

# Molybdenum Schiff base complex supported on MNPs as an efficient and easily recyclable catalyst in threecomponent Strecker reaction for synthesis of $\alpha$ -aminonitrile derivatives

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Abstract An efficient and straight procedure has been described for one-pot multicomponent synthesis of  $\alpha$ -aminonitrile derivatives in the presence of a molybdenum Schiff base complex supported on magnetite nanoparticles as a heterogeneous catalyst. The synthesized catalyst was characterized by Fourier transform infrared, X-ray powder diffraction, vibrating sample magnetometry, scanning electron microscopy, energy dispersive X-ray and inductively coupled plasma atomic emission spectroscopy. The extensive substrate scopes, easy recoverability of the magnetite catalyst, solvent-free conditions, short reaction time and high yields of products make this protocol environmentally friendly, practical and economically attractive.

**Graphical Abstract** Synthesis of molybdenum Schiff base complex supported on metal nanoparticles and its efficient and green application as a recyclable heterogeneous catalyst for the synthesis of  $\alpha$ -aminonitrile derivatives is reported.



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#### Introduction

α-Aminonitriles are very important intermediates, particularly in the preparation of natural and unnatural α-amino acids, a variety of nitrogen-containing heterocycles and other biologically useful molecules. For example, they are the key precursors for the synthesis of proteins and have several applications as the chiral building blocks in the pharmaceutical industry [1, 2]. One of the most important multicomponent reactions in organic chemistry for the direct one-pot synthesis of  $\alpha$ -aminonitriles is the Strecker reaction [3]. The Strecker reaction includes the threecomponent coupling of an amine, an aldehyde and either hydrogen cyanide or its alkaline metal cyanides [4]. One of the initial drawbacks of this reaction is the use of highly toxic cyanide derivatives. In order to partially avoid this inconvenience, the use of trimethylsilyl cyanide has been introduced [5]. The Strecker reaction has been studied extensively by using various Lewis acids [6, 7], Lewis bases [8] and metal complexes and metal-salen complexes [9, 10] in stoichiometric or catalytic amounts under mild conditions. Also, a literature survey has shown the use of several heterogeneous catalysts which are more advantageous in terms of catalyst/ product separation and continuous production. The examples include MCM-41anchored sulfonic acid [11], sulfamic acid-functionalized magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) [12], polymer-supported scandium triflate [13], heteropoly acid [14] sulfonic acid functionalized nanoporous SBA-15 [15] graphene oxide and its functionalized derivatives [16], and the new MOFs with the general formula  $[In_xGa_{1-x}(O_2C_2H_4)_{0.5}(hfipbb)]$  [17]. However, many of these reported methods involve the use of expensive reagents, hazardous solvents, longer reaction times and tedious workup procedures.

Many Schiff base complexes of transition metal ions are efficient catalysts in both homogeneous and heterogeneous reactions, and play a significant role in various reactions to enhance their yield and product selectivity [18–20]. However, homogeneous catalysis suffers from the problematic separation of the catalyst from the product for reuse [21]. Thus, several insoluble materials have frequently been applied as heterogeneous catalytic supports for these complexes [22–24]. Recently, the use of magnetite NPs has attracted a lot of attention in the field of catalysis due to unique advantages such as chemical stability, strong magnetization, high activities and easy reparability in heterogeneously catalytic processes [25–27]. The presence of hydroxyl groups on the NPs' surface allows the attachment of different functional groups. In addition, the use of 3-aminopropyltrimethoxysilane having a primary amine group allows post-conjugation with different ligands, metals or metal complexes [28–31].

In continuation of our efforts in developing new catalysts for multi-component reactions [32, 33], we report the synthesis and characterization of a  $MoO_2(acac)_2$ -Schiff base complex supported on MNPs which acts as an efficient catalyst in the synthesis of  $\alpha$ -aminonitrile derivatives under mild conditions (Scheme 1).



Scheme 1 The synthesis of  $\alpha$ -aminonitrile derivatives using molybdenum complex supported on functionalized Fe<sub>3</sub>O<sub>4</sub> magnetite nanoparticles containing a Schiff base ligand

### Experimental

#### Materials

All the reagents and solvents were of analytical grade and used as received without further purification.

