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MCM-41@Schiff base-$Co(OAc)_2$ as an efficient catalyst for the synthesis of pyran derivatives

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Abstract

Heterogeneous ordered mesoporous silica materials catalyst, MCM-41@Schiff base-$Co(AcO)_2$, reveals high catalytic performance within the synthesis of pyran derivatives using the multicomponent reaction of aldehydes, malononitrile and 2-naphthol (or cyclohexane-1,3-dione) in water. The reactions afforded the desired products in high yields (up to 97% and 95%). The substantial feature is that the mesoporous-complex catalyst could be easily separated from the reaction mixture by centrifugation and reused at least 6 times with more than 80% yield in activity. The gram-scale experiments were achieved with good yields and implied that the catalytic method was effective and convenient for heterocyclic synthesis. What is more, the synthesized catalyst was characterized using various spectroscopic techniques to obtain the structural and functional features. The analysis results confirmed that the Co-Schiff base complex immobilized on the surface of mesoporous materials MCM-41. Finally, a plausible reaction mechanism was proposed.

Keywords MCM-41 · Schiff base · Heterogeneous · Pyran · Catalysis

Introduction

Pyran is an important structural units of six-membered oxygen heterocyclic compounds, which can build various active structures of biopharmacological molecules and natural products [1], such as antiproliferative activity of pyranoxanthone [2], antibacterial agents [3, 4] and apoptosis-inducing agents [5, 6]. With the further

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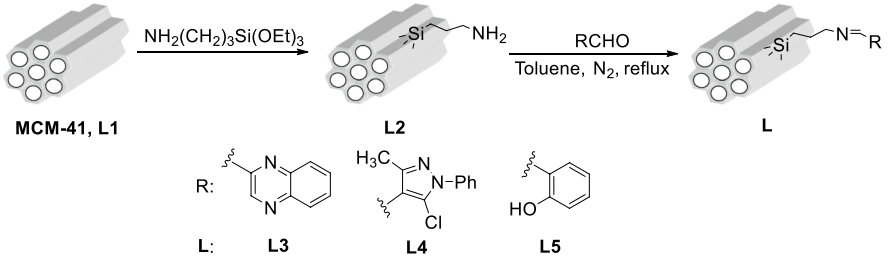
study of these compounds, pyran derivatives can be widely applied not only in medicine and biochemistry, but also in these fields of dyes [7, 8], pH sensitizers [9], semiconductors [10, 11] and materials [12, 13]. Therefore, due to their wide application value, they have attracted much attention. The new synthetic methods of pyran derivatives using different catalysts have been reported, for instance Brønsted acid [14], BINOL based [15], Lewis acids [16], ionic liquids [17], nanomaterials [18–20], etc. And good results were obtained. But the development of simply, environment and convenient procedures for the synthesis of pyran or xanthene derivatives continues to be a challenging endeavor in organic catalytic.

In recent years, following the increasing consciousness of "green chemistry," remarkable studies have been focused on finding environmental, atomic economy, recycling and reuse technology, etc., in the field of organic synthesis. The ordered mesoporous silica materials, as heterogeneous catalysts, have attracted particular attention due to their environmentally friendly nature, low cost, recovery and recyclability [21]. This kind of materials has been applied in various fields such as drug delivery, gas absorption, energy storage, catalysis [22, 23]. We previously reported some studies with the aim of designing functional MCM-41, as classic heterogeneous catalysts, that can be used to the organic catalysis [24]. And among them, Schiff base-supported MCM-41 shows good catalytic activity [25]. In view of the great potential of MCM-41, we have designed a new heterogeneous MCM-41@Schiff base-$Co(AcO)_2$ catalytic system. In continuance, further investigation was carried out by using catalyzing the reactions of aldehyde and malononitrile with 2-naphthol (or cyclohexane-1,3-dione) to confirm the catalytic activity and reusablity. MCM-41@Schiff base-$Co(AcO)_2$ has shown high catalytic performance in this reaction in water and with high yields (up to 97% and 95%) (Scheme 1).

Experimental

All chemicals and MCM-41 were obtained from Adamas-Beta and used without further purification. The samples were analyzed using FTIR spectroscopy (using a Bruker equinx 55 in KBr matrix in the range of 4000–400 cm^{-1}). Scanning electron microscope (SEM) images were recorded on LEO1430VP. Transmission electron microscope (TEM) images were obtained from a Hitachi H-600 instrument. ^{1}H and ^{13}C NMR spectra were recorded on an INOVA 400 MHz in $CDCl_3$ as solvent and TMS as internal reference (chemical shifts, in ppm). Purification



Scheme 1 Synthesis of ligands

of reaction products was carried out by column chromatography using Qingdao silica gel (300–400 mesh). Analytical thin-layer chromatography (TLC) was performed on silica gel GF254 (Qingdao, China) with ethyl acetate and petroleum ether (60–90 °C). Melting points were determined on an elemental digital melting points apparatus and were uncorrected.

Preparation of L2 and L4

In a typical procedure, 1 g of calcined MCM-41 was added to free three-necked bottle, and then, 50 mL ethanol and 3 mL 3-aminopropyltriethoxysilane were injected slowly under nitrogen protection. Afterward, refluxing lasted for 12 h and the mixture was recovered by centrifugation. It was washed carefully with diethyl ether and dichloromethane. The Schiff base ligand **L4** was synthesized from the reaction with 1 mmol modification of MCM-41 (**L2**) and 1 mmol aldehyde in 40 mL toluene, in the presence of nitrogen under reflux for 12 h. The mixture was cooled to room temperature and filtered to give the corresponding crude product. The pure product was washed by dichloromethane and petroleum ether.

General procedure for synthesis of pyran derivatives

Aldehyde **1a** (0.2 mmol, 28.1 mg), malonitrile **2a** (0.2 mmol, 13.2 mg), 2-naphthol **3** (0.2 mmol, 28.8 mg) (or 5,5-dimethylcyclohexane-1,3-dione **5a** (0.2 mmol, 28.0 mg)) and **L4** (0.01 g)-Co(OAc)$_2$ (10 mol%) were added in water (1.0 mL) and stirred at 100 °C for 3 h until completion (monitored by TLC). Then, the reaction mixture was extracted with ethyl acetate (5 mL × 3). The combined organic was dried with anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography to give the corresponding adducts **4a** and **6c**.

Physical and spectroscopic data for 4a–4q and 6a–6v

3-Amino-1-(4-chlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (4a) White solid, yield: 69.90 mg (97%); m.p: 210–211 °C (lit. [26] 207–209 °C); 1H NMR (400 MHz, DMSO) δ 7.96–7.91 (m, 2H), 7.82–7.80 (m, 1H), 7.47–7.41 (m, 2H), 7.35–7.30 (m, 3H), 7.24–7.18 (m, 2H), 7.00 (s, 2H), 5.36 (s, 1H).

