



***H*-imidazolium Acidic Ionic Liquids as Efficient Catalysts in the Synthesis of Xanthenes under Solvent-Free Conditions**

Moslem Mansour Lakouraj *, Zari Fallah, Mahmood Tajbakhsh, Vahid Hasantabar

Department of Organic Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar 47416, Iran

Corresponding author: E-mail: lakouraj@umz.ac.ir

Tel: +98112 5342350 Fax: +98 112 5342350

Received 29 April 2014 | Received in revised form 26 July 2014 | Accepted 12 August 2014

Abstract:

Bifunctional acidic ionic liquids, having both *H*-imidazolium and -SO₃H groups as cation moieties (H-BFAILs) and CF₃SO₃⁻ as anion, were synthesized in high yields. These H-BFAILs showed significant hydrophilic properties, lower acidity and higher thermal stability relative to common ionic liquids, due to their unique structures. The (propyl or butyl-3-sulfonic) imidazolium trifluoromethane sulfonates ([IMPS][TfO] and [IMBS][TfO]) were employed as efficient catalysts for the synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthene derivatives via the condensation of β-naphthol with aromatic aldehydes at 80°C under solvent-free conditions. The workup procedure is green, involving only washing the reaction mixture with water to remove the ionic liquid. The acidic ionic liquids were easily recovered and reused for at least seven successive runs without significant loss of catalytic activity.

Key words: Acidic ionic liquids; Dibenzoxyanthenes; One-pot reaction; Solvent-free; Recyclable catalyst

©2014 Published by University of Mazandaran. All rights reserved.

1. Introduction

Ionic liquids (ILs) have been one of the most attractive and rapidly growing areas of chemistry research in the past decade. Ionic liquids, as environmentally benign solvents and catalysts, have found much attention in various fields including synthesis, catalysis, separation, electrochemistry, biochemistry, and polymerization [1], because of their unique

physical and chemical properties such as air and moisture stability, negligible vapor pressure [2], high thermal and chemical stability, and recyclability [3]. In addition, the wide range of possible cation and anion combinations represents a variety of tunable interactions and applications [4, 5]. In recent years, research of ionic liquids is focused on functionalized ionic liquids (FILs)

which can provide better specialized functions with functional group linked with its cation or anion [6]. Along this, the research and application of various acidic functionalized ionic liquids with strong bronsted acidity have received special attention [7]. Among them, the HO₃S-functionalized ionic liquids have exhibited great potential in replacement of conventional homogeneous and heterogeneous acidic catalysis because they are non volatile, non corrosive and immiscible with many organic solvents [8, 9]. These compounds are also readily recycled and are tunable to specific chemical tasks [10].

Xanthenes and benzoxanthenes are biologically important compounds, due to antiviral [11], antibacterial [12], anti-inflammatory activities [13] and antagonists for paralyzing action of zoxazolamine [14]. These heterocycles can be used as dyes [15], in laser technology [16], and as pH-sensitive fluorescent materials for the visualization of biomolecules [17]. It is also noteworthy that dibenzoxanthenes are applied as sensitizer in photodynamic therapy (PDT) for treatment of tumours by combined use of a photosensitizer and light [18]. Xanthene dyes are extracted naturally from soil and plants [19]. A number of synthetic methods have been developed for the synthesis of xanthenes and benzoxanthenes [20]. The synthesis of dibenzoxanthenes by treating aldehydes with β -naphthol is the most convenient method, and many catalysts including *p*-toluenesulfonic acid [21], sulfamic acid [22], Fe(HSO₄)₃ [23], H₃PO₄ or HClO₄ [24], SelectfluorTM [25], Sc[N(SO₂C₈F₁₇)₂]₃ [26], Dowex-50w [27], silica and cellulose sulfuric acid [28, 29], and K₅CoW₁₂O₄₀.3H₂O [30] have been reported for this purpose.

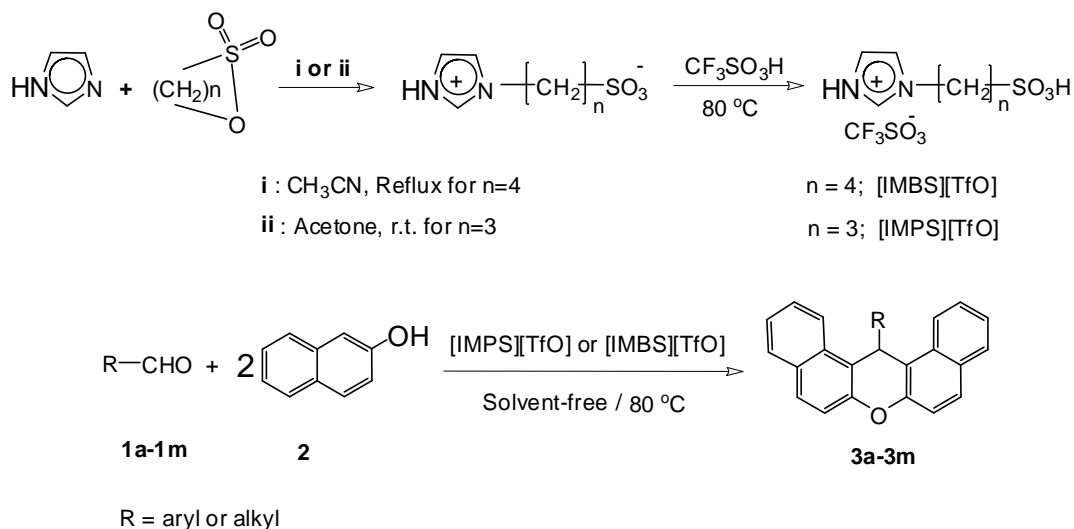
Although many of these methods are effective but some of them suffer from disadvantages such as low yield, prolonged reaction times, use of toxic

