

# Nano-Fe<sub>3</sub>O<sub>4</sub> -encapsulated silica particles bearing sulfonic acid groups as a magnetically separable catalyst for the green and efficient synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione derivatives

Mohammad Ali Ghasemzadeh<sup>1</sup> • Mina Azimi-Nasrabad<sup>1</sup>

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Abstract In this research, an efficient and environmentally friendly ("green") method for one-pot synthesis of xanthene derivatives was developed in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H nanoparticles. The functionalization of silica-coated Fe<sub>3</sub>O<sub>4</sub> magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) using chlorosulfonic acid was afforded by nano-Fe<sub>3</sub>O<sub>4</sub> encapsulated-silica particles bearing sulfonic acid (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H) that could be applied as a reusable and efficient heterogeneous nanocatalyst. The multicomponent reactions of 2-hydroxy-1,4-naphthoquinone, β-naphthol and aldehydes were carried out under reflux conditions to obtain some 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione derivatives. Being a simple procedure with environmental benignness, excellent yields, short reaction times, simple purification and facile catalyst separation are the advantages of this protocol. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H was readily recovered using an external magnet and could be reused several times without significant loss of reactivity. The catalyst was fully characterized by vibratingsample magnetometry (VSM), Fourier transform-infrared (FT-IR) spectrometry, scanning electron microscopy (SEM), X-ray diffraction (XRD) spectroscopy, energy dispersive X-ray spectroscopy (EDAX) and transmission electron microscopy (TEM).

Mohammad Ali Ghasemzadeh Ghasemzadeh@qom-iau.ac.ir

<sup>&</sup>lt;sup>1</sup> Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Islamic Republic of Iran

# Introduction

The aim of science and technology in recent years has been to shift toward more environment friendly and reusable catalysts and sustainable resources in order to decrease waste and the use of raw materials. The development of new catalysts by nano-scale design has emerged as a fertile field suitable for research and varied innovation [1]. Magnetite nanoparticles (MNPs) have been intensively studied because of their broad application in several fields such as ferrofluids, digital media recording, targeted drug delivery, magnetic hyperthermia, magnetic resonance imaging (MRI), etc. [2, 3]. Magnetite, Fe<sub>3</sub>O<sub>4</sub>, is also a facile reductant for various environmental contaminants found in groundwater [4, 5]. However, bare  $Fe_3O_4$ nanoparticles (NPs) tend to aggregate into large clusters, are easily oxidated in air, have high dispersion, a loss of magnetism, and agglomeration because of their high specific area and strong inter particle interaction, limiting their usage. In this regard, great attention has recently been paid to the preparation of Fe<sub>3</sub>O<sub>4</sub>-based NPs with a core-shell structure [6-9]. Coating MNPs with an amorphous silica layer is a promising and significant approach in the expansion of MNPs for both basic study and technological applications [10]. A silica shell on a nanocomposite is chemically inert and has high stability versus aggregation.

Furthermore, the presence of silanol moieties on the surface can readily be functionalized through suitable surface modifications, enabling introduction of a variety of various functionalities [11]. Therefore, the outer shell of silica not only protects the inner magnetite core from oxidation but also provides sites for surface functionalization using various groups such as guanidine [12], proline [13], sulfamic acid [14] and sulfonic acid [15].

Recently, nano-Fe<sub>3</sub>O<sub>4</sub> encapsulated-silica particles bearing sulfonic acid (Fe<sub>3-O4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H) NPs were used as an active catalyst in the synthesis of 1,8-dioxo-octahydroxanthene [16], indazolo[2,1-b]phthalazine-triones and pyrazolo[1,2-b]phthalazine-diones [17], functionalized pyrimido[4,5-b]quinolines and indeno-fused pyrido[2,3-d]pyrimidines [18] and 3,4-dihydropyrimidinones/thiones [19].

In this research, sulfonic acid-functionalized silica-coated nano-Fe<sub>3</sub>O<sub>4</sub> particles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>–SO<sub>3</sub>H) were prepared as effective acid catalysts in our laboratory and were used for the synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione. It could easily be separated from the media using a simple external magnet and reused several times. The process is more efficient than filtration and centrifugation in preventing loss of the solid catalyst.

Multicomponent coupling reactions have become significant tools in organic, combinatorial and medicinal chemistry [20] with their fast production of molecular complexity and variety with predefined functionality [21].

Recently, three-component reaction of aldehydes,  $\beta$ -Naphthol and 2-hydroxy-1, 4-naphthoquinone has received a great deal of attention in organic synthesis. The synthesis of xanthene derivatives has received much attention due to their various range of therapeutic and biological attributes, including antiviral [22, 23], antibacterial [24, 25] and anti-inflammatory properties [26, 27]. Also, these

compounds are applied extensively in laser technologies [28], dyes [29] and as pH-sensitive fluorescent material for embodiment of biomolecules [30].

Many synthetic methods exist for the synthesis of xanthenes and benzoxanthenes, including condensation of aldehydes and acetophenones [31], 2-hydroxyaromatic aldehydes and 2-tetralone [32], and  $\beta$ -naphthol with alkyl or aryl aldehydes [33]. There are some methods reported in the literature for the synthesis of 14-aryl-14H-dibenzo[a,i] xanthene-8,13-dione involving the three-component reaction of  $\beta$ -naphthol, 2-hydroxy-1, 4-naphthoquinone with various aldehydes catalyzed by different catalysts such as poly(4-vinylpyridinium) hydrogen sulfate [34], silica supported perchloric acid [35], xanthan sulfuric acid [36], silica chloride [37], Amberlyst-15 [38], acetic acid [39], and sulfuric acid [40].

In view of our interest in sustainable protocols in the synthesis of heterocyclic compounds using multi-component reactions and nanocatalysts [41–46], here, we report a new and efficient method for the preparation of 14-aryl-14H-dibenzo[a,i]x-anthene-8,13-dione derivatives via multi-component synthesis of  $\beta$ -naphthol, 2-hydroxy-1,4-naphthoquinone and various aldehydes using an Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> sulfuric acid core–shell composite (Scheme 1).

## **Experimental**

Chemicals were purchased from Sigma–Aldrich and Merck in high purity. All materials were of commercial reagent grade and were used without further purification. All melting points are uncorrected and were determined in capillary tubes on a Boetius melting point microscope. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Bruker 400 MHz spectrometer with CdCl<sub>3</sub> as the solvent using tetramethylsilane as an internal standard; the chemical shift values are in  $\delta$ . FT-IR spectra were recorded on Nicolet Magna 550 IR spectrometer in KBr pellets in the range of 400–4000 cm<sup>-1</sup>. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Powder XRD was carried out on a Philips diffractometer (X'pert Company) with mono chromatized Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). Microscopic morphology of products was visualized by SEM (LEO 1455VP). Mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV. Magnetic properties were obtained via VSM using a BHV-55 vibrating sample magnetometer. Compositional analysis was done by X-ray energy dispersive analysis (Scheme 2).



 $\label{eq:scheme1} \begin{array}{l} \mbox{Scheme 1} \quad \mbox{Fe}_3O_4@SiO_2-SO_3H \ \mbox{NPs catalyzed one-pot synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione derivatives} \end{array}$ 



Scheme 2 Preparation steps for fabricating Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H

# Preparation of Fe<sub>3</sub>O<sub>4</sub> NPs

Fe<sub>3</sub>O<sub>4</sub> NPs were prepared according to the procedure reported by Zhang et al. [47]. To a solution of FeCl<sub>2</sub>.4H<sub>2</sub>O (2.5 g) and FeCl<sub>3</sub>.6H<sub>2</sub>O (6 g) in 30 ml of deionized water was added dropwise 1.0 mL of concentrated hydrochloric acid at room temperature. The solution was added to 300 mL of 1.5 mol L<sup>-1</sup> NaOH and then the solution was stirred vigorously at 80 °C until precipitation. Afterwards, the prepared magnetic NPs were separated magnetically, washed with deionized water and then dried at 70 °C for 8 h.

# Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs

The core–shell  $Fe_3O_4@SiO_2$  microspheres were prepared according to the previously reported method [48]. Briefly, 1 g of  $Fe_3O_4$  NPs was treated with 0.5-M HCl aqueous solution (25 mL) by sonication. After treatment for 10 min, the magnetite particles were separated and washed with deionized water, and then homogeneously dispersed in a mixture of ethanol (60 mL), deionized water (100 mL) and concentrated ammonia aqueous solution (10 mL, 28 wt%), followed by the addition of tetraethylorthosilicate (TEOS, 0.22 g, 0.144 mmol). After stirring at room temperature for 2 h, the  $Fe_3O_4@SiO_2$  microspheres were separated using an external magnet and washed with ethanol and water.

## Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>–SO<sub>3</sub>H MNPs were prepared according to a previously reported procedure by Kiasat and Davarpanah [17]. A suction flask was equipped with a constant-pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution functioning as an alkali trap. Firstly, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (1 g) was added to the flask and dispersed in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) ultrasonically for 30 min. Subsequently, chlorosulfonic acid (1 mL) was added drop-wise to a cooled (ice-bath) solution of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (1 g) over a period of 30 min at room temperature. After completion of the addition, the mixture was stirred for an additional 6 h until complete dissipation of HCl from the reaction vessel. The resulted MNPs were separated using an external magnet and washed with ethanol and water before being dried in an oven at 70 °C, giving Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H as a brown powder.

The chemical purity of the samples as well as their stoichiometry was tested by EDAX studies. The EDAX spectrum given in Fig. 1a shows the presence of Fe and O



Fig. 1 EDAX spectra of Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H (c) NPs



Fig. 2 SEM images of Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H (c) NPs

as the only elementary components of  $Fe_3O_4$  NPs. The EDAX spectrum of  $Fe_3O_4@SiO_2$  in Fig. 1b shows the elemental compositions are (Fe, Si and O) of coreshell NPs. The EDAX spectrum of  $Fe_3O_4@SiO_2-SO_3H$  in Fig. 1c shows the elemental compositions are (Fe, Si, O and S) of sulfuric acid functionalized silicacoated MNPs with a core-shell structure.

In order to study the morphology and particle size of  $Fe_3O_4$  (a),  $Fe_3O_4@SiO_2$ (b) and  $Fe_3O_4@SiO_2-SO_3H$  (c) NPs, SEM images were prepared (Fig. 2). As shown in Fig. 2b,  $Fe_3O_4@SiO_2$  NPs retain the morphological properties of  $Fe_3O_4$  (Fig. 2a), except for a slightly larger particle size and smoother surface, while silica are uniformly coated on the  $Fe_3O_4$  particles to form a silica shell compared to the  $Fe_3O_4@SiO_2$ . The SEM image shown in Fig. 2c demonstrates that  $Fe_3O_4@SiO_2-SO_3H$  NPs are nearly spherical, about 30 nm in size.

The structure of Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>(b) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> sulfuric acid(c) were analyzed by XRD spectroscopy (Fig. 3). An XRD diagram of the bare Fe<sub>3</sub>O<sub>4</sub> NPs displayed patterns consistent with the patterns of spinel ferrites described in the literature (Fig. 3) [14]. The same peaks were observed in the both of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> sulfuric acid XRD patterns, indicating retention of the crystalline spinel ferrite core structure during the silica-coating process. The average MNP core diameter of 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>@SiO<sub>2</sub> sulfuric acid were calculated to be about 18, 25 and 32 nm, respectively, from the XRD results by Scherrer's equation.

The FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> NPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> sulfuric acid are shown in Fig. 4. The FT-IR analysis of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> sulfuric acid exhibits two basic characteristic peaks at  $\sim$  3300 cm<sup>-1</sup> (O–H



Fig. 3 XRD patterns of Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H (c) NPs



Fig. 4 The comparative FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H (c) NPs

stretching) and 580 cm<sup>-1</sup> (Fe–O vibration) [49]. The band at 1081 cm<sup>-1</sup> comes from the Si–O–Si group. The presence of a saulfonyl group in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> sulfuric acid was confirmed by 1217 and 1124 cm<sup>-1</sup> bands, which were covered by a stronger absorption of Si–O bonds at 1081 cm<sup>-1</sup> [14]. A wide bond at 2500–3409 cm<sup>-1</sup> is due to the stretching of OH groups in the SO<sub>3</sub>H.

The magnetic properties of the samples containing a magnetite component were studied via VSM at 300 K. Figure 5 shows the absence of the hysteresis phenomenon and indicates that all of the products have superparamagnetism at room temperature. The saturation magnetization values for  $Fe_3O_4$  (a),  $Fe_3O_4@SiO_2$  (b),  $Fe_3O_4@SiO_2-SO_3H$  (c) were 48.49, 38.16 and 35.82 emu/g, respectively. These results indicated that the magnetization of  $Fe_3O_4$  decreased considerably with the increase of SiO<sub>2</sub> and SO<sub>3</sub>H groups.

The size and morphology of  $Fe_3O_4@SiO_2-SO_3H$  NPs were analyzed by TEM (Fig. 6). The results show that these nanocatalysts consist of spherical particles with a crystallite size of about 30 nm, confirming the results calculated from Scherrer's formula based on the XRD pattern.



Fig. 5 Magnetization curves for the prepared Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H (c) NPs



Fig. 6 TEM images of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H NPs

*Typical procedure for the systhesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione(4a–4p).* 

A mixture of 2-naphthol (1 mmol) and 2-hydroxynaphthalene-1,4-dione (1 mmol), aldehyde (1 mmol) and  $Fe_3O_4@SiO_2-SO_3H$  NPs (0.005 gr) in 2.5 mL of ethanol and 2.5 mL of water was refluxed at 80 °C. After completion of the reaction, the reaction mixture was diluted with chloroform (10 mL) and the catalyst was recovered by using an external magnet. The solvent was evaporated and the obtained solid was recrystallized using ethanol. All of the products were fully charactrisized by FT-IR and NMR spectroscopy.

#### Spectral data of the new products:

14-(4-hydroxyphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (4e) Red solid; m.p. = 265–267 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 5.20 (1H, s), 5.72 (1H, s), 6.54–6.56 (2H, m), 6.63–6.64 (2H, m), 7.09–7.16 (4H, m), 7.31–7.56 (4H, m), 8.01–8.09 (2H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 38.2, 110.1, 114.2, 116.1, 117.9, 118.6, 122.3, 124.2, 126.1, 126.6, 128.1, 128.9, 129.5, 130.3, 131.7, 135.4, 140.2, 151.8, 152.0, 155.9, 156.0, 159.9, 178.2, 183.0. FT-IR (KBr, cm<sup>-1</sup>): 3352 (O–H), 1660 (C = O), 1379 (C = C), 1220 (C-O), Anal. Calcd. For  $C_{27}H_{16}O_4$ : C 80.19, H 3.99. Found C 80.27, H 3.92; MS (EI) (m/z): 404 (M<sup>+</sup>).

14-(4-isopropylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (4l) Yellow powder; m.p. = 190–193 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.2–1.3 (6H, m), 2.74 (1H, s), 5.92 (1H, s), 7.03–7.05 (2H, m), 7.29–7.32 (2H, m), 7.43–7.50 (2H, m), 7.52–7.56 (2H, m), 7.58–7.60 (1H, m), 7.76–7.80 (2H, m), 7.84–7.86 (1H, m), 7.87–7.89 (1H, m), 8.02–8.04 (1H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 22.8, 32.7, 38.4, 108.5, 112.5, 115.9, 117.9, 118.3, 121.9, 125.4, 127.1, 127.9, 128.1, 129.9, 130.3, 132.7, 134.1, 136.3, 141.3, 144.9, 152.9, 157.1, 160.1, 177.9, 181.1. FT-IR (KBr, cm<sup>-1</sup>): 1691 (C = O), 1426 (C = C), 1226 (C-O); Anal. Calcd. For  $C_{30}H_{22}O_3$ : C 83.70, H 5.15. Found C 83.64, H 5.21; MS (EI) (m/z): 430 (M<sup>+</sup>).

14-(4-formylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (4n) Yellow solid; m.p = 271–272 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 5. 90 (1H, s), 7.15 (3H, t), 7.34 (3H, m), 7.45–7.62 (4H, m), 7.77–7.91 (4H, m), 9.81 (1H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 39.5,113.5, 115.1, 115.3, 116.6, 119.6, 123.1, 124.8, 126.8, 127.3, 128.9, 129.1, 130.5, 131.6, 132.3, 136.2, 142.4, 148.8, 152.8, 158.8, 160.3, 177.6, 184.1, 198.6. FT-IR (KBr, cm<sup>-1</sup>): 3078, 1692 (C = O), 1595 (C = C), 1232 (C-O); Anal. Calcd. for  $C_{28}H_{16}O_4$ : C 80.76, H 3.87. Found C 80.84, H 3.79; MS (EI) (m/z): 416 (M<sup>+</sup>).

14-(4-thiomethylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (4m) Yellow solid; m.p = 283-284 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.32 (3H, s), 5.90 (1H, s), 7.31 (3H, m), 7.43-7.60 (4H, m), 7.76-7.89 (2H, m), 7.98 (3H, m), 8.12 (2H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 21.4, 35.1, 112.3, 114.7,115.11, 118.1, 121.9, 122.6, 125.8, 126.5, 128.2, 129.1, 129.8, 130.3, 131.4, 133.6, 138.2, 140.25, 150.9, 152.75, 156.1, 159.7, 178.7, 182.4. FT-IR (KBr, cm<sup>-1</sup>): 1662 (C = O), 1367 (C = C), 1200 (C–O) cm<sup>-1</sup>; Anal. Calcd. for:  $C_{28}H_{18}O_3S$ : C 77.40, H 4.18, S 7.38. Found: C 77.31, H 4.28, S 7.31; MS (EI) (m/z): 434 (M<sup>+</sup>).

#### **Results and discussion**

In order to optimize the reaction conditions, the model reaction was carried out by using 4-chlorobenzaldehyde,  $\beta$ -naphthol and 2-hydroxy-1,4-naphthoquinone under various conditions (Scheme 3). The reaction conditions were optimized on the basis of the solvent, catalyst, and different temperatures for synthesis of 14-(4-chlorophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (4b).

The influence of the solvent was studied when the model reaction was performed using  $Fe_3O_4@SiO_2-SO_3H$  NPs under various solvents and also solvent-free conditions at different temperatures (Table 1). The best results were obtained under reflux conditions (Table 1, entries 4–10). As shown in Table 1, in the reflux conditions, the time of the reaction significantly decreased, but the yield of the product formation increased in comparison with solvent-free conditions. Table 1 shows that the solvent has a great effect on the acceleration of the reaction. The best results (97 % yield, 40 min) were obtained in water/ethanol under reflux for this multicomponent reaction (Table 1, entry 4). The significant results presented in Table 1 are related to the hydrogen bonding between water/ethanol and substrates that promote the nucleophilic attack of the reactants.

Then, to show the merit of the present approach in comparison with other catalysts, the model reaction was performed in the presence of various nanocatalysts such as CuO, MgO, ZnO, CuI, 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>@SiO<sub>2</sub>–SO<sub>3</sub>H. As shown in Table 2, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>–SO<sub>3</sub>H NPs were the best catalysts with respect to reaction time and yield of the obtained product.

In continuation of our research, we ran the study model using different amounts of  $Fe_3O_4@SiO_2-SO_3H$  nanocatalyst under reflux conditions. No product was obtained in the absence of the catalyst (Table 3, entry 1). As shown in Table 3, the optimum concentration of  $Fe_3O_4@SiO_2-SO_3H$  NPs was obtained at 0.005 g in the model reaction. Increasing the amount of the catalyst did not change the time and yield of the reaction (Table 3, entry 5).



Scheme 3 The model reaction for the synthesis of 14-(4-chlorophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione in the presence of  $Fe_3O_4@SiO_2-SO_3H$  NPs

Table 1 Preparation of 14-(4-chlorophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione in different solvents	Entry	Solvent	T/°C	Time (min)	Yield (%) <sup>a</sup>
	1	Solvent-free	25	120	Trace
	2	Solvent-free	100	100	25
	3	Water/EtOH	25	95	35
	4	Water/EtOH	Reflux	40	97
	5	EtOH	Reflux	60	60
	6	Water	Reflux	80	54
Reaction conditions: β-naphthol (1 mmol), 2-hydroxy-1,4-	7	CH <sub>3</sub> CN	Reflux	120	45
	8	DMF	Reflux	140	38
naphthoquinone (1 mmol) and	9	$CH_2Cl_2$	Reflux	150	35
<sup>a</sup> Isolated vields	10	Toluene	Reflux	160	30

Table 2   The model reaction	
was carried out by various	
catalysts	

Entry	Catalyst	Time (min)	Yield (%) <sup>a</sup>	
1	Fe <sub>3</sub> O <sub>4</sub>	60	60	
2	MgO	120	25	
3	ZnO	75	65	
4	CuO	100	38	
5	CuI	80	70	
6	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	55	85	
7	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H	40	97	

Water/ethanol as solvent under reflux conditions

<sup>a</sup> Isolated yields

Table 3 The effect of the amount of $Fe_3O_4@SiO_2-SO_3H$ on the model reaction	Entry	Catalyst amount (gr)	Time (min)	Yield (%) <sup>a</sup>
	1	None	240	None
	2	0.001	90	30
	3	0.003	70	68
Water/ethanol as solvent under reflux conditions <sup>a</sup> Isolated vields	4	0.005	40	97
	5	0.006	40	97

After optimization of the reaction conditions, we used a diversity of aldehydes to investigate three-component reactions in the presence of  $Fe_3O_4@SiO_2-SO_3H$  NPs under reflux conditions. We observed that various aryl aldehydes could be introduced at a high efficiency and produced high yields of products at a high purity (-97 % by <sup>1</sup>H NMR). When this research was carried out using aliphatic aldehyde including butanal and pentanal, TLC and <sup>1</sup>H NMR spectra of the reaction mixture showed a combination of the starting materials and numerous products, the yield of the expected product was very poor. Data in Table 4 show that sterically hindered aromatic aldehydes required longer reaction times in comparison with *p*-substituted aryl aldehydes. In addition, aromatic aldehydes bearing electron-withdrawing groups such as Cl, Br, and NO<sub>2</sub> in the p-position reacted very smoothly, in short

Entry	Ar	Product	Time(min)	Yield (%) <sup>a</sup>	m.p. °C	Lit. m.p.ºC
1	C <sub>6</sub> H <sub>5</sub>	4a	60	91	317-319	(319–320) [34]
2	4-ClC <sub>6</sub> H <sub>4</sub>	4b	40	97	303-305	(305–306) [34]
3	$4-BrC_6H_4$	4c	55	94	290-295	(284–295) [40]
4	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4d	70	90	256-258	(255–256) [34]
5	4-HOC <sub>6</sub> H <sub>4</sub>	4e	70	90	265–269 <sup>b</sup>	_
6	4-MeOC <sub>6</sub> H <sub>4</sub>	4f	65	92	280-282	(279–280) [31]
7	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	4g	40	95	332-335	(332–333) [34]
8	2-ClC <sub>6</sub> H <sub>4</sub>	4h	75	87	280-282	(281–282) [37]
9	2,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	4i	70	88	300-303	(301–302) [37]
10	$4-FC_6H_4$	4j	50	96	304-305	(>300) [40]
11	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	4k	45	95	303-306	(304–305) [37]
12	4-(CH <sub>3</sub> ) <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub>	41	65	90	190–195 <sup>b</sup>	_
13	4-MeSC <sub>6</sub> H <sub>4</sub>	4m	60	92	283-284 <sup>b</sup>	_
14	4-OHCC <sub>6</sub> H <sub>4</sub>	4n	50	94	271–272 <sup>b</sup>	_

Reaction conditions: aldehyde (1 mmol), 2-naphthol (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol) and  $Fe_3O_4@SiO_2-SO_3H$  NPs (0.005 g)

<sup>a</sup> Isolated yield

<sup>b</sup> New compounds

Cycle	First	Second	Third	Fourth	Fifth
Yield (%) <sup>a</sup>	97	95	90	88	82

Table 5 Recoverability of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H NPs

<sup>a</sup> Yields refer to the isolated pure product

reaction times and with high yields while reactants with electron-releasing groups, such as methoxy and isopropyl, decreased both the rate of the reaction and the yield of corresponding product, as shown in Table 4.

After completion of the reaction, the reaction mixture was dissolved in chloroform and the catalyst was then separated magnetically. The  $Fe_3O_4@SiO_2-SO_3H$  NPs were washed three to four times with chloroform and methanol and dried at 60 °C for 8 h. The separated catalyst was used for six cycles with a slightly decreased activity, as shown in Table 5. In conclusion, we were able to demonstrate that a range of 14-aryl-14H-dibenzo[a,i] xanthene-8,13-dione derivatives could be obtained by the catalytic application of  $Fe_3O_4@SiO_2-SO_3H$  NPs under reflux conditions.

## Proposed mechanism

A plausible mechanism for the synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13diones using  $Fe_3O_4@SiO_2-SO_3H$  NPs has been shown in Scheme 4, on the basis of



 $\label{eq:scheme 4} \begin{array}{l} \mbox{The proposed mechanism for the synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-diones catalyzed by $Fe_3O_4@SiO_2-SO_3H NPs$ \end{array}$ 

our experimental results together with some literature (Scheme 4) [36, 37]. The reaction proceeds via a reaction sequence of condensation, addition, cyclization and dehydration. First, the condensation of aldehyde and 2-naphthol gave the intermediate (A). The addition of 2-hydroxynaphthalene-1,4-dione to (A) led to the formation of (B), which, after intermolecular cyclization and dehydration, gave rise to the desired 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione derivatives.

## Conclusions

We have developed a novel and highly efficient method for the synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione derivatives by treatment of  $\beta$ -naphthol and aromatic aldehydes with 2-hydroxy-1,4-naphthoquinone in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H NPs as the catalyst. This active catalyst is thermally stable, environmentally friendly ("green"), inexpensive, and easy to prepare. In addition, it could be easily separated from the reaction mixture and recycled without any significant impact on its activity or the reaction yields. The operational simplicity, high yields, and facile work-up procedures associated with this catalytic process represent some of the other advantages of this methodology.

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#### References

- 1. A. Ghosal, J. Shah, R.K. Kotnala, S. Ahmad, J. Mater. Chem. A. 1, 12868 (2013)
- 2. K. Raj, R. Moskowitz, J. Magn. Magn. Mater. 85, 233 (1990)
- 3. Q.A. Pankhurst, J. Connolly, S.K. Jones, J. Dobson, J. Phys. D Appl. Phys. 36, R167 (2003)
- 4. M.L. McCormick, E.J. Bouwer, P. Adriaens, Environ. Sci. Technol. 36, 403 (2002)
- P.I. Girginova, A.L. Daniel-da-Silva, C.B. Lopes, P. Figueira, M. Otero, V.S. Amaral, E. Pereira, T. Trindade, J. Colloid Interface Sci. 345, 234 (2010)
- 6. A.R. Kiasat, S. Nazari, J Mol Catal A. 365, 80 (2012)
- 7. J. Davarpanah, A.R. Kiasat, S. Noorizadeh, M. Ghahremani, J Mol Catal A. 376, 78 (2013)
- 8. W. Zhang, S.Y. Jia, Y. Liu, S.H. Wu, Q. Wu, Mater. Lett. 65, 1973 (2011)
- 9. S. Rostamizadeh, M. Azad, N. Shadjou, M. Hasanzadeh, Catal. Commun. 25, 83 (2012)
- 10. J. Kim, J.E. Lee, J. Lee, J.H. Yu, B.C. Kim, K. An, Y. Hwang, C.-H. Shin, J.E.-G. Park, J. Kim, T. Hyeon, J. Am. Chem. Soc. 128, 688 (2006)
- 11. H. Shen, J. Chen, H. Dai, L. Wang, M. Hu, Q. Xia, Ind. Eng. Chem. Res. 52, 12723 (2013)
- 12. B. Atashkar, A. Rostami, B. Tahmasbi, Catal Sci Technol. 21, 44 (2013)
- H. Yang, S. Li, X. Wang, F. Zhang, X. Zhong, Z. Dong, J. Ma, J. Mol. Catal. A: Chem. 363–364, 404 (2012)
- 14. M.Z. Kassaee, H. Masrouri, F. Movahedi, Appl Catal A: Gen. 395, 28 (2011)
- 15. F. Nemati, M.M. Heravi, R. Saeedirad, Chin. J. Catal. 33, 1825 (2012)
- 16. H. Naeimi, Z.S. Nazifi, J. Nanopart. Res. 15, 2026 (2013)
- 17. A.R. Kiasat, J. Davarpanah, J. Mol. Catal. A: Chem. 373, 46 (2013)
- 18. F. Nemati, R. Saeedirad, Chin. Chem. Lett. 24, 370 (2013)
- 19. A.R. Kiasat, J. Davarpanah, Res. Chem. Intermed. (2011). doi:10.1007/s11164-013-1407-6
- 20. X.N. Zhang, Y.X. Li, Z.H. Zhang, Tetrahedron 67, 7426 (2011)
- 21. A. Schätz, O. Reiser, W.J. Stark, Chem. Eur. J. 16, 8950 (2010)
- 22. T. Hideo, J. Teruomi, Jpn. Tokkyo Koho JP56005480, 1981; Chem. Abstr. 1981, 95, 80922b
- 23. V. Peres, T. Nagem, F.F. de Oliveira, Phytochem. 5, 683 (2000)
- 24. R.W. Lambert, J.A. Martin, J.H. Merrett, K.E.B. Parkes, G.J. Thomas, "Pyrimidine nucleosides", PCT Int. Appl. WO9706178, 1997., Chem. Abstr., 1997, 126, p212377y
- 25. G.J. Bennett, H.H. Lee, Phytochem. 28, 967 (1989)
- H.N. Hafez, M.I. Hegab, I.S. Ahmed-Farag, A.B.A. El-Gazzar, Bioorg. Med. Chem. Lett. 18, 4538 (2008)
- 27. M.M.M. Pinto, M.E. Sousa, M.S. Nascimento, J Curr Med Chem. 12, 2517 (2005)
- 28. M. Behforouz, J. Haddad, W. Cai, Z. Gu, J. Org. Chem. 63, 343 (1998)
- 29. M.F. Sartori, Chem. Rev. 63, 279 (1963)
- A.S. Hammam, M.S.K. Youssef, M. Radwansh, M.A. Abdel-Rahman, Bull. Korean Chem. Soc. 25, 779 (2004)
- 31. C.W. Kuo, J.M. Fang Synth (2001) Chem Commun. 31, 877
- 32. A. Jha, J. Beal, Tetrahedron Lett. 45, 8999 (2004)
- 33. R. Kumar, G.C. Nandi, R.K. Verma, M.S. Singh, Tetrahedron Lett. 51, 442 (2010)
- 34. N.G. Khaligh, Catal Sci Technol. 2, 2211 (2012)
- 35. L.Q. Wu, Y.F. Wu, C.G. Yang, L.M. Yang, L.J. Yang, J. Braz. Chem. Soc. 21, 941 (2010)
- 36. K.B. Suresh, P.A. Crooks, B. Rajitha, Adv Appl Sci Res. 3, 1 (2012)
- 37. L. Wu, J. Zhang, L. Fang, C. Yang, F. Yan, Dye Pigment. 86, 93 (2010)
- 38. S. Chao, G. Lu, L. Wu, Asian J. Chem. 23, 3865 (2011)
- 39. V. Srinivas, R.V. Rajeswar, Synth. Commun. 42, 388 (2012)
- 40. J.M. Khurana, A. Chaudhary, A. Lumb, B. Nand, Can. J. Chem. 90, 739 (2012)
- 41. M.A. Ghasemzadeh, J. Safaei-Ghomi, H. Molaei, C R Chimie. 15, 69 (2012)
- 42. M.A. Ghasemzadeh, J. Safaei-Ghomi, J. Chem. Res. 38, 313 (2014)
- 43. M.A. Ghasemzadeh, J. Safaei-Ghomi, S. Zahedi, J. Serb. Chem. Soc. 78, 769 (2013)
- 44. J. Safaei-Ghomi, M.A. Ghasemzadeh, Chin. Chem. Lett. 23, 1225 (2012)
- 45. J. Safaei-Ghomi, M.A. Ghasemzadeh, J. Sulfur Chem. 34, 233 (2013)
- 46. J. Safaei-Ghomi, M.A. Ghasemzadeh, J. Chem. Sci. 125, 1003 (2013)
- 47. H.Y. Lu, S.H. Yang, J. Deng, Z.H. Zhang, Aust. J. Chem. 63, 1290 (2010)
- 48. X.Q. Xu, C.H. Deng, M.X. Gao, W.J. Yu, P.Y. Yang, X.M. Zhang, Adv. Mater. 18, 3289 (2006)
- 49. Y. Lin, H. Chen, K. Lin, B. Chen, C. Chiou, J Environ Sci. 23, 44 (2011)