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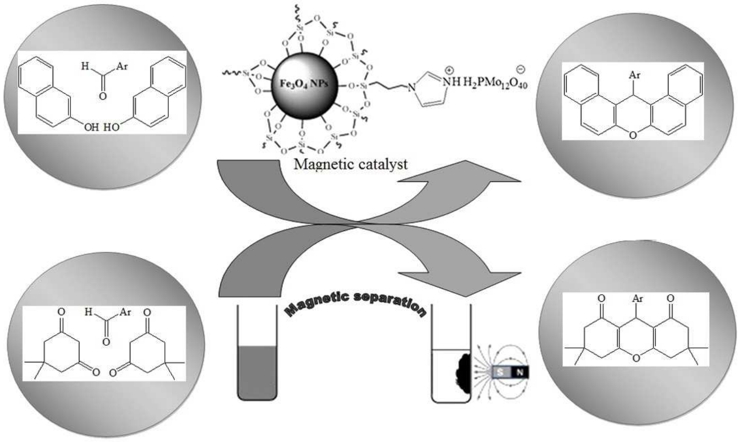
Graphical abstract

Synthesis of 14-aryl- or alkyl -14H-dibenzo[a,j]xanthenes and 1,8 dioxooctahydro xanthene derivatives by Fe3O4@SiO2-imid-PMA nanocatalysts



$Fe_3O_4@SiO_2$-imid-PMA^n magnetic porous nanosphere as recyclable catalyst for the one-pot synthesis of 14-aryl- or alkyl -14H-dibenzo[a,j]xanthenes and 1,8 dioxooctahydro xanthene derivatives under various conditions

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Abstract

A facile, efficient and environmentally-friendly protocol for the synthesis of 14-aryl- or alkyl-14H-dibenzo[a,j] xanthenes and 1,8-dioxooctahydroxanthenes has been developed by one-pot condensation of various aldehydes with (i) β-naphthol and (ii) cyclic 5,5-dimethyl-1,3-cyclohexanedion, in the presence of $Fe_3O_4@SiO_2$-Imid- $H_3PMo_{12}O_{40}$ nanoparticles as magnetic catalyst under various conditions. Different types of aromatic and aliphatic aldehydes are used in the reaction and in all cases the products synthesized successfully. The present approach offers several advantages such as short reaction times, high yields, easy purification, a cleaner reaction and ease of recovery and reusability of the catalyst by magnetic field. Also, the aforementioned nanocatalyst can be easily recovered by a magnetic field and reused for subsequent reactions for at least 5 times without noticeable deterioration in catalytic activity.

Keywords

Magnetic catalyst, One-pot synthesis, Aldehydes, β-Naphthol, 5,5-dimethyl-1,3-cyclohexanedion

1. Introduction

In recent years, Keggin-type heteropolyacids (HPAs) such as $H_3PMo_{12}O_{40}$ (PMA) have been used as efficient catalysts for a variety of organic reactions because of their superacidic and redox properties, low toxicity, ease of handling, low cost, high thermal stability, high proton mobility, water tolerance, recoverability and reusability [1]. Although HPAs are versatile compounds in their acidic form, their main disadvantages are high solubility in polar solvents and low surface area (<10 m^2/g). Therefore, in a homogeneous reaction the isolation of the products and the reuse of the catalyst after reaction become difficult [1]. Therefore, in order to overcome this problem, these materials disperse on supports (such as silica, acidic ion-exchange resins, active carbon and nano-titania) which possess large surface area. The use of support allows the heteropolyacids to be dispersed over a large surface area and increases theirs catalytic activity [2-3]. Conventionally, heterogeneous catalysis is favored over homogeneous catalysis due to its ease of handling and regenerability [3-5]. However, in practice, the separation and recovery of these heterogeneous nanocatalysts from the reaction medium by using standard techniques such as filtration and centrifugation is not always easy due to the nanometric size of the particles [6-8]. To overcome this drawback, magnetic nanomaterials are supported over a variety of organic and inorganic supports, and their magnetic properties enables the simple and efficient recovery of the catalyst by means of an external magnet [9-14].

The magnetic nanoparticles utilized as supports usually consist of core-shell structures; being iron oxides (FexOy) the most commonly used ones. The coating of these magnetic nanomaterials prevents aggregation/oxidation and serves as platform for the catalyst. For this purpose, silica has been widely used because of its stability under different reaction conditions and due to the fact that it can be easily functionalized for diverse applications. Recently, a number of functionalized Fe_3O_4 nanoparticles have been employed in a range of organic transformations [15-18].

Xanthene and its derivatives are known as an important class of heterocyclic compounds which have been investigated extensively in recent years because they have wide range of biological and pharmaceutical properties such as anti-inflammatory [19], antibacterial [20] and antimalarial agents [21]. Furthermore, these compounds can be used as dyes [22], fluorescent materials for visualization of biomolecules [23], in laser technologies [24] and are useful in the photodynamic therapy [25]. Because of their wide range of pharmacological, industrial and synthetic application, many methods for their preparation are reported in the literature [26].

One of these methods is the condensation reaction of aldehydes with β-naphthol for the synthesis of 14-aryl or alkyl-14H-dibenzo[a,j]xanthenes, many catalysts such as $H_5PW_{10}V_2O_{40}$ [27] $KAl(SO_4)_2.12H_2O$ (alum) [28], Nano-TiO_2 [29]. Succinimide-N-sulfonic acid [30], $MeSO_3H$ [31], iodine [32], silica sulfuric acid [33], boric acid [34], cyanuric chloride [35] and $[Et_3N\text{-}SO_3H]Cl$ [36] have been used for the synthesis of 14-aryl or alkyl-14H-dibenzo[a,j]xanthenes derivatives.

Another method to synthesis of these compounds is the condensation reaction of aldehydes with cyclic 1,3-dicarbonyl compounds for the synthesis of 1,8-dioxoocta hydroxanthene. Many alternative catalysts such as Fe^{3+}-montmorilonite [37], p-toluenesulfonic acid [38], $InCl_3$/ionic liquid [39], *p*-dodecylbenzenesulphonic acid [40], pentafluorophenyl ammonium triflate (PFPAT) [41], triethylbenzylammonium chloride [42], diammoniumhydrogen phosphate under various conditions [43], sulfonic acid under ultrasonic irradiation [44], $NaHSO_4$–SiO_2 or silica chloride [45], amberlyst-15 [46], montmorilonite [47], P_2O_5 [48], and silica sulfuric acid [49], have been used for the synthesis of 1,8-dioxooctahydroxanthene derivatives. Unfortunately, many of these methods have various drawbacks, such as, low yields, prolonged reaction time, use of hazardous catalysts or organic solvents and tedious work-up processes. Therefore, to avoid these limitations, the development of a new procedure for the synthesis of xanthene derivatives would be highly desirable.