organic solvents, the requirement of special apparatus, or harsh reaction conditions, high cost and corrosive nature of the reagents, and use of excess of catalyst. Thus, there is a certain need for the development of new alternative route for the production of xanthene derivatives, which surpasses those limitations. During the course of our systematic studies directed towards the development of environmentally friendly procedures for several important organic transformations [31], herein, we report the synthesis of two bifunctional acidic ionic liquids of (propyl-3-sulfonic) imidazolium trifluoromethane sulfonate [IMPS][TfO] and (butyl-4-sulfonic) imidazolium trifluoromethane sulfonate [IMBS][TfO] consisting of *H*-imidazolium-based cation bearing alkylsulfonic acid group and triflate anion, and introduce a convenient and efficient condensation reaction of various aldehydes with β -naphthol to corresponding 14-alkyl or aryl-14*H*-dibenzo [*a,j*] xanthenes using [IMPS][TfO] or [IMBS][TfO] in the absence of organic solvents at 80 °C. In addition, the work-up procedure is very simple, involving only washing the reaction mixture with water to remove the ionic liquid (Scheme 1).

2.1. Experimental

General. Acetone and acetonitrile were distilled from K₂CO₃ and calcium hydride respectively, and stored over 3Å molecular sieves. In all the syntheses, distilled and deionized water were used. Imidazole, trifluoromethane sulfonic acid and 1,4-butanediol were purchased from Merck company (Darmstadt), and 1,3-propanediol was obtained from Fkuka (Switzerland). All other solvents and chemicals were commercially available and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on

Bruker 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm).



Scheme 1: Synthesis of H-BFAILs and 14-substituted-14H-dibenzo[*a,j*]xanthenes

IR spectra were recorded on a Bruker FTIR spectrometer using liquid film and/or KBr pellet. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Decomposition temperature was determined by T.G.A (Perkin-Elmer TGA pyrisl instrument, 10 °C min⁻¹ heating rate). All the products were characterized by comparing their IR, ¹H NMR, ¹³C NMR spectra and melting points with those reported in literature.

Preparation of functionalized ionic liquids

Synthesis of 3-(1-imidazolium) propanesulfonate [IMPS]

To a solution of 1, 3-propanesultone (1.0 mmol) in anhydrous acetone (5 ml), an equimolar amount of imidazole was added in drop wise under cooling in an ice-bath, and the mixture was slowly heated up to room temperature and stirred for 6h. The formed white precipitate was filtered and washed with ethanol, then diethyl ether three times to remove non ionic residues.

After drying in vacuum at 120 °C for 2h, the white hygroscopic solid was obtained in 91% yield with a melting point (*T_m*) of 186 °C. Spectroscopic data

for [IMPS]- ¹H NMR (400 MHz, DMSO-*d*₆): 2.10 (m, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 4.32 (t, *J* = 7Hz, 2H), 7.65 (t, *J* = 1.6 Hz, 1H), 7.78 (t, *J* = 1.6 Hz, 1H), 9.08 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): 26.69, 47.86, 48.35, 120.50, 122.47, 135.94. IR (KBr, cm⁻¹): 2500- 3500 (br), 1645, 1583, 1457, 1194, 1030, 865, 794, 536.

Synthesis of 4-(1-imidazolium) butanesulfonate [IMBS]

1,4-Butanesultone and imidazole were mixed in a 1:1 molar ratio in anhydrous acetonitrile and stirred at 80 °C for 24h. The resulting white precipitate was pulverized, washed with ethanol and diethyl ether to remove any unreacted starting materials.

The precipitate dried in vacuum to give IMBS as a white hygroscopic solid in 90% yield with a melting point (*T_m*) of 193 °C.

Spectroscopic data for [IMBS]; ¹H NMR (400 MHz, DMSO-*d*₆): 1.53 (m, 2H), 1.89 (m, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 4.22 (t, *J* = 7.2 Hz, 2H), 7.68 (t, *J* = 1.6 Hz, 1H), 7.79 (t, *J* = 1.6 Hz, 1H), 9.15 (t, *J* = 1.4 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): 22.16, 29.07, 48.67, 50.89, 120.41, 122.48, 135.75.

