



Preparation of a new, green and recyclable catalyst, silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride, and a solvent- and metal-free protocol for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives

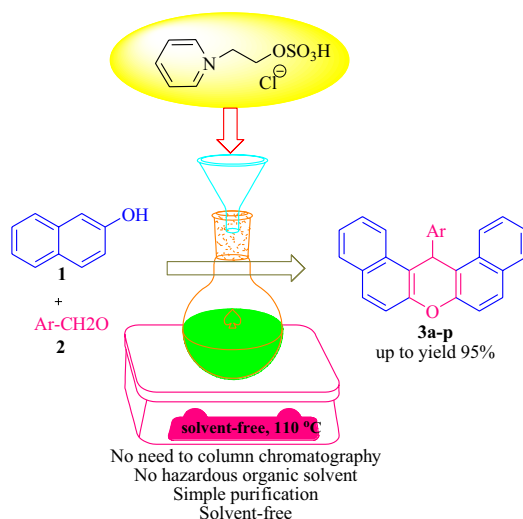
Sami Sajjadifar¹ · Maryam Pornuroz¹

Received: 28 February 2017 / Accepted: 18 March 2018 / Published online: 2 April 2018
© The Author(s) 2018

Abstract

A cost-effective and convenient procedure for the synthesis of silica-supported 1-(2-sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride $\text{SiO}_2/[\text{SEP}]\text{Cl}$ as a recoverable heterogeneous and Brønsted acid catalyst is described, and was used for the one-pot synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes under solvent- and metal-free conditions at 110 °C in short reaction time with a yield of up to 95%. The present method offers several advantages such as simplicity in operation, ease of preparation and recycling of Brønsted acidic ionic liquid (BAIL), solvent-free reaction conditions, and no hazardous organic solvents are used in the entire procedure including workup and purification.

Graphical abstract



Keywords 1-(2-Sulfooxy)ethyl)1*H*-pyridine-1-ium-chloride · One-pot reaction · 14-Aryl-14*H*-dibenzo[*a,j*]xanthene · Solvent- and metal-free conditions · Brønsted acidic ionic liquid

✉ Sami Sajjadifar
sami.sajjadifar@gmail.com

¹ Department of Chemistry, Payame Noor University, P.O. Box 19395-4697, Tehran, Iran

Introduction

Recently ionic liquids (ILs) are considered as dual reagents (catalysts and solvents) and a greener alternative for a range of various organic reactions, but the application of them as

catalyst in the absence of solvent is vital and important in organic and inorganic chemistry [1]. As well as, ILs are an appropriate alternative instead of volatile and toxic organic solvents in the future due to high polarity, solubility with certain organic solvents and/or water, low vapor pressure, and excellent solubility in organic and inorganic materials [2]. On the other hand, ILs have been frequently used as solar cell, catalysts, biocatalysts, in nanomaterial synthesis, liquid–liquid separations, polymerization reactions, extraction, dissolution processes, electrochemistry and electro-deposition, and as supercapacitors [3–10].

Among organic compounds, the synthesis of xanthene and its derivatives has received specific attention among pharmacological activities and organic chemists due to having a wide range of biological and therapeutic properties such as antioxidant [11], cytotoxic [12], anti-proliferative [13], antifungal [14], anti-inflammatory, antiviral [15], and antibacterial properties [16]. Furthermore, xanthene and its derivatives would be used in laser technologies [17], as pH-sensitive fluorescent materials for visualization of biomolecules [18], sensitizers in dye-sensitized solar cells (DSSCs) [19], in photodynamic therapy [20], as hole-transporting materials in organic light-emitting devices (OLEDs) [21], and in the food industry as additives [22]. Xanthene and its derivatives are available in natural plants [23, 24]. For instance, examples of natural xanthenes are 3-isopropyl-9a-methyl-1,2,4a,9a-tetrahydroxanthene **A**, used as an antidote for all snake venoms, blumeaxanthene **B** and lumeaxanthene **C**, used to treat gynecological disorders (Scheme 1).

Different procedures have been employed for the preparation of xanthenes and benzoxanthenes [25–29]. In addition, one of the best, easiest, and cost-effective procedures for the synthesis of xanthene derivatives is condensation between aldehydes with 2-naphthols under different conditions in the presence of various Lewis and Brønsted acid catalysts such as $\text{Fe}_2(\text{SO}_4)_{3.7}\text{H}_2\text{O}$ [30], polyvinylpolypyrrolidone-bound boron trifluoride [31], pentafluorophenyl ammonium triflate [32], silica sulfuric acid [33], $\gamma\text{-Fe}_2\text{O}_3\text{-HAp-Fe}^{2+}$ NPs [34], $\text{H}_3\text{PW}_{10}\text{V}_2\text{O}_{40}$ [35], cellulose sulfuric acid [36], $\text{Yb}(\text{OTf})_3$ [37], 2,6-Pyridinedicarboxylic acid [38], silica-supported [2-(sulfoxy)ethyl]sulfamic acid [39], Selectfluor™ [40], carbon-based solid acid [41], I_2 [42], ZnO NPs [43], *p*-toluenesulfonic acid/ionic liquid [44], trityl chloride [45], and

polytungstozincate acid [46]. Although several of these procedures suffer from disadvantages such as the use of excess reagents/catalysts, tedious workup procedures, toxicity of the reagent, unsatisfactory yields, low yields of products, use of organic solvents, prolonged reaction time, use of the often expensive catalysts and non-recyclability, the focus on introducing efficient, economical, and solvent-free procedures with high activity, simple reaction workup, and reusability of the catalyst to overcome these problems is still in demand for the synthesis of xanthene derivatives.

It is necessary to introduce milder, simple reaction workup, solvent- and metal-free, faster, reusability of the catalyst, and generally a greener approach accompanied with higher yields for the synthesis of xanthene derivatives. Therefore, and according to the above-mentioned notes, it seems that silica-supported 1-(2-sulfoxy)ethyl)1*H*-pyridine-1-ium-chloride $\text{SiO}_2/[\text{SEP}]\text{Cl}$ as a catalyst can be an appropriate in the synthesis of these organic compounds.

