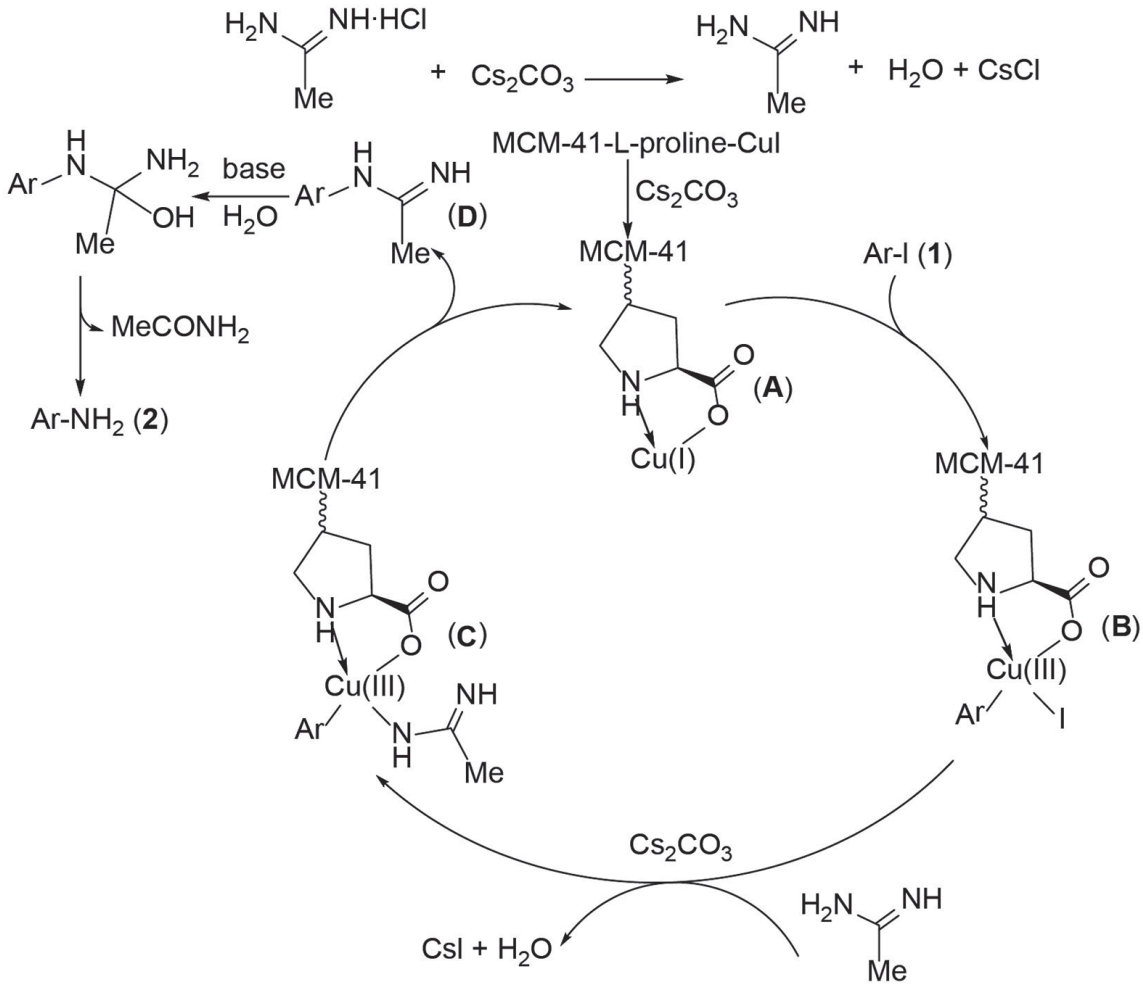
[b] Isolated yield.

[c] Acetamidine hydrochloride (2 mmol) and Cs_2CO_3 (3 mmol) were used.



