



One-pot three-component synthesis of 1,8-dioxooctahydroxanthenes and 14-Aryl-14Hdibenzo[*a,j*]xanthenes using a new nanostructure zeolite

SEYEDEH FATEMEH HOJATI^{a,*}, MARYAM MOOSAVIFAR^b and NASRIN MOEINIEGHBALI^a

^aDepartment of Chemistry, University of Sabzevar, Sabzevar, Iran

^bDepartment of chemistry, University of Maragheh, Maragheh, Iran

E-mail: hojatee@yahoo.com

MS received 15 April 2019; revised 7 October 2019; accepted 14 October 2019

Abstract. A new modified zeolite containing Fe nanoparticles loaded in zeolite X (Fe-X) has been synthesized and characterized by FT-IR, XRD, EDX and SEM techniques and its catalytic activity has been investigated in the synthesis of two series of xanthene derivatives. We have described an efficient and novel method using Fe-X as a new and reusable catalyst for the synthesis of 1,8-dioxooctahydroxanthenes and 14-aryl-14H-dibenzo[*a,j*]xanthenes derivatives from one-pot three-component condensation of aromatic aldehyde and dimedone or β -naphthol under solvent-free conditions. The significant advantages of the present method are high yields of products, short reaction time, easy separation of the catalyst from the reaction mixture, easy product isolation, solvent-free condition and reusability of the catalyst.

Keywords. Nanostructure zeolite X; one-pot synthesis; 1,8-dioxooctahydroxanthene; 14-aryl-14H-dibenzo[*a,j*]xanthene.

1. Introduction

Zeolites are hydrated aluminosilicate frames based on an extremely large three-dimensional network of AlO_4 and SiO_4 tetrahedral that are linked together by oxygen atoms. The exceptional properties of zeolites include ion exchange capability, thermal stability and recyclability. Furthermore, they have been applied as catalyst in the petroleum refining and industrial processes.¹⁻³ The basic formula of zeolites can be represented as: $\text{M}_{x/n}[(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_y]w\text{H}_2\text{O}$ where, M is the alkaline or alkaline earth metal. Structurally, zeolites contain small cavities like alkaline and alkaline earth metal cations in a non-framework position such as sodium, potassium, magnesium, calcium, strontium and barium that can be replaced by transition metals *via* ion exchange process.⁴ Zeolites with transition metal ions have the potential to show novel catalytic behavior as these cations are coordinately unsaturated, possess variable oxidation states and can form complexes with guest molecules more selectively than filled shell cations such as Na.^{5,6} Zeolite X has an

aluminosilicate framework analogous to the naturally occurring mineral faujasite including sodalite cages and a 12-membered ring inner cavity which is surrounded by sodalite cages.⁷

Xanthene derivatives are known as an important class of O-containing heterocyclic compounds that received considerable attention as they have a wide range of valuable biological and pharmaceutical properties such as antibacterial,⁸ antiviral,⁹ anti-inflammatory,¹⁰ anti-depressants and antimalarial activities.¹¹ These compounds have been also found to be as antagonists for paralyzing action of zoxazolamine.¹² As well as, these compounds can be used as dyes,¹³ in laser technology,¹⁴ photodynamic therapy,¹⁵ pH-sensitive fluorescent materials for the visualization of biomolecules assemblies.¹⁶ In recent years, many different methods have been reported for the synthesis of xanthene derivatives *via* three-component reaction promoted by various catalysts such as silica chloride,¹⁷ alum,¹⁸ p-dodecylbenzenesulfonic acid,¹⁹ cyanuric chloride,²⁰ $\text{FeCl}_3/\text{SiO}_2$,²¹ $\text{SbCl}_3/\text{SiO}_2$,²² $\text{HClO}_4/\text{SiO}_2$,²³ sulfamic acid-ionic liquid,²⁴ iodine,²⁵ $\text{ZrO}(\text{OTf})_2$,²⁶ selectfluorTM,²⁷ $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$,²⁸ silica sulfuric acid²⁹ and so on. Although some of the

*For correspondence

procedures reported for the synthesis of these heterocyclic compounds are valuable, most of them have problems such as moderate yields of products, long reaction times, harsh reaction conditions, the use of toxic organic solvents and expensive catalyst.

Therefore, we now wish to report a simple and efficient method for the synthesis of xanthene derivatives *via* one-pot three-component reaction of aromatic aldehyde and dimedone or β -naphthol using a novel nanostructure zeolite X (Fe-X) as an efficient, reusable and non-toxic catalyst.

2. Experimental

2.1 General information

All materials were prepared from Merck or Fluka Company. The IR spectra of the compounds were recorded on a Shimadzu 435-U-04 spectrophotometer (KBr pellets). ^1H NMR and ^{13}C NMR data were obtained using a Bruker AVANCE 300 MHz. A Bamstead Electrothermal apparatus was used to measure the melting points and was uncorrected. The structure of Fe-NaX zeolite was determined using a Holland Philips Xpert X-ray powder diffraction (XRD). Analysis of elemental content of the catalyst was determined by energy dispersive X ray spectroscopy (EDX) model MIRA III. The morphology of Fe-NaX and size of nano-particles were determined by scanning electron microscopy (SEM) model MIRA III.

2.2 Catalyst preparation

First, $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ (1.5 g) was dissolved in 100 mL distilled water and zeolite X (3 g) was added and then stirred at 50 °C for 24 h. After that, the precipitate was filtered. Then distilled water (100 mL) was added to the separated precipitate and the reaction mixture was stirred at room temperature and during stirring, hydrazine was added. Then, the obtained product was filtered and washed with distilled water and dried in oven for 3 h at 150 °C. For complete reduction of iron ions, the obtained precipitate containing iron particles was dissolved in distilled water (100 mL), and stirring at room temperature and then a solution of NaBH_4 (0.3 g) in distilled water was added dropwise to the mixture. After 30 min the reaction mixture was filtered and dried in oven for 4 h at 150 °C.

2.3 General procedure for the preparation of xanthenes derivatives

A mixture of dimedone **1a** (2 mmol) or β -naphthol **1b** (2 mmol), aromatic aldehyde **2** (1 mmol) and Fe-X (25 mg) was prepared and heated at 90 °C under solvent-free

condition. After the completion of the reaction as monitored by TLC (*n*-hexane/EtOAc, 3:1), hot ethanol (10 mL) was added to the reaction mixture and filtrated for catalyst separation. Then the catalyst washed with ethanol and dried at 120 °C for 2 h. The reaction mixture was cooled to room temperature and the obtained precipitate was filtered and washed with ethanol. Further purification was down by recrystallization in ethanol (Table 2).

