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Fe_3O_4 nanoparticle-supported copper(I): magnetically recoverable and reusable catalyst for the synthesis of quinazolinones and bicyclic pyrimidinones

Lin Yu[a], Min Wang[a], Pinhua Li[a] and Lei Wang[a,b]*

A highly efficient, easily recoverable and reusable Fe_3O_4 magnetic nanoparticle-supported Cu(I) catalyst has been developed for the synthesis of quinazolinones and bicyclic pyrimidinones. In the presence of supported Cu(I) catalyst (10 mol%), amidines reacted with substituted 2-halobenzoic acids and 2-bromocycloalk-1-enecarboxylic acids to generate the corresponding *N*-heterocycle products in good to excellent yields at room temperature in DMF. In addition, the supported Cu(I) catalyst could be recovered at least 10 times without significant loss of its catalytic activity. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: supported Cu(I) catalyst; magnetic nanoparticles; amidines; 2-halobenzoic acids; quinazolinones

Introduction

The use of efficient and clean catalysts is becoming a hot research field for chemists because it represents a new strategy to meet the challenges of energy and sustainability. Although homogeneous catalysts have many advantages, such as high turnover number, good activity and selectivity, and are widely used in a variety of industries, separation of the soluble catalyst from the product and reaction medium remains difficult, especially for expensive and/or toxic heavy metal complex. Furthermore, it is essential to remove toxic metals from the final product because metal contamination is highly regulated, especially in the drug and pharmaceutical industry. Catalyst recovery and reuse are the two most important features for many green synthetic methods. Heterogenization of the existing homogeneous catalysts, thus creating a heterogeneous catalytic system, has become one powerful way to solve these problems.[1] Over the past few decades, various inorganic and organic supports have been explored, such as mesoporous silica,[2] ionic liquids[3] and polymers,[4] and the grafting of such supports with homogeneous catalysts often provides catalyst systems that can be efficiently recycled and reused by filtration or liquid/liquid extraction while keeping the inherent catalytic activity.[5]

Recently, new smart supports – magnetic nanoparticles (MNPs) – have emerged and have great potential for catalyst recovery, because magnetic separation from the reaction mixture with an external permanent magnet is typically simpler and more effective than filtration or centrifugation as it prevents loss of the catalyst.[6] In recent years, fabrication of core–shell magnetic nanoparticles made up of a magnetic iron oxide core coated by a layer of cross-linked polymer[7] or silica[8] shell has been the subject of research, since such materials combine the stabilization of magnetic nanoparticles by preventing aggregation of oxide cores together with the possibility of further functionalizing the surface for immobilization of catalysts. In particular, as robust and high-surface-area heterogeneous catalyst supports, Fe_3O_4 nanoparticles have successfully demonstrated the application of various strategies.[9]

Nitrogen-containing heterocycles, especially quinazolinone and bicyclic pyrimidinone derivatives, represent a predominant structural motif in a wide array of biologically active natural compounds, pharmaceuticals and organic functional materials.[10] There is therefore considerable attention to the development of practical methods for the synthesis of this structural element. The traditional synthetic routes to such compounds depend on the common starting materials *ortho*-amino- or -nitrobenzoic acid derivatives, which are not readily available or are difficult to prepare.[11] Alternatively, Fu[12] and others[13] have developed efficient copper-catalyzed Ullmann *N*-arylations for the preparation of *N*-heterocycles. Following that, Fu described an iron-catalyzed cascade synthesis of 1,2,4-benzothiadiazine 1,1-dioxide and quinazolinone derivatives.[14] In 2010, Liu *et al*. developed an iron/copper co-catalyzed synthesis of 2-methylquinazolin-4(3*H*)-one under microwave irradiation.[15] Most recently, Fu[16] also reported a novel and useful domino method for construction of quinazolinones using readily available α-amino acids as the nitrogen-containing motifs. All of these protocols use homogeneous

