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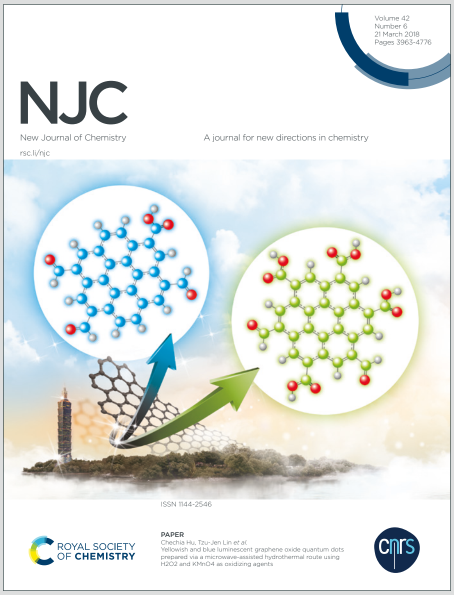

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PAPER
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ARTICLE TYPE

MOF-5 as a highly efficient and recyclable catalyst for one pot synthesis of 2,4-disubstituted quinoline derivatives

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A MOF-5-catalyzed three-component coupling reaction was developed as an efficient approach for the synthesis of 2,4-disubstituted quinoline derivatives via one pot three-component reaction of aromatic amine, aldehyde and alkyne with excellent yields. The easy recovery of the catalyst and reusability, broad substrate scopes, short reaction time, high yields of products and solvent-free conditions make this protocol practical, environmentally friendly and economically attractive.

Introduction

Nitrogen containing heterocycles are important natural products and can be pharmaceutically active. In particular, quinolines and their derivatives is present in many natural products,[1] biologically active molecules,[2] and they play important roles in medicinal chemistry, which have been found to be associated with wide ranging pharmaceutical activities, such as, antitumor,[3] antimalarial,[4] antiasthmatic,[5] antiinflammatory,[6] and antidiabetic[7] activities. The classical method for synthesis of quinoline is Skraup's procedure.[8] Also, many methods of quinoline synthesis have been developed,[9] including Doebner-von Miller,[10] Conrad-Limpach,[11] Friedländer,[12] and Combes[13] reactions. However, they usually involve arduous processes, which are incompatible with the environment, generate large amounts of waste, give relatively large amounts of undesirable by-products. Recently, the A^3-coupling reaction of alkyne, aldehyde and amine was widely used to synthesize 2,4-disubstitued-quinoline,[14] which offers a number of advantages: (i) simple materials, (ii) high atom economy, (iii) reduce reaction steps, and (iv) easy work-up procedure. But the use of corrosive, expensive and non-reusable catalysts limits the usefulness of this method, especially for large scale operation and leads to serious environmental and safety problems. Consequently, the design of efficient, neat conditions, environmentally friendly approach by using a reusable catalyst for the A^3-coupling reaction of alkyne, aldehyde and amine is in great demand.

Heterogeneous catalysts have many advantages, such as easy separation from the reaction mixture, recyclability and less pollution in the final product. Metal-organic frameworks (MOFs), an emerging new class of porous materials constructed by metal ions and organic building units, have drawn significant attention because of their applications in gas storage,[15] separation,[16] magnetics,[17] sensing[18] and heterogeneous biomimetic catalysis.[19] In particular, the specific porous structure of MOFs containing organic and inorganic active sites and their ductility make them effective heterogeneous catalysts.[20] Furthermore, heterogeneous catalysts based on MOFs have exhibited remarkable advantages with respect to analogous homogeneous transition-metal catalysts because of their zeolite-like properties, such as high internal surface area and microporosity, and well-ordered porous structures. Applications of MOFs in the synthesis of the organic compounds have also been widely explored.[20] However, the exploration of their applications in different reactions is yet interesting.