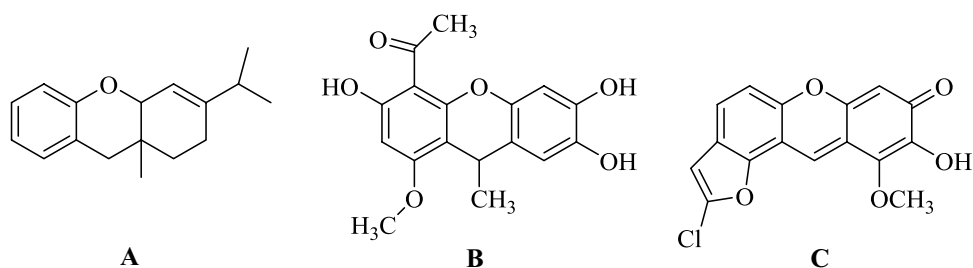
In this research, we wish to report a rapid and cost-effective procedure for the synthesis of silica-supported 1-(2-sulfoxy)ethyl)1*H*-pyridine-1-ium-chloride $\text{SiO}_2/[\text{SEP}]\text{Cl}$ as a new, highly efficient, and Brønsted acid catalyst for the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthene **3a–p** derivatives under solvent-, metal-free and thermal conditions (Scheme 2).

Experimental

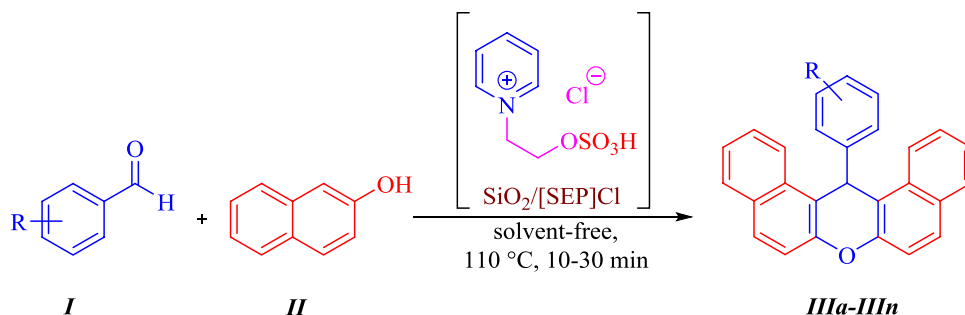
General

All of the reagents used in the current study were purchased from Merck, Aldrich, and Fluka and used without further purification. All the products are known compounds and were characterized by comparing the IR (KBr), ^1H NMR, and ^{13}C NMR spectroscopic data and their melting point to the literature values. Nuclear magnetic resonance (^1H NMR and ^{13}C NMR) was recorded in CDCl_3 solvent on a Bruker DRX-300 and -400 spectrometer using tetramethylsilane (TMS) as an internal reference. IR spectra were recorded on a Frontier FT-IR (PerkinElmer) spectrometer using a KBr disk. The purities of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/

Scheme 1 Examples of natural xanthenes



Scheme 2 One-pot synthesis of xanthenes derivatives in the presence of BAIL under solvent-free conditions



UV 254 plates. Melting points (MP) were determined on a Thermo Scientific 9300 melting point apparatus.

Preparation of silica-supported 1-(2-sulfoxyethyl)1*H*-pyridine-1-ium-chloride SiO₂/[SEP]Cl

In this study, silica-supported 1-(2-sulfoxyethyl)1*H*-pyridine-1-ium-chloride SiO₂/[SEP]Cl as a BAIL catalyst was prepared according to the literature procedure (Fig. 1) [47]. Spectral data of 1-(2-sulfoxyethyl)1*H*-pyridine-1-ium-chloride are as follows: viscous brown oil: IR (KBr): OH (3200–3600 cm⁻¹), C=N (1658 cm⁻¹), C=C (1426 cm⁻¹), S=O (1232 cm⁻¹), and S–O (614 cm⁻¹). ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.13–3.16 (t, *J* = 5.6 Hz, 2H), 3.93–3.970 (t, *J* = 8 Hz, 2H), 8.10–8.17 (t, *J* = 12 Hz, 2H), 8.61 (s, 1H), 8.92–8.99 (t, *J* = 6.4 Hz, 2H), 9.00–9.42 (d, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): 60.7, 61.8, 128.2, 142.2, 146.0.

General procedure for the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes

A mixture of 2-naphthol (1 mmol), various aldehydes (1 mmol) and SiO₂/[SEP]Cl (20 mol%) in a 10-mL round-bottomed flask connected to a reflux condenser was stirred in an oil bath at 110 °C. Completion of the reaction was indicated by TLC (monitored by TLC, ethylacetate:*n*-hexane 1:3). After completion, the solvent was removed under reduced pressure and the crude product was recrystallized with ethanol to afford the pure product in 81–95% yield. All the products were known compounds and characterized by

comparing the melting point, ¹H NMR and ¹³C NMR spectra with those reported in the literature.

14-(4-Bromophenyl)-14*H*-dibenzo[*a,j*]xanthenes (Table 4, entry 3e)

¹H NMR (300 MHz, CDCl₃): δ 5.34 (1H, s, CH), 6.16–6.48 (10H, m, Ar–H), 6.68–6.75 (4H, m, Ar–H), 7.19–7.22 (2H, m, *J* = 7.8, Ar–H). ¹³C NMR (75 MHz, CDCl₃): δ 37.46, 116.65, 118.01, 120.21, 122.39, 124.37, 126.92, 128.91, 129.11, 129.88, 131.04, 131.24, 131.58, 143.98, 148.67.