2.4 Physical and spectral data of products

2.4a 3,3,6,6-Tetramethyl-9-phenyl-1,8-dioxooctahydroxanthene (**3a**): IR (KBr, ν_{max} cm^{-1}): 3028, 2961, 1662, 1624, 1454, 1197. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, ppm): δ 1.00 (s, 6H, 2CH₃); 1.11 (s, 6H, 2CH₃), 2.19–2.22 (m, 4H, 2CH₂), 2.48 (s, 4H, 2CH₂), 4.76 (s, 1H, CH), 7.22–7.13 (m, 5H, ArH).

2.4b 3,3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxooctahydroxanthene (**3b**): IR (KBr, ν_{max} cm^{-1}): 3044, 2964, 1661, 1624, 1469, 1198. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, ppm): δ 1.00 (s, 6H, 2CH₃), 1.11 (s, 6H, 2CH₃), 2.20–2.23 (m, 4H, 2CH₂), 2.47 (s, 4H, 2CH₂), 4.72 (s, 1H, CH), 7.20–7.27 (m, 4H, ArH).

2.4c 3,3,6,6-Tetramethyl-9-(4-Bromophenyl)-1,8-dioxooctahydroxanthene (**3c**): IR (KBr, ν_{max} cm^{-1}): 3081, 2966, 1659, 1623, 1470, 1199. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, ppm): δ 1.00 (s, 6H, 2CH₃), 1.13 (s, 6H, 2CH₃), 2.15–2.28 (m, 4H, 2CH₂), 2.52 (s, 4H, 2CH₂), 4.85 (s, 1H, CH), 7.27–8.02 (m, 4H, ArH).

2.4d 3,3,6,6-Tetramethyl-9-(3-Bromophenyl)-1,8-dioxooctahydroxanthene (**3d**): IR (KBr, ν_{max} cm^{-1}): 3078, 2960, 1669, 1620, 1460, 1189. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, ppm): δ 1.00 (s, 6H, 2CH₃), 1.14 (s, 6H, 2CH₃), 2.19–2.21 (m, 4H, 2CH₂), 2.49 (s, 4H, 2CH₂), 4.85 (s, 1H, CH), 7.28–8.09 (m, 4H, ArH).

2.4e 3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxooctahydroxanthene (**3e**): IR (KBr, ν_{max} cm^{-1}): 3058, 2962, 1666, 1615, 1519, 1467, 1352, 1200. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, ppm): δ 0.99 (s, 6H, 2CH₃), 1.12 (s, 6H, 2CH₃), 2.14–2.29 (m, 4H, 2CH₂), 2.51 (t, $j = 18.7$ Hz, 4H, 2CH₂), 4.83 (s, 1H, CH), 7.48 (d, $J = 9$ Hz, 2H, ArH), 7.62 (d, $J = 8$ Hz, 2H, ArH), 8.09 (d, $J = 8$ Hz, 2H, ArH).

2.4f 3,3,6,6-Tetramethyl-9-(3-nitrophenyl)-1,8-dioxooctahydroxanthene (**3f**): IR (KBr, ν_{max} cm^{-1}): 3060, 2961, 1666, 1622, 1529, 1474, 1351, 1200. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, ppm): δ 1.01 (s, 6H, 2CH₃), 1.13 (s, 6H, 2CH₃), 2.18–2.22 (m, 4H, 2CH₂), 2.51 (d, 4H, 2CH₂), 4.85 (s, 1H, CH), 7.56 (t, $J = 7.7$ Hz, 1H, ArH), 7.66 (d, $J = 7.6$ Hz, 1H, ArH), 7.99 (d, $j = 8.2$, 1H, ArH), 8.00 (s, 1H, ArH).

2.4g 3,3,6,6-Tetramethyl-9-(4-Cyanophenyl)-1,8-dioxooctahydroxanthene (**3g**): IR (KBr, ν_{max} cm^{-1}): 3050, 2950, 2210, 1660, 1620, 1460, 1200. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, ppm): δ 0.99 (s, 6H, 2CH₃), 1.13 (s, 6H, 2CH₃),

2.17–2.23 (m, 4H, 2CH₂), 2.5 (d, 4H, 2CH₂), 4.78 (s, 1H, CH), 7.43 (d, $J = 9.6$ Hz, $J = 1.6$ Hz, 2H, ArH), 7.54 (d, $J = 6.6$ Hz, $J = 1.6$ Hz, 2H, ArH).

2.4h 3,3,6,6-Tetramethyl-9-(4-Hydroxyphenyl)-1,8-dioxooctahydroxanthene (**3h**): IR (KBr, ν_{\max} cm⁻¹): 3498, 3078, 2929, 1719, 1645, 1465, 1166. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 1.00 (s, 6H, 2CH₃), 1.11 (s, 6H, 2CH₃), 2.12–2.18 (m, 4H, 2CH₂), 2.45 (s, 4H, 2CH₂), 4.61 (s, 1H, CH), 6.77 (d, $j = 8$ Hz, 2H, ArH.), 6.93 (d, $j = 8$ Hz, 2H, ArH).

2.4i 3,3,6,6-Tetramethyl-9-(4-Methoxyphenyl)-1,8-dioxooctahydroxanthene (**3i**): IR (KBr, ν_{\max} cm⁻¹): 3050, 2958, 1658, 1625, 1439, 1261, 1195. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 1.00 (s, 6H, 2CH₃), 1.11 (s, 6H, 2CH₃), 2.20–2.22 (m, 4H, 2CH₂), 2.47 (s, 4H, 2CH₂), 3.74 (s, 3H, OCH₃), 4.71 (s, 1H, CH), 6.76 (d, $J = 9$ Hz, 2H, ArH), 7.22 (d, $J = 9$ Hz, 2H, ArH).

2.4j 3,3,6,6-Tetramethyl-9-(3-Methoxyphenyl)-1,8-dioxooctahydroxanthene (**3j**): IR (KBr, ν_{\max} cm⁻¹): 3020, 2950, 1650, 1618, 1459, 1235, 1160. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 0.99 (s, 6H, 2CH₃), 1.12 (s, 6H, 2CH₃), 2.30–2.45 (m, 4H, 2CH₂), 2.54–2.71 (m, 4H, 2CH₂), 3.81 (s, 3H, OCH₃), 4.83 (s, 1H, CH), 6.69–6.71 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 1H), 6.89–6.95 (m, 2H), 7.17 (t, $J = 8.0$ Hz, 1H).

