

Fe²⁺ supported on hydroxyapatite-core-shell- γ -Fe₂O₃ nanoparticles: Efficient and recyclable green catalyst for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives

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Received: 28 July 2015 / Accepted: 8 October 2015 / Published online: 23 October 2015
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Abstract In this work, Fe²⁺ supported on hydroxyapatite-core-shell- γ -Fe₂O₃ nanoparticles (γ -Fe₂O₃-HAp-Fe²⁺ NPs) has been prepared and characterized by Fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and vibrating sample magnetometry spectra. Then, γ -Fe₂O₃-HAp-Fe²⁺ NPs were used as an efficient, reusable and heterogeneous nanocatalyst for one-pot synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes via the one-pot condensation reaction of arylaldehydes and 2-naphthol under solvent-free conditions in good to excellent yields. This procedure has a lot of advantages such as very easy reaction conditions, simplicity in operation, short reaction time, high yield, and green aspects by avoiding toxic conventional catalysts and solvents. Additionally, γ -Fe₂O₃-HAp-Fe²⁺ NPs were easily recycled from the reaction mixture and were reused seven times without any loss in activity.

Keywords γ -Fe₂O₃-HAp-Fe²⁺ · Magnetic nanoparticle ·
14H-dibenzo[a,j]xanthenes · Lewis acid · Nanocatalyst · Reusable catalyst

Introduction

The synthesis of xanthene and benzoxanthene compounds has received great attention from various pharmacological activities and organic chemists because of their broad spectrum of biological and pharmaceutical properties, such as anti-viral [1], antioxidant [2], anti-cancer [3], antibacterial and antifungal [4, 5], analgesic and

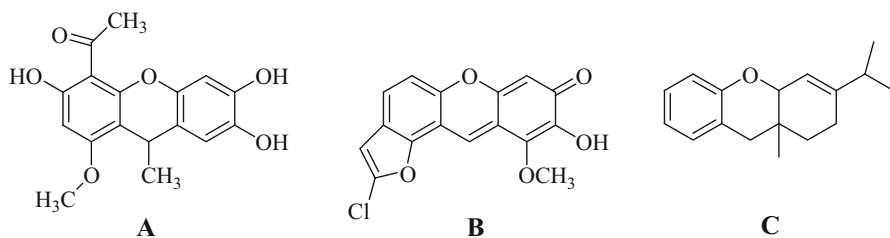
Electronic supplementary material The online version of this article (doi:10.1007/s11164-015-2318-5) contains supplementary material, which is available to authorized users.

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anti-inflammatory [6, 7], cytotoxic [8], and anti-proliferative properties [9]. Moreover, xanthene and benzoxanthene derivatives can be used as sensitizers in dye-sensitized solar cells (DSSCs) [10–12], in the food industry as additives [13], in laser technologies [14], in photodynamic therapy [15], as fluorescent materials for the visualization of biomolecules [16], and also as hole-transporting materials in organic light-emitting devices (OLEDs) [17]. Xanthenes and their derivatives are rare in natural plants [18, 19]. Blumeaxanthene (**A**), blumeaxanthene (**B**), and 3-isopropyl-9a-methyl-1,2,4a,9a-tetrahydroxanthene (**C**) are examples of natural xanthenes (Scheme 1). Compounds **A** and **B** have been used to treat gynecological disorders, and compound **C** has been used in traditional Indian medicine as an antidote for all snake venoms.