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* Correspondence to: L. Wang, Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, People's Republic of China. Email: leiwang@chnu.edu.cn

a Department of Chemistry, Huaibei Normal University, Anhui 235000, People's Republic of China

b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

catalysts. Engaged in the development of greener and sustainable pathways for organic transformations,[17] herein we wish to report an efficient magnetically recoverable and reusable Fe_3O_4 nanoparticle-supported copper(I) catalyst and its application in cascade reactions of amidines with substituted 2-halobenzoic acids and 2-bromocycloalk-1-enecarboxylic acids to synthesize *N*-heterocycles. It was found that the Fe_3O_4 nanoparticle-supported copper(I) catalyst exhibits high reactivity and a wide range of substrate applicability. Recovery of the catalyst by decantation of the reaction mixture in the presence of an external magnet is easy and efficient. We demonstrated that it is possible to recover and reuse this grafted catalyst at least 10 times without significant loss of its reactivity (Scheme 1).

Experimental

General Methods

All reactions were carried out under nitrogen atmosphere. All chemical reagents were purchased from commercial suppliers and used without further purification. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz and 100 MHz, respectively) with DMSO-d_6 or $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in hertz (Hz). IR spectra were obtained by using a Nicolet NEXUS 470 spectrophotometer. High-resolution mass spectroscopic data of the products were collected on a Waters Micromass GCT instrument.

Preparation of Fe_3O_4 Nanoparticle-Supported Copper(I) catalyst, Catal. A

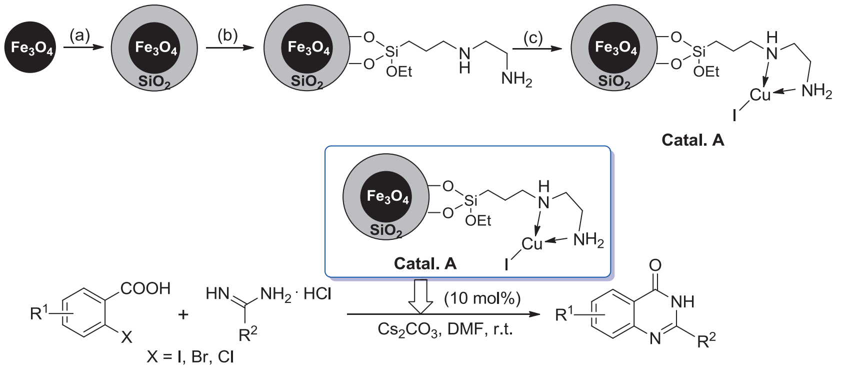
Fe_3O_4 magnetic nanoparticles (0.60 g, with an average diameter of 20 nm, purchased from Aldrich) were diluted with 8.0 ml deionized water and 40.0 ml *i*-PrOH, and the mixture was sonicated for approximately 30 min (the average diameter of Fe_3O_4 was about 10 nm according to the transmission electron microscope (TEM) image). To this well-dispersed magnetic nanoparticle solution, 1.0 g tetraethyl orthosilicate and 0.60 g [3-(2-aminoethyl) aminopropyl]trimethoxysilane in 2.0 ml *i*-PrOH was slowly added and stirred for half an hour. Then 1.5 ml $NH_3.H_2O$ was added to the mixture drop by drop with mechanical stirring for a further 5 h at room temperature. The collected material was purified by repeated washing with H_2O (5 × 2.5 ml) until the pH of the solution reached 7, and then washed with ethanol (2 × 3.0 ml) and CH_3CN (2 × 3.0 ml), respectively. The obtained nanosphere was subsequently added to CuI (0.50 mmol) in CH_3CN (10.0 ml) solution, which ultrasonically dispersed until no solid was observed. The mixture was shaken at room temperature for 4 h until the solution became clarified. Then the solid catalyst was magnetically separated, and the solid was washed thoroughly with THF (3 × 3.0 ml) and CH_3CN (2 × 3.0 ml), and dried under vacuum at 50°C for 3 h. The Fe_3O_4 nanoparticle-supported Cu(I) catalyst, **Catal. A**, was obtained with a loading of copper 0.158 mmol g^{-1} determined via inductively coupled plasma (ICP) analysis. IR (KBr, cm^{-1}): ν_{O-H} and $\nu_{N-H} = 3419$ (br), $\nu_{C-H} = 2935$, $\nu_{Si-O} = 1056$.

