

Fe₃O₄@SiO₂ nanoparticles: An efficient, green and magnetically reusable catalyst for the one-pot synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione derivatives

Mohammad Ali Ghasemzadeh*, Mina Azimi-Nasrabad, Javad Safaei-Ghomi

Department of Chemistry, Qom Branch, Islamic Azad University, Qom, P.O. Box 364/37185, I.R. Iran.

Received 14 June 2015; received in revised form 13 September 2015; accepted 27 September 2015

ABSTRACT

An efficient and eco-friendly method for the one-pot synthesis of 14-aryl-14H-dibenzo [a,i]xanthene-8,13-dione derivatives has been developed in the presence of Fe₃O₄@SiO₂ core-shell nanoparticles. The multi-component reactions of 2-hydroxy-1,4-naphthoquinone, β-naphthol and aldehydes were efficiently catalyzed using novel nano-scale materials under reflux conditions. The present method offers several advantages such as environmentally benign, simple work-up, excellent yield of products, short reaction times, little catalyst loading and facile catalyst separation. The nanomagnetic catalyst could be readily recovered using a simple external magnet and reused several times without any significant loss in activity. The catalyst was fully characterized by FT-IR, SEM, XRD, EDX and VSM analysis.

Keywords: Multi-component reactions, Nanoparticles, Core-shell, Fe₃O₄@SiO₂, Xanthene.

1. Introduction

During the recent decades, nanotechnology has developed to such an extent that it has become conceivable to characterize, fabricate and specially tailor the functional attributes of nanoparticles for diagnostics and biomedical applications [1-4]. Nanocrystalline metal oxide has interested considerable attention as effective catalysts in several organic reactions because of their significant surface-to-volume ratio and coordination parts which provide a great number of active sections per unit area compared to their heterogeneous counter parts [5,6].

Solid acids have attracted great attention in organic synthesis due to their simple work-up procedures, easy purification and minimization of price and wastage generation due to reusing and recycling of these catalysts [7]. In recent years, silica coating of magnetic nanoparticles has been applied as an effective heterogeneous catalyst with a number of advantages such as low price, simplicity of preparation, and catalyst recycling [8,9].

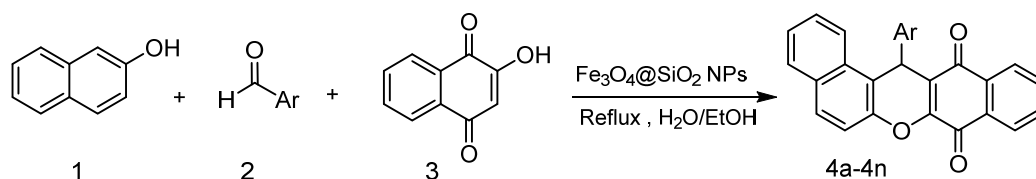
Core-shell nanostructures have recently been subject to extensive research for the combined functionalities of cores and shells which endow them with great application potentials in various fields [10]. The core/shell nanostructure is a perfect composite system that combines the advantages of together the core and the shell to offer increase physical and chemical attributes. Recently, magnetic nanoparticles (MNPs) (e.g. Fe₃O₄) have been extensively investigated as inorganic cores for the synthesis of organic/inorganic core-shell compound particles, because of their possible applications in some industrial and biological areas [11]. Multi-component reactions (MCRs) are effective tools for the synthesis of many complex molecules in an only reaction from easily available starting substrates without the difficult purification steps; thus, MCRs are time-effective processes and therefore economically favorable procedure in diversity generation [12]. Furthermore MCRs are effective, environmentally friendly, quick, atom economic and time-saving. They supply an efficient tool for the preparation of different compounds with biological and pharmaceutical properties [13]. Recently, three-component reaction of aldehydes, β-Naphthol and 2-Hydroxy-1, 4-naphthoquinone has

*Corresponding author email: ghasemzadeh@qom-iau.ac.ir
Tel./Fax: +98 25 3778 0001

received a great deal attention in organic synthesis. The synthesis of xanthene derivatives has received extreme attention due to their various range of therapeutic and biological attributes including antiviral [14], antibacterial [15] and anti-inflammatory properties [16]. Also, these compounds are applied extensively in laser technologies [17], dyes [18], and as pH sensitive fluorescent material for embodiment of biomolecules [19]. Many synthetic methods exist for the synthesis of xanthenes and benzoxanthenes, which include the condensation of aldehydes and acetophenones [20], 2-hydroxyaromatic aldehydes and 2-tetralone [21], β -naphthol with alkyl or aryl aldehydes [22]. 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 β -naphthol, 2-hydroxy-1,4-naphthoquinone with various aldehydes which catalyzed by different catalysts such as poly(4-vinylpyridinium) hydrogen sulfate [23], silica supported perchloric acid [24], xanthan sulfuric acid [25], silica chloride [26], Amberlyst-15 [27], acetic acid [28], and sulfuric acid [29]. But, some of these methods suffer from disadvantages such as long reaction times, unsatisfactory yields, toxic organic solvents, expensive catalysts, the requirement of special apparatus, laborious work-up procedures, and harsh reaction conditions. Thus, the development of efficient, easy, high-yielding and eco-friendly methods using novel catalysts for the synthesis of these compounds would be highly desirable. With the purpose to develop more effective synthetic processes, minimize by-products and reduce the number of separate reaction steps and in continuation of our efforts to develop efficient processes in organic synthesis using nanoparticles as catalyst [30-36], here we report a new and efficient method for the preparation of 14-aryl-14H-dibenzo[a,i] xanthene-8,13-dione derivatives via multi-component synthesis of β -naphthol, 2-hydroxy-1,4-naphthoquinone with various aldehydes using silica-coated magnetite nanoparticles (Scheme 1). $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs as a non-volatile, efficient, non-explosive, recyclable, simple to handle, and eco-friendly catalyst can be used as catalyst in many organic reactions.