IR (KBr, cm^{-1}): 2500- 3500, 1646, 1581, 1457, 1305, 1202, 1039, 822, 606.

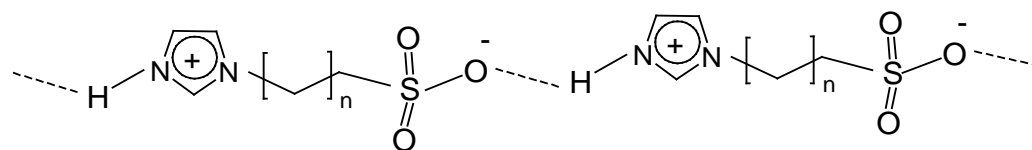
Preparation of HO_3S -functionalized ionic liquids

[IMPS] or [IMBS] was dissolved in deionized water under stirring, and a stoichiometric amount of trifluoromethane sulfonic acid was added slowly at 0 °C. The system was slowly heated up to 80 °C and stirred for 6 h. Then, water was evaporated using a rotary evaporator. The IL phase was washed repeatedly with diethyl ether to remove non ionic residues and dried in vacuum (150 °C, 60 cm^{-2} Hg). The product was formed quantitatively as a hydrophilic light yellow viscous liquid. Spectroscopic data for [IMPS][TfO]; ^1H NMR (400 MHz, DMSO-d_6): 2.12 (m, 2H), 2.46 (t, $J = 7.4\text{Hz}$, 2H), 4.32 (t, $J = 7\text{Hz}$, 2H), 7.68 (t, $J = 1.6\text{Hz}$, 1H), 7.79 (t, $J = 1.6\text{Hz}$, 1H), 9.11 (s, 1H), 14.25 (br s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 26.54, 47.91, 48.28, 120.36, 121.34 (q, $J_{\text{C-F}} = 317\text{Hz}$, CF_3), 122.50, 135.90.

Spectroscopic data for [IMBS][TfO]; ^1H NMR (400 MHz, DMSO-d_6): 1.54 (m, 2H), 1.89 (m, 2H), 2.63 (t, $J = 7.6\text{ Hz}$, 2H), 4.20 (t, $J = 7\text{ Hz}$, 2H), 7.66 (t, $J = 1.6\text{ Hz}$, 1H), 7.75 (t, $J = 1.6\text{Hz}$, 1H), 9.09 (t, $J = 1.4\text{Hz}$, 1H), 4.25 (br s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 21.76, 28.83, 48.59, 50.76, 120.38, 121.06 (q, $J_{\text{C-F}} = 320\text{ Hz}$, CF_3), 122.41, 135.63. IR (lf, cm^{-1}): 3161, 2963, 2917, 2862, 1714, 1587, 1551, 1460, 1379, 1292, 1237, 1171, 1028, 764, 517.

Synthesis of 14-alkyl or aryl-dibenzo[*a,j*]xanthenes

General procedure



Scheme 2: Intermolecular hydrogen bonding in zwitterionic salts.

Procedure A: A mixture of aldehyde (1 mmol), β -naphthol (2 mmol) and H-BFAILs (0.1 mmol for liquid aldehyde, and 0.2 mmol for solid aldehyde) was stirred at 80 °C for appropriate time indicated in table 3. The progress of reactions was monitored by TLC (ethyl acetate/ *n*-Hexane; 1:3). After completion of the reaction, the reaction mixture was rubber like solid that was cooled to room temperature. Then, water (10 ml) was added and mixture was stirred until triturated with water. The crude product was collected by filtration and purified by recrystallization from ethanol to give the pure product in high yield (Table 3).

Procedure B: the solvent-catalyst method is the same as procedure A, but to solve the substrate an excess amount (1.0 mmol) of the catalyst was used.

3. Results and discussion

Two *H*-imidazolium zwitterionic salts, [IMPS] and [IMBS], were prepared from imidazole and corresponding sultones (propanesultone and/or butanesultone) via a procedure similar to those reported in the literature with slight modification [32]. The obtained zwitterions were characterized by NMR and IR spectroscopy and confirmed the expected structures. We typically observed a higher thermal stability for the *H*-imidazolium zwitterions and H-BFAILs than alkyimidazolium type salts and their acidic ionic liquids, probably could be due to the presence of a proton in imidazol ring which enhances the intermolecular interaction through hydrogen bonding (Scheme 2).

Both new synthesized zwitterionic salts are crystalline solids and the melting point for [IMPS] and [IMBS] are 186 and 193°C respectively, which are higher than that of methylimidazolium butylsulfonate [MIMBS] [33] and ethylimidazolium propylsulfonate [EIMPS] [34]. To convert the *H*-imidazolium salts [IMPS] and [IMBS] to their corresponding H-BFAILs, trifluoromethane sulfonic acid was chosen as a donor acid because of the resistance of its anion toward hydrolytic decomposition, a common problem with some strong acid anions (e. g. PF_6^-) [8]. In addition, ionic liquids with triflate anions

showed better catalytic activity than acidic ILs bearing other counter ions [35].

