J IRAN CHEM SOC
DOI 10.1007/s13738-017-1155-4

ORIGINAL PAPER

Trityl bromide versus nano-magnetic catalyst in the synthesis of henna-based xanthenes and bis-coumarins

Mahmoud Zarei[1] · Mohammad Ali Zolfigol[1] · Ahmad Reza Moosavi-Zare[2] · Ehsan Noroozizadeh[1]

Received: 28 December 2016 / Accepted: 12 June 2017
© Iranian Chemical Society 2017

Abstract In this work, trityl bromide (TrBr) as a new, efficient, mild and neutral catalyst was used for the synthesis of henna-based xanthenes (aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13H)-tetraones) and bis-coumarins by in situ generation of trityl carbocation under solvent-free conditions in comparison with $[Fe_3O_4@SiO_2@(CH_2)_3\text{-Im-}SO_3H]Cl$ as an acidic and reusable catalyst for the first time.

Graphical Abstract

Electronic supplementary material The online version of this article (doi:10.1007/s13738-017-1155-4) contains supplementary material, which is available to authorized users.

✉ Mahmoud Zarei
mahmoud8103@yahoo.com

✉ Mohammad Ali Zolfigol
zolfi@basu.ac.ir; mzolfigol@yahoo.com

✉ Ahmad Reza Moosavi-Zare
moosavizare@yahoo.com

[1] Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran

[2] Sayyed Jamaleddin Asadabadi University, Asadabad 6541835583, Iran

Published online: 14 August 2017

Keywords Trityl bromide · [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl · Bis-coumarin · Henna-based xanthene · Organocatalyst

Introduction

Among catalysts, organocatalysts can be used as a powerful synthetic paradigm which could be replaced with metal to catalyze chemical transformations. Also, in comparison with transition-metal catalysts, the cost and toxicity of organocatalysts are low [1]. Therefore, making new organocatalysts is useful to prepare pharmaceutical intermediates and biological products [2]. Recently, comprehensive reviews have covered the recent development in designing, improvement and validation of more efficient organocatalytic domino, tandem and cascade strategies as effective alternative tools for the creation of at least one chiral center [3–5]. Biological-based organocatalysts such as urea- or thiourea-based catalysts [6], chitosan, chemically modified chitosan, blended chitosan, or other biopolymers, such as alginate with its carboxylic groups or carrageenan with its sulfonate groups, have been emerged that are tightly connected to green and sustainable chemistry [7]. On the other hand, limitations in the recyclability and reusability of organocatalysts are the major drawback for their applications in chemical processes: chemists design, synthesis and development of magnetic nanoparticles (MNPs) and their derivatives as a reusable catalysts for solving the above mentioned limitation of organocatalysts. Moreover, applications of MNPs, as versatile inorganic support for organic and inorganic materials, have appeared as a potent branch in the field of green chemistry. Utilizing MNPs as supports for immobilization of organocatalysts can add various merits to homogeneous nature of them and make them powerful and easy recoverable heterogeneous active catalysts [8–18].

Henna (2-hydroxynaphthalene-1,4-dione) refers to the dye which is derived from the henna plant. It has been used for various purposes such as dyeing of skin, hair, fingernails, fabrics, silk, wool and leather. 2-Hydroxynaphthalene-1,4-dione has been also used in the synthesis of azo dyes and their copper complexes [19, 20], leuco-dye [21–23], spiro[dibenzo[*b*,*i*]xanthene-13,30-indoline]-pentaones and 5*H*-dibenzo[*b*,*i*]xanthene-tetraones [24].

Bis-coumarins, as an important kind of vitamin K antagonists, have various biological activities such as anti-HIV, anti-bacterial, antioxidant, anticancer, and anticoagulant activities [25]. Recently, Li and coworkers have reported a good range of bis-coumarin derivatives which successfully show anti-tumor and anti-bacterial activities [25–27]. Several methods have been reported for the synthesis of bis-coumarins through the Domino Knoevenagel–Michael condensation reactions of aldehydes with two equivalents of 4-hydroxycoumarin. This reaction can be catalyzed by both acidic and basic catalysts such as silica-supported Preyssler nanoparticles [28], CuO–CeO_2 nano-composite [29], basic ionic liquid tetramethylguanidinium acetate [30], poly(4-vinylpyridine) and 1,4-butanesultone) [31], propane-1,2,3-triyl tris(hydrogen sulfate) [32], silica-supported perchloric acid nanoparticles [33], $RuCl_3{\cdot}nH_2O$ [34], SO_3H-functionalized ionic liquids based on benzimidazolium cation [35], sodium dodecyl sulfate (SDS) [36] and tetrabutylammonium bromide [37]. Most of these catalytic systems have acidic or basic nature and often suffer from high reaction temperature, low yield, long reaction time and necessary refluxing in volatile organic solvents. Thus, a great demand is needed to develop neutral catalytic systems which can efficiently catalyze this type of reactions under mild reaction conditions.

With this issue in our mind and in our continuous research on the use of trityl chloride [38–46] and magnetic nanoparticles (MNPs) [47–54] as catalysts in the organic synthesis, we have reported the first catalytic application of trityl bromide as an organocatalyst versus nano-magnetic particles catalyst of [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (Scheme 1) in the synthesis of aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone leuco-dye and bis-coumarins by the condensation reaction of 2-hydroxynaphthalene-1,4-dione (2 mmol) or 4-hydroxy cumarin (2 mmol) with various aldehyde(1 mmol) under solvent-free conditions (Schemes 2, 3).

