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ORIGINAL ARTICLE

Nano-Fe₃O₄ encapsulated-silica particles bearing sulfonic acid groups as an efficient, eco-friendly and magnetically recoverable catalyst for synthesis of various xanthene derivatives under solvent-free conditions



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KEYWORDS

Magnetic nanoparticle;
1,8-Dioxo-octahydroxanthene;
14H-dibenzo[a,j]xanthenes;
12-Aryl-tetrahydrobenzo[a]xanthenes-11-one;
13-Aryl-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone;
2-Hydroxynaphthalene-1,4-dione

Abstract This report describes an efficient method for the synthesis of 1,8-dioxo-octahydroxanthene, 14H-dibenzo[a,j]xanthene, 12-aryl-tetrahydrobenzo[a]xanthenes-11-one and 13-aryl-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone derivatives in the presence of a catalytic amount of nano-iron oxide encapsulated silica particles bearing sulfonic acid groups. Results present an efficient, environmentally friendly and magnetically recoverable catalyst under solvent-free conditions at 110–130 °C.

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1. Introduction

Xanthene and benzoxanthene derivatives are important as biologically and pharmacologically active compounds. Research has shown that these properties include antiplasmodial [41], antiviral [18] and anti-inflammatory activities [28]. Xanthene and benzoxanthene derivatives are also useful in photodynamic therapy [12] and for antagonism of the paralyzing action of zoxazolamine [33]. Furthermore, due to the useful spectroscopic properties of these derivatives they also have application in industries related to the production of dyes and fluorescent materials, particularly for products

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that require visualization of bio-molecules [2,19]. Other useful applications of these heterocycles are as leucodyes [19] and in laser technologies [1].

In accordance with these useful properties and related applications as above-mentioned, a number of methods have been reported for the synthesis of such compounds. For example, 14-aryl-14H-dibenzo[a,i]xanthenes have been synthesized by the one-pot multi-component condensation of β -naphthol (2 eq.) with various aldehydes (1 eq.) [8,20,30]. The best method for the preparation of tetra-hydrobenzo[a]xanthene-11-ones is a one-pot condensation reaction between β -naphthol, arylaldehydes and dimedone [36,39], and the most common protocol for the preparation of 1,8-dioxo-octahydroxanthenes involves the reaction of two molecules of dimedone with one molecule of aldehyde [11,13,14,21]. In addition, the synthesis of 13-aryl-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraones was reported from the reaction of 2 mmol 2-hydroxynaphthalene-1,4-dione and 1 mmol aldehyde [34,38]. Many of these reported that synthetic methods are limited because they involve only one class of xanthene; accordingly there is a crucial need to develop a novel catalyst to synthesize various xanthene derivatives, indicating a strong demand for this research.

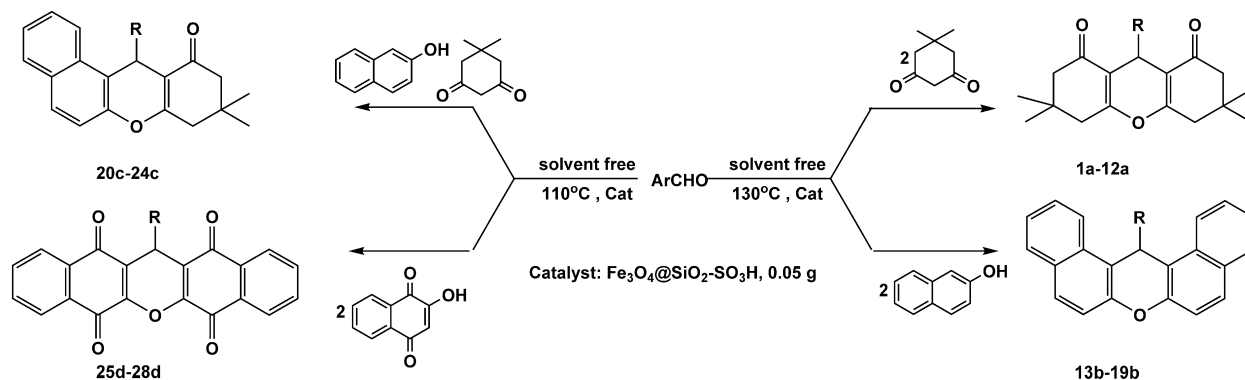
The recent trend of green chemistry has contributed to a recent increase in research attention directed toward the synthesis of magnetic nanoparticles and their application in catalysis [7,22]. Properties of nano-sized particles such as high

surface area show a remarkable level of catalytic performance. In addition, due to their magnetic properties, the catalyst could be quickly and easily recovered by means of an external magnet [29]. However simplicity of the catalyst preparation is very important in terms of practicality and considerations for application.