Recently, some MOFs have been employed for the A^3-coupling reaction of alkyne, aldehyde and amine. Li and co-workers reported sulfonate-based Cu(I) metal-organic framework (Cu(I)-MOF) as a highly efficient and reusable catalyst for the synthesis of propargylamine compounds via the three-component reaction of aldehydes, alkynes and secondary amines under solvent-free conditions (Scheme 1a).[21] In 2018, Kassymova et al prepared a new heterogeneous NHC catalyst (Ag-NHC-MOF) by the post-synthetic modification of an azolium-containing metal–organic framework. This catalyst showed an excellent activity towards above A^3-coupling reaction under ambient conditions (Scheme 1b).[22] These efforts focused on the coupling reaction of using secondary amines to produce propargylamine. MOF-5, one of the most studied MOFs prepared from Zn ions and 1,4-benzene dicarboxylic acid (H_2BDC), is a typical MOFs reported by Yaghi and co-workers and exhibits considerable potential application in catalytic organic reaction owing to its remarkably large pore volume, large surface area and relatively high thermal stability.[24] In continuation of our effort to

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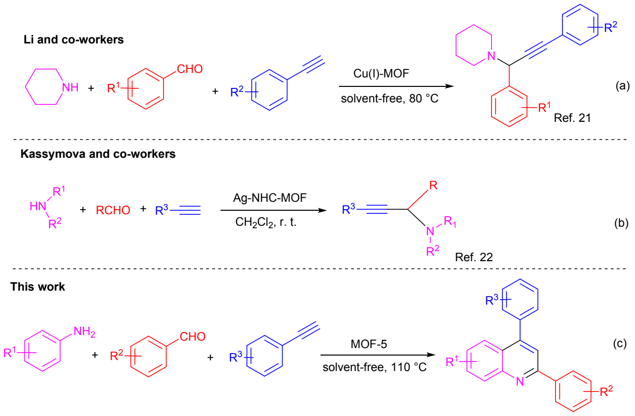
develop efficient and reusable heterogeneous for green synthetic method,[25] herein, a MOF-5-catalyzed three-component coupling reaction of aromatic amine, aldehyde and alkyne was developed under solvent-free conditions. As far as we know, the present work is the first example where the coupling reaction is followed by an intramolecular hydroarylation/oxidative aromatization using MOF-5 as an efficient catalyst, leading to 2,4-disubstituted quinoline derivatives (Scheme 1c).



Scheme 1 MOF catalyzed three-component reaction of amine, aldehyde and alkyne

Results and discussion

Synthesis and crystal structure determination. Solvothermal reaction of $Zn(NO_3)\cdot 6H_2O$ and 1,4-benzenedicarboxylate in *N,N*-dimethylformamide at 100 °C produced MOF-5. The powder XRD pattern of the MOF-5 is given in Fig. 1, which basically consisitented with the result reported by Howard.[26] MOF-5 has good thermal stability, as can be learned from the thermogram shown in Fig. 2. The weight loss below 300°C resulted from the occluded solvent DEF and water. MOF-5 began to decompose above 450 °C, which is much higher than the reaction temperatures of the A^3-coupling reaction (110 °C). The FTIR spectrum of the MOF-5 is provided in Fig. 3. IR spectra show the expected strong characteristic adsorptions for the symmetrical stretching vibration and the asymmetric stretching vibrations of the carboxyl group which is one of the main functional group of 1,4-benzenedicarboxylic (BDC) ligands (1375 and 1597 cm^{-1}). The broad absorption peak apparent around 3400 cm^{-1} corresponds to the absorption peak of water molecules in the sample. As shown in Fig. 4, the SEM of MOF-5 catalyst demonstrates that the particles is highly crystalline cubic structure with a particle size of 2.0-3.0 μm, which was also in a good agreement with the results from TEM (Fig. 5). The EDS elemental analysis indicates the presence of O, C and Zn (Fig. 6). The nitrogen absorption–desorption measurements indicates that the catalyst had a specific surface area of 240 m^{2}g^{-1} (Fig. 7).

