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MCM-41-SO_3H: an efficient, reusable, heterogeneous catalyst for the one-pot, three-component synthesis of pyrano[3,2-*b*]pyrans

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Abstract MCM-41-SO_3H, ordered mesoporous silica material MCM-41 with covalently anchored sulfonic acid groups, was used as a solid acid catalyst for the convenient, efficient, and 'green' synthesis of 2-amino-6-(hydroxymethyl)-8-oxo-4-aryl-4,8-dihydropyrano[3,2-*b*]pyrans via a one-pot, three-component reaction of 5-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one, aldehydes and malononitrile in aqueous media.

Keywords 2-Amino-6-(hydroxymethyl)-8-oxo-4-aryl-4 · 8-Dihydropyrano[3,2-*b*]pyran · MCM-41-SO_3H · Multicomponent reactions · Aqueous media

Introduction

Multicomponent reactions (MCRs) have proved to be very influential and efficient bond-forming tools for the synthesis of biologically active compounds. MCRs are extremely convergent, producing a remarkably high increase of molecular complexity in just one step [1–3].

Kojic acid [5-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one], which was first isolated from the mycelia of *Aspergillus oryzae* grown on steamed rice (koji), is widely used as a food additive for preventing enzymatic browning of raw crabs and shrimps, and as a skin-whitening agent because of its tyrosinase inhibitory activity on melanin synthesis. Kojic acid derivatives possess wide-ranging pharmacological activities such as antifungal [4], anti-neoplastic [5], antiproliferative [6], anti-HIV

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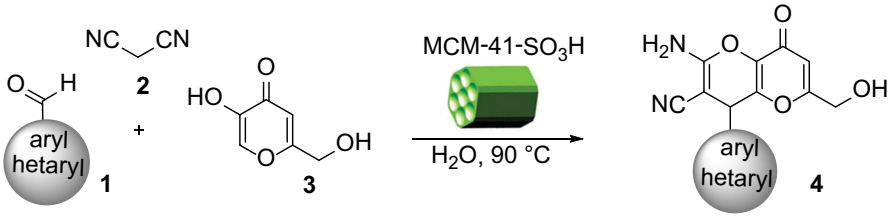
[7], anticonvulsant [8], anti-inflammatory [9], antioxidative [10], antibacterial [11], and tyrosinase inhibitory activities [12]. Because of these valuable properties, kojic acid derivatives are of great interest for the pharmaceutical chemistry. On the other hand, 2-amino-4*H*-pyran derivatives are the core structure of many pharmacological agents and are favorite compounds for medicinal chemists due to their potential biomedical application as a novel anticancer agent for human use. Giving attention to the synthetic feasibility of 2-amino-4*H*-pyran and kojic acid derivatives it appeared useful to fuse both these scaffolds as a single molecular entity in view of enhanced biological activity.

In 1997, Piao et al. [13] reported the two step synthesis of 2-amino-6-(hydroxymethyl)-8-oxo-4-aryl-4,8-dihydropyrano[3,2-*b*]pyranes using amine-based catalyst. This method is associated with some disadvantages such as the use of a toxic and non-recyclable catalyst, high reaction temperature, and two step synthesis. Litvinov et al. have described a three-component Et_3N-catalyzed procedure for the synthesis of similar compounds [14]. Recently, ultrasound-assisted synthesis of these compounds has also been reported [15]. However, only a few methods have been developed for the synthesis of this class of compounds, but, also, 2-amino-6-(hydroxymethyl)-8-oxo-4-aryl-4,8-dihydropyrano[3,2-*b*]pyranes have not been widely explored. Thus, the development of environmental, efficient, and facile process for the synthesis of these compounds is of current interest.

In recent years, replacement of hazardous and corrosive homogeneous catalysts with environmental compatible and reusable heterogeneous catalysts has been one of the key areas of green chemistry [16]. In this context, organically functionalized ordered mesoporous silica with a tunable pore structure and tailored composition have gained much research interest because of their several advantages such as reusability, environmental compatibility, non-corrosiveness and easy separation, compared to homogeneous counterparts [16–22]. Ever since the discovery of MCM-41 mesoporous silica, these structurally ordered materials have been regarded as the ideal solid support for various catalysts due to their high surface areas and tunable pore size.