2.4k 3,3,6,6-Tetramethyl-9-(2-Methoxyphenyl)-1,8-dioxooctahydroxanthene (**3k**): IR (KBr, ν_{\max} cm⁻¹): 3015, 2950, 1660, 1623, 1490, 1250, 1198. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 0.97 (s, 6H, 2CH₃), 1.11 (s, 6H, 2CH₃), 2.14–2.23 (m, 4H, 2CH₂), 2.39–2.48 (d, $j = 17.4$, 4H, 2CH₂), 3.79 (s, 3H, OCH₃), 4.87 (s, 1H, CH), 6.77 (d, $J = 8$ Hz, 1H, ArH), 6.89 (dt, $J = 7.4$ Hz, $J = 1.2$ Hz, 1H, ArH), 7.12 (m, 1H, ArH), 7.43 (dd, $J = 7.4$ Hz, $J = 1.6$ Hz, 1H, ArH).

2.4l 3,3,6,6-Tetramethyl-9-(4-Hydroxy-3-methoxyphenyl)-1,8-dioxooctahydroxanthene (**3l**): IR (KBr, ν_{\max} cm⁻¹): 3694, 3065, 2972, 1665, 1608, 1410, 1169. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 1.00 (s, 6H, 2CH₃), 1.09 (s, 6H, 2CH₃), 2.20 (s, 4H, 2CH₂), 2.44 (s, 4H, 2CH₂), 3.88 (s, 3H, OCH₃), 4.65 (s, 1H, CH), 5.46 (s, 1H), 6.53–6.58 (dd, $J = 2.0$, 8.1 Hz, 1H), 6.71 (d, $J = 8.2$ Hz, 1H), 7.00 (d, $J = 2.0$ Hz, 1H).

2.4m 14-(Phenyl)-14H-dibenzo[*a,j*]xanthene (**4a**): IR (KBr, ν_{\max} cm⁻¹): 3050, 1620, 1470, 1250. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 6.51 (s, 1H, CH), 6.99–8.43 (m, 17H, ArH).

2.4n 14-(4-chlorophenyl)-14H-dibenzo[*a,j*]xanthene (**4b**): IR (KBr, ν_{\max} cm⁻¹): 3069, 1622, 1459, 1240. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 6.49 (s, 1H, CH), 7.11–8.35 (m, 16H, ArH).

2.4o 14-(3-chlorophenyl)-14H-dibenzo[*a,j*]xanthene (**4c**): IR (KBr, ν_{\max} cm⁻¹): 3073, 2900, 1619, 1456, 1239. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 6.51 (s, 1H, CH), 6.96–8.37 (m, 16H, ArH).

2.4p 14-(2-chlorophenyl)-14H-dibenzo[*a,j*]xanthene (**4d**): IR (KBr, ν_{\max} cm⁻¹): 3055, 2920, 1625, 1410, 1256. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 5.69 (s, 1H, CH), 5.82–7.65 (m, 16H, ArH).

2.4q 14-(4-Bromophenyl)-14H-dibenzo[*a,j*]xanthene (**4e**): IR (KBr, ν_{\max} cm⁻¹): 3030, 1624, 1429, 1254. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 6.63 (s, 1H, CH), 7.32–8.44 (m, 16H, ArH).

2.4r 14-(4-Nitrophenyl)-14H-dibenzo[*a,j*]xanthene (**4f**): IR (KBr, ν_{\max} cm⁻¹): 3065, 1621, 1458, 1250. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 6.62 (s, 1H, CH), 7.46–8.31 (m, 16H, ArH).

2.4s 14-(3-Nitrophenyl)-14H-dibenzo[*a,j*]xanthene (**4g**): IR (KBr, ν_{\max} cm⁻¹): 3070, 1619, 1452, 1254. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 6.64 (s, 1H, CH), 7.29–8.44 (m, 16H, ArH).

2.4t 14-(4-Methoxyphenyl)-14H-dibenzo[*a,j*]xanthene (**4h**): IR (KBr, ν_{\max} cm⁻¹): 3060, 1634, 1457, 1399, 1247, 1200. ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ 6.40 (s, 1H, CH), 7.32–8.35 (m, 16H, ArH).

2.4u 9-(4-Formylphenyl)-1,8-dioxooctahydroxanthene: IR (KBr, ν_{\max} cm⁻¹): 3021, 2968, 2845, 2756, 1661, 1620, 1454, 1197. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.91 (s, 6H, 2CH₃), 1.07 (s, 6H, 2CH₃), 2.09–2.35 (m, 8H, 4CH₂), 5.3 (s, 1H, CH), 6.85 (d, 1H, ArH), 7.06 (d, 1H, ArH), 7.63 (d, 1H, ArH), 9.78 (d, 1H, CH), 11.68 (s, 1H). ¹³C NMR (300 MHz, CDCl₃, ppm): δ 27.45, 27.5, 29.62, 31.44, 31.49, 32.39, 33.33, 46.41, 46.99, 115.13, 115.27, 115.55, 126.63, 126.74, 127.44, 129.79, 134.32, 135.5, 145.93, 189.34, 190.54, 191.78.

3. Results and Discussion

3.1 Characterization of the catalyst

The Fe nanoparticles were loaded in zeolite X and the new nanostructure zeolite (Fe-X) was characterized by FT-IR, XRD, EDS and SEM techniques.

Figure 1 shows the FT-IR spectra of Fe-X catalyst. The observed peaks at 3440 cm⁻¹ and 1620 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibration of the OH and H-O-H groups. The absorption showed at about 1080 cm⁻¹ is related to the asymmetric stretching vibration of the Si-O and Al-O bonds and the weak peak located at 470 cm⁻¹ assign the bending vibrations of O-Si-O and O-Al-O.³⁰

As shown in Figure 2, the XRD pattern of Fe-X catalyst (Figure 2, b) is identical to that of NaX zeolite (Figure 2, a) which proved the zeolite structure retained unchanged based on incorporation of Fe nanoparticles into the X zeolite. However, relative decreasing in the peak intensity can be related to the

loading of Fe nanoparticles which its presence proved by EDS technique. Furthermore, the peak appearing at $2\theta=45$ clearly demonstrate the presence of Fe NPs in the zeolite X structure.³¹

Figure 3 shown the EDS spectrum of Fe-X catalyst, that confirms the presence of Fe nanoparticles in the new zeolite structure. The Si/Al ratio in the Fe-X catalyst based on EDS data is estimated about 1.07 which is in accordance with the NaX zeolite.