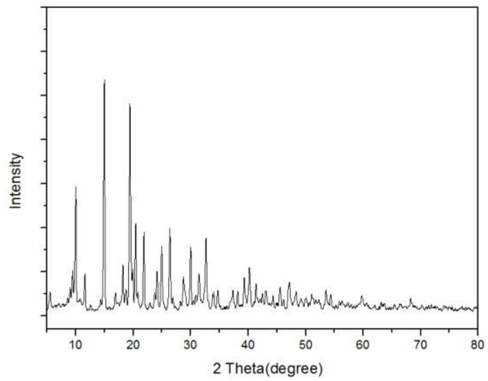


Fig. 1 XRD pattern of MOF-5.

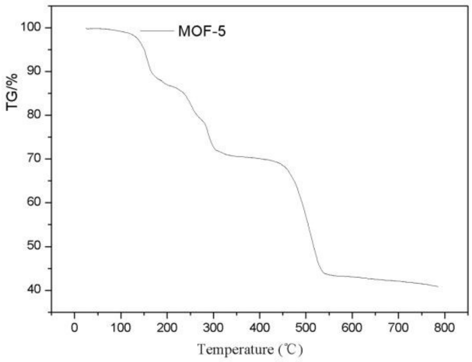


Fig. 2 Thermogram of MOF-5.

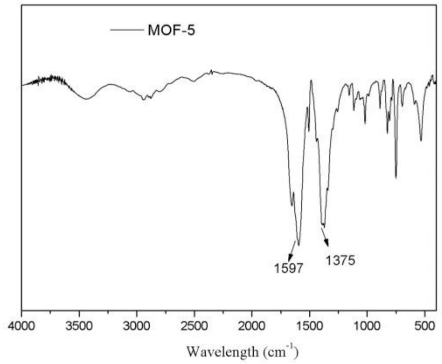


Fig. 3 FTIR spectra of MOF-5.

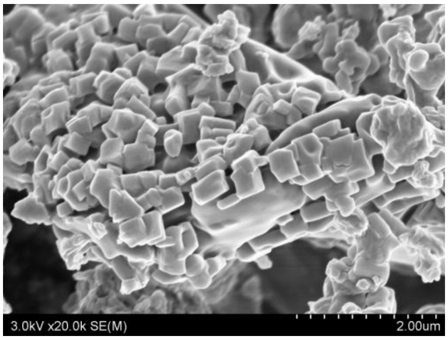


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Fig. 4 SEM image of MOF-5.

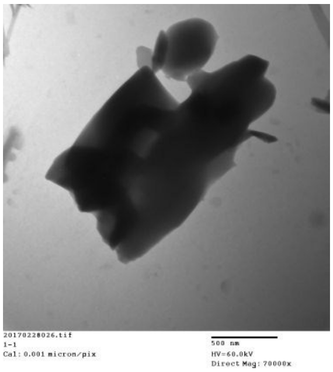


Fig. 5 TEM image of MOF-5.

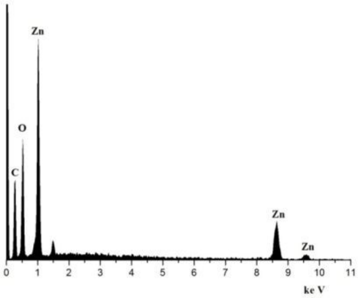


Fig. 6 EDS spectrum of MOF-5.

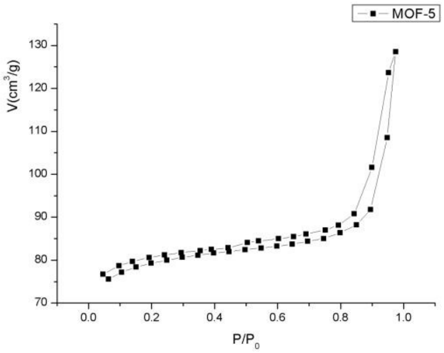
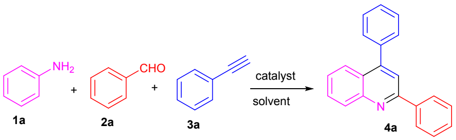


Fig. 7 SEM image of MOF-5.