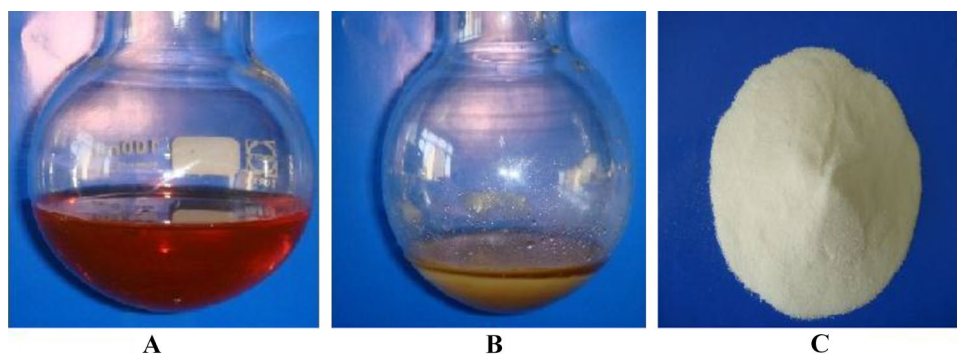
4-(4-Methoxyphenyl)-14*H*-dibenzo[*a,j*]xanthenes (Table 4, entry 3 g)

¹H NMR (300 MHz, CDCl₃): 2.49 (3H, s, OMe), 5.36 (1H, s, CH), 5.59–5.61 (2H, d, *J* = 8.66 Hz, Ar–H), 6.32–6.45 (6H, m, Ar–H), 6.49–6.55 (2H, m, Ar–H), 6.69–6.76 (4H, m, Ar–H), 7.31–7.33 (2H, d, *J* = 8.48, Ar–H); ¹³C NMR (75 MHz, CDCl₃): 37.17, 55.05, 113.89, 117.58, 118.06, 122.77, 124.28, 126.81, 128.80, 128.87, 129.23, 131.13, 131.47, 137.45, 148.69, 157.89.

14-(2-Chlorophenyl)-14*H*-dibenzo[*a,j*]xanthenes (Table 4, entry 3 l)

¹H NMR (300 MHz, CDCl₃): δ 5.69 (1H, s, CH), 5.81–5.82 (2H, d, Ar–H), 6.27–6.40 (5H, m, Ar–H), 6.50 (2H, d, Ar–H), 6.55–6.67 (4H, m, Ar–H), 7.63–7.66 (2H, *J* = 8.5, d, Ar–H). ¹³C NMR (75 MHz, CDCl₃): δ 34.63, 118.02, 118.11,

Fig. 1 Pictures of reaction between pyridine and 2-chloroethanol (a), 1-(2-sulfoxyethyl)1*H*-pyridine-1-ium-chloride (b), and silica-supported 1-(2-sulfoxyethyl)1*H*-pyridine-1-ium-chloride (c)



123.46, 124.44, 126.93, 127.87–127.94, 128.66, 129.08, 129.60, 130.13, 130.89, 131.76, 131.81, 143.57, 148.95.

Results and discussion

For this work, BAIL **C** as a green and reusable catalyst was prepared by condensation reaction between pyridine and 2-chloroethanol that led to ionic liquid **B**, following which chlorosulfonic acid was added dropwise and slowly to ionic liquid **B** for 45–60 min at 0 °C, which afforded BAIL **C** (Scheme 3) [47].

The structure of 1-(2-sulfoxy)ethyl)1*H*-pyridine-1-ium-chloride [SEP]Cl was characterized on the basis of its IR (KBr), ¹H and ¹³C NMR data, which were presented in the “Experimental” section. The characterization of BAIL **C** in comparison to compounds **A** and **B** was further conducted by FT-IR spectrum (Fig. 2). As it can be seen from Fig. 2, the broad peak is at around 3200–3600 cm⁻¹ which is related to the OH group. On the other hand, the spectra show that the broad peak is at around 1658 cm⁻¹ for C=N and 1426 cm⁻¹ for C=C, which imply both are related to pyridine ring, and the strong peak at 1232 cm⁻¹ is related to the stretching vibration of S=O bond.

¹H and ¹³C NMR spectra of the BAIL **C** are presented in Figs. 3 and 4. The important peaks of ¹H NMR spectrum of BAIL **C** were related to the acidic hydrogen (SO₃H) which was observed in 8.61 ppm. The ¹³C NMR spectrum of the BAIL **C** exhibited five signals in agreement with the proposed structure.

The activity of the new BAIL **C** as a reusable and green catalyst was tested using a one-pot condensation reaction of various aromatic aldehydes (1 mmol) with 2-naphthol (2 mmol) under solvent-free conditions for the preparation of biologically active 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives (Scheme 2).

For this purpose, to optimize the reaction conditions for the synthesis of compound **3a**, the condensation reaction of benzaldehyde (1 mmol) and 2-naphthol (2 mmol) was chosen using different amounts of BAIL as a heterogeneous and Brønsted acid catalyst under solvent-free conditions at room temperature (Table 1). As it can be seen in Table 1, when reaction was carried out in the absence of the catalyst, after 120 min the reaction was without yield (Table 1, entry 1). The best results were achieved when 20 mol% of the BAIL was appropriate to promote the reaction efficiently and give the product in excellent yield and in short reaction time (Table 1, entry 6). Additionally, it is worth noting that

Scheme 3 The synthesis of 1-(2-sulfoxy)ethyl)1*H*-pyridine-1-ium-chloride [SEP]Cl

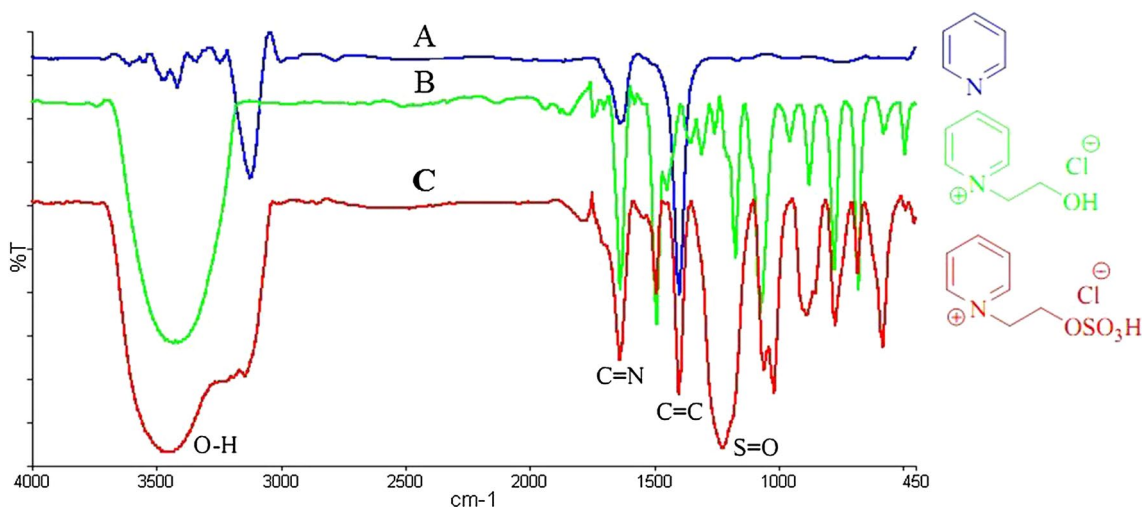
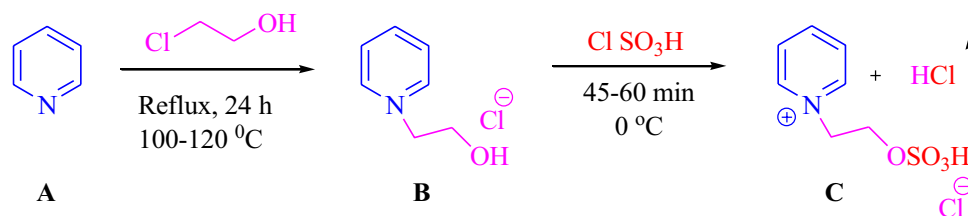


Fig. 2 Comparison of IR spectrum of compounds **A** and **B** with BAIL **C**

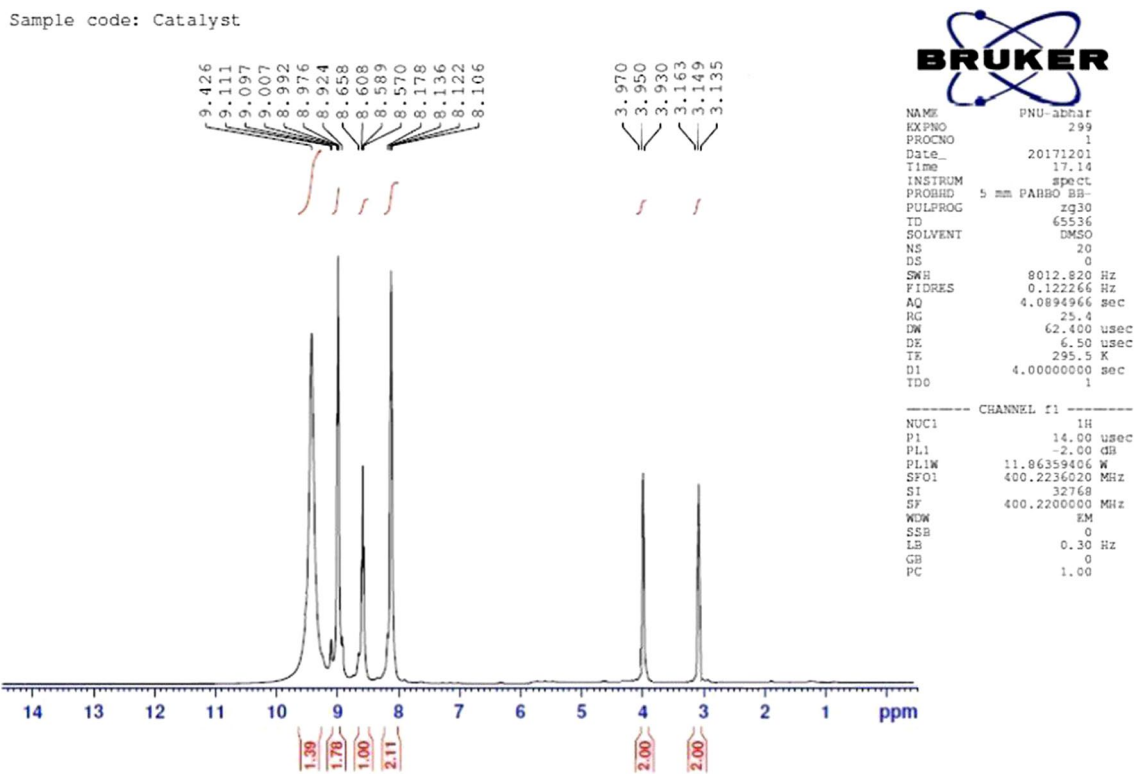


Fig. 3 ¹H NMR spectrum of [SEP]Cl

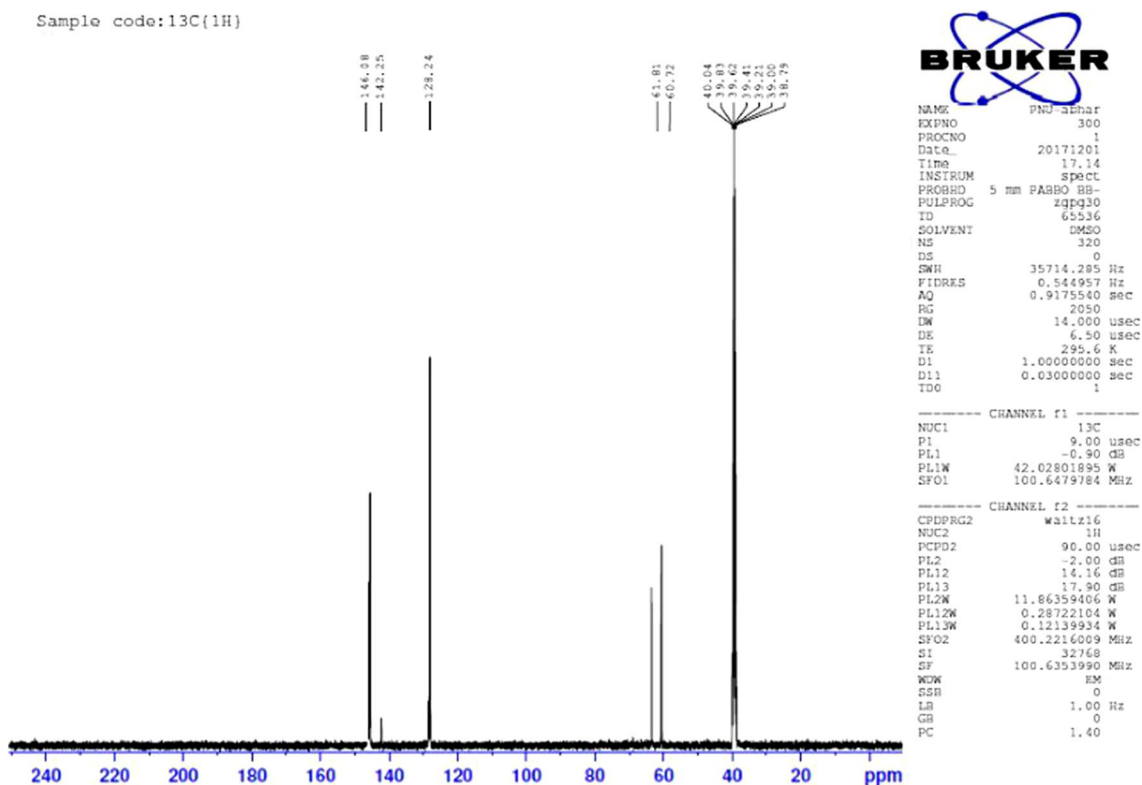


Fig. 4 ¹³C NMR spectrum of [SEP]Cl

Table 1 Result of the amount of the catalyst in the synthesis of compound **3a** under solvent-free conditions

Entry	Catalyst loading (%)	Reaction time (min)	Yield (%) ^a
1	None	120	–
2	1	100	35
3	5	90	54
4	10	90	75
5	15	45	80
6	20	20	85
7	25	20	85

^aYield of isolated products

when a higher percentage of loading of the BAIL was used, the yields did not improve (Table 2, entry 6).

To optimize the temperatures, the condensation of benzaldehyde (1 mmol) and 2-naphthol (2 mmol) in the presence of 20 mol% of BAIL was checked, and the results are tabulated in Table 2. As it can be seen in Table 2, temperature increase was appropriate for the synthesis of compound **3a**. Therefore, the model reaction in solvent-free conditions at 110 °C leads to the highest yield (94%) and shortest reaction time (15 min) compared to the other temperatures.

In the next study, to compare the efficiency of solvent-free conditions versus solvent conditions, the condensation reaction between benzaldehyde (1 mmol) and 2-naphthol (2 mmol) using BAIL (20 mol%) was tested in various solvents such as ethanol, methanol, chloroform, dichloromethane, and ethyl acetate under reflux conditions, and the results are summarized in Table 3. As it can be seen in Table 3, low yields of the product and longer reaction time rather than solvent-free conditions were obtained. Hence, performing the reaction under solvent-free conditions and in the presence of 20 mol% of BAIL at 110 °C was determined as the optimal condition.

To assess the efficiency and the scope of BAIL for the synthesis of biologically active 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives, a variety of aromatic aldehydes

Table 2 Optimization of temperature in the synthesis of compound **3a** under solvent-free conditions

Entry	Temperature (°C)	Reaction time (min)	Yield (%) ^a
1	60	55	81
2	80	40	87
3	100	30	94
4	110	15	94
5	120	20	94

^aYield of isolated products**Table 3** Optimization of various solvents in the synthesis of compound **3a** on the model reaction under reflux condition

Entry	Solvent (5 ml)	Reflux conditions (°C)	Reaction time (min)	Yield (%) ^a
1	EtOH	78.3	60	44
2	MeOH	65	60	40
3	CHCl ₃	61.2	60	51
4	CH ₂ Cl ₂	39.6	60	45
5	EtOAc	77.1	60	30

^aYield of isolated products

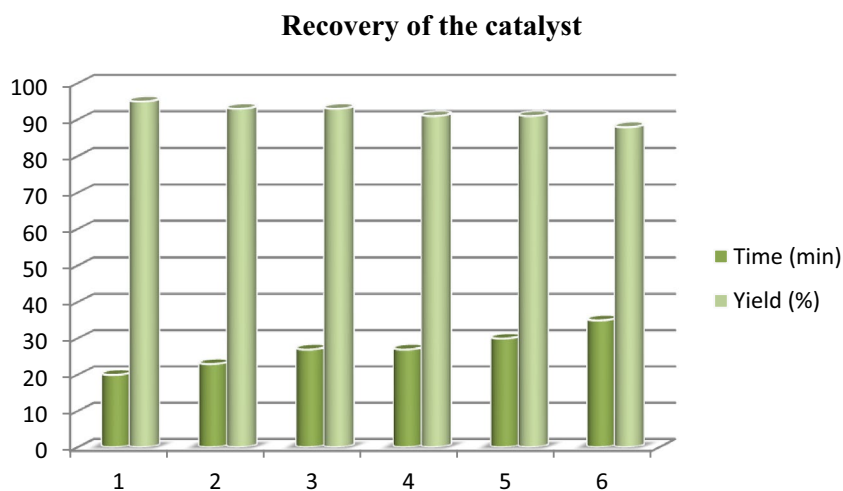
(containing electron-withdrawing, electron-donating groups, and halogens on their aromatic ring) were reacted with 2-naphthol in the optimal reaction conditions to produce the desired products **3a–p** in excellent yields and in short reaction time (Table 4). As it can be seen in Table 4, in all cases, aromatic aldehydes **3a–p** containing both electron-donating and electron-withdrawing groups (–NO₂, –Me, –OMe, –Br, –Cl, –OH, –NR₂) reacted with 2-naphthol under solvent-free conditions at 110 °C for an appropriate time (10–30 min) and good to excellent yields (81–95%) to generate 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives.