2. Experimental

Chemicals were purchased from the Sigma-Aldrich and Merck in high purity. All of the materials were of commercial reagent grade and were used without



Scheme 1. Three-component reaction of aldehydes, 2-hydroxy-1,4-naphthoquinone and β -naphthol catalyzed by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles.

further purification. All melting points are uncorrected and were determined in capillary tubes on a Boetius melting point microscope. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker 400MHz spectrometer with CDCl_3 as solvent using tetramethylsilane as an internal standard; the chemical shift values are in δ . FT-IR spectrum was recorded on Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of $400\text{--}4000\text{ cm}^{-1}$. 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 of X'pert Company with monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). Microscopic morphology of products was visualized by SEM (LEO 1455VP). The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV. Magnetic properties were obtained on a BHV-55 vibrating sample magnetometer (VSM) made by MDK-I.R. Iran. The compositional analysis was done by energy dispersive analysis of X-ray.

2.1. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared according to the procedure reported by Zhang et al [37]. To a solution of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (2.5 g) and $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (6 g) in 30 ml deionized water was added dropwise 1.0 mL of concentrated hydrochloric acid at room temperature. The solution was added in to 300 mL of 1.5 mol L^{-1} NaOH and then the solution was stirred vigorously at 80°C until precipitation. Afterwards, the prepared magnetic nanoparticles were separated magnetically, washed with deionized water and then dried at 70°C for 8 h.

2.2. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles

The core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres were prepared according to the previously reported method [38]. Briefly 1g of Fe_3O_4 nanoparticles were treated with 0.5 M HCl aqueous solution (25 mL) by sonication. After the treatment for 10 min, The magnetite particles were separated and washed with deionized water, and then homogeneously dispersed in the 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 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres were separated using an external magnet and washed with ethanol and water.

2.3. Typical procedure for the synthesis 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 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (0.02 g, 8 mol %) in 2.5 mL ethanol and 2.5 mL 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 solid obtained was recrystallized using ethanol. All of the products were fully characterized by FT-IR and NMR spectroscopy.

Spectral data of the new products

14-(4-hydroxyphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione. (4e):

m.p.= 265-270°C. FT-IR: $\bar{\nu}$ = 3352 (O-H), 1660 (C=O), 1379 (C=C), 1220 (C-O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 5.20 (1H, s, OH), 5.72 (1H, s, CH), 6.54-6.56 (2H, m, Ar-H), 6.63-6.64 (2H, m, Ar-H), 7.09-7.16 (4H, m, Ar-H), 7.31-7.56 (4H, m, Ar-H), 8.01-8.09 (2H, m, Ar-H) ppm. ^{13}C NMR (100MHz, CDCl_3): δ = 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 ppm. Anal. Calcd. for $\text{C}_{27}\text{H}_{16}\text{O}_4$: C, 80.19; H, 3.99. Found: C, 80.27; H, 3.92.

14-(4-isopropylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione. (4l):

m.p.=190-195°C. FT-IR: $\bar{\nu}$ = 1661 (C=O), 1426 (C=C), 1226 (C-O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.2-1.3 (6H, m, 2CH₃), 2.74 (1H, s, CH), 5.92 (1H, s, CH), 7.03-7.05 (2H, m, Ar-H), 7.29-7.32 (2H, m, Ar-H), 7.43-7.50 (2H, m, Ar-H), 7.52-7.56 (2H, m, Ar-H), 7.58-7.60 (1H, m, Ar-H), 7.76-7.80 (2H, m, Ar-H), 7.84-7.86 (1H, m, Ar-H), 7.87-7.89 (1H, m, Ar-H), 8.02-8.04 (1H, m, Ar-H) ppm. ^{13}C NMR (100MHz, CDCl_3): δ = 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 ppm. Anal. Calcd. for $\text{C}_{30}\text{H}_{22}\text{O}_3$: C, 83.70; H, 5.15. Found: C, 83.64; H, 5.21.