The activity of the prepared catalyst was tested for the reaction of benzaldehyde (**1a**, 1.0 mmol), aniline (**2a**, 1.0 mmol) and phenyl acetylene (**3a**, 1.2 mmol) at 110 °C. The reaction, as shown in Table 1, proceeded very slowly in the absence of catalyst and only a trace of desired product was found after heating for 8 h (Table 1, entry 1). As expected, the desired 2,4-disubstitued-quinoline product **4a** was isolated in 91% yield after reaction at 110 °C for 3 h (Table 1, entry 9). Moreover, a higher reaction temperature (130 °C) does not make an obvious difference in the yield of the product (Table 1, entry 10), but lowering the temperature to 70 °C resulted in a lower yield (Table 1, entry 8). A number of common solvents were examined and the screening results implied that the use of these solvent resulted in lower yields of the quinoline product **4a** along with a mixture of propargylamine product and unreacted starting materials (from HPLC-MS) (Table 1, entry 2-7). Lowering the catalyst amount to 15 mg, the yield was decreased to 87% (Table 1, entry11). The use of 5.0 wt% (5.3 mg) of MOF-5 resulted in a lower yield (82%) even under a longer reaction (Table 1, entry12). Whereas an increasing in catalyst amount to 25 mg did not produce better results (Table 1, entry 13). It should be mentioned that the presence of various Lewis acid catalysts led to a decreased yield of product. Under similar reaction conditions, the use of 1:1:1 of **1a**/**2a**/**3a** resulted in a slightly lower yield. (**4a**, 89%, Table 1; entry 19). Therefore, the optimal reaction conditions for this MOF-5-catalyzed A^3-coupling reaction was use of 1:1:1.2 of **1a**, **2a** and **3a** under solvent-free condition at 110 °C for 3 h.

Table 1. Optimization of the Reaction Conditions[a]



Entry	catalyst	Solvent	Temperature (°C)	Time/h	Yield/%[b]
1	no	no	110	8	trace
2	MOF-5	EtOH	reflux	3	34
3	MOF-5	MeOH	reflux	3	35
4	MOF-5	$CHCl_3$	reflux	3	28
5	MOF-5	DMF	reflux	3	29
6	MOF-5	EtOAc	reflux	3	31
7	MOF-5	H_2O	reflux	3	trace
8	MOF-5	no	90	3	78
9	MOF-5	no	110	3	91
10	MOF-5	no	130	3	91
11[c]	MOF-5	no	110	3	87
12[d]	MOF-5	no	110	8	82
13[e]	MOF-5	no	110	3	91
14	$FeCl_3$	no	110	3	62
15	$ZnCl_2$	no	110	3	59
16	$CuCl_2$	no	110	3	58
17	$AgNO_3$	no	110	3	56
18	MgO	no	110	3	43
19[f]	MOF-5	no	110	3	89

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), **3a** (1.2 mmol) and MOF-5 (20 mg, 18.9 wt%) in the solvent (2.0 mL) or neat condition for 3 h under air atmosphere. [b] Isolated yields. [c] 15 mg catalyst was used. [d] 5.3 mg catalyst (5.0 wt%) was used. [e] 25 mg catalyst was used. [f] Using 1:1:1 of **1a**/**2a**/**3a**.