A number of methods have been developed and reported for the synthesis of xanthenes and benzoxanthenes. These methods include the cyclocondensation reaction between 2-tetralone and 2-hydroxyarylaldehydes under acidic conditions [20], the palladium-catalysed cyclisation of polycyclic aryltriflate esters [21], the reaction of alkylphenoxy magnesium halides with triethylorthoformate [22], and the reaction of the condensation of cyclic 1,3-diketones with aryl aldehydes catalysed by molybdate sulphonic acid [23]. Also, 14-aryl-14H-dibenzo[a,j]xanthene derivatives can be prepared by condensation of 2-naphthol with aldehydes in the presence of different catalysts, including Lewis acids and Brønsted acids. For example, carbon-based solid acid [24], functionalized mesoporous materials [25], cellulose sulfuric acid [26], P_2O_5/Al_2O_3 [27], amberlyst-15 [28], silica sulfuric acid [29], $HClO_4-SiO_2$ [30], heteropoly acid [31], montmorillonite K-10 [32], $Yb(OTf)_3$ [33], phospho sulfonic acid (PSA) [34], boron sulfonic acid (BSA) [35], molecular iodine [36], and boric acid [37] have been used as catalysts for the synthesis of xanthenes. However, some of these methods suffer from drawbacks such as strongly acidic wastes, high cost, reagent toxicity, unsatisfactory yields, tedious work-up procedures, harsh conditions and nonrecyclable reagents. Recently, the application of nanoparticles (NPs) has received great attention from organic chemists because of their high surface area and unique magnetic properties. Moreover, they have a wide range of usage in various fields, such as data storage [38], environmental remediation [39], biology and medical applications [40], magnetic resonance imaging (MRI) [41], and magnetic fluids [42]. $\gamma-Fe_2O_3-HAp-Fe^{2+}NPs$ are important both environmentally and economically, because they can be conveniently handled, making the experimental procedure simple, low cost and eco-



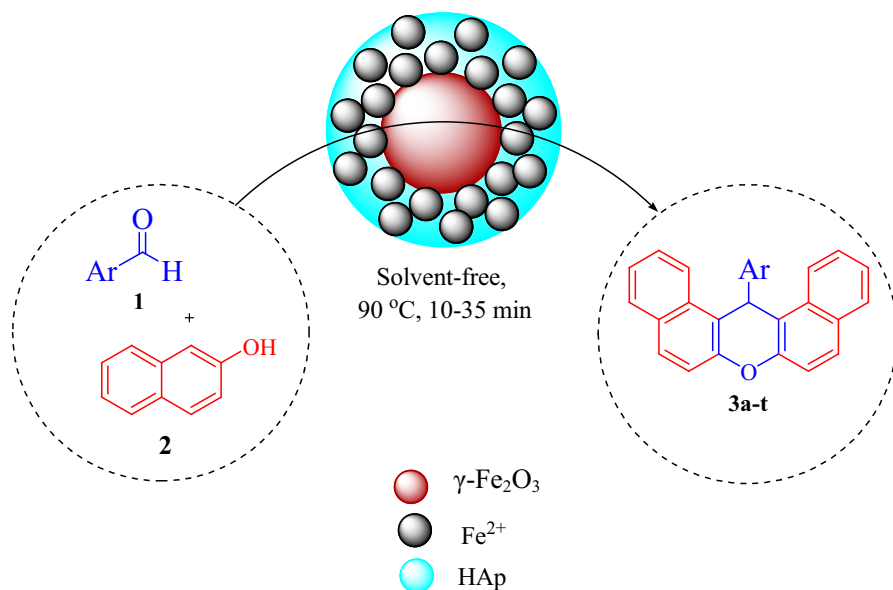
Scheme 1 Examples of natural xanthenes

friendly. Also, the catalyst can be recovered from the reaction mixtures and reused. Recently, we used a magnetic NP with a high surface area, narrow pore size distribution and large pore volume as a recoverable heterogeneous catalyst in some organic transformations [43–49]. Therefore, in the current work, it seems that the major task of current research is developing more acceptable methods based on the use of Fe²⁺ supported on hydroxyapatite-core-shell-Fe₂O₃ (γ -Fe₂O₃-HAp-Fe²⁺) NPs as an efficient and reusable Lewis acid catalyst for the one-pot synthesis of 14-aryl-14H-dibenzo[a,j] xanthenes in good to excellent yields and in short reaction times under solvent-free conditions at 90 °C (Scheme 2). (Please see supporting information for experimental procedures for the synthesis of γ -Fe₂O₃-HAp-Fe²⁺ NPs, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), vibrating sample magnetometry (VSM), and Fourier transform infrared spectroscopy, (FTIR)].