The recovery and reusability of the catalyst is a very important factor in industry and green chemistry, and also one of the advantages of heterogeneous catalyst. It is also worth noting that silica-supported 1-(2-sulfooxy)ethyl-1*H*-pyridine-1-ium-chloride SiO₂/[SEP]Cl as a catalyst can be recovered at the end of the reaction and can be used six times without losing its activity (Fig. 5). The yields of 4-(4-nitrophenyl)-14*H*-dibenzo[*a,j*]xanthenes **3i** obtained after 15 min include 95, 93, 93, 91, 91 and 88%, respectively.

The advantages of BAIL were compared (solvent, catalyst loading, time, yield, and temperature) with some other catalysts for the synthesis of compound **3a** from the reaction between benzaldehyde with 2-naphthol, and the results are represented in Table 5. In 2012, Rao et al. (Table 5, entry 3) reported the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes using ZnO NPs; in this procedure, the yield of products are low (80%) and reaction time is long (60 min). On the other hand, this procedure needs high temperature (150 °C) to complete the reaction. In 2008, Khaksar et al. (Table 5, entry 5) reported a highly efficient method for the synthesis of 14-aryl(alkyl)-14*H*-dibenzo[*a,j*]xanthenes using pentafluorophenyl ammonium triflate (PFPAT); this method relies on the use of toxic solvent like toluene, and requires very long reaction time (4.5 h). In addition, one of the other problems is that the catalyst used in this method is non-recyclable. Recently, Kumara et al. in 2006 reported the use of Selectfluor™ (Table 5, entry 7) as a catalyst for the preparation of 14-aryl(alkyl)-14*H*-dibenzo[*a,j*]xanthene derivatives in which the reaction completion time

Table 4 The solvent-free synthesis of biologically active 14-aryl-14H-dibenzo[*a,j*]xanthene derivatives using silica supported 1-(2-sulfooxyethyl)1H-pyridine-1-ium-chloride

Entry	Aldehydes	Time (min) ^a	Yield (%) ^b	M.p. °C (Lit)	
				Found	Reported
3a	C ₆ H ₅	15	94	188–190	191–193 [34]
3b	2-NO ₂ C ₆ H ₄	30	84	308–310	309–311 [34]
3c	3-NO ₂ C ₆ H ₄	30	89	211–213	210–212 [34]
3d	3-OCH ₃ C ₆ H ₄	12	90	261–263	260–262 [34]
3e	4-BrC ₆ H ₄	25	94	295–296	294–295 [34]
3f	4-CH ₃ C ₆ H ₄	20	88	225–227	226–228 [34]
3g	4-OCH ₃ C ₆ H ₄	15	85	201–203	203–205 [34]
3h	4-ClC ₆ H ₄	10	93	282–284	285–287 [34]
3i	4-NO ₂ C ₆ H ₄	20	95	309–311	310–312 [34]
3j	3-OHC ₆ H ₄	25	84	171–173	169–171 [34]
3k	4-OHC ₆ H ₄	22	87	140–141	1387–139 [34]
3l	2-ClC ₆ H ₄	17	85	221	219–220 [34]
3m	2,4-ClC ₆ H ₃	13	95	86–88	87–89 [34]
3n	4-C ₆ H ₅ C ₆ H ₄	30	81	279–281	281–283 [34]
3o	2,3-ClC ₆ H ₃	15	94	220–222	221–224 [48]
3p	4- <i>N,N</i> -(CH ₃) ₂ C ₆ H ₄	30	90	222–224	224–226 [49]

^aReactions were run till the completion as indicated by TLC^bYield of isolated products**Fig. 5** Recyclability of the SiO₂/[SEP]Cl for the synthesis of compound **3i** after 15 min

was very long and tedious (8 h), and also requires high temperature (125 °C). Wang et al. in 2009 reported the use of iodine (Table 5, entry 9) as a catalyst for the synthesis of 14-aryl(alkyl)-14H-dibenzo[*a,j*]xanthene derivatives under neat conditions; one of the main problems of this method is the use of iodine, which is toxic and biodegradable, and the reaction time is long. As it can be seen in Table 5, the reaction in the presence of BAIL was simpler, solvent free, economical, eco-friendly, the catalyst used was recyclable, and the reaction time was shorter. On the whole, it seems that this catalytic system can be an appropriate alternative method for the synthesis.

Conclusion

In summary, silica-supported 1-(2-sulfooxyethyl)1H-pyridine-1-ium-chloride SiO₂/[SEP]Cl as a new and recoverable heterogeneous catalyst was employed for the synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthene derivatives by the one-pot condensation reaction of various aldehydes with 2-naphthol under thermal and solvent-free conditions. This methodology offers very attractive features such as economic viability of catalyst, short reaction time, high yield of products, operational simplicity, easier workup

Table 5 Comparison of various catalysts used for the synthesis of compound **3a**

Entry	Reaction condition	Time (h)	Yield (%) ^a	Refs.
1	Silica sulfuric acid (0.05 g)/solvent free/125 °C	20 ^b	90	[33]
2	Yb(OTf) ₃ /[BPy]BF ₄ (0.01 mmol)/110 °C	7	89	[37]
3	ZnO NPs (0.3 mmol)/solvent free/150 °C	60 ^b	80	[43]
4	PVPP-BF ₃ /solvent free (0.05 g)/120 °C	1.5	94	[31]
5	PFPAT (10 mol%)/toluene/25–30 °C	4.5	90	[32]
6	H ₃ PW ₁₀ V ₂ O ₄₀ (0.5 mol%)/solvent-free/100 °C	1	67	[35]
7	Selectfluor™ (0.1 m mol)/neat conditions/125 °C	8	93	[40]
8	Polytungstozincate acid (0.05 g)/solvent free/80 °C	1	81	[46]
9	Iodine (0.1 mmol)/neat conditions/90 °C	2.5	90	[42]
10	SiO ₂ /[SEP]Cl (20 mol%)/solvent free/110 °C	15 ^b	94	–

^aYield of isolated products^bIn minute

procedure, ease of recovering and reusing of the catalyst, and higher turn-over frequency of the catalyst in comparison to previously reported catalysts.