Having the optimal conditions in hand, we investigated the substrate scope of this reaction provided good yields between 78-91% as summarized in Table 2. Phenyl acetylene and aniline were initially used as substrates for exploring the scope of aromatic aldehyde substrates with different substituents (para, ortho, meta). All of aromatic aldehyde with electrondonating or

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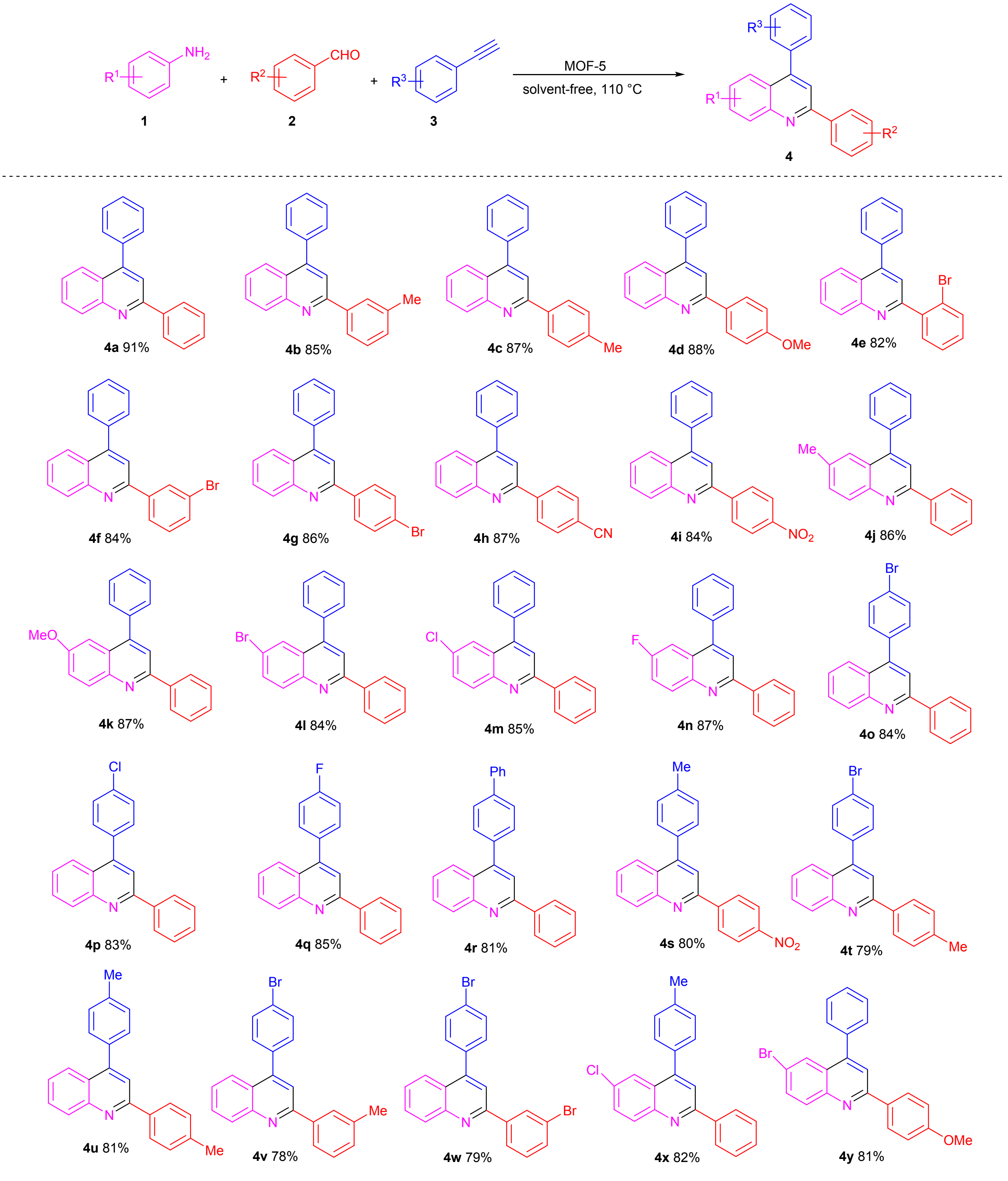
Table 2 Substrate scope examination.



