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Original article

One-pot synthesis of various xanthene derivatives using ionic liquid 1,3-disulfonic acid imidazolium hydrogen sulfate as an efficient and reusable catalyst under solvent-free conditions

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ABSTRACT

In this study, 1,3-disulfonic acid imidazolium hydrogen sulfate (DSIMHS) is used as an efficient and reusable ionic liquid for the green, mild, and efficient synthesis of xanthenes under solvent-free conditions. Simple and easy work-up, low cost, green process, short reaction times and excellent yields of the products are the advantages of this procedure. Further, the catalyst can be recycled and reused at least for four times without a noticeably decrease in its catalytic activity.

1. Introduction

The principles of green chemistry have been introduced to eliminate or reduce the use or generation of hazardous materials in chemical processes. One of the key areas of green chemistry is the replacement of hazardous solvents with environmentally benign ones or the elimination of solvents altogether [1–3]. One strategy is the use of ionic liquids (ILs) that are defined as salts in liquid form at or below 100 °C. ILs have gained much attention as "designer solvents and/or catalysts" for a diversity of chemical applications due to their special properties such as high polarity, good solvating capability, wide liquid range, high thermal stability, negligible vapour pressure, great selectivity, ease of isolation and reusability [4–6]. Among the different kinds of ILs, Brønsted acidic ionic liquids, which have a functional group such as $-SO_3H$ in their framework, have been designed as green substitute for solid acids and traditional mineral liquid acids such as sulfuric acid and hydrochloric acid in chemical processes [7–11].

In recent years, considerable efforts from both academic and industrial researchers have been focused especially on the design and development of multi-component reactions (MCRs) for the generation of libraries of heterocyclic compounds [12].

There has been a renewed and growing interest in MCRs as notable synthetic tools for the synthesis of structurally diverse complex molecules, such as novel biologically and pharmaceutically active compounds. MCRs offer several attractive features to the chemists, including access to a large number of novel and diverse structures, low production and environmental costs due to high convergence, atom economy, high selectivity and simple purification [13–16].

Xanthenes and their derivatives have received special attention due to their wide range of biological and pharmaceutical activities such as antibacterial [17], antiviral [18] and antitumor effects [19]. In addition, they can be employed as dyes [20], pH sensitive fluorescent materials for visualization of biomolecules [21] and utilized in laser technology [22]. Thus, the synthesis of xanthene derivatives currently is of much importance.

Various approaches have been reported for the synthesis of xanthene derivatives in the literature [23–26]. One of the most simple and general methods for the synthesis of this type of compounds involves a one-pot MCR of aldehydes (1 equiv.) with β-naphthol (1 or 2 equiv.) and dimedone (1 or 2 equiv.), in the presence of an acidic or other type of catalysts. A variety of catalysts have been applied for this reaction, such as ferric hydrogen sulfate [27], proline triflate [28], $NaHSO_4{\cdot}SiO_2$ [29], strontium triflate [30], $Zr(HSO_4)_4$ [31], $RuCl_4$ [32], P_2O_5/Al_2O_3 [33], $BF_3{\cdot}SiO_2$ [34], oxalic acid [35], (DBH)/kaolin [36], ZnO nanoparticles [37], molecular iodine [38,39], heteropoly acid [40,41], silica sulfuric acid [42,43], amberlyst-15 [44], nano-TiO_2 [45],

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$KAl(SO_4)_2 \cdot 12H_2O$ (alum) [46], $NaHSO_4$/ionic liquid ([bmim]BF_4) [47], montmorillonite K-10 [48], *p*-TSA [49], cyanuric chloride [50], $H_4[SiW_{12}O_{40}]$ [51], $Yb(OTf)_3$ [52] and SuSA [53]. However, many of these procedures suffer from one or more disadvantages including the use of toxic metals and volatile organic solvents, low yields, long reaction times, tedious work-up procedures, expensive reagents, high catalyst loading, high temperature and hash reaction conditions.

To avoid these drawbacks and develop useful synthetic methodologies, herein, we wish to report a simple, green and efficient method for the synthesis of xanthene derivatives using DSIMHS as an eco-friendly catalyst with high catalytic activity under solvent-free conditions. To the best of our knowledge, this methodology has not been reported in the literature.

2. Experimental

All chemicals were purchased from Merck or Fluka Chemical Companies. All yields refer to the isolated products. Products were characterized by their physical constants and comparison with authentic samples. Progress of the reactions was monitored by thin layer chromatography (TLC) analyses using silica gel SIL G/UV 254 plates.

Melting points were recorded on an electrothermal digital melting point apparatus model IA9100 in open capillary tubes. IR spectra were recorded on a Perkin-Elmer model Spectrum One FT-IR Spectrometer. The ^1H NMR (300 or 400 MHz) was run on a Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm).

Synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes: A mixture of β-naphthol (2 mmol), aldehyde (1 mmol) and DSIMHS (0.25 mmol) was stirred and heated in an oil-bath at 90 °C for an appropriate period of time. The progress of the reaction was followed by TLC analyses. After the completion of the reaction, the reaction mixture was cooled to room temperature, 10 mL of H_2O was added, stirred for 5 min and filtered to remove the catalyst. DSIMHS is soluble in water and the product precipitated with high purity. Then, 2 mL of hot EtOH was added to the resulting solid product, stirred for 5 min, and filtered. Finally, the solid residue was recrystallized from EtOH to give the pure product.

Synthesis of 12-aryl-tetrahydrobenzo[a]xanthene-11-ones: A mixture of β-naphthol (1 mmol), dimedone (1 mmol), aldehyde (1 mmol) and DSIMHS (0.25 mmol) was stirred and heated in an oil-bath at 55 °C for an appropriate period of time. The reaction was monitored by TLC analyses. After the completion of the reaction, the reaction mixture was cooled to room temperature, 10 mL of H_2O was added, stirred for 5 min and filtered to remove the catalyst. Then, 2 mL of hot EtOH was added to the resulting solid product, stirred for 5 min, and filtered. Finally, the solid residue was recrystallized from EtOH to give the pure product.

Synthesis of 1,8-dioxo-octahydroxanthenes: A mixture of dimedone (2 mmol), aldehyde (1 mmol) and DSIMHS (0.25 mmol) was stirred and heated in an oil-bath at 55 °C for an appropriate period of time. After the completion of the reaction, as monitored by TLC analyses, the reaction mixture was cooled to room temperature, 10 mL of H_2O was added, stirred for 5 min and filtered to remove the catalyst. Then, 2 mL of hot EtOH was added to the resulting solid product, stirred for 5 min, and filtered. Finally, the solid residue was recrystallized from EtOH to give the pure product. Spectroscopic data for the selected products are as follows:

14-(Phenyl)-14*H*-dibenzo[*a*,*j*]xanthene (Table 2, entry 1): IR (KBr, cm^{-1}): ν 3070, 3020, 1620, 1590, 1430, 1400, 1250, 1150, 1075, 825, 740; ^1H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 1H), 6.96 (t, 1H, J = 7.2 Hz), 7.12 (t, 2H, J = 7.2 Hz), 7.36–7.58 (m, 8H), 7.74–7.81 (m, 4H), 8.37 (d, 2H, J = 8.4 Hz).

14-(4-Methylphenyl)-14*H*-dibenzo[*a*,*j*]xanthene (Table 2, entry 9): IR (KBr, cm^{-1}): ν 3068, 3022, 1620, 1590, 1512, 1395, 1248, 1110, 810, 740; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.11 (s, 3H), 6.43 (s, 1H), 6.93 (d, 2H, J = 7.8 Hz), 7.22–7.36 (m, 8H), 7.42–7.81 (m, 4H), 8.37 (d, 2H, J = 8.4 Hz).

12-(4-Isoprpylphenyl)-9,9-dimethyl-8,9,10,12 tetrahydrobenzo[*a*]xanthen-11-one(Table 4, entry 12): IR (KBr, cm^{-1}): ν 3050, 2950, 2900, 2870, 1642, 1618, 1590, 1504, 1460, 1368, 1220, 1140, 1020, 830, 815, 740; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.01 (s, 3H), 1.14 (s, 6H), 1.16 (s, 3H), 2.23 and 2.30 (AB system, 2H, J = 30 Hz), 2.48–2.59 (d, 2H, J = 45 Hz), 2.77 (t, 1H, J = 6.8 Hz), 5.70 (s, 1H), 7.03 (d, 1H, J = 7.2 Hz), 7.19–7.46(m, 5H), 7.78 (t, 3H, J = 10 Hz), 8.05 (d, 1H, J = 8 Hz).

12-(4-Cyanophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (Table 4, entry 13): IR (KBr, cm^{-1}): ν 3070, 2956, 2931, 2869, 2220, 1651, 1618, 1594, 1515, 1460, 1370, 1220, 1175, 1140, 1020, 838, 802, 740; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.97 (s, 3H), 1.15 (s, 3H), 2.25 and 2.37 (AB system, 2H, J = 16 Hz), 2.61 (s, 2H), 5.78 (s, 1H), 7.37 (d, 1H, J = 8.8 Hz), 7.41–7.49 (m, 6H), 7.84 (t, 3H, J = 8.4 Hz).

9-(2-Mehtoxyphenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (Table 6, entry 12): IR (KBr, cm^{-1}): ν 3010, 2950, 2870, 1650, 1620, 1590, 1490, 1460, 1360, 1250, 1020, 1200, 1000, 1160, 1140, 1118, 750; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.97 (s, 6H), 1.11 (s, 6H), 2.14 and 2.23 (d, 2H, J = 6.4 Hz), 2.39 and 2.48 (d, 2H, J = 17.4 Hz), 3.79 (s, 3H), 4.87 (s, 1H), 6.77 (d, 1H, J = 8 Hz), 6.89 (dt, 1H, J = 7.4 Hz, J = 1.2 Hz), 7.12 (m, 1H), 7.43 (dd, 1H, J = 7.4 Hz, J 1.6 Hz).

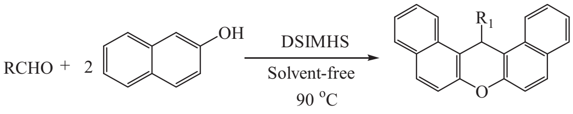
9-(4-Cyanophenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (Table 6, entry 13): IR (KBr, cm^{-1}): ν 3050, 2950, 2870, 2210, 1660, 1620, 1600, 1500, 1460, 1360, 1200, 1160, 1140, 1105, 850; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.99 (s, 6H), 1.13 (s, 6H), 2.17 and 2.26 (d, 2H, J = 16.4 Hz), 2.5 (d, 2H, J = 1.2 Hz), 4.78 (s, 1H), 7.43 (dd, 2H, J = 9.6 Hz, J = 1.6 Hz), 7.54 (dd, 2H, J = 6.6 Hz, J = 1.6 Hz).

3. Results and discussion

In continuation of our ongoing research program on the development of new applications of DSIMHS in organic synthesis [54,55], we decided to study the preparation of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes from aldehydes and β-naphthol in the presence of this catalyst (Scheme 1). For this purpose, the condensation of β-naphthol (2 mmol) with benzaldehyde (1 mmol) was selected as a model reaction and the optimization of the reaction conditions was performed using various amounts of DSIMHS at different temperatures under solvent-free conditions. The results are summarized in Table 1.

As it shown in Table 1, the best result was obtained by carrying out the reaction using 0.25 mmol of DSIMHS at 90 °C (Table 1, entry 5). Increasing the amount of the catalyst and the temperature of the reaction did not improve the yields and reaction times. In addition, results indicated that when the reaction proceeded at room temperature in 240 min, the yield of the corresponding product was low (Table 1, entry 1). The solvent-free reaction was also tested at 90 °C in the absence of the catalyst and no significant amount of product was observed after long reaction time (Table 1, entry 2).

In order to study the generality of this procedure, a variety of aromatic aldehydes were applied under the optimal reaction conditions. The results are shown in Table 2. The nature of the



Scheme 1. Synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes in the presence of DSIMHS under solvent-free conditions.

Table 1

The effect of different amounts of DSIMHS and temperature on the synthesis of 14-(phenyl)-14*H*-dibenzo[*a*,*j*]xanthene.[a]

Entry	Catalyst (mmol)	Temperature (°C)	Time (min)	Yield (%)[b]
1	0.25	25	240	25
2	–	90	360	18
3	0.15	90	10	80
4	0.25	100	3	92
5	0.25	90	3	94
6	0.25	80	8	85
7	0.35	90	3	94

[a] Reaction conditions: β-naphthol (2 mmol) and benzaldehyde (1 mmol) under solvent-free conditions.

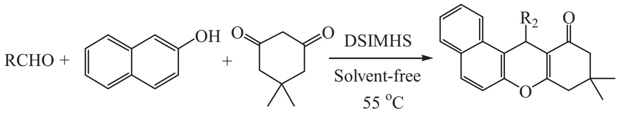
[b] Isolated yield.

functional group on the aromatic ring of the aldehyde exerted a strong influence on the reaction time. It could be concluded that the aldehydes substituted with electron-withdrawing groups reacted very well and produced the corresponding xanthenes in good to excellent yields in shorter times than aldehydes with electron-donating groups.

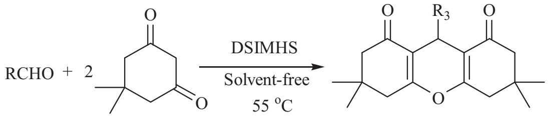
After the successful synthesis of a series of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes, we turned our attention toward the synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones, in the presence of DSIMHS (Scheme 2). In order to determine the optimal conditions, we investigated the MCR of β-naphthol (1 mmol) with dimedone (1 mmol) and benzaldehyde (1 mmol) in the presence of various amounts of the catalyst, at different temperatures ranging from 25 °C to 65 °C in the absence of solvent (Table 3).

According to Table 3, we found that 0.25 mmol of DSIMHS was adequate to accomplish the reaction effectively at 55 °C (Table 3, entry 4). Using smaller amounts of the catalyst resulted in lower yields, while higher amounts of the catalyst did not affect the reaction times and yields and in the absence of the catalyst, no appreciable product could be detected. Moreover, when the same reaction was performed at 25 °C, the corresponding product was obtained in very low yield after prolonged reaction time.

To generalize the suitability of this protocol, the reaction was extended to different substituted aromatic aldehydes to prepare a series of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones. In all cases, aldehydes bearing electron-donating groups needed slightly longer time to complete the reaction as compared to aldehydes containing halogens or other electron-withdrawing groups. The results are summarized in Table 4.



Scheme 2. Three-component synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones in the presence of DSIMHS under solvent-free conditions.



Scheme 3. Ionic liquid catalyzed synthesis of 1,8-dioxo-octahydroxanthenes in the presence of DSIMHS under solvent-free conditions.

Table 3

The effect of different amounts of DSIMHS and temperature on the synthesis of 12-phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one.[a]

Entry	Catalyst (mmol)	Temperature (°C)	Time (min)	Yield (%)[b]
1	0.25	25	240	22
2	–	55	360	14
3	0.15	55	35	87
4	0.25	65	20	92
5	0.25	55	20	93
6	0.25	45	40	84
7	0.35	55	20	93

[a] Reaction conditions: β-naphthol (1 mmol), dimedone (1 mmol) and benzaldehyde (1 mmol) under solvent-free conditions.

[b] Isolated yield.

Finally, we evaluated the catalytic activity of DSIMHS in the synthesis of 1,8-dioxo-octahydroxanthenes. In this regard, the reaction between dimedone (2 mmol) and benzaldehyde (1 mmol) was chosen as a model reaction using different amounts of the catalyst, at various temperatures under solvent-free conditions (Scheme 3). As can be seen from Table 5, the shortest time and best yield was achieved using 0.25 mmol of the reagent at 55 °C. It is interesting to note that the yield of the reaction was not significantly affected by increasing the amount of the catalyst and temperature. Also, in the absence of the catalyst or at room temperature, only a trace amount of the product was obtained indicating that the catalyst and elevated temperature are necessary for the reaction.

After the optimization of the reaction, we extended the condensation of dimedone with various aromatic aldehydes to further explore the scope and limitations of this reaction. The results showed that the reaction proceeds very efficiently and in all

Table 2

DSIMHS catalyzed synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes.[a]

Entry	R	Time (min)	Yield (%)[b]	Mp (°C)		Ref.
				Found	Reported	
1	C_6H_5	3	94	184–185	183–185	[56]
2	4-$OMeC_6H_4$	9	91	204–205	204–207	[56]
3	4-OHC_6H_4	8	90	133–135	135–136	[57]
4	2-ClC_6H_4	4	88	213–215	211–213	[56]
5	4-ClC_6H_4	2	95	290–292	289–291	[56]
6	3-BrC_6H_4	5	93	192–194	190–192	[58]
7	4-BrC_6H_4	3	95	297–298	298–300	[56]
8	4-FC_6H_4	2	92	239–240	241–243	[58]
9	4-$CH_3C_6H_4$	8	88	227–228	226–228	[56]
10	3-$O_2NC_6H_4$	5	91	213–215	211–213	[56]
11	4-$O_2NC_6H_4$	4	94	312–314	312–314	[56]
12	4-$(CH_3)_2CHC_6H_4$	6	90	154–156	153–155	[59]
13	4-CNC_6H_5	2	94	292–294	293–295	[56]

[a] The products were characterized by the used spectroscopic data and melting point. These data closely matched with the reported data.

[b] Isolated yield.

Table 4
DSIMHS catalyzed synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones.[a]

Entry	R	Time (min)	Yield (%)[b]	Mp (°C)		Ref.
				Found	Reported	
1	C_6H_5	20	93	148–150	148–151	[60]
2	4-OMeC_6H_4	35	90	202–204	201–203	[60]
3	4-OHC_6H_4	35	91	222–223	223–225	[61]
4	2-ClC_6H_4	20	91	181–183	180–181	[58]
5	4-ClC_6H_4	12	93	176–178	178–179	[60]
6	3-BrC_6H_4	22	90	161–163	161–164	[60]
7	4-BrC_6H_4	16	93	184–186	185–187	[60]
8	4-FC_6H_4	14	91	193–195	191–193	[62]
9	4-$CH_3C_6H_4$	30	87	171–173	170–172	[63]
10	3-$O_2NC_6H_4$	15	89	168–170	167–170	[60]
11	4-$O_2NC_6H_4$	14	92	174–176	175–178	[60]
12	4-$(CH_3)_2CHC_6H_4$	35	90	152–154	154–155	[63]
13	4-CNC_6H_5	10	92	196–198	196–199	[63]

[a] The products were characterized by the used spectroscopic data and melting point. These data closely matched with the reported data.
[b] Isolated yield.

Table 5
The effect of different amounts of DSIMHS and temperature on the synthesis of 9-(phenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthenes.[a]

Entry	Catalyst (mmol)	Temperature (°C)	Time (min)	Yield (%)[b]
1	0.25	25	240	30
2	–	55	360	15
3	0.15	55	10	80
4	0.25	65	3	93
5	0.25	55	3	95
6	0.25	45	8	80
7	0.35	55	3	95

[a] Reaction conditions: dimedone (2 mmol) and benzaldehyde (1 mmol) under solvent-free conditions.
[b] Isolated yield.

Table 6
DSIMHS catalyzed synthesis of 1,8-dioxo-octahydroxanthenes.[a]

Entry	R	Time (min)	Yield (%)[b]	Mp (°C)		Ref.
				Found	Reported	
1	C_6H_5	4	95	206–208	205–206	[64]
2	4-OMeC_6H_4	10	93	239–241	241–243	[64]
3	4-OHC_6H_4	10	90	245–247	246–248	[64]
4	2-ClC_6H_4	6	89	227–228	226–228	[64]
5	4-ClC_6H_4	4	94	231–233	230–232	[65]
6	3-BrC_6H_4	6	91	189–191	190–192	[65]
7	4-BrC_6H_4	3	92	240–242	240–241	[65]
8	4-FC_6H_4	3	93	221–223	223–224	[65]
9	4-$CH_3C_6H_4$	12	89	211–213	216–218	[66]
10	3-$O_2NC_6H_4$	8	90	165–167	167–168	[64]
11	4-$O_2NC_6H_4$	5	93	222–224	221–223	[64]
12	2-OMeC_6H_4	14	86	205–207	199–200	[67]
13	4-CNC_6H_5	5	91	226–228	220–222	[66]

[a] The products were characterized by the used spectroscopic data and melting point. These data closely matched with the reported data.
[b] Isolated yield.

Table 7
Comparison of the efficiency of various ILs in synthesis of 14-(phenyl)-14*H*-dibenzo[*a,j*]xanthene.

Entry	IL	Conditions	Time (min)	Yield (%)[a]	Ref.
1	DSIMHS (0.25 mmol)	Solvent-free, 90 °C	3	94	This work
2	[Dsim]Cl (10 mol%)	Solvent-free, 110 °C	5	90	[68]
3	[Msim]PF_6 (10 mol%)	Solvent-free, 110 °C	7	85	[68]
4	[Msim]BF_4 (10 mol%)	Solvent-free, 110 °C	8	88	[68]
5	[MIMPS]HSO_4 (0.25 mmol)	Water, 100 °C	7	93	[69]
6	[Et_3N-SO_3H]Cl (15 mol%)	Solvent-free, 120 °C	30	96	[66]
7	[Hmim]HSO_4 (12 mol %)	Solvent-free, 125 °C	90	85	[56]

[a] Yields refer to isolated pure products.

cases, aromatic aldehydes substituted with either electron-donating or electron-withdrawing groups underwent the reaction successfully and gave the desired products in good to excellent yields (Table 6).

In Scheme 4, a plausible mechanism has been offered for the synthesis of xanthene derivatives in the presence of DSIMHS under solvent-free conditions. On the basis of this mechanism, DSIMHS donates the proton to the oxygen atom of the aldehyde and

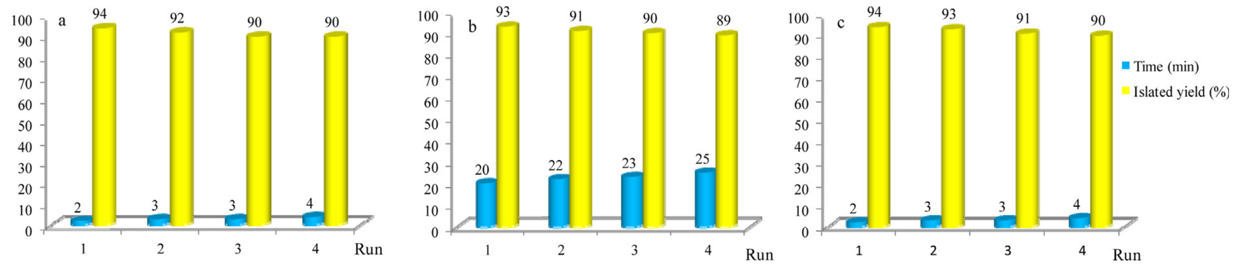
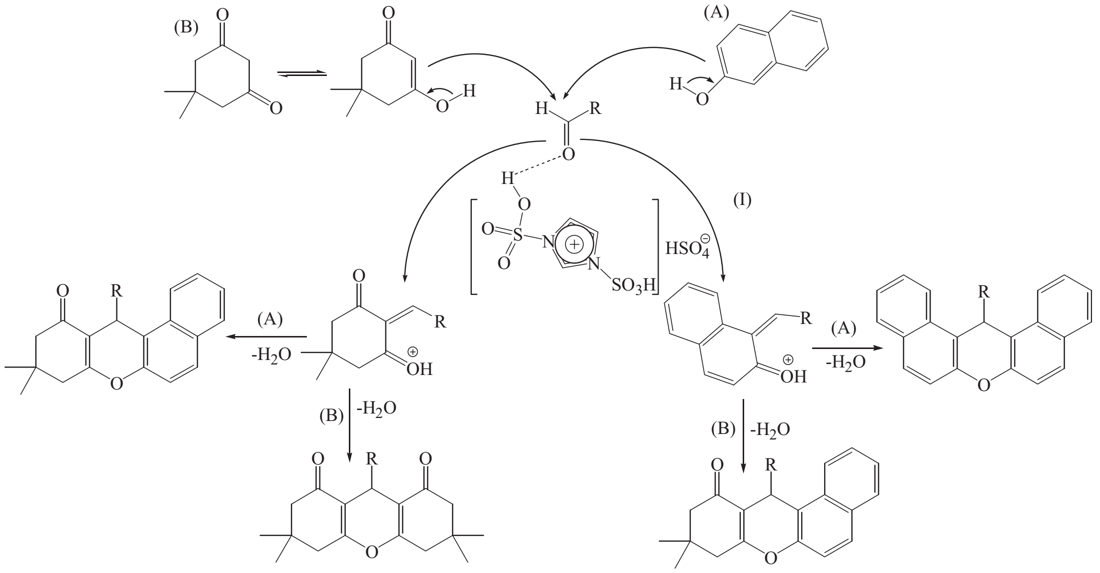


Fig. 1. Reusability of DSIMHS in the synthesis of (a) 14-(phenyl)-14*H*-dibenzo[*a*,*j*]xanthenes, (b) 12-phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one and (c) 9-(phenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthenes.



Scheme 4. Proposed mechanism for the synthesis of xanthene derivatives in the presence of DSIMHS under solvent-free conditions.

Table 8
Comparison of the efficiency of various ILs in synthesis of 12-(4-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one.

Entry	IL	Conditions	Time (min)	Yield (%) [a]	Ref.
1	DSIMHS (0.25 mmol)	Solvent-free, 90 °C	12	93	This work
2	[BSMIM]Ts (5 mol%)	MW oven at 240 W	10	84	[70]
3	[(4-sulfobutyl)tris(4-sulfophenyl)phosphonium-hydrogen sulfate (10 mol%)	Solvent-free, 80 °C	15	98	[71]
4	[bmim]BF_4 (0.5 mL)	Solvent-free, 80 °C	120	85	[72]
5	Py$(HSO_4)_2$ (10 mol%)	Solvent-free, 100 °C	30	87	[73]
6	[Et_3N-SO_3H]Cl (25 mol%)	Solvent-free, 120 °C	40	89	[74]

[a] Yields refer to isolated pure products.

activates it. Then, nucleophilic *β*-naphthol (A) or dimedone (B) attacks the carbonyl group of the activated aldehyde and by removing H_2O, the Knoevenagel products (I or II) is generated. The following addition of these intermediates to A or B, gives the acyclic adduct intermediate, which undergoes an intramolecular cyclization with the participation of two hydroxyl groups to afford the xanthene derivatives (Scheme 4).

It is noteworthy to mention that the catalyst is recyclable and could be reused without significant loss of activity. Hence, we decided to examine the reusability and recycling performance of

Table 9
Comparison of the efficiency of various ILs in synthesis of 9-(4-bromophenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthenes under solvent-free conditions.

Entry	IL	Temperature (°C)	Time (min)	Yield (%) [a]	Ref.
1	DSIMHS (0.25 mmol)	90	3	92	This work
2	[Dsim]Cl (10 mol%)	70	4	96	[68]
3	[Msim]PF_6 (10 mol%)	70	6	91	[68]
4	[Msim]BF_4 (10 mol%)	70	8	95	[68]
5	[bmim]HSO_4 (100 mg)	80	210	90	[75]
6	[Hmim]TFA (100 mg)	80	180	91	[76]
7	[Et_3NH][H_2PO_4] (400 mg)	100	5	94	[77]

[a] Yields refer to isolated pure products.

DSIMHS for the synthesis of xanthene derivatives. For this purpose, all the water added for filtering and washing the product was collected and washed with CH_2Cl_2 (2×10 mL) to remove organic impurities. Then, water was evaporated and the extracted catalyst was dried. It was found that the recovered catalyst could be reused directly in the next run without any loss of its activity even after the fourth run (Fig. 1).

As shown in Tables 7–9 the performance of DSIMHS was compared with the efficiency of other ILs reported in the literature. It is clear from these data that DSIMHS can act as an efficient and beneficial catalyst compared with the other mentioned reagents. For example, in Table 7, amount of the catalyst, reaction times and temperature in this work have been reduced relative to the other ILs. In addition, Table 9 shows that the reaction can be carried out using smaller amounts of DSIMHS in shorter reaction times compared to the other catalysts.

4. Conclusion

In conclusion, herein we described DSIMHS as an inexpensive, easily available, efficient, reusable and green catalyst for the synthesis of xanthenes in a simple one-pot protocol under solvent-free conditions with excellent yields. The obtained results show that the catalytic activity of DSIMHS is convincingly superior to other recently reported catalysts. In addition, other advantages of this methodology such as short reaction times, simplicity of operation and easy work-up, high reaction rates, lack of side reactions, ease of preparation and handling of the catalyst and simple experimental procedure makes it attractive for organic chemists. Further work to explore this novel catalyst in other organic transformations is in progress.

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