In continuation of our efforts for the developing of new and eco-friendly synthetic methodologies [23–27], herein, we disclose the application of sulfonic acid functionalized MCM-41 as a recyclable catalyst for the synthesis of 2-amino-6-(hydroxymethyl)-8-oxo-4-aryl-4,8-dihydropyrano[3,2-*b*]pyranes (Scheme 1).



Scheme 1 MCM-41-SO_3H-catalyzed synthesis of 2-amino-dihydropyrano[3,2-*b*]pyrane derivatives

Experimental

All the chemicals were purchased from Merck, Fluka, and Sigma-Aldrich. The reactions were monitored by thin layer chromatography (TLC). Melting points were measured on an electrothermal 9100 apparatus. NMR spectra were recorded with a Bruker DRX-400 AVANCE instrument (400.1 MHz for ^1H and 100.6 MHz for ^{13}C). IR spectra were recorded on a FT-IR Bruker vector 22 spectrometer. Mass spectra were measured on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 30 eV.

Synthesis of sulfonic acid functionalized MCM-41

The MCM-41 (60.0 g) were dispersed in dry CH_2Cl_2 (5 mL) and $ClSO_3H$ (81.13 g, 0.70 mol) was then added dropwise over a period of 60 min at r.t. Hydrogen chloride gas evolved from the reaction vessel immediately. After completion of the addition, the mixture was shaken for 30 min and the obtained MCM-41-SO_3H was washed three times with dry CH_2Cl_2 to remove the unattached substrates. The solid material was finally dried at 60 °C overnight [28]. The amount of sulfonic acid groups of MCM-41-SO_3H, which were determined by acid–base titration, was found to be 0.95 mmol g^{-1}.

General procedure for preparation of 2-amino-4,8-dihydropyrano[3,2-b]pyran-3-carbonitriles

A mixture of benzaldehyde (1 mmol), malonitrile (1 mmol), kojic acid (1 mmol), and MCM-41-SO_3H (30 mg) in water (5 mL) was stirred at 90 °C. After completion of the reaction (as monitored by TLC), the catalyst was filtered out using filter paper and washed with hot ethanol. Then, the solvent of the filtrate was evaporated, and the crude product was purified by recrystallization from ethanol. The new compounds were identified by their ^1H and ^{13}CNMR spectra and elemental analysis. The known products were characterized by comparison of their physical and spectroscopic data with the literature [13–15].

Physical and spectral data of new products

*2-amino-4,8-dihydro-6-(hydroxymethyl)-4-(4-nitrophenyl)-8-oxopyrano[3,2-b]pyran-3-carbonitrile (**4c**)* MP: 230–232 °C; IR (KBr, cm^{-1}) ν_{max}: 3538, 3452, 3329, 2195, 1650, 1521, 1352; ^1H NMR (400 MHz, DMSO-d_6) δ: 4.17 (2H, AB_qd, $J = 16.4$, 6 Hz, CH_2), 5.08 (1H, s, CH_{aliph}), 5.69 (1H, t, $J = 6$ Hz, OH), 6.35 (1H, s, CH_{vinyl}), 7.39 (2H, s, NH_2), 7.62 (2H, d, $J = 8.8$ Hz, ArH), 8.26 (2H, d, $J = 8.8$ Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 55.12, 59.51, 111.96, 124.64, 129.82, 137.15, 147.62, 148.19, 148.44, 159.82, 168.81, 169.99; $[M]^+$ 341.

*2-amino-4-(4-cyanophenyl)-4,8-dihydro-6-(hydroxymethyl)-8-oxopyrano[3,2-b]pyran-3-carbonitrile (**4d**)* MP: 228–230 °C; IR (KBr, cm^{-1}) ν_{max}: 3520, 3424, 3325,

2229, 2191, 1653; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.16 (2H, AB_qd, J = 16, 6 Hz, CH_2), 4.99 (1H, s, CH_{aliph}), 5.68 (1H, t, J = 6 Hz, OH), 6.34 (1H, s, CH_{vinyl}), 7.35 (2H, s, NH_2), 7.53 (2H, d, J = 8 Hz, ArH), 7.88 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 55.20, 59.52, 111.26, 111.96, 119.00, 119.46, 129.46, 133.44, 137.15, 146.55, 148.28, 159.83, 168.75, 169.98; [M] $^{+}$ 321.