#### Instrumentation

Reaction progress and purity determination of the compounds were checked by TLC using silica gel SIL G/UV 254 plates. Infrared spectra were recorded on a Jusco 300 FT-IR Spectrometer using compressed KBr discs. The <sup>1</sup>H NMR (400.13) and <sup>13</sup>C NMR (100.62 MHz) were recorded on a Bruker spectrometer ( $\delta$  in ppm). Nanostructure observations were conducted with a field emission scanning electron microscope (FESEM). Melting points are uncorrected and were recorded on a Buchi B-545 apparatus in open capillary tubes. Mass spectra of new compounds were obtained on an Agilent Technologies 5975C VL MSD spectrometer. Magnetic measurement of materials was investigated with a vibrating sample magnetometer (VSM-4 inch; DaghighMeghnatis Kashan, Kashan, Iran) at room temperature. XRD patterns were collected using a Bruker D8ADVANCE diffractometer. The samples were scanned at a rate of  $0.05^{\circ}$ /min from  $10^{\circ}$  to  $90^{\circ}$  of  $2\theta$ . The metal content of nanocatalyst was measured using inductively coupled plasma (ICP; Labtam 8440 plasmalab) after leaching the molybdenum ions with concentrated HNO<sub>3</sub>, then heating and diluting to specific volumes. The resulting solutions were filtered and exposed to ICP analysis.

A schematic representation for the synthesis of the  $MoO_2(acac)_2$  Schiff base complex immobilized on functionalized silica-coated  $Fe_3O_4$  NPs is shown in Scheme 2.



Scheme 2 The sequence of events in the preparation of a  $MoO_2(acac)_2$  Schiff base complex supported on MNPs

#### Synthesis of iron oxide nanoparticle

The Fe<sub>3</sub>O<sub>4</sub> NPs were prepared according to a previously published method with a slight modification [34]. Magnetic NPs were prepared by chemical co-precipitation technique. An aqueous solution of salts FeCl<sub>3</sub>·6H<sub>2</sub>O (2 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (1 mmol) were mixed in deionized water at 80 °C with the rapid addition of NH<sub>4</sub>OH (25%, 15 mL) under ultrasonication to yield a black powder. The black precipitate was separated magnetically and washed with ethanol (10 mL) and water (5 mL) and dried at 60 °C.

#### Synthesis of silica-coated iron oxide nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs)

The silica-coated NPs were prepared according to the Stober method [35, 36]. Sonication of a Fe<sub>3</sub>O<sub>4</sub> NPs suspension of a mixture of 100 mL of ethanol, 10 mL of deionized water, 2.5 mL of 25 wt% concentrated aqueous ammonia solution and tetraethylorthosilicate (TEOS) causes rapid coating of the magnetic core with a silica shell. After stirring for 12 h at room temperature, the brown precipitate was collected from the solution using a magnet, and then washed several times with water and ethanol and dried at 25 °C under vacuum.

#### Synthesis of magnetite nanoparticles coated by 3aminoopropyltrimethoxysilane (APTMS)

The obtained  $Fe_3O_4@SiO_2$  MNPs (1 g) was suspended in ethanol (100 ml), and then 3-aminopropyltrimethoxysilane (APTMS) (2 ml) was added under dry nitrogen

atmosphere. The mixture was refluxed for 24 h and the resultant solid was separated and washed with ethanol to remove the unreacted residue of silylating reagent, and then dried at 60  $^{\circ}$ C.

### Synthesis of Schiff-base ligand and its complex supported on MNPs $(Fe_3O_4@Si@MoO_2(acac)_2)$

To a solution of thiophene-2-carbaldehyde (2.5 mmol, 280 mg) in absolute ethanol (100 ml) was added  $Fe_3O_4@Si@NH_2$  (2.0 g) and then the mixture was stirred under a  $N_2$  atmosphere at 60 °C for 24 h. The product was separated and washed with ethanol and dried under vacuum at 60 °C overnight. Then, an excess amount of  $MoO_2(acac)_2$  was added to a mixture of the above product (1 g) in ethanol (100 ml) and the resulting mixture was irradiated with ultrasonics for 20 min and then refluxed under  $N_2$  for 24 h. The resulting precipitate was separated with an external magnet and washed with hot water and ethanol until the solution became colorless. The obtained product was dried and stored in a vacuum desiccator.