14-(4-formylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione. (4n):

m.p.= 271-272°C. FT-IR: $\bar{\nu}$ = 3078, 1692 (C=O), 1662 (C=O), 1595 (C=C), 1232 (C-O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 5.90 (1H, s, CH), 7.15 (3H, t, Ar-H), 7.34 (3H, m, Ar-H), 7.45-7.62 (4H, m, Ar-H), 7.77-7.91 (4H, m, Ar-H), 9.81 (1H, s, CHO) ppm. ^{13}C NMR (100MHz, CDCl_3): δ = 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 ppm. Anal. Calcd. for $\text{C}_{28}\text{H}_{16}\text{O}_4$: C, 80.76; H, 3.87. Found: C, 80.84; H, 3.79.

14-(4-thiomethylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (4m):

m.p.= 283-284°C. FT-IR: $\bar{\nu}$ = 1662 (C=O), 1367 (C=C), 1200 (C-O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 2.32 (3H, s, SCH₃), 5.90 (1H, s, CH), 7.31 (3H, m, Ar-H), 7.43-7.60 (4H, m, Ar-H), 7.76-7.89 (2H, m, Ar-H), 7.98 (3H, m, Ar-H), 8.12(2H, m, Ar-H) ppm. ^{13}C NMR (100MHz, CDCl_3): δ = 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 ppm. Anal. Calcd. for $\text{C}_{28}\text{H}_{18}\text{O}_3\text{S}$: C, 77.40; H, 4.18; S, 7.38. Found: C, 77.31; H, 4.28; S, 7.31.

3. Results and Discussion

3.1. Characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ as a solid acid catalyst

The Fe_3O_4 NPs were prepared by co-precipitation via the reaction of iron (II) and iron (III) ions. The crystallite size of magnetite nanoparticles were obtained in the range of between 20-30 nm. For the surface modification, the MNPs coated with a layer of silica using the (TEOS) by co-precipitation method to provide reaction sites for further functionalization and thermal stability (Fig. 1).

Initially, in order to study the morphology and particle size of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles, scanning electron microscopy (SEM) images of them are shown in Fig. 2a and Fig. 2b. As shows $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles still keep the morphological properties of Fe_3O_4 except for a slightly larger particle size and smoother surface, which silica are uniform coated on the Fe_3O_4 particles to form silica shell in compared to the $\text{Fe}_3\text{O}_4@\text{SiO}_2$.

Fig. 3 shows the FT-IR spectra for the samples of Fe_3O_4 NPs and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres catalysts. For the bare magnetic nanoparticle (Fig. 3a), the vibration band at 575 cm^{-1} is the typical IR absorbance induced by structure Fe-O vibration.

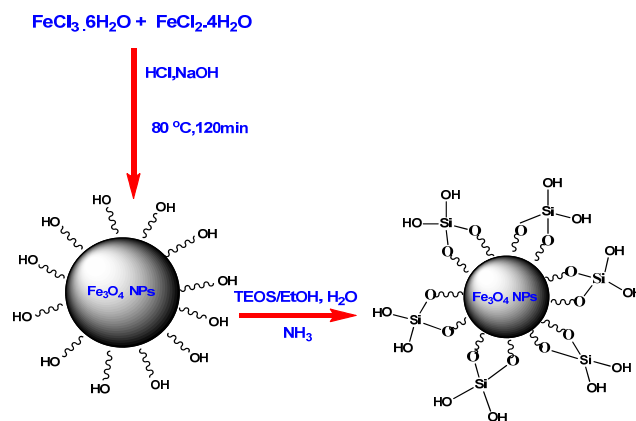


Fig. 1. Preparation steps for fabricating of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles

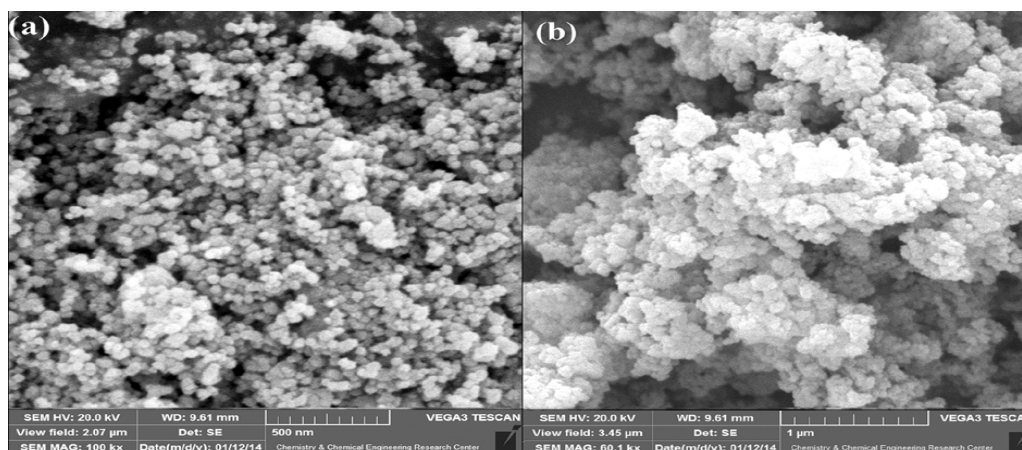


Fig. 2. SEM images of Fe_3O_4 (a) and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (b) nanoparticles.

