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Synthesis of SCMNPs@imine/\(\text{SO}_3\text{H}\) magnetic nanocatalyst by chlorosulfonic acid as sulfonating agents and their application for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one and 1,8-dioxooctahydroxanthene derivatives

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Abstract

In this survey, new recoverable sulfonated magnetic nanocatalysts (SCMNPs@imine/\(\text{SO}_3\text{H}\)) was synthesized by covalent attachment of a Schiff base ligand on the surface of SCMNPs@APTES/sucanh through reaction with 4-[(Pyridin-2-ylmethylene)-amino]-phenol and subsequent reaction with chlorosulfonic acid. The synthesized nanocatalyst was characterized by several techniques such as FTIR, TGA, VSM, XRD, UV—vis and EDX analysis. The nanocatalyst was evaluated in the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one and 1,8-dioxooctahydroxanthene derivatives with pharmacologically and biologically remarkable activity. 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one and 1,8-dioxooctahydroxanthene derivatives were respectively prepared via one-pot, three-component reactions of 2-naphthol, dimedone and aldehydes, as well as the reaction between dimedone and aldehydes in the presence of SCMNPs@imine/\(\text{SO}_3\text{H}\) under solvent-free conditions. The merits of this synthesis are high-to-excellent yields, short reaction time, mild basic conditions and high catalytic activity. Also, the SCMNPs@imine/\(\text{SO}_3\text{H}\) with suitable magnetic strength can be easily separated from the reaction solution using an external magnetic field.

Introduction

During the last decades, magnetic nanoparticles (MNPs) have attracted the attention of researchers due to their particular features in terms of catalytic activity like high dispersion, high reactivity, highly stability, durability in the catalytic processes and effective separation without any significant changes in their activity [1—5]. To avoid reducing the efficiency of these unique characteristics, magnetic nanoparticles have been modified with organic or inorganic layers such as silica, polymer, carbon, zeolite, and metal oxides [6—10]. Additionally, magnetic nanoparticles can be used in adsorption of heavy metals, proteins, drug delivery, dyes, beneficial supports, biosensors, hyperthermia activity for cancer treatment and environmental remediation [11—16].

Multicomponent reactions (MCRs) are well-appointed techniques to design the product in a single pot from three or more substrates with high yield for accessing a vast number of synthetic and pharmacologically relevant compounds [17]. This illustrative method has many advantages such as selectivity, efficiency, high reaction rates, high variability, simplicity, low costs, and environmentally friendly properties [18]. Xanthenes have a broad spectrum of approved biological and pharmaceutical activities; e.g., they have been used as anti-inflammatory [19], antibacterial [20], antiviral [21] agents, and as antagonists for inhibiting the action of zoxalamine [22]. Moreover, xanthe derivatives have also been applied in laser technology [23], pH sensitive fluorescent materials [24] and photodynamic therapy [25]. The one-pot multi-component condensation reaction between 2-naphthol, dimedone, arylaldehydes and, also, between dimedone and arylaldehydes, have been used as the
best procedures for synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one and 1,8-dioxooctahydroxanthene derivatives, respectively. Several catalysts have been utilized to promote this reaction, including N-sulfonic acid PVP Cl [26], TrCl [27], p-TSA [28], Succinimide-N-sulfonic acid [29], Cellulose sulfonic acid [30], Polytungstozincate acid [31] and Selectfluor™ [32].

Experimental

General
All of the chemicals, reagents, and solvents used in our research work were entirely purchased from Merck and Fluka Chemical Companies. Melting points were done on a Büchi B-545 apparatus. FT-IR spectra were measured through the method of KBr pellets in the range 400–4000 cm$^{-1}$ with a Shimadzu IR-470 spectrometer. TGA spectra were characterized using a TGA thermoanalyzer (PerkinElmer) instrument. VSM analyses of the samples were characterized by a Lakeshore 7407 at room temperature. Energy-dispersive analysis of x-ray (EDX) was provided on an ESEM, Philips, and XL30. X-ray powder diffraction (XRD) patterns of samples were obtained using a Siemens D-5000 x-ray diffractometer.