The morphology of Fe-X catalyst and the size distribution of the Fe NPs were determined by SEM technique (Figure 4). As clearly shown in this micrograph, nanoparticles of Fe are almost spherical and have a regular shape and the average size of nanoparticles was estimated about 21 nm in Fe-X nanostructure. The uniform distribution of Fe NPs on the zeolite surface is also observable.

3.2 Catalytic activity studies

3.2a Synthesis of xanthen derivatives

In continuation of our efforts on the development of new and efficient catalytic system for the green syntheses of biologically active heterocycles,^{32–38} herein we wish to report a simple and highly efficient method for the preparation of two classes of xanthen derivatives by condensation of aromatic aldehyde with

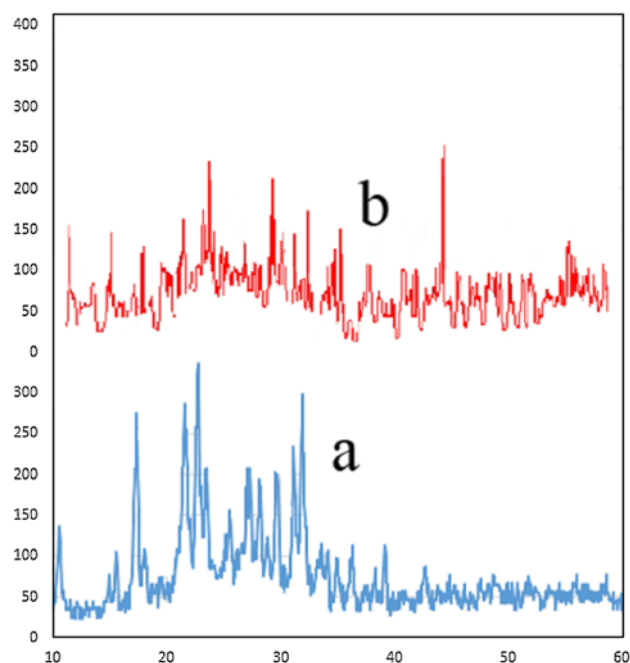


Figure 2. XRD patterns of (a) zeolite X and (b) Fe-X catalyst.

2 equivalents of dimedone or β -naphthol using Fe-X as a new nanostructure catalyst.

At first, to optimize the reaction condition for the synthesis 1,8-dioxooctahydroxanthen, the reaction of dimedone (2 mmol) and benzaldehyde (1 mmol) in the

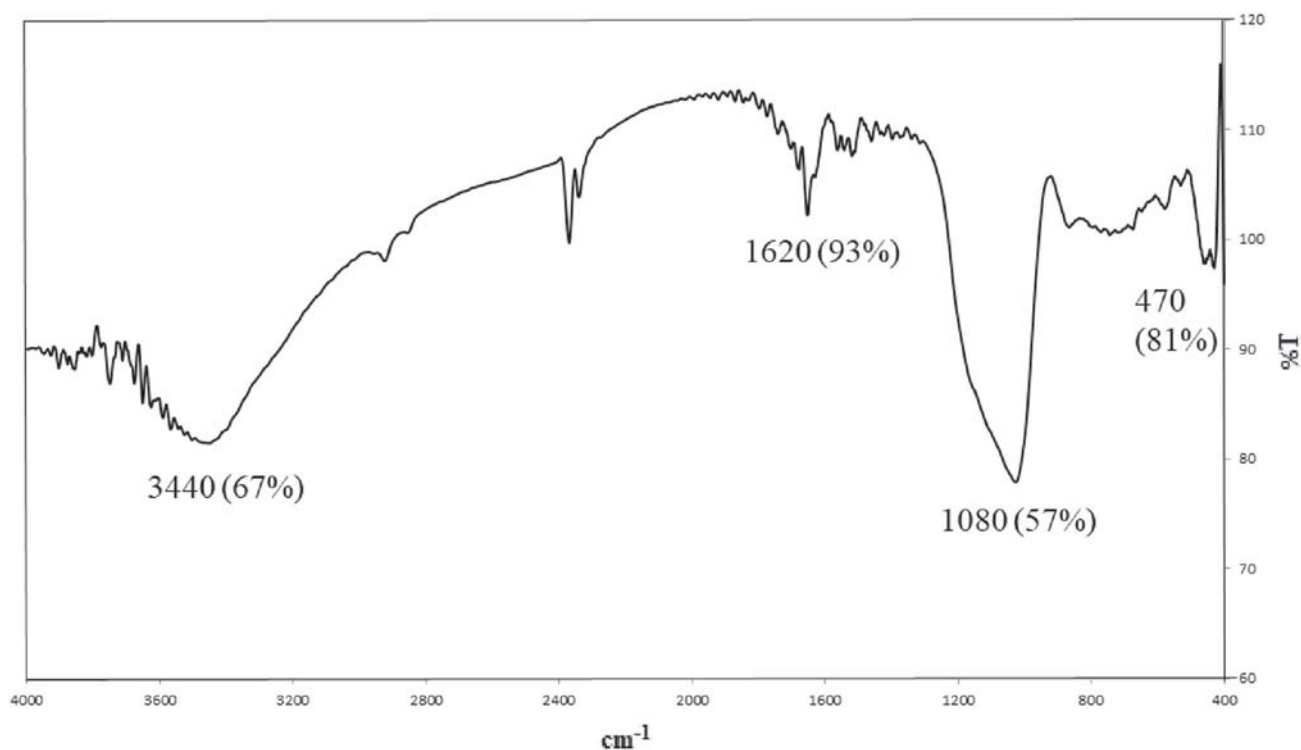


Figure 1. FT-IR spectra of Fe-X catalyst.