In the present research, we wish to describe an efficient, facile, and convenient procedure for the rapid preparation of 14-aryl- or alkyl-14H-dibenzo[a,j] xanthenes and 1,8-dioxooctahydroxanthene by one-pot condensation of various aldehydes with (i) β-naphthol and (ii) cyclic 5,5-dimethyl-1,3-cyclohexanedion, in the presence of $H_3PMo_{12}O_{40}$ (PMA) as catalyst (Scheme1). Compared to other substrates (silica, acidic ion-exchange resins, active carbon and nano titania [3]), Fe_3O_4@SiO_2-Imid nanoparticles have various advantages such as high loading capacity, low leaching and the simple and efficient recovery procedure.

2. Experimental

2.1. General

Chemical materials were purchased from the Merck Chemical Company in high purity. All the solvents were distilled, dried and purified by standard procedures. Fourier transform infrared (FT-IR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. The NMR spectra were recorded on a Bruker avance DPX 250 MHz spectrometer in chloroform ($CDCl_3$) using tetramethylsilane (TMS) as an internal reference. All products were characterized by their melting points and comparison with literature values. The progress of the reaction was monitored by TLC and purification was achieved by silica gel column chromatography.

2.2. Preparation of Fe_3O_4@SiO_2-Imid- $H_3PMo_{12}O_{40}$ nanoparticles (Fe_3O_4@SiO_2-Imid-PMA^n)

The catalyst (Fe_3O_4@SiO_2-Imid-PMA^n) was synthesized by the reported procedure [50]. Briefly, firstly Fe_3O_4@SiO_2 core–shell was prepared by coprecipitation method. The mixture of $FeCl_3.6H_2O$ (1.3g, 4.8mmol) in water (15ml) was added to the solution of polyvinyl alcohol (PVA 15000), as a surfactant, and $FeCl_2.4H_2O$ (0.9g, 4.5mmol) in water (15 ml), which was prepared by completely dissolving PVA in water followed by addition of $FeCl_2.4H_2O$. The resultant solution was left to be stirred for 30 min in 80°C. Then, hexamethylentetraamine (1.0mol/l) was added dropwise with vigorous stirring to produce a black solid product when the reaction media reaches pH 10. The resultant mixture was heated on water bath for 2h at 60°C and the black magnetite solid product was separated and washed with ethanol three times and was then dried at 80°C for 10h.Then Fe_3O_4 nanoparticle (0.50g, 2.1mmol) was dispersed in the mixture of ethanol (50mL), deionized water (5mL) and tetraethoxysilane (0.20mL), followed by the addition of 5.0mL of NaOH (10wt%). This solution was stirred mechanically for 30 min at room temperature. Then the product, Fe_3O_4@SiO_2, was separated by an external magnet, and was washed with deionized water and ethanol three times and dried at 80°C for 10 h.

In the second step Fe_3O_4@SiO_2-Imid was synthesis. Fe3O4@SiO2 (1g) was added to the solution of 3-chlorotriethoxypropylsilane (1 mmol, 0.241 g) and imidazole (1 mmol, 0.0680 g) in p-xylene (20 mL) and the resultant mixture was under reflux for 24h under nitrogen atmosphere. After refluxing for about 24 h, the mixture was cooled to room temperature, filtered by an external magnet and the product was washed with xylene to remove any reacted species and dried at 70 ^{o}C for 6 h.
PMA^n nanoparticles were prepared in tertiary step. In a typical procedure, 5 mmol of bulk $H_3PMo_{12}O_{40}$ (PMA^b) was dispersed in 50 mL n-Octane and the resulting dispersion was stirred vigorously for 30 min at room temperature to form a homogeneous dispersion. This dispersion was transferred into a Teflon-lined stainless autoclave filling 80% of the total volume. The autoclave was sealed and maintained at 150^{o}C for 12 h. The autoclave was then cooled to room temperature. Finally, the resulted powder was filtered and washed for several times by Octane, and dried in a vacuum at 80^{o}C for 12 h.
In last step, Fe3O4@SiO2-Imid (1.0g) was added to an acetonitrile solution of PMA^n (1.0mmol) in 20mL was taken in a round-bottom flask. The mixture was refluxed for 24h under nitrogen atmosphere. After 24h, the mixture was filtered by an external magnet, washed with acetonitrile and dichloromethane, and dried at 70^{o}C for 6h. FT-IR spectrum of the catalyst showed the expected bands, including distinctive bands due to anchoring of PMA^n onto Fe3O4@SiO2-Imid. Fig. 1 represents the procedure for the preparation of Fe_3O_4@SiO_2-Imid-PMA^n step by step.

2.3. General procedure for the synthesis of alkyl or aryl-14H-dibenzo[a,j]xanthenes (Method A)

A mixture of β-naphthol (2 mmol), aldehyde (1 mmol), and Fe_3O_4@SiO_2-Imid-PMA^n (0.03g) in 1,2-dichloroethane (5mL) was refluxed for the appropriate time. Progress of the reaction was monitored by TLC utilizing petroleum ether and ethyl acetate with a molar ratio of 2:1 acts as mobile solvent. After completion of the reaction, the mixture was cooled and diluted with hot ethanol (20 mL). The catalyst was removed by using magnetic field or filtration and then the solvent was evaporated and the crude product was recrystallized from ethanol to afford the corresponding pure product.

2.4. General procedure for the synthesis of alkyl or aryl-14H-dibenzo[a,j]xanthenes (Method B)

To a mixture of aldehyde (1 mmol) and β-naphthol (2 mmol), Fe_3O_4@SiO_2-Imid-PMA^n (0.03g) was added and the mixture was heated on an oil bath at 110 ^{o}C with good stirring for the appropriate time. The progress of the reaction was monitored by TLC (n-hexane:ethyl acetate, 7:2), after completion of the reaction, hot EtOH (10 mL) was added and the mixture stirred for 10 min. Then, the catalyst was removed by using magnetic field. A solid precipitated that was collected by filtration and washed with H_2O and then dried to give the corresponding 14-aryl or alkyl-14H-dibenzo[a,j] xanthenes **(3a-o)**. For further purification this product was recrystallized from ethanol to afford the pure products.

2.5. General procedure for the synthesis of 1,8-dioxooctahydroxanthene Derivatives

A mixture of 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), aldehyde (1 mmol) and Fe_3O_4@SiO_2-Imid-PMA^n (0.03g) in ethanol (5mL) was refluxed for the appropriate time. During the procedure, the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and diluted with hot ethanol (20 mL). The catalyst was removed by using magnetic field or filtration and then the solvent was evaporated and the crude product was recrystallized from ethanol to afford the corresponding pure product.