Catalyst synthesis

Preparation of the Fe$_3$O$_4$ magnetic nanoparticles (Fe$_3$O$_4$ MNPs)
First, FeCl$_3$·6H$_2$O (4.8 g) and FeCl$_2$·4H$_2$O (1.7 g) were dispersed in 100 ml of deionized water containing 0.9 ml of concentrated HCl and sonicated for 30 min. Then, 250 ml of NaOH solution (1.5 M) was added slowly to the reaction solution and the mixture was stirred for 30 min with a magnetic stirrer in the absence of temperature. The formed black magnetic nanoparticles were collected by a powerful magnet, washed several times with 150 ml deionized water, and dried under vacuum at 60 °C for 15h.

Preparation of the silica-coated Fe$_3$O$_4$ magnetic nanoparticles (Fe$_3$O$_4$@SCMNPs)
A mixture of 50 ml ethanol, 8 ml deionized water, and 3 ml concentrated aqueous ammonia (25 wt %) was added to about 1g of the synthesized Fe$_3$O$_4$ magnetic nanoparticles and the contents of the reaction vessel were ultrasonicated for 15 min. After the time required for the reaction passed, 0.6 ml of tetraethylorthosilicate (TEOS) was added to the reaction vessel and ultrasonication was done again for 15 min. To achieve the target product, the contents of the reaction vessel were mechanically stirred at 80 °C for 12h. After the passage of the desired time, the precipitates of silica-coated magnetic nanoparticles were separated using an external magnetic field that were then washed with ethanol (3 × 10 ml) and dried in the absence of temperature under vacuum.

Preparation of the silica-coated Fe$_3$O$_4$ magnetic nanoparticles bonded propyl chloride (SCMNPs@APTESi)
Following the successful coating procedure of the magnetic nanoparticles, 1g of SC@ Fe$_3$O$_4$ MNPs was added to the reaction vessel containing 20 ml dry toluene and dispersed with the aid of ultrasonication for 30 min. Next, a certain amount of aminopropyltriethoxysilane (APTESi) (2 ml) was added dropwise to the reaction solution and refluxed under argon atmosphere with vigorous stirring for 24h. After the appearance of the bright solid magnetic nanoparticles in the reaction vessel, the desired product was magnetically separated from the solution, consecutively washed with ethanol, and then dried in a vacuum oven at 50 °C.

Preparation of the SCMNPs@APTES/sucanh
The prepared SCMNPs@APTESi (2 g) was added to the reaction vessel containing 100 ml of dry toluene and dispersed for 30 min with sonication. After dispersing the magnetic nanoparticles in the desired solvent, more succinimicyanohydride (3 mmol) and triethylamine (3.5 mmol) were poured to the reaction solution and the resulting mixture was refluxed for 36h with stirring. The residue solid (SCMNPs@APTES/sucanh) was extracted using an appropriate magnet, consecutively washed with ethanol, and dried in a vacuum oven.

Preparation of the 4-[[Pyridin-2-ylmethylene]-amino]-phenol
Iminopyridine was prepared using procedure reported in literature [33]. A mixture of Pyridine-2-carbaldehyde (1 mmol), 4-aminophenol (1 mmol), and MeOH (10 ml) was stirred magnetically under reflux conditions for 3h. After this period and completion of the reaction, as controlled by thin-layer chromatography (TLC), the solution was cooled to room temperature, and the resulting yellow crystals were separated by filtration. The solid residue was rinsed several times with methanol and dried under vacuum.
Preparation of the SCMNPs@APTES/imine

To a dispersed solution of SCMNPs@APTES/sucan (2 g) in dry DMF (10 ml) was added a solution of iminopyridine (0.2 g), NaH (0.006 g) and DMF (7 ml), and the mixture was refluxed under vigorous stirring for 24 h. The obtained Schiff base immobilized on SCMNPs@APTES/sucan was extracted with magnetic decantation in the presence of the powerful magnetic field that was consecutively washed with DMF and dried in a vacuum oven.