These new H-BFAILs are relatively viscous liquids at room temperature, and do not lose any triflic acid under reduced pressure at 150 °C. Furthermore, in keeping with the behavior of common ionic liquids, neither of these species fumes or emit noxious vapors. This means that triflic acid being fully incorporated into their respective ionic liquid structure. Some physicochemical properties of the [IMBS][TfO], [IMPS][TfO] and of the already reported alkyl imidazolium ionic liquids are compared in table 1.

Table 1. Comparison of physicochemical properties of FAILs and the zwitterionic salts with those of reported in literature.

Entry	ILs / zwitterions	$T_g / (T_m)$	T_d	H_0	Ionic conductivity (Scm^{-1})	Ref.
1	[IMBS][TfO]	-	365	0.688	4.01×10^{-2}	-
2	[IMPS][TfO]	-	370	0.667	3.98×10^{-2}	-
3	[MIMBS][TfO]	-	350	0.424	1.21×10^{-3}	33
4	[IMBS]	(193)	389	-	3.1×10^{-6}	-
5	[IMPS]	(186)	397	-	3.7×10^{-6}	-
6	[EIMPS]	(150)	-	-	7.46×10^{-6}	34
7	[MIMBS]	-41	350	-	3.8×10^{-5}	34
8	GDAIL1	-30.1	313.7	-0.016	7.23×10^{-2}	33
9	GDAIL2	-29.2	339.7	-0.115	6.41×10^{-2}	33

The H-BFAILs are viscous liquids at room temperature and showed high thermal stability up to 380 °C. The thermal decomposition temperatures T_d (with mass loss of 10%) of [IMBS] and [IMPS] (entries 4 and 5) and their acidic forms [IMBS][TfO] and [IMPS][TfO] (entries 1 and 2) are higher than of [MIMBS][TfO] (entry 3), and geminal dicationic acidic ionic liquids GDAIL1 and GDAIL2 (entries 8 and 9) [33]. The Bronsted acidity of the H-BFAILs were evaluated from the determination of the Hammett acidity functions

using UV/VIS spectroscopy [36]. In the present case, this method consists of evaluating the protonation extent of uncharged indicator bases [I] in a solution, in terms of the measurable ratio [I]/[HI]. The chosen indicators belong to the same chemical family, mainly substituted dinitroanilines. As evident in table 1, the acidity functions (H_0) of the H-BFAILs are relatively greater than those of common alkylimidazolium based sulfonic acids and geminal dicationic acidic ionic liquids. This indicated that H-BFAILs exhibit lower bronsted

acidity than the other ionic liquids. We also investigated the ionic conductivity of the H-BFAILs and their corresponding zwitterionic salts. The ionic conductivity of [IMBS][TfO] and [IMPS][TfO] (table 1, entries 1 and 2) are considerably higher than that of zwitterionic salts [IMBS] and [IMPS] (entries 4 and 5) but slightly lower than that of geminal dicationic acidic ionic liquids at 25 °C (entries 8 and 9).

Table 2. Temperature effect on yield and reaction time ^a

Entry	Temperature (°C)	Time (min)	Yield (%)
1	60	150	75
2	80	75	93
3	100	60	93
4	120	30	88

^aReaction conditions: benzaldehyde (1mmol), β -naphthol (2 mmol), [IMPS][TfO] (0.1 mmol).

As was expected the bulk ionic conductivity of zwitterionic salts was very low since both the cation and the anion are connected intermolecularly, and therefore have no ion migration induced by potential gradient.

The H-BFAILs are soluble in water and highly polar protic solvents such as ethanol, but insoluble in ether, acetone, dichloromethane, n-hexane, and acetonitrile. Therefore, the immiscibility in common organic solvents offers special advantages of simple workup procedure and recyclability of the catalyst. In order to achieve an environmentally friendly solvent-free method and to study the possibility of using *H*-imidazolium based ionic liquids bearing sulfonic acid group for acid catalysis transformations, both prepared BAFILs were screened as catalyst/solvent-catalyst for condensation of 2-naphthol with various aldehydes to synthesis of xanthene derivatives.

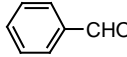
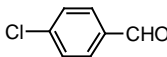
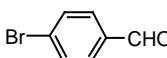

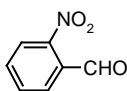
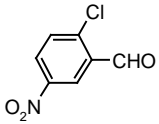
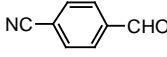
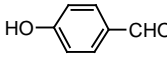
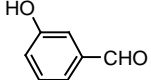
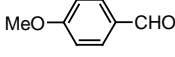
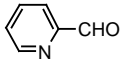
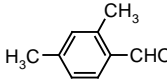
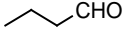
Initially, to optimize the reaction conditions, we studied reaction between β -naphthol (2 mmol) and benzaldehyde (1 mmol) as a model reaction using catalytic amount of [IMPS][TfO] (0.1 mmol) under different temperatures (Table 2).

