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A highly efficient heterogeneous copper-catalyzed cascade reaction of 2-halobenzoic acids and amidines leading to quinazolinones†

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The heterogeneous cascade reaction of 2-halobenzoic acids and amidines was achieved in DMF at 60 °C in the presence of 10 mol% of MCM-41-immobilized tridentate nitrogen copper(I) complex [MCM-41-3N–CuI] using Cs_2CO_3 as base, yielding a variety of quinazolinone derivatives in good to excellent yields. This heterogeneous copper catalyst can be easily prepared from commercially available and inexpensive reagents, and recovered by a simple filtration of the reaction solution and reused for at least 10 times without any decreases in activity.

Introduction

The quinazolinone scaffold is present in a plethora of natural products such as luotonin A, 2-methyl-4(3*H*)-quinazolinone, 2-(4-hydroxybutyl)quinazolin-4-one, and bouchardatine.[1] Many quinazolinone derivatives are proven to have useful biological and medicinal activities and can be used as hypnotic, sedative, analgesic, anti-convulsant, antitussive, antibacterial, antidiabetic, anti-inflammatory, and antitumor agents.[2] Therefore, considerable attention has been devoted to the development of efficient and practical methods for their construction. The traditional methods for the synthesis of quinazolinone derivatives depend on the requisite starting materials *ortho*-amino- or -nitrobenzoic acid derivatives, which are not readily available or are difficult to prepare.[2a,b,3] Recently, the copper-catalyzed Ullmann-type *N*-arylations have attracted much attention[4] and have been widely used to prepare N-heterocycles.[5] However, these methods are not suitable for preparing some quinazolinone derivatives due to too high reaction temperatures. Therefore, the development of milder copper-catalyzed *N*-arylations is highly desirable. The groups of Buchwald and Fu have developed copper-catalyzed *N*-arylations at room temperature by using suitable ligands.[6]

Recently, Fu and co-workers have developed a novel copper-catalyzed cascade reaction for the synthesis of quinazolinone derivatives from 2-halobenzoic acids and amidines in the absence of ligands or additives [eqn (1), in Scheme 1].[7] In the presence of 20 mol% CuI, the tandem reaction of 2-halobenzoic acids with amidines in DMF with Cs_2CO_3 as base at room temperature gave quinazolinone derivatives in good to excellent yields. Although the ligand-free copper-catalyzed cascade reaction of 2-halobenzoic acids with amidines is highly efficient, 20 mol% of CuI was used to obtain high yields. Moreover, the problem with homogeneous catalysis is the difficulty to separate the catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. It is generally accepted that homogeneous catalysis might result in heavy metal contamination of the desired isolated product, which is a particularly significant drawback for its application in the pharmaceutical industry. These problems are of particular environmental and economic concerns in large-scale syntheses and in industry. To overcome these problems, the development of highly efficient and recyclable heterogeneous catalysts, for example by immobilization of catalytically active species onto a solid support to produce a molecular heterogeneous catalyst is essential.[8] Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes.[9] In spite of tremendous effort dedicated to the immobilization of homogeneous palladium complexes over the last two decades,[10] the carbon–carbon or carbon-heteroatom bond formation reactions catalyzed by heterogeneous copper catalysts have received less attention[11] apart from many examples of azide–alkyne cycloaddition reactions promoted by heterogeneous copper systems.[12] Therefore, the development of a stable heterogeneous copper catalyst that allows for highly efficient synthesis of quinazolinone derivatives from a wide range of substrates (2-halobenzoic acids and amidines) is worthwhile.

The discovery of mesoporous material MCM-41 has given an enormous stimulus to research in heterogeneous catalysis and provided a new possible candidate for a solid support for

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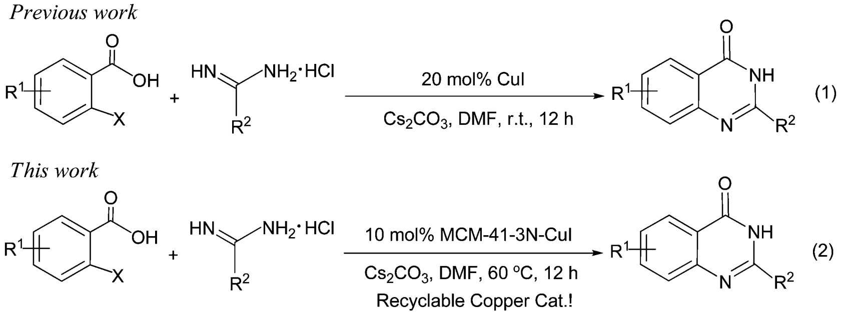