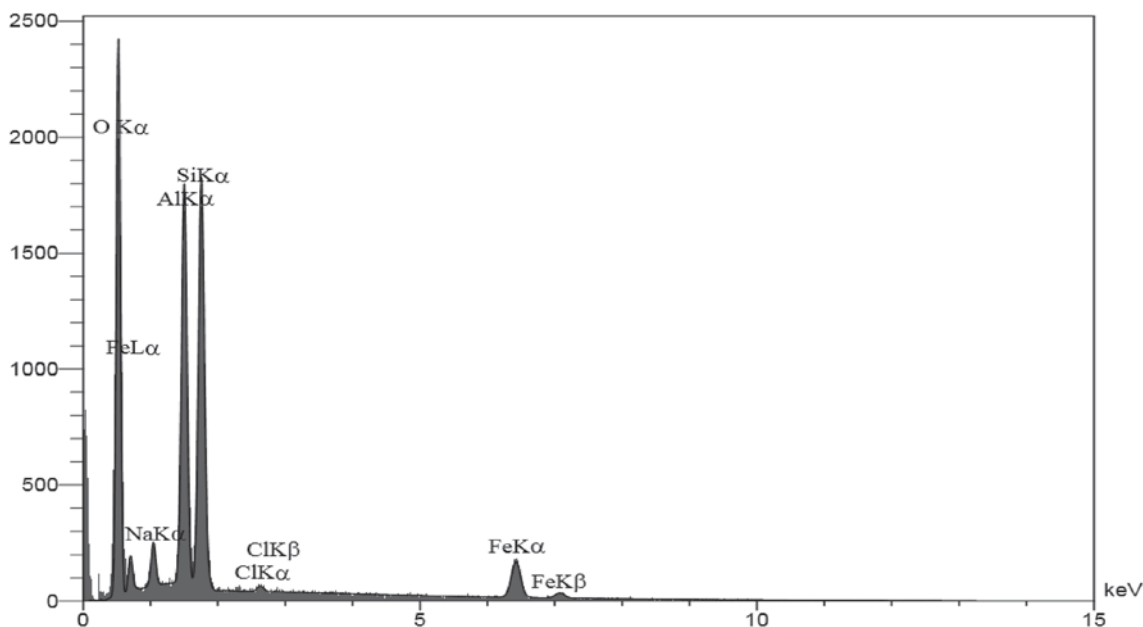


Figure 3. EDS spectra of Fe-X catalyst.

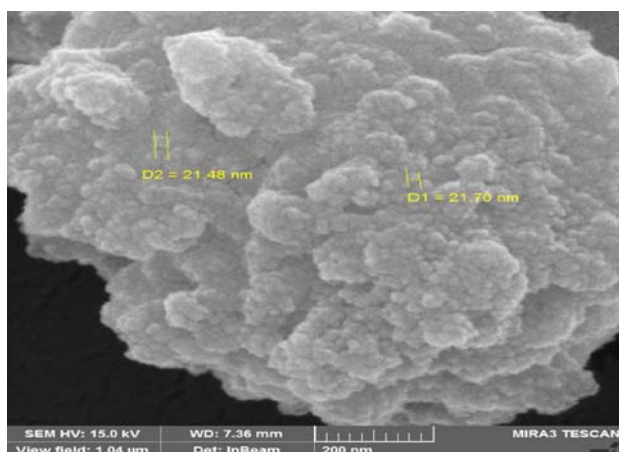


Figure 4. SEM micrograph of Fe-X zeolite.

presence of Fe-X catalyst was selected as a model reaction. The effect of solvent, amount of the catalyst and the temperature were investigated in the model reaction. As shown in Table 1, the best result was obtained in the presence of 25 mg of Fe-X at 90 °C under solvent-free condition, which led to 95% yield after 15 min (Table 1, entry 3). Also, the model reaction was performed in the presence of zeolite NaX as the catalyst and without the catalyst under optimized reaction conditions. The results show that zeolite X has low catalytic activity (Table 1, entry 13) and in the absence of catalyst, a trace amount of the product was obtained after 120 min (Table 1, entry 14).

After optimization of the reaction conditions, this procedure was extended to various aromatic aldehydes

with either electron-donating or electron-withdrawing groups and dimedone under optimized reaction conditions and the corresponding 1,8-dioxooctahydroxanthenes derivative were formed in high to excellent yields and in very short times (Scheme 1, Table 2, entry 1–12).

After the successful application of Fe-X nanostructure catalyst in the synthesis of 1,8-dioxooctahydroxanthenes, we examined its applicability for preparation of 14-aryl-14H-dibenzo[*a,j*]xanthenes derivatives, by studying the reaction between β -naphthol (2 mmol) and different aromatic aldehydes (1 mmol) under optimized reaction condition (Scheme 2). As is shown in Table 2, the products were obtained in good yields and short times (Table 2, entry 13–20).

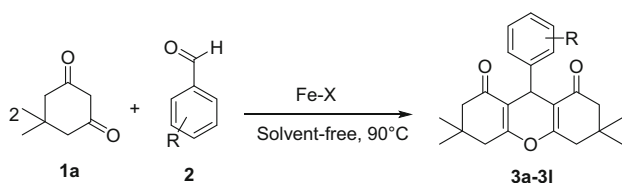
In Scheme 3, a reasonable mechanism has been proposed for the preparation of xanthene derivatives in the presence of Fe-X nanostructure composite.

3.3 Chemoselectivity of the catalyst

In order to investigate the selectivity of the current method terphthalaldehyde was treated with 2 and 4 equivalence dimedone under optimized conditions. It was found that in both experiments 9-(4-formylphenyl)-1,8-dioxooctahydroxanthene was exclusively generated in 90% yield after 15 min and phenylene-bis-xanthene was not observed in these reaction mixtures (Scheme 4).

Table 1. Optimization of the reaction conditions.

| Entry ^a | Catalyst (mg) | Solvent | Condition | Time (min) | Yield ^b (%) |
|--------------------|----------------|-------------------------------|-----------|------------|------------------------|
| 1 | Fe-X (10) | – | 90 °C | 28 | 85 |
| 2 | Fe-X (15) | – | 90 °C | 20 | 90 |
| 3 | Fe-X (25) | – | 90 °C | 15 | 95 |
| 4 | Fe-X (35) | – | 90 °C | 15 | 90 |
| 5 | Fe-X (25) | – | rt | 100 | 25 |
| 6 | Fe-X (25) | – | 60 °C | 30 | 90 |
| 7 | Fe-X (25) | H ₂ O | Reflux | 50 | 75 |
| 8 | Fe-X (25) | Ethanol | Reflux | 80 | 55 |
| 9 | Fe-X (25) | H ₂ O/Ethanol(1:1) | Reflux | 50 | 60 |
| 10 | Fe-X (25) | Chloroform | Reflux | 40 | 48 |
| 11 | Fe-X (25) | <i>n</i> -hexane | Reflux | 40 | 40 |
| 12 | Fe-X (25) | Ethyl acetate | Reflux | 90 | 30 |
| 13 | Zeolite X (25) | – | 90 °C | 15 | 50 |
| 14 | – | – | 90 °C | 120 | Trace |

^aDimedone (2 mmol), benzaldehyde (1 mmol).^bIsolated yields.**Scheme 1.** Synthesis of 1,8-dioxo-octahydroxanthens derivatives catalyzed by Fe-X.