*2-amino-4-(4-(trifluoromethyl)phenyl)-4,8-dihydro-6-(hydroxymethyl)-8-oxopyrano [3,2-b]pyran-3-carbonitrile (**4e**)* MP: 240–242 °C; IR (KBr, cm^{-1}) ν_{max}: 3408, 2197, 1639; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.10–4.23 (2H, m, CH_2), 4.99 (1H, s, CH_{aliph}), 5.68 (1H, t, J = 6 Hz, OH), 6.34 (1H, s, CH_{vinyl}), 7.33 (2H, s, NH_2), 7.55 (2H, d, J = 8 Hz, ArH), 7.77 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 40.43, 55.45, 59.54, 111.94, 119.54, 124.59 (q, ^{1}J = 270.6 Hz),128.89 (q, ^{3}J = 3.8 Hz),129.26,129.89 (q, ^{2}J = 31.3 Hz), 137.08, 145.80, 148.57, 159.79, 168.78, 170.01; [M] $^{+}$ 364.

*2-amino-4-(3-chlorophenyl)-4,8-dihydro-6-(hydroxymethyl)-8-oxopyrano[3,2-b]pyran-3-carbonitrile (**4g**)* MP: 238–240 °C; IR (KBr, cm^{-1}) ν_{max}: 3317, 2201, 1644; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.10–4.24 (2H, m, CH_2), 4.99 (1H, s, CH_{aliph}), 5.68 (1H, t, J = 6 Hz, OH), 6.34 (1H, s, CH_{vinyl}), 7.27 (1H, dt, J = 7.6, 1.6 Hz, ArH), 7.30 (2H, s, NH_2), 7.37–7.45 (3H, m, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 55.64, 59.56, 111.95, 127.11, 128.12, 128.44, 131.38, 133.94, 137.01, 143.71, 148.67, 159.76, 168.70, 170.02; [M] $^{+}$ 330.

*2-amino-4,8-dihydro-6-(hydroxymethyl)-4-(3-methoxyphenyl)-8-oxopyrano[3,2-b]pyran-3-carbonitrile (**4h**)* MP: 225-227 °C; IR (KBr, cm^{-1}) ν_{max}: 3189, 2202, 1630, 1260, 1032; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.34 (1H, s, CH_{aliph}), 4.07–4.22 (2H, m, CH_2), 4.99 (1H, s, CH), 5.66 (1H, t, J = 6 Hz, OH), 6.32 (1H, s, CH_{vinyl}), 6.96 (1H, td, J = 7.6, 0.8 Hz, ArH), 7.05 (1H, d, J = 8 Hz, ArH), 7.11 (2H, s, NH_2), 7.13 (1H, dd, J = 7.6, 1.6 Hz, ArH), 7.28–7.32 (1H, m, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 35.84, 55.59, 56.28, 59.54, 111.82, 112.48, 119.83, 121.42, 128.91, 129.67, 129.77, 137.39, 149.77, 157.53, 160.12, 168.50, 170.01; [M] $^{+}$ 326.

*2-amino-4,8-dihydro-6-(hydroxymethyl)-4-(2-nitrophenyl)-8-oxopyrano[3,2-b]pyran-3-carbonitrile (**4i**)* MP: 223–225 °C; IR (KBr, cm^{-1}) ν_{max}: 3378, 3318, 3210, 2192, 1678, 1529, 1354; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.03–4.19 (2H, m, CH_2), 5.50 (1H, s, CH_{aliph}), 5.67 (1H, t, J = 6 Hz, OH), 6.32 (1H, s, CH_{vinyl}), 7.38 (2H, s, NH_2), 7.57–7.63 (2H, m, ArH), 7.77 (1H, td, J = 7.8, 1.2 Hz, ArH), 7.98 (1H, dd, J = 8, 1.2 Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 36.55, 54.16, 59.42, 111.85, 119.26, 125.20, 130.03, 131.64, 133.92, 134.44, 137.10, 147.94, 149.68, 160.18, 168.75, 169.92; [M] $^{+}$ 342.