4a 91% **4b** 85% **4c** 87% **4d** 88% **4e** 82%

4f 84% **4g** 86% **4h** 87% **4i** 84% **4j** 86%

4k 87% **4l** 84% **4m** 85% **4n** 87% **4o** 84%

4p 83% **4q** 85% **4r** 81% **4s** 80% **4t** 79%

4u 81% **4v** 78% **4w** 79% **4x** 82% **4y** 81%

Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), **3** (1.2 mmol), and 20 mg MOF-5 under solvent-free condition at 110 ºC for 3 h. Isolated yield.

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weakly electron-withdrawing substituents were found to be applicable to this reaction and gave the expected products in high to excellent yields (**4b-4g**). Remarkably, strongly electron-poor aromatic aldehyde such as 4-formylbenzonitrile and 4-nitrobenzaldehyde afforded the desired product in high yields. The position of substituents has no obvious effect (**4e, 4f**, **4g**). To our disappointment, under these reaction conditions, aliphatic aldehyde such as cyclohexanal is not a suitable substrate, and an inseparable mixture is formed.

Next, various substituted phenyl acetylene and anilines, such as para substituents (F, Cl, Br, OMe and CH_3), were examined. Electronwithdrawing and electron-donating substituents were generally well-tolerated, affording the desired products **4j**–**4q** bearing alkyl, halide, and alkoxyl functionalities in good yields. Moreover, 4-ethynyl-1,1'-biphenyl was compatible in the reaction, and product **4r** was obtained. Stimulated by these results, the reactions of substituted aromatic aldehydes or substituted anilines was tested under the above optimal conditions and the corresponding quinolines (**4s-4y**) were obtained in high yields.

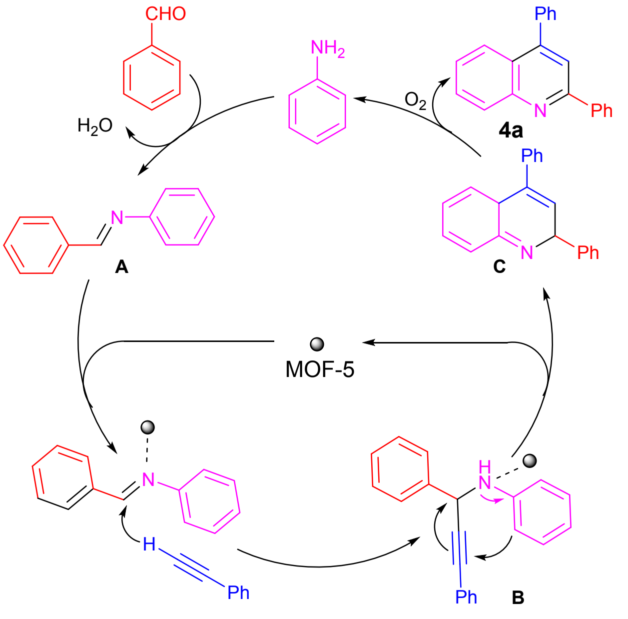
The recyclability and reusability of the catalyst MOF-5 are very important for commercial and industrial applications. Finally, the reusability of the catalyst has been tested in the reaction of benzaldehyde, aniline and phenyl acetylene. After completion of the reaction, the mixture was cooled to room temperature and diluted with cold ethyl acetate. The catalyst was easily recovered by simple filtration and the recover catalyst was washed with ethyl acetate, drying under vacuum and then reused directly in model reaction for the next round without further purification. As shown in Table 3, the catalyst can be reused at least five times with essentially no loss of catalytic activity, which indicates that the prepared catalyst possessed excellent activity and reusability.

Table 3 Recycling of the catalyst

Entry	Recycle	Yield (%)[a]
1	1st	91
2	2nd	90
3	3rd	91
4	4th	86
5	5th	85

[a] Isolated yield.