Preparation of the SCMNPs@imine/\textsubscript{SO\textsubscript{3}H}

2 g of SCMNPs@APTES/imine was dispersed in 50 ml dry dichloromethane with the aid of ultrasonication for 15 min and 10 mmol chlorosulfonic acid was added dropwise into the resulting solution. The resulting mixture was stirred vigorously for 6 h and after collecting sediments in the bottom of the container, the sediments were separated with magnetic decantation in the presence of the powerful magnetic field. The resultant SCMNPs@imine/\textsubscript{SO\textsubscript{3}H} was rinsed twice with water and ethanol and dried at 60 °C for 17 h under a vacuum oven. All stages of the SCMNPs@imine/\textsubscript{SO\textsubscript{3}H} synthesis are exhibited in scheme 1.

General process for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one derivatives (4)

The condensation of 2-naphthol (1 mmol), dimeredone (1 mmol), and 3-nitrobenzaldehyde (1 mmol) was tested in the presence of SCMNPs@imine/\textsubscript{SO\textsubscript{3}H} (10 mg) at 90 °C under solvent-free conditions. After solidification of the reaction solution and in order to ensure its completion, the reaction mixture was controlled by the TLC. After viewing the product spot on TLC, the reaction solution was cooled to 25 °C and the catalyst was separated by an external magnet and the solid residue was achieved from the reaction container by recrystallization from aqueous ethanol (90%).

General process for the preparation of 1,8-dioxooctahydroxanthene derivatives (5)

The condensation of dimeredone (1 mmol) and aldehyde (1 mmol) was tested in the presence of SCMNPs@imine/\textsubscript{SO\textsubscript{3}H} (10 mg) at 90 °C under solvent-free conditions. After solidification of the reaction solution and in order to ensure its completion, the reaction mixture was controlled by the TLC. After viewing the product spot on TLC, the reaction solution was cooled to 25 °C and the catalyst was separated by an external magnet and the solid residue was achieved from the reaction container by recrystallization from aqueous ethanol (90%).

Results and discussion

Catalyst characterization

**FTIR analysis of SCMNPs@imine/\textsubscript{SO\textsubscript{3}H}**

Figure 1 exhibits the infrared spectra of MNPs, SCMNPs@APTES/imine, and SCMNPs@imine/\textsubscript{SO\textsubscript{3}H}. In the case of MNPs, a broad peak at 3443 cm\(^{-1}\) can be related to the OH stretching vibration of the which are bonded to the surface of MNPs. In addition, the successful synthesis of MNPs is confirmed with 550 and 472 cm\(^{-1}\) peaks relating to the Fe-O band of the Fe\textsubscript{3}O\textsubscript{4} lattice. In the spectrum of SCMNPs@APTES/imine, the characteristic peaks at 1538 cm\(^{-1}\) and 1615 cm\(^{-1}\) corresponds to the C=\text{N} stretching vibrations. The peak at 2961 cm\(^{-1}\) can be allocated to the aliphatic C-H stretching vibrations. The absorption peak corresponding to the stretching vibrations of the Si-O-Si group appeared at 1091 cm\(^{-1}\). Moreover, the absorption peak at 1400–1500 cm\(^{-1}\) is attributable to the C=C stretching vibrations of the aromatic rings. In the spectrum of SCMNPs@imine/\textsubscript{SO\textsubscript{3}H},
the functionalization of SO$_3$H group on the SCMNPs@APTES/imine surface is confirmed by the peaks at 3409 cm$^{-1}$ and 1228 cm$^{-1}$ dedicate to the O–H and O–SO$_2$ stretching vibration, respectively.

**UV-visible spectrum of SCMNPs@imine/SO$_3$H**

Calculating the Hammett acidity function ($H_0$), which can express the acidity of an acid in an organic solvent, can be achieved using the following equation:

$$H_0 = pK(I)_{aq} + \log ([II]/[IH^+])$$

Where ‘T’ shows the indicator base and [II], and [IH$^+$], are molar concentration of the indicator in the absence and presence of acid, respectively. In this study, 4-nitroaniline (pK (I)$_{aq} = 0.99$) as an indicator to abstract proton was used in CCl$_4$. In electron spectra of the 4-nitroaniline in CCl$_4$, indicator unprotonated form illustrated maximum absorption at 331 nm. According to the Lambert-Beer’s Law, the value of [II]/[IH$^+$], could be obtained using the UV-visible spectrum.