1 **2**

Scheme 2



Scheme 3

aryl iodide **1** to the MCM-41-L-proline-Cu(I) complex **A** provides an MCM-41-immobilised L- proline–Ar–Cu(III)–I complex intermediate **B**, which reacts with free acetamidine in the presence of Cs_2CO_3 to form intermediate **C**. The latter undergoes a reductive elimination to give intermediate **D** and regenerates the MCM-41-L-proline-Cu(I) complex **A**. Finally, intermediate **D** undergoes addition with water in base medium and subsequent removal of acetamide to afford the target product **2**. During the purification of the product, acetamide could be isolated as a white solid in support of the proposed mechanism.

For the practical application of a heterogeneous transition-metal catalyst system, its stability and recyclability are important factors. We next investigated the reusability of the MCM-41-L-proline-CuI complex by using the amination reaction of 3-iodonitrobenzene (1.0 mmol) with acetamidine hydrochloride (1.2 mmol) and Cs_2CO_3 (2 mmol) in the presence of MCM-41-L-proline-CuI (0.1 mmol) in DMF (3 mL) at 130 ºC under Ar for 20 h. After completion of the reaction, the catalyst was separated by simple filtration of the reaction solution and washed with distilled water and EtOH. After being air-dried, it was reused directly without further purification in the next run and almost consistent activity was observed for eight consecutive reactions (Fig 3). In addition, copper leaching in the supported catalyst was also determined. The copper content of the catalyst was found by ICP-AES analysis to be 0.82 mmol g^{-1} after eight consecutive reactions and only 1.2% of copper had been lost from the MCM-41 support. The high stability and excellent reusability of the catalyst can be attributed to the chelating action of the bidentate L-proline ligand on copper and the mesoporous structure of the MCM-41 support. The result is important from industrial and environmental points of view. The high catalytic activity and excellent reusability of the new MCM-41-L-proline-CuI complex make it a highly attractive heterogeneous copper catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

In conclusion, we have successfully developed a novel, practical and environmentally friendly method for the synthesis

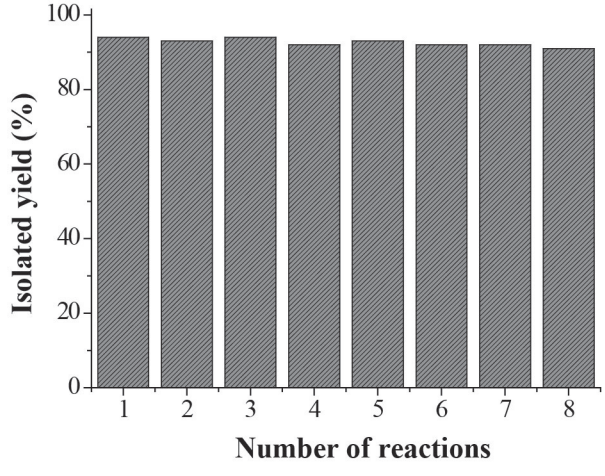


Fig. 3 Recycling of the MCM-41-L-proline-CuI catalyst.

of primary arylamines through the amination reaction of aryl iodides with acetamidine hydrochloride as the ammonia surrogate in DMF by using an MCM-41-immobilised L-proline-copper(I) complex (MCM-41-L-proline-CuI) as catalyst. The reactions were performed under simple and safe experimental conditions and generated a variety of primary arylamines in good to excellent yields and were applicable to a range of aryl iodides. Importantly, this new heterogeneous copper catalyst can be easily prepared from commercially available and inexpensive reagents, recovered by a simple filtration and used at least seven more times without a significant loss of activity, thus making this procedure economically and environmentally more acceptable.