In accordance with reports from the literature[14b], a plausible mechanism for the current MOF-5-catalyzed tandem reaction is proposed (Scheme 2). Intermediate **A** is generated in situ from aromatic aldehyde and aniline. The nitrogen atom of the intermediate **A** is coordinated by the MOF-5 and enhances the electrophilicity of the imine, and then addition of alkyne to intermediate **A** forms the propargylamine intermediate **B**, which then undergoes an intramolecular hydroarylation of alkyne to give dihydroquinoline intermediate **C**, followed by oxidized aromatization with O_2 to afford the quinoline **4a**.



Scheme 2 A plausible mechanism for the synthesis of quinoline derivative **4a.**

Conclusions

In summary, we have developed an efficient, selective and green one-pot synthesis of quinolines using the recoverable MOF-5 catalyst under solvent-free condition. A variety of aromatic amine, aldehyde and alkyne can be tolerated, giving the structural diversity of quinolines in good to excellent yields. Besides, the catalyst could be reused five times without significant loss of activity, showing good potential for industrial application.

Experimental Section

General Methods: All solvents and chemicals were obtained commercially and were used without further purification. X-ray diffraction analysis was carried out using a PANalytical X'Pert Pro X-ray diffractometer. The surface morphology and particle size were studied using a Hitachi S-4800 SEM instrument. Transmission electron microscopy (TEM) observation was performed using a Hitachi H-7650 microscope at 80 kV. Melting points were determined on X-5 apparatus and were uncorrected. IR spectra were obtained with KBr pellets in the range of 400–4000 cm^{-1} using a Thermo Fisher iS50 spectrometer. Elemental compositions were determined using a Hitachi S-4800 scanning electron microscope equipped with an INCA 350 energy dispersive spectrometer (SEM-EDS) presenting a 133 eV resolution at 5.9 keV. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV III-500 or Zhongke Niujin AS 400 spectrometer using TMS as an internal standard. Mass spectra were recorded on a 3200 Qtrap instrument with an ESI source. High resolution mass spectra (HR-MS) were measured on a Brukter Impact II instrument using ESI source.

Preparation of the MOF-5. In a typical preparation, a solid mixture of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) (0.1188 g, 0.4 mmol) and 1,4-benzenedicarboxylic acid (H_2BDC) (0.0216 g,

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0.13 mmol) was dissolved in *N,N*-dimethylformamide (10 ml) in a 20 ml vial. The vial was tightly capped and heated at 100 °C in an isothermal over for 24 h to yield pale yellow crystals. After unassisted cooling of the vial to room temperature, the solid product was removed by decanting with mother liquor and washed with *N,N*-dimethylformamide (DMF) (3 × 10 ml). After the solid product had been obtained, solvent exchange was carried out with dichloromethane (DCM) (3 × 10 ml) at room temperature. The product was then dried under vacuum at 125 °C for 6 h. X-ray diffraction patterns, thermograms, and FTIR spectra of the MOF-5 prepared in this work agree well with those reported by other authors.

General procedure for the synthesis of 2,4-disubstitued-quinoline product 4a. The mixture of benzaldehyde (1.0 mmol), aniline (1.0 mmol) and phenyl acetylene (1.2 mmol) and MOF-5 (20 mg) under solvent-free condition at 110 °C for 3 h (monitored by TLC). Upon completion of the reaction, the reaction mixture was cooled to room temperature and 5 ml of ethyl acetate was added. The quinoline derivatives were dissolved in ethyl acetate and the catalyst was separated by simple filtration, washed with ethyl acetate, and used for subsequent cycles after drying under vacuum. Pure products were obtained by evaporation of the solvent, followed by column chromatography on silica gel using ethyl acetate/hexane as the eluent.

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Graphical Abstract:

MOF-5 as a highly efficient and recyclable catalyst for one pot synthesis of 2,4-disubstituted quinoline derivatives

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An approach was developed for synthesis of 2,4-disubstituted quinoline derivatives via one pot three-component reaction of aromatic amine, aldehyde and alkyne catalyzed by MOF-5 under solvent-free condition.