3. Results and discussion

In our previous work [50] the Fe_3O_4@SiO_2-Imid-PMA^n nano catalysts were characterized by various methods such Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Dynamic light scattering (DLS), Fourier transform infrared (FT-IR) and etc. As shown in Fig. 1 Fe_3O_4@SiO_2-Imid-PMA^n nanoparticles have spherical shapes with approximately 50 nm diameters. The size distribution of it is centered at a value of 55 nm. The presence of vibration bands in 556, 794, 864, 956, 1055, 1095, 1454 and 2792-2985 cm^{-1} in FT-IR spectrum of it relevanted to the Fe-O, Mo-O$_e$-MO, Mo-O$_c$-MO, Mo-O$_t$, P-O, Si-O-Si, C=N and CH respectively. The band at 1443 cm^{-1} for Fe_3O_4@SiO_2-Imid is assigned to the C=N of the imidazole group, which is shifted toward 1454 cm^{-1} in Fe_3O_4@SiO_2-Imid-PMA^n which could be due to the change in environment of the double-bonded nitrogen in imidazole. Also, a small band between at 1400-1420 cm^{-1} is the characteristic band of the C-N bond which can be attributed to anchoring of imidazole to the propyl group.

At the first stage for the synthesis of 14-aryl or alkyl-14H-dibenzo-[a,j]xanthenes, the reaction of 2-naphthol (2 mmol) and benzaldehyde (1 mmol) was investigated in the presence of Fe_3O_4@SiO_2-Imid-PMA^n as a catalyst in various solvents and also under solvent free conditions in present of various amount of catalyst and different temperature .

The results were summarized in Table 1.

In order to evaluate the optimum amount of catalyst required for this condensation, the reaction was carried out in the presence varying amount of the nanocatalysts and the results are presented in Table 1. The best result was achieved by carrying out the reaction with 0.03g of Fe_3O_4@SiO_2-imid-PMA^n nanocatalyst (Table1, entries 1,9). The results show clearly that nanocatalyst is effective for this transformation and in the absence of it, the reaction did not take place even after higher reaction time

(Table1, entry10). Use of a higher amount of catalysts did not improve the yield (Table1, entries 13) while a decrease in the amount of catalysts decreases the yield (Table1, entries 11,12). As it was shown in Table 1, solvent free condition at 110 ºC (Table1, entry 9) and using 1,2-dichloro ethane as a solvent at reflux with 0.03g catalyst (Table1, entry 1) are obviously the best choices for these reactions. The use of other organic solvents like THF, H_2O, MeOH, CH_3CO_2Et, CH_3CN and EtOH afforded the desired product in lower yields (Table1, entries 2-8).

Then, we also briefly examined the effect of different temperatures. The effect of temperature was studied by carrying out the model reaction at different temperatures in the presence of Fe_3O_4@SiO_2-Imid-PMA^n under solvent free conditions (Table1, entries 14-18) and the best result was obtained at 110ºC (Table1, entry9).

After optimizing the reaction conditions, we next investigated the generality of this condition using 2-naphthol (2 mmol) and several aldehydes (1 mmol) in 1,2-dichloro ethane as a solvent at reflux (Method A) and solvent free condition at 110ºC with 0.03 g catalyst (Method B). The results are summarized in Table2. A wide range of aldehydes containing electron-withdrawing and electron-donating groups were investigated. Aldehydes containing electron-withdrawing groups such as, chloro, bromo, flouro and nitro underwent condensation in short reaction times with excellent isolated yields with both of conditions (Table2, entries 4-10). Aldehydes containing electron-donating groups such as methyl, methoxy and hydroxyl required longer reaction time. (Table2, entries 2,3 and 11). The catalytic system also worked well with aliphatic aldehydes (Table2, entries 12-15) to generate the corresponding xanthenes.

In order to show the advantage of Fe_3O_4@SiO_2-Imid-PMA^n over some of the reported catalysts in the literature, we showed a reaction of 2-naphthol (2 mmol) and benzaldehyde (1 mmol) in the presence of Fe_3O_4@SiO_2-Imid-PMA^n (Table3). In comparison with the other reported catalysts in literature, we observed that Fe_3O_4@SiO_2-Imid-PMA^n gives better yield in shorter reaction time in compare with some of these catalysts and is comparable with some another ones (Table3, entries1,2).

For optimization of the reactions parameters for 1,8-dioxooctahydroxanthene derivatives the reaction of benzaldehyde (1mmol), 5,5-dimethyl-1,3-cyclohexanedione (2mmol) was investigated in the presence of Fe_3O_4@SiO_2-Imid-PMA^n as a catalyst in various solvents and also under solvent free conditions in present of various amount of catalyst and different temperature. The results were summarized in Table4.

As it was shown in Table4, ethanol as a solvent at reflux with 0.03g catalyst is obviously the best choices for this reaction (Table4, entry 1). The use of other organic solvents like toluene, THF, H_2O, MeOH, CH_3CO_2Et and also solvent free conditions afforded the desired product in lower yields (Table4, entries 2-8).

After optimizing the reaction conditions, we next investigated the generality of this condition using 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) and several aldehydes (1 mmol) in ethanol as a solvent at reflux with 0.03g catalyst. The results are summarized in Table5. A wide range of aromatic aldehydes containing electron-withdrawing and electron-donating groups such as, chloro, bromo,flouro,hydroxyl, methyl, methoxy, and nitro were investigated. In all of theme excellent isolated yields were obtained in short reaction times (Table5).

A plausible mechanism for the synthesis of 14-aryl- or alkyl -14H-dibenzo[a,j] xanthenes and 1,8-dioxooctahydroxanthenes catalyzed by Fe_3O_4@SiO_2-Imid-PMA^n is shown in Scheme2. As it is shown in Scheme2A, prior activation of the carbonyl group of aldehyde by H^+ to give intermediate [I], followed by a nucleophilic attack from C1 of β-naphthol, provides intermediate [II], which serves as an electrophile, ready for attack by a second molecule of β-naphthol. Then, cyclodehydration of intermediate [III] and dehydration afford the desired product. Also, we propose that one molecule of 5,5-dimethyl-1, 3-cyclohexanedione was firstly condensed with an activated aldehyde [I] to afford intermediate [II]' (Scheme2B). Then another molecule of 5,5-dimethyl-1,3-cyclohexanedione reacted with [II]' via Michael addition reaction to give the intermediate [III]'. Finally, cyclodehydration of the intermediate [III]' gave the expected products 1,8-dioxo-octahydroxanthenes.

A comparison among Fe_3O_4@SiO_2-imid-PMA^n and the other catalysts, which were reported in the literature, in the synthesis of 1,8-dioxooctahydroxanthene, revealed advantages of Fe_3O_4@SiO_2-imid-PMA^n over the most of them in term of higher yield and shorter reaction time (Table6, entry 10). According to these findings, it can be seen that Fe_3O_4@SiO_2-imid-PMA^n is a very efficient catalysts useful in the synthesis of xanthene derivatives (Table6).

The reusability of the catalyst is an important benefit especially for commercial applications. Thus, the recovery and reusability of nanocatalyst was investigated forpreparation of 14-(Phenyl)-14H-dibenzo[a,j]xanthene (Method A), (Method B) and 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione under optimized conditions (Fig. 2). The catalyst was recovered by a magnetic field and the remaining solid was washed with ethyl acetate (3×10 mL), dried and the catalyst reused for subsequent reactions for at least 5 times without any activation process.