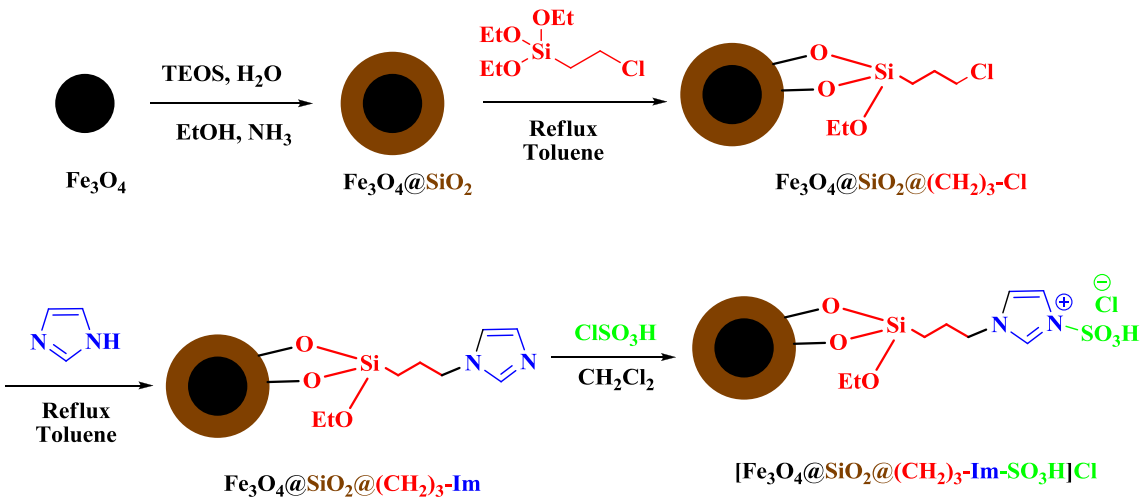
Experimental

General

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H NMR spectra were recorded by a Bruker BioSpin GmbH spectrometer at 400 MHz and ^{13}C NMR spectrometer at 100 MHz. IR spectra were recorded by a Bomem MB-Series FTIR spectrophotometer. All chemicals used in this work were purchased from Merck chemical company.

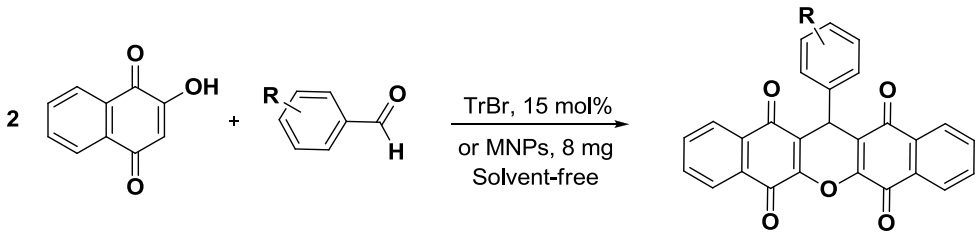
General procedure for the preparation of [nano-Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl as a heterogeneous acidic catalyst

At first magnetic nanoparticles of Fe_3O_4 and Fe_3O_4@SiO_2 were synthesized according to the previous reported literature. Then, a mixture of Fe_3O_4@SiO_2 (1 mmol), (3-chloropropyl) triethoxysilane (0.806 g, 3.3 mmol) and 30 mL of dry toluene was added in a 50-mL round-bottomed

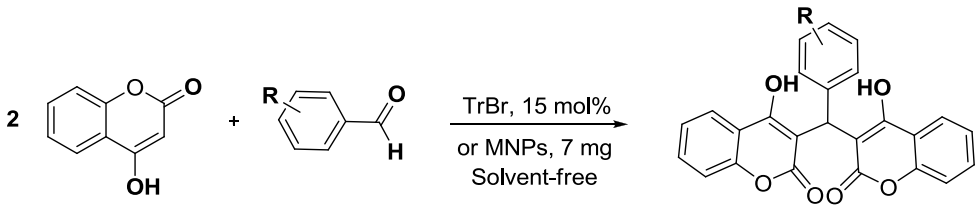


Scheme 1 Preparation of [nano-Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (NMPs)

Scheme 2 The preparation of henna-based xanthenes (aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13H)-tetraones) catalyzed by TrBr or [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl



Scheme 3 The preparation of bis-coumarins catalyzed by TrBr or [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl



flask connected to a reflux condenser and refluxed under nitrogen for 12 h. The obtained Fe_3O_4@SiO_2@$(CH_2)_3$Cl (grafted with chloropropyl group) was filtered, washed twice with dry toluene and anhydrous diethyl ether and dried at 80 °C for 6 h under vacuum. In the next step, imidazole (0.491 g, 7 mmol) in 50 mL of dry toluene was added to the Fe_3O_4@SiO_2@$(CH_2)_3$Cl and the prepared mixture was refluxed for 12 h. The obtained solid was filtered, washed and dried according to same procedure to create Fe_3O_4@SiO_2@$(CH_2)_3$-Im. Finally, a solution of chloro sulfonic acid (0.456 mL, 1.165 g, 7 mmol) in dry dichloromethane (10 mL) was added dropwise to the suspension of {Fe_3O_4@SiO_2@$(CH_2)_3$-Im}, and the reaction mixture was stirred for 6 h, then filtered and washed to give [nano-Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (Scheme 1).

Typical procedure for the preparation of 13-aryl-5*H*-dibenzo [*b*,*i*] xanthene-5,7,12,14(13*H*)-tetraone in the presence of TrBr (A) and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (B)

Method A A mixture of 2-hydroxynaphthalene-1,4-dione (0.348 g, 2 mmol), aldehyde (1 mmol) and TrBr ((0.0483 g, 15 mol%), in a 10-mL round-bottomed flask connected to a reflux condenser was heated and stirred at 100 °C in the absence of solvent. The reaction was monitored by TLC. After the completion of the reaction as monitored by TLC, the reaction mixture was washed with petroleum ether (15 mL) and filtered to separate the catalyst (the catalyst was soluble in petroleum ether and the product was not soluble in this solvent). The residue was recrystallized from EtOH to afford the pure product (Scheme 2).

Method B A mixture of 2-hydroxynaphthalene-1,4-dione (0.348 g, 2 mmol), aldehyde (1 mmol) and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (8 mg), in a 10-mL round-bottomed flask connected to a reflux condenser, was heated and stirred at 100 °C in the absence of solvent. After the completion of the reaction as monitored by TLC, the reaction mixture was dissolved in hot EtOH and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl catalyst was recovered magnetically. The crude product was recrystallized from ethanol to afford the pure product (Scheme 2).