Typical Procedure for the Cascade Reaction of Acetamidine with 2-Iodobenzoic Acid to Synthesize Quinazolinone 3a

Under nitrogen atmosphere, a sealable reaction tube was charged with 2-iodobenzoic acid (**1a**, 0.50 mmol), acetamidine hydrochloride (**2a**, 0.75 mmol), **Catal. A** (317 mg, containing Cu 0.05 mmol), Cs_2CO_3 (1.0 mmol) and DMF (3.0 ml). The mixture was shaken at room temperature for 10 h. After magnetic separation of the catalyst, the organic material was extracted with ethyl acetate. The resulting solution was dried by Na_2SO_4, then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether–ethyl acetate, 1:1–1:3, v/v) to give the desired product quinazolinone **3a** (white solid, 78 mg, 97% yield).

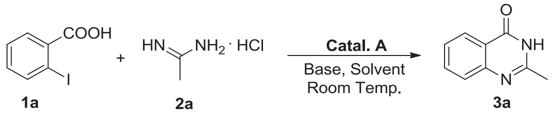
The following compounds have been characterized by comparing their ^1H and ^{13}C spectral data (see supporting information) with those reported in the literature:

2-methylquinazolin-4(3 *H*)-one (**3a**)[12a]
2-phenylquinazolin-4(3 *H*)-one (**3b**)[12a]
2-cyclopropylquinazolin-4(3 *H*)-one (**3c**)[12a]
6-fluoro-2-methylquinazolin-4(3 *H*)-one (**3d**)[18]
6-fluoro-2-phenylquinazolin-4(3 *H*)-one (**3e**)[19]
7-methoxy-2-methylquinazolin-4(3 *H*)-one (**3 g**)[20]
7-methoxy-2-phenylquinazolin-4(3 *H*)-one (**3 h**)[20]
2,8-dimethylquinazolin-4(3 *H*)-one (**3j**)[21]
8-methyl-2-phenylquinazolin-4(3 *H*)-one (**3 k**)[21]
2-methyl-5,6,7,8-tetrahydronquinazolin-4(3 *H*)-one (**3 m**)[12o]
2-phenyl-5,6,7,8-tetrahydronquinazolin-4(3 *H*)-one (**3n**)[12o]
2-cyclopropyl-5,6,7,8-tetrahydronquinazolin-4(3 *H*)-one (**3o**)[12o]
2-methyl-6-nitroquinazolin-4(3 *H*)-one (**3p**)[12a]



Scheme 1. Synthesis of magnetic nanoparticle-supported copper(I) catalyst and its application in the synthesis of quinazolinones and bicyclic pyrimidinones: (a) $Si(OEt)_4/NH_3.H_2O$; (b) $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OEt)_3$/toluene; (c) CuI/CH_3CN

Table 1. Optimization of the reaction conditions[a]



Entry	Base	Solvent	Yield[b] (%)
1	Cs_2CO_3	DMF	97
2	Na_3PO_4	DMF	90
3	K_3PO_4	DMF	85
4	Na_2CO_3	DMF	80
5	K_2CO_3	DMF	88
6	KF	DMF	31
7	NaOAc	DMF	43
8	Et_3N	DMF	30
9	Cs_2CO_3	MeOH	Trace
10	Cs_2CO_3	THF	Trace
11	Cs_2CO_3	Dioxane	Trace
12	Cs_2CO_3	EtOH	77
13	Cs_2CO_3	*i*-PrOH	69
14	Cs_2CO_3	CH_3CN	88
15	Cs_2CO_3	Toluene	83
16	Cs_2CO_3	DMA	75
17	Cs_2CO_3	DMSO	85
18	Cs_2CO_3	DMF	63[c]
19	Cs_2CO_3	DMF	72[d]
20	Cs_2CO_3	DMF	76[e]

[a] Reaction conditions: 2-iodobenzoic acid (**1a**, 0.50 mmol), acetamidine hydrochloride (**2a**, 0.75 mmol), $Fe_3O_4@SiO_2$–Cu(I) (**Catal. A**, 317 mg, containing Cu 0.05 mmol), base (1.0 mmol) in solvent (3.0 ml) at room temperature under nitrogen atmosphere for 10 h.