The amounts of the nano heteropolyacid leaching for the reactions under the optimized conditions were detected. The molybdenum (Mo) amount in reaction medium after each reaction cycle was measured through ICP and details are shown in Table 7. The analysis of the reaction mixture by the ICP technique showed the leaching of $H_3PMo_{12}O_{40}$ was negligible.

Additionally, size of catalysts after each reaction cycle was investigated by DLS and results are shown in Table 8. As show, the size of catalysts will be increased after each cycle. Generally, leaching of $H_3PMo_{12}O_{40}$ and increasing of catalyst size lead to the yield of reaction will decreased.

4. Conclusion

In summary, we have developed a simple, convenient, and efficient procedure for preparing a variety of 14-substituted- 14H-dibenzo[a,j]xanthenes by the reactions of various aldehydes with β-naphthol in the presence of a catalytic amount of $Fe_3O_4@SiO_2$-Imid-PMA^n nanoparticles under dichloroethane and solvent-free conditions. Also, the present methodology shows that $Fe_3O_4@SiO_2$-Imid-PMA^n is an efficient magnetic catalyst in the one-pot synthesis of 1,8-dioxooctahydroxanthene derivatives in ethanol under reflux conditions. The procedure offers several advantages including cleaner reaction profiles, high reaction rates and excellent yields, simple experimental and work-up procedures, no side reactions and use of recyclable and environmentally benign nature of catalyst.

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References

[1] Aany Sofia LT, Krishnan A, Sankar M, Kala Raj NK, Manikandan P, Rajamohanan PR, Ajithkumar TG. *J Phys Chem C*, 2009, 113: 21114-21122.
[2] Zhang Z, Zhang F, Zhu Q, Zhao W, Ma B, Ding Y. *J Colloid Interf Sci*, 2011, 360: 189-194.
[3] Davood A., Seyed-Mola K. , Razieh N. *J Chem Sci, 2014, 126: 95-101.*
[4] He Y, Cai C. *Catal Commun*, 2011, 12: 678-683.
[5] Ma M, Zhang Q, Yin D, Dou J, Zhang H, Xu H. *Catal Commun*, 2012, 17: 168-172.
[6] Nador F, Volpe MA, Alonso F, Feldhoff A, Kirschning A, Radivoy G. *Appl. Catal A: Gen,* 2013, 455: 39-45.
[7] Zhang J, Wang Y, Ji H, Wei Y, Wu N, Zuo B, Wang Q. *J Catal*, 2005, 229: 114-118.
[8] Stevens PD, Li G, Fan J, Yen M, Gao Y. *Chem Commun*, 2005, 35: 4435-4437.
[9] Laska U, Frost CG, Price GJ, Plucinski PK. *J Catal*, 2009, 268: 318-328.
[10] Gardimalla HMR, Mandal D, Stevens PD, Yen M, Gao Y. *Chem Commun*, 2005,35: 4432-4434.
[11] Yoon TJ, Kim JS, Kim BG, Yu KN, Cho MH, Lee JK. *Angew Chem Int Ed*, 2005, 44: 1068-1071.
[12] Lee J, Lee D, Oh E, Kim J, Kim YP, Jin S, Kim HS, Hwang Y, Kwak JH, Park JG, Shin CH, Kim J, Hyeon T. *Angew Chem Int Ed*, 2005, 44: 7427-7432.
[13] Esmaeilpour M, Sardarian AR, Javidi J. *Appl Catal A: Gen*, 2012, 445-446: 359-367.
[14] Javidi J, Esmaeilpour M. *Colloid Surfaces B*, 2013, 102: 265-272.
[15] Polshettiwar V, Luque R, Fihri A, Zhu H, Bouhrara M, Basset JM. *Chem Rev*, 2011, 111: 3036-3075.
[16] Schatz A, Hager M, Reiser O. *Adv Funct Mater*, 2009, 19: 2109-2115.
[17] Shylesh S, Schunemann V, Thiel WR. *Angew Chem Int Ed*, 2010, 49: 3428-3459.
[18] Schatz A, Reiser O, Stark WJ. *Chem Eur J*, 2010, 16: 8950-8967.
[19] Poupelin JP, Saint-Rut G, Fussard-Blanpin O, Narcisse G, Uchida-Ernouf G, Lakroix R. *Eur J Med Chem*, 1978,13: 67-71.
[20] Hideo T, Teruomi J. *Chem. Abstr*. Jpn. Tokkyo Koho JP56005480, 1981 95: 80922b.
[21] Chibale K, Visser M, Schalkwyk DV, Smith PJ, Saravanamuthu A, Fairlamb AH. *Tetrahedron*, 2003, 59: 2289-2296.
[22] Menchen SM, Benson SC, Lam JYL, Zhen W, Sun D, Rosenblum BB, Khan SH, Taing M. *Chem Abstr*, 2003, 139: p54287f, U.S. Patent, US6583168.
[23] Knight CG, Stephens T. *Biochem*, J. 1989, 258: 683-687.

[24] Ahmad M, King TA, Ko DK, Cha BH, Lee J. *J Phys D: Appl Phys*, 2002, 35: 1473-1476.
[25] Ion RM, Planner A, Wiktorowicz K, Frackowiak D. *Acta Biochim Pol*, 1998, 45: 833-845.
[26] Wang JQ, Harvey RG. *Tetrahedron*, 2002, 58: 5927-5931.
[27] Tayebee R, Tizabi Sh. *Chin J Catal*, 2012, 33: 962-969.