Selected spectra of compounds

13-Phenyl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone Red powder; Mp 304–306 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 5.17 (*s*, 1H), 7.21–7.27 (*m*, 1H), 7.30–7.34 (*m*, 2H), 7.52 (*d*, J = 7.2 Hz, 2H), 7.79 (*s*, 1H), 7.93–7.96 (*m*, 2H), 8.00–8.05 (*m*, 2H), 8.01 (*d*, J = 4.8 Hz, 1H), 8.15–8.19 (*m*, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 33.05, 115.22, 123.16, 124.17, 125.98, 126.16, 127.11, 128.3, 128.69, 129.08, 129.31, 130.4, 130.66, 131.07, 131.71, 134.38, 134.69, 135.15, 141.38, 148.76, 155.04, 176.66, 176.83, 177.69, 182.69.

13-(4-Fluorophenyl)-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone Yellow powder; Mp 268–270 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 5.3 (*s*, 1H), 7.27 (*t*, J = 8 Hz, 2H), 7.69–7.70 (*m*, 2H), 7.99–8.20 (*m*, 8H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 33.05, 115.22, 123.16, 124.17, 125.98, 126.16, 127.11, 128.3, 128.69, 129.08, 129.31, 130.4, 130.66, 131.07, 131.71, 134.38, 134.69, 135.15, 141.38, 148.76, 155.04, 176.66, 176.83, 177.69, 182.69.

Typical procedure for the preparation of bis-coumarin in the presence of TrBr (A) and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (B)

Method A A mixture of 4-hydroxycoumarin (0.324 g, 2 mmol), aldehyde (1 mmol) and TrBr ((0.0483 g, 15 mol %)), in a 10-mL round-bottomed flask connected to a reflux condenser, was heated and stirred at 100 °C in the absence of solvent. After the completion of the reaction as monitored by TLC, the reaction mixture was washed with petroleum ether (15 mL) and filtered to separate the catalyst (the catalyst was soluble in petroleum ether and the product was not soluble in this solvent). The residue was recrystallized from EtOH to afford the pure product. (Scheme 3)

Method B A mixture of 4-hydroxycoumarin (0.324 g, 2 mmol), aldehyde (1 mmol) and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (7 mg) in a 10-mL round-bottomed flask connected to a reflux condenser, was heated and stirred at 100 °C in the absence of solvent. After the completion of the reaction as monitored by TLC, the reaction mixture was dissolved in hot EtOH and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl catalyst was recovered magnetically. The crude product was recrystallized from ethanol to afford the pure product (Scheme 3).

Selected spectra of compounds

3,3′-((4-chlorophenyl)methylene)bis(4-hydroxychroman-2-one) White powder; Mp 260–262 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 6.38 (*s*, 1H), 7.20–7.23 (*d*, *m*, 2H), 7.28–7.4 (*m*, 6H), 7.59–7.63 (*m*, 2H), 7.93–7.96 (*m*, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): 35.6, 104.6, 116.0, 117.2, 123.8, 123.9, 128.0, 128.7, 130.3, 132.2, 138.3, 152.1, 164.5, 164.7.

3,3′-(pyridin-4-ylmethylene)bis(4-hydroxychroman-2-one) White powder; Mp: 270–274 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 6.45 (*s*, 1H), 7.24–7.33 (*m*, 4H), 7.56 (*t*, J = 7.2 Hz, 2H), 7.81 (*t*, J = 8 Hz, 4H), 8.68 (*d*, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): 37.7, 101.2, 115.7, 119.2, 123.2, 124.1, 125.2, 131.6, 140.7, 152.6, 164.0, 164.8, 168.0.

Results and discussion

At first, to optimize the reaction conditions, the reaction between 4-chloro benzaldehyde and 2-hydroxynaphthalene-1,4-dione was selected as a model reaction and various

Table 1 Optimization reaction between 4-chloro benzaldehyde and 2-hydroxynaphthalene-1,4-dione using TrBr under solvent-free condition

Entry	Catalyst (mol%)	Temperature °C	Time (min)	Yield[a] (%)
1	5	100	120	35
2	7	100	90	54
3	10	100	75	65
4	12	100	60	82
5	15	100	45	90
6	17	100	45	90
7	20	100	45	90
8	15	90	65	78
9	15	70	80	60
10	15	50	90	45
11	15	rt	120	Trace
12	–	100	120	–

[a] Isolated yield

Table 2 Optimization reaction between 4-chloro benzaldehyde and 2-hydroxynaphthalene-1,4-dione using [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl under solvent-free condition

Entry	Catalyst (mg)	Temperature °C	Time (min)	Yield[a] (%)
1	1	100	50	35
2	3	100	35	54
3	6	100	28	65
4	8	100	12	92
5	10	100	11	92
6	12	100	11	92
7	8	70	24	73
8	8	50	30	61
9	8	rt	60	21
10[b]	8	100	60	70

[a] Isolated yield. [b] This reaction was carried out in the presence of Fe_3O_4 in comparison with [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl

amounts of TrBr as a neutral organocatalyst and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl as a heterogeneous nano-catalyst were investigated on this reaction at different temperatures up to 100 °C under solvent-free conditions (Tables 1, 2). The worthy results were attained when the reaction was achieved in the presence of 15 mol% of TrBr (Table 1, entry 5) or 8 mg of [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl at 100 °C (Table 2, entry 4). No improvement was obtained in the yield and reaction time using increasing the amount of the catalyst (Table 1, entries 6, 7, Table 2, entries 5, 6). Table 1 clearly shows that in the absence of catalyst, the product was produced with low yield (Table 1, entry 12). The acidic content of [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl was characterized by the determination of its H^+ of the catalyst, through the titration with NaOH (0.01 mol/L). For this purpose, 8 g of catalyst titrated by 1 mL of NaOH (0.01 mol/L) and amounts of H^+ in catalyst was obtained 0.01 mmol.