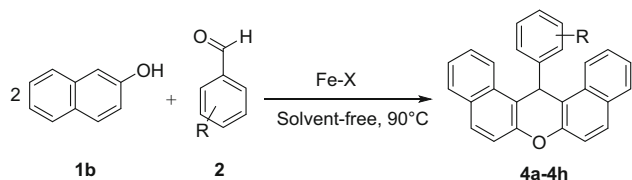
3.4 Reusability of the catalyst

The reusability of the catalyst was also examined in the model reaction under optimized reaction condition. After completion of the reaction, EtOH (10 mL) was added to the reaction mixture and the catalyst was separated by filtration, washed with acetone and dried at 120 °C under vacuum for 2 h. The recovered

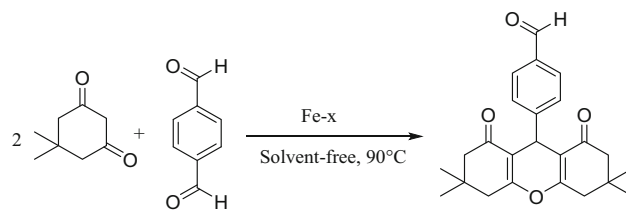
Table 2. Synthesis of xanthene derivatives catalyzed by Fe-X nanostructure composite.

| Entry | 1 | 2 | Product | Time (min) | Yield (%) ^a | M.p. (°C) | |
|-------|----|--|-----------|------------|------------------------|-----------|-----------------------|
| | | | | | | Found | Reported |
| 1 | 1a | PhCHO | 3a | 15 | 95 | 200-203 | 203-205 ³⁹ |
| 2 | 1a | 4-Cl-C ₆ H ₄ CHO | 3b | 25 | 93 | 232-234 | 233-235 ³⁹ |
| 3 | 1a | 4-Br-C ₆ H ₄ CHO | 3c | 25 | 90 | 236-238 | 237-239 ³⁹ |
| 4 | 1a | 3-Br-C ₆ H ₄ CHO | 3d | 29 | 87 | 190-193 | 190-192 ⁴⁰ |
| 5 | 1a | 4-NO ₂ -C ₆ H ₄ CHO | 3e | 20 | 93 | 223-226 | 224-226 ³⁹ |
| 6 | 1a | 3-NO ₂ -C ₆ H ₄ CHO | 3f | 23 | 90 | 166-169 | 168-170 ³⁹ |
| 7 | 1a | 4-CN-C ₆ H ₄ CHO | 3g | 25 | 90 | 219-221 | 220-222 ⁴¹ |
| 8 | 1a | 4-OH-C ₆ H ₄ CHO | 3h | 40 | 83 | 245-247 | 246-248 ⁴⁰ |
| 9 | 1a | 4-MeO-C ₆ H ₄ CHO | 3i | 60 | 80 | 243-246 | 243-245 ⁴¹ |
| 10 | 1a | 3-MeO-C ₆ H ₄ CHO | 3j | 50 | 80 | 189-192 | 190-191 ⁴² |
| 11 | 1a | 2-MeO-C ₆ H ₄ CHO | 3k | 50 | 80 | 208-210 | 210-212 ⁴² |
| 12 | 1a | 4-OH-3-OMe-C ₆ H ₄ CHO | 3l | 40 | 85 | 225-228 | 225-227 ⁴⁰ |
| 13 | 1b | PhCHO | 4a | 30 | 85 | 185-187 | 186-187 ³⁹ |
| 14 | 1b | 4-Cl-C ₆ H ₄ CHO | 4b | 40 | 85 | 289-291 | 290-292 ³⁹ |
| 15 | 1b | 3-Cl-C ₆ H ₄ CHO | 4c | 45 | 80 | 204-206 | 207-209 ⁴¹ |
| 16 | 1b | 2-Cl-C ₆ H ₄ CHO | 4d | 45 | 80 | 215-217 | 216-218 ³⁹ |
| 17 | 1b | 4-Br-C ₆ H ₄ CHO | 4e | 40 | 85 | 292-294 | 294-295 ⁴² |
| 18 | 1b | 4-NO ₂ -C ₆ H ₄ CHO | 4f | 40 | 85 | 310-313 | 312 ³⁹ |
| 19 | 1b | 3-NO ₂ -C ₆ H ₄ CHO | 4g | 45 | 83 | 214-217 | 212-213 ³⁹ |
| 20 | 1b | 4-MeO-C ₆ H ₄ CHO | 4h | 70 | 75 | 198-201 | 200-202 ³⁹ |

^aIsolated yields.



Scheme 2. Synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthenes derivatives catalyzed by Fe-X.



Scheme 4. Selective synthesis of 9-(4-formylphenyl)-1,8-dioxooctahydroxanthene using Fe-X.

catalyst was reused in the same reaction. Recovery and reuse of the catalyst were repeated for 10 times, without significant decrease in this nanostructure catalyst activity. Results are summarized in Table 3.