#### General procedure for the synthesis of $\alpha$ -aminonitriles derivatives

To a 10-mL round-bottomed flask were added sequentially aldehyde (1.0 mmol), amine (1.0 mmol), TMSCN (1 mmol) and dioxomolybdenum complexes supported on MNPs as nanocatalyst (0.02 g). The reaction was stirred vigorously under solvent-free conditions at 50 °C. After completion of the reaction, as monitored by TLC, *n*-hexane/ethyl acetate (5:3) and ethyl acetate (10 mL) were added to reaction mixture, stirred and refluxed for 3 min, and then the catalyst was separated from the other materials by an external magnet. The separated catalyst was used for alternative reactions. The solvent of the organic layer was evaporated and the crude product was purified by recrystallization from ethanol/water (10:1).

#### Spectral data analysis for compounds

#### 2-((4-Bromophenyl)amino)-2-(thiophen-2-yl)acetonitrile (Table 3, entry 1)

IR (KBr): v 3431, 3101, 2920, 2251, 1663, 1617, 1567, 1432, 1107 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.27 (*d*, *J* = 8.6 Hz, 1H), 8.01 (dd, *J* = 19.8, 11.0 Hz, 3H), 7.59 (dd, *J* = 9.1, 4.9 Hz, 2H), 7.20 (*d*, *J* = 7.0 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.76 (*d*, *J* = 7.9 Hz, 1H), 6.60 (t, *J* = 7.5 Hz, 1H); <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  162.77, 152.39, 139.31, 127.33, 127.13, 118.57, 117.25, 116.36, 114.45, 113.65, 111.86, 55.11; MS: m/z = 292 [M]<sup>+</sup>.

2,2'-(1,4-Phenylene)bis(2-((4-bromophenyl)amino)acetonitrile) (Table 3, entry 2)

IR (KBr): v 3377, 3347, 2215, 1593, 1492, 1397, 1297, 1071 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.71 (s, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 7.2 Hz, 1H); <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  143.41, 136.39,

130.20, 129.26, 128.50, 127.48, 122.54, 121.40, 118.70, 110.95, 15.18; MS:  $m/z = 496 \text{ [M]}^+$ .

2-((4-Bromophenyl)amino)-2-(perfluorophenyl)acetonitrile (Table 3, entry 3)

IR (KBr): v 3435, 2135, 1650, 1608, 1473, 1119 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  7.29 (d, J = 1.3 Hz, 1H), 7.27 (d, J = 1.3 Hz, 2H), 7.25 (d, J = 1.6 Hz, 2H), 7.24 (d, J = 1.4 Hz, 2H), 7.22 (d, J = 1.1 Hz, 2H), 7.20 (d, J = 1.1 Hz, 1H); <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  155.79, 142.30, 139.33, 135.68, 129.14, 129.03, 127.96, 127.60, 126.89, 126.77, 116.93, 116.15, 114.61, 21.79; MS: m/z = 376 [M]<sup>+</sup>.

2-((4-Bromophenyl)amino)-2-(ferroceneyl)acetonitrile (Table 3, entry 4)

IR (KBr): v 3401, 3339, 3084, 2961, 2045, 1723, 1637, 1591, 1384, 1105 cm<sup>-1</sup>.; MS: m/z = 394 [M]<sup>+</sup>. Due to paramagnetic nature of ferrocene moiety a useful NMR spectrum of this compound was not obtained.

2-((4-Bromophenyl)amino)-2-(5-fluoro-2-hydroxyphenyl)acetonitrile (Table 3, entry 5)

IR (KBr): v 3334, 3121, 2969, 2131, 1662, 1617, 1571, 1484, 1190 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  7.22 (*d*, *J* = 7.7 Hz, 1H), 7.18 (s, 1H), 6.93 (*d*, *J* = 8.1 Hz, 1H), 6.67 (*d*, *J* = 8.1 Hz, 1H), 6.63 (s, 1H); <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  135.07, 132.73, 130.69, 128.59, 128.28, 127.81, 127.67, 127.42, 126.72, 123.85, 116.90, 116.18, 114.67, 24.81; MS: m/z = 320 [M]<sup>+</sup>.