To compare the effect of the solution in comparison with solvent-free condition, a mixture of 4-chloro benzaldehyde and 2-hydroxynaphthalene-1,4-dione, as model reaction, was tested using 15 mol% of TrBr, as a neutral organocatalyst or [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl in several solvents such as H_2O, C_2H_5OH, CH_2Cl_2, $CHCl_3$ and toluene under reflux condition. The results are summarized in Table 3. The results displayed that solvent-free condition was the best condition for this reaction (Table 3, entry 6).

To optimize the reaction conditions, the reaction between benzaldehyde and 4-hydroxycoumarin (Scheme 3) was chosen as a model reaction and various amounts of TrBr as a neutral organocatalyst and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl as a heterogeneous nano-catalyst were investigated in this reaction at different temperatures up to

Table 3 The reaction of 2-hydroxynaphthalene-1,4-dione and 4-chlorobenzaldehyde using TrBr (15 mol%) (method A) and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (8 mg) (method B) in different solvents under reflux conditions

Entry	Solvent	A: Catalyst (mol%)/B: (mg)	Temperature °C	Time (min) A/B	Yield[a] (%)
1	Ethanol	15/8	Reflux	120/60	40/78
2	H_2O	15/8	Reflux	120/60	50/81
3	CH_2Cl_2	15/8	Reflux	120/60	30/54
4	$CHCl_3$	15/8	Reflux	120/60	35/59
5	Toluene	15/8	Reflux	120/60	62/82
6	–	15/8	100	45/12	90/92

[a] Isolated yield

Table 4 Effect of different amounts of the catalysts and temperatures on the reaction between 4-hydroxycoumarin and benzaldehyde

Entry	A: Catalyst (mol%)/B: (mg)	Temperature °C	Time (min) A/B	Yield[a] (%)
1	–	80	120	25
2	5/2	80	35/30	54/47
3	10/4	80	30/22	65/68
4	12/5	80	27/18	82/80
5	15/7	80	20/12	92/93
6	15/7	90	19/12	92/93
7	15/7	70	20/12	92/93
8	15/7	50	30/32	70/72
9	15/7	rt	60/60	Trace
10	20/10	70	20/12	92/93

[a] Isolated yield

Table 5 The preparation of aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone by using TrBr (method A) and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (method B)

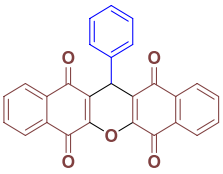
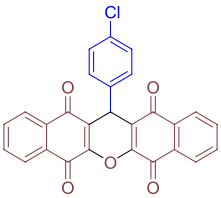
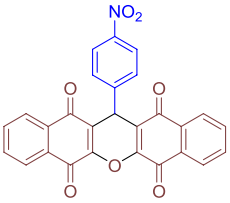
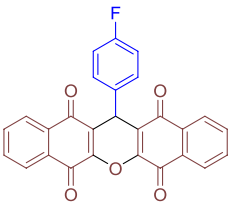
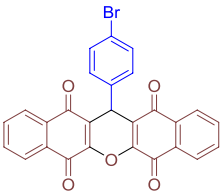
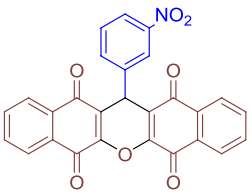
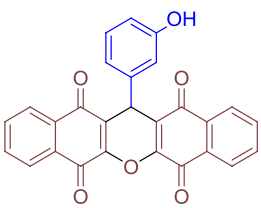
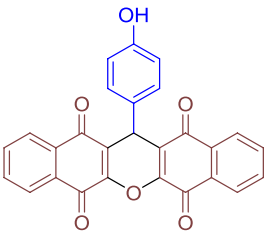
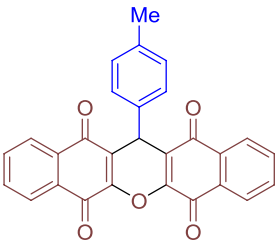
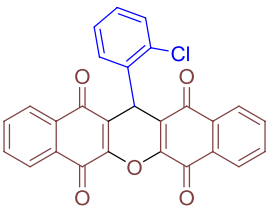
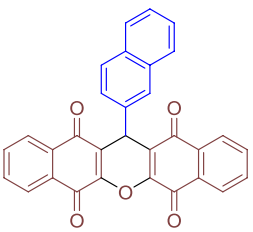
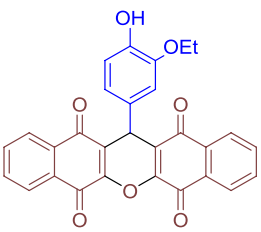
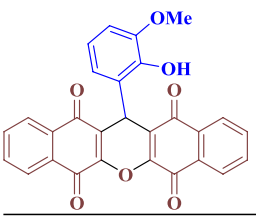
Product	Time (min) Method A/B	Yield[a] (%) Method A/B	Mp. °C (Lit.)
	50/15	85/87	304–306 (305–307) [21]
	45/12	90/92	329–331 (330–332) [21]
	50/10	85/92	350–353 (354–356) [36]
	35/15	80/86	268–270 (270–272) [21]
	40/14	86/88	330–333 (333–335) [21]
	55/10	80/89	338–341 (340–342) [21]
	60/18	90/91	243–246

Table 5 continued

Product	Time (min) Method A/B	Yield[a] (%) Method A/B	Mp. °C (Lit.)
	60/15	90/91	262–265
	55/14	84/90	303–306 (304–307) [21]
	60/15	75/86	307–309 (307–309) [36]
	55/17	78/84	248–251
	50/17	82/86	265–268
	60/15	83/85	238–240

[a] Isolated yield

Table 6 The preparation of biscoumarins using TrBr (method A) and $[Fe_3O_4@SiO_2@(CH_2)_3\text{-Im-}SO_3H]Cl$ (method B)