*2-amino-4-(2-chloro-5-nitrophenyl)-4,8-dihydro-6-(hydroxymethyl)-8-oxopyrano[3,2-b]pyran-3-carbonitrile (**4j**)* MP: 260–262 °C; IR (KBr, cm^{-1}) ν_{max}: 3425, 3310, 3209, 2200, 1623, 1527, 1348; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.17 (2H, AB_q,

J = 15.6 Hz, CH_2), 5.50 (1H, s, CH_{aliph}), 5.66 (1H, s, OH), 6.35 (1H, s, CH_{vinyl}), 7.44 (2H, s, NH_2), 7.84 (2H, d, J = 8.8 Hz, ArH), 8.21 (2H, dd, J = 8.8, 2.8 Hz, ArH), 8.26 (2H, d, J = 2.8 Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 38.95, 53.88, 59.48, 111.99, 119.18, 125.17, 126.28, 132.31, 137.61, 139.32, 140.09, 147.13, 147.36, 160.24, 168.83, 169.89; [M] $^+$ 375.

*2-amino-4-(4-(2-amino-3-cyano-4,8-dihydro-6-(hydroxymethyl)-8-oxopyrano[3,2-b]pyran-4-yl)phenyl)-4,8-dihydro-6-(hydroxymethyl)-8-oxopyrano[3,2-b]pyran-3-carbonitrile (**4m**)* MP: 270–272 °C; IR (KBr, cm^{-1}) ν_{max}: 3320, 2191, 1644; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.12 (2H, AB_qd, J = 16.8, 6 Hz, CH_2), 4.81 (1H, s, CH_{aliph}), 5.69 (1H, t, J = 6 Hz, OH), 6.33 (1H, s, CH_{vinyl}), 7.25 (2H, s, NH_2), 7.30 (2H, s, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_c 55.92, 59.58, 111.93, 119.78, 128.75, 136.98, 140.81, 149.31, 159.85, 168.71, 170.03; [M] $^+$ 510.7

Results and discussion

Powder X-ray diffraction patterns of MCM-41, MCM-41-SO_3H, and reused MCM-41-SO_3H are shown in Fig. 1. For MCM-41, four well-defined Brag peaks at low angles can be seen, which can be indexed to the (1 0 0), (1 1 0), (2 0 0), and (2 1 0) reflections corresponding to a hexagonal lattice (i.e., MCM-41). When the surface of mesoporous silica is functionalized with the sulfonic groups, a decrease in the intensity of the peaks is observed; however, the two-dimensional hexagonal array of mesoporous structure is retained. Also, the used MCM-41-SO_3H XRD diagram revealed that mesopore channels during catalytic reaction were stable as physical structure damage had not been observed.

As illustrated in Fig. 2, N_2 adsorption–desorption measurement for the sulfonated MCM-41 demonstrated a type IV isotherm, which is the characteristic of mesoporous materials. The specific surface area and total pore volume of the catalyst determined from the BET equation were 390 m^2/g and 0.38 cm^3/g, respectively. Furthermore, the TEM micrograph of MCM-41-SO_3H (Fig. 3) showed an ordered hexagonal pore system.