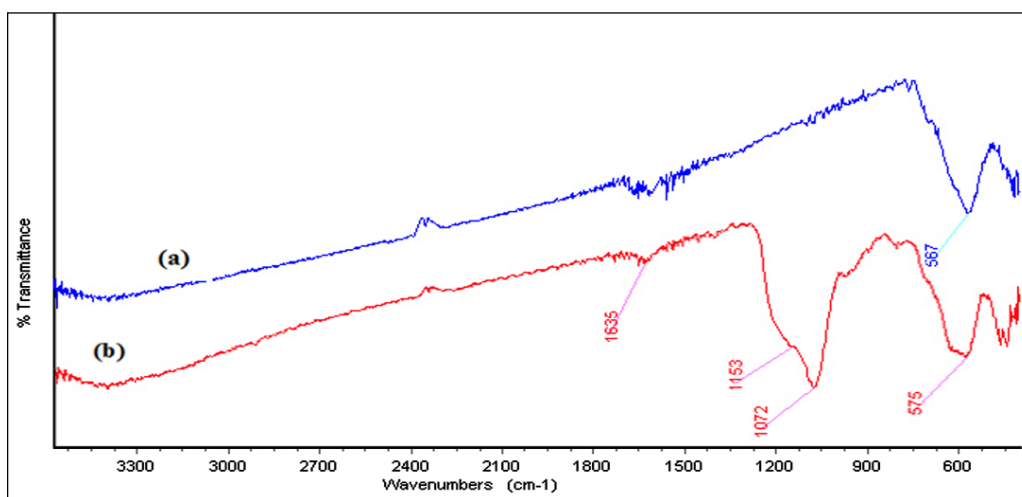


Fig. 3. The comparative FT-IR spectra of Fe_3O_4 (a), and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (b) nanoparticles.

In the case of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles (Fig. 3b), the band at 1072 cm^{-1} is corresponding to Si-O-Si antisymmetric stretching vibrations, being indicative of the existence of SiO_2 in the nanoparticles.

The X-ray diffraction patterns of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ are shown in Fig. 4 (a, b). The position and relative intensities of all peaks confirm well with standard XRD pattern of Fe_3O_4 indicating retention of

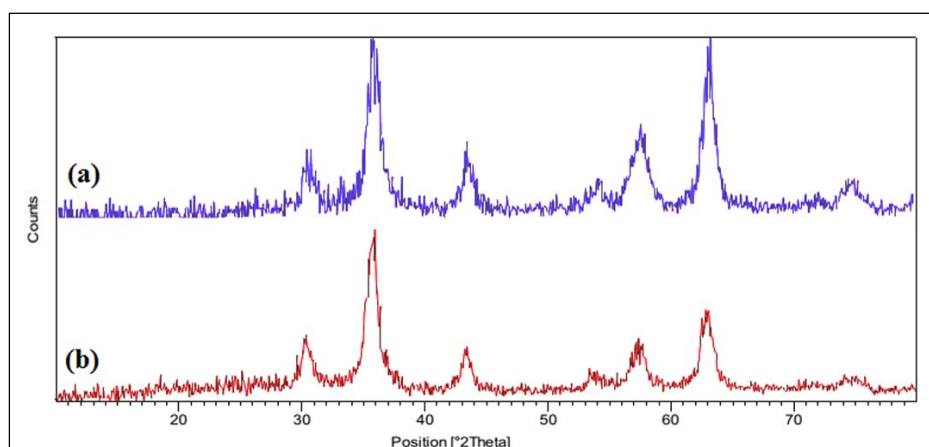


Fig. 4. XRD patterns of Fe_3O_4 (a) and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (b) nanoparticles.

the crystalline cubic spinel structure during functionalization of MNPs. Characteristic peak of SiO_2 in core shell structure has been hidden under weak peak of Fe_3O_4 at $2\theta = 30$. The average MNPs core diameter was calculated to be 25 nm from the XRD results by Scherrer's equation, $D = K\lambda/\beta\cos\theta$ where k is a constant (generally considered as 0.94), λ is the wavelength of Cu K α (1.54 \AA), β is the corrected diffraction line full-width at half-maximum (FWHM), and θ is Bragg's angle.

The magnetic properties of the samples containing a magnetite component were studied by a vibrating sample magnetometer (VSM) at 300 K. Fig. 5 show the absence of hysteresis phenomenon and indicates that all of the products have superparamagnetism at room temperature. The saturation magnetization values for Fe_3O_4 (a), $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (b) were 48.49 and 38.16 emu/g, respectively. These results indicated that the magnetization of Fe_3O_4 decreased considerably with the increase of SiO_2 .