The best result was obtained when the reaction was carried out at 80 °C (Table 2, entry 2). It was found that the desired product was obtained in excellent yield using only 3.3 mol % of the catalyst, although a higher amount of catalyst (10 mol %) reduced the reaction time to a few minutes. It is noteworthy that nearly no product could be detected when the reaction mixture was heated at 80 °C for 12 h in the absence of BFAIL, indicating the crucial role of the catalyst on the reaction progress.

To show the generality of this method, the optimized conditions was applied for the synthesis of other derivatives of xanthenes (Table 3, method A). The electronic effects and the nature of the functional group on the aromatic ring of the aldehyde affected the yield and reaction time. An increase of the reaction rate was observed for aldehydes bearing electron-withdrawing group in the *p*-position (Table 3, entries 2-4 and 7), in comparison with the unsubstituted benzaldehyde. The presence of an electron donating group (Table 3, entries 8, 9 and 10) reduced both rate and yield of the reaction. Reaction with aliphatic aldehyde provided lower yield than those with aromatic aldehydes (Table 3, entry 13).

Though meta- and para- substituted aromatic aldehydes gave good yields, ortho-substituted aromatic aldehydes (such as 2-nitro benzaldehyde) gave lower yields due to the steric effects. It should be pointed out that hindered benzaldehydes such as 2, 6-dimethoxy benzaldehyde did not react with β -naphthol under the present reaction conditions even after 5 h. The condensation reaction of ketones with β -naphthol did not occur as it was expected according to the previous reports in literature [37].

Table 3. Synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes in presence of H-BFALs

Entry	Aldehyde	Product	Method A ^a		Method B ^b		mp (°C)	
			Time (min)	Yield (%) ^c	Time (min)	Yield (%) ^c	Found	Reported
1		3a	75	93	7	92	184-186	184-185 [39]
2		3b	30	94	4	93	286-288 [40]	287-288
3		3c	35	96	5	94	292-294	295-296 [27]
4		3d	30	94	4	91	312-315	308-310 [41]
5		3e	50	90	11	87	293-295	293 [22]
6		3f	85	80	13	84	249-250	-
7		3g	40	88	7	90	290-293	291-292 [42]
8		3h	55	85	10	88	143-145	140 [27]
9		3i	40	90	9	89	244-246	242-246 [40]
10		3j	90	91	13	88	204-206	204-205 [30]
11		3k	100	80	14	82	237	236-237 [43]
12		3l	75	88	11	89	196-198	-
13		3m	135	50	15	45	153-155	152-154 [39]

^a Aldehyde (1 mmol), β -naphthol (2 mmol), [IMPS][CF₃SO₃] (0.1-0.2 mmol); 80°C. ^b Aldehyde (1 mmol), β -naphthol (2 mmol), [IMBS][CF₃SO₃] (1 mmol); 80°C. ^c Yields refer to isolated pure products.

The reaction conducted with α -naphthol instead of β -naphthol did not afford any product, similar to the reaction of phenol with substituted benzaldehydes [38].

Heterocyclic carbaldehydes such as furan-2-carboxaldehyde, thiophen-2-carboxaldehyde, and pyrrole-2-carboxaldehyde did not give the desired xanthenes, but polymerized under reaction conditions which could be attributed to the acidic nature of the covalently bounded sulfonic acid group in [IMPS][TfO]. When [IMBS][CF₃SO₃] has been applied as both solvent and catalyst at 80 °C, excellent yields of the corresponding xanthenes were obtained in shorter reaction times (table 3, method B).

Absence of OH absorption and appearance of the characteristic peak of 14-*H* xanthenes at 6.44–7.34 ppm region as a singlet in the ¹H NMR spectra, confirmed the structure of products.

To show the merit of the present work in comparison with reported methods in the literature, we have compared our results with those reported for some other catalysts in the synthesis of 14-phenyl-14*H*-dibenzo [*a,j*] xanthene. As seen in table 4, among the acyclic HO₃S-functional bronsted acidic ionic liquids, [IMPS][TfO] and [IMBS][TfO] were found to be the most effective catalyst and solvent-catalyst with respect to the reaction time, amount of catalyst, and milder reaction conditions.

Table 4. Comparison of H-BFAILs with reported catalysts for the synthesis of 14- phenyl-14*H*-dibenzoxanthene (3a)

No	Catalyst (mol %)	Conditions	Temp. (°C)	Time (h)	Yield (%)	Ref.
1	<i>P</i> -TSA, (0.1mmol)	CH ₂ Cl ₂ solvent-free	Reflux 125	20 4	93 89	[21]
2	Sulfamic acid, (0.1mmol)	solvent-free	125	8	93	[22]
3	Selectfluor™, (0.1mmol)	solvent-free	125	8	93	[25]
4	Sc[N(SO ₂ C ₈ F ₁₇) ₂] ₃ , (0.01mmol)	solvent-free	110	5	93	[26]
5	N-Bu ₄ NBr, (0.1mmol)	neat	125	1	96	[44]
6	[MIMPS][HSO ₄], (0.25mmol)	solvent-free	100	0.1	93	[35]
7	[MIMPS][H ₂ PO ₄], (0.25mmol)	solvent-free	100	2	76	[35]
8	[MIMBS][P-TsO], (2.5mmol)	AIL (excess)	125	0.15	89	[45]
9	[MIMBS][TfO], (2.5mmol)	AIL (excess)	125	0.25	a	[45]
10	[IMPS][TfO], (0.1mmol)	solvent-free	80	75 min.	93	Table 3
11	[IMBS][TfO], (1mmol)	solvent-free	80	7 min.	92	Table 3

Finally, the recovery and reusability of the catalysts, [IMPS][TfO], [IMBS][TfO], and solvent-catalyst were investigated. The immiscibility of xanthenes with water and the good solubility of H-BFAILs in water makes the separation of the catalyst from the product quite facile. These H-BFAILs are soluble in water and could therefore be recycled as the filtrate. The catalyst was recovered by evaporation of the water, washed with diethyl ether to remove any organic impurity, dried in vacuum at 100 °C for 2 h and reused in the subsequent reactions without any further treatment. This procedure applied for 14*H*-dibenzo[*a,j*]xanthene in eight subsequent runs (table 5).

Table 5. Reusability of [IMPS][TfO] on yield of 14-phenyl-14*H*-dibenzoxanthene^a

Run	Cycle	Isolated Yield (%)
1	0	93
2	1	93
3	2	90
4	3	90
5	4	87
6	5	87
7	6	85
8	7	80

^a Reaction conditions: benzaldehyde (1mmol), β-naphthol (2 mmol), [IMPS][TfO] (0.1 mmol), 80 °C .

As it is clear in this table the catalytic activity was slightly decreased after seven cycles. In summary, the *H*-imidazolium ionic liquids (H-BFAILs) were easily prepared in high yield and used as efficient catalyst and solvent-catalyst for synthesis of dibenzoxanthenes. No organic solvent was used, resulting in eco-friendly process. Therefore, it is possible to apply the tenets of green chemistry to the generation of biologically interesting products

under solvent-free media that is less expensive and less toxic than those with organic solvents. This method is important from both environmental point of view and economic considerations; because it produces little waste, good yield, and short reaction time using H-BFAILs. Greener conditions and simple work-up procedure, including simple filtration and recrystallization, recovery and reusability of ionic liquids are other advantages of this method. The catalyst is recyclable and could be reused for at least seven times without significant loss of its activity.

4. Acknowledgements

The authors are grateful to the research council of Mazandaran University for the financial support of this work.

5. References

- [1] Swindall, W. J. Ionic liquids come of age-almost. *Clean Techn. Environ. Policy.*, 6 (2004) 149.
- [2] Zhao, D.; Wu, M.; Kou, Y.; Min, E. Ionic liquids: applications in catalysis. *Catal. Today.*, 74 (2002) 157.
- [3] Leadbeater, N. E.; Torenius, H. M. A study of the ionic liquid mediated microwave heating of organic solvents. *J. Org. Chem.*, 67(2002) 3145.
- [4] Jastorff, B.; Molter, K.; Behrend, P.; Filser, J. Progress in evaluation of risk potential of ionic liquids-basis for an eco-design of sustainable products. *Green Chem.*, 7 (2005) 362.
- [5] Anderson, J. L.; Ding, R.; Ellern, A.; Armstrong, D. W. Structure and properties of high stability geminal dicationic ionic liquids. *J. Am. Chem. Soc.*, 127 (2005) 593.
- [6] Whitehead, J. A.; Lawrance, G. A.; McCluskey, A. Green leaching: recyclable and selective leaching of gold-bearing ore in an ionic liquid. *Green Chem.*, 6 (2004) 313.