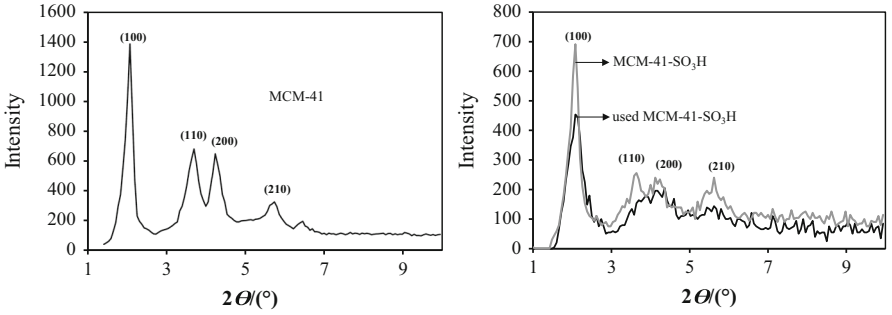


Fig. 1 XRD patterns of MCM-41, MCM-41-SO_3H and used MCM-41-SO_3H

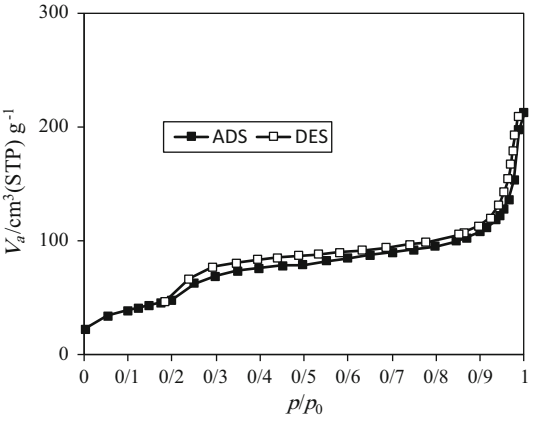


Fig. 2 N_2 adsorption–desorption isotherm of the MCM-41-SO_3H

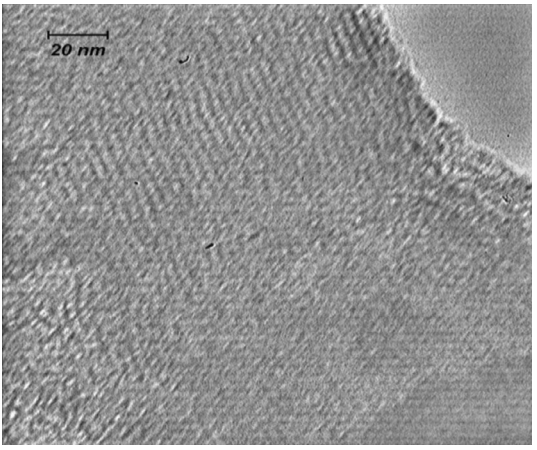
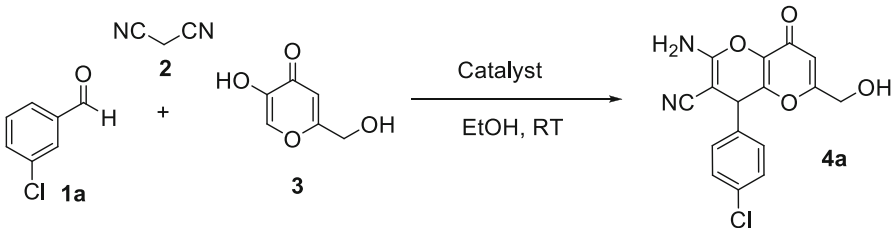


Fig. 3 The TEM image of MCM-41-SO_3H

Our study began with a one-pot three-component reaction of 4-chloro-benzaldehyde 1a, malononitrile 2, and kojic acid 3 in EtOH at room temperature. The choice of the catalyst played a crucial role and the use of solid catalysts was at the center of our study. As shown in Table 1, the best result was obtained with the MCM-41-SO_3H catalyst in terms of yield and reaction time (entry 7). The commercial ion-exchange sulfonic resins such as Amberlist-15 gave moderate yields of the corresponding product (entry 1). The Alum-catalyzed reaction gave a much lower yield. The observed meaningful catalytic activity of MCM-41-SO_3H compared to the mentioned acid catalysts may be due to the higher surface area of the MCM-41-SO_3H, which enhanced the chemical accessibility of substrates to the anchored acid groups. The use of SiO_2, TiO_2 and Al_2O_3 nanoparticles and H_2SO_4 were also examined whereby a moderate yield of product was obtained in a relatively longer reaction time (entries 3, 4, 5, 9). This reaction was also carried out with MCM-41 that required longer reaction times and resulted in a significantly lower yield (entry 6).

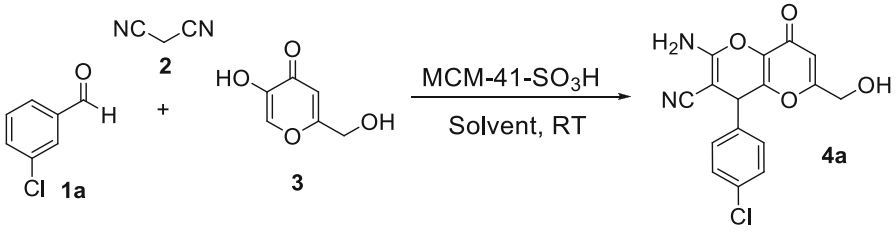
Table 1 Effect of different catalysts on the reaction of 4-chloro-benzaldehyde **1a**, malononitrile **2**, and kojic acid **3** in EtOH at room temperature



Entry	Cat. (0.02 g)	Time (h)	Yield (%)[a]
1	Amberlyst-15	12	50
2	Alum	12	25
3	Nano-SiO_2	9	45
4	Nano-Tio_2	10	40
5	Nano-Al_2O_3	10	43
6	MCM-41	5.5	65
7	MCM-41-SO_3H	3	75
8	–	12	Trace
9	H_2SO_4	10	45