[b] Isolated yield.

[c] $Fe_3O_4@SiO_2$–Cu(I) catalyst (159 mg, containing Cu 0.025 mmol) was added.

[d] Cs_2CO_3 (0.50 mmol) was added.

[e] Reaction time was 6 h.

6-nitro-2-phenylquinazolin-4(3 *H*)-one (**3q**)[12a]
2-cyclopropyl-6-nitroquinazolin-4(3 *H*)-one (**3r**)[12a]

2-Cyclopropyl-6-fluoroquinazolin-4(3 *H*)-one (**3f**). White solid, m.p. 253.6–254.3°. ^{1}H NMR (400 MHz, DMSO-d$_6$): $\delta = 12.46$ (s, br, 1 H, N-*H*), 7.65–7.62 (m, 1 H, Ar-*H*), 7.51–7.46 (m, 2 H, Ar-*H*), 1.94–1.90 (m, 1 H, -C*H*), 1.10–0.97 (m, 4 H, -C*H$_2$*); ^{13}C NMR (100 MHz, DMSO-d$_6$): $\delta = 161.4$, 159.6 (d, $J_{C-F} = 242.8$ Hz), 158.8, 146.4, 129.6, 122.9 (d, $J_{C-F} = 20.6$ Hz), 122.1, 110.6 (d, $J_{C-F} = 22.7$ Hz), 13.8, 9.8. Elemental analysis: Calcd for $C_{11}H_9N_2OF$: C, 64.70; H, 4.44; N, 13.72%. Found: C, 64.43; H, 4.70; N, 13.68%. HRMS (EI) ([M]$^+$). Calcd for $C_{11}H_9N_2OF$: 204.0699. Found 204.0697.

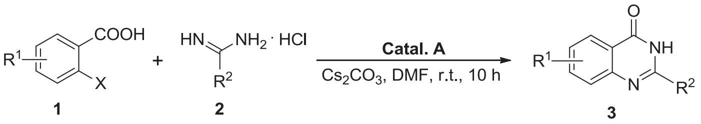
2-Cyclopropyl-7-methoxyquinazolin-4(3 *H*)-one (**3i**). White solid, m.p. 237.2–239.6 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): $\delta = 12.30$ (s, br, 1 H, N-*H*), 7.41–7.38 (m, 2 H, Ar-*H*), 7.29–7.26 (m, 1 H, Ar-*H*), 3.80 (s, 3 H, -OC*H$_3$*), 1.94–1.88 (m, 1 H, -C*H*), 1.05–0.93 (m, 4 H, -C*H$_2$*); ^{13}C NMR (100 MHz, DMSO-d$_6$): $\delta = 161.9$, 157.2, 156.9, 143.9, 128.5, 124.1, 121.7, 106.2, 55.9, 13.7, 9.5. Elemental analysis: Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96%. Found: C, 66.93; H, 5.28; N, 12.80%. HRMS (EI) ([M]$^+$). Calcd. for $C_{12}H_{12}N_2O_2$: 216.0899. Found 216.0898.

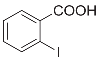
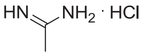
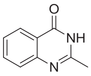
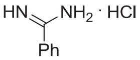
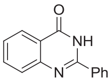
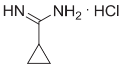
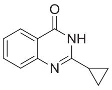
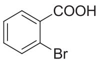
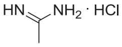
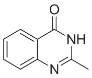
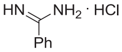
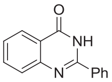
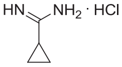
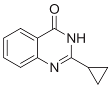
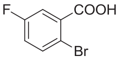
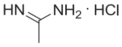
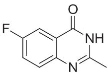
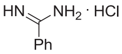
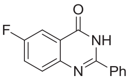
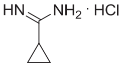
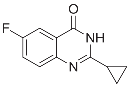
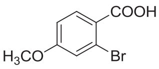
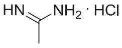
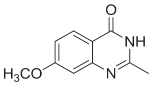
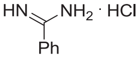
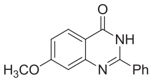
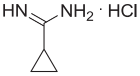
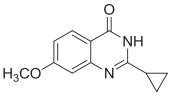
2-Cyclopropyl-8-methylquinazolin-4(3 *H*)-one (**3 l**). White solid, m.p. 227.6–229.4 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): $\delta = 12.33$ (s, br, 1 H, N-*H*), 7.85 (d, $J = 4.0$ Hz, 1 H, Ar-*H*), 7.49 (d, $J = 8.0$ Hz, 1 H, Ar-*H*), 7.20 (t, $J = 8.0$ Hz, 1 H, Ar-*H*), 2.37 (s, 3 H, -C*H$_3$*), 1.97–1.91 (m, 1 H, -C*H*), 1.11–0.97 (m, 4 H, -C*H$_2$*); ^{13}C NMR (100 MHz, DMSO-d$_6$): $\delta = 162.4$, 158.2, 147.9, 134.8, 134.7, 125.0, 123.8, 120.9, 17.3, 13.9, 10.1. Elemental analysis: Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99%. Found: C, 71.59; H, 5.92; N, 13.78%. HRMS (EI) ([M]$^+$). Calcd for $C_{12}H_{12}N_2O$: 200.0950. Found 200.0949.

Results and Discussion

The magnetic nanoparticle-supported Cu(I) catalyst was prepared according to the synthetic route in Scheme 1. The Fe_3O_4 with an average diameter of 10 nm (TEM result) after sonication was coated with silica as shell to produce $Fe_3O_4@SiO_2$ nanoparticles.[22] The obtained silica coating not only protects the magnetic cores but can also be easy modified with other functional groups through the reaction of OH groups on the surface. TEM images of the $Fe_3O_4@SiO_2$ show the core–shell structure of the particles, and the silica coating has a uniform thickness of 10 nm. Treatment of the silica-coated nanoparticles with excess *N*-(3-(triethoxysilyl) propyl)ethane-1,2-diamine in toluene at refluxing temperature for 24 h afforded silica nanospheres functionalized with 1,2-diamine groups. The magnetically Fe_3O_4 nanoparticle-supported Cu(I) catalyst was obtained by simply dissolving CuI in CH_3CN and treating it with the above amine-functionalized $Fe_3O_4@SiO_2$. The

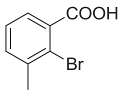
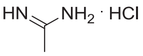
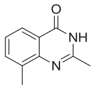
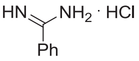
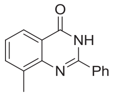
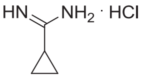
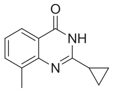
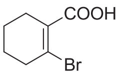
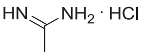
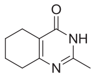
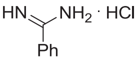
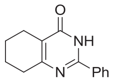
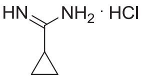
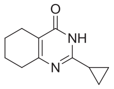
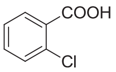
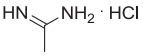
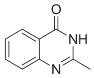
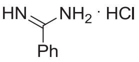
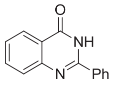
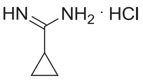
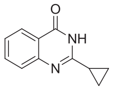
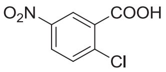
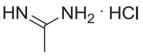
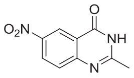
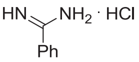
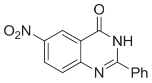
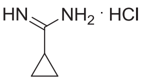
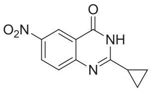
Table 2. The cascade reactions for the preparation of quinazolinone and bicyclic pyrimidinone derivatives[a]



Entry	1		2		Product, **3**		Yield (%)[b]
1		**1a**		**2a**		**3a**	97
2		**1a**		**2b**		**3b**	99
3		**1a**		**2c**		**3c**	99
4		**1b**		**2a**		**3a**	90
5		**1b**		**2b**		**3b**	95
6		**1b**		**2c**		**3c**	94
7		**1c**		**2a**		**3d**	84
8		**1c**		**2b**		**3e**	90
9		**1c**		**2c**		**3f**	93
10		**1d**		**2a**		**3g**	81
11		**1d**		**2b**		**3h**	92
12		**1d**		**2c**		**3i**	98

(Continues)

Table 2. ***(Continued)***

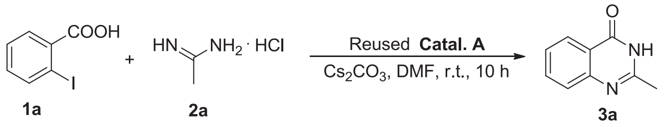
13		**1e**		**2a**		**3j**	73
14		**1e**		**2b**		**3k**	82
15		**1e**		**2c**		**3l**	87
16		**1f**		**2a**		**3m**	72
17		**1f**		**2b**		**3n**	78
18		**1f**		**2c**		**3o**	86
19		**1g**		**2a**		**3a**	74[c]
20		**1g**		**2b**		**3b**	85[c]
21		**1g**		**2c**		**3c**	90[c]
22		**1h**		**2a**		**3p**	68[c]
23		**1h**		**2b**		**3q**	76[c]
24		**1h**		**2c**		**3r**	80[c]

[a] Reaction conditions: **1** (0.50 mmol), **2** (0.75 mmol), $Fe_3O_4@SiO_2$–Cu(I) (**Catal. A**, 317 mg, containing Cu 0.05 mmol), Cs_2CO_3 (1.0 mmol), DMF (3.0 ml) at room temperature under nitrogen atmosphere for 10 h.

[b] Isolated yield.

[c] Reaction temperature was 50 °C.

Table 3. Recycling of Fe_3O_4 nanoparticle-supported Cu(I) **Catal. A**[a]



Run	Yield[b] (%)	Run	Yield[b] (%)
1	97	6	94
2	97	7	93
3	96	8	94
4	97	9	94
5	95	10	93

[a]Reaction conditions: 2-iodobenzoic acid (**1a**, 0.50 mmol), acetamidine hydrochloride (**2a**, 0.75 mmol), reused Fe_3O_4@SiO_2–Cu(I) (**Catal. A**, 317 mg, containing Cu 0.05 mmol), Cs_2CO_3 (1.0 mmol), DMF (3.0 ml) at room temperature under nitrogen atmosphere for 10 h.

[b]Isolated yields.

generated **Catal. A** was found to be with a loading of 0.158 mmol of Cu g^{-1} determined via ICP analysis. X-ray diffraction measurements of **Catal. A** exhibit diffraction peaks corresponding to the typical spinal magnetite structure; the diffraction peak of the layered amorphous silica was not obvious and no peaks characteristic for Cu(0) nanoparticles were observed.

To evaluate the efficiency of supported Cu(I) catalyst, it was tested by means of the cascade reaction of 2-halobenzoic acid with amidine (Table 1). To our delight, the reaction of 0.50 mmol of 2-iodobenzoic acid (**1a**) with 0.75 mmol acetamidine hydrochloride (**2a**) in DMF in the presence of **Catal. A** (10 mol%, relative to the amount of **1a**) using 2 equiv. of Cs_2CO_3 as the base afforded the quinazolinone **3a** in 98% yield (Table 1, entry 1). We then began the following investigation on the model reaction to optimize the other reaction parameters, including base and solvent, and the results are summarized in Table 1. It is evident that Cs_2CO_3 is the most effective base for the model reaction (Table 1, entry 1), and lower yields were obtained by using Na_3PO_4, K_3PO_4, Na_2CO_3 or K_2CO_3 as base (Table 1, entries 2–5). Poor results were observed using KF, NaOAc or Et_3N (Table 1, entries 6–8). The effect of solvents on the reaction was also screened. Only trace amounts of quinazolinone **3a** were observed when the reaction was carried out in MeOH, THF or dioxane (Table 1, entries 9–11) although the reactions in EtOH, *i*-PrOH, CH_3CN, toluene, *N*,*N*-dimethyl acetamide (DMA) and DMSO gave the desired product in moderate yields (Table 1, entries 12–17). Decreasing the amount of catalyst or base or shortening the reaction time also decreased the yield (Table 1, entries 18–20). After surveying a variety of catalysts, bases and solvents, we found that the combination of 10 mol% Fe_3O_4 nanoparticle-supported **Catal. A** and 2 equiv of Cs_2CO_3 in DMF at room temperature for 10 h served as the optimal conditions for this transformation.