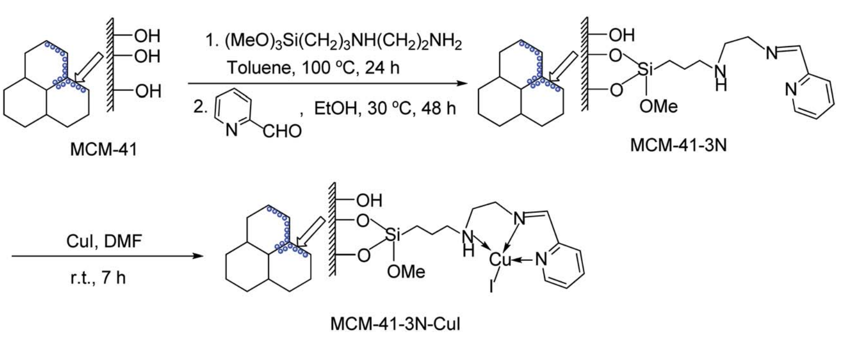
Scheme 1 Synthesis of quinazolinone derivatives *via* copper-catalyzed cascade reaction of 2-halobenzoic acids and amidines.

immobilizing homogeneous catalysts.[13] The hexagonally-ordered material MCM-41 has large and uniform pore size, ultrahigh surface area, big pore volume and rich silanol groups in the inner walls.[14] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach the surface of the channel.[15] To date, some functionalized MCM-41-immobilized palladium or rhodium complexes have been prepared and successfully used in organic reactions.[16] Recently, we have reported the first synthesis of 3-(2-aminoethylamino)-propyl-functionalized MCM-41-immobilized copper(I) complex and found that it is a highly efficient and recyclable heterogeneous catalyst for the homo- and heterocoupling of terminal alkynes[11e] and Buchwald *N*-arylation reaction of indoles with aryl halides.[11f] In continuing our efforts to develop greener synthetic pathways for organic transformations, herein we wish to report a highly efficient, heterogeneous cascade reaction of 2-halobenzoic acids and amidines catalyzed by an MCM-41-immobilized tridentate nitrogen copper(I) complex [MCM-41-3N–CuI] with Cs_2CO_3 as base and DMF as solvent [eqn (2), in Scheme 1].

Results and discussion

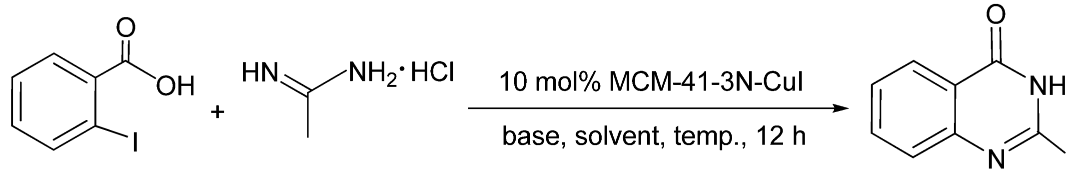
The novel MCM-41-immobilized tridentate nitrogen copper(I) complex [MCM-41-3N–CuI] was conveniently prepared from commercially available and inexpensive 3-(2-aminoethylamino)-propyltrimethoxysilane *via* immobilization on MCM-41, followed by reacting with pyridine-2-carboxaldehyde and CuI (Scheme 2). Firstly, the mesoporous material MCM-41 reacted with 3-(2-aminoethylamino)propyltrimethoxysilane in toluene at 100 °C for 24 h, followed by the condensation with pyridine-2-carboxaldehyde in dry ethanol at 30 °C for 48 h to give the tridentate nitrogen-functionalized MCM-41 (MCM-41-3N). The latter was subsequently treated with CuI in DMF at room temperature for 7 h to generate an MCM-41-immobilized tridentate nitrogen copper(I) complex [MCM-41-3N–CuI] as pale blue powder, the copper content of the catalyst was found to be 0.47 mmol g^{-1} according to the ICP-AES measurements.

