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ARTICLE

Synthesis and characterization of novel nanosilica molybdic acid and its first catalytic application in synthesis of new and known pyranocoumarins

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Nanosilica molybdic acid (nano-SMA) was prepared and employed as a novel, recyclable and safe catalyst for the one-pot, three-component condensation of 4-hydroxycoumarin with aldehydes and malononitrile to produce new and known pyrano[2,3-*c*]chromenes as potent biologically active compounds. This novel method has many advantages, such as the high product yield and a simple work-up procedure.

Introduction

It is well known in the protocol of green chemistry that its main objective is to perform reactions using heterogeneous catalysts, in order to generate environmentally friendly chemical transformations.[1] In this context, substantial research efforts have been devoted to develop catalysts with high efficacy. In the case of heterogeneous catalysis, the catalytic ability of materials mainly depends on their microscopic structure which directly impacts the activity, selectivity and thermal or chemical stability of the catalyst.[2] Use of efficient nanocatalysts plays a promising role towards achieving these objectives of green chemistry.[3]

The recent emergence of nanocatalysis has received a lot of attention because it opens new perspectives for the mild catalysis of important reactions with lower environmental impact.[4] Nanocatalysts have distinguishing features than bulk case. For example, nano sized systems dramatically increase the contact between reactants and catalyst.[5]

Multicomponent reactions (MCRs) are special types of synthetically useful organic reactions in which three or more various substrates react to give a final product in a one-pot procedure.[6] These reactions are valuable assets in the organic synthesis and pharmaceutical chemistry due to their wide range of usage in the preparation of various structural scaffolds and discovery of new drugs.[7]

Pyranocoumarins are well recognized due to their importance in biological and pharmaceutical researches.[8] A considerable effort has been made for the synthesis of pyran-annulated heterocycles due to their wide applications.[9]

Several methods have been reported for the synthesis of pyrano[2,3-*c*]coumarin as biologically active compounds. In recent studies, the synthesis of pyrano[2,3-*c*]chromenes via a three-component reaction has been described using various reagents, such as $Ca(OTf)_2$,[10] $Bi(OTf)_3$,[11] meglumine,[12] Mohr's salt,[13] $Cu(OTf)_2$,[14] $[BMIm]BF_4$,[15] [2-aemim][PF_6],[16] sodium dodecyl sulfate (SDS),[17] $H_6P_2W_{18}O_{62}.18H_2O$,[18] cetyltrimethylammonium chloride/bromide,[19,20] Titanium dioxide nanowires,[21] tetrabutylammonium bromide (TBAB),[22] triethylbenzylammonium chloride (TEBA),[23] chitosan,[24] K_3PO_4,[25] Na_2CO_3 under grinding,[26] Mg/Al hydrotalcite,[27] DBU[28] and piperidine under microwave irradiation.[29] However, some proposed methods suffer from disadvantages including relying on multi-step conditions, the use of toxic organic solvents or catalysts containing transition metals, tedious work-up procedure, troublesome waste discarding, high reaction time, and low yields.[30]

In this work, a new methodology to obtain some pyrano[2,3-c]chromene, via a one-pot three-component condensation, is reported. In this paper, we introduce nano silica molybdic acid (nano-SMA) as a novel and safe catalyst for the synthesis of novel and known pyranocoumarin derivatives.

Experimental

Methods and materials

The chemicals were purchased from Merck and Aldrich chemical companies. The silica chloride **1** was synthesized according to the published procedure.[31] The reactions were monitored by TLC (silica–gel 60 F 254 , hexane: EtOAc). Fourier transform infrared (FT-IR) spectroscopy spectra were recorded on a Shimadzu-470 spectrometer, using KBr pellets and the melting points were determined on a KRUSS model instrument. ^{1}H NMR spectra were recorded on a Bruker Avance II 400 NMR spectrometer at 400 MHz, in which DMSO-d_6 was used as solvent and TMS as the internal standard. X-ray diffraction (XRD) pattern was obtained by Philips X Pert Pro X diffractometer operated with a Ni filtered Cu-Kα radiation

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source. X-ray fluorescence (XRF) spectroscopy was recorded by X-Ray Fluorescence Analyzer, Bruker, S_4 Pioneer, Germany. The varioEl CHNS Isfahan Industrial University was used for elemental analysis. Transmission electron microscopy (TEM) images of the electrocatalyst were recorded using a Philips CM-10 TEM microscope operated at 100 kV.