2-((4-Bromophenyl)amino)-2-(1H-pyrrol-2-yl)acetonitrile (Table 3, entry 6)

IR (KBr): v 3326, 2963, 2249, 1654, 1609, 1559, 1487, 1097 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  7.90 (dd, J = 6.1, 3.5 Hz, 1H), 7.38 (dd, J = 6.1, 3.3 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.87 (d, J = 6.2 Hz, 1H), 6.45 (t, J = 7.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  142.53, 135.98, 127.82, 122.17, 121.98, 121.89, 121.03, 118.78, 118.54, 115.56, 114.04, 14.53; MS: m/z = 274 [M]<sup>+</sup>.

#### **Results and discussion**

The structure of a new MoO<sub>2</sub>(acac)<sub>2</sub> Schiff base complex supported on MNPs as a heterogeneous catalyst was studied and characterized by FT-IR, XRD, SEM, EDX, ICP and VSM analysis.

FT-IR spectra of compounds  $Fe_3O_4$ ,  $Fe_3O_4@SiO_2$ ,  $Fe_3O_4@Si@NH_2$ ,  $Fe_3O_4@-Si@Schiff$  base, and  $Fe_3O_4@Si@MoO_2(acac)_2$  are illustrated in Fig. 1. The band around 593 cm<sup>-1</sup> is due to the presence of magnetite NPs and corresponds to the Fe–O bond [34]. The Si–O absorption appearing at 1053 cm<sup>-1</sup> confirms the successful functionalization of the NPs with 3-aminopropyltrimethoxysilane (see

Fig. 1b). The bands in the ranges of 2915–2930 and 2844–2870 cm<sup>-1</sup> are assigned to the stretching mode of the CH<sub>2</sub> groups (see Fig. 1c), indicating that the amine functional groups are successfully grafted onto the surface of the magnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs. As shown in Fig. 1d, the FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@Si@Schiff base exhibits the C=N stretching vibration band at 1639 cm<sup>-1</sup>. Upon treatment with  $MoO_2(acac)_2$ , the above band shifts to a lower frequency (1631 cm<sup>-1</sup>; Fig. 1e) and shows the involvement of the C=N group in complexation with molybdenum.

The XRD patterns of the initial magnetic NPs and silica-coated magnetite as well as the resulting catalyst are collected in Fig. 2 and are helpful for the identification of the catalyst. The XRD patterns of all the samples shows characteristic peaks of magnetite NPs, and the sharp and strong peaks confirm that the products are well crystallized. All the compounds showed seven peaks at 35.5, 43.2, 53.7, 57.2, 62.9, 74 and 87.7°, attributed to Miller index values {h k l} of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) diffractions of  $Fe_3O_4$ , respectively, which are in agreement with the patterns of the crystalline spinel ferrites of Fe<sub>3</sub>O<sub>4</sub> MNPs characterized in the literature data (JCPDS NO. 85-1436) [37]. The silica-layered systems of magnetite NPs show an additional broad band at  $2\theta = 20-30$  (Fig. 2b, c) for the amorphous silica. Similar peaks are detected in the XRD patterns of both metal complexes immobilized on MNPs and naked magnetite NPs, indicating the retention of the crystalline spinel ferrite core structure through the reaction procedure. The Debye-Scherrer's equation  $[D = K\lambda/(\beta \cos\theta)]$  can be used to calculate the crystallite size of the Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub> in the form of a powder. Also, the interplaner distance was attained via the Bragg equation:  $dhkl = \lambda/(2\sin\theta)$ . Crystallite sizes from several diffraction lines by the Debye-Scherrer equation were found to be in the nanometer range (10.46-55.08 nm), which are in good accordance with the data obtained from scanning electron microscopy (Fig. 3). The size and the distance between the crystal plates and peak breadth (FWHM) at a distance of above-mentioned range in the XRD pattern were evaluated and the results are given in Table 1.