In our initial screening experiments, the coupling of 2-iodobenzoic acid with acetamidine hydrochloride was chosen as the model reaction to optimize the reaction conditions, which include base, solvent, and reaction temperature and the results are summarized in Table 1. At first, the temperature effect was examined by using Cs_2CO_3 (2.0 equiv.) as the base in DMF (Table 1, entries 1–4). The reaction at 60 °C gave the best result and other temperatures were substantially less effective. Our next studies focused on the effect of base on the model reaction. It is evident that good to excellent yields were obtained when Na_2CO_3, Cs_2CO_3, K_2CO_3, K_3PO_4 and Na_3PO_4 were used as the base and Cs_2CO_3 was the most effective (Table 1, entries 3 and 4–8), whereas Et_3N, NaOAc, and KF afforded low yields (Table 1, entries 9–11), so Cs_2CO_3 was finally selected as the base for the reaction. The effect of the solvent on the model reaction was also investigated (Table 1, entries 3 and 12–19). Among the solvents examined, DMF was found to be the best choice (Table 1, entry 3), DMAc, MeCN and DMSO also afforded good yields (Table 1, entries 12–14). While other solvents such as toluene, EtOH, and i-PrOH were substantially less effective



Scheme 2 Preparation of MCM-41-3N–CuI complex.

Table 1 Heterogeneous copper-catalyzed coupling of 2-iodobenzoic acid with acetamidine hydrochloride: optimization of reaction conditions[a]



Entry	Base	Solvent	Temp. (°C)	Yield[b] (%)
1	Cs_2CO_3	DMF	25	18
2	Cs_2CO_3	DMF	40	78
3	Cs_2CO_3	DMF	60	96
4	Cs_2CO_3	DMF	80	90
5	K_2CO_3	DMF	60	89
6	Na_2CO_3	DMF	60	82
7	K_3PO_4	DMF	60	86
8	Na_3PO_4	DMF	60	84
9	KF	DMF	60	34
10	NaOAc	DMF	60	37
11	Et_3N	DMF	60	29
12	Cs_2CO_3	MeCN	60	87
13	Cs_2CO_3	DMSO	60	83
14	Cs_2CO_3	DMAc	60	81
15	Cs_2CO_3	Toluene	60	67
16	Cs_2CO_3	EtOH	60	72
17	Cs_2CO_3	i-PrOH	60	65
18	Cs_2CO_3	Dioxane	60	Trace
19	Cs_2CO_3	THF	60	Trace
20[c]	Cs_2CO_3	DMF	60	57
21[d]	Cs_2CO_3	DMF	60	64

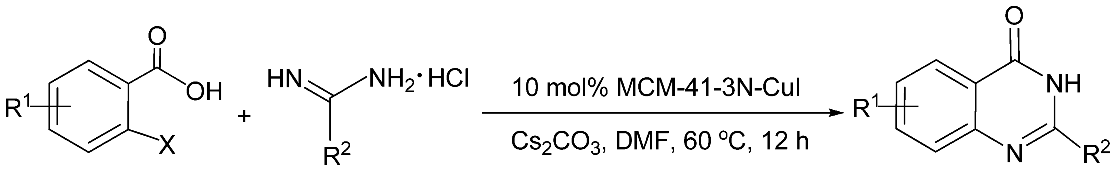
[a] Reaction conditions: 2-iodobenzoic acid (0.5 mmol), acetamidine hydrochloride (0.75 mmol), MCM-41-3N–CuI (0.05 mmol), base (1 mmol), solvent (3 mL) under Ar for 12 h. [b] Yield of isolated product. [c] MCM-41-3N–CuI (0.025 mmol) was used. [d] Cs_2CO_3 (0.5 mmol) was used.

(Table 1, entries 15–17) and THF and dioxane were ineffective (Table 1, entries 18 and 19). Reducing the amount of the catalyst or base resulted in a decrease in yield (Table 1, entries 20 and 21). Thus, the optimized reaction conditions for this transformation are the MCM-41-3N–CuI (10 mol%) in DMF using Cs_2CO_3 (2.0 equiv.) as base at 60 °C under Ar for 12 h (Table 1, entry 3).