General procedure for the preparation of nanosilica molybdic acid 2

To an oven-dried (125 °C, vacuum) sample of silica–gel 60 (10 g) in a round bottomed flask (250 mL) equipped with a condenser and a drying tube, thionyl chloride (40 mL) was added and the mixture in the presence of $CaCl_2$ as a drying agent was refluxed for 48 h. The resulting white-grayish powder was filtered and stored in a tightly capped bottle.[31] 0.1g of silica chloride **1** was dissolved in toluene (10 ml) and stirred for 30 min. The solution of 0.084 g sodium molybdate in 10 ml toluene was added to the first solution and stirred for 10 min. The resulting mixture was sonicated in ultrasonic bath for 1h at room temperature. The mixture was transferred to a 70 ml autoclave, heated at 140 °C for 4 h. White precipitate obtained, washed with distilled water and then separated by filtration, dried at 30 ˚C for 2 h. The white powder was dissolved in HCl (0.1 N) and stirred for 1h. The white powder was separated by filtration, washed with distilled water and dried at 30 ˚C for 2 h.

General procedure for the preparation of pyrano[2,3-c]coumarin derivatives 6

Malononitrile **3** (1.1 mmol), aromatic aldehyde **4** (1 mmol), 4-hydroxycoumarin **5** (1 mmol), and SMA **2** (5 mol %) were added to a 10 mL mixture EtOH/H_2O (50/50) in a 25-mL pyrex flask and refluxed for an appropriate time (Table 3). The reaction progress was controlled by thin layer chromatography (TLC) using hexane/EtOAc (1:1). After completion of the reaction, the solvent was removed under vacuum, the crude products **6** were obtained after recrystalization from EtOH.

Spectral data

Compound 6i. IR (KBr): 3396, 3321, 3195, 2202, 1706, 1671, 1607, 1381, 1053 cm^{-1}. ^{1}H NMR (DMSO, 400 MHz): δ 7.90 (dd, 1H, J = 7.8, 1.2 Hz), 7.75–7.70 (m, 1H), 7.52–7.43 (m, 6H), 7.30–7.28 (m, 2H), 4.50 (s, 1H) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 159.55, 157.94, 153.70, 152.18, 146.02, 132.99, 130.69, 130.39, 130.05, 126.94, 124.65, 122.54, 121.68, 119.05, 116.57, 112.98, 103.15, 57.31, 36.59 ppm. Anal. Calcd. for $C_{19}H_{11}BrN_2O_3$: C, 57.74; H, 2.81; N, 7.09%. Found: C, 58.05; H, 2.68; N, 7.16%.

Compound 6j. IR (KBr): 3408, 3280, 3175, 2203, 1705, 1674, 1602, 1381, 1055 cm^{-1}. ^{1}H NMR (DMSO, 400 MHz): δ 7.90 (dd, 1H, J = 7.8, 1.2 Hz), 7.76–7.72 (m, 1H), 7.55–7.48 (m, 4H), 7.55–7.19 (m, 3H), 5.19 (d, 1H, J = 1.6 Hz). ^{13}C NMR (DMSO, 100 MHz): δ 159.38, 158.77, 152.11, 133.14 (d, J = 8.9 Hz), 129.88 (d, J = 10.4 Hz), 124.84, 124.68 (d, J = 4.2 Hz), 122.29, 118.73, 116.68, 115.25, 112.56, 38.83 ppm. Anal. Calcd. for $C_{19}H_{10}ClFN_2O_3$: C, 61.89; H, 2.73; N, 7.60%. Found: C, 61.90; H, 2.55; N, 7.72%.