4. Conclusions

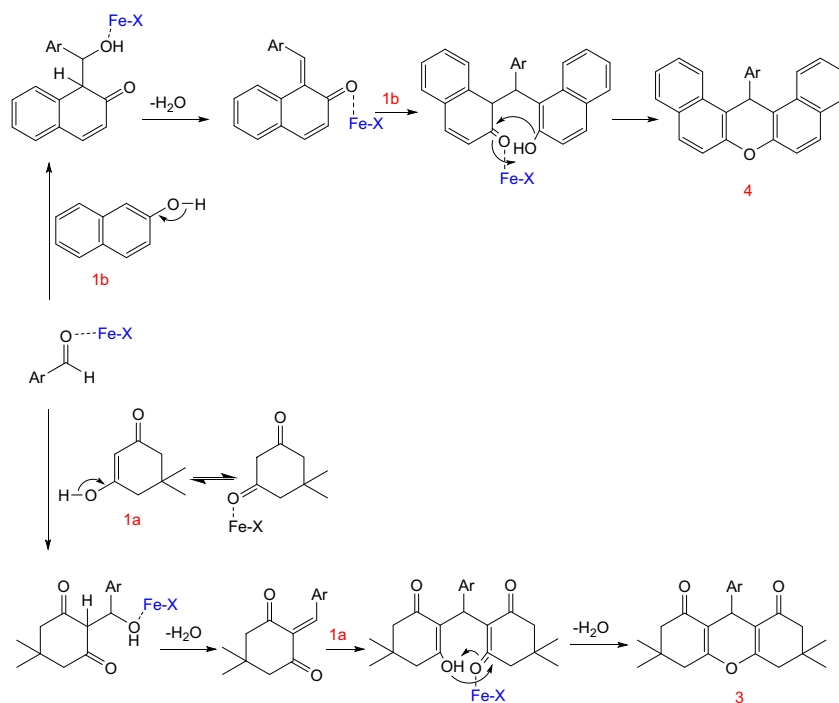
In conclusion, Fe nanoparticles loaded zeolite X (Fe-X) has been synthesized and characterized by FT-IR, XRD, EDS and SEM techniques. Spectroscopic analyses not only confirm the proposed structure of the catalyst but also, demonstrate the nano nature and crystalline character of this nanostructure zeolite. The catalytic activity of nanostructure Fe-X zeolite has been investigated in the synthesis of two series of xanthene derivatives; 1,8-dioxooctahydroxanthenes and 14-aryl-14H-dibenzo[*a,j*]xanthenes, from one-pot

Table 3. Reusability of Fe-X in the preparation of 1,8-dioxooctahydroxanthenes from benzaldehyde and dimedone.

| Run no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|------------------------|----|----|----|----|----|----|----|----|----|----|
| Yield ^a (%) | 93 | 93 | 90 | 90 | 87 | 85 | 85 | 85 | 85 | 85 |

^aIsolated yield.

three-component condensation of aromatic aldehydes and dimedone or β -naphthol. High yields of products, short reaction time, easy work-up procedure, absence of solvent, in combination with non-toxicity, easy separation, high activity, nano character and reusability of the catalyst are a valuable advantage of this method.



Scheme 3. Proposed mechanism for the synthesis of xanthene derivatives using Fe-X.

Acknowledgements

The author is grateful to the research council of Hakim Sabzevari University for partial support of this work.

References

- Sersale R 1985 Natural zeolites: processing, present and possible applications *Stud. Surf. Sci. Catal.* **24** 503
- Parveen A, Ahmed M R S, Shaikh K A, Deshmukh S P and Pawar R P 2007 Efficient synthesis of 2, 4, 5-triaryl substituted imidazoles under solvent free conditions at room temperature *Arkivoc.* **16** 12
- Breck D W 1974 *Zeolite Molecular Sieves* (New York: Wiley)
- Flanigen E M 1991 Zeolites and molecular sieves: an historical perspective *Stud. Surf. Sci. Catal.* **58** 13
- Choi E Y, Kim Y, Han Y W and Seff K 2000 Structure of a cyclopropane sorption complex of dehydrated fully Cd²⁺-exchanged zeolite A *Micropor. Mesopor. Mat.* **41** 61
- Bae D and Seff K 1999 Structures of cobalt (II)-exchanged zeolite X *Micropor. Mesopor. Mat.* **33** 265
- Sebastian J, Jinka K M and Jasra R V 2006 Effect of alkali and alkaline earth metal ions on the catalytic epoxidation of styrene with molecular oxygen using cobalt(II)-exchanged zeolite X *J. Catal.* **244** 208
- Veljović E, Špirtović-Halilović S, Kahrović E, Roca S, Novaković I, Osmanović A, Salihović M, Alagić D, Hastor B, Ljubunčić Dž and Završnik D 2016 Solvent-free synthesis and antibacterial activity of 14-aryl substituted dibenzoxanthene derivatives *Bull. Chem. Technol. Bosnia Herzegovina* **46** 33
- Naidu K R M, Krishna B S, Kumar M A, Arulselvan P, Khalivulla S I and Lasekan O 2012 Design, synthesis and antiviral potential of 14-aryl/heteroaryl-14H-dibenzo[a,j]xanthenes using an efficient polymer-supported catalyst *Molecules* **17** 7543
- Poupelin J P, Saint-Rut G, Fussard-Blanpin O, Narcisse G, Uchida-Ernouf G and Lakroix R 1978 Synthesis and antiinflammatory properties of bis(2-hydroxy-1-naphthyl) methane derivatives. I. Monosubstituted derivatives *Eur. J. Med. Chem.* **13** 67
- Chibale K, Visser M, Schalkwyk D V, Smith P J, Saravanamuthu A and Fairlamb A H 2003 Exploring the potential of xanthene derivatives as trypanothione reductase inhibitors and chloroquine potentiating agents *Tetrahedron* **59** 2289
- Saint-Ruf G, Hieu H T and Poupelin J P 1975 The effect of dibenzoxanthenes on the paralyzing action of zoxazolamine *Naturwissenschaften* **62** 584
- Peters A T and Bide M J 1985 Amino derivatives of 1,8-naphthalic anhydride and derived dyes for synthetic-polymer fibres *Dyes Pigm.* **6** 349
- Ahmad M, King T A, Ko D K, Cha B H and Lee J 2002 Performance and photostability of xanthene and pyrromethene laser dyes in sol-gel phases *J. Phys. D: Appl. Phys.* **35** 1473
- Ion R M, Frackowiak D, Planner A and Wiktorowicz K 1998 The incorporation of various porphyrins into blood cells measured via flow cytometry, absorption and emission spectroscopy *Acta Biochim. Pol.* **45** 833
- Knight C G and Stephens T 1989 Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH. Studies in phospholipid vesicles *Biochem. J.* **258** 683
- Das B, Thirupathi P, Reddy K R, Ravikanth B and Nagarapu L 2007 An efficient synthesis of 1,8-dioxooctahydroxanthenes using heterogeneous catalysts *Catal. Commun.* **8** 535
- Madje B R, Ubale M B, Bharad J V and Shingare M S 2010 Alum-promoted synthesis of 1,8-dioxooctahydroxanthenes in water *Afr. J. Chem.* **63** 36
- Jin T S, Zhang J S, Xiao J C, Wang A Q and Li T S 2004 Clean synthesis of 1,8-dioxooctahydroxanthene derivatives catalyzed by p-dodecylbenzenesulfonic acid in aqueous media *ChemInform* **35**
- Zhang Z H and Tao X Y 2008 2,4,6-Trichloro-1,3,5-triazine-promoted synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions *Aust. J. Chem.* **61** 77
- Shaterian H R, Hosseini A and Ghashang M 2008 Reaction in dry media: silica gel supported ferric chloride catalyzed synthesis of 1,8-dioxooctahydroxanthene derivatives *Phosphor. Sulfur Silicon.* **183** 3136
- Zhang Z H and Liu Y H 2008 Antimony trichloride/SiO₂ promoted synthesis of 9-ary-3,4,5,6,7,9-hexahydroxanthene-1,8-diones *Catal. Commun.* **9** 1715
- Kantevari S, Bantu R and Nagarapu L J 2007 HClO₄-SiO₂ and PPA-SiO₂ catalyzed efficient one-pot Knoevenagel condensation, Michael addition and cyclo-dehydration of dimedone and aldehydes in acetonitrile, aqueous and solvent free conditions: Scope and limitations *J. Mol. Catal. A Chem.* **269** 53
- Wu H, Chen X M, Wan Y, Xin H Q, Xu H H, Yue C H, Pang L L and Ma R 2009 Synthesis and Luminescence of 14-Aryl- or Alkyl-14H-dibenzo[a,j]xanthenes catalyzed by 2-1'-methylimidazolium-3-yl-1-ethyl sulfate *Synth. Commun.* **39** 3762
- Das B, Ravikanth B, Ramu R, Laxminarayana K and Rao B V 2006 Iodine catalyzed simple and efficient synthesis of 14-aryl or alkyl-14-H-dibenzo[a,j]xanthenes *J. Mol. Catal. A: Chem.* **255** 74
- Mohammadpoor-Baltork I, Moghadam M, Mirkhani V, Tangestaninejad S and Tavakoli H R 2011 Highly efficient and green synthesis of 14-aryl(alkyl)-14H-dibenzo[a,j]xanthene and 1,8-dioxooctahydroxanthene derivatives catalyzed by reusable zirconyl triflate [ZrO(OTf)₂] under solvent-free conditions *Chin. Chem. Lett.* **22** 9
- Kumar P S, Kumar B S, Rajitha B, Reddy P N, Sreenivasulu N and Reddy Y T 2006 A novel one pot synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes catalyzed by SelectfluorTM under solvent free conditions *Arkivoc.* **12** 46
- Dabiri M, Baghbanzadeh M, Nikcheh M S and Arzroomchilar E 2008 Eco-friendly and efficient one-pot synthesis of alkyl- or aryl-14H-dibenzo[a,j]xanthenes in water *Bioorg. Med. Chem. Lett.* **18** 436
- Wu L, Zhang J, Fang L, Yang C and Yan F 2010 Silica chloride catalyzed synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-diones *Dyes Pigm.* **86** 93
- Baghbanian S M, Rezaei N and Tashakkorian H 2013 Nanozeolite clinoptilolite as a highly efficient