With this promising result in hand, we started to investigate the scope of this cascade reaction under the optimized conditions. The scope of both 2-halobenzoic acids and amidines was explored, and the results are summarized in Table 2. As shown in Table 2, the cascade reactions of 2-iodobenzoic acid **1a** with a variety of amidines **2a–e** proceeded smoothly under mild conditions affording the corresponding quinazolinone derivatives **3a–3e** in excellent yields (Table 2, entries 1–5). Although the reactivity of aryl bromides was lower than that of aryl iodides in copper-catalyzed *N*-arylation,[4,5] 2-bromobenzoic acid **1b** and substituted 2-bromobenzoic acids **1c–g** are also good substrates and the cascade reactions of 2-bromobenzoic acids **1b–g** with a variety of amidines performed effectively under the optimized conditions, affording the corresponding quinazolinone derivatives **3a** and **3f–3y** in good to excellent yields (Table 2, entries 6–26). 2-Chlorobenzoic acid **1h** is weak substrate in this reaction and gave lower yields, however, good yields were obtained when the reaction was carried out at 80 °C for 24 h (Table 2, entries 27 and 28). The *N*-arylation of 2-bromo-5-chlorobenzoic acid **1c** with amidines occurred selectively at the C–Br bond *ortho* to the carboxyl group, indicating that there is an *ortho*-substituent effect in this reaction. Generally, the electronic natures of the substituent on the 2-bromobenzoic acids have limited influence on this heterogeneous copper-catalyzed cascade reaction and various electron-withdrawing and electron-donating substituents such as nitro, chloro, fluoro, and methyl were well tolerated. As for amidines, they are all good substrates and no obvious reactivity difference was observed. It is well known that quinazolinones can be readily transformed into the corresponding quinazolines, which have various biological and medicinal activities,[17] so our catalytic system provides a novel, practical and environmentally friendly method for the synthesis of a diverse array of quinazolinone and quinazoline derivatives.

To verify whether the observed catalysis was due to the heterogeneous catalyst MCM-41-3N–CuI or to a leached copper species in solution, we performed the hot filtration test.[18] We focused on the cascade reaction of 2-iodobenzoic acid with acetamidine hydrochloride. We filtered off the MCM-41-3N–CuI

Table 2 Heterogeneous copper-catalyzed synthesis of quinazolinone derivatives[a]



1 + **2** → **3**

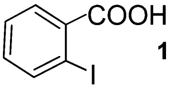
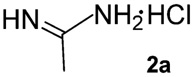
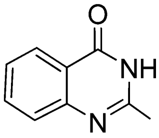
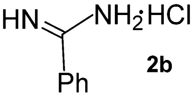
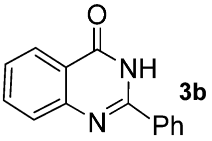
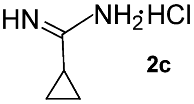
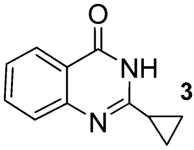
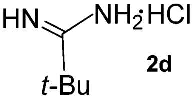
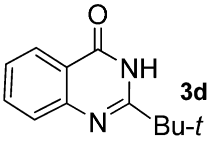
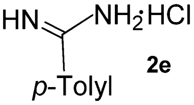
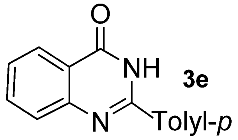
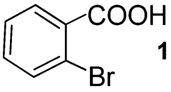
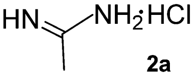
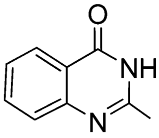
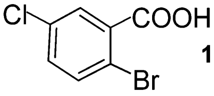
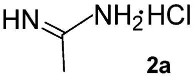
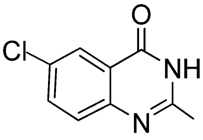
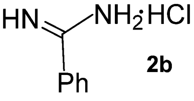
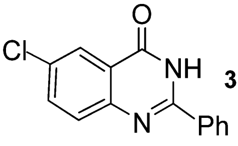
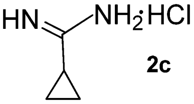
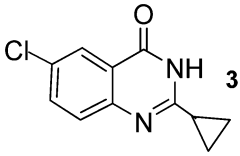
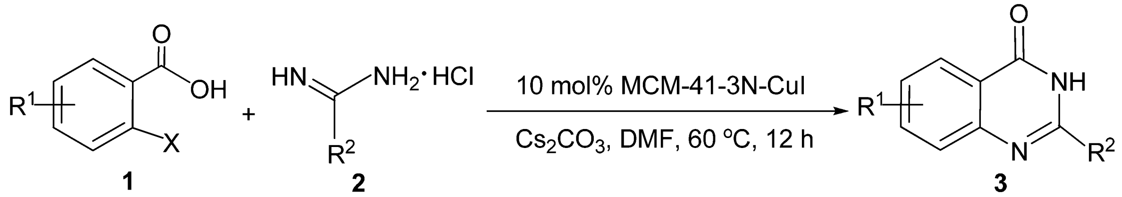
Entry	2-Halobenzoic acid	Amidine	Product	Yield[b] (%)
1	 **1a**	 **2a**	 **3a**	96
2	**1a**	 **2b**	 **3b**	99
3	**1a**	 **2c**	 **3c**	97
4	**1a**	 **2d**	 **3d**	98
5	**1a**	 **2e**	 **3e**	95
6	 **1b**	 **2a**	 **3a**	87
7	 **1c**	 **2a**	 **3f**	88
8	**1c**	 **2b**	 **3g**	71
9	**1c**	 **2c**	 **3h**	80