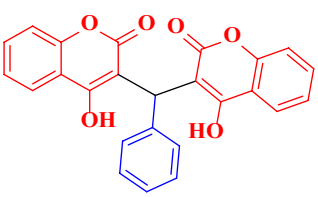
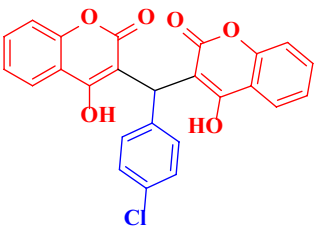
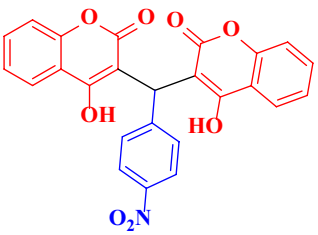
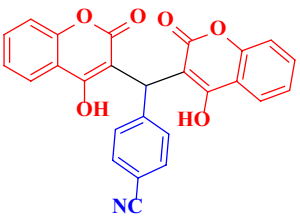
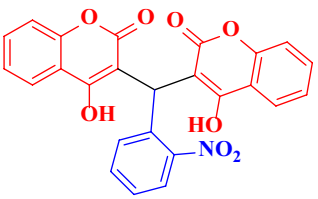
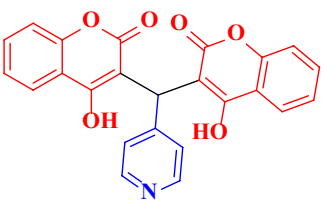
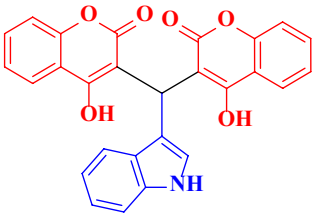
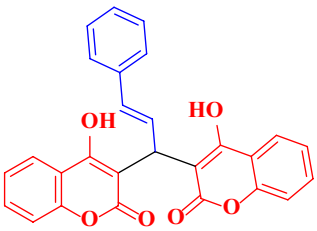
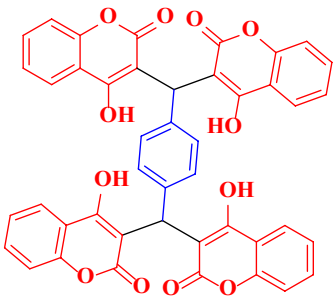
Product	Time (min) Method A/B	Yield[a] (%) Method A/B	M p. °C (Lit.)
	20/12	92/93	231–233 (230–232) [25]
	18/10	91/94	259–261 (256–258) [25]
	19/11	92/94	232–234 (232–234) [25]
	22/14	89/91	260–262 (260–262) [25]
	28/18	85/87	205–207 (200–202) [25]
	30/22	78/81	270–274 [25]

Table 6 continued

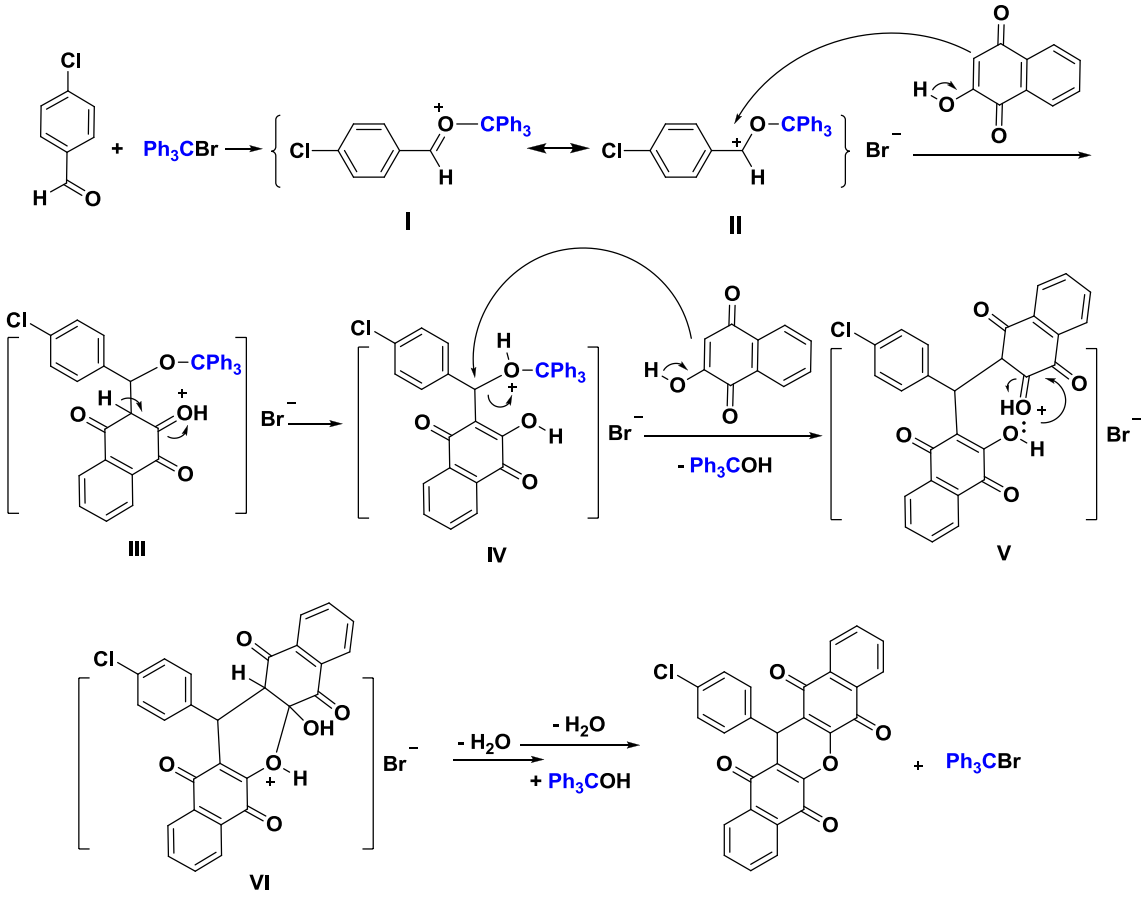
Product	Time (min) Method A/B	Yield[a] (%) Method A/B	M p. °C (Lit.)
	28/19	82/85	132–136 (133) [25]
	35/22	85/86	188–191 (190) [25]
	40/27	76/79	188–191 [25]

[a] Isolated yield

100 °C under solvent-free conditions (Table 4). As shown in Table 4, the worthy results were obtained when the reaction was carried out in the presence of 15 mol% of TrBr or 7 mg of [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl at 70 °C (Table 4, entry 7). No improvement was shown in the yield and reaction time using increasing the amount of catalyst and temperature (Table 4, entry 10). Table 4 clearly shows that in the absence of catalyst, the product was produced with low yield (Table 4, entry 1).