Next, a variety of substituted 2-halobenzoic acids with amidines were examined under the optimized reaction conditions, and the results are listed in Table 2. In all cases, the reactions took place smoothly, giving quinazolinone derivatives in high yields. The most probable reason for the higher reactivity of Fe_3O_4 nanoparticle-supported copper(I) catalyst is that nanoparticles have a much larger surface area to volume ratio, which can provide a higher catalytic activity. As expected, due to the relative higher strength of C-Cl bond, 2-chlorobenzoic acid showed lower reactivity than 2-iodo- and 2-bromobenzoic acids in the cascade reactions under the same reaction conditions, while 2-iodobenzoic acid showed the highest reactivity (Table 2, entries 1–3). We were delighted that moderate to good yields were obtained when the reaction temperature was increased to 50 °C in the reactions of 2-chlorobenzoic acid and 2-chloro-5-nitrobenzoic acid with amidines (Table 2, entries 19–24). Generally, the reaction efficiency was insensitive to the electronic properties of the groups on the phenyl ring of 2-halobenzoic acid **1**, while unsubstituted 2-halobenzoic acids gave higher yields than that of substituted ones, whether electron-withdrawing or electron-donating groups (Table 2, entries 4 vs. 7, 10 and 13; 5 vs. 8, 11 and 14). The hindrance of the phenyl ring of **1** had a slight effect on the efficiency (Table 2, entries 13–15). Moreover, 2-bromocyclohex-1-enecarboxylic acid could also react with amidines under the present reaction conditions, and bicyclic pyrimidinone derivatives were isolated in good yields (Table 2, entries 16–18). As for amidines, it is obvious that benzimidamide and cyclopropanecarboximidamide exhibited higher reactivity than acetimidamide. For example, the reaction of 2-iodobenzoic acid with benzimidamide or cyclopropanecarboximidamide, or 2-bromo-4-methoxybenzoic acid with cyclopropanecarboximidamide, provided the corresponding quinazolinones in almost quantitative yields (Table 2, entries 2, 3 and 12).

Recovery of the catalyst is easy and efficient. After the reaction was completed, Fe_3O_4 nanoparticle-supported Cu(I) **Catal. A** was recovered by decantation of the reaction mixture in the presence of an external magnet. The catalyst was then washed with ethyl acetate, dried under high vacuum, and used directly for the next round of reaction without further purification. For the reaction of 2-iodobenzoic acid with acetamidine, the supported copper catalyst could be recycled and reused for 10 consecutive trials without any significant loss in activity (Table 3).

Conclusions

We have developed a Fe_3O_4 nanoparticle-supported copper(I) catalyst which exhibits excellent reactivity in the cascade reactions of 2-halobenzoic acids and 2-bromocyclohex-1-enecarboxylic acid with amidines. The reactions generated the corresponding quinazolinone and bicyclic pyrimidinone derivatives in good to excellent yields. Magnetically, nanocatalyst has a much larger surface area to volume ratio, which can provide a higher catalytic activity. Recovery of the catalyst by decantation of the reaction mixture in the presence of an external magnet is easy and efficient. The catalyst was recycled over ten times in reactions without any obvious loss in its activity.

Acknowledgments

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