Table 2 (*Contd.*)



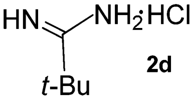
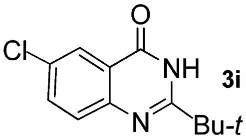
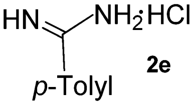
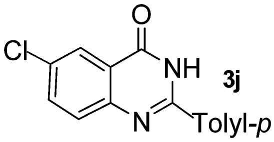
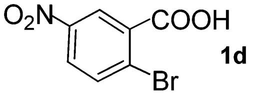
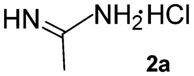
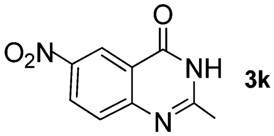
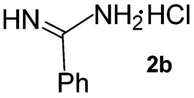
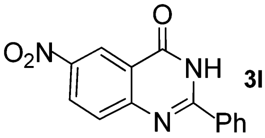
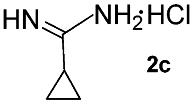
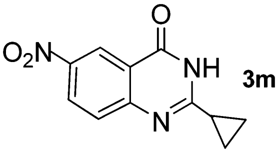
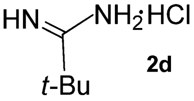
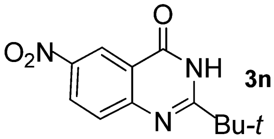
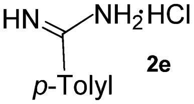
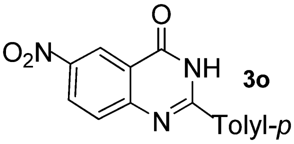
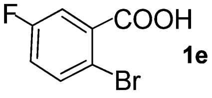
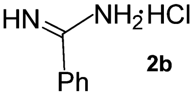
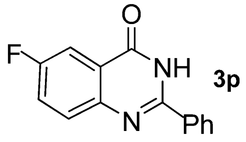
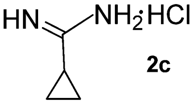
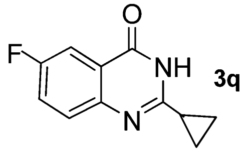
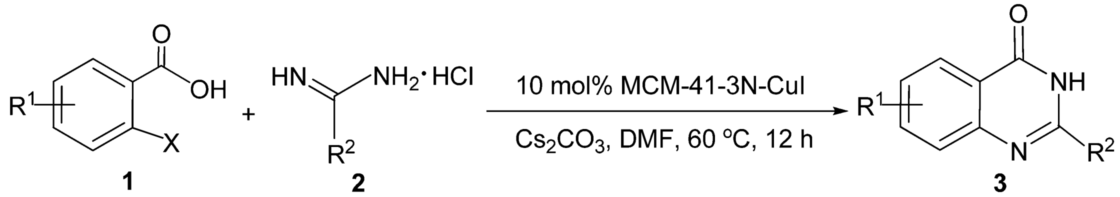
Entry	2-Halobenzoic acid	Amidine	Product	Yield^b (%)
10	**1c**	 **2d**	 **3i**	84
11	**1c**	 **2e**	 **3j**	88
12	 **1d**	 **2a**	 **3k**	72
13	**1d**	 **2b**	 **3l**	78
14	**1d**	 **2c**	 **3m**	71
15	**1d**	 **2d**	 **3n**	80
16	**1d**	 **2e**	 **3o**	83
17	 **1e**	 **2b**	 **3p**	95
18	**1e**	 **2c**	 **3q**	87

