

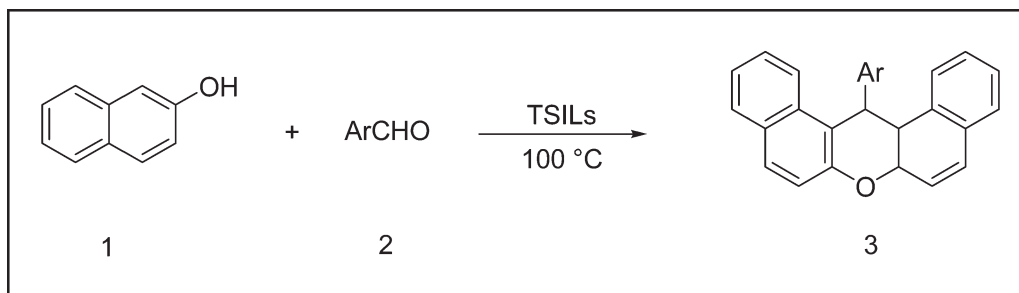
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Some recyclable acyclic SO_3H -functionalized ionic liquids have been used as novel catalysts for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes *via* the one-pot condensation of β -naphthol and aromatic aldehydes in aqueous medium. The condensation reaction was accomplished successfully with various aromatic aldehydes with good to excellent yields ranged from 86 to 96% within 5–30 min. After the reaction, the products could simply be separated from the catalysts by filtration. When separated from the reaction mixture, the catalysts could be recycled and reused for several times without noticeably reducing catalytic activity. The methodology gives the advantages of high yields, short reaction time, and easy work-up procedure.

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INTRODUCTION

The synthesis of xanthenes derivatives is of much importance because of their wide range of biological and pharmaceutical properties, such as antiviral, and anti-inflammatory activities as well as efficacy in photodynamic therapy [1,2]. Furthermore, these compounds can be used as dyes [3], pH-sensitive fluorescent materials for visualization of bimolecular [4] and used in laser technologies [5]. Recently, many synthetic methods for synthesis of these compounds have been reported by the condensation of aldehydes with β -naphthol in the presence of *p*-toluenesulfonic acid [6], sulfamic acid [7], fluoroboric acid/silica-gel [8], cellulose sulfuric acid [9], zirconium(iv) oxide chloride [10], CBr_4 [11], molecular iodine [12], heteropoly acid [13], silica sulfuric acid [14], Amberlyst-15 [15], and cyanuric chloride [16] as catalysts. However, the search for the new readily available and green catalysts is still being actively pursued.

With the increasing public concern over environmental degradation and future resources, it is of great importance for chemists to come up with new approaches that are less hazardous to human health and environment. Being used in large amounts and are usually vol-

atile liquids, the solvents used in organic synthesis are high on the list of environmental pollutants. For overcoming these problems; one approach is to use the water as the green medium, another approach is to develop new processes involving the solvent-free conditions. In recent years, ionic liquids have been emerged as a powerful alternative to conventional molecular organic solvents because of their particular properties, such as undetectable vapor pressure, wide liquid range, as well as ease of recovery and reuse, and making them a greener alternative to volatile organic solvents. Combining the useful characteristics of solid acids and mineral acids, Brønsted acidic task-specific ionic liquids (TSILs) are designed to replace traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid in chemical processes [17]. Such acidic TSILs have dual role (solvent and catalyst) in organic reactions [18–21]. In fact, the use of Brønsted-acidic TSILs as catalysts is an area of ongoing activity; however, development and exploration of acidic TSILs are currently in the preliminary stage.

We are especially interested in developing the potential use of efficient, simple, and inexpensive TSILs

Table 1Synthesis of 14-phenyl-14*H*-dibenzo[*a,j*]xanthenes catalyzed by acidic ionic liquids.^a

Entry	Catalyst	TSILs (mol %) ^b	Time (min)	Yields (%) ^c
1	—	—	180	—
2	[TMPSA][HSO ₄]	1	60	80
3	[TMPSA][HSO ₄]	3	30	86
4	[TMPSA][HSO ₄]	5	5	93
5	[TMPSA][HSO ₄]	7	5	94
6	[TMPSA][HSO ₄]	9	5	95
7	[TMPSA][HSO ₄]	15	5	94
8	[TEPSA][HSO ₄]	5	5	90
9	[TBPSA][HSO ₄]	5	5	92
10	[TMBSA][HSO ₄]	5	5	94
11	[TEBSA][HSO ₄]	5	5	93
12	[PyPSA][HSO ₄]	5	5	91
13	[MIMPSA][HSO ₄]	5	5	93
14	[bmim][HSO ₄]	5	30	85

^a 5 mmol benzaldehyde, 10 mmol β-naphthol, water is used as a solvent.^b Molar ratio of TSILs to benzaldehyde.^c Isolated yields.

catalysts. In our previous work, some novel and relatively cheap SO₃H-functional halogen-free acidic ionic liquids that bear an alkane sulfonic acid group in an acyclic trialkylammonium cation have been synthesized and their catalytic activity for acid-catalyzed reactions have also been investigated [22–24]. In continuation of our work in studying acid-catalyzed reactions in ionic liquids, we report here the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes in acidic ionic liquids.

RESULTS AND DISCUSSION

For the beginning of this study, benzaldehyde and β-naphthol were used as the model reactants to compare the catalytic performance of the TSILs. As shown in Table 1, nearly no xanthenes could be detected in the

Table 2Reusing of the ionic liquid [TMPSA][HSO₄].^a

Entry	Run	Isolated yield (%)
1	Fresh	93
2	1	94
3	2	93
4	3	91
5	4	92
6	5	90
7	6	90

^a 5 mmol benzaldehyde, 10 mmol β-naphthol, 0.25 mmol catalyst, 100°C, 5 min.

absence of ionic liquids (entry 1), which indicated that the catalyst was absolutely necessary for this condensation reaction. All the prepared eight TSILs proved to be very active, leading to 86–95% yield of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes in the presence of 5% TSILs (entries 4, 8–14). In addition, ionic liquids containing the shorter length of alkyl chain are relatively cheaper. Further, the better immiscibility of the resulted xanthenes with the shorter length of alkyl chain should facilitate the separation in work-up procedure. Hence, [TMPSA][HSO₄] should be the best catalyst for this condensation among the five acyclic TSILs, and the optimized reaction conditions were presented in Table 1 (entry 4).

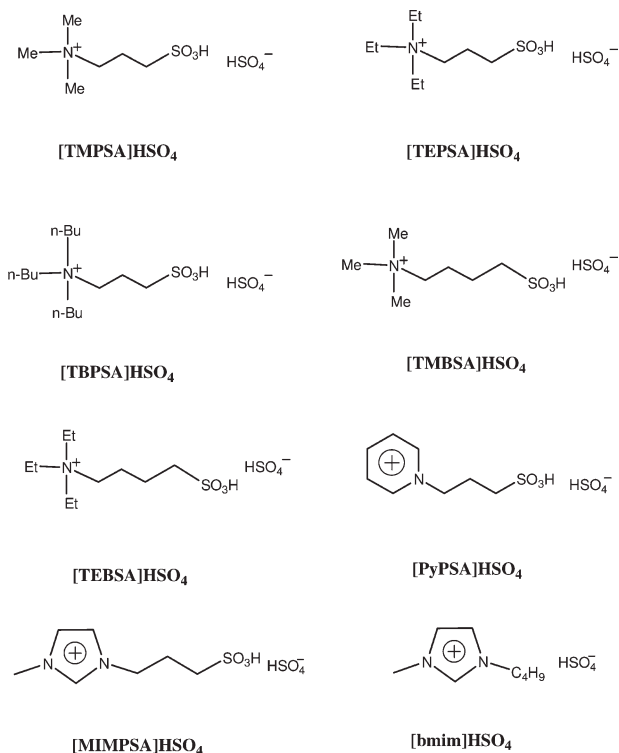
Compared with the traditional methods, use of volatile solvents and catalysts, which is complex, and time and energy consuming, and environmentally malign, the easy recycling is an attractive property of the TSILs for the environmental protection and economic reasons. So, the recycling performance of [TMPSA][HSO₄] in the same model condensation reaction was subsequently explored. After the reaction, the products were isolated from the catalytic system by filtration, the catalyst was reused in the next run directly without further

Table 3Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes catalyzed by [TMPSA][HSO₄].^a

Entry	Ar	Product	Time (min)	m.p. (°C) [lit.]	Yields (%) ^b
1	C ₆ H ₅	3a	5	184–185 [8]	93
2	<i>o</i> -ClC ₆ H ₄	3b	10	213–215 [6]	92
3	<i>p</i> -ClC ₆ H ₄	3c	5	286–288 [6]	96
4	2,4-Cl ₂ C ₆ H ₃	3d	10	228–229 [10]	95
5	<i>p</i> -FC ₆ H ₄	3e	5	238–239 [6]	95
6	<i>o</i> -NO ₂ C ₆ H ₄	3f	10	213–215 [8]	90
7	<i>m</i> -NO ₂ C ₆ H ₄	3g	10	211–212 [6]	91
8	<i>p</i> -NO ₂ C ₆ H ₄	3h	5	310–312 [8]	95
9	<i>p</i> -CH ₃ C ₆ H ₄	3i	10	227–229 [6]	92
10	<i>p</i> -CH ₃ OC ₆ H ₄	3j	30	202–204 [6]	86

^a 5 mmol benzaldehyde, 10 mmol β-naphthol, 0.25 mmol catalyst, 100°C.^b Isolated yields.

Scheme 1



purification. As shown in Table 2, the catalyst can be reused at least six times without appreciable decrease in yield and reaction rate, and the yield ranged from 94–90%.

The condensation reactions of other substituted benzaldehydes and β -naphthol in the presence of [TMPSA][HSO₄] were accomplished under the optimized reaction conditions described above and the results are presented in Table 3. It can easily be seen that all aromatic aldehydes with either electro-withdrawing or electro-donating substituents, such as nitro and methoxy groups gave reasonable to good yields ranged from 85–96% with 30 min. However, aromatic aldehydes with electron-withdrawing group are more actively than that with electro-donation one. Their physical properties were determined and structures were confirmed by ¹H NMR spectral data.

In conclusion,, it was demonstrated that some readily available, economic TSILs have been used as recyclable catalysts for the condensation of benzaldehydes and β -naphthol to synthesis 14-aryl-14*H*-dibenzo[*a,j*]xanthenes. The merit of this methodology is that it is simple, high efficient, and eco-friendly.

EXPERIMENTAL

Melting points were determined on X-6 microscope melting apparatus. ¹H NMR spectra were recorded on Bruker DRX300 (300 or 500 MHz) and ¹³C NMR spectra on Bruker DRX300 (75.5 MHz) spectrometer. Mass spectra were obtained with automated FININIGAN Trace Ultra-Trace DSQ GC/MS spectrometer. All chemicals (AR grade) were commercially available and used directly without further purification.

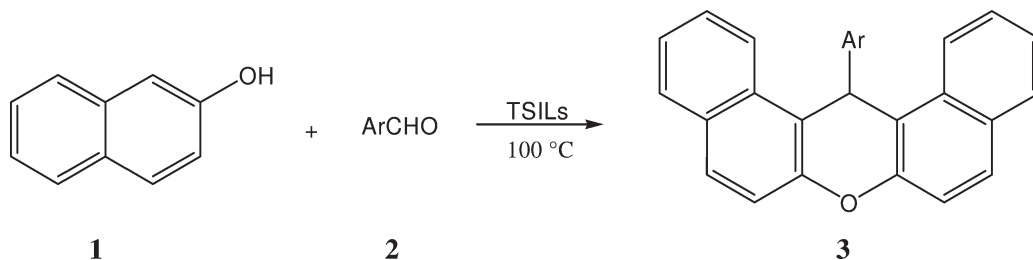
Synthesis of SO₃H-functional halogen-free acidic ionic liquid (TSILs). All acyclic SO₃H-functionalized halogen-free acids, such as [TMPSA][HSO₄], [TEPSA][HSO₄] were synthesized according to our previous methods [18], the pyridine, imidazole-based SO₃H-functionalized ionic liquids for comparison were obtained according to reported methods [16]. The structures of TSILs were analyzed by ¹H NMR, ¹³C NMR, and MS spectral data (Scheme 1).

The selected spectral data for SO₃H-functionalized halogen-free TSILs. *N,N,N*-trimethyl-*N*-propanesulfonic acid ammonium hydrogen sulfate [TMPSA][HSO₄]. ¹H NMR (300 MHz, D₂O): δ 3.22 (t, J = 7.2 Hz, 2H, N—CH₂—C—SO₃), 2.90 (s, 9H, N—CH₃), 2.73 (t, J = 7.8 Hz, 2H, N