As shown in figure 2, the maximum wavelength of the indicator in the presence of SCMNPs@imine/SO$_3$H was decreased compared with the indicator sample in CCl$_4$, and this is a confirmation of the acidic strength of SCMNPs@imine/SO$_3$H. The obtained outcomes of the catalyst acidity strength are tabulated in table 1.

**XRD analysis of SCMNPs@imine/SO$_3$H**

Characterization by x-ray diffraction (XRD) was carried out to survey the synthesis of magnetite crystal phase of MNPs, SCMNPs@APTES/sucanah and SCMNPs@imine/SO$_3$H in the 2$\theta$ range of 10–80°. As shown in figure 3, the XRD patterns of all samples had six reflections at 2$\theta = 30.31, 35.49, 43.63, 54.11, 57.35, 62.95$, and $74.53$ that were corresponding to the (220), (311), (400), (422), (511), and (440) planes, respectively. Moreover, the
XRD patterns of SCMNPs@APTES/sucanh and SCMNPs@imine/\textSO_3\textH illustrated additional reflections at 2\theta = 16°–28°, which are relevant to an amorphous silica shell. It is indicated that the SCMNPs@imine/\textSO_3\textH catalyst was achieved successfully with retention of the MNPs crystalline structure.

EDX analysis of SCMNPs@imine/\textSO_3\textH

Energy dispersive x-ray (EDX) spectrum was accomplished to verify the elemental composition of SCMNPs@imine/\textSO_3\textH nanocatalyst (figure 4). The EDX analysis proves the presence of Fe, N, O, Si and S characteristic peaks and confirms the functionalization of SCMNPs@APTES/imine shift base with the \textSO_3\textH groups (figure 4).

VSM analysis of SCMNPs@imine/\textSO_3\textH

To investigate the saturation magnetization of the MNPs and SCMNPs@imine/\textSO_3\textH, magnetic measurements were accomplished by a vibrating sample magnetometer (VSM) to assay the loading of various functional groups on the MNPs with an applied magnetic field of 10000 Oersted at room temperature (figure 5). As can be seen from the VSM patterns, the values of saturation magnetization (Ms) for MNPs and SCMNPs@imine/\textSO_3\textH are 61.20 and 36.78 emu g⁻¹, respectively. This difference in the saturation magnetization value (Ms) can be attributed to the quenching of surface moments with the formation of silica layer and functional groups around the MNPs core.

Thermal analysis of SCMNPs@imine/\textSO_3\textH

The thermal behaviors of MNPs, SCMNPs@APTES/sucanh, SCMNPs@APTES/imine and SCMNPs@imine/\textSO_3\textH are studied by Thermogravimetric analysis (TGA). As shown in all thermogram in figure 6, the mass loss up to the temperature of 250 °C is correlated with the evaporation of the adsorbed water molecules. Moreover, TGA data for SCMNPs@APTES/sucanh, SCMNPs@APTES/imine and SCMNPs@imine/\textSO_3\textH samples exhibit 2 mass loss at the temperature up to 600 °C because of losing functional groups around the MNPs core.

| Entry | Catalyst | [I]₀ (%) | [H⁺]₀ (%) | H₀ |
|-------|----------|----------|-----------|----|
| 1     | —        | 100.0    | 0.0       | —  |
| 2     | \textSO_3\textH@imineZCMNPs | 78.7     | 21.2      | 1.6 |

Conditions for the measurement of UV-visible spectrum: Solvent, CCl₄; indicator, 4-nitroaniline (pK(\textIaq) = 0.99), 3.00 × 10⁻⁵ mol L⁻¹; SCMNPs@imine/\textSO_3\textH (10 mg) room temperature for 1 day.

Table 1. Calculation of Hammett acidity function (H₀) of SCMNPs@imine/\textSO_3\textH.
In order to show the semiconductor property of the synthesized SCMNPs@imine/\(\text{SO}_3\text{H}\), the energy band gap of the catalyst was plotted using the Tauc relation. The energy band gap of semiconductors is between 0 to 3 eV. On the other hand, according to the exhibited diagram in figure 7, the band gap of the catalyst was obtained at 2.53 eV, confirming the semiconductor of the synthesized SCMNPs@imine/\(\text{SO}_3\text{H}\).