Table 2 (*Contd.*)



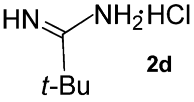
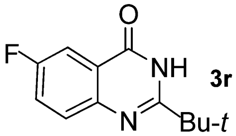
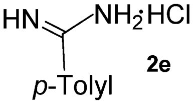
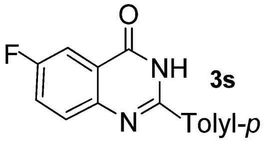
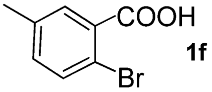
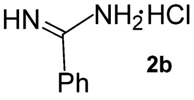
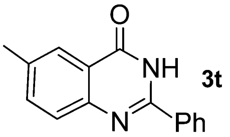
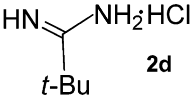
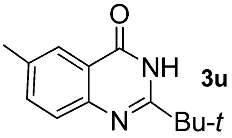
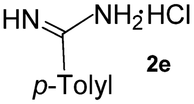
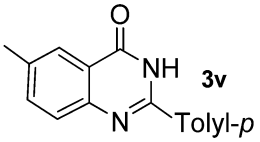
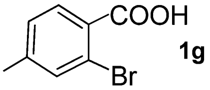
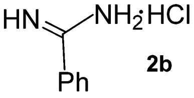
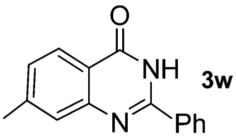
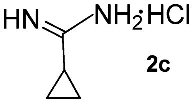
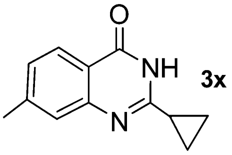
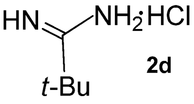
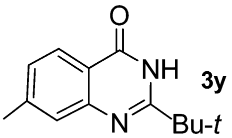
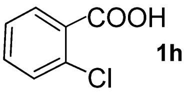
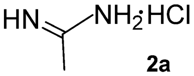
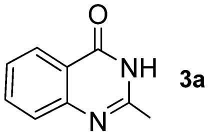
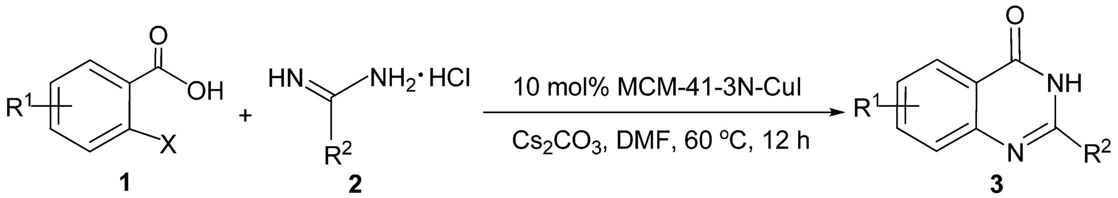
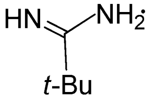
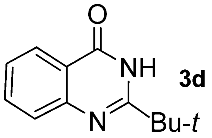
Entry	2-Halobenzoic acid	Amidine	Product	Yield^b (%)
19	**1e**	 **2d**	 **3r**	94
20	**1e**	 **2e**	 **3s**	89
21	 **1f**	 **2b**	 **3t**	87
22	**1f**	 **2d**	 **3u**	92
23	**1f**	 **2e**	 **3v**	85
24	 **1g**	 **2b**	 **3w**	87
25	**1g**	 **2c**	 **3x**	90
26	**1g**	 **2d**	 **3y**	95
27	 **1h**	 **2a**	 **3a**	76^c