- [7] Li, D.; Shi, F.; Peny, J.; Guo, S.; Deng, Y. Application of functional ionic liquids possessing two adjacent acid sites for acetalization of aldehydes. *J. Org. Chem.*, 69 (2004) 3582.
- [8] Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weave, K. J.; Forbes, D. C.; Davis, J. H. Novel brønsted acidic ionic liquids and their use as dual solvent-catalysts. *J. Am. Chem. Soc.*, 124 (2002) 5962.
- [9] Fraga-Dubreuil, J.; Bourahla, K.; Rahmouni, M.; Bazureau, J. P.; Hamelin, J. Catalysed esterifications in room temperature ionic liquids with acidic counteranion as recyclable reaction media. *Catal. Commun.*, 3 (2002) 185.
- [10] Wang, Y.; Jiang, D.; Dai, L. Novel brønsted acidic ionic liquids based on benzimidazolium cation: synthesis and catalyzed acetalization of aromatic aldehydes with diols. *Catal. Commun.*, 9 (2008) 2475.
- [11] Jamison, J.; Krabill, M. K.; Hatwalkar, A. Potentiation of the antiviral activity of poly r(A-U) by xanthene dyes. *Cell Biol. Int. Rep.*, 14 (1990) 1075.
- [12] EL-Brashy, A. M.; Metwally, M. E.; EL-Sepai, F. A. Spectrophotometric determination of some fluoroquinolone antibacterials by binary complex formation with xanthene dyes. *Farmaco.*, 59 (2004) 809.
- [13] Chibale, K.; Visser, M.; Schalkwyk, D. V.; Smith, P. J.; Saravanamuthu, A.; Fairamb, A. H. Exploring the potential of xanthene derivatives as trypanothione reductase inhibitors and chloroquine potentiating agents. *Tetrahedron*, 59 (2003) 2289.
- [14] Santi-Ruf, G.; Hieu, H. T.; Poupelin, J. P. The effect of dibenzoxanthenes on the paralyzing action of zoxazolamine. *Naturwissenschaften*, 62 (1975) 584.
- [15] Bhowmik, B. B.; Ganguly, P. Photophysics of xanthene dyes in surfactant solution. *Spectrochimica Acta part A: Molecul. and Biomolecul. Spect.*, 61 (2005) 1997.
- [16] Ahmad, M.; King, T. A.; Ko, D. K.; Cha, B. H.; Lee, J. Performance and photostability of xanthene and pyrromethene laser dyes in sol-gel phases. *J. Phys. D: Appl. Phys.*, 35 (2002) 1473.
- [17] Knight, C. G., Stephens, T. Xanthene-dye-labeled phosphatidylethanolamines as probes of interfacial pH-studies in phospholipid vesicles. *Biochem. J.*, 258 (1989) 683.
- [18] Ion, R. M.; Frackowiak, D.; Wiktorowicz, P. K. The incorporation of various porphyrins into blood cells measured via flow cytometry, absorption and emission spectroscopy. *Acta Biochim. Pol.*, 45 (1998) 833.
- [19] Licudine, P. J. A.; Kawate, M. K.; Li, Q. X. Method for the analysis of phloxine B, uranine, and related xanthene dyes in soil using supercritical fluid extraction and high-performance liquid chromatography. *J. Agric. Food Chem.*, 45 (1997) 766.
- [20] Jha, A.; Beal, J. Convenient synthesis of 12H-benzo[a]xanthenes from 2-tetralone. *Tetrahedron Lett.*, 45 (2004) 8999.
- [21] Khosropour, A. R.; Khodaei, M. M.; Moghannian, H. A facile, simple, and convenient method for the synthesis of 14-alkyl or aryl-14H dibenzo[a,j]xanthenes catalyzed by p-TSA in solution and solvent-free conditions. *Synlett*, (2005) 955.
- [22] Rajitha, B.; Kumar, B. S.; Reddy, Y. T.; Reddy, P. N.; Sreenivasulu, N. A novel and efficient catalyst for the synthesis of aryl-14H-dibenzo[a,j]xanthenes under conventional heating and microwave irradiation. *Tetrahedron Lett.*, 46 (2005) 8691.
- [23] Eshghi, H.; Bakavoli, M.; Moradi, H. Fe(HSO₄)₃: An efficient, heterogeneous and reusable catalyst for the synthesis of 14-aryl- or