[a] Isolated yields

Table 2 Effect of solvent on the MCM-41-SO_3H -catalyzed synthesis of 2-amino-dihydropyrano[3,2-*b*]pyrane **4a**



Entry	Solvent[a,b]	Time (h)	Yield (%)[c]
1	H_2O	2.5	80
2	EtOH	3	75
3	MeOH	6	70
4	MeCN	24	Trace
5	$CHCl_3$	24	Trace

[a] Reaction conditions: aromatic aldehydes (1 mmol), malononitrile (1 mmol), kojc acid (1 mmol) and MCM-41-SO_3H (0.02 g) at RT

[b] Solvent: 5 ml

[c] Isolated yields

Table 3 Effect of temperature on the MCM-41-SO_3H-catalyzed synthesis of 2-amino-dihydropyrano[3,2-*b*]pyrane **4a**[a]

Entry	Temperature (°C)	Time (h)	Yield (%)[b]
1	RT	2.5	80
2	50	2	80
3	90	1	85
4	100	1	85

[a] Reaction conditions: aromatic aldehydes (1 mmol), malononitrile (1 mmol), kojc acid (1 mmol), and MCM-41-SO_3H (0.02 g) in H_2O (5 mL)

[b] Isolated yields

Table 4 Influence of the amount of MCM-41-SO_3H in synthesis of 2-amino-dihydropyrano[3,2-*b*]pyrane **4a**[a]

Entry	MCM-41-SO3H (g)	Time	Yield (%)[b]
1	0.04	60 min	96
2	0.03	40 min	97
3	0.02	1 h	85
4	–	10 h	25

[a] Reaction conditions: aromatic aldehydes (1 mmol), malononitrile (1 mmol), and kojc acid (1 mmol) in H_2O (5 mL) at 90 °C

[b] Isolated yields

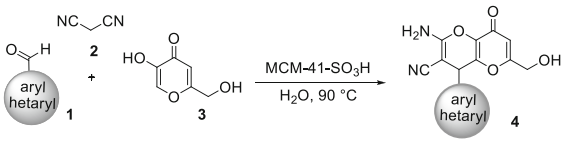
When the reaction was attempted without a catalyst, trace product formation was observed.

We then tried to screen the reaction in various solvents in order to optimize the reaction conditions using MCM-41-SO_3H as catalyst (Table 2). The results revealed that solvents show great effect on the catalytic activity of MCM-41-SO_3H. The highest yield was obtained with water as solvent.

During the optimization of the reaction condition, the effect of temperature on the reaction rate as well as the yields of products was investigated (Table 3). In this regard, the reactions were carried out at different temperatures ranging from room temperature to 100 °C. We found that the yield of product 3a was improved, and the reaction time was shortened as the temperature was increased to 90 °C (Table 3, entry 3).

We also evaluated the amount of catalyst required for this transformation. It was found that 0.03 g of MCM-41-SO_3H was enough to afford 3a with 97 % isolated yield in suitable time (Table 4, entry 2). The yield remained nearly unaffected when the catalyst loading was increased to 0.04 g (Table 4, entry 1). However, the yield was dramatically decreased when the catalyst-free reaction was performed (Table 2, entry 4).

Table 5 Synthesis of different 2-amino-dihydropyrano[3,2-*b*]pyrane derivatives **4** catalyzed by MCM-41-SO_3H[a]



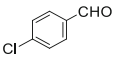
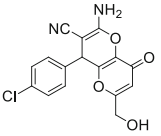
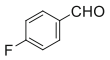
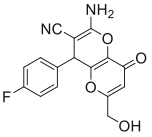
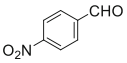
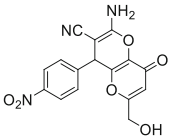
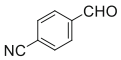
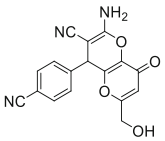
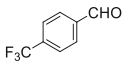
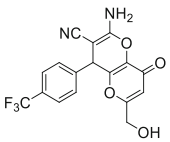
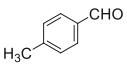
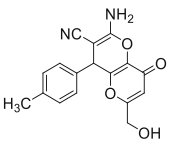
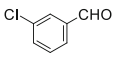
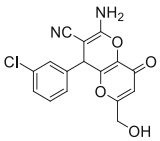
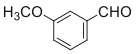
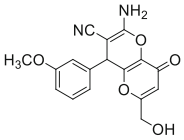
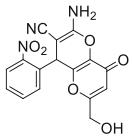
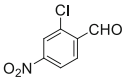
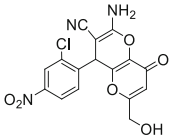
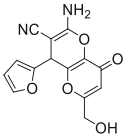
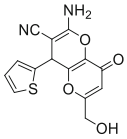
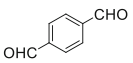
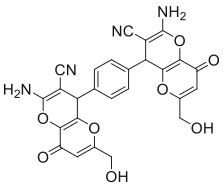
Entry	Aromatic aldehydes	Product	Time (min)	Yield (%)[b]	Mp °C
1		 **4a**	40	97	235–237
2		 **4b**	45	91	247–249
3		 **4c**	35	98	230–232
4		 **4d**	35	98	228–230
5		 **4e**	45	94	240–242
6		 **4f**	50	90	221–223
7		 **4g**	50	95	238–240

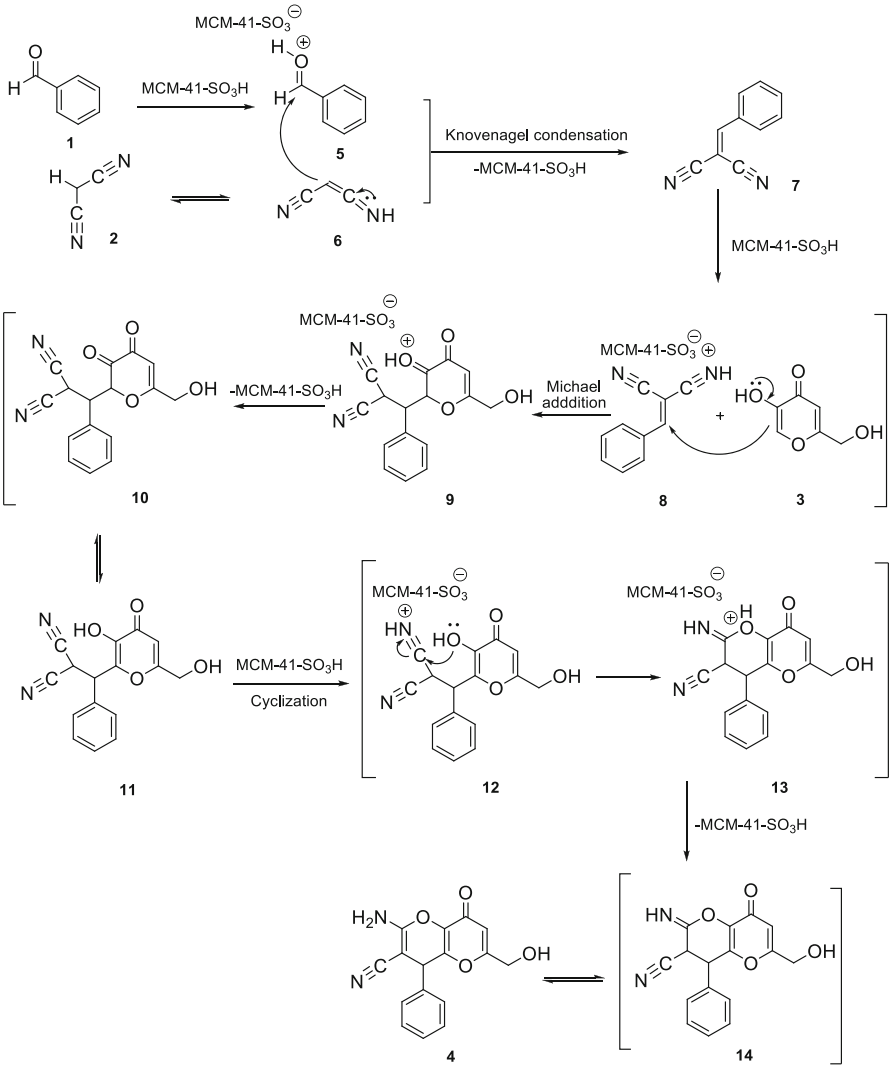
Table 5 continued

Entry	Aromatic aldehydes	Product	Time (min)	Yield (%)[b]	Mp °C
8		 **4h**	45	89	225–227
9		 **4i**	10	95	223–225
10		 **4j**	50	89	260–262
11		 **4k**	50	89	222–224
12		 **4l**	50	87	234–236
13		 **4m**	45	95	270–272

[a] Reaction conditions: aromatic aldehydes (1 mmol), malononitrile (1 mmol), kojc acid (1 mmol) and MCM-41-SO_3H (0.03 g) in H_2O (5 mL) at 90 °C

[b] Isolated yields

To evaluate the versatility of this methodology, a series of aromatic aldehydes were studied under the optimal reaction conditions and the results are collected in Table 5. In all cases, the reactions gave the products in good to excellent yields in very short reaction times. The aromatic aldehydes with both electron-withdrawing



Scheme 2 A plausible reaction mechanism

and electron-donating substituents such as CN, NO_2, halogens, and CH_3 were performed smoothly under optimized conditions to afford the corresponding products in high yields (Table 5). However, the aromatic aldehydes having a strong electron-donating substituent such as *p*-OCH_3 provided the lower yields of product. Acid sensitive electron-rich heterocyclic aldehydes such as furfural and thiophene-2-carbaldehyde also reacted very efficiently with no side reaction (entries 11 and 12).

The suggested mechanism for the synthesis of 2-amino-4*H*-pyran derivatives **4** is described in (Scheme 2). The unsaturated nitrile 7 is formed via a Knoevenagel

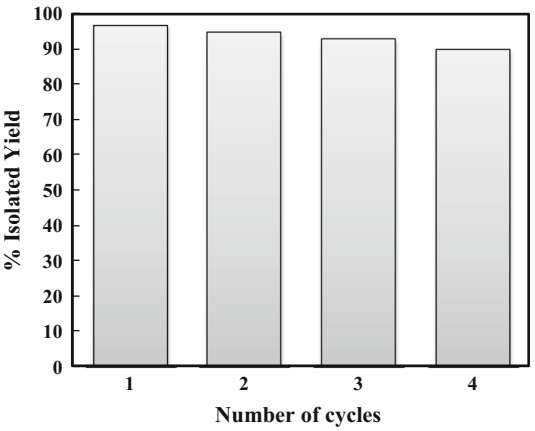


Fig. 4 Reusability study of the catalyst in the model reaction

condensation reaction of benzaldehyde **1** and malononitrile **2**. This step was regarded as a rapid Knoevenagel condensation. Compound 7 is gained through Michael addition in which kojc acid **3** is employed as nucleophile attacks on unsaturated nitriles 7. As the result of the intramolecular addition reaction, including the hydroxyl group and the cyano group in compound **11**, the imine **14** is generated. Finally, following a tautomeric proton shift of imine **14**, 2-amino-6-(hydroxymethyl)-8-oxo-4-aryl-4,8-dihydropyrano[3,2-*b*]pyrane **4** is formed.

The recovery and reuse of MCM-41-SO_3H were studied by using the preparation of **4a** as a model. The result indicated that the catalyst could be reused several times without significant loss of its activity and any prolonging of reaction time (Fig. 4). Furthermore, leaching of sulfur during the catalytic reaction was found to be negligible and decreased activity was attributed to catalyst weight loss in recycling. The amount of sulfonic acid groups of the catalyst before reaction indicated 0.95 mmol g^{-1}. After reaction at 90 °C, the amount of sulfonic acid groups of MCM-41-SO_3H was found to be 0.93 mmol g^{-1}.

Conclusion

In summary, we have demonstrated an environmentally benign and simple protocol for the synthesis of pyrano[3,2-*b*]pyrans derivatives by a one-pot three-component reaction of aldehydes or malononitrile, and kojic acid in the presence of MCM-41-SO_3H as efficient and recoverable catalyst. The catalyst can be recycled and reused without losing the original activity.

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Compliance with ethical standards

We confirm that the manuscript has been submitted solely to this journal and is not published, in press, or submitted elsewhere. We confirm that all the research meets the ethical guidelines, including adherence to the legal requirements of the study country.

Conflicts of interest We certify that we have no affiliation with or financial involvement with any organization or entity with a direct financial or any other interest in the subject matter or materials discussed in the manuscript. We declare no conflicts of interest.

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