To explore the generality, scope and efficiency of the catalyst, we extended our study using TrBr (15 mol %) and [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl (8 mg) with different aromatic aldehydes under solvent-free conditions to prepare a series of aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone derivatives (Table 5) and of bis-coumarin derivatives (Table 6). Various aromatic aldehydes containing electron withdrawing substituents, electron-releasing substituents, halogens and hetero-aromatic aldehydes on their aromatic rings were utilized successfully in the reaction and gave the corresponding products in high yields and in short reaction times (Tables 5, 6). The structures of the desired obtained products were confirmed by the IR, ^{1}H and ^{13}C NMR.

In a plausible mechanism (Scheme 4), aldehyde was activated by the trityl bromide catalysts. Two resonance forms of activated aldehyde could be produced and converted together in a reversible reaction. To prove the formation of **I** and **II**, 4-chlorobenzaldehyde was reacted with trityl bromide at room temperature. Then, UV spectra of the 4-chlorobenzaldehyde, trityl bromide and activated 4-chlorobenzaldehyde with trityl bromide were recorded and maximum absorptions of them were appeared at 263, 235 and 314 nm, respectively (Fig. 1). **I** and **II** were introduced by Oikawa et al. as cationic intermediates for the first time [38–46]. 2-Hydroxynaphthalene-1,4-dione reacted with the carbonyl group of the aldehyde, which was activated by trityl carbocation to afford intermediate **III** and **IV,** respectively. In the next step, intermediate **IV**,



Scheme 4 The plausible mechanism for the reaction of 2-hydroxynaphthalene-1,4-dione with 4-chlorobenzaldehyde catalyzed by TrBr

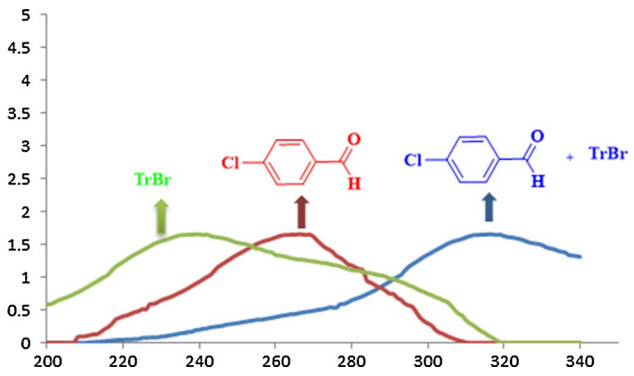


Fig. 1 UV spectra of TrBr, 4-chlorobenzaldehyde and mixture of 4-chlorobenzaldehyde with TrBr

as a Michael acceptor, reacted with another molecule of 2-hydroxynaphthalene-1,4-dione to give intermediate **V**. Finally, by intra molecular nucleophilic addition reaction to carbonyl group, 13-(4-chlorophenyl)-5H-dibenzo[*b*,*i*]xanthene-5,7,12,14(13H)-tetraone was prepared (Scheme 4). To confirm that TrBr cannot convert to TrOH and HBr by very few water present in the reaction medium from environment and consequently HBr is not the real catalyst of the process, the model reaction was tested in the presence of pyridine as a base besides TrBr as a catalyst in which no changes in the reaction were observed. The preparation of bis-coumarins was catalyzed using TrBr by similar mechanism as given in Scheme 4.

Recyclability of $[Fe_3O_4@SiO_2@(CH_2)_3\text{-Im-}SO_3H]Cl$ was tested on the synthesis of 13-(4-Chlorophenyl)-5H-dibenzo[*b*,*i*]xanthene-5,7,12,14(13H)-tetraone and (phenylmethylene) bis (4-hydroxy-2H-chromen-2-one). Catalytic activity of the catalyst was restored within the limits of the experimental errors for 7 successive recycle runs (Fig. 2).

In order to compare the catalytic activity of trityl chloride and trityl bromide in the synthesis of