The chemical purity of the samples as well as their stoichiometry was tested by energy dispersive X-ray spectroscopy (EDX) studies. The EDX spectrum given in Fig. 6 (a) shows the presence of Fe and O as the only elementary components of Fe_3O_4 NPs. EDX spectrum $\text{Fe}_3\text{O}_4@\text{SiO}_2$ in Fig. 6 (b) shows the elemental compositions are (Fe, Si and O) of core-shell nanoparticles.

Firstly, in order to optimize the reaction conditions, the model reaction was carried out by using 4-nitrobenzaldehyde, β -naphthol and 2-hydroxy-1,4-naphthoquinone under various conditions (Scheme 2). The reaction conditions were optimized on the basis of the solvent, catalyst, and different temperatures for synthesis 14-(4-nitrophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (4g).

The influence of solvent was studied when the model reaction was performed using $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles (10 mol %) in the presence of various solvents and also solvent-free conditions in different temperatures (Table 1). The best results were obtained under reflux conditions (Table1, Entry1-6). As shown

in Table 1, the time of reaction was significantly decreased, but the yield of product formation increased in comparison with solvent-free conditions. Table1 shows that, the solvent has a great effect on the accelerating of the reaction. The best results (95% yield, 45 min) were obtained in water/ethanol under reflux for this multicomponent reaction (Table 1, entry 6). The significant results presented in Table 1 are related to the hydrogen bonding between water and ethanol and also hydrogen bonding of substrates and solvents 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_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$. As shown in Table 2, the silica-coated magnetite nanoparticles were the best catalysts with respect to reaction time and yield of the obtained product.

In continuation of our research, we run the model study using different amounts of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ 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 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs was chosen 8 mol% in the model reaction. Increase in the amount of the catalyst did not change the time and yield the reaction.

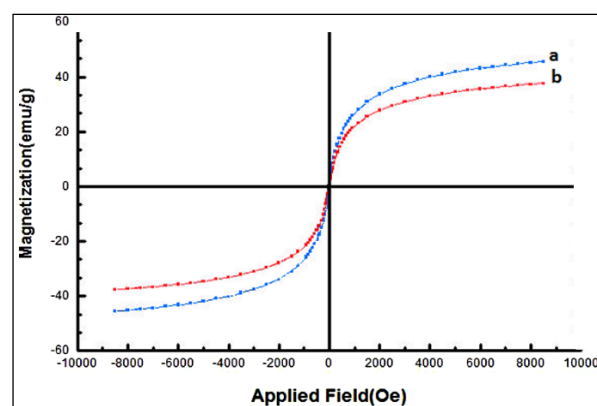


Fig. 5. Magnetization curves for the prepared Fe_3O_4 (a) and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (b) nanoparticles.

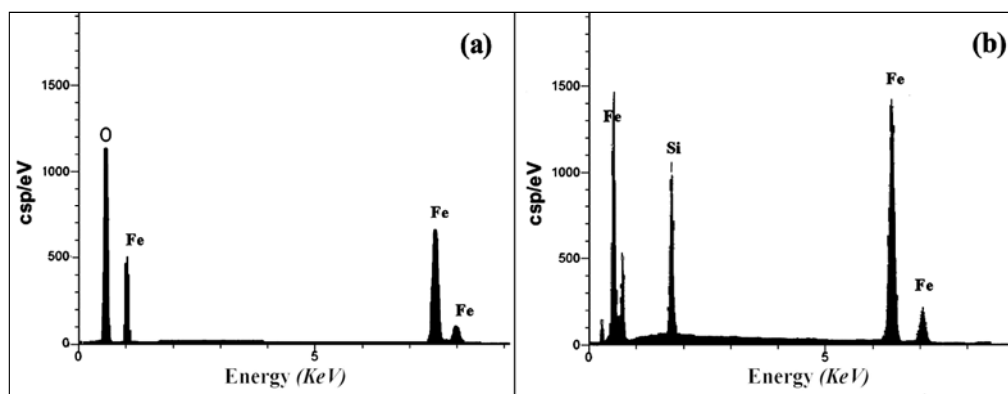
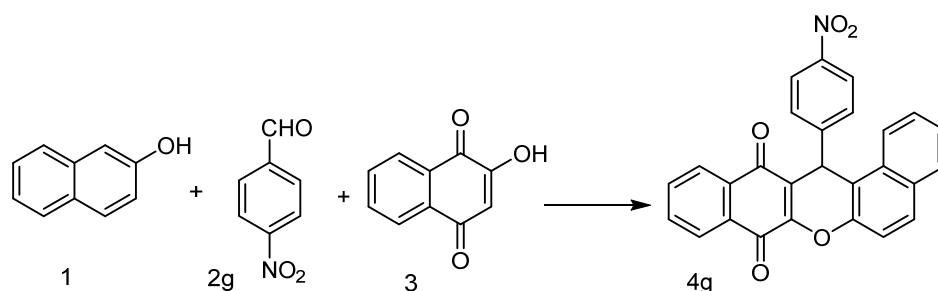


Fig. 6. EDX spectra of Fe_3O_4 (a), and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (b) nanoparticles.



Scheme 2. The model reaction for the preparation of 14-(4-nitrophenyl)-14H-dibenzo[*a,i*]xanthene-8,13-dione (4g).

Table 1. Preparation of 14-(4-nitrophenyl)-14H-dibenzo[*a,i*]xanthene-8,13-dione in different solvents.^a

Entry	Solvent	Temp. (°C)	Time (min)	Yield (%) ^b
1	EtOH	Reflux	60	60
2	Water	Reflux	80	54
3	CH ₃ CN	Reflux	120	45
4	DMF	Reflux	140	38
5	Toluene	Reflux	150	30
6	Water/EtOH	Reflux	45	95
7	Water/EtOH	25	95	35
8	Solvent-free	25	120	trace
9	Solvent-free	100	100	25

^aβ-naphthol (1mmol), 2-hydroxy-1,4-naphthoquinone (1mmol) and 4-nitrobenzaldehyde (1mmol) using Fe₃O₄@SiO₂ NPs (10 mol %).

^bIsolated yields.

After optimization of the reaction conditions, we used a diversity of aldehydes to investigate three-component reactions in the presence of Fe₃O₄@SiO₂ NPs under reflux conditions. We observed that various aryl aldehydes could be introduced in high efficiency and produced high yields of products in high purity (—95 % by ¹H NMR). The data of Table 4 show 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 NO₂, Br, and Cl

in the *p*-position reacted very smoothly, in short reaction times and 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).

The formation of dibenzoxanthenes could be explained by a reaction sequence similar to the literature reports (Scheme 3) [24,26]. The reaction proceeds via a reaction sequence of condensation, addition, cyclization and dehydration.

Table 2. The model reaction was carried out by various catalysts.^a

Entry	Catalyst	Time (min)	Yield (%) ^b
1	Fe ₃ O ₄	60	60
2	MgO	120	25
3	ZnO	75	65
4	CuO	100	38
5	CuI	80	70
6	Fe ₃ O ₄ @SiO ₂	45	95

^aWater/ethanol as solvent under reflux conditions using 10 mol % of each catalyst.

^bIsolated yields.

Table 3. The effect of the amount of Fe₃O₄@SiO₂ nanoparticles on the model reaction.^a

Entry	Catalyst amount (mol %)	Time (min)	Yields (%) ^b
1	None	120	None
2	2	90	30
3	5	70	68
4	8	45	95
5	10	45	95

^aWater/ethanol as solvent under reflux conditions.^bIsolated yields.

We suppose that Fe₃O₄@SiO₂ nanoparticles behave as the Lewis acid and coordinate with carbonyl and hydroxyl groups to promote cyclization reaction. First, the condensation of aldehyde and 2-naphthol gave the intermediate (A). The addition of 2-hydroxy naphthalene-1,4-dione to (A) leading to the formation of (B), which on intermolecular cyclization and dehydration gave rise to the desired 14-aryl-14H-dibenzo [a,i]xanthene-8,13-dione derivatives (4).

3.2. Catalyst recovery

After completion of the reaction, the reaction mixture was dissolved in chloroform and then the catalyst was separated magnetically. The Fe₃O₄@SiO₂ 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 Fig. 7. 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 silica-coated magnetite nanoparticles under reflux conditions.

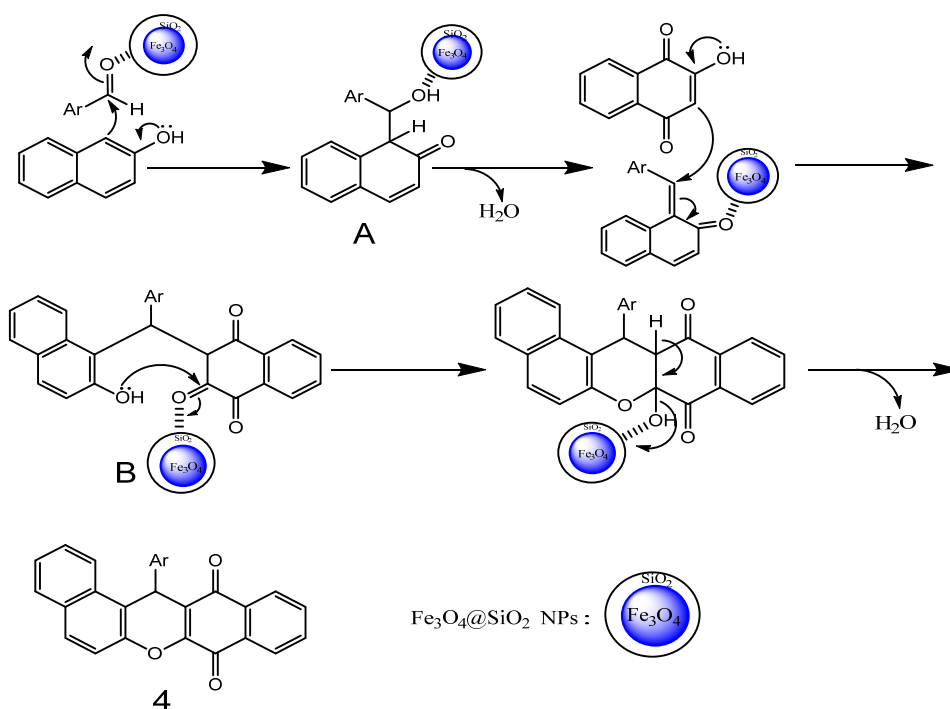
4. Conclusion

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 β-naphthol, aromatic aldehydes with 2-hydroxy-1,4-naphthoquinone in the presence of Fe₃O₄@SiO₂ nanoparticles as catalyst. The significant advantages of this methodology are high yields, a cleaner reaction, simple work-up procedure, short time and easy preparation and handling of the catalyst. The catalyst can be recovered by filtration and reused.

Table 4. Fe₃O₄@SiO₂ NPs catalyzed one-pot synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione derivatives.^a

Products	Ar	Time (min)	Yield (%) ^b	m.p. (°C)		Ref.
				Found	Reported	
4a	C ₆ H ₅	60	91	317-319	319-320	[23]
4b	4-ClC ₆ H ₄	45	97	303-305	305-306	[23]
4c	4-BrC ₆ H ₄	55	94	290-295	284-295	[29]
4d	4-CH ₃ C ₆ H ₄	70	90	256-258	255-256	[23]
4e	4-HOC ₆ H ₄	70	90	265-269 ^c	-	This work
4f	4-MeOC ₆ H ₄	65	90	280-282	279-280	[23]
4g	4-O ₂ NC ₆ H ₄	45	95	332-335	332-333	[23]
4h	2-ClC ₆ H ₄	75	87	280-282	281-282	[26]
4i	2,4-Cl ₂ -C ₆ H ₃	70	88	300-303	301-302	[26]
4j	4-FC ₆ H ₄	50	96	304-305	>300	[29]
4k	3-O ₂ NC ₆ H ₄	45	95	303-306	304-305	[26]
4l	4-(CH ₃) ₂ CHC ₆ H ₄	65	90	190-195 ^c	-	This work
4m	4-MeSC ₆ H ₄	60	92	283-284 ^c	-	This work
4n	4-OHCC ₆ H ₄	50	94	271-272 ^c	-	This work

^aReaction conditions: aldehyde (1mmol), 2-naphthol (1mmol), 2-hydroxy-1,4-naphthoquinone (1mmol) and Fe₃O₄@SiO₂ NPs (0.02g).^bIsolated yield.^cNew compounds.



Scheme 3. Proposed reaction pathway for the synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-dione derivatives by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles.

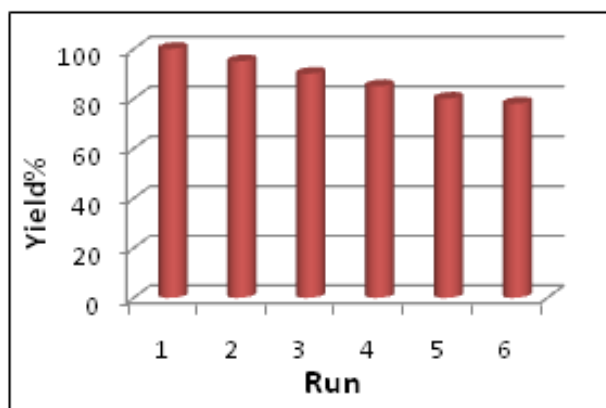


Fig. 7. Recoverability of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles.

Acknowledgment

The authors gratefully acknowledge the financial support of this work by the Research Affairs Office of the Islamic Azad University, Qom Branch, Qom, I. R. Iran.

References

- [1] S.M. Moghimi, A.C.H. Hunter, J.C. Murray, *Pharm. Rev.* 53 (2001) 283-318.
- [2] A.S.G. Curtis, C. Wilkinson, *Trends Biotech.* 19 (2001) 97-101.
- [3] J.M. Wilkinson, *Med. Device Technol.* 14 (2003) 29-31.
- [4] M.G. Dekamin, Z. Mokhtari, Z. Karimi, *Sci. Iran. Trans. C* 18 (2011) 1356-1364.
- [5] Z. Bing, H. Scott, R. Raja, G.A. Somorjai, *Nanotechnology in Catalysis*, Springer, Ottawa, 2007.
- [6] Y. Min, M. Akbulut, K. Kristiansen, Y. Golan, J. Israelachvili, *Nat. Mater.* 7 (2008) 527-538.
- [7] (a) M.H. Alizadeh, H. Razavi, F.F. Bamoharram, *J. Mol. Catal. A: Chem.* 206 (2003) 89-93. (b) G.M. Ziarani, A. Badiei, F. Shahjafari, T. Pourjafar, *S. Afr. J. Chem.* 65 (2012) 10-13.
- [8] N. Ahmed, J.E. Van Lier, *Tetrahedron Lett.* 47 (2006) 2725-2729.
- [9] Q. Dang, B.S. Brown, M.D. Erion, *Tetrahedron Lett.* 41 (2000) 6559-6562.
- [10] Y.H. Deng, W.L. Yang, C.C. Wang, S. K. Fu, *Adv. Mater.* 15 (2003) 1729-1732.
- [11] L.M. Liz-Marzán, M. Giersig, P. Mulvaney, *Langmuir* 12 (1996) 4329-4335.
- [12] G. Eyanom, N. Blanchard, M. Toumi, *Chem. Rev.* 108 (2008) 3054-3131.
- [13] (a) L. A. Thompson, J. A. Ellman, *Chem. Rev.* 96 (1996) 555-600. (b) G. I. Shakibaei, A. Feiz, A. Bazgir, *C.R. Chim.* 14 (2011) 556-562.
- [14] (a) T. Hideo, J. Teruomi, *Jpn. Tokkyo Koho* (1981) JP56005480. (b) V. Peres, T. Nagem, F.F. de Oliveira, *Phytochemistry* 5 (2000) 683-710.
- [15] (a) R.W. Lambert, J.A. Martin, J.H. Merrett, K.E.B. Parkes, G.J. Thomas, *PCT Int. Appl.* (1997) WO9706178. (b) G.J. Bennett, H.H. Lee, *Phytochemistry* 28 (1989) 967-998.

- [16] (a) H.N. Hafez, M.I. Hegab, I.S. Ahmed-Farag, A.B. A. El-Gazzar, *Bioorg. Med. Chem. Lett.* 18 (2008) 4538-4543. (b) M.M.M. Pinto, M.E. Sousa, M.S.J. Nascimento, *Curr. Med. Chem.* 12 (2005) 2517-2538.
- [17] M. Behforouz, J. Haddad, W. Cai, Z. Gu, *J. Org. Chem.* 63 (1998) 343-346.
- [18] M.F. Sartori, *Chem. Rev.* 63 (1963) 279-296.
- [19] A.S. Hammam, M.S.K. Youssef, M. Radwansh, M.A. Abdel-Rahman, *Bull. Korean Chem. Soc.* 25 (2004) 779-785.
- [20] C.W. Kuo, J.M. Fang *Synth. Chem. Commun.* 31 (2001) 877-892.
- [21] A. Jha, J. Beal, *Tetrahedron Lett.* 45 (2004) 8999-9001.
- [22] R. Kumar, G.C. Nandi, R.K. Verma, M.S. Singh, *Tetrahedron Lett.* 51 (2010) 442-445.
- [23] N.G. Khaligh, *Catal. Sci. Technol.* 2 (2012) 2211-2215.
- [24] L. Q. Wu, Y.F. Wu, C.G. Yang, L.M. Yang, L.J. Yang, *J. Braz. Chem. Soc.* 21 (2010) 941-945.
- [25] K.B. Suresh, P.A. Crooks, B. Rajitha, *Adv. Appl. Sci. Res.* 3 (2012) 1-5.
- [26] L. Wu, J. Zhang, L. Fang, C. Yang, F. Yan, *Dyes Pigm.* 86 (2010) 93-96.
- [27] S. Chao, G. Lu, L. Wu, *Asian J. Chem.* 23 (2011) 3865-3869.
- [28] V. Srinivas, R. Rajeswar, V. *Synth. Commun.* 42 (2012) 388-393.
- [29] J.M. Khurana, A. Chaudhary, A. Lumb, B. Nand, *Can. J. Chem.* 90 (2012) 739-746.
- [30] J. Safaei-Ghomi, S. Zahedi, M.A. Ghasemzadeh, *Iran. J. Catal.* 2 (2012) 27-30.
- [31] J. Safaei-Ghomi, M.A. Ghasemzadeh, *J. Chem. Sci.* 125 (2013) 1003-1008.
- [32] M.A. Ghasemzadeh, J. Safaei-Ghomi, *J. Chem. Res.* 38 (2014) 313-316.
- [33] M.A. Ghasemzadeh, J. Safaei-Ghomi, *Acta Chim. Slov.* 62 (2015) 103-110.
- [34] M.A. Ghasemzadeh, J. Safaei-Ghomi, S. Zahedi, *J. Serb. Chem. Soc.* 78 (2013) 769-779.
- [35] M.A. Ghasemzadeh, J. Safaei-Ghomi, H. Molaei, *C.R. Chim.* 15 (2012) 969-974.
- [36] M.A. Ghasemzadeh, J. Safaei-Ghomi, *J. Chem. Res.* 38 (2014) 313-316.
- [37] H.Y. Lu, S.H. Yang, J. Deng, Z.H. Zhang, *Aust. J. Chem.* 63 (2010) 1290-1296.
- [38] X.Q. Xu, C.H. Deng, M.X. Gao, W.J. Yu, P.Y. Yang, X.M. Zhang, *Adv. Mater.* 18 (2006) 3289-3293.