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

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Li TS, Zhang ZH, Yang F, Fu CG (1998) Montmorillonite clay catalysis. Part 7. 1 an environmentally friendly procedure for the synthesis of coumarins via pechmann condensation of phenols with ethyl acetoacetate. *J Chem Res* 1:38–39
- Ngo HL, LeCompte K, Hargens L, McEwen AB (2000) Thermal analysis of polyethylene graft copolymers. *Thermochim Acta* 97:357–361
- Zhao D, Wu M, Kou Y, Min E (2002) Ionic liquids: applications in catalysis. *Catal Today* 74:157–189
- Sheldon RA, Maderia-Lau L, Sorgedragher MJ, Van Rantwijk F, Seddon KR (2002) Biocatalysis in ionic liquids. *Green Chem* 4:147–151
- Yang C, Sun Q, Qiao J, Li Y (2003) Ionic liquid doped polymer light-emitting electrochemical cells. *J Phys Chem B* 107:12981–12988
- Swatloski RP, Spear SK, Holbrey JD, Rogers RD (2002) Dissolution of cellulose with ionic liquids. *J Am Chem Soc* 124:4974–4975
- Zhang S, Zhang Q, Zhang ZC (2004) Extractive desulfurization and denitrogenation of fuels using ionic liquids. *Ind Eng Chem Res* 43:614–622
- Vygodskii YS, Shaplov AS, Lozinskaya EI, Filippov OA, Shubina ES, Bandari R, Buchmeiser MR (2006) Ring-Opening Metathesis Polymerization (ROMP) in ionic liquids: scope and limitations. *Macromolecules* 39:7821–7830
- Liu ZM, Sun SY, Han BX, Zhang JL, Huang J, Du JM, Miao SD (2006) Microwave-assisted synthesis of Pt nanocrystals and deposition on carbon nanotubes in ionic liquids. *J Nanosci Nanotechnol* 6:175–179
- Swatloski RP, Visser AE, Reichert WM, Broker GA, Facina LM, Holbrey JD, Rogers RD (2002) On the solubilization of water with ethanol in hydrophobic hexafluorophosphate ionic liquids. *Green Chem* 4:81–87
- Nishiyama T, Sakita K, Fuchigami T, Fukui T (1998) Antioxidant activities of fused heterocyclic compounds, xanthene-2,7-diols with BHT or catechol skeleton. *Polym Degrad Stab* 62:529–534
- Bhattacharya AK, Rana KC, Mujahid M, Sehar I, Saxena AK (2009) Synthesis and in vitro study of 14-aryl-14H-dibenzo[a, j]xanthenes as cytotoxic agents. *Bioorg Med Chem Lett* 19:5590–5593
- Bhattacharya AK, Rana KC, Mujahid M, Sehar I, Saxena AK (2009) Synthesis and in vitro study of 14-aryl-14H-dibenzo[a, j]xanthenes as cytotoxic agents. *Bioorg Med Chem Lett* 19:5590–5593
- Kumar A, Sharma S, Maurya RA, Sarkar JJ (2010) Diversity oriented synthesis of benzoxanthene and benzochromene libraries via one-pot, three-component reactions and their anti-proliferative activity. *Comb Chem* 12:20–24
- Omolo JJ, Johnson MM, Van Vuuren SF, de Koning CB (2011) The synthesis of xanthenes, xanthenediones, and spirobenzofurans: their antibacterial and antifungal activity. *Bioorg Med Chem Lett* 21:7085–7088
- Chibale K, Visser M, Schalkwyk DV, Smith PJ, Saravanamuthu A, Fairlamb AH (2003) Exploring the potential of xanthene derivatives as trypanothione reductase inhibitors and chloroquine potentiating agents. *Tetrahedron* 59:2289–2296
- El-Brashy AM, El-Sayed Metwally M, El-Sepai FA (2004) Spectrophotometric determination of some fluoroquinolone antibacterials by binary complex formation with xanthene dyes. *Farmaco* 59:809–817
- Ahmad M, King TA, Ko DK, Cha BH, Lee J (2002) Performance and photostability of xanthene and pyromethene laser dyes in sol-gel phases. *J Phys D Appl Phys* 35:1473–1476
- Knight CG, Stephens T (1989) Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH. studies in phospholipid vesicles. *Biochem J* 258:683–687