Compound 6k. IR (KBr): 3391, 3180, 2196, 1712, 1674, 1608, 1381, 1240, 1054 cm^{-1}. ^{1}H NMR (DMSO, 400 MHz): δ 7.90 (dd, 1H, J = 8.0 Hz), 7.73–7.69 (m, 1H), 7.44–7.38 (m, 7H), 7.18 (d, 2H, J = 8.8 Hz), 6.95 (d, 2H, J = 8.8 Hz), 5.06 (s, 2H), 4.40 (s, 1H). ^{13}C NMR (DMSO, 100 MHz): δ 159.51, 157.87, 157.45, 153.09, 152.06, 137.05, 135.60, 132.83, 128.76, 128.40, 127.79, 127.64, 124.63, 122.41, 119.30, 116.53, 114.61, 112.97, 104.19, 69.17, 58.09, 36.13 ppm. Anal. Calcd. for $C_{26}H_{18}N_2O_4$: C, 73.92; H, 4.29; N, 6.63%. Found: C, 74.15; H, 4.15; N, 6.79%.

Compound 6l. IR (KBr): 3340, 3312, 2188, 1697, 1669, 1598, 1379, 1066 cm^{-1}. ^{1}H NMR (DMSO, 400 MHz): δ 8.44(d, 1H, J = 6.4 Hz), 7.96 (d, 2H, J = 8.0 Hz), 7.83 (d, 1H, J = 8.0 Hz), 7.76–7.33 (m, 8H), 5.48 (s, 1H). ^{13}C NMR (DMSO, 100 MHz): δ 159.55, 157.83, 153.80, 152.07, 133.26, 132.93, 130.93, 128.47, 127.43, 126.10, 126.00, 125.85, 125.75, 124.74, 123.43, 122.43, 119.15, 116.61, 112.96, 104.65, 58.49 ppm. Anal. Calcd. for $C_{23}H_{14}N_2O_3$: C, 75.40; H, 3.85; N, 7.65%. Found: C, 75.65; H, 3.70; N, 7.53%.

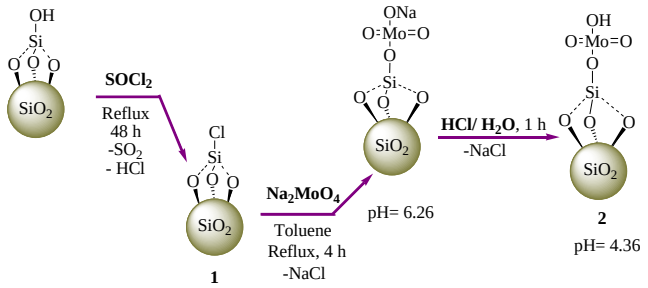
Compound 6m. IR (KBr): 3389, 3310, 2201, 1713, 1671, 1606, 1374, 1049 cm^{-1}. ^{1}H NMR (DMSO, 400 MHz): δ 7.90 (dd, 1H, J = 6.5, 1.3 Hz), 7.73–7.69 (m, 1H), 7.51–7.44 (m, 2H), 7.38 (s, 2H), 7.19–7.15 (m, 4H), 4.41 (s, 1H), 2.84 (m, 1H, 6.92 Hz), 1.17 (d, 6H, 6.92 Hz). ^{13}C NMR (DMSO, 100 MHz): δ 159.54, 158.00, 157.95, 153.28, 152.08, 147.11, 140.70, 132.88, 127.45, 126.42, 124.65, 122.41, 119.29, 116.54, 112.95, 104.18, 58.03, 38.85, 36.50, 33.23, 23.79 ppm. Anal. Calcd. for $C_{22}H_{18}N_2O_3$: C, 73.74; H, 5.03; N, 7.82%. Found: C, 73.45; H, 5.12; N, 7.74%.

Compound 6n. IR (KBr): 3427, 3280, 2188, 1720, 1669, 1594, 1389, 1048 cm^{-1}. ^{1}H NMR (DMSO, 400 MHz): δ 7.82 (dd, 1H, J = 6.44, 1.36 Hz), 7.72–7.67 (m, 1H), 7.48–7.43 (m, 2H), 7.35 (s, 2H), 4.43 (s, 1H), 1.74 (m, 1H), 1.63-1.57 (m, 4H), 1.38-1.32 (m, 2H), 1.18-0.94 (m, 4H). ^{13}C NMR (DMSO, 100 MHz): δ 160.64, 160.06, 154.63, 152.02, 132.67, 124.56, 122.05, 116.53, 116.00, 113.00, 104.60, 52.48, 43.18, 36.66, 30.51, 27.52, 26.11, 25.85, 25.52 ppm. Anal. Calcd. for $C_{19}H_{18}N_2O_3$: C, 70.80; H, 5.59; N, 8.69%. Found: C, 70.53; H, 5.22; N, 8.38%.

Results and discussion

Nanosilica molybdic acid was synthesized and characterized by X-ray fluorescence (XRF), X-ray diffraction pattern (XRD), Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM).

In continuation of our previous studies on the development of various catalysts in synthesis of organic compounds,[32-34] as can be seen in Scheme 1, from the reaction of readily available materials such as silica gel and thionyl chloride, silica chloride **1** has been prepared.[35] Accordingly, we found that anhydrous sodium molybdate can react with **1** to give silica molybdic acid (and subsequently nano SMA) **2**. From the synthetic point of view, the nucleophilic substitution at silicon is also attractive.



Scheme 1. Preparation of nano silica molybdic acid **2**.

As can be seen in Table 1, the XRF data for the nano-SMA **2** show the composition of catalyst as 71.14 (%W/W) SiO_2 and 25.62 (%W/W) MoO_4 (Fig. 1).

Table 1. XRF data of nano-SMA **2**.

Compound	Concentration (%W/W)
SiO_2	71.14
MoO_4	25.62
Na_2O	1.90
Cl	0.460
ZnO	0.355
CaO	0.289
Fe_2O_3	0.046
Al_2O_3	0.045
CuO	0.027
GeO_2	0.023
MnO	0.022
TiO_2	0.022
Total	99.95

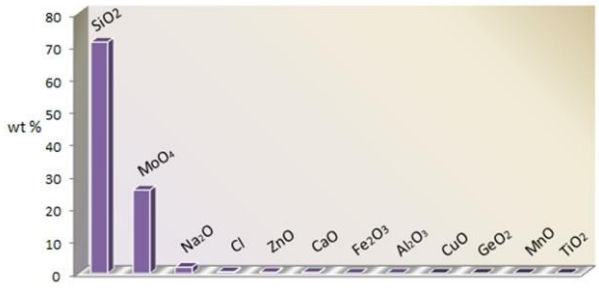


Fig. 1. XRF analysis of nano-SMA **2**.

Fig. 2 shows the XRD patterns for the silica molybdic acid 2 which exhibits the presence of molybdic acid crystalline phase supported on amorphous silica as a broad peak around 23° (2 θ) (θ is the Bragg's angle). The three peaks in the 35–40° region of the XRD spectrum could be attributed to the presence and linking of MoO_3 to the silica gel.[36]

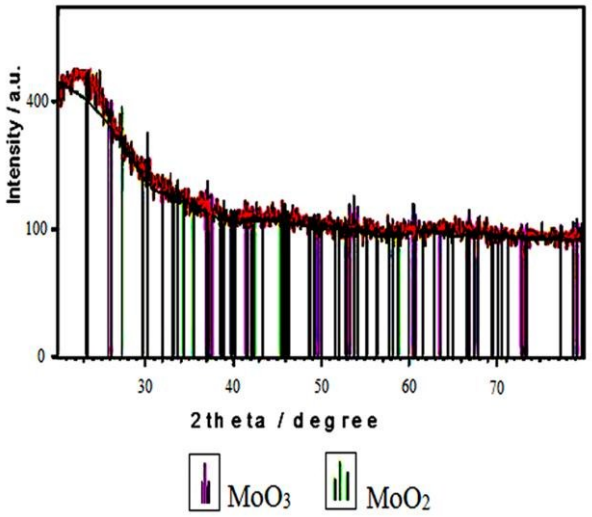


Fig. 2. XRD pattern for nano-SMA **2**.

The FT-IR spectra for the anhydrous sodium molybdate, silicachloride, and silica molybdic acid **2** are shown in Fig. 3. This spectrum shows the characteristic bonds of anhydrous sodium molybdate and silica chloride.