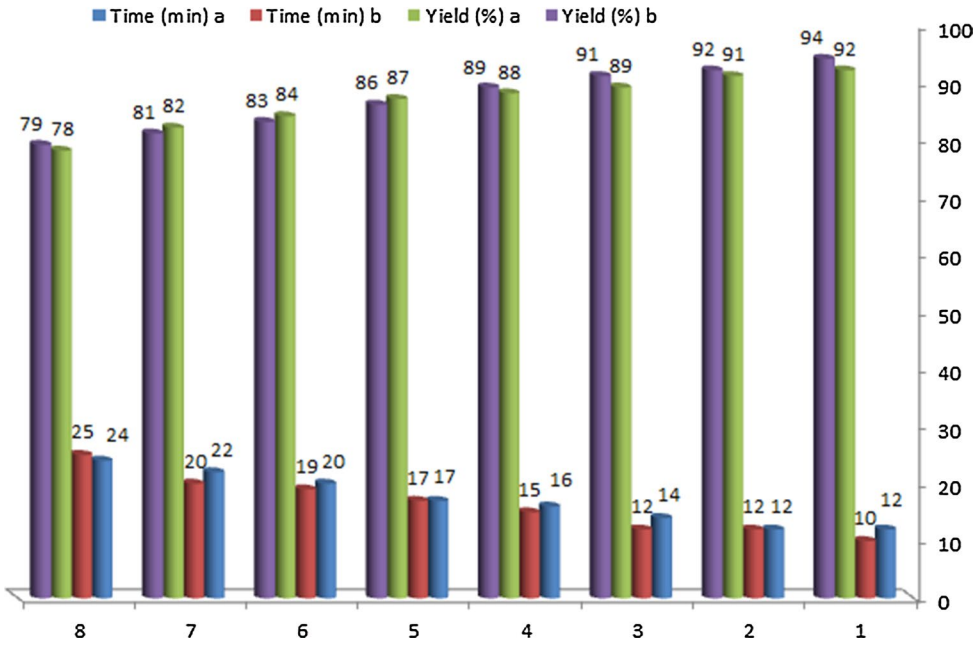


Fig. 2 Recycled [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl catalyst in the synthesis of aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone and (phenylmethylene) bis(4-hydroxy-2H-chromen-2-one). [a]13-(4-Chlorophenyl)-5H-dibenzo[*b*,*i*]xanthene-5,7,12,14(13H)-tetraone. [b](Phenylmethylene) bis (4-hydroxy-2H-chromen-2-one)

Table 7 Comparison of TrBr and TrCl in the synthesis of aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone and (phenylmethylene) bis(4-hydroxy-2H-chromen-2-one)

Catalyst	Time (min)[a]	Yield (%)[a]	Time (min)[b]	Yield (%)[b]
TrBr	45	90	20	92
TrCl	65	70	35	85

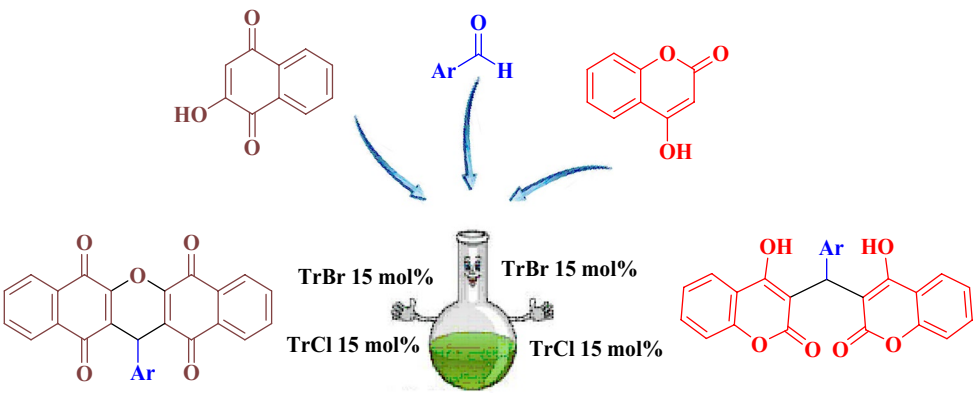
[a] 13-(4-Chlorophenyl)-5H-dibenzo[*b*,*i*]xanthene-5,7,12,14(13H)-tetraone

[b] (Phenylmethylene) bis (4-hydroxy-2H-chromen-2-one)

13-(4-chlorophenyl)-5H-dibenzo[*b*,*i*]xanthene-5,7,12,14(13H)-tetraone and 3,3′(phenylmethylene) bis(4-hydroxy-2H-chromen-2-one), 15 mol% of these catalysts were used for the synthesis of these products (Table 7) (Scheme 5). Table 7 indicates that the catalytic activity of TrBr was more than that of TrCl in the mentioned reactions.

Conclusions

In summary, we have developed new catalytic methods for the preparation of biological henna-based xanthenes (aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone) and bis-coumarin derivatives via the reaction between 2-hydroxynaphthalene-1,4-dione (henna) or 4-hydroxycoumarin with aromatic aldehydes in the presence of trityl bromide as a homogenous and neutral organocatalyst or [Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H]Cl as a heterogeneous, acidic and nano-magnetic catalyst under solvent-free conditions. The advantages of the described method are efficiency, generality, high yields, short reaction times, cleaner reaction profile and simplicity.



Scheme 5 Incorporation of TrBr and TrCl as catalysts in the synthesis of aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone and (phenylmethylene) bis(4-hydroxy-2H-chromen-2-one)

Acknowledgements We thank Bu-Ali Sina University and Iran National Science Foundation (INSF) for financial support (The Grant Number: 940124) to our research group.