3-Amino-1-(4-fluorophenyl)-1H-benzo[f]chromene-2-carbonitrile (4b) White solid, yield: 64.74 mg (94%); m.p: 230–231 °C (lit. [26] 226–228 °C); 1H NMR (400 MHz, DMSO) δ 7.96–7.91 (m, 2H), 7.84–7.82 (m, 1H), 7.48–7.40 (m, 2H), 7.31 (d, $J = 9.0$ Hz, 1H), 7.25–7.19 (m, 2H), 7.15–7.09 (m, 2H), 6.99 (s, 2H), 5.35 (s, 1H).

3-Amino-1-(4-nitrophenyl)-1H-benzo[f]chromene-2-carbonitrile (4c) White solid, yield: 66.84 mg (90%); m.p: 168–170 °C (lit. [26] 168–170 °C); 1H NMR (400 MHz, DMSO) δ 8.18–8.12 (m, 2H), 8.01–7.97 (m, 1H), 7.95–7.92 (m, 1H),

7.81–7.78 (m, 1H), 7.49–7.43 (m, 4H), 7.37 (d, J = 8.6 Hz, 1H), 7.12 (s, 2H), 5.55 (s, 1H).

3-Amino-1-(4-methoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (4d) White solid, yield: 66.23 mg (93%); m.p: 193–195 °C (lit. [26] 195–197 °C); 1H NMR (400 MHz, DMSO) δ 7.94–7.90 (m, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.46–7.40 (m, 2H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.10 (d, J = 8.7 Hz, 2H), 6.89 (s, 2H), 6.81 (d, *J*–8.6 Hz, 2H), 5.24 (s, 1H), 3.67 (s, 3H).

3-Amino-1-(2-chlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (4e) White solid, yield: 67.83 mg (94%); m.p: 255–256 °C (lit. [26] 265–267 °C); 1H NMR (400 MHz, DMSO) δ 7.99–7.90 (m, 2H), 7.66–7.62 (m, 1H), 7.51–7.40 (m, 3H), 7.37–7.32 (m, 1H), 7.22–7.15 (m, 2H), 7.06–6.96 (m, 3H), 5.72 (s, 1H).

3-Amino-1-(2-bromophenyl)-1H-benzo[f]chromene-2-carbonitrile (4f) White solid, yield: 68.08 mg (84%); m.p: 245–246 °C (lit. [26] 229–231 °C); 1H NMR (400 MHz, DMSO) δ 7.98–7.91 (m, 2H), 7.66–7.62 (m, 2H), 7.50–7.40 (m, 2H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13–7.03 (m, 3H), 6.92 (d, *J* = 7.5 Hz, 1H), 5.68 (s, 1H).

3-Amino-1-(2-methoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (4g) White solid, yield: 65.57 mg (92%); m.p: 224–225 °C (lit. [26] 222–224 °C); 1H NMR (400 MHz, DMSO) δ 7.94–7.85 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.46–7.38 (m, 2H), 7.33–7.29 (m, 1H), 7.17–7.07 (m, 1H), 7.05–7.01 (m, 1H), 6.88–6.75 (m, 4H), 5.60 (s, 1H), 3.89 (s, 3H).

3-Amino-1-(3-chlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (4h) White solid, yield: 66.39 mg (92%); m.p: 230–231 °C (lit. [26] 234–236 °C); 1H NMR (400 MHz, DMSO) δ 8.02 (d, J = 8.4 Hz, 1H), 7.9–7.88 (m, 2H), 7.73 (d, *J* = 5.3 Hz, 2H), 7.53–7.48 (m, *J* = 8.4, 1H), 7.44–7.36 (m, 2H), 7.36–7.33 (m, 1H), 7.20–7.17 (m, 2H), 7.13–7.10 (m, 1H), 5.54 (s, 1H).

3-Amino-1-(2,4-dichlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (4i) White solid, yield 72.72 mg (92%); m.p: 211–212 °C (lit. [27] 214–216 °C); 1H NMR (400 MHz, DMSO) δ 8.02–7.89 (m, 2H), 7.76–7.54 (m, 2H), 7.52–7.40 (m, 2H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.30–7.24 (m, 1H), 7.08 (s, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.70 (s, 1H).

3-Amino-1-(naphthalen-2-yl)-1H-benzo[f]chromene-2-carbonitrile (4j) White solid, yield: 69.26 mg (92%); m.p: 230–231 °C (lit. [28] 210–214 °C); 1H NMR (400 MHz, DMSO) δ 7.99–7.76 (m, 7H), 7.49–7.35 (m, 5H), 7.24 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.04 (s, 2H), 5.49 (s, 1H).

Ethyl 3-amino-1-(4-chlorophenyl)-1H-benzo[f]chromene-2-carboxylate (4k) White solid, yield: 72.17 mg (95%); m.p: 190–192 °C (lit. [29] 193 °C); 1H NMR (400 MHz, DMSO) δ 7.99 (d, J = 8.3 Hz, 1H), 7.93–7.87 (m, 2H), 7.67 (s, 2H),

7.52–7.46 (m, 1H), 7.44–7.35 (m, 2H), 7.30–7.21 (m, 4H), 5.52 (s, 1H), 4.16–4.03 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H).

Ethyl 3-amino-1-(4-bromophenyl)-1H-benzo[f]chromene-2-carboxylate (4l) White solid, yield: 76.37 mg (90%); m.p: 234–235 °C (lit. [29] 231–232 °C); 1H NMR (400 MHz, DMSO) δ 7.98 (d, J = 8.5 Hz, 1H), 7.89 (dd, J = 8.5, 3.0 Hz, 2H), 7.69 (s, 2H), 7.52–7.45 (m, 1H), 7.43–7.33 (m, 4H), 7.23 (t, J = 5.4 Hz, 2H), 5.52 (s, 1H), 4.22–3.96 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H).

Ethyl 3-amino-1-(4-nitrophenyl)-1H-benzo[f]chromene-2-carboxylate (4m) White solid, yield: 69.49 mg (89%); m.p: 226–227 oC (lit. [29] 233–234 °C); 1H NMR (400 MHz, DMSO) δ 8.07–8.97 (m, 3H), 7.95–7.88 (m, 2H), 7.77 (s, 2H), 7.58–7.46 (m, 3H), 7.45–7.38 (m, 2H), 5.66 (s, 1H), 4.19–4.00 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H).

Ethyl 3-amino-1-(4-methoxyphenyl)-1H-benzo[f]chromene-2-carboxylate (4n) White solid, yield: 69.08 mg (92%); m.p: 150–152 °C (lit. [29] 145–146 °C); 1H NMR (400 MHz, DMSO) δ 8.01 (d, J = 8.5 Hz, 1H), 7.91–7.81 (m, 2H), 7.56 (s, 2H), 7.53–7.48 (m, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 8.9 Hz, 1H), 7.18–7.14 (m, 2H), 6.76–6.71 (m, 2H), 5.46 (s, 1H), 4.14–4.07 (m, 2H), 3.63 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H).