[28] Dabiri M, Baghbanzadeh M, Nikcheh MS, Arzroomchilar E. *Bioorg Med Chem Lett*, 2008, 18: 436-438.
[29] Mirjalili BF, Bamoniri A, Akbari A, Taghavinia N. *J Iran Chem Soc*, 2011, 8: 129-134.
[30] Shirini F, Ghaffari Khaligh N, Shirini F, Khaligh NG. *Dyes Pigments*, 2012, 95: 789-794.
[31] Bhattacharya AK, Rana KC. *Mendeleev Commun*, 2007,17: 247-248.
[32] Das B, Ravikanth B, Ramu R, Laxminarayana K, Rao BV. *J Mol Catal A Chem*, 2006, 255: 74-77.
[33] Hunnur RK, Sunilkumar B, Kumar PS, Srinivasulu N, Udupi RH, Himabindu V. *Chem Heterocycl Compd*, 2008, 44: 143-147.
[34] Karimi-Jaberi Z, Keshavarzi M. *Chinese Chem Lett*, 2010, 21: 547-549.
[35] Bigdeli MA, Heravi MM, Mahdavinia GH. *Catal Commun*, 2007, 8: 1595-1598.
[36] Zare A, Moosavi-Zare AR, Merajoddin M, Zolfigol MA, Hekmat-Zadeh T, Hasaninejad AR, Khazaei A, Mokhlesi M, Khakyzadeh V, Derakhshan-Panah F, Beyzavi MH, Rostami E, Argoon A, Roohandeh R. *J Mol Liq*, 2012, 167: 69-77.
[37] Song G, Wang B, Luo H, Yang L. *Catal Commun*, 2007, 8: 673-676.
[38] Khosropour AR, Khodaei MM, Moghannian H. *Synlett*, 2005, 6: 955-958.
[39] Fan X, Hu X, Zhang X, Wang J. *Can J Chem*, 2005, 83: 16-20.
[40] Jin T, Zhang JS, Xiao JC, Wang AQ, Li TS. *Synlett*, 2004, 5: 866-870.
[41] Khaksar S, Behzadi N. *Chinese J Catal*, 2012, 33: 982–985.
[42] Wang XS, Shi DQ, Li YL, Chen H, Wei XY, Zong ZM. *Synth Commun*, 2005, 35: 97-104.
[43] Darvish, S. Balalaei, F. Chadegani, P. Salehi, *Synth Commun*, 2007, 37: 1059-1067.
[44] Jin TS, Zhang JS, Wang AQ, Li TS. *Ultrason Sonochem*, 2006, 13: 220-224.
[45] Das B, Thirupathi P, Mahender I, Reddy KR, Ravikanth B, Nagarapu L. *Catal Commun*, 2007, 8: 535-538.
[46] Das B, Thirupathi P, Mahender I, Reddy VS, Rao YK. *J Mol Catal A: Chem*, 2006, 247: 233-239.

[47] Dabiri M, Azimi SC, Bazgir A. *Chem Pap*, 2005, 62: 522-526.
[48] Kumar R, Nandi GC, Verma RK, Singh MS. *Tetrahedron Lett*, 2010, 51: 442-445.
[49] Seyyedhamzeh M, Mirzaei P, Bazgir A. *Dyes Pigments*, 2008, 76: 836-839.
[50] M. Esmaeilpour, J. Javidi, M. Zandi, Mater Res Bull, 2014, 55: 78-87
[51] Amini, MM, Seyyedhamzeh M, Bazgir A. (2007). *Appl Catal A: Gen*, 323, 242-245.

[52] Nagarapu L, Kantevari S, Mahankhali VC, Apuri S. *Catal Commun*, 2007, 8: 1173-1177.
[53] Madhav JV, Reddy VT, Reddy PN, Reddy MN, Kuarm S, Crooks PA, Rajitha B. *J Mol Catal A: Chem*, 2009, 304: 85-87.
[54] Rajitha B, Kumar BS, Reddy YT, Reddy PN. *Tetrahedron Lett*, 2005, 46: 8691-8693.
[55] Imani Shakibaei G, Mirzaei P, Bazgir A. *Appl Catal A Gen*, 2007, 325: 188-192.
[56] Ko S, Yao CF. *Tetrahedron Lett*, 2006, 47: 8827-8829.
[57] Niknam K, Damya M. *J Chin Chem Soc*, 2009, 56: 659-665.
[58] Ma JJ, Li JC, Tang R, Zhou X, Wu Q, Wang C, Zhang M, Li Q. *Chin J Org Chem*, 2007, 27: 640-642.
[59] Bigdeli MA, Nemati F, Mahdavinia GH, Doostmohammadi H. *Appl Organometal Chem*, 2009, 23: 165-169.
[61] Maleki B, Gholizadeh M, Sepehr Z. *Bull Korean Chem Soc*, 2011, 32: 1697-1702.
[62] Mahdavinia GH. *J Iran Chem Res*, 2008, 1: 11-17.
[63] Srihari, P, Mandal SS, Reddy JSS, Rao RS, Yadav JS. *Chin Chem Lett*, 2008, 19: 771-774.
[64] Karade HN, Sathe M, Kaushik MP. *Arkivoc*, 2007, 13: 252-258.
[65] Kantevari S, Bantu R, Nagarapu L. *J Mol Catal A: Chem*, 2007, 269: 53-57.

[66] Kantevari S, Bantu R, Nagarapu L. *Arkivoc*, 2006, 16: 136-148.