- alkyl-14*H*-dibenzo[*a,j*]xanthenes. *Chin. Chem. Lett.*, 19 (2008) 1423.
- [24] Zad, A. K.; Kazemi, Z.; Rudbari, H. A. Conversion of cyclic acetals to hydroxy esters by MCPBA oxidation. *J. Korean Chem. Soc.*, 46 (2002) 541.
- [25] Kumar, P. S.; Sunil-Kumar, B.; Rajitha, B.; Narsimha-Reddy, P.; Sreenivasulu, N.; Thirupathi-Reddy, Y. One-pot synthesis of xanthene derivatives under solvent-free conditions. *Arkivoc*, XII (2006) 46.
- [26] Hong, M.; Cai, C. Sc[N(SO₂C₈F₁₇)₂]₃ catalyzed condensation of β-naphthol and in fluoros solvent: One-pot synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes. *J. Fluorine Chem.*, 130 (2009) 989.
- [27] Amini, M. M.; seyedhamzeh, M.; Bazgir, A. Heteropolyacid: An efficient and eco-friendly catalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene. *Appl. Catal A: General.*, 323 (2007) 242.
- [28] Shaterian, H. R.; Ghashang, M.; Hassankhani, A. One-pot synthesis of aryl 14*H*-dibenzo[*a,j*]xanthene leuco-dye derivatives. *Dyes Pigments*, 76 (2008) 564.
- [29] Madhav, J. V.; Reddy, Y. T.; Reddy, P. N.; Reddy, M. N.; Kuarm, S.; Crooks, P. A.; Rajitha, B. Cellulose sulfuric acid: novel and efficient biodegradable and recyclable acid catalyst for the solid-state synthesis of thiadiazolo benzimidazoles. *J. Mol. Catal. A: Chem.*, 304 (2009) 85.
- [30] Nagarapu, L.; Kantevari, S.; Mahankhali, V. C.; Apuri, S. Potassium dodecatungstocobaltate trihydrate (K₅CoW₁₂O₄₀ · 3H₂O): A mild and efficient reusable catalyst for the synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes under conventional heating and microwave irradiation. *Catal. Commun.*, 8 (2007) 1173.
- [31] Lakouraj, M. M.; Mokhtary, M. Polyvinylpyrrolidone-supported boron trifluoride: a high-loaded, polymer-supported lewis acid for the Ritter reaction. *Monatsh. Chem.*, 140 (2009) 53.
- [32] Kundu, D.; Kumar, R.; Majee, A.; Hajra, A. Zwitterionic-type molten salt-catalyzed syn-selective aza-Henry reaction: solvent-free one-pot synthesis of β-nitroamines. *Tetrahedron Lett.*, 50 (2009) 6998.
- [33] Liu, X.; Xiao, L.; Wu, H.; Chen, J.; Xia, C. Synthesis of novel gemini dicationic acidic ionic liquids and their Catalytic Performances in the Beckmann rearrangement. *Helv. Chem. Acta.*, 92 (2009) 1014.
- [34] Yoshizawa, M.; Hirao, M.; Ito-Akita, K.; Ohno, H. Ion conduction in zwitterionic-type molten salts and their polymers. *J. Mater. Chem.*, 11 (2001) 1057.
- [35] Gong, K.; Fang, D.; Wang, H. L.; Zhou, X. L.; Liu, Z. L. The one-pot synthesis of 14-alkyl- or aryl-14*H*-dibenzo[*a,j*]xanthenes catalyzed by task-specific ionic liquid. *Dyes Pigments*, 80 (2009) 30.
- [36] Thomazeau, C.; Olivier-Bourbigou, H.; Magna, L.; Luts, S.; Gilbert, B. Determination of an acidic scale in room temperature ionic liquids. *J. Am. Chem. Soc.*, 125 (2003) 5264.
- [37] Shaterian, H. R.; Ghashang, M.; Mir, N. Aluminium hydrogensulfate as an efficient and heterogeneous catalyst for preparation of aryl 14*H*-dibenzo[*a,j*]xanthene derivatives under thermal and solvent-free conditions. *Arkivoc*, xv (2007) 1.
- [38] Seyyedhamzeh, M.; Mirzaei, P.; Bazgir, A. Solvent-free synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes and 1,8-dioxo-octahydro-xanthenes using silica sulfuric acid as catalyst. *Dyes Pigments*, 76 (2008) 836.
- [39] Bigdeli, M. A.; Heravi, M. M.; Mahdavinia, G. H. Silica supported perchloric acid (HClO₄-SiO₂): A mild, reusable and highly efficient heterogeneous catalyst for the synthesis of 14-aryl or alkyl-14*H*-

dibenzo[*a,j*]xanthenes. *J. Mol. Catal A: Chem.*, 275 (2007) 25.

[40] Kumar, R.; Nandi, G. C.; Verma, R. K.; Singh, M. S. A facile approach for the synthesis of 14-aryl- or alkyl-14*H*-dibenzo[*a,j*]xanthenes under solvent-free condition. *Tetrahedron Lett.*, 51 (2010) 442.

[41] Dabiri, M.; Baghbanzadeh, M.; Shakouri-Nikcheh, M.; Arzroomchilar, E. Ecofriendly and efficient one-pot synthesis of alkyl-or aryl-14*H*-dibenzo[*a,j*]xanthenes in water. *Bioorg. Med. Chem. Lett.*, 18 (2008) 436.

[42] Su, W.; Yang, D.; Jin, C.; Zhang, B. Yb(OTf)₃ catalyzed condensation reaction of β- naphthol and aldehyde in ionic liquids: a green synthesis of aryl-14*H*- dibenzo[*a,j*] xanthenes. *Tetrahedron Lett.*, 49 (2008) 3391.

[43] Zarei, A.; Hajipour, A. R.; Khazdooz, L. The one-pot synthesis of 14-aryl or alkyl- 14*H*-dibenzo[*a,j*]xanthenes catalyzed by P₂O₅/Al₂O₃ under microwave irradiation. *Dyes Pigments*, 85 (2010) 133.

[44] Kantevari, S.; Chary, M. V.; Das, A. P. R.; Vuppalapati, S. V. N.; Lingaiah, N. Catalysis by an ionic liquid: Highly efficient solvent-free synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes by molten tetrabutylammonium bromide under conventional and microwave heating. *Catal. Commun.*, 9 (2008) 1575.

[45] Kumari, P.; Yathindranth, V.; Chauhan, S. M. S. Facile and efficient synthesis of 14-alkyl- or aryl-14*H*-dibenzo[*a,j*]xanthenes using sulfonyl-functionalized ionic liquids. *Synth. Commun.*, 38 (2008) 637.