This study aimed at publishing the operative and one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[\(a\)]xanthen-11-one and 1,8-dioxooctahydroxanthene derivatives using the novel, recyclable and reusable magnetic nanoparticles of SCMNPs@imine/\(\text{SO}_3\text{H}\) under solvent-free conditions (scheme 2).

To optimize the reaction conditions, we conducted the condensation of 2-naphthol (1), dimedone (2) and 3-nitrobenzaldehyde (3) as a model reaction for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[\(a\)]xanthen-11-one derivatives in the presence of SCMNPs@imine/\(\text{SO}_3\text{H}\) (10 mg) in different solvents (EtOH, \(\text{H}_2\text{O}\), THF, and EtOAc) and also under solvent-free condition (table 2, Entries 1–4). The results showed that the best optimal condition was obtained in the absence of solvent (table 2, Entry 5). To determine the effect of temperature on the model reaction, the reaction was carried out in a range of various temperatures, including 25, 70, 80, 90, 100, 110 and 120 °C, in the presence of 10 mg of SCMNPs@imine/\(\text{SO}_3\text{H}\) catalyst under solvent-free conditions (table 2, entries 5–11). Increasing the reaction temperature to 120 °C made no obvious difference in the product yield (table 2, Entries 9–11). To optimize the amount of magnetic

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**Figure 4.** EDX spectra of SCMNPs@imine/\(\text{SO}_3\text{H}\).

**Figure 5.** Magnetization curves for MNPs and SCMNPs@imine/\(\text{SO}_3\text{H}\) nanoparticles at room temperature.

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Figure 6. TGA curves of MNPs, SCMNPs@APTES/sucanah, SCMNPs@APTES/imine and SCMNPs@imine/SO$_3$H.

Figure 7. Determination of the optical energy band by the Tauc relation.

Scheme 2. Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one and 1,8-dioxooctahydroxanthene derivatives using SCMNPs@imine/SO$_3$H.
Table 2. Optimization of the three-component reaction of 2-naphthol (1), dimedone (2) and 3-nitrobenzaldehyde (3h) under various conditions.*

| Entry | Solvent        | Catalyst (mg)                  | Temp.      | Time (min) | Yield (%)\(^b\) | References |
|-------|----------------|--------------------------------|------------|------------|-----------------|------------|
| 1     | H\(_2\)O       | SCMNPs@imine/SO\(_3\)H/10      | Reflux     | 80         | 32              | This work  |
| 2     | EtOH           | SCMNPs@imine/SO\(_3\)H/10      | Reflux     | 60         | 75              | This work  |
| 3     | THF            | SCMNPs@imine/SO\(_3\)H/10      | Reflux     | 50         | 78              | This work  |
| 4     | EtOAc          | SCMNPs@imine/SO\(_3\)H/10      | Reflux     | 50         | 69              | This work  |
| 5     | Solvent-free   | SCMNPs@imine/SO\(_3\)H/10      | 90 °C      | 15         | 95              | This work  |
| 6     | Solvent-free   | SCMNPs@imine/SO\(_3\)H/10      | 25 °C      | 60         | 56              | This work  |
| 7     | Solvent-free   | SCMNPs@imine/SO\(_3\)H/10      | 70 °C      | 35         | 80              | This work  |
| 8     | Solvent-free   | SCMNPs@imine/SO\(_3\)H/10      | 80 °C      | 25         | 89              | This work  |
| 9     | Solvent-free   | SCMNPs@imine/SO\(_3\)H/10      | 100 °C     | 15         | 94              | This work  |
| 10    | Solvent-free   | SCMNPs@imine/SO\(_3\)H/10      | 110 °C     | 15         | 92              | This work  |
| 11    | Solvent-free   | SCMNPs@imine/SO\(_3\)H/10      | 120 °C     | 15         | 91              | This work  |
| 12    | Solvent-free   | SCMNPs@imine/SO\(_3\)H/15      | 90 °C      | 15         | 93              | This work  |
| 13    | Solvent-free   | SCMNPs@imine/SO\(_3\)H/5       | 90 °C      | 25         | 77              | This work  |
| 14    | EtOH           | RuCl\(_3\).H\(_2\)O            | Reflux     | 35         | 86              | [34]       |
| 15    | Solvent-free   | Orange peel                     | 120 °C     | 40         | 90              | [35]       |
| 16    | H\(_2\)O       | Fe\(_3\)O\(_4\)/ch-Ag NPs      | 80 °C      | 30         | 91              | [36]       |
| 17    | Solvent-free   | [Et\(_3\)N-SO\(_3\)H]Cl        | 120 °C     | 60         | 85              | [37]       |
| 18    | Toluene        | PVP-Tf                          | 110 °C     | 300        | 85              | [38]       |