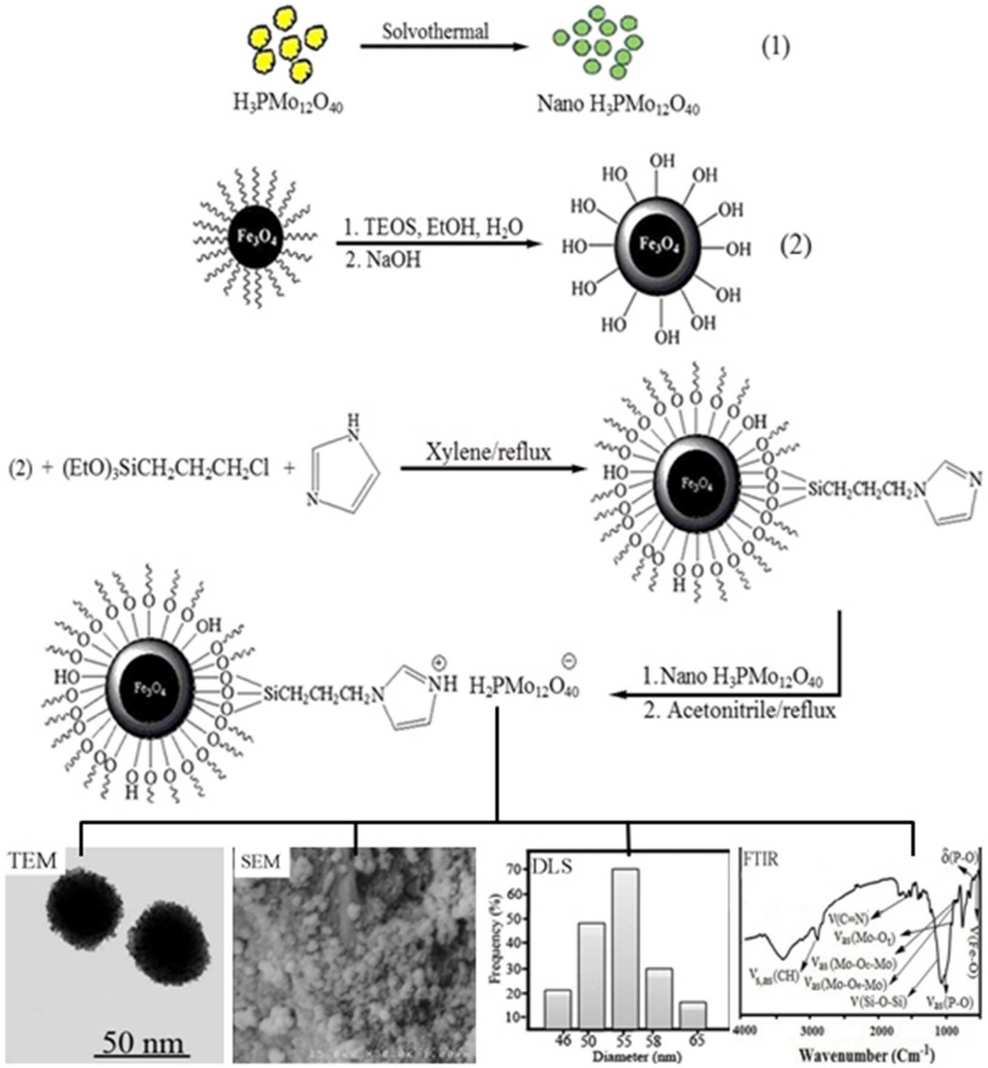
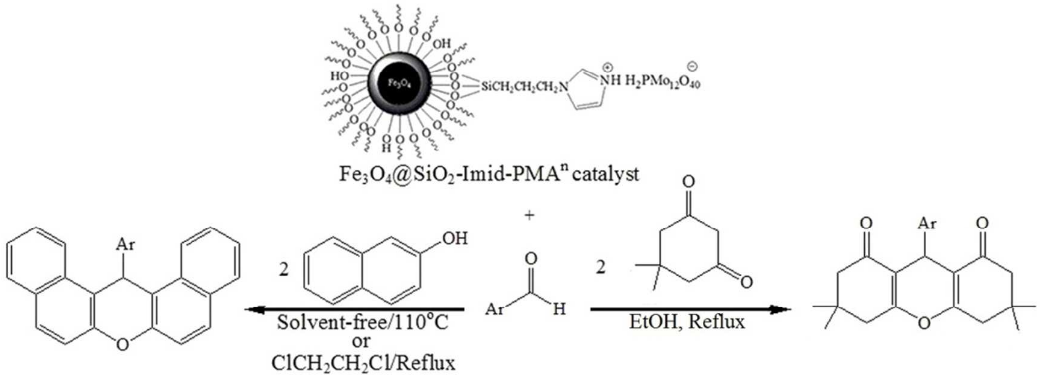
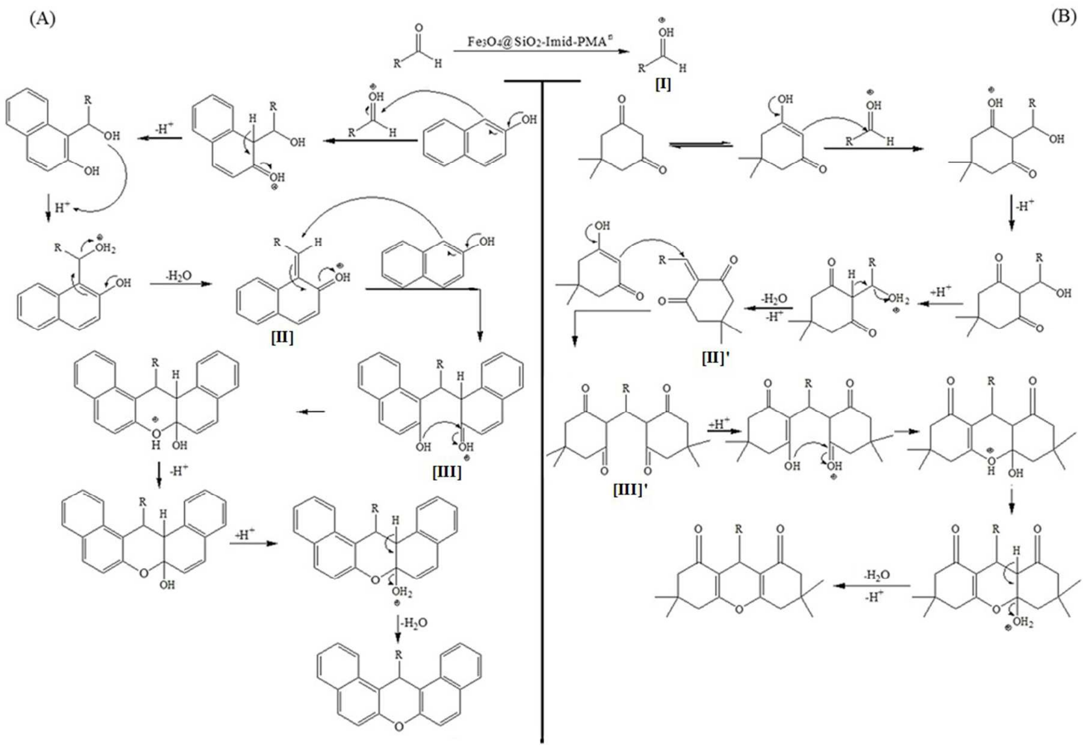


Fig. 1. Preparation and characterization of $Fe_3O_4@SiO_2$-Imid-PMA^n.



Scheme.1: $Fe_3O_4@SiO_2$-Imid-PMA^n-catalyzed synthesis of xanthenes derivatives.



Scheme.2: (A) Plausible mechanism for the synthesis of 14-aryl- or alkyl -14H-dibenzo[a,j] xanthenes and (B) 1,8 dioxooctahydro xanthenes catalyzed by Fe$_3$O$_4$@SiO$_2$-imid-PMA^n nanoparticles.