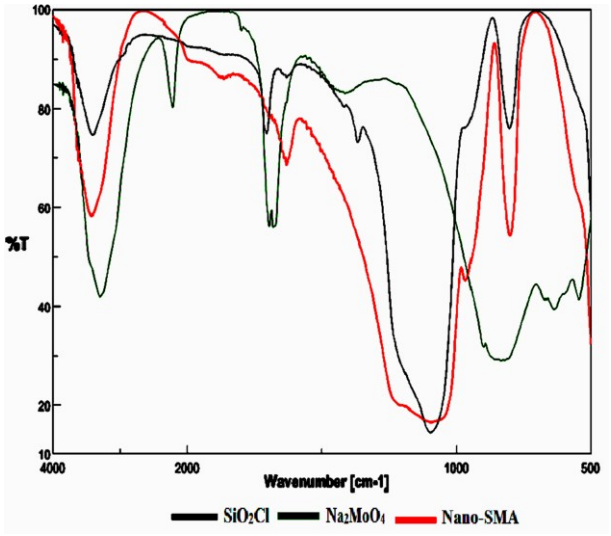


Fig. 3. FT-IR spectra for the comparison of SiO_2Cl, Na_2MoO_4 and nano-SMA **2**.

The adsorption in 3452, 1634, 1086, 800 cm^{-1} in the catalyst spectrum reveals both bonds in SiO_2–Cl and MoO_4 group. We evaluated the amounts of molybdic acid supported on SiO_2 using two methods, including (a) titration with 0.1 N NaOH (neutralization reaction) and (b) calculating the weight difference between primary solid acid loosed chloride and new silica molybdic acid **2**. After these experiments, we found that 1 g catalyst includes 0.04 g $–OMoO_3H$. Regarding to the molecular weight of MoO_4H (161 g), therefore, 1 g of catalyst is equal to 0.25 mmol.

The structural information about nanosilica molybdic acid such as particle size and shape was provided by transmission electron microscopy (TEM). As shown in Fig. 4., the TEM image

revealed the formation of mesostructured nanoparticles with an average size in the range of 15-30 nm.

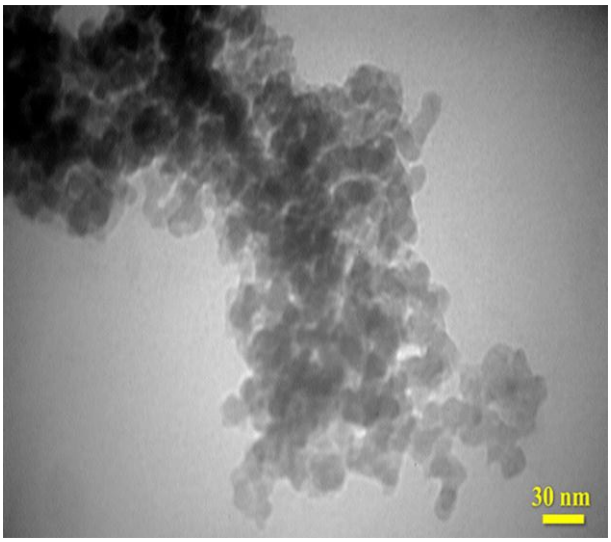


Fig. 4. TEM image of nano-SMA **2**.

In continuation of our previous studies on the development of green synthetic methodologies for the preparation of organic compounds,[37-40] herein, we report a new green condition for the synthesis of some pyrano[2,3-*c*]**coumarins 6** from the condensation reaction of malononitrile **3**, aromatic aldehydes **4**, and 4-hydroxycoumarin **5** in the presence of catalytic amount of nano-SMA **2** (Scheme 2).

Scheme. 2 Synthesis of pyrano[2,3-c]chromenes using nano-SMA **2**.

From the perspective of green chemistry, equal mixture of H_2O/EtOH (1:1) was opted as reaction medium. It should be noted that the reaction progress in absolute water and/or absolute ethanol was not better than mixture of these solvents. From different ratio of H_2O/EtOH mixtures, equal mixture H_2O/EtOH (1:1) was considered as the most effective ratio. Initially, the model reaction was established under reflux in an equal mixture of H_2O/EtOH (1:1) in the presence of various amounts of nano-SMA. This reaction was firstly examined in the absence of catalyst which did not show any appreciable progress even after 360 min. Upon screening, the results well showed that the this reaction proceeds efficiently by adding 5 mol% of nano-SMA. Also, increasing the catalyst amount did not improve the results (Figure 5).

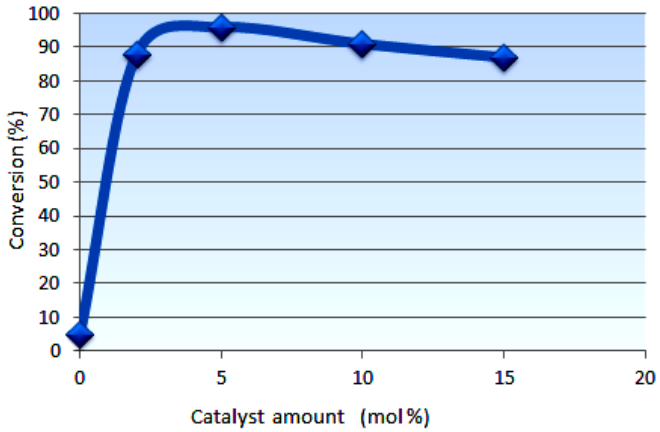


Fig. 5. Optimization of the catalyst amount.

After optimization of the reaction conditions, in order to extend the scope of this reaction, a wide range of aromatic aldehydes were used with **3** and **5** (Table 2). All the products were characterized by comparison of their spectra and physical data with those reported in the literature.[41-43]

Table 2. Synthesis of pyrano[2,3-*c*]coumarin derivatives using nano-SMA **2**.

Entry	Ar	Time (min)	Yield[a] (%)	Mp (°C)
6a	C_6H_5	30	96	262-264
6b	4-MeO-C_6H_4	18	92	240-242
6c	2-Cl-C_6H_4	25	78	260-262
6d	3-NO_2-C_6H_4	35	81	255-257
6e	4-NO_2-C_6H_4	75	73	248-250
6f	4-Me-C_6H_4	70	87	250-252
6g	4-Cl-C_6H_4	50	90	258-260
6h	thiophene-2-yl	75	70	234-236
6i	3-Br-C_6H_4	20	91	272-274
6j	2-Cl-6-F-C_6H_3	30	95	288-290
6k	4-benzyloxy-C_6H_4	450	84	275-277
6l	1-Naphthyl	90	90	260-262
6m	4-isopropyl-C_6H_4	40	92	239-241[b]
6n	cyclohexyl	25	86	265-267[b]

[a]Isolated yield.
[b]Novel compounds.

Table 3 demonstrates the merit of this method for the synthesis of pyrano[2,3-*c*]coumarins in comparison with previously reported results. As it can be seen from Table 3, piperidine was employed as a basic catalyst under refluxing EtOH, but this method could not afford good yields (entry 1). In the case of (S)-proline (entry 4), the product was obtained in low yield in a long time. Using some catalysts, such as DAHP

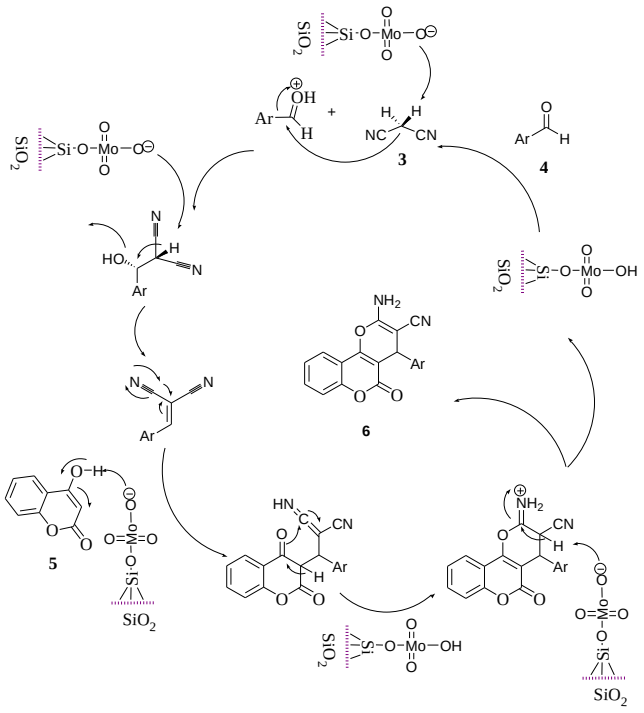
(entry 3), KF–Al_2O_3(entry 5), and TEBA (entry 6) needs too long reaction times. We believe that these reactions can be efficiently carried out under our suggested conditions with respect to reaction times and product yield.