Figure 3 shows the nanoparticle size and typical field emission scanning electron microscopy (FE-SEM) image of  $Fe_3O_4@Si@dioxomolybdenum$ . As can be seen, most of the prepared NPs are spherical-shaped and have a mean diameter of about 15–35 nm which shows close agreement with the values calculated by XRD analysis.

The energy dispersive X-ray spectroscopy (EDS) results, obtained from SEM/ EDS analysis of the  $Fe_3O_4@Si@MoO_2(acac)_2$  samples, are shown in Fig. 4, and clearly indicate the presence of Mo in the above catalyst. Moreover, the presence of C, N, O, S, Si and Fe signals indicates that the iron oxide particles are loaded into the silica. According to the above analysis, it can be deduced that the  $Fe_3O_4@Si@MoO_2(acac)_2$  have been prosperity synthesized. ICP analysis of the catalyst found that the weight percentage of Mo is 2.1%.

Magnetic measurements of the samples were carried out at room temperature using a vibrating sample magnetometer (VSM). The measured magnetization curves for Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub> are compared in Fig. 5. The hysteresis curve allows the determination of the saturation magnetization ( $M_s$ ), remanent magnetization ( $M_r$ ) and coercivity ( $H_c$ ). The magnetization of the samples



**Fig. 1** FT-IR spectra of *a* Fe<sub>3</sub>O<sub>4</sub>, *b* Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, *c* Fe<sub>3</sub>O<sub>4</sub>@Si@NH<sub>2</sub>, *d* Fe<sub>3</sub>O<sub>4</sub>@Si-H<sub>2</sub>azosaldien, e Fe<sub>3</sub>O<sub>4</sub>@Si@MOO<sub>2</sub>(acac)<sub>2</sub>



Fig. 2 XRD diffraction pattern of Fe<sub>3</sub>O<sub>4</sub> MNPs (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b) and Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub> (c)

could be completely saturated at high fields of up to  $\pm 8500.0 \text{ O}_e$  and the  $M_s$  of the samples changed from 58.31 emu/g for Fe<sub>3</sub>O<sub>4</sub> to 50 and 48 emu/g for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub>, respectively, due to the formation of a silica shell around the Fe<sub>3</sub>O<sub>4</sub> core. Although, with the above reduction in the saturation magnetization, strong magnetization of the NPs was also revealed by simple attraction with an external magnet, the catalyst could still be efficiently and easily separated from the reaction system.



Fig. 3 SEM image of Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub>

## Application of dioxomolybdenum complex supported on $\mathrm{Fe_3O_4}$ as a heterogeneous catalyst

With the idea of developing a green procedure for the synthesis of  $\alpha$ -aminonitriles derivatives, the optimization of the reaction condition (Table 1) was performed by considering the model reaction including thiophene-2-carbaldehyde, 4-bromoaniline and TMSCN with an equimolar ratio under neat condition. Also, the effects of catalyst and temperature were investigated in the presence of various amounts of  $Fe_3O_4@Si@MoO_2(acac)_2$  (0–0.04 g) at temperatures ranging from 25 to 100 °C. Stirring the reaction mixture at 25 °C/50 °C/100 °C aerobically (2 h) and in the absence of a catalyst did not lead to any product (Table 2, entries 1–3). Thus, we investigated the reaction by using the nanocatalyst (0.005-0.04 g) at different temperatures, under solvent-free and various time conditions. The optimal amounts of the catalyst were 0.02 g for all conditions. The best result was obtained when the reaction was conducted at 50 °C and the reaction time was kept at 30 min (Table 2, entry 11). The reactions were lazy and gave poor yields with longer reaction times. Also, a further increase in temperature and catalyst amount did not improve the product yield. We then examined the above reaction in different solvents and made a comparison with the solvent-free condition (Table 3). We found that the solventfree condition is the best choice.

In order to understand the reaction scope and generality of this interesting protocol, a series of  $\alpha$ -aminonitriles were prepared in high yields using various aldehydes, TMSCN and aniline in the presence of the Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub> catalyst under optimized conditions. The outcomes are summarized in Table 4.