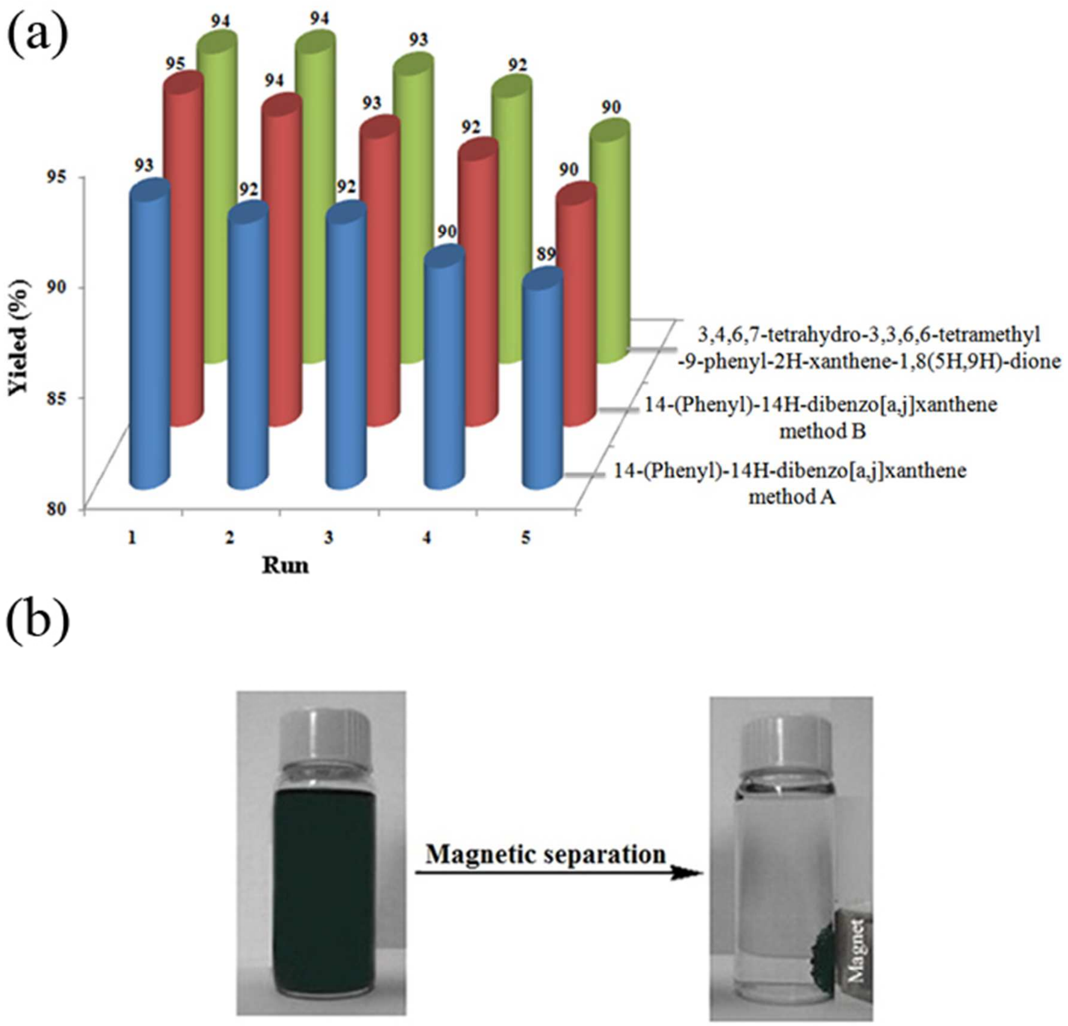


Fig. 2: a) Recyclability of the catalyst for the one-pot synthesis of 14-(Phenyl)-14H-dibenzo[a,j]xanthene (a) Method A[a], (b) Method B[b] and 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione[c]. b) Photo images of magnetic field-responsive of $Fe_3O_4@SiO_2$-imid-PMA^n nanoparticles (before magnetic field and under magnetic field).

[a] Reaction condition: benzaldehyde (1 mmol), β-naphthol (2 mmol), $Fe_3O_4@SiO_2$-Imid-PMA^n (0.03g), $ClCH_2CH_2Cl$ (5mL), reflux.

[b] Reaction condition: benzaldehyde (1 mmol), β-naphthol (2 mmol), $Fe_3O_4@SiO_2$-Imid-PMA^n (0.03g), Solvent-free, 110°C.

[c] Reaction condition: benzaldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), $Fe_3O_4@SiO_2$-Imid-PMA^n (0.03g), EtOH (5mL), reflux.

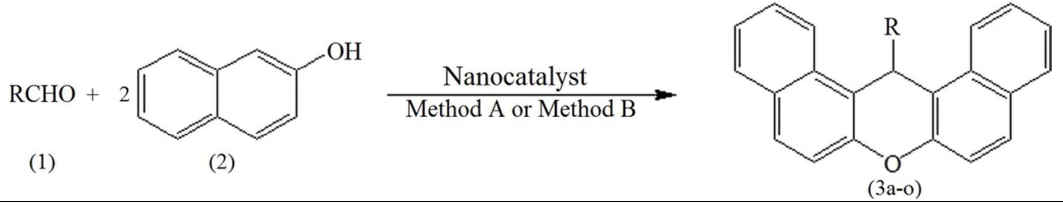
Table.1: Effect of solvent, temperature and catalyst amount on the reaction of 2-naphthol and benzaldehyde.[a]

Entry	Solvent	Catalyst (g)	Temperature (^oC)	Time (h)	Yield (%)[b]
1	$ClCH_2CH_2Cl$	0.03	Reflux	1.5	93
2	EtOH	0.03	Reflux	2.5	82
3	CH_2Cl_2	0.03	Reflux	2.5	51
4	CH_3CN	0.03	Reflux	2.5	58
5	CH_3CO_2Et	0.03	Reflux	2.5	54
6	MeOH	0.03	Reflux	2.5	67
7	H_2O	0.03	Reflux	2.5	14
8	THF	0.03	Reflux	2.5	23
9	Solvent-free	0.03	110^oC	1.5	95
10	Solvent-free	-	140^oC	10	-
11	Solvent-free	0.01	110^oC	1.5	17
12	Solvent-free	0.02	110^oC	1.5	45
13	Solvent-free	0.04	110^oC	1.5	93
14	Solvent-free	0.03	r.t	5	18
15	Solvent-free	0.03	60^oC	4	46
16	Solvent-free	0.03	90^oC	2.5	81
17	Solvent-free	0.03	100^oC	1.5	89
18	Solvent-free	0.03	120^oC	1.5	95

[a] Reaction condition: 2-naphthol (2 mmol) and benzaldehyde (1 mmol).

[b] Isolated yield.

Table.2: The one-pot synthesis of 14-aryl or alkyl-14H-dibenzo-[a,j]xanthenes using Fe_3O_4@SiO_2-Imid-PMA^n.



Entry	R	Product	Method A		Method B		Mp (°C)	
			Time (h)	Yield (%)[a]	Time (h)	Yield (%)[a]	Found	Reported
1	C_6H_5	**3a**	2	93	1.5	95	183-185	(185)[51]
2	4-MeC_6H_4	**3b**	2.5	89	2	91	228-229	(229)[51]
3	4-$MeOC_6H_4$	**3c**	3	86	2	91	204-206	(204)[51]
4	4-BrC_6H_4	**3d**	2.5	95	1.5	94	206-207	(297)[51]
5	2-ClC_6H_4	**3e**	1.5	92	o.75	93	214-216	(215)[51]
6	4-ClC_6H_4	**3f**	1.5	88	0.5	94	290-291	(289)[51]
7	4-FC_6H_4	**3g**	1.5	90	0.5	92	239-240	(238-240)[48]
8	2-$O_2NC_6H_4$	**3h**	2	92	1.5	94	214	(213)[51]
9	3-$O_2NC_6H_4$	**3i**	2	86	1.5	87	212-213	(210-211)[48]
10	4-$O_2NC_6H_4$	**3j**	2	90	1	91	312-313	(310-311)[51]
11	4-HOC_6H_4	**3k**	3	91	2	93	138-140	(139-140)[48]
12	$C_6H_5CH_2$	**3l**	3	83	2	85	181-182	(178-180)[48]
13	CH_3CH_2	**3m**	3	84	2.5	83	149-150	(150-151)[51]
14	$CH_3CH_2CH_2$	**3n**	4	82	2.5	84	153-154	(152-154)[51]
15	$(CH_3)_2CH$	**3o**	4	80	3	79	152-153	(155-157)[51]

Method A: $ClCH_2CH_2Cl$. Method B: Solvent-free.

[a] Isolated yield.