Table 3. Comparison of the present work with other methods reported in the literature.[a]

Catalyst/amount	Conditions	Time (min)	Yield (%)[Ref.]
SDS/20 mol%	H_2O/60 °C	120	85[17]
TEBA/0.07 g	H_2O/90 °C	420	96[23]
Piperidine/0.5 mL	EtOH /reflux	30	70[44]
DAHP/10 mol%	H_2O:EtOH /r.t	180	81[45]
(S)-Proline/10 mol%	H_2O:EtOH/reflux	240	72[45]
KF–Al_2O_3/0.125 g	EtOH /reflux	240	90[46]
nano-SMA/5 mol%	H_2O:EtOH/reflux	30	96[b]

[a] Synthesis of **6a.**
[b] Present work.

A mechanistic rationale for the formation of pyranochromenes **6** is suggested in Scheme 3. It seems that the reaction takes place in three steps. It is reasonable to assume that the initial event involves the generation of the arylmethylene via a Knoevenagel condensation of the aldehyde and malononitrile catalyzed by nano-SMA **2**. In the next steps, a Michael-type addition to the arylmethylene and subsequent heterocyclization promoted by nano-SMA **2** gives the corresponding products **6**.



Scheme 3 A plausible mechanism for the formation of pyranocoumarins **6** catalyzed by nano-SMA **2**.

The main disadvantage of many reported methods for these reactions is that the catalysts are destroyed in the work-up procedure and cannot be recovered or reused. In these processes, as outlined in Fig. 6, the nano-SMA **2** showed recyclability up to four cycles, during which there are a little losses in the catalytic activity.

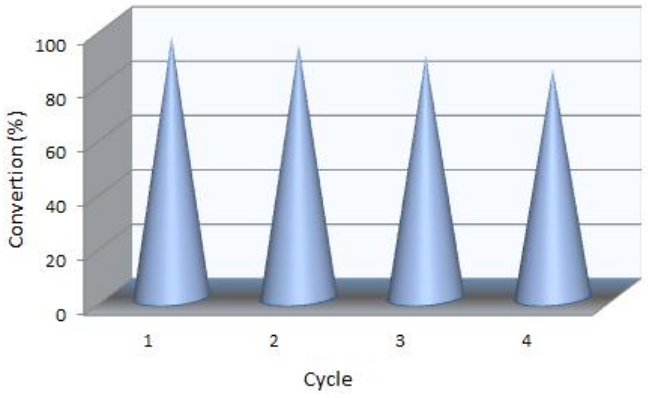


Fig. 6. Recyclability of nano-SMA **2** in the synthesis of **6a** (reaction time = 30 min).

Conclusions

In summary, we found nanosilica molybdic acid as an effective and environmentally safe heterogeneous catalyst which successfully catalyzed the reaction between 4-hydroxycoumarin, various aromatic aldehydes and malononitrile to produce new and known pyrano[2,3-*c*]chromens of potential synthetic and pharmaceutical interest. The present protocol not only originates the products with excellent yields in short reaction times, but also avoids some problems such as catalyst cost, pollution, handling, and safety. Also, conventional product work-up and high recyclability of catalyst are other attractive features of this procedure.

Acknowledgements

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Table of Content (ToC)

Nanosilica molybdic acid as an effective and environmentally safe heterogeneous catalyst has been developed for the synthesis of pyranocoumarins