During the course of our recent research program on the development of new condition for organic transformations [3,4,23,25], recently, sulfonic acid-functionalized silica-coated nano- Fe_3O_4 particles have been prepared in our laboratory [24,26]. It displayed a high stability and an impressive catalytic activity in the synthesis of tetraketones, pyrimido[4,5-b]quinolines and indeno fused pyrido[2,3-d]pyrimidines in water under mild condition [27]. The performance and recyclability behavior of this nano magnetic catalyst in the preparation of various xanthene derivatives under solvent-free condition are reported in this study to extend possibilities of this new catalyst (Scheme 1).

2. Results and discussion

At the outset of our study, to examine the catalytic activity of the catalyst, the reaction of benzaldehyde (1 mmol) with dimedone (2 mmol) was performed under refluxing in various solvents as shown in Table 1. Then, with particular reference to the current importance of green chemistry, this transformation was attempted without the presence of a solvent. Interestingly,



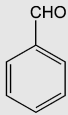
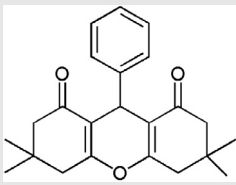
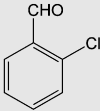
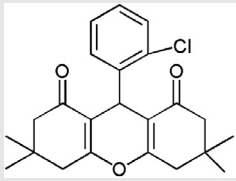
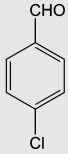
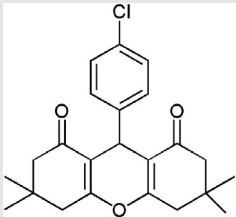
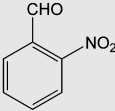
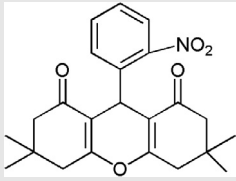
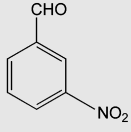
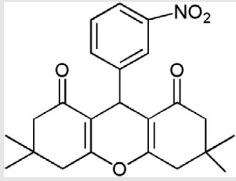
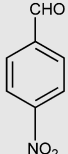
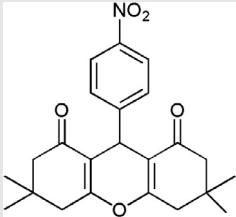
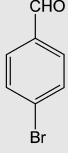
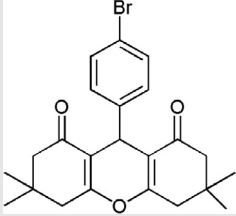
Scheme 1 Synthesis of various xanthene derivatives in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ under solvent free condition.

Table 1 Optimization of the model reaction.^a

Entry	Catalyst	Catalyst loading (g)	Condition	Time (min)	Yield (%)
1	No	–	Neat/130 °C	15	Trace
2	$\text{Fe}_3\text{O}_4@\text{SiO}_2$	0.05	Neat/130 °C	60	56
3	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	0.05	EtOH/reflux	60	35
4	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	0.05	H_2O /reflux	60	Nil
6	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	0.05	CH_3CN /reflux	60	45
7	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	0.05	Toluene/reflux	60	55
8	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	0.05	Neat/110 °C	15	72
9	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	0.05	Neat/120 °C	15	81
10	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	0.05	Neat/130 °C	4	94
11	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	0.025	Neat/130 °C	35	94
12	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	0.075	Neat/130 °C	4	94

^a Reaction condition: dimedone (2 mmol), benzaldehyde (1 mmol), catalyst (0.05 g) at 130 °C under solvent free condition.

Table 2 Fe₃O₄@SiO₂-SO₃H catalyzed synthesis of various xanthene derivatives.

Entry	Aldehyde	Product	Yield (%) ^a	Time (min)	M.p. (Lit.) (°C)
1a			94	4	202–204 (202–204) [31,32]
2a			95	5	224–227 (225–227) [11]
3a			93	5	235–238(228–239) [35]
4a			52	11	250–256(248–249)[31,32]
5a			95	6	171–172(166–168) [31,32]
6a			92	8	226–228(225–226) [31,32]
7a			95	3	239–241(240–241) [31,32]

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Table 2 (continued)

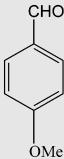
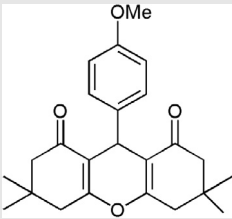
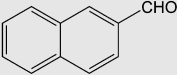
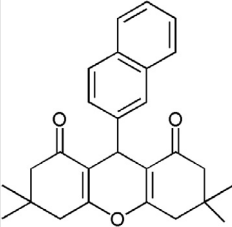
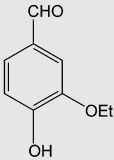
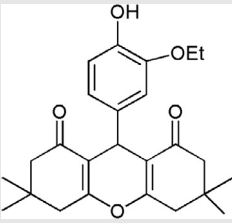
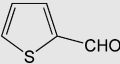
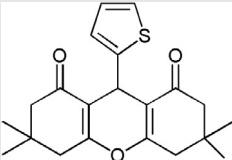
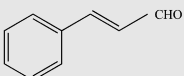
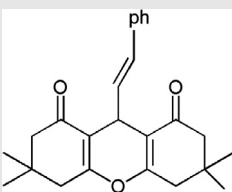
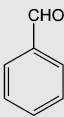
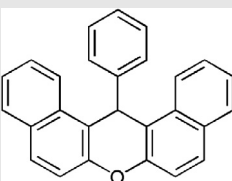
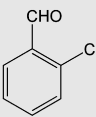
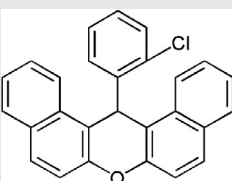
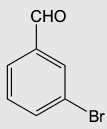
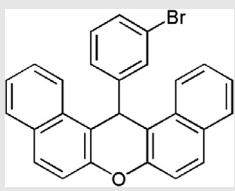
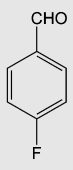
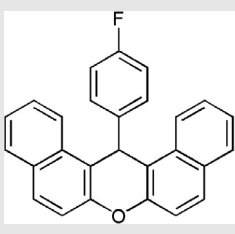
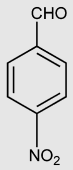
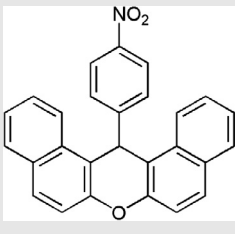
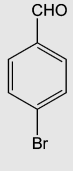
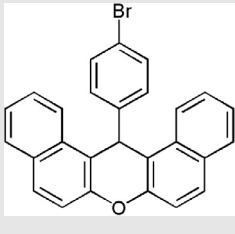
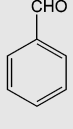
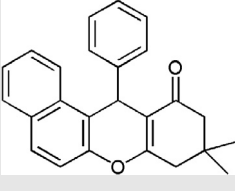
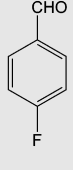
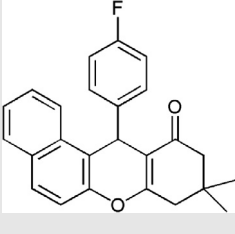
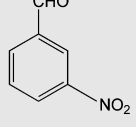
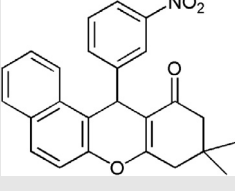
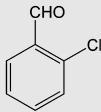
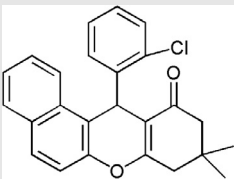
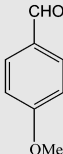
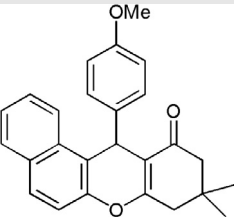
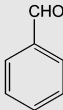
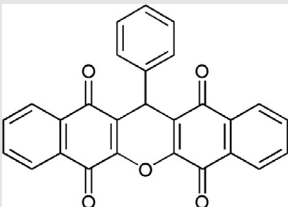
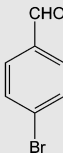
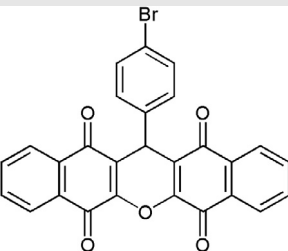
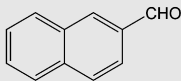
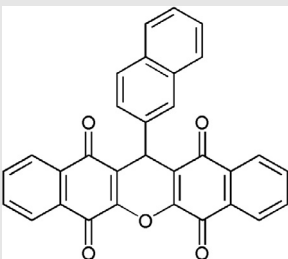
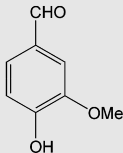
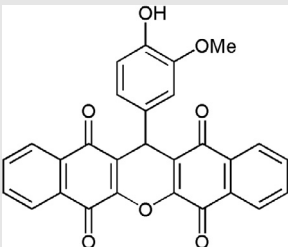
Entry	Aldehyde	Product	Yield (%) ^a	Time (min)	M.p. (Lit.) (°C)
8a			94	5	241–243(241–243) [31,32]
9a			94	12	197–198(197–199) [35]
10a			95	10	193–194
11a			95	12	197–199(198–200) [21]
12a			92	12	175–176(176–177) [13]
13b			94	30	181–183(181–183) [31,32]
14b			93	55	215(214–215) [10]

Table 2 (continued)

Entry	Aldehyde	Product	Yield (%) ^a	Time (min)	M.p. (Lit.) (°C)
15b			90	60	191–193(192–194) [31,32]
16b			90	45	240–241(240–242) [31,32]
17b			92	25	311–313(312–314) [40]
18b			92	45	295–297(295–296) [31,32]
19c			95	30	149–151(149–151) [24,26]
20c			94	20	184–185(184–186) [17]
21c			98	50	167–169(167–170) [15]

(continued on next page)

Table 2 (continued)

Entry	Aldehyde	Product	Yield (%) ^a	Time (min)	M.p. (Lit.) (°C)
22c			96	30	178–179(179–180) [24,26]
23c			90	45	204–206(204–205) [17]
24d			95	30	304–306(305–307) [38]
25d			94	20	335–336(333–335) [38]
26d			91	60	292–293
27d			97	40	303–304

^a All yields refer to isolated products after crystallization.

as demonstrated by the results shown in Table 1, product yield was increased to 94% under the solvent-free condition. To study the function of SO_3H , an experiment was conducted in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and the results showed that the reaction proceeded for a longer period and produced a lower yield (Table 1, entry 2). However when $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ was used, the reaction afforded the desired product in high yield (94% yields). In addition, a trace amount of the product was formed in the absence of the catalyst. Thus it can be determined that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ was essential to obtain the desired product.

Screenings of temperature and amounts of catalyst were investigated and presented (Table 1, entries 8–12). The best results were obtained by using 0.05 g $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ at 130 °C (Table 1, entry 10). No significant improvement in yield was obtained past that point, so 130 °C was chosen as the most appropriate reaction temperature for all further studies. Likewise, increasing the amount of catalyst did not lead to any change in yield of **1a**.

Hence, performing the reaction without a solvent and in the presence of 0.05 g catalyst at 130 °C was determined as the optimal condition.

Using the optimized reaction condition, the scope and limitations of this methodology were evaluated using a variety of aromatic aldehydes. In general, aromatic aldehydes bearing electron-donating or electron-withdrawing functional groups reacted smoothly with dimedone and within a short reaction time to generate 1,8-dioxo-octahydroxanthene derivatives with good to excellent yields (Table 2, entries 1a–12a). Only using aldehyde with the strongly electron-withdrawing group ($-\text{NO}_2$) at *ortho* position afforded the desired product with a moderate yield (entry 4a). Moreover, this reaction also worked well with aliphatic aldehyde, heteroaromatic aldehyde and hindered aldehyde (Table 2, entries 9a, 11a and 12a).

Preparation of 14H-dibenzo[a,j]xanthenes was also examined to further expand the scope of this nano-magnetic catalyst in the synthesis of xanthene derivatives (Scheme 1). The reaction of 2-naphthol (2 mmol) and arylaldehydes (1 mmol) (carrying both electron-donating and electron-withdrawing functional groups), in the presence of 0.05 g $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ proceeded efficiently to furnish the corresponding 14H-dibenzo[a,j]xanthene derivatives producing high yields, as summarized in Table 2, entries 13b–18b. The reactions were completed in 25–65 min at 130 °C under solvent-free conditions.

Subsequently, application of the catalyst was successfully extended on the condensation of aldehyde with 2-naphthol and dimedone. The obtained results demonstrated efficiency of this method in the synthesis of 12-aryl-tetrahydrobenzo[a]xanthenes-11-ones at 110 °C under solvent-free conditions (Table 2, entries 19c–23c).

Also 13-aryl-5-H-dibenzo[b,j]xanthenes-5,7,12,14(13H)-tetraones were synthesized using $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ under the same conditions from the reaction of 2-hydroxynaphthalene-1,4-dione with aryl and naphthyl aldehydes, the results of which are given in Table 2, entries 24d–27d.

Good reusability of the catalyst is an important aspect of green chemistry so the potential for recovery of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ was investigated. After completion of the reaction of benzaldehyde and dimedone, hot ethanol was added to the reaction mixture and the catalyst was recovered simply by application of an external magnet. Then the recovered catalyst

was first washed with diethyl ether and then with methanol, and dried at 60 °C for 1 h. The recovered catalyst was added to a fresh reaction mixture under the same conditions for five runs with only a slight loss of its catalytic activity (Fig. 1). The recoverability and reusability of catalyst was also checked for the synthesis of other xanthene derivatives, the results are summarized in Table 3. The results confirm that the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ has good stability and recyclable applicability for the synthesis various xanthene derivatives. As depicted in Table 3, after four runs, a minor decline contributing ca. 10–15% is observed. The decrease in the activity could be mainly attributed to unavoidable loss of the catalyst during the process of collection and washing.

Another test was done to determine the percentage of leaching of the SO_3H group; the reaction of benzaldehyde and 2-naphthol was carried out in the presence of the nano-magnetic catalyst for 10 min in the reaction condition, and then at that point the catalyst was removed by an external magnet. The reaction was then allowed to proceed further, but no meaningful progress was observed even after 80 min of heating at 130 °C. Thus it can be concluded that no homogeneous catalyst was involved.

The TEM image of the used catalyst showed that size and shape of the catalyst particles remained almost the same after five runs (Fig. 2) [24,26]. Furthermore, the intensity and peak positions between the used and fresh catalyst in the FTIR spectra after the reaction, indicated that structure of the catalyst had remained the same as that of fresh catalyst (Fig. 3).

The XRD pattern of a reused catalyst (Fig. 4) exhibits a broad peak at $2\theta = 25.5$, which is typical for amorphous silica [5]. Some distinct peaks at 2θ values of 30.24, 35.60, 43.24, 53.7, 57.6 and 62.8 are assigned to the (220), (311), (400), (422), (511) and (440) planes of Fe_3O_4 [37].

The rationale sequence of events is depicted in Scheme 2 according to the commonly accepted mechanism for such reactions. Initially SO_3H groups, as acid sites, are active in protonating the carbonyl group of aldehyde. This intermediate is attacked by 2-naphthol, dimedone or 2-hydroxynaphthalene-1,4-dione to form the Knoevenagel products. In the next step, each of these intermediates is converted to the desired product via Michael type addition and cyclization with the removal of a molecule of water (Scheme 2).

Table 4 compares efficiency of the present method for the synthesis of various xanthenes with results recently reported

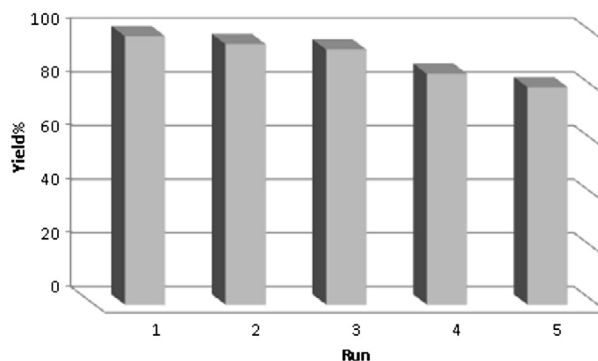
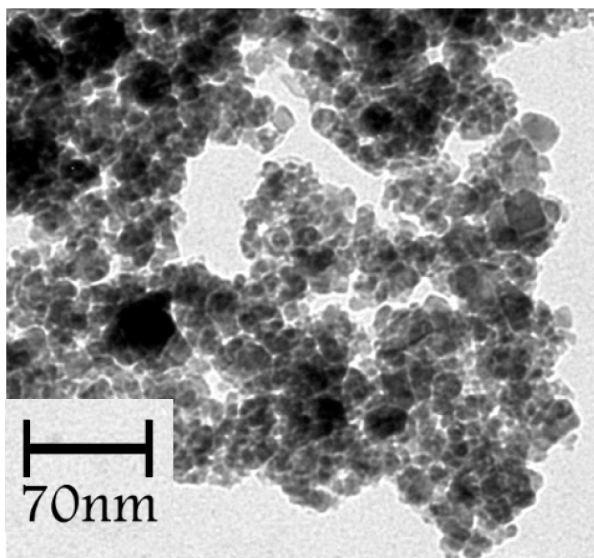


Figure 1 The reusability of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ for the preparation of tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione (**1a**).

Table 3 Effect of reusability of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ on the xanthenes yields.

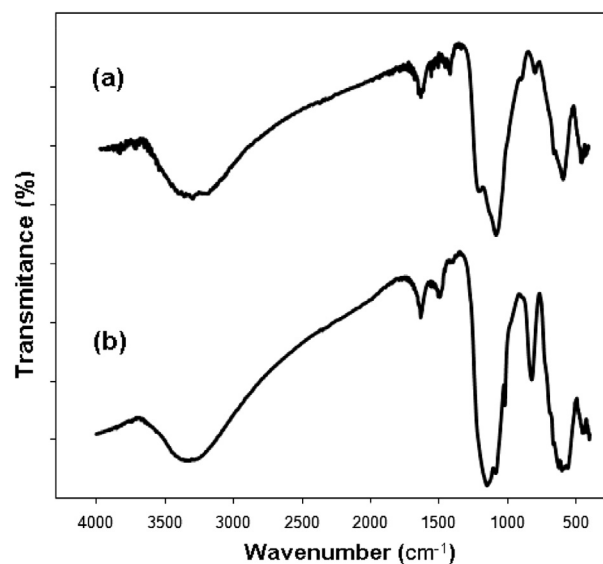
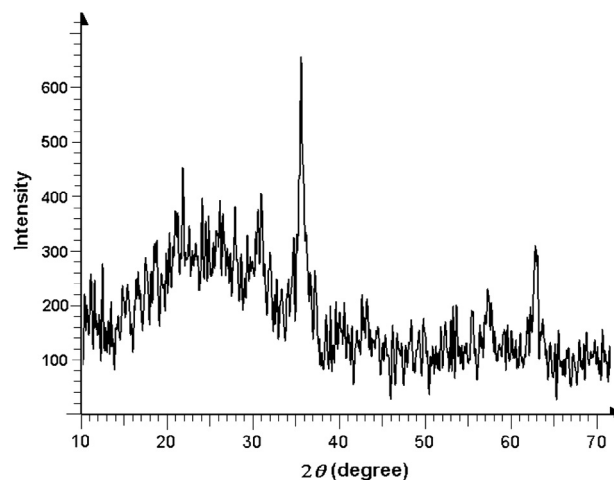
Product	Yield % (cycle 1)	Yield % (cycle 2)	Yield % (cycle 3)	Yield % (cycle 4)
13b	94	90	86	79
19c	95	93	90	86
24d	95	92	87	79

**Figure 2** TEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ after 5 runs.

by other catalysts in the related literature. Each of these methods has its own merits, but some of them often suffer from some troubles such as the use of organic solvents (entries 3, 9, 10, and 15), long reaction times (entries 7, 8, 9, 10, 14, and 15) and employ of non-recyclable or expensive catalyst (entries 3, 8, 9, 10, and 11). So $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ acts as a highly effective and economical catalyst in terms of time and yield produced by the reaction.

3. Experimental

Chemicals were purchased from the Fluka, Merck and Aldrich chemical companies. Melting points were determined on an Electrothermal 9100 without further corrections. TLC on commercial aluminum-backed plates of silica gel 60 F254 was used to monitor the progress of reactions. Infrared spectra were recorded on a Shimadzu 8400s spectrometer with KBr plates. Only representative absorptions are given. NMR spectra were taken in CDCl_3 or $\text{DMSO-}d_6$ on a Bruker Avance 3–400 MHz instrument at 20–25 °C. Elemental analyses were performed by a Perkin-Elmer CHN analyzer, 2400 series II. The wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a PW 1800 diffractometer (Philips) with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5401 \text{ \AA}$). The scanning rate was $0.08^\circ/\text{s}$ over a range of $2\theta = 4\text{--}80^\circ$. The sizes of MNPs were evaluated using a transmission electron microscope (TEM, 100 kV, Philips-CM 10).

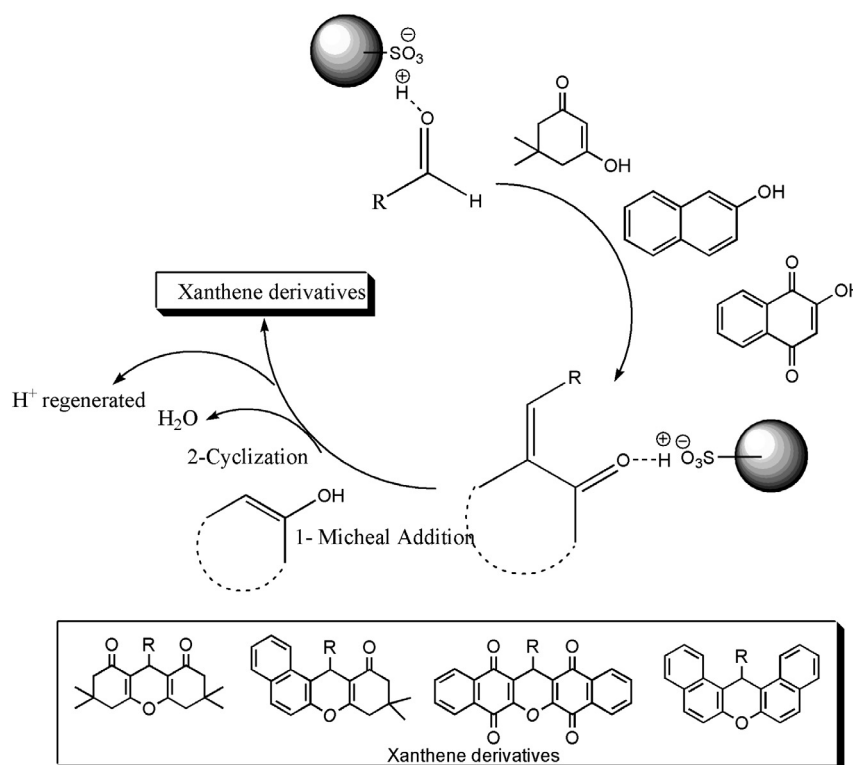
**Figure 3** FTIR spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ (a) fresh, and (b) after 5 runs recycle.**Figure 4** The XRD pattern of reused $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$.

3.1. Preparation of the catalyst

The $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ was prepared in accordance to our earlier report [24,26].

3.2. General procedure for the synthesis of xanthenes derivatives

In a 25 mL flask, a mixture of aldehyde (1 mmol), desired substrate (according to Scheme 1) and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ (0.05 g) was heated in an oil bath at appropriate temperature under solvent-free conditions (Table 1). After completion of the reaction as monitored by TLC, the resulting solid product was cooled, hot ethanol was added to it and stirred for 10 min. Then the catalyst was removed magnetically. The remained alcoholic solution was kept overnight to afford the pure product. The removed catalyst was washed exhaustively with diethyl ether and methanol and dried at 60 °C for 1 h prior



Scheme 2 Plausible mechanism.

Table 4 Comparison of the results obtained for the synthesis of 3,3,6,6-tetramethyl-9-(4-chloro-phenyl)-1,8-dioxo-octahydroxanthene (3a), tetra-hydrobenzo[a]xanthene-11-ones (13b), 9,10-dihydro-9,9-dimethyl-12-phenyl-8H-benzo[a]xanthene-11(12H)-one (19c) and 13-aryl-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraones (24d) catalyzed by $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ with those recently reported catalysts.