20. Sharma GD, Balraju P, Kumar M, Roy MS (2009) Quasi solid state dye sensitized solar cells employing a polymer electrolyte and xanthene dyes. *Mater Sci Eng B* 162:32–39
21. Chang CC, Yang YT, Yang JC, Wu HD, Tsai T (2008) Absorption and emission spectral shifts of rose bengal associated with DMPC liposomes. *Dyes Pigment* 79:170–175
22. Chu ZZ, Wang D, Zhang C, Wang FH, Wu HW, Lv ZB, Hou SC, Fan X, Zou DC (2012) Synthesis of spiro[fluorene-9,9'-xanthene] derivatives and their application as hole-transporting materials for organic light-emitting devices. *Synth Met* 162:614–620
23. Qi H, Zhu BW, Abe N, Shin Y, Murata Y, Nakamura Y (2012) Involvement of intracellular oxidative stress-sensitive pathway in phloxine B-induced photocytotoxicity in human Tlymphocytic leukemia cells. *Food Chem Toxicol* 50:1841–1847
24. Thangadurai D, Ramesh N, Viswanathan MB, Prasad DX (2001) A novel xanthene from *Indigofera longiracemosa* stem. *Fito-terapia* 72:92–94
25. Huang L, Lei T, Lin CW, Kuang XC, Chen HY, Zhou H (2010) Blumeaxanthene II, a novel xanthene from *Blumea riparia* DC. *Fito-terapia* 81:389–392
26. Knight DW, Little PB (1998) The first high-yielding benzyne cyclisation using a phenolic nucleophile: a new route to xanthenes. *Synlett* 1998:1141–1143
27. Wang JQ, Harvey GR (2002) Synthesis of polycyclic xanthenes and furans via palladium-catalyzed cyclization of polycyclic aryltriflate esters. *Tetrahedron* 58:5927–5931
28. Casiraghi G, Casnati G, Cornia M (1973) Regiospecific reactions of phenol salts: reaction-pathways of alkylphenoxy-magnesiumhalides with triethylorthoformate. *Tetrahedron Lett* 14:679–682
29. Kuo CW, Fang JM (2001) Synthesis of xanthenes, indanes, and tetrahydronaphthalenes via intramolecular phenyl-carbonyl couplings reactions. *Synth Commun* 31:877–892
30. Khoeiniha R, Ezabadi A, Olyaei A (2016) An efficient solvent-free synthesis of 1,8-dioxo-octahydroxanthenes by using $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ as catalyst. *Iran Chem Commun* 4:237–282
31. Mokhtary M, Refahati S (2013) Polyvinylpyrrolidone-supported boron trifluoride (PVPP-BF₃): mild and efficient catalyst for the synthesis of 14-aryl-14H-dibenzo [a, j] xanthenes and bis(naphthalen-2-yl-sulfane) derivatives. *Dyes Pigm* 99:378–381
32. Khaksar S, Behzadi N (2012) Mild and highly efficient method for synthesis of 14-aryl(alkyl)-14H-dibenzo[a, j]xanthenes and 1,8-Dioxooctahydroxanthene derivatives using pentafluorophenyl ammonium triflate as a novel organocatalyst. *Chin J Catal* 33:982–985
33. Shaterian HR, Ghashang M, Hassankhani A (2008) One-pot synthesis of aryl 14H-dibenzo[a, j]xanthene leuco-dye derivatives. *Dyes Pigment* 76:564–568
34. Haeri HS, Rezayati S, Rezaee Nezhad E, Darvishi H (2016) Fe^{2+} supported on hydroxyapatite-core-shell- $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles: efficient and recyclable green catalyst for the synthesis of 14-aryl-14H-dibenzo[a, j]xanthene derivatives. *Res Chem Intermed* 42:4773–4784
35. Tayebee R, Tizabi Sh (2012) Highly efficient and environmentally friendly preparation of 14-aryl-14H dibenzo[a, j]xanthenes catalyzed by tungsto-divanado-phosphoric acid. *Chin J Catal* 33:962–969
36. Venu-Madhav J, Thirupathi-Reddy Y, Narsimha-Reddy P (2009) Cellulose sulfuric acid: an efficient biodegradable and recyclable solid acid catalyst for the one-pot synthesis of aryl-14H-dibenzo[a, j]xanthenes under solvent-free conditions. *J Mol Catal A Chem* 304:85–87
37. Su W, Yang D, Jin C, Zhang B (2008) $\text{Yb}(\text{OTf})_3$ catalyzed condensation reaction of β -naphthol and aldehyde in ionic liquids: a green synthesis of aryl-14H-dibenzo[a, j]xanthenes. *Tetrahedron Lett* 49:3391–3394
38. Rezayati S, Seifournia H, Mirzajanzadeh E (2017) 2,6-Pyridinedicarboxylic acid as an efficient and mild organocatalyst for the one-pot synthesis of xanthene derivative. *Asian J Green Chem* 1:24–33
39. Sajjadifar S, Fadaeian M, Bakhtiyari M, Rezayati S (2014) One-pot synthesis of xanthene derivatives using silica supported [2-(sulfooxy)ethyl]sulfamic acid as a novel and efficient catalyst under solvent-free condition. *Chem Sci Trans* 3:107–116
40. Kumara PS, Sunil Kumara B, Rajithaa B, Narsimha Reddy P, Sreenivasulua N, Thirupathi Reddy Y (2006) A novel one pot synthesis of 14-aryl-14H-dibenzo[a, j]xanthenes catalyzed by selectfluorTM under solvent free conditions. *Arkivoc* 2006(XII):46–50
41. Mirkhani V, Moghadam M, Tangestaninejad S, Mohammad-poor-Baltork I, Mahdavi M (2009) Highly efficient synthesis of 14-Aryl-14H-dibenzo[a, j]xanthenes catalyzed by carbon-based solid acid under solvent-free conditions. *Synth Commun* 39:4328–4340
42. Wang RZ, Zhang LF, Cui ZS (2009) Iodine-catalyzed synthesis of 12-Aryl-8,9,10,12-tetrahydro-benzo[a]xanthene-11-one derivatives via multicomponent reaction. *Synth Commun* 39:2101–2107
43. Rao GBD, Kaushik MP, Halve AK (2012) An efficient synthesis of naphtha[1,2-e]oxazinone and 14-substituted-14H-dibenzo[a, j]xanthene derivatives promoted by zinc oxide nanoparticle under thermal and solvent-free conditions. *Tetrahedron Lett* 53:2741–2744
44. Khurana JM, Magoo D (2009) pTSA-catalyzed one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-ones in ionic liquid and neat conditions. *Tetrahedron Lett* 50:4777–4780
45. Khazaei A, Zolfigol MA, Moosavi-Zare AR, Zare A, Khojasteh M, Asgari Z, Khakyzadeh V, Khalafi-Nezhad A (2012) Organocatalyst trityl chloride efficiently promoted the solvent-free synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]-xanthene-11-ones by in situ formation of carbocationic system in neutral media. *Catal Commun* 20:54–57
46. Mohammadpour Amini M, Fazaeli Y, Yassae Z, Feizi Sh, Bazgir A (2009) Polytungstozincate acid: a new and efficient catalyst for the synthesis of xanthenes under solvent-free conditions. *Open Catal J* 2:40–44
47. Klass DL (1964) Addition of sulfur trioxide—pyridine to aldehydes. *J Org Chem* 29:2666–2669
48. Moosavi-Zare AR, Zolfigol MA, Zarei M, Zare A, Khakyzadeh V (2015) Application of silica-bonded imidazolium-sulfonic acid chloride (SBISAC) as a heterogeneous nanocatalyst for the domino condensation of arylaldehydes with 2-naphthol and dimedone. *J Mol Liq* 211:373–380
49. Shaterian HR, Hosseinian A, Ghashang M (2009) Ferric hydrogen sulfate as an efficient heterogeneous catalyst for environmentally friendly greener synthesis of 1,8-dioxo-octahydroxanthenes. *Turk J Chem* 33:233–240

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.