Experimental

Materials and methods

All chemicals were purchased from Merck or Fluka chemical companies. All the products are known compounds and were characterized by comparing the proton nuclear magnetic resonance (¹H-NMR) and carbon-13 (¹³C)-NMR spectroscopic data and their melting point literature values. The uncorrected melting points of all



Scheme 2 The reaction of 2-naphthol with aldehydes catalyzed by γ -Fe₂O₃-HAp-Fe²⁺ NPs under solvent-free conditions

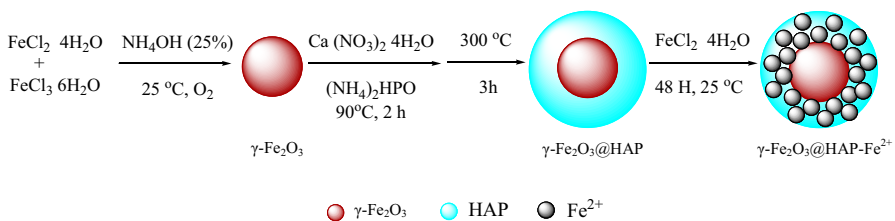
compounds were measured in an open capillary in a paraffin bath. NMR chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS, $d = 0.00$) with the residual solvent as an internal reference [deuterated chloroform (CDCl_3), δ 7.26 ppm for $^1\text{H-NMR}$ and δ 77.0 for $^{13}\text{C-NMR}$]. Data are reported as follows: chemical shift, multiplicity ($s = \text{singlet}$, $d = \text{doublet}$, $t = \text{triplet}$, $q = \text{quartet}$, $m = \text{multiplet}$), coupling constants (Hz) and integration. Mass spectrometry (MS) analyses were performed on a PerkinElmer Clarus 680 gas chromatograph (GC) equipped with a Clarus SQ 8T mass spectrometer. Infrared (IR) spectra were recorded on a Frontier FT-IR (Perkin Elmer) spectrometer using a potassium bromide (KBr) disk. The phases present in the magnetic materials were analyzed using a powder X-ray diffractometer, Philips (Holland), model X0 Pert with X Pert with $\text{CuK}\alpha 1$ radiation ($\lambda = 1.5401 \text{ \AA}$), and the X-ray generator was operated at 40 kV and 30 mA. Diffraction patterns were collected from 2 h = $20^\circ\text{--}80^\circ$.

Preparation of $\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$ NPs

In this study, $\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$ NPs were prepared in two steps. The iron oxide magnetic particles (IOMPs) were synthesized by a chemical co-precipitation technique of ferric and ferrous chlorides in aqueous solution. Solutions of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (0.25 mol L^{-1}) and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (0.125 mol L^{-1}) were mixed and precipitated with NH_4OH solution (25 %) at pH 12, while stirring vigorously. The black suspension, which formed immediately, was maintained at 70°C for approximately 1 h and washed several times with ultrapure water until the pH decreased to 7. IOMP/HAP was prepared by the impregnation method according to known procedures with some modifications [50]. Then hydroxyapatite-encapsulated $\gamma\text{-Fe}_2\text{O}_3$ (0.6 g) was introduced into 100 ml of distilled water containing 6.4 mmol of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$. The mixture was stirred (500 rpm) for 24 h, filtered, and washed several times with ethanol. The recovered solid was dried at 70°C overnight (Scheme 3). The mean size and the surface morphology of the $\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$ NPs were characterized by TEM, SEM, VSM, XRD and FTIR techniques [43].

Procedure for preparation of 14-aryl-14H-dibenzo[a,j]xanthenes 3a-t

To a mixture of aldehyde (1 mmol) and 2-naphthol (2 mmol), $\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$ NPs (20 mg) were added and the mixture was inserted in an oil bath and heated at



Scheme 3 The synthesis of Fe^{2+} supported on hydroxyapatite-core-shell $\gamma\text{-Fe}_2\text{O}_3$ ($\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$ NPs)

90 °C for the appropriate time (Table 3). Completion of the reaction was indicated by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled to room temperature. The reaction mixture was dissolved in ethylacetate and the catalyst was separated by simple filtration. Excess solvent was removed under reduced pressure and the crude product was recrystallized with ethanol to afford the pure product in 81–95 % yield. All the products were known compounds and characterized by comparing Melting points, ¹H-NMR ¹³C-NMR, and Mass spectra with those reported in the literature. The spectral data for some selected compounds are given below.

14-(Phenyl)-14H-dibenzo[a,j]xanthenes (3a)

Pale yellow solid; ¹H-NMR (300 MHz, CDCl₃): δ 5.39 (1H, s, CH), 7.28–7.31 (d, 2H, J = 8.5 Hz, Ar–H), 6.68–6.74 (4H, m, Ar–H), 5.89–6.80 (11H, m, Ar–H); ¹³C-NMR (75 MHz, CDCl₃): δ 38.03, 117.31, 118.01, 122.68, 124.23, 126.37, 126.78, 128.25, 128.47, 128.79, 128.85, 131.04, 131.44, 144.98, 148.71; MS (EI), m/z : 358 (M⁺), 282, 281, 252, 250, 179.

14-(2-Nitrophenyl)-14H-dibenzo[a,j]xanthenes (3b)

Yellow solid; ¹H-NMR (300 MHz, CDCl₃): δ 5.91 (1H, s, CH), 6.08–6.43 (8H, m, Ar–H), 6.48–6.51 (2H, m, Ar–H), 6.68–6.72 (4H, m, Ar–H), 7.41–7.44 (2H, d, J = 8.53, Ar–H); ¹³C-NMR (75 MHz, CDCl₃): δ 32.5, 117.5, 118.0, 122.5, 124.6, 124.9, 127.3, 127.5, 128.7, 129.4, 130.9, 131.7, 132.2, 134.1, 140.8, 147.0, 149.3; MS (EI), m/z : 403 (M⁺), 282, 281, 252, 250, 178, 141.

14-(4-Bromo)-14H-dibenzo[a,j]xanthenes (3e)

Pink solid; ¹H-NMR (300 MHz, CDCl₃): δ 7.19–7.22 (m, 2H), 6.16–6.75 (m, 4H), 6.15–6.75 (m, 10H), 5.34 (s, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ 37.18, 115.18, 115.47, 117.07, 118.03, 122.46, 124.33, 126.88, 128.89, 129.56, 129.67, 131.04, 131.26, 140.80, 148.68; MS (EI), m/z : 438, 436 (M⁺), 282, 281, 252, 250, 179.

14-(4-Methyl)-14H-dibenzo[a,j]xanthenes (3f)

White solid; ¹H-NMR (300 MHz, CDCl₃): δ 7.32–7.29 (m, 2H), 6.74–6.67 (m, 4H), 6.51–6.15 (m, 8H), 5.87–5.85 (m, 2H), 5.36 (s, 1H), 1.04 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃): δ 20.91, 37.63, 117.44, 118.01, 122.71, 124.21, 126.76, 128.11, 128.79, 129.18, 131.07, 131.45, 135.90, 142.13, 148.67; MS (EI), m/z : 372 (M⁺), 282, 281, 252, 250, 186.

14-(4-methoxyphenyl)-14H-dibenzo[a,j]xanthenes (3g)

Pink solid; ¹H-NMR (300 MHz, CDCl₃): δ 2.49 (3H, s, OMe), 5.36 (1H, s, CH), 5.59–5.61 (2H, d, J = 8.66 Hz, Ar–H), 6.32–6.45 (6H, m, Ar–H), 6.49–6.55 (2H, m, Ar–H), 6.69–6.76 (4H, m, Ar–H), 7.31–7.33 (2H, d, J = 8.48, Ar–H); ¹³C-NMR

(75 MHz, CDCl_3): δ 37.17, 55.05, 113.89, 117.58, 118.06, 122.77, 124.28, 126.81, 128.80, 128.87, 129.23, 131.13, 131.47, 137.45, 148.69, 157.89; MS (EI), m/z : 388 (M^+), 282, 281, 252, 250, 194, 187.

14-(4-Nitrophenyl)-14H-dibenzo[a,j]xanthenes (3i)

Pale yellow solid; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 5.44 (1H, s, CH), 6.33–6.57 (8H, m, Ar-H), 6.71–6.76 (4H, m, Ar-H), 6.85–6.89 (2H, d, Ar-H), 7.15–7.18 (2H, $J = 8.3$, Ar-H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 37.88, 115.75, 118.06, 122.04, 123.86, 124.58, 127.19, 128.96, 129.06, 129.59, 131.07, 146.27, 148.75, 152.01; MS (EI), m/z : 388 (M^+), 282, 281, 252, 250, 178, 177.

14-(2-Chlorophenyl)-14H-dibenzo[a,j]xanthenes (3p)

White solid; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 5.69 (1H, s, CH), 5.81–5.82 (2H, d, Ar-H), 6.27–6.40 (5H, m, Ar-H), 6.50 (2H, d, Ar-H), 6.55–6.67 (4H, m, Ar-H), 7.63–7.66 (2H, $J = 8.5$, d, Ar-H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 34.63, 118.02, 118.11, 123.46, 124.44, 126.93, 127.87–127.94, 128.66, 129.08, 129.60, 130.13, 130.89, 131.76, 131.81, 143.57, 148.95; MS (EI), m/z : 394, 392 (M^+), 282, 281, 252, 250, 178, 177.

Results and discussion

In this study, initially the Fe^{2+} supported on hydroxyapatite-core-shell- $\gamma\text{-Fe}_2\text{O}_3$ NPs were prepared according to the reported procedures (Scheme 3). Then, they were fully characterized by TEMSEM, XRD, VSM, and FTIR techniques.

Herein, we wish to report for the condensation of 2-naphthol and various aromatic aldehydes in the presence of $\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$ NPs as a green, reusable and Lewis acid catalyst for the preparation of 14-aryl-14H-dibenzo[a,j]xanthenes derivatives under solvent-free conditions (Scheme 2).

To optimize the reaction conditions for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives, the reaction between 2-naphthol and benzaldehyde under solvent-free conditions was selected as a model reaction to provide compound **3a** (Table 4, entry 1). At first, we examined the catalytic activity of various acids in a model reaction (Table 1). As it can be seen in Table 1, the high yield and short reaction time of compound **3a** was obtained when $\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$ was utilized as catalyst (Table 1, entry 6).

In the next step, the model reaction was tested using different amounts of $\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$ at the various temperatures. The results are summarized in Table 2. It can be seen in Table 2 that this reaction was strongly influenced by the amount of catalyst and temperature. The best results were obtained using 20 mg of catalyst in 15 min at 90 °C. (Table 2, entry 4). Accordingly, 20 mg of catalyst was selected for use in these reactions due to its low concentration, which resulted in excellent yields and short reaction times. Moreover, the product yield was not changed by increasing the amount of the catalyst and increasing the reaction

Table 1 Synthesis of compound **3a** using different catalysts

Entry	Catalyst	Time (min)	Yield (%) ^c
1	Citric acid ^a	90	55
2	Silicagel	180	Not completed reaction
3	Cyanuric choride ^b	90	45
4	TBBDA ^c	120	65
5	PBBS ^d	120	63
6	γ -Fe ₂ O ₃ -HAp-Fe ²⁺	60	78

^a 5 mol% of citric acid was used

^b 5 mol% of cyanuric choride was used

^c 0.25 g of *N,N,N',N'*-tetrabromobenzene-1,3-disulfonamide was used

^d 0.25 g of poly(*N,N'*-dibromo-*N*-ethyl-benzene-1,3-disulfonamide) was used

^e Yield of isolated products

Table 2 Optimization of reaction conditions

Entry	Amount of catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)
1	5	90	50	51
2	10	90	35	63
3	15	90	15	75
4	20	90	15	95
5	20	100	15	93
6	20	120	20	90
7	25	90	30	85

temperature. In the next part, using these optimized reaction conditions, other benzaldehydes (**3b–3t**) were examined in the presence of γ -Fe₂O₃-HAp-Fe²⁺NPs.

It was found that all the reactions proceeded smoothly to give the corresponding 14-aryl-14H-dibenzo[a,j]xanthene derivatives in good to excellent yields and short reaction times (Table 3). The results given in Table 3 show that, in all cases, aromatic aldehydes containing both electron-donating and electron-withdrawing groups reacted under solvent-free conditions with 2-naphthol and within a short reaction time (10–35 min) to generate 14-aryl-14H-dibenzo[a,j]xanthene derivatives with good to excellent yields (81–95 %). *Ortho*-substituted aromatic aldehydes, however, did not react as smoothly, likely because of steric hindrance, and longer reaction times were required to get the corresponding products in good yields (Table 2, entries 2 and 15–16).

In order to show the merit of the present work, the advantages of γ -Fe₂O₃-HAp-Fe²⁺NPs were compared (reaction condition, time and yield) with some homogeneous and heterogeneous catalysts for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes, and the results are presented in Table 4. Based on previous research using

Table 3 Synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives promoted by γ -Fe₂O₃-HAP-Fe²⁺ NPs

Entry	Aldehydes	Product ^a	Time (min) ^b	Yield (%) ^c	M.p./°C	
					Found	Reported
1	C ₆ H ₅	3a	15	95	191–193	190–191 [51]
2	2-NO ₂ C ₆ H ₄	3b	30	81	309–311	310–331 [52]
3	3-NO ₂ C ₆ H ₄	3c	20	89	210–212	210–211 [52]
4	3-OCH ₃ C ₆ H ₄	3d	10	87	260–262	261–263 [52]
5	4-BrC ₆ H ₄	3e	35	94	294–295	295–296 [52]
6	4-CH ₃ C ₆ H ₄	3f	15	86	226–228	227–228 [52]
7	4-OCH ₃ C ₆ H ₄	3g	15	85	203–205	202–203 [52]
8	4-ClC ₆ H ₄	3h	10	92	285–287	287–288 [52]
9	4-NO ₂ C ₆ H ₄	3i	15	93	310–312	310–311 [52]
10	3-CH ₃ C ₆ H ₄	3j	15	90	195–197	197–198 [53]
11	4Cl-3NO ₂ C ₆ H ₃	3k	10	95	230–231	232–234 [54]
12	3-OHC ₆ H ₄	3l	25	90	169–171	172–173 [54]
13	4-OHC ₆ H ₄	3m	20	85	138–139	137–138 [54]
14	3-BrC ₆ H ₄	3n	30	95	193–195	194–195 [55]
15	2-CH ₃ C ₆ H ₄	3o	20	88	205–206	208 [56]
16	2-ClC ₆ H ₄	3p	20	85	219–220	221 [56]
17	2,4-ClC ₆ H ₃	3q	10	90	87–89	89–90 [57]
18	4-[(CH ₃) ₃ C]C ₆ H ₄	3r	30	88	301–302	303 [58]
19	4-C ₆ H ₅ C ₆ H ₄	3s	30	90	281–283	285 [59]
20	4-SCH ₃ C ₆ H ₄	3t	20	86	210–212	213 [59]

^a Products are characterized by spectral data (¹H-NMR, ¹³C-NMR, and mass spectrometry)

^b Reactions were run till the completion as indicated by TLC

^c Yield of isolated products

M.p. melting point

cellulose sulfuric acid (Table 4, entry 1), Polyvinylpyrrolidone-bound boron trifluoride (PVPP-BF₃; Table 4, entry 5), zinc oxide NP (Table 4, entry 6), and *p*-Toluene sulfonic acid (Table 4, entry 8) for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes derivatives, which requires long reaction time and high temperature to complete the reaction. In the recent years, Khaksar and et al. reported the synthesis of xanthene derivatives using Pentafluorophenyl Ammonium Triflate (Table 4, entry 9). This method requires long reaction time and the use of hazardous organic solvents such as toluene to complete the reaction. In the 2011, Rahmatpour and et al. reported using Polystyrene-supported aluminium chloride (Table 4, entry

Table 4 Comparison of the efficiencies of various catalysts used in the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes

Entry	Catalyst/solvent/temperature	Time (h)	Yield (%) ^b	Refs.
1	Cellulose sulfuric acid (0.08 g)/solvent-free/110 °C	1.5–3	81–97	[26]
2	Amberlyst-15 (1 mmol)/solvent-free/125 °C	0.5–2	80–94	[28]
3	Silica sulfuric acid (0.05 g)/solvent-free/80 °C	15–120 ^a	80–96	[29]
4	Yb(OTf) ₃ /[BPy]BF ₄ (0.01 mmol)/110 °C	5–7	80–95	[33]
5	PVPP-BF ₃ /solvent-free (0.05 g)/120 °C	1.5–2	92–98	[57]
6	ZnO-NPs (0.3 mmol)/solvent-free/150 °C	40–80 ^a	82–92	[60]
7	<i>p</i> -Toluenesulfonic acid (0.1 equiv)/CH ₂ Cl ₂ /reflux	15–24	83–95	[61]
8	<i>p</i> -Toluenesulfonic acid (0.1 equiv)/solvent-free/125 °C	2.5–6	80–96	[61]
9	PFPAT (10 mol%)/toluene/25–30 °C	3–5	85–97	[62]
10	Poly(AMPS-co-AA) (0.04 g)/solvent-free/110 °C	20–30	75–92	[63]
11	γ -Fe ₂ O ₃ -HAp-Fe ²⁺ NPs (20 mg)/solvent-free/90 °C	10–35	81–95	– ^c

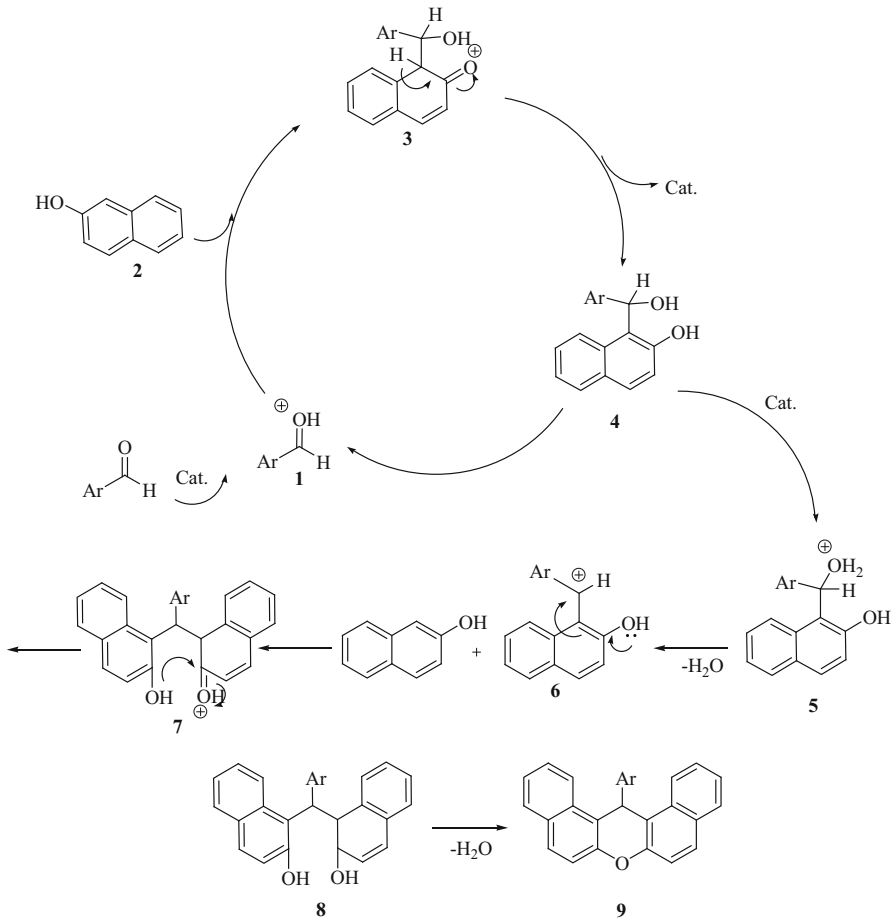
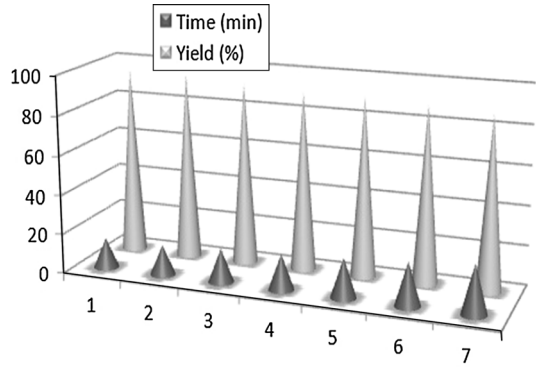
^a In a minute^b Yield of isolated products^c Our manuscript

10) and in the 2005, Khosropour and et al. using *p*-toluene sulfonic acid (Table 4, entry 7) for the one-pot synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes derivatives. This methods requires long reaction times, and requires harsh reaction conditions like use of reflux conditions and also use hazardous organic solvents such as dichloromethane. As shown in Table 4, γ -Fe₂O₃-HAp-Fe²⁺ NPs can act as effective catalyst with respect to reaction times, amount of the catalyst, and yields of the obtained products. Thus, the present protocol with γ -Fe₂O₃-HAp-Fe²⁺ NPs catalysts is convincingly superior to the some reported catalytic methods.

The reusability of catalysts is of major importance in green chemistry and also is of major importance for large scale operations and from an industrial point of view. Thus, the recovery and reusability of γ -Fe₂O₃-HAp-Fe²⁺ NPs was investigated. Catalyst reusability was also examined for the preparation of 14-(phenyl)14H-dibenzo[a,j]xanthenes (**3a**) from the reaction between 2-naphthol with benzaldehyde as a model reaction. When the reaction was completed (monitored by TLC), ethylacetate was added until the solid crude product was dissolved. Then, γ -Fe₂O₃-HAp-Fe²⁺ NPs as the catalyst were isolated from the reaction mixture by simple filtration and reused again after washing with ethylacetate. The recovered catalyst was reused in seven similar subsequent runs. For each of the runs, the product yield was 95, 95, 93, 91, 91, 90 and 88 %, respectively, which verifies that the activity of the catalyst remained unchanged throughout these seven runs (Fig. 1).

The suggested mechanism for the γ -Fe₂O₃-HAp-Fe²⁺ NP-catalyzed transformation is shown in Scheme 4. According to the mechanism, γ -Fe₂O₃-HAp-Fe²⁺ NPs readily catalyzed the in situ formation of 14-aryl-14H-dibenzo[a,j]xanthenes **9**. The activated aromatic aldehyde **1** reacted with one molecule of 2-naphthol **2** to provide intermediate **3**, which can be regarded as a fast Knoevenagel addition. Then the

Fig. 1 Recyclability of the γ - Fe_2O_3 -HAp- Fe^{2+} NPs for the model reaction after 10 min



Scheme 4 The plausible mechanism for the condensation reaction of 2-naphthol with aldehydes catalyzed by the γ - Fe_2O_3 -HAp- Fe^{2+} NPs

active methylene of the second molecule of 2-naphthol reacted with intermediate **3** via conjugate Michael addition to produce the intermediate **7**, which underwent intramolecular cyclodehydration to give the 14-aryl-14H-dibenzo[a,j]xanthenes **9**.

Conclusion

We have synthesized Fe²⁺ supported on hydroxyapatite-core-shell- γ -Fe₂O₃ NPs as a green and non-toxic nanocatalyst, and successfully used the compound as a catalyst for one-pot condensation of arylaldehydes with 2-naphthol. Some important advantages of this work are high yield, ease of product isolation, non-use of hazardous organic solvents, short reaction times, use of various substrates, and ease of catalyst recovery and reuse, which make it a useful, attractive, and green strategy for the preparation of xanthene derivatives.

Acknowledgments The authors gratefully acknowledge partial support of this study by the Payame Noor University (PNU) of Ilam, I.R. Iran.

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