Entry	Catalyst	Condition	Product	Time (min)	Yield (%)	Refs.
1	Succinimide-N-sulfonic acid	Neat/80 °C	3a	18	92	[35]
2	Tungstate sulfuric acid	Neat/100 °C	3a	45	90	[13]
3	CAN/ultra son.	2-Propanol/50 °C	3a	40	93	[21]
4	Nano-ZnO	Neat/80 °C	3a	15	96	[31,32]
5	$[\text{Et}_3\text{N-SO}_3\text{H}]\text{Cl}$	Neat/80 °C	3a	40	93	[40]
6	Nano-TiO ₂	Neat/100 °C	3a	60	92	[16]
7	$(\text{NH}_4)_2\text{HPO}_4$ then H_2SO_4	Water/25 °C	3a	90	70	[6]
8	SmCl_3	Neat/120 °C	3a	9h	97	[11]
9	PFPAT ^a	Toluene/25–30 °C	3a	3h	97	[14]
10	CAN/ultra son.	DCM, EtOH	19c	120	85	[36]
11	SSWC nano tube ^b	Neat/70 °C	13b	8	93	[8]
12	Nano-ZnO	Neat/80 °C	13b	28	87	[31,32]
13	$[\text{H-NMP}][\text{HSO}_4]$	Neat/110 °C	13b	12	94	
14	<i>p</i> -TSA	Neat/100 °C	24d	180	81	[38]
15	PFPAT ^a	Toluene/25–30 °C	13b	4.5h	90	[14]
16	Thiamine hydrochloride	Rt /aqueous micellar system	19c	25	92	[9]
17	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	Neat/130 °C	3a	5	93	This work
18	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	Neat/130 °C	13b	30	94	This work
19	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	Neat/110 °C	19c	30	95	This work
20	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	Neat/110 °C	24d	30	95	This work

^a Pentafluorophenyl ammonium triflate.

^b Sulfonated single-walled carbon nanotubes.

to reuse in subsequent reaction. All the desired products were characterized by comparison of their physical data with those

reported compounds. The spectral data of new compounds are given below:

3.3. The spectral data of new products

3.3.1. 9-(3-Ethoxy-4-hydroxyphenyl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-2H-xanthene-1,8 (5H,9H)-dione (Table 2, 10a)

m.p. 193–194 °C, IR (KBr, cm^{-1}): ν_{max} : 3434, 1666, 1623; ^1H NMR (400 MHz, CDCl_3): δ_{H} 1.02 (s, 6H), 1.12 (s, 6H), 1.43 (t, $J = 6.8$ Hz, 3H), 2.22 (q, $J = 7.2$ Hz, 4H), 2.47 (s, 4H), 4.16 (q, $J = 7.2$ Hz, 2H), 4.67 (s, 1H), 5.57 (s, br, 0.82H), 6.58 (dd, $J = 8$ Hz, $J = 2$ Hz, 1H), 6.57 (d, $J = 8$ Hz, 1H), 7.01 (d, $J = 2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 14.89, 27.31, 29.32, 31.32, 32.21, 40.87, 50.79, 64.34, 113.16, 113.84, 115.83, 119.88, 136.37, 144.10, 145.14, 162.07, 196.61; Anal. calcd for $\text{C}_{25}\text{H}_{30}\text{O}_5$: C 73.17, H 7.31; found: C 72.99, H 7.11.

The followed products have very low solubility in DMSO, so we cannot report appropriate spectral data for these compounds.

3.3.2. 13-(Naphthalen-2-yl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (Table 2, 26d)

m.p. 292–293 °C, IR (KBr, cm^{-1}): ν_{max} : 3061, 1662, 1610; calcd for $\text{C}_{31}\text{H}_{16}\text{O}_5$: C 79.48, H 3.41; found: C 79.32, H 3.31.

3.3.3. 13-(4-Hydroxy-3-methoxyphenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (Table 2, 27d)

m.p. 303–304 °C, IR (KBr, cm^{-1}): ν_{max} : 3482, 1661, 1652; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ_{H} 3.71 (s, 3H), 4.99 (s, 1H), 6.61 (d, $J = 8$ Hz, 1H), 6.77 (d, $J = 8$ Hz, 1H), 6.93 (s, 1H), 7.88 (m, 2H), 7.95 (m, 2H), 8.00 (d, $J = 7.2$ Hz, 2H), 8.09 (m, 2H), 8.91 (s, br, 1H); Anal. calcd for $\text{C}_{28}\text{H}_{16}\text{O}_7$: C 72.41, H 3.44; found: C 72.29, H 3.35.

4. Conclusion

In summary, an efficient and environmentally benign procedure has been developed for the synthesis of various xanthene derivatives using $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-SO}_3\text{H}$ as a nano magnetic catalyst under thermal and solvent-free conditions. The reaction produced corresponding products with excellent yield and within a short reaction time. The most noteworthy aspects of this methodology are simplicity of its operation, easy isolation of the product and excellent reusability potential of the catalyst. The attractiveness of this protocol lies in its green approach in that the catalyst is easily recoverable using an external magnet, which makes the process economical.

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