Entry	20	Peak width (FWHM) (°)	Size (nm)	Interplaner distance (nm)
1	35.50	0.80	10.46	0.252571
2	43.20	0.62	13.80	0.209168
3	53.70	0.42	21.28	0.170483
4	57.20	0.72	12.62	0.160855
5	62.90	0.60	15.62	0.147651
6	74.00	0.23	43.25	0.127949
7	87.70	0.20	55.08	0.111155



Fig. 4 EDS diagram of the Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub>

Most of the reactions launched very efficiently and no side-products were observed. As Table 4 shows, in the case of all aldehyde derivatives having electron-donating or electron-withdrawing substituents, the yield of reaction is good.

Reusability of the catalyst was also investigated. For this purpose, the same model reaction was again studied under optimized conditions. After completion of the reaction, the catalyst was recovered by an external magnet and the remaining solid was washed with hot ethanol ( $2 \times 10$  mL). Then, the recovered catalyst was dried under vacuum at 60 °C for 4 h and reused for similar reactions. The catalyst could be reused at least eight times without significant loss of activity (Fig. 6). Analysis by ICP-AES of Mo in the crude product after isolation of the catalyst showed no loss of metal during the catalytic reaction, indicating that no metal leaching occurred. Furthermore, the XRD of the catalyst after eight cycles demonstrated that the structure of the catalyst is maintained during the reaction.



Fig. 5 The magnetic hysteresis loops of  $Fe_3O_4$  MNPs (a),  $Fe_3O_4@SiO_2$  (b) and  $Fe_3O_4@Si@MoO_2(acac)_2$  (c)

 $\label{eq:Table 2} \mbox{Table 2 optimization reaction between thiophene-2-carbaldehyde, TMSCN and 4-bromoaniline under solvent-free conditions^a$ 

$H_{3}C$ $I_{3}C$ $J_{3}C$ $I_{3}C$ $H$ $NH_{2}$ $H$ $Br$	Nanocatalyst (?) Temperature (?) Solvent-free	Br Br H		
Catalyst amount (g)	Temperature (°C) <sup>b</sup>	Time (min)	Yield <sup>c</sup> (%)	
-	r.t.	120	Trace	
-	50	120	Trace	
-	100	120	Trace	
0.005	r.t.	90	15	
0.005	50	90	20	
0.005	100	90	20	
0.01	r.t.	60	45	
0.01	50	60	60	
0.01	100	60	60	
0.02	r.t.	30	75	
0.02	50	30	85	
0.02	100	30	85	
0.04	r.t.	30	70	
0.04	50	30	85	
0.04	100	30	80	
	H <sub>3</sub> C I <sub>3</sub> C I <sub>3</sub> C Si CH <sub>3</sub> H NH <sub>2</sub> Br Catalyst amount (g) - - - 0.005 0.002 0.02 0.02 0.02 0.04 0.04 0.04	H <sub>3</sub> C       Nanocatalyst (?)         H       Nanocatalyst (?)         Temperature (?)       Solvent-free         Catalyst amount (g)       Temperature (°C) <sup>b</sup> -       r.t.         -       50         -       100         0.005       r.t.         0.005       100         0.01       r.t.         0.02       r.t.         0.02       50         0.02       100         0.04       7.t.	H <sub>3</sub> C       Nanocatalyst (?) $femperature (?)$ $femperature (?)$ Br       Nanocatalyst (?)       Temperature (?) $femperature (?)$ Catalyst amount (g)       Temperature (°C) <sup>b</sup> Time (min)         -       r.t.       120         -       50       120         -       100       120         0.005       r.t.       90         0.005       50       90         0.005       100       90         0.01       r.t.       60         0.01       50       60         0.02       r.t.       30         0.02       50       30         0.02       100       30         0.04       50       30	

<sup>a</sup> Reaction condition: Thiophene-2-carbaldehyde (1 mmol), TMSCN (1 mmol), 4-bromoaniline (1 mmol)

<sup>b</sup> This is the temperature of the oil bath and not inside the reaction medium

<sup>c</sup> Isolated yield

$ \begin{array}{c}     H_{3}C \\     H_{3}C \\     H_{3}C \\     S \\     H_{3}C \\     S \\     S \\     Br \\ \end{array} $	$ \begin{array}{c}  H_{3}C \\  H_{3}C \\  S \\  S \\  H \\  S \\  S \\  Br \\  H \\  S \\  S \\  Br \\  S \\  $			), 50 °C ?)	Br N H		
	Solvent-free	$H_2O$	C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> CN	$CH_2Cl_2$	CH <sub>3</sub> CO <sub>2</sub> Et	n-Hexane
Yield (%) <sup>c</sup>	85	Trace	80	75	70	45	30
Reaction time (min)	30	60	30	30	45	60	60

**Table 3** Solvent effect in the reaction between thiophene-2-carbaldehyde, TMSCN and 4-bromoaniline at 50  $^{\circ}$ C<sup>a</sup> using 0.02 g catalyst<sup>b</sup>

<sup>a</sup> This is the temperature of the oil bath and not inside the reaction medium

<sup>b</sup> Thiophene-2-carbaldehyde (1 mmol), TMSCN (1 mmol), 4-bromoaniline (1 mmol) under reflux condition

c Isolated yield

The proposed mechanism for the synthesis of  $\alpha$ -aminonitriles in the presence of Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub> as a promoter is given in Scheme 3. The mechanism of the reaction begins with the activation of the carbonyl group of the aldehyde (1) by this catalyst (3). The amines (2) used are better nucleophiles than TMSCN (6), and therefore they react first with the carbonyl compound of aldehydes to produce the imine band. Water elimination from the intermediate (4) can also be considered as a driving force for the imine bond formation. In the next step, TMSCN (6) is reacted to generate an imine bond (5) which was polarized by the heterogeneous catalyst making the imine carbon more disposed to the attack by cyanide, producing the  $\alpha$ -aminonitriles derivatives. These compounds were readily hydrolyzed with water to give the desired products (7) [39, 40].

To compare the reactivity of the Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub> with some of those reported in the literature, a comparative chart is presented in Table 5. In comparison with other catalysts employed for the synthesis of  $\alpha$ -aminonitriles from 4-chlorobenzaldehdye, aniline and TMSCN, our catalyst showed a much higher catalytic activity in terms of short reaction time, amount of nanocatalyst required and mild conditions. The table shows that the yield of the model reaction in the case of all the catalysts (except entries 5 and 9) is lower than Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub>, and also the required reaction time for all the catalysts (except entries 1, 3 and 12) are usually much longer than our catalyst, indicating that the nanocatalyst synthesized here is convincingly superior to the recently reported catalytic methods. Additionally, it can be easily separated magnetically after the reaction and has shown great reusability. Table 4 Strecker synthesis of  $\alpha$ -aminonitrile derivatives using 0.02 g catalyst under solvent-free conditions

O Ar	$H_{3}C$ $H_{3}C$ $H_{3}C$ $H_{3}C$ $H_{3}C$ $H_{3}C$ $H_{3}C$ $H_{3}C$ $H_{2}$ $H_{2}$ $H_{3}$ $H_{2}$ $H_{3}$ $H_{2}$ $H_{3}$ $H_{2}$ $H_{3}$ $H_{3$	talyst (0.02 g), 50 °C Solvent-free	+ Ar	NH R
	R = H or Br			
Entry	Product	Time (min)	Yield <sup>a</sup> (%)	M.p (°C) [Lit.]
1	Br H	30	85	154–156 <sup>b</sup>
2		ir 20	90	146–148 <sup>b</sup>
3	Br F F F F F F	15	95	148–150 <sup>b</sup>
4		30	85	153–155 <sup>b</sup>
5		20	88	163–165 <sup>b</sup>
6	Br	30	85	151–153 <sup>b</sup>
7		30	85	76–78 [38]
8		20	93	118–120 [38]
9		30	88	65–67 [38]

Entry	Product	Time (min)	Yield <sup>a</sup> (%)	M.p (°C) [Lit.]
10		15	95	Oil [38]
11		20	91	91–93 [38]
12		25	88	73–75 [38]
13		25	88	93–95 [38]
14		20	94	100–102 [38]
15		30	82	105–107 [38]

#### Table 4 continued

Reaction conditions: Aldehyde (1 mmol), aniline derivatives (1 mmol), TMSCN (1 mmol), 50 °C, solvent-free

<sup>a</sup> Isolated yield

<sup>b</sup> New derivatives



Fig. 6 Reusability of Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub> as a heterogeneous catalyst in 20 min



Scheme 3 The proposed mechanism for the synthesis of  $\alpha$ -aminonitriles derivatives using Fe<sub>3</sub>O<sub>4</sub>@Si@MoO<sub>2</sub>(acac)<sub>2</sub> as a heterogeneous catalyst

#### Conclusion

In summary, we have described a general and highly efficient methodology for the synthesis of  $\alpha$ -aminonitriles compounds by one-pot multi-component condensation using magnetic NPs supported by a Schiff base complex under solvent-free conditions. The advantageous points for the present methodology are the short reaction time, efficiency, potential for recycling of the catalyst, high yield, easy experimental workup, ease of handling of the catalyst with an external magnet, ease

Entry	Amount of catalyst	Solvent	Temp (°C)	Time (min)	Yield <sup>a</sup> (%)	References
1	Sulfuric acid-modified PEG-6000 (3 mol%)	H <sub>2</sub> O	r.t	10	92	[41]
2	Tin-exchanged zeolite (10 mg)	Solvent free	r.t	45	86	[42]
3	γ-Al <sub>2</sub> O <sub>3</sub> -Supported 12-Tungstosilicic acid (10 g)	CH <sub>3</sub> CN	r.t	8	92	[43]
4	Xanthan sulfuric acid (0.1 g)	CH <sub>3</sub> CN	r.t	60	90	[44]
5	Guanidine hydrochloride (6 mg)	CH <sub>3</sub> OH	40	60	98	[45]
6	Palladium(II) complex (3 mol%)	$CH_2Cl_2$	r.t	24 h	84	[46]
7	Montmorillonite clay	$CH_2Cl_2$	r.t	3.5 h	91	[47]
8	InI <sub>3</sub> (10 mol%)	$H_2O$	r.t	30	91	[48]
9	MCM-41 anchored sulfonic acid (5 mg)	CH <sub>3</sub> CH <sub>2</sub> OH	r.t	30	98	[11]
10	Fe(Cp) <sub>2</sub> PF <sub>6</sub> (5 mol%)	Solvent free	r.t	20	91	[39]
11	K <sub>2</sub> PdCl <sub>4</sub> (10 mol%)	$H_2O$	r.t	30	91	[49]
12	Zr(HSO <sub>4</sub> ) <sub>4</sub> (2 mol%)	Solvent free	r.t	10	85	[50]
13	Cyanuric acid (10 mol%)	CH <sub>3</sub> CN	r.t	40	92	[51]
14	PVP-SO <sub>2</sub> complex (0.1 g)	$CH_2Cl_2$	50	6 h	89	[52]
15	Magnetic nanoparticles with urea or urethane moieties (1 mg)	Solvent free	50	20	91	[40]
16	Trimethylsilyl trifluoromethane sulfonate (5 mol%)	CH <sub>2</sub> Cl <sub>2</sub>	r.t	3 h	87	[53]
17	Bi(NO <sub>3</sub> ) <sub>3</sub> (10 mol%)	CH <sub>3</sub> CN	r.t	75	87	[54]
18	Fe <sub>3</sub> O <sub>4</sub> @Si@MoO <sub>2</sub> (acac) <sub>2</sub> (0.02 g)	Solvent free	50	20	93	-

Table 5 Comparison of various catalysts in the synthesis of  $\alpha$ -aminonitriles with our catalyst

Reaction conditions: 4-chlorobenzaldehyde (1 mmol), aniline (1 mmol), TMSCN (1 mmol)

<sup>a</sup> Isolated yield

of product isolation and minimal environmental impact, which all make it a useful process for the synthesis of the above derivatives.

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