Table 2 (*Contd.*)



Entry	2-Halobenzoic acid	Amidine	Product	Yield[b] (%)
28	**1h**	 **2d**	 **3d**	85[c]

[a] Reaction conditions: 2-halobenzoic acid (0.5 mmol), amidine (0.75 mmol), MCM-41-3N–CuI (0.05 mmol), Cs_2CO_3 (1 mmol), DMF (3 mL) at 60 °C under Ar for 12 h. [b] Yield of isolated product. [c] Reaction was performed at 80 °C for 24 h.

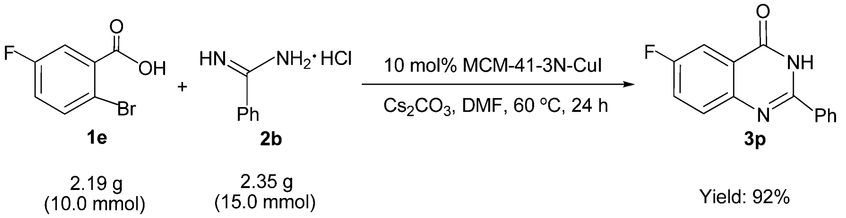
complex after 4 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (60 °C) in order to avoid possible recoordination or precipitation of soluble copper upon cooling. We found that, after this hot filtration, no further reaction was observed, indicating that leached copper species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that no copper could be detected in the hot filtered solution. This result suggests that the copper catalyst remains on the support at elevated temperature during the reaction.

In order to further show the practical utility of this heterogeneous copper-catalyzed cascade reaction of 2-halobenzoic acids and amidines for the synthesis of quinazolinone derivatives, we next explored the possibility for large-scale synthesis. As shown in Scheme 3, we scaled up the reaction of 2-bromo-5-fluorobenzoic acid (**1e**) to 2.19 g (10.0 mmol) in the presence of 10 mol% MCM-41-3N–CuI (1.0 mmol) with Cs_2CO_3 (20.0 mmol) as base and 60 mL of DMF as solvent. The reaction took place smoothly under the given conditions and the desired product **3p** was isolated in 92% yield by recrystallization from ethanol.

For a heterogeneous transition-metal catalyst, it is important to examine its ease of separation, recoverability and reusability. We therefore investigated the recyclability of the MCM-41-3N–CuI by using the cascade reaction of 2-bromo-4-methylbenzoic acid with trimethylacetamidine hydrochloride. After carrying out the reaction, the catalyst was separated by simple filtration and washed with distilled water, ethanol and diethyl ether. After being air-dried, it can be reused directly without further purification. The recovered copper catalyst was used in the next run, and almost consistent activity was observed for 10 consecutive cycles (Table 3, entries 1–10). The high stability and excellent reusability of the catalyst should result from the chelating action of tridentate nitrogen 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, excellent reusability and the easy accessibility of the MCM-41-3N–CuI complex make it a highly attractive heterogeneous copper catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

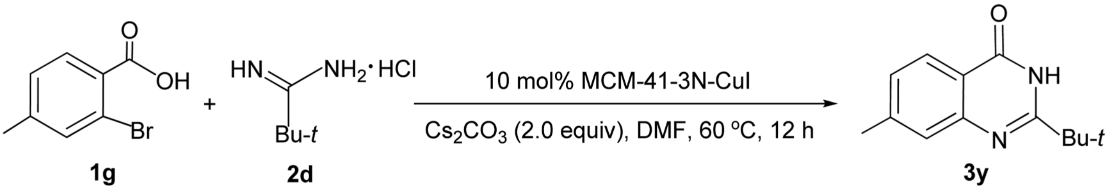
Conclusions

In summary, we have successfully developed a novel, practical and environmentally friendly method for the synthesis of quinazolinone derivatives through the cascade reaction of 2-halobenzoic acids with amidines by using an MCM-41-immobilized tridentate nitrogen copper(I) complex [MCM-41-



Scheme 3 Scaling up the reaction of 2-bromo-5-fluorobenzoic acid (**1e**) with **2b** to a multi-gram scale.

Table 3 Cascade reaction of 2-bromo-4-methylbenzoic acid with trimethylacetamidine hydrochloride catalyzed by the recycled catalyst[a]



Cycle	Yield[b] (%)	Cycle	Yield[b] (%)
1	95	2	95
3	94	4	95
5	94	6	94
7	94	8	93
9	94	10	93

[a] Reaction was carried out with **1g** (0.5 mmol), **2d** (0.75 mmol), MCM-41-3N–CuI (0.05 mmol), Cs_2CO_3 (1 mmol), DMF (3 mL) at 60 °C under Ar for 12 h. [b] Isolated yield.

3N–CuI] as catalyst with Cs_2CO_3 as base and DMF as solvent. The reactions generated a variety of quinazolinone derivatives in good to excellent yields and were applicable to various 2-halobenzoic acids and amidines. This heterogeneous copper catalyst can be conveniently prepared by a simple procedure from commercially available and inexpensive reagents. In addition, this methodology offers the competitiveness of recyclability of the catalyst without loss of catalytic activity, and the catalyst could be easily recovered and reused for at least 10 cycles, thus making this procedure 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 characterized by comparison of their spectra and physical data with authentic samples. ^1H NMR spectra were recorded on a Bruker Vance 400 (400 MHz) spectrometer with TMS as an internal standard in DMSO-d_6 as solvent. ^{13}C NMR spectra were recorded on a Bruker Vance 400 (100 MHz) spectrometer in DMSO-d_6 as solvent. Melting points are uncorrected. Copper content was determined with inductively coupled plasma atom emission Atomscan 16 (ICP-AES, TJA Corporation). Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer.

Preparation of MCM-41-3N

A solution of 1.54 g of 3-(2-aminoethylamino)propyltrimethoxysilane in 18 mL of dry chloroform was added to a suspension of 2.2 g of the MCM-41 in 180 mL of dry toluene. The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried in vacuum at 160 °C for 5 h. The dried white solid (1.725 g) was then reacted with pyridine-2-carboxaldehyde (0.251 g, 2.34 mmol) in 10 mL of dry ethanol at 30 °C for 48 h. The solid product was filtered, washed with ethanol (3 × 20 mL) and diethyl ether (20 mL), and dried in vacuum at 120 °C for 5 h to obtain 1.874 g of hybrid material MCM-41-3N. The nitrogen content was found to be 2.65 mmol g^{-1} by elemental analysis.

Preparation of MCM-41-3N–CuI

In a small Schlenk tube, 1.50 g of the above-functionalized MCM-41 (MCM-41-3N) was mixed with 0.15 g (0.78 mmol) of CuI in 15 mL of dry DMF. The mixture was stirred at room temperature for 7 h under an argon atmosphere. The solid product was filtered by suction, washed with DMF and acetone and dried at 40 °C/26.7 Pa under Ar for 5 h to give 1.543 g of a pale blue copper complex (MCM-41-3N–CuI). The nitrogen and copper contents were found to be 2.43 mmol g^{-1} and 0.47 mmol g^{-1}, respectively.

General procedure for the heterogeneous copper-catalyzed synthesis of quinazolinone derivatives

A two-neck round bottom was charged with a magnetic stirrer, evacuated and backfilled with argon. 2-Halobenzoic acid (0.5 mmol) and amidine hydrochloride (0.75 mmol) in DMF (3 mL) were added under argon atmosphere. After being stirred for 10 min, Cs_2CO_3 (1 mmol) and MCM-41-3N–CuI (106 mg, 0.05 mmol) were added and the mixture was stirred at 60 °C under argon atmosphere for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (5 mL), and filtered. The MCM-41-3N–CuI complex was washed with distilled water (2 × 5 mL), ethanol (2 × 5 mL), and Et_2O (2 × 5 mL) and reused in the next run. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether–ethyl acetate = 3 : 1 to 1 : 1) to provide the desired product.

Acknowledgements

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