\(^a\) Reaction conditions: 2-naphthol (1 mmol), dimedone (1 mmol), 3-nitrobenzaldehyde (1 mmol), and required amount of the catalysts.

\(^b\) The yields refer to the isolated product.
| Entry | RCHO (2) | Product | Yield(%)<sup>b</sup>/Time (min) | M.P(Obsd)(°C) | M.P(Lit)(°C) |
|-------|----------|---------|---------------------------------|---------------|--------------|
| 1     | ![RCHO1](image1.png) | ![Product1](image2.png) | 94/20 | 151–153 | 150–152 [38] |
| 2     | ![RCHO2](image3.png) | ![Product2](image4.png) | 96/12 | 180–182 | 178–180 [38] |
| 3     | ![RCHO3](image5.png) | ![Product3](image6.png) | 94/17 | 181–184 | 180–182 [38] |
| 4     | ![RCHO4](image7.png) | ![Product4](image8.png) | 93/20 | 180–183 | 183–185 [37] |
| 5     | ![RCHO5](image9.png) | ![Product5](image10.png) | 97/20 | 169–171 | 168–170 [38] |
Table 3. (Continued.)

| Entry | RCHO (2) | Product | Yield(%)\[^{b}\]/Time (min) | M.P(Obsd)(°C) | M.P(Lit)(°C) |
|-------|----------|---------|-----------------------------|---------------|--------------|
| 6     | ![Image](image1) | ![Image](image2) | 95/25 | 160–163 | 159–162 [37] |
| 7     | ![Image](image3) | ![Image](image4) | 97/15 | 187–189 | 186–187 [39] |
| 8     | ![Image](image5) | ![Image](image6) | 95/15 | 170–172 | 169–171 [37] |
| 9     | ![Image](image7) | ![Image](image8) | 92/12 | 177–180 | 176–179 [39] |
| Entry | RCHO (2) | Product | Yield (%)<sup>b</sup>/Time (min) | M.P (Obsd) °C | M.P (Lit) °C |
|-------|----------|---------|-------------------------------|----------------|--------------|
| 10    | ![Image 1](image1.png) | ![Image 2](image2.png) | 91/25                         | 175–178        | 176–179 [39] |
| 11    | ![Image 3](image3.png) | ![Image 4](image4.png) | 93/20                         | 200–203        | 199–201 [37] |

*Reaction conditions: 2-naphthol (1 mmol), dimedone (1 mmol), aldehyde (1 mmol), and SCMNPs@imine/SO<sub>3</sub>H (10 mg).*
Table 4. Optimization of the three-component reaction of dimeredone (1) and 4-chlorobenzaldehyde (3g) under various conditions.

| Entry | Solvent        | Catalyst (mg)                      | Temp.         | Time (min) | Yield (%)\(^b\) | References |
|-------|----------------|------------------------------------|---------------|------------|-----------------|------------|
| 1     | H₂O            | SCMNP@imine/SO₃H/10                | Reflux        | 80         | 37              | This work  |
| 2     | EtOH           | SCMNP@imine/SO₃H/10                | Reflux        | 60         | 65              | This work  |
| 3     | CH₃CN          | SCMNP@imine/SO₃H/10                | Reflux        | 50         | 56              | This work  |
| 4     | EtOAc          | SCMNP@imine/SO₃H/10                | Reflux        | 50         | 49              | This work  |
| 5     | Solvent-free   | SCMNP@imine/SO₃H/10                | 90 °C         | 8          | 96              | This work  |
| 6     | Solvent-free   | SCMNP@imine/SO₃H/10                | 70 °C         | 30         | 83              | This work  |
| 7     | Solvent-free   | SCMNP@imine/SO₃H/10                | 80 °C         | 15         | 90              | This work  |
| 8     | Solvent-free   | SCMNP@imine/SO₃H/10                | 100 °C        | 8          | 95              | This work  |
| 9     | Solvent-free   | SCMNP@imine/SO₃H/10                | 110 °C        | 8          | 93              | This work  |
| 10    | Solvent-free   | SCMNP@imine/SO₃H/10                | 120 °C        | 8          | 92              | This work  |
| 11    | Solvent-free   | SCMNP@imine/SO₃H/15                | 90 °C         | 15         | 94              | This work  |
| 12    | Solvent-free   | [bmim][HSO₄]                       | FeC₃⁶₆H₂O      | 80 °C      | 3h              | [40]       |
| 13    | [bmim][HSO₄]   | CH₃CN                              | Amberlyst-15  | 120 °C     | 5h              | [41]       |
| 14    | [bmim][HSO₄]   | H₂O                                | β-cyclodextrin | 60 °C      | 10h             | [42]       |
| 15    | [bmim][HSO₄]   | Solvent-free                       | Silica sulphuric acid | 80 °C | 60 | [43] |

\(^a\) Reaction conditions: dimeredone (1 mmol), 4-chlorobenzaldehyde (1 mmol), and required amount of the catalysts. \(^b\) The yields refer to the isolated product.
Table 5. SCMNPs@imine/\(\text{SO}_3\text{H}\)-Catalyzed synthesis of 1,8-dioxooctahydroxanthene derivatives\(^a\).

| Entry | RCHO (2) | Product | Yield(%)\(^b\)/Time (min) | M.P.(Obsd)\(^o\text{C}\) | M.P.(Lit)\(^o\text{C}\) |
|-------|----------|---------|---------------------------|-------------------------|------------------------|
| 1     |          | ![4a](image) | 92/8 | 198–201 | 201–202 [32] |
| 2     | ![NO2](image) | ![4b](image) | 93/12 | 250–253 | 251–252 [26] |
| 3     | ![O2N](image) | ![4c](image) | 95/10 | 163–166 | 164–165 [26] |
| 4     | ![O2N](image) | ![4d](image) | 97/8 | 220–223 | 222 [44] |
| 5     | ![Br](image) | ![4d](image) | 93/8 | 278–280 | 281–282 [26] |
| Entry | RCHO (2) | Product | Yield(%)/Time (min) | M.P.(Obsd)(°C) | M.P.(Lit)(°C) |
|-------|----------|---------|---------------------|----------------|---------------|
| 6     | ![Image](4e) | 96/8    | 235–237             | 256–238        | [45]          |
| 7     | ![Image](4f) | 96/8    | 228–231             | 230–232        | [32]          |
| 8     | ![Image](4g) | 93/8    | 186–189             | 188–190        | [46]          |
| 9     | ![Image](4h) | 94/10   | 190–193             | 192–194        | [29]          |
Table 5. (Continued.)

| Entry | RCHO(2) | Product | Yield(%)$/Time (min)$ | M.P(Obsd)(°C) | M.P(Lit)(°C) |
|-------|---------|---------|-----------------------|---------------|--------------|
| 10    | ![4i](image) | ![4j](image) | 95/8                  | 200–203       | 205–207 [44] |

$^a$ Reaction conditions: dimedone (1 mmol), aldehyde (1 mmol), and SCMNPs/imine/\(\text{SO}_3\text{H}\) (10 mg).
nanocatalyst, the model reaction was investigated in the range of 5–15 mg of SCMNPs@imine/\(\text{SO}_3\text{H}\) (table 2, Entries 5 and 12–13). The results indicated that 10 mg of SCMNPs@imine/\(\text{SO}_3\text{H}\) was found to be sufficient to complete the reaction. Decreasing the amounts of the catalyst from 10 to 5 mg led to a decrease in the yield of product and an increase in the reaction time. Notably, enhancing the concentration of catalyst beyond 10–15 mg did not show any significant changes in yield and time of reaction. Finally, to compare the efficiency of this synthesized catalyst with the previously reported catalysts for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (a) and 1,8-dioxo-octahydroxanthene (b) derivatives, we used the results for these catalysts in the preparation of 4h as a model reaction. The results clearly demonstrate that
SCMNPs@imine/\text{SO}_3\text{H} is superior with respect to the reported catalysts in terms of saving time, energy, and high yields of the products.