References

1. S. Verma, L.S. Jain, B. Sain, Tetrahedron Lett. **51**, 6897 (2010)
2. S. Das, S. Santra, P. Mondal, A. Majee, A. Hajr, Synthesis **48**, 1269 (2016)
3. K.L. Jensen, G. Dickmess, H. Jiang, L. Albrecht, K.A. Jorgensen, Acc. Chem. Res. **45**, 248 (2012)
4. F. Vetica, R.M. de Do Figueire, M. Orsini, D. Tofani, T. Gasperi, Synthesis **47**, 2139 (2015)
5. T. Kano, Y. Yamaguchi, K. Keiji, Maruoka. Chem. Eur. J. **15**, 6678 (2009)
6. Y.B. Huang, W.B. Yi, C. Cai, Top Curr Chem. **308**, 191 (2012)
7. A. El Kadib, Chemsuschem **8**, 217 (2014)
8. B. Karimi, F. Mansouri, H.M. Mirzaei, ChemCatChem **7**, 1736 (2015)
9. S.G. Babu, R. Karvembu, Catal. Surv. Asia **17**, 156 (2013)
10. D. Zhang, C. Zhou, Z. Sun, L.Z. Wu, C.H. Tung, T. Zhang, Nanoscale **4**, 6244 (2012)
11. S. Shylesh, V. Schunemann, W.R. Thiel, Angew. Chem. Int. Ed. **49**, 3428 (2010)
12. S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L.V. Elst, R.N. Muller, Chem. Rev. **108**, 2064 (2008)
13. A.H. Lu, E.L. Salabas, F. Schith, Angew. Chem. Int. Ed. **46**, 1222 (2007)
14. T. Cheng, D. Zhang, H. Li, G. Liu, Green Chem. **16**, 3401 (2014)
15. R. Hudson, Y. Feng, R.S. Varma, A. Moores, Green Chem. **16**, 4493 (2014)
16. M.B. Gawande, R. Luque, R. Zboril, ChemCatChem. **6**, 3312 (2014)
17. R. Mrowczynski, A. Nan, J. Liebscher, RSC Adv. **4**, 5927 (2014)
18. M. Mokhtary, J. Iran. Chem. Soc. (2016). doi:10.1007/s13738-016-0900-4
19. A.L. Romanyuk, O.P. Polishchuk, B.L. Litvin, N.I. Ganushchak, Russ. J. Gen. Chem **72**, 251 (2002)
20. A.G.F. Shoair, J. Coord. Chem. **65**, 3511 (2012)
21. Z.N. Tisseh, S.C. Azimi, P. Mirzaei, A. Bazgir, Dyes Pigments **79**, 73 (2008)
22. D. Liu, S. Zhou, J. Gao, L. Li, D. Xu, J. Mex. Chem. Soc. **57**, 345 (2013)
23. A. Rahmati, Chin. Chem. Lett. **76**, 121 (2010)
24. A. Bazgir, Z.N. Tisseh, P. Mirzaei, Tetrahedron Lett. **49**, 5165 (2008)
25. M.A. Zolfigol, A.R. Moosavi-Zare, M. Zarei, C. R. Chim. **17**, 1264 (2014)
26. J. Li, C.W. Lv, X.J. Li, D. Qu, Z. Hou, M. Jia, X.X. Luo, X. Li, M.K. Li, Molecules **17**, 46920 (2015)
27. J. Li, Y.P. Sui, J.J. Xin, X.L. Du, J.T. Li, H.R. Huo, H. Ma, W.H. Wang, H.Y. Zhou, H.D. Zhan, Z.J. Wang, C. Li, F. Sui, X. Li, Bioorg. Med. Chem. Lett. **25**, 5520 (2015)
28. M.M. Heravi, F. Nahavandi, S. Sadjadi, H.A. Oskooie, F.F. Bamoharram, Synth. Commun. **40**, 498 (2010)
29. J. Albadi, A. Mansournezhad, S. Salehnasab, Res. Chem. Intermed. **41**, 5713 (2015)
30. A. Zhu, M. Wang, L. Li, Wang. RSC Adv. **5**, 73974 (2015)
31. K. Parvanak Boroujeni, P. Ghasemi, Z. Rafienia, Monatsh. Chem. **145**, 1023 (2014)
32. R. Rezaei, F. Moezzi, M.M. Doroodmand, Chin. Chem. Lett. **25**, 183 (2014)
33. B. Sadeghi, J. Chem. Res. **3**, 171 (2013)
34. K. Tabataeian, H. Heidari, A. Khorshidi, M. Managhani, N.O. Mahmoodi, J. Serb. Chem. Soc. **77**, 407 (2012)
35. W. Li, Y. Wang, Z. Wang, L. Dai, Y. Wang, Catal. Lett. **141**, 1651 (2011)
36. H. Mehrabi, H. Abusaidi, J. Iran. Chem. Soc. **7**, 890 (2010)
37. L. Shastri, S. Kalegowda, M. Kulkarni, Tetrahedron Lett. **48**, 7215 (2007)
38. A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, F. Abi, A. Zare, H. Kaveh, V. Khakyzadeh, M. Kazem- Rostami, A. Parhami, Tetrahedron **69**, 212 (2013)
39. A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, A. Zare, A. Parhami, A. Khalafi-Nezhad, Appl. Catal. A Gen. **386**, 179 (2010)
40. A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, A. Zare, M. Khojasteh, Z. Asgari, V. Khakyzadeh, A. Khalafi-Nezhad, Catal. Commun. **20**, 54 (2012)
41. A. Zare, M. Merajoddin, A. Hasaninejad, A.R. Moosavi-Zare, V. Khakyzadeh, C. R. Chim. **16**, 380 (2013)
42. A. Zare, M. Merajoddin, A.R. Moosavi-Zare, M. Zarei, Chin. J. Catal. **35**, 85 (2014)
43. M. Zarei, Iran. J. Catal. **5**, 293 (2015)
44. A.R. Moosavi-Zare, Z. Asgari, A. Zare, M.A. Zolfigol, M. Shekouhy, RSC Adv. **4**, 60636 (2014)
45. A.R. Moosavi-Zare, M.A. Zolfigol, A. Mousavi-Tashar, Res. Chem. Intermed. **42**, 7305 (2016)
46. A.R. Moosavi-Zare, M.A. Zolfigol, Z. Rezanejad, Can. J. Chem. **94**, 626 (2016)
47. M.A. Zolfigol, V. Khakyzadeh, A.R. Moosavi-Zare, A. Rostami, A. Zare, N. Iranpoor, M.H. Beyzavi, R. Luque, Green Chem. **15**, 2132 (2013)
48. M.A. Zolfigol, T. Azadbkht, V. Khakizadeh, R. Nejatyami, D. Perrin, RSC Adv. **4**, 40036 (2014)
49. T. Azadbakht, M.A. Zolfigol, R. Azadbakht, V. Khakizadeh, D. Perrin, New J. Chem. **39**, 439 (2015)
50. A. Khazaei, A.R. Moosavi-Zare, H. Afshar-Hezarkhani, V. Khakyzadeh, RSC Adv. **4**, 32142 (2014)
51. M.A. Zolfigol, A.R. Moosavi-Zare, P. Moosavi, V. Khakyzadeh, A. Zare, C. R. Chim. **16**, 962 (2013)
52. A. Khazaei, F. Gholami, V. Khakyzadeh, A.R. Moosavi- Zare, J. Afsar, RSC Adv. **5**, 14305 (2015)
53. A. Khazaei, F. Gholami, V. Khakyzadeh, A.R. Moosavi- Zare, J. Afsar, RSC Adv. **5**, 14305 (2015)
54. A. Khazaei, A.R. Moosavi-Zare, F. Gholami, V. Khakyzadeh, Appl. Organometal. Chem. **30**, 691 (2016)