Ethyl 3-amino-1-(2-chlorophenyl)-1H-benzo[f]chromene-2-carboxylate (4o) White solid, yield: 71.41 mg (94%); m.p: 170–172 °C (lit. [30] 170–172 °C); 1H NMR (400 MHz, DMSO) δ 8.22 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.7 Hz, 2H), 7.76 (s, 2H), 7.54–7.48 (m, 1H), 7.45–7.39 (m, 1H), 7.38–7.26 (m, 3H), 7.18–7.04 (m, 2H), 5.85 (s, 1H), 4.14–4.04 (m, 2H), 1.18 (t, J = 7.1 Hz, 3H).

Ethyl 3-amino-1-(2-nitrophenyl)-1H-benzo[f]chromene-2-carboxylate (4p) White solid, yield: 71.05 mg (91%); m.p: 240–241 °C (lit. [29] 248–250 °C); 1H NMR (400 MHz, DMSO) δ 8.56 (d, J = 8.3 Hz, 1H), 8.02–7.85 (m, 3H), 7.78 (s, 2H), 7.56–7.39 (m, 4H), 7.37–7.30 (m, 1H), 7.11–7.07 (dd, J = 7.9, 1.3 Hz, 1H), 6.33 (s, 1H), 4.19–4.12 (m, 1H), 3.90–3.83 (m, 1H), 1.15 (t, J = 7.0 Hz, 3H).

Ethyl3-amino-1-(2,4-dichlorophenyl)-1H-benzo[f]chromene-2-carboxylate(4q) White solid, yield: 76.23 mg (92%); m.p: 200–201 °C (lit. [29] 196 °C); 1H NMR (400 MHz, DMSO) δ 8.13 (d, J = 8.4 Hz, 1H), 7.88 (dd, J = 8.2, 3.2 Hz, 2H), 7.81 (s, 2H), 7.53–7.46 (m, 1H), 7.43–7.38 (m, 2H), 7.34 (d, J = 8.9 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H), 7.20 (dd, J = 8.5, 2.2 Hz, 1H), 5.81 (s, 1H), 4.08 (q, J = 7.1 Hz, 2H), 1.18 (t, J = 9.2, 3H).

2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6a) White solid, yield: 55.34 mg (94%); m.p: 220–222 °C (lit. [31] 229–230 °C); 1H NMR (400 MHz, DMSO) δ 7.29 (t, J = 7.4 Hz, 2H), 7.21–7.11 (m, 3H),

6.97 (s, 2H), 4.17 (s, 1H), 2.51 (dd, $J = 4.9$, 3.0 Hz, 2H), 2.18 (dd, $J = 59.1$, 16.1 Hz, 2H), 1.04 (s, 3H), 0.96 (s, 3H).

2-Amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6b) White solid, yield: 56.22 mg (90%); m.p: 232–234 °C (lit. [32] 230–232 °C); 1H NMR (400 MHz, DMSO) δ 7.20–7.15 (m, 2H), 7.10 (t, $J = 8.6$ Hz, 2H), 6.95 (s, 2H), 4.21 (s, 1H), 2.60–2.45 (m, 2H), 2.18 (dd, J = 54.1, 16.1 Hz, 2H), 1.04 (s, 3H), 0.96 (s, 3H).

2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6c) White solid, yield: 61.16 mg (93%); m.p: 210–211 °C (lit. [32] 213–215 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.37–7.32 (m, 2H), 7.20–7.15 (m, 2H), 7.04 (s, 2H), 4.20 (s, 1H), 2.51–2.47 (m, 2H), 2.18 (dd, J = 57.2, 16.1 Hz, 2H), 1.04 (s, 3H), 0.95 (s, 3H).

2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6d) White solid, yield: 66.44 mg (89%); m.p: 206–208 °C (lit. [31] 195–197 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.50–7.46 (m, 2H), 7.13–7.08 (m, 2H), 7.04 (s, 2H), 4.18 (s, 1H), 2.18 (dd, $J = 57.7$, 15.9 Hz, 2H), 1.24 (s, 2H), 1.04 (s, 3H), 0.95 (s, 3H).

2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6e) White solid, yield: 61.08 mg (90%); m.p: 186–188 °C (lit. [31] 180–182 °C); ^{1}H NMR (400 MHz, DMSO) δ 8.20–8.13 (m, 2H), 7.47–7.42 (m, 2H), 7.16 (s, 2H), 4.35 (d, $J = 18.7$ Hz, 1H), 2.54 (s, 2H), 2.19 (dd, J = 59.5, 16.1 Hz, 2H), 1.05 (s, 3H), 0.96 (s, 3H).

2-Amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6f) White solid, yield: 59.04 mg (91%); m.p: 200–202 °C (lit. [31] 200–203 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.09–7.02 (m, 2H), 6.92 (s, 2H), 6.85–6.82 (m, 2H), 4.12 (s, 1H), 3.72 (s, 3H), 2.51 (d, $J = 1.8$ Hz, 2H), 2.17 (dd, $J = 60.4$, 16.1 Hz, 2H), 1.04 (s, 3H), 0.95 (s, 3H).

2-Amino-7,7-dimethyl-5-oxo-4-(p-tolyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6g) White solid, yield: 57.98 mg (94%); m.p: 212–214 °C (lit. [31] 208–210 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.05 (dd, $J = 25.9$, 8.0 Hz, 4H), 6.93 (s, 2H), 4.13 (s, 1H), 2.50 (s, 3H), 2.28–2.22 (m, 4H), 1.04 (s, 3H), 0.95 (s, 3H).

2-Amino-4-(3-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6h) White solid, yield: 60.50 mg (92%); m.p: 211–213 °C (lit. [31] 210–212 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.35–7.31 (m, 1H), 7.27–7.25 (m, 1H), 7.17–7.16 (m, 1H), 7.14–7.11 (m, 1H), 7.07 (s, 2H), 4.22 (s, 1H), 2.55–2.49 (m, 2H), 2.28–2.11 (m, 2H), 1.04 (s, 3H), 0.96 (s, 3H).

2-Amino-7,7-dimethyl-5-oxo-4-(m-tolyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6i) White solid, yield: 56.13 mg (91%); m.p: 220–222 °C (lit. [26] 204–206 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.17 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.96–6.91 (m, 4H), 4.13 (s, 1H), 2.52 (s, 2H), 2.27 (s, 3H), 2.24–2.09 (m, 2H), 1.04 (s, 3H), 0.97 (s, 3H).

2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6j) White solid, yield: 61.81 mg (94%); m.p: 215–216 °C (lit. [31] 190–192 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.36 (dd, J = 7.8, 1.3 Hz, 1H), 7.27 (td, J = 7.4, 1.4 Hz, 1H), 2.23–7.16 (m, 2H), 7.00 (s, 2H), 4.70 (s, 1H), 2.52–2.49 (m, 2H), 2.17 (dd, J = 67.8, 16.0 Hz, 2H), 1.05 (s, 3H), 0.99 (s, 3H).

2-Amino-4-(2-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6k) White solid, yield: 67.19 mg (90%); m.p: 151–152 °C (lit. [33] 150–152 °C); 1H NMR (400 MHz, DMSO) δ 7.55–7.51 (m, 1H), 7.31 (dd, J = 10.9, 4.2 Hz, 1H), 7.12 (ddd, J = 12.9, 6.8, 2.8 Hz, 2H), 7.00 (s, 2H), 4.71 (s, 1H), 2.53 (d, J = 3.5 Hz, 2H), 2.16 (dd, J = 66.6, 16.0 Hz, 2H), 1.05 (s, 3H), 0.99 (s, 3H).

2-Amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6l) White solid, yield: 62.44 mg (92%); m.p: 222–224 °C (lit. [31] 230–232 °C); 1H NMR (400 MHz, DMSO) δ 7.82 (dd, J = 8.1, 1.3 Hz, 1H), 7.66 (td, J = 7.7, 1.3 Hz, 1H), 7.46–7.39 (m, 1H), 7.36 (dd, J = 7.9, 1.4 Hz, 1H), 7.16 (s, 2H), 4.94 (s, 1H), 2.56 (d, J = 1.5 Hz, 1H), 2.46 (d, J = 17.6 Hz, 1H), 2.11 (dd, J = 73.5, 16.2 Hz, 2H), 1.02 (s, 3H), 0.89 (s, 3H).

2-Amino-4-(2-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6m) White solid, yield: 60.33 mg (93%); m.p: 202–204 °C (lit. [31] 190–194 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.18–7.13 (m, 1H), 7.00–7.93 (m, 2H), 6.85 (td, J = 7.4, 1.1 Hz, 1H), 6.79 (s, 2H), 4.48 (s, 1H), 3.75 (s, 3H), 2.55 (d, J = 17.5, 1H), 2.45 (d, J = 17.6 Hz, 1H), 2.27–2.04 (m, 2H), 1.05 (s, 3H), 0.97 (s, 3H).

2-Amino-4-(2,4-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6n) White solid, yield: 69.02 mg (95%); m.p: 200–201 °C (lit. [31] 200–202 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.52 (d, J = 2.2 Hz, 1H), 7.36 (dd, J = 8.4, 2.2 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.07 (s, 2H), 4.68 (s, 1H), 2.51–2.50 (m, 2H), 2.17 (dd, J = 65.0, 16.0 Hz, 2H), 1.04 (s, 3H), 0.98 (s, 3H).

2-Amino-7,7-dimethyl-4-(naphthalen-1-yl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6o) White solid, yield: 60.62 mg (88%); m.p: 230–232 °C (lit. [34] 232–233 °C); ^{1}H NMR (400 MHz, DMSO) δ 8.37 (d, J = 8.6 Hz, 1H), 7.94–7.89 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.59–7.50 (m, 2H), 7.48–7.42 (m, 1H), 7.24 (d, J = 6.6 Hz, 1H), 6.94 (s, 2H), 5.14 (s, 1H), 2.60 (s, 2H), 2.16 (dd, J = 68.7, 16.1 Hz, 2H), 1.07 (s, 3H), 1.00 (s, 3H).

2-Amino-4-(furan-2-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6p) White solid, yield: 51.18 mg (90%); m.p: 222–224 °C (lit. [34] 219–221 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.49–7.46 (m, 1H), 7.05 (s, 2H), 6.32 (dd, J = 3.2, 1.9 Hz, 1H), 6.07–6.03 (m, 1H), 4.33 (s, 1H), 2.53 (d, J = 14.5 Hz, 1H), 2.45 (d, J = 17.7 Hz, 1H), 2.23 (dd, J = 46.5, 16.1 Hz, 2H), 1.05 (s, 3H), 0.99 (s, 3H).

2-Amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6q) White solid, yield: 49.53 mg (93%); m.p: 215–217 °C (lit. [35] 211–212 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.28 (dd, J = 10.4, 4.3 Hz, 2H), 7.21–7.18 (m, 1H), 7.16 (d, J = 1.4 Hz, 1H), 7.15 (s, 1H), 6.96 (s, 2H), 4.18 (s, 1H), 2.65–2.60 (m, 2H), 2.32–2.24 (m, 2H), 2.00–1.92 (m, 2H).

2-Amino-4-(4-fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6r) White solid, yield: 53.45 mg (94%); m.p: 190–191 °C (lit. [35] 209–210 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.22–7.16 (m, 2H), 7.13–7.07 (m, 2H), 7.00 (s, 2H), 4.21 (s, 1H), 2.63–2.58 (m, 2H), 2.34–2.23 (m, 2H), 1.99–1.86 (m, 2H).

2-Amino-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6s) White solid, yield: 55.34 mg (92%); m.p: 223–224 °C (lit. [26] 224–226 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.34 (dd, J = 8.7, 2.1 Hz, 2H), 7.20–7.17 (m, 2H), 7.03 (s, 2H), 4.20 (s, 1H), 2.64–2.59 (m, 2H), 2.32–2.23 (m, 2H), 1.97–1.87 (m, 2H).

2-Amino-4-(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6t) White solid, yield: 53.34 mg (90%); m.p: 190–192 °C (lit. [26] 190–192 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.09–7.04 (m, 2H), 6.92 (s, 2H), 6.86–6.81 (m, 2H), 4.14 (s, 1H), 3.72 (s, 3H), 2.64–2.55 (m, 2H), 2.33–2.22 (m, 2H), 2.00–1.85 (m, 2H).

2-Amino-4-(3-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6u) White solid, yield: 57.14 mg (95%); m.p: 253–255 °C (lit. [26] 254 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.33 (t, J = 7.8 Hz, 1H), 7.27–7.24 (m, 1H), 7.18 (t, J = 1.9 Hz, 1H), 7.14 (dd, J = 7.5, 1.2 Hz, 1H), 7.06 (s, 2H), 4.22 (s, 1H), 2.69–2.57 (m, 2H), 2.23–2.24 (m, 2H), 1.98–1.86 (m, 2H).

2-Amino-4-(2-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6v) White solid, yield: 54.13 mg (90%); m.p: 212–214 °C (lit. [31] 212–214 °C); ^{1}H NMR (400 MHz, DMSO) δ 7.38–7.34 (m, 1H), 7.29–7.24 (m, 1H), 7.22–7.17 (m, 2H), 6.99 (s, 2H), 4.71 (s, 1H), 2.66–2.59 (m, 2H), 2.34–2.20 (m, 2H), 1.99–1.87 (m, 2H).

Results and discussion

The FTIR spectra of MCM-41 (**L1**), amine-functionalized MCM-41 (**L2**), MCM-41@Schiff base (**L4**) and MCM-41@Schiff base-M (**L4**-$Co(OAc)_2$) are shown in Fig. 1. The FTIR spectrum of mesoporous materials catalysts exhibited characteristic peaks at 1085 cm^{-1} and 799 cm^{-1} corresponding to Si–O–Si band. A new weak adsorption peak around 2950 cm^{-1} was corresponding to vibration of N–H band of amine-functionalized MCM-41. In the FTIR spectrum of **L4**, the presence of the C=N group was confirmed at 1670 cm^{-1}. The C=N band absorption shifts to lower frequency of the spectrum of **L4**/M ($Co(OAc)_2$) compared with the spectrum of **L4**, which indicates that C=N coordinates with cobalt successfully. XRD spectra of **L1**–**L4**/M are shown in Fig. 2. In the range of 15°–30°, the basic pore structure was kept. In the spectrum of **L4**/M, a significant decrease in intensity was observed because of placing Schiff base group and metal salt into the MCM-41 pores that change the internal structure of the mesoporous [36, 37]. SEM (Fig. 3) and TEM (Fig. 4) of the different catalysts indicated that the nanoparticles showed uniform

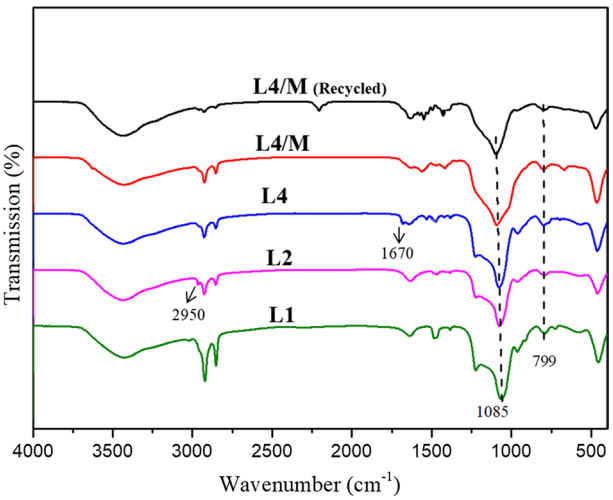


Fig. 1 IR patterns of MCM-41 **L1**, amine-functionalized MCM-41 **L2, L4**, **L4**/M and **L4**/M (recycled) catalyst)

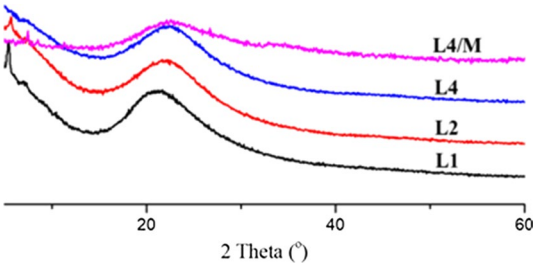


Fig. 2 XRD patterns of MCM-41 **L1**, amine-functionalized MCM-41 **L2, L4** and **L4**/M

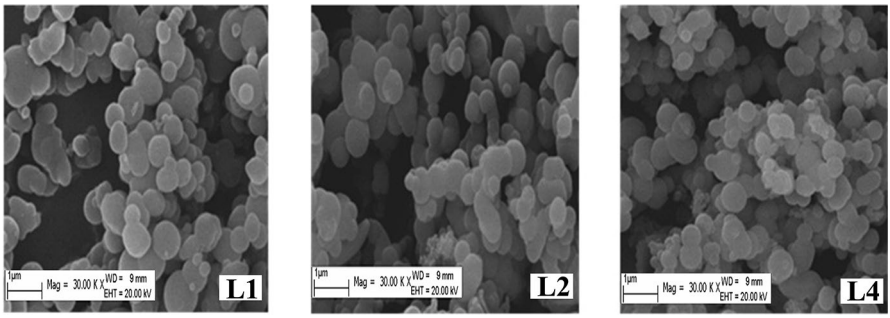


Fig. 3 SEM patterns of MCM-41 **L1**, amine-functionalized MCM-41 **L2** and **L4**

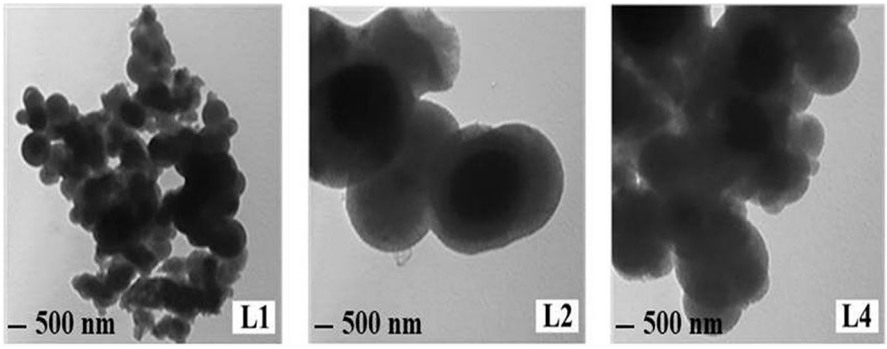


Fig. 4 TEM patterns of MCM-41 **L1**, amine-functionalized MCM-41 **L2** and **L4**

spherical shape. And the TEM image showed the hierarchical hollow mesoporous structure of material.

The binding energies of the catalyst **L4**/M were 284.8 eV which were shown in the deconvoluted XPS spectra in Fig. 5. In C 1*s* XPS spectra, there are three peaks around 284.8, 286.4 and 288.0 eV which represented the C=C, C=N and C–Cl groups, respectively [38]. In N 1*s* XPS spectra, there is a signal around 402.68 eV which confirmed the C=N group of Schiff base formation involves the condensation of 5-chloro-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde and amine-functionalized MCM-41 **L2**. In O 1*s* XPS spectra, there is a peak at 532.28 eV that is Si–O–C group. And, there is a peak around 399.48 eV that is the electron pair effect of nitrogen atoms and cobalt ions. The satellite peak of Co 2*p* 1/2 and Co 2*p* 3/2 spectra of the catalyst complex shows two typical bands at 797.48 and 781.28 eV confirmed the binding energy of Cobalt atom with Co^{2+} ion and the coordination of cobalt metal with the C=N of Schiff base and heterocycle groups. There is a satellite peak around 797.48 eV, i.e., Co 2*p* 3/2, which confirmed the electrostatic interaction with the **L4** and $Co(OAc)_2$. Furthermore, the wide survey of XPS spectra confirms that there were C, O, N, Co and Si atoms on the synthesized catalyst.

In our initial study, we screened various catalysts to the reaction of 4-chlorobenzaldehyde **1a** and malononitrile **2a** with 2-naphthol **3**. First, the catalytic

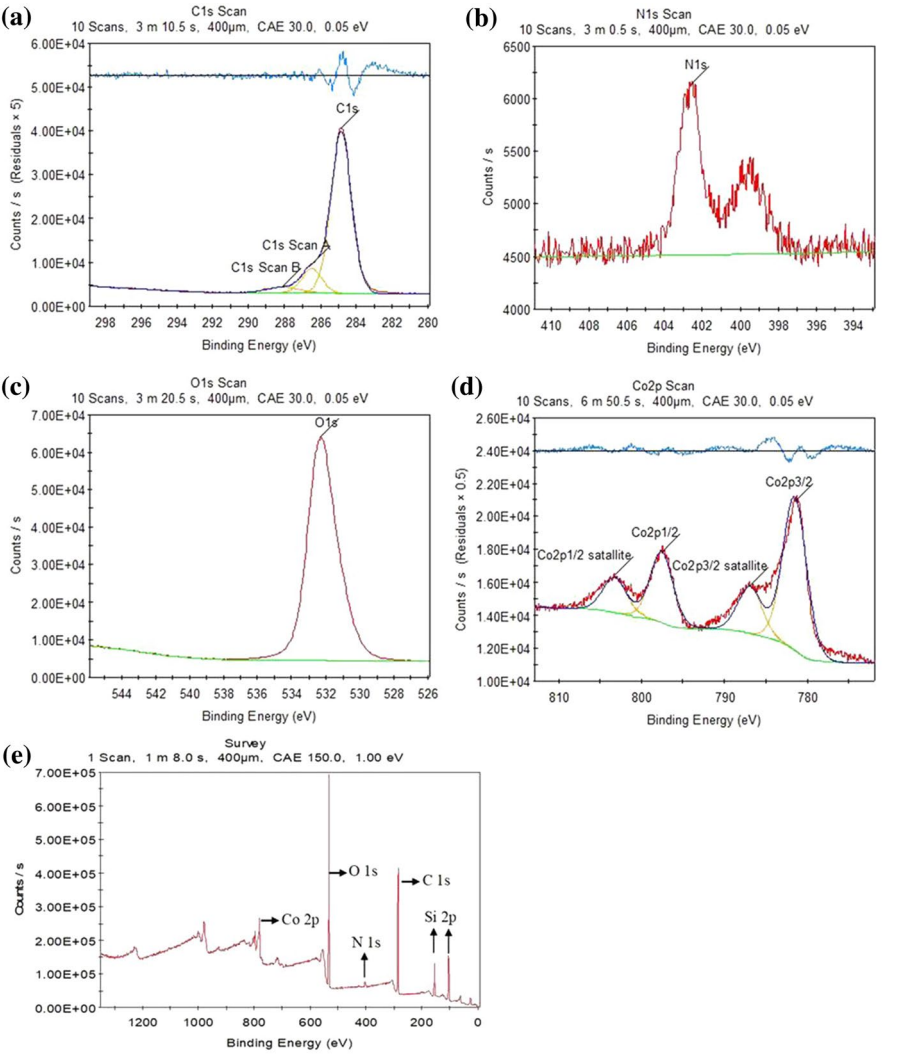


Fig. 5 XPS analysis of **L4/**M with **a** C 1*s* scan, **b** N 1*s* scan, **c** O 1 s scan, **d** Co 2*p* scan, and **e** elemental survey

activity of SiO_2, MCM-41 and MCM-41@Schiff bases in the multicomponent reaction was tested. MCM-41 and MCM-41@Schiff bases exhibited better catalytic activity than SiO_2, and **L4** was found to be the most suitable for the reaction and gave the highest reactivity (Table 1, entries 2–7). Comparative results indicated that the pores indeed facilitated the reaction.

Following, the catalytic activity of a series of Lewis acids such as $Zn(OAc)_2$, $Ni(OAc)_2$, $Cu(OAc)_2$ and $Co(OAc)_2$ was examined. **L4**-$Co(OAc)_2$ gave the best result, 95% yield (Table 1, entries 8–11). However, only 37% yield was achieved

Table 1 Optimization of the reaction conditions

Entry	Catalyst	Solvent	Time (h)	Temp (°C)	Yield (%)[a]
1	None	Water	3	100	–
2	SiO_2	Water	3	100	–
3	**L1**	Water	3	100	20
4	**L2**	Water	3	100	31
5	**L3**	Water	3	100	32
6	**L4**	Water	3	100	60
7	**L5**	Water	3	100	41
8	**L4**/$Zn(OAc)_2$	Water	3	100	36
9	**L4**/$Ni(OAc)_2$	Water	3	100	45
10	**L4**/$Cu(OAc)_2$	Water	3	100	35
11	**L4**/$Co(OAc)_2$	Water	3	100	95
12	$Co(OAc)_2$	Water	3	100	37
13	**L4**/$Co(OAc)_2$	Water	3	90	79
14	**L4**/$Co(OAc)_2$	Water	3	80	75
15	**L4**/$Co(OAc)_2$	Water	3	50	68
16	**L4**/$Co(OAc)_2$	Water	1/2/5	100	30/54/94
17[b]	**L4**/$Co(OAc)_2$	water	3	100	97
18[c]	**L4**/$Co(OAc)_2$	Water	3	100	90
19[d]	**L4**/$Co(OAc)_2$	Water	3	100	90/80

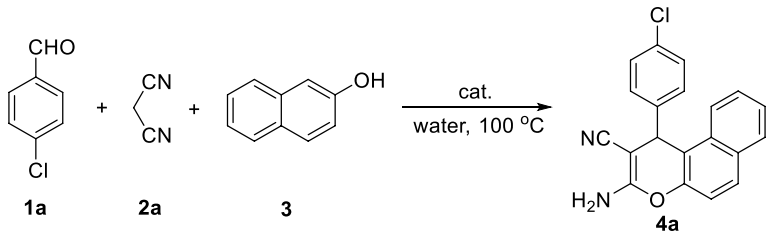
Reaction conditions (unless noted otherwise): All the reactions were performed with 4-chlorobenzaldehyde (0.20 mmol), malononitrile (0.20 mmol), 2-naphthol (0.20 mmol), **L** (0.01 g) and $Co(OAc)_2$ (10 mol%) in water (1 mL) at 100 °C for 3 h

[a]Isolated yield

[b]**1a**:**2a**:**3** = 1:1.2:1

[c]**1a**:**2a**:**3** = 1.1:1:1

[d]Use 5 mol% and 2.5 mol% $Co(OAc)_2$



Scheme 2 Synthesis of 2-amino benzo[*H*] chromene with 2-naphthol

when the catalyst was $Co(OAc)_2$ (Table 1, entry 12). Finally, some parameters were considered to obtain higher yield. The effect of temperature, time, substrate ratio and the catalyst loading was examined (Table 1, entries 13–18). It is noteworthy when the substrate ratio was 1:1.2:1, 97% yield was achieved (Table 1,

Table 2 Synthesis of 2-amino benzo[*h*] chromenes **4** from 2-naphthol

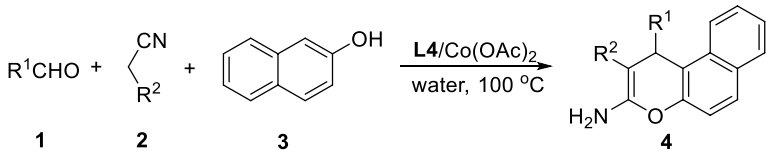
Entry	R^1	R^2	Product	Yield(%)[a]
1	4-Cl–C_6H_4	CN	**4a**	97
2	4-F–C_6H_4	CN	**4b**	94
3	4-NO_2–C_6H_4	CN	**4c**	90
4	4-CH_3O–C_6H_4	CN	**4d**	93
5	2-Cl–C_6H_4	CN	**4e**	94
6	2-Br–C_6H_4	CN	**4f**	84
7	2-CH_3O–C_6H_4	CN	**4g**	92
8	3-Cl–C_6H_4	CN	**4h**	92
9	2,4-Cl–C_6H_3	CN	**4i**	92
10	2-Naphthyl	CN	**4j**	92
11	4-Cl–C_6H_4	COOEt	**4k**	95
12	4-Br–C_6H_4	COOEt	**4l**	90
13	4-NO_2–C_6H_4	COOEt	**4m**	89
14	4-CH_3O–C_6H_4	COOEt	**4n**	92
15	2-Cl–C_6H_4	COOEt	**4o**	94
16	2-NO_2–C_6H_4	COOEt	**4p**	91
17	2,4-Cl–C_6H_3	COOEt	**4q**	92

Reaction conditions (unless noted otherwise): All the reactions were performed with **1** (0.20 mmol), **2** (0.24 mmol), **3** (0.20 mmol), **L4** (0.01 g) and $Co(OAc)_2$ (10 mol%) in water (1 mL) at 100 °C for 3 h

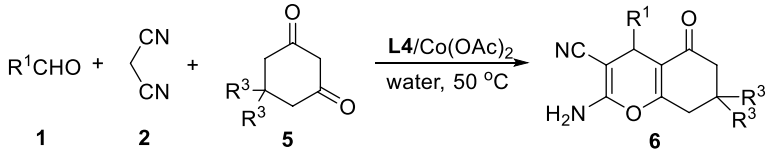
[a]Isolated yield

entry 17). Extensive screening showed that the optimized conditions were **1a** (0.20 mmol), **2a** (0.24 mmol), **3** (0.20 mmol), **L4** (0.01 g)/$Co(OAc)_2$ (10 mol%) in water (1 mL) at 100 °C for 3 h (Scheme 2).

Under the optimized conditions, the substrate scope of the aromatic aldehyde and malononitrile (or ethyl cyanoacetate) was investigated, and the corresponding products were obtained in good yields. As shown in Table 2, whether R^2 was CN or COOEt, the electronic nature and the position of the different substituents on the aromatic ring had little influence on yields. Moreover, fused-ring and multisubstituted aldehydes were also suitable substrates for the reaction (Table 2, entries 9, 10 and 17) (Scheme 3).



Scheme 3 Synthesis of 2-amino benzo[*H*] chromene derivatives



Scheme 4 Synthesis of 2-amino-4*H*-pyran derivatives

Table 3 Synthesis of 2-amino-4*H*-pyrans 6 from cyclohexane-1,3-dione

Entry	R^1	R^3	Product	Yield (%)[a]
1	C_6H_4	CH_3	**6a**	94
2	4-F–C_6H_5	CH_3	**6b**	90
3	4-Cl–C_6H_4	CH_3	**6c**	93
4	4-Br–C_6H_4	CH_3	**6d**	89
5	4-NO_2–C_6H_4	CH_3	**6e**	90
6	4-CH_3O–C_6H_4	CH_3	**6f**	91
7	4-CH_3–C_6H_4	CH_3	**6g**	94
8	3-Cl–C_6H_4	CH_3	**6h**	92
9	3-CH_3–C_6H_4	CH_3	**6i**	91
10	2-Cl–C_6H_4	CH_3	**6j**	94
11	2-Br–C_6H_4	CH_3	**6k**	90
12	2-NO_2–C_6H_4	CH_3	**6l**	92
13	2-CH_3O–C_6H_4	CH_3	**6m**	93
14	2,4-Cl–C_6H_3	CH_3	**6n**	95
15	2-Naphthyl	CH_3	**6o**	88
16	2-Furyl	CH_3	**6p**	90
17	C_6H_5	H	**6q**	93
18	4-F–C_6H_5	H	**6r**	94
19	4-Cl–C_6H_4	H	**6s**	92
20	4-CH_3O–C_6H_4	H	**6t**	90
21	3-Cl–C_6H_4	H	**6u**	95
22	2-Cl–C_6H_4	H	**6v**	90

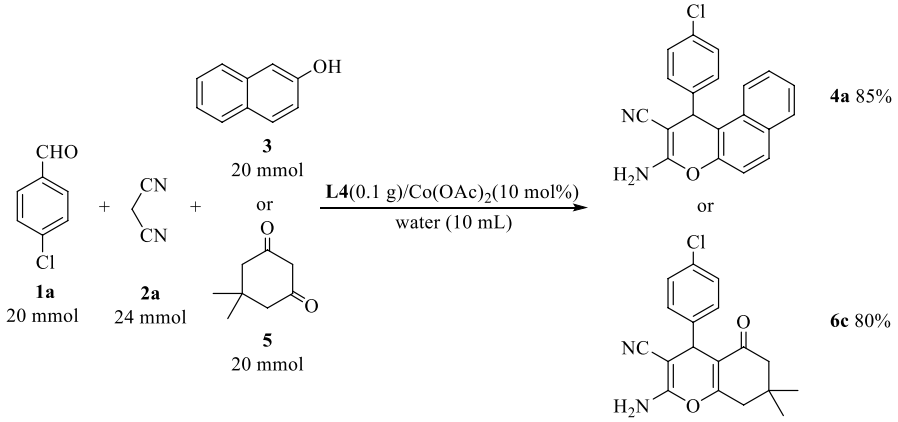
Reaction conditions (unless noted otherwise): All the reactions were performed with **1** (0.20 mmol), **2** (0.24 mmol), **5** (0.20 mmol), **L4** (0.01 g) and $Co(OAc)_2$ (10 mol%) in water (1 mL) at 50 °C for 3 h

[a]Isolated yield

To expand the application of the present synthetic strategy, catalytic xanthene of cyclohexane-1,3-dione was performed, and the corresponding products were obtained with 88–95 yields. Similarly, fused-ring, multisubstituted and heteroaromatic-substituted aldehydes were also suitable substrates for the reaction of xanthenes. Furthermore, a scale-up version of the catalytic xanthenes of 2-naphthol **3** or cyclohexane-1,3-dione **5** was also performed to test the synthetic potential. As

Table 4 Comparison of literature and this work methods for synthesis of 2-amino benzo[*h*] chromenes **4a** and 2-amino-4*H*-pyrans **6c**

Product	Catalyst	Reaction conditions	Time (min)	Yield (%)	References
4a	Nanosilica-bonded aminoethylpiperazine (SB-APP)	Solvent-free/80 °C	30 min	95	[28]
	Nanopolypropylenimine dendrimer (PPI)	Solvent-free/110 °C	15 mine	92	[39]
	Triazine-based porous organic polymer (TPOP-2)	H_2O/80 °C	6 h	88	[40]
	MCM-41@Schiff base-Co(OAc)$_2$	H_2O/100 °C	3 h	97	This work
6c	Ionic liquid	r.t.	24-30 h	80	[32]
	Fe_3O_4@SiO_2@TiO_2	Solvent-free/100 °C	10 min	96	[41]
	Fe_3O_4@SiO_2-Imid-PMA^n	H_2O/reflux	10 min	95	[34]
	MCM-41@Schiff base-Co(OAc)$_2$	H_2O/50 °C	3 h	93	This work



Scheme 5 Synthesis of xanthene derivatives on a gram scale

shown in Scheme 5, by treatment of 20 mmol of 4-chlorobenzaldehyde under the optimal reaction conditions, the desired synthesis of **4a** or **6c** was accomplished in 85% or 80% yield using **L4**(0.1 g)/$Co(OAc)_2$ (10 mol%) complex catalyst (Scheme 4, Table 3).

As pyran is an important heterocyclic unit, many heterogeneous catalyst systems have been developed to catalyze the synthesis of pyran derivatives. Table 4 shows the catalytic data reported in the literature and this work. The present method using MCM-41@Schiff base-$Co(OAc)_2$ as catalyst offers several advantages, such as greener conditions, simple procedure, excellent yields and ideal recyclable catalyst (Scheme 5).

Out of the advantages of the organic mesoporous materials is its ability to function as a recyclable catalyst, recyclability of **L4**-$Co(OAc)_2$ was investigated under

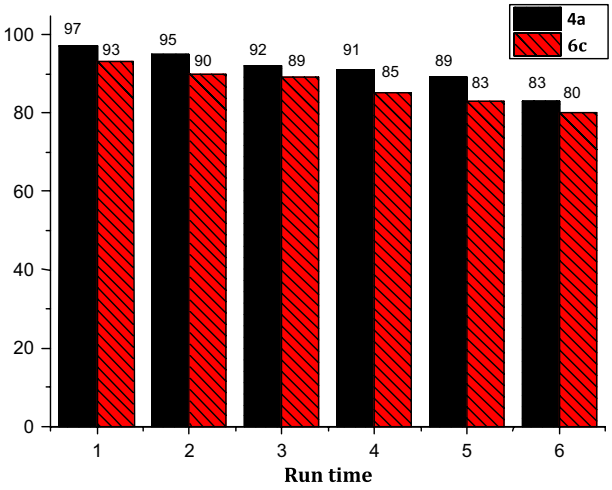
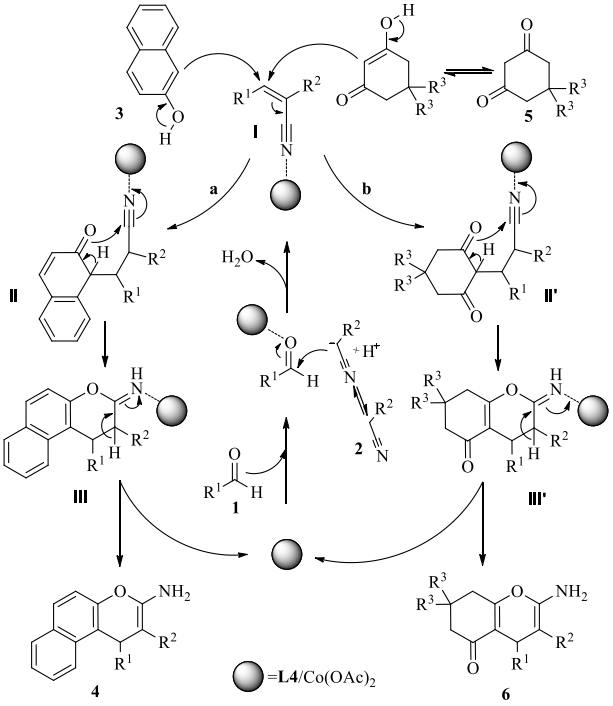


Fig. 6 Catalyst recycling studies



Scheme 6 Proposed catalytic mechanism

the optimized conditions (Fig. 6). After six cycles of reaction, **4a** and **6c** were still afforded with 83% and 80% yields. The heterogeneity of **L4**-Co(OAc)$_2$ in these two reactions was confirmed by the "hot filtration" test. After a reaction run, the solid and water were separated and separately used as catalyst for the reactions. Compared with the previous catalytic activity, a slightly lower yield was gained in the solid, and a small amount of products were observed for the water. This "hot filtration" test indicated the dissolved cobalt salt leads to the slight decrease in the activity. And the FTIR of catalyst after recycling of it for six times showed the intensity of C=N adsorption peak decreased, which confirmed the loss of active components. So, in the recycling experiments, the mixture of solid and water was stirred and dried and used as catalyst for the next reaction run.

The formation of **4** and **6** could be explained by a possible mechanism shown in Scheme 6. Firstly, the complex **L4**/Co(OAc)$_2$ catalyzed the Knoevenagel condensation of aldehyde (**1**) and malononitrile (or ethyl cyanoacetate) (**2**) to give the intermediate **I** [42]. And then, 2-naphthol (**3**) or cyclohexane-1,3-dione (**5**) attacked **I** to provide intermediate **II** or **II'**. Tautomerism of **II** or **II'** followed by intramolecular nucleophilic addition of oxygen to the cyano group and protonation provides **III** or **III'**, finally, which undergoes isomerization to give the xanthenes of **4** and **6**.

Conclusion

In summary, a novel, green and efficient catalytic system has been developed for the direct one-spot synthesis of xanthenes via MCM-41@Schiff base-$Co(OAc)_2$-mediated three-component reaction of 2-naphthol (or cyclohexane-1,3-dione) with aromatic aldehyde and malononitrile (or ethyl cyanoacetate). The corresponding products were obtained in high yields (up to 97% and 95%) in water. Compared with the methods described in the literature, the heterogeneous catalyst showed good levels of recyclability and reusability, and it could be recovered at least six cycles still maintained the yields at more than 80%. Further applications of MCM-41@Schiff base catalysts to other reactions are underway.

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