After optimizing the reaction parameters such as solvent, temperature and catalyst loading, we have synthesized different derivatives of 12-aryl-8,9,10,12-tetrahydrobenzo[\text{a}]xanthen-11-one derivatives (4a-k) from a variety of substrates including aldehydes, 2-naphthol, and dimedone in the presence of 10 mg of SCMNPs@imine/\text{SO}_3\text{H} as catalyst. As clearly shown in table 3, the aryl aldehydes with both electron-withdrawing and electron-donating substituents proceeded smoothly and afforded the corresponding products with high purity in good yields.

Also, we focused on a rapid and efficient one-pot three-component synthesis of 1,8-dioxooctahydroxanthenes via the condensation of dimedone with 4-chlorobenzaldehyde in the presence of SCMNPs@imine/\text{SO}_3\text{H} as a model reaction. For optimization of the reaction conditions, various conditions using various concentration of catalyst at different temperatures under solvent-free conditions were investigated (table 4). We found that the best result was obtained using 1 mmol aldehyde, 1 mmol dimedone and 10 mg SCMNPs@imine/\text{SO}_3\text{H} at 90 °C under solvent-free conditions (table 4, Entry 5). To highlight the advantages of our developed procedures, we have compared our result obtained from the synthesis of 1,8-dioxooctahydroxanthenes catalyzed with SCMNPs@imine/\text{SO}_3\text{H} with the previously reported catalysts in the literature. As shown in this table, this method is superior in the term of saving time, energy, and high yields of the products.

Under the optimal conditions and to establish the effectiveness and the acceptability of the method, we surveyed the procedure with a variety of simple readily available substrates. As presented in table 5, wide ranges of aromatic aldehydes containing electron-withdrawing and electron-donating groups were condensed with dimedone under the optimal conditions with high yields and very short reaction times.

A plausible mechanism for one-pot three-component condensation of 2-naphthol (1) / dimedone (2), dimedone (2), various aryl aldehydes (3), and SCMNPs@imine/\text{SO}_3\text{H} is exhibited in scheme 3. Firstly, 2-naphthol (1) / dimedone (2) and activated carbonyl group of aldehyde 3 react with each other via a Knoevenagel condensation reaction to afford intermediate 6 and 7. After that, Michael addition of dimedone 2, as a cyclic 1,3-diketones to intermediate 6 and 7 afford the polar transition state 8 and 9. Intermediates 8 and 9 are unstable and convert to desired products 4 and 5 after intermediates 10 and 11 dehydrations.

An effective characteristic of the SCMNPs@imine/\text{SO}_3\text{H} is the ease with which it can be separated from the reaction mixtures by an external magnetic field. Thus, the recyclability of the SCMNPs@imine/\text{SO}_3\text{H} in the model reaction between 2-naphthol, dimedone and 3-nitrobenzaldehyde, also, between dimedone and 4-chlorobenzaldehyde were tested. After completion of the reaction and separation of the catalyst from the mixture, ethanol was added and the catalyst was rinsed several times. The washed catalyst was dried before being reused in the next run of the same model reaction. As figure 8 shows, the catalytic activity of the SCMNPs@imine/\text{SO}_3\text{H} was not significantly changed at least 6 runs consecutive recycling in the same model reactions.

**Conclusion**

Results show that functional groups have been supported on the Fe$_3$O$_4$ MNPs surfaces and a heterogeneous magnetic nanocatalyst is formed (SCMNPs@imine/\text{SO}_3\text{H}). Then the SCMNPs@imine/\text{SO}_3\text{H}, as a non-toxic, efficient and green catalyst, has been used for one pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo [\text{a}]xanthen-11-one and 1,8-dioxooctahydroxanthen derivatives under solvent free conditions with good to high yield and short reaction times. The SCMNPs@imine/\text{SO}_3\text{H} was extracted using a permanent magnetic field and reused efficiently for the six runs without any significant decrease in catalytic activities.

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