Experimental

All chemicals were reagent grade and used as purchased. All solvents were dried and distilled before use. The products were purified by flash chromatography on silica gel. A mixture of light petroleum ether (30–60 °C) and ethyl acetate was generally used as eluent. All products were characterised by comparison of their spectra and physical data with authentic samples. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard in DMSO-d_6 or $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer in $CDCl_3$ as solvent. Melting points are uncorrected. Copper content was determined with by ICP-AES using an Atomscan16 instrument (TJA Corporation). Microanalyses were carried out using a Yanaco MT-3 CHN microelemental analyser. XRD patterns were obtained on a Damx-rA instrument (Rigaku). EDS was performed using a JSM-6510 scanning electron microscope. Mesoporous material MCM-41 was prepared according to a literature method.[47]

Synthesis of MCM-41-CH_2Cl

A solution of 4-(chloromethyl)phenyltrichlorosilane (5.0 g) in dry toluene (20 mL) was added to a suspension of MCM-41 (5.5 g) in dry toluene (100 mL). The mixture was stirred for 24 h at 100 °C under Ar. Then the solid was filtered off, washed with $CHCl_3$ (20 mL) and dried under reduced pressure at 100 °C for 2 h. The dried white solid was then treated with dry ethanol (50 mL) at 80 °C for 5 h under Ar. The solid product was filtered off, washed with diethyl ether (3 × 20 mL) and then soaked in a solution of Me_3SiCl (5.0 g) in dry toluene (100 mL) at room temperature with stirring for 24 h. Then the solid was filtered off, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL) and dried under reduced pressure at 120 °C for 5 h to obtain the hybrid material MCM-41-CH_2Cl (7.43 g). The chlorine content was found to be 1.65 mmol g^{-1} by elemental analysis.

Synthesis of MCM-41-L-proline

NaH (0.28 g, 11.6 mmol) was added to a solution of *N*-Boc-*trans*-4-hydroxy- L-proline (1.27 g, 5.5 mmol) in dry THF (100 mL) and the reaction mixture was stirred at room temperature for 2 h under Ar. Then MCM-41-CH_2Cl (2.23 g) was added and the mixture was refluxed for 24 h. After being cooled to room temperature, the solid was filtered off, washed with distilled water (2 × 20 mL) and ethanol (2 × 20 mL) and then dried under reduced pressure at 100 °C for 5 h. The white solid (1.5 g) was treated with TFA (8 mL) in CH_2Cl_2 (10 mL) at reflux for 3 h and then filtered off. It was washed with Et_3N (6 mL), CH_2Cl_2 (10 mL) and Et_2O (10 mL) and then dried under reduced pressure at 100 °C for 5 h to afford the hybrid material MCM-41-L-proline (1.27 g). The nitrogen content was found to be 1.06 mmol g^{-1} by elemental analysis.

Synthesis of MCM-41-L-proline-CuI

In a small Schlenk tube, the L-proline-functionalised MCM-41 (MCM-41-L-proline) (1.10 g) was mixed with CuI (0.19 g, 1.0 mmol) in dry acetone (10 mL). The mixture was stirred at room temperature for 12 h under Ar. The solid product was filtered off by suction, washed with acetone and dried at 60 °C/26.7 Pa under Ar for 5 h to give the copper complex (MCM-41-L-proline-CuI) (1.15 g) as a light blue powder. The copper content was found to be 0.83 mmol g^{-1}.

Heterogeneous copper-catalysed synthesis of primary arylamines; general procedure

A two-necked flask equipped with a magnetic stirring bar was charged with Cs_2CO_3 (2 or 3 mmol), MCM-41-L-proline-CuI (0.1 mmol), aryl iodide (1.0 mmol), acetamidine hydrochloride (1.2 or 2 mmol) and DMF (3.0 mL) under Ar. The reaction mixture was stirred at 130 or 140 ºC for 20 h. After being cooled to room temperature, the mixture was diluted with CH_2Cl_2 (10 mL) and filtered. The catalyst was washed with distilled water (2 × 5 mL) and EtOH (2 × 5 mL) and air-dried when reused in the next run. The filtrate was concentrated with the aid of a rotary evaporator and the residue was purified by column chromatography on silica gel using petroleum ether (30–60 °C)/ethyl acetate (10:1 to 1:1) as eluent to give the desired product **2**. All the products **2a–z** are known compounds.

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Electronic Supplementary Information

The ESI (characterisation details of the products) is available through
stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data

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