- heterogeneous catalyst for the synthesis of various 2-amino-4H-chromene derivatives in aqueous media *Green Chem.* **15** 3446
31. Singhal R K, Gangadhar B, Basu H and Manisha V 2012 Remediation of malathion contaminated soil using zero valent iron nano-particles *Am. J. Anal. Chem.* **3** 76
 32. Hojati S F, Amiri A and Raouf H 2017 Efficient four-component synthesis of spiroindole derivatives catalysed by a versatile and reusable nano-paramagnetic catalyst *Appl. Organomet. Chem.* **31** 3595
 33. Hojati S F and Raouf H 2016 Ionic Liquid for One-pot Synthesis of Spiro [indoline-3,4'-pyrano[2,3-c]pyrazoles] *Org. Prep. Proc. Int.* **48** 474
 34. Hojati S F, Moosavifar M and Ghorbanipoor T 2017 The improvement in nano composite host (nano cavity of dealuminated zeolite Y)-gest (12-molibdophosphoric acid) catalytic activity and its application in one-pot three-component synthesis of tetrahydrobenzo[b]pyrans *C. R. Chem.* **20** 520
 35. Hojati S F, Amiri A, Mohamadi S and Moeini Eghbali N 2018 Novel organometallic nanomagnetic catalyst for multicomponent synthesis of spiroindoline derivatives *Res. Chem. Int.* **44** 2275
 36. Hojati S F, Amiri A, Moeini Eghbali N and Mohamadi S 2018 Polypyrrole/Fe₃O₄/CNT as a recyclable and highly efficient catalyst for one-pot three-component synthesis of pyran derivatives *Appl. Organomet. Chem.* **32** 4235
 37. Keshavarz M, Abdoli-Senejani M, Hojati S F and Moosavifar M 2017 Novel and highly efficient heteropoly acids for one-pot mild and green synthesis of xanthene derivatives *Org. Prep. Proc. Int.* **49** 549
 38. Keshavarz M, Abdoli-Senejani M, Hojati S F and Askari S 2018 Fe₃O₄ magnetic nanoparticles coated with a copolymer: a novel reusable catalyst for one-pot three-component synthesis of 2-amino-4H-chromen *React. Kin. Mech. Catal.* **124** 757
 39. Maleki B, Gholizadeh M and Bull Z 2011 1,3,5-Trichloro-2,4,6-triazinetriion: a versatile heterocycle for the one-pot synthesis of 14-aryl-or alkyl-14H-dibenzo[a,j]xanthene, 1,8-dioxooctahydroxanthene and 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one derivatives under solvent-free conditions *Korean Chem. Soc.* **32** 1697
 40. Venkatesan K, Pujari S S, Lahoti R J and Srinivasan K V 2008 An efficient synthesis of 1,8-dioxo-octahydroxanthene derivatives promoted by a room temperature ionic liquid at ambient conditions under ultrasound irradiation *Ultrason. Sonochem.* **15** 548
 41. Zolfigol M A, Khakyzadeh V, Moosavi-Zare A R, Zare A, Azimi S B, Asgari Z and Hasaninejad A 2012 *C. R. Chemie.* **15** 719
 42. Shirini F, Abedini M and Pourhasan R 2013 A novel polymeric and reusable catalyst for the preparation of xanthenes derivatives *Dyes Pigm.* **99** 250