Table.3: Comparing the catalytic activity of Fe_3O_4@SiO_2-Imid-PMA^n with the reported catalysts in the preparation of 14-(phenyl)-14H-dibenzo[a,j]xanthene.

Entry	Catalyst	Condition	Time (h)	Yield (%)	Ref.
1	Fe_3O_4@SiO_2-Imid-PMA^n	Solvent-free/110 °C	1.5	95	This work
2	Fe_3O_4@SiO_2-Imid-PMA^n	$ClCH_2CH_2Cl$, reflux	2	93	This work
3	Heterohpolyacid	Solvent-free/100 °C	0.5-1.5	80-91	51
4	I_2	Solvent-free/90 °C	2.5	90	32
5	$K_5CoW_{12}O_{40}\_3H_2O$	Neat/125 ^oC	2	91	52
6	Cellulose sulfuric acid	Neat/110 ^oC	1.5	81	53
7	Sulfamic acid	Neat/125 ^oC	8	93	54
8	*p*-TsOH	Neat/125 ^oC	4	89	33
10	Silica sulfuric acid	$ClCH_2CH_2Cl$, reflux	9	90	33
11	Dowex-50W	Neat/100 ^oC	1.5	78	55
12	Amberlyst-15	Neat/125 ^oC	2	94	56

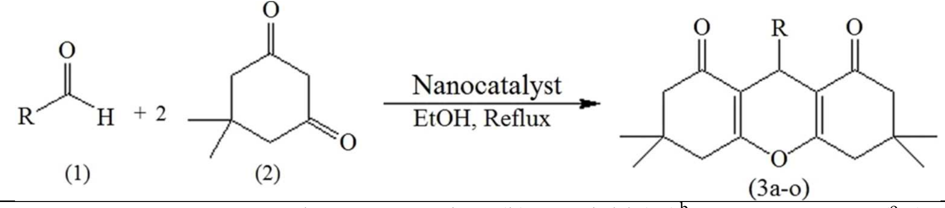
Table.4: Effect of solvent, temperature and catalyst amount on the condensation of 5,5-dimethyl-1,3-cyclohexanedione with benzaldehyde over $Fe_3O_4@SiO_2$-imid-PMA^n nanocatalyst.[a]

Entry	Solvent	Catalyst(g)	Conditions	Time (h)	Yield (%)[b]
1	EtOH	0.03	reflux	1.5	94
2	CH_3CN	0.03	reflux	2	85
3	CH_3CO_2Et	0.03	reflux	2	76
4	MeOH	0.03	reflux	2	66
5	Toluene	0.03	reflux	2	56
6	THF	0.03	reflux	2	48
7	H_2O	0.03	reflux	2	28
8	Solvent-free	0.03	110°C	2	87
9	EtOH	-	reflux	10	-
10	EtOH	0.01	reflux	3	33
11	EtOH	0.02	reflux	2	79
12	EtOH	0.04	reflux	1.5	94
13	EtOH	0.03	r.t	8	17
14	EtOH	0.03	60°C	5	62

[a] Reaction condition: benzaldehyde (1mmol), 5,5-dimethyl-1,3-cyclohexanedione (2mmol).

[b] Isolated yield.

Table.5 : $Fe_3O_4@SiO_2$-Imid-PMA^n catalyzed synthesis of 1,8-dioxo-octahydroxanthenes.[a]



Entry	R	Product	Time (h)	Yield (%)[b]	Mp (°C)	
					Found	Reported
1	C_6H_5	**3a**	1.5	94	204-205	(203-204)[57]
2	4-MeC_6H_4	**3b**	2	87	207-208	(208-209)[58]
3	4-MeOC_6H_4	**3c**	2	84	245-247	(242-244)[57]
4	3-MeOC_6H_4	**3d**	2	85	180-182	(177-180)[59]
5	4-BrC_6H_4	**3e**	1.5	93	238-240	(240-241)[57]
6	4-FC_6H_4	**3f**	1.25	95	225-227	(226-227)[60]
7	2-ClC_6H_4	**3g**	1.25	90	224-226	(225-227)[57]
8	4-ClC_6H_4	**3h**	1	91	231-233	(230-232)[57]
9	2-$NO_2C_6H_4$	**3i**	1.25	90	245-246	(251-253)[61]
10	3-$NO_2C_6H_4$	**3j**	1.5	88	169-170	(170-172)[57]
11	4-$NO_2C_6H_4$	**3k**	1.25	94	224-226	(225-227)[59]
12	2,4-$Cl_2C_6H_4$	**3l**	1.25	92	250-251	(248-251)[60]
13	4-HOC_6H_4	**3m**	2	86	249	(248-250)[58]
14	2-HOC_6H_4	**3n**	2	82	203-204	(202-205)[58]
15	PhCH=CH_2	**3o**	2.5	85	178-180	(177-178)[62]

[a] Reaction condition: aromatic aldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), $Fe_3O_4@SiO_2$-Imid-PMA^n (0.03g) , EtOH (5mL), reflux.

Table.6: Comparison of the efficiency of Fe_3O_4@SiO_2-Imid-PMA^n with reported catalysts for the synthesis of 1, 8-dioxooctahydroxanthene.

Entry	Catalyst	Condition	Time (h)	Yield (%)	Ref.
1	PMA/SiO_2	CH_3CN/Reflux	4-5	88-96	63
2	TBAHS	Solvent-free/110 °C	3-3.5	88-94	64
3	HPWA/MCM-41	EtOH/90 °C	5	81-94	65
4	PPA/SiO_2	CH_3CN/Reflux	10-12	54-82	66
5	Amberlyst-15	CH_3CN/Reflux	5	90-96	46
6	Fe^{+3}-montmorillonite	EtOH /100 °C	6	84-94	37
7	Dowex-50W	Solvent-free/100 °C	2–5	78–91	55
8	Montmorillonite K10	Solvent-free/100 °C	1-2	75–90	47
9	$NaHSO_4$-SiO_2	CH_3CN/Reflux	6	90–98	45
10	Fe_3O_4@SiO_2-Imid-PMA^n	EtOH/ Reflux	1-2.5	82-95	This work

Table 7. Ratio of PMA leaching (%) in each reaction cycle.

Run	Ratio of PMA leaching (%)		
	14-aryl-14H-dibenzo-[a,j]xanthenes[a]		1,8-dioxooctahydroxanthene[b]
	Method A	Method B	
1	0.10	0.12	0.15
2	0.15	0.19	0.26
3	0.26	0.29	0.35
4	0.30	0.33	0.43
5	0.43	0.46	0.50

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

[b] 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione

Table 8. The size of catalysts in each reaction cycle.

Run	Size of catalysts by DLS (nm)		
	14-aryl-14H-dibenzo-[a,j]xanthenes[a]		1,8-dioxooctahydroxanthene[b]
	Method A	Method B	
1	55	55	55
2	58	59	58
3	60	63	61
4	65	67	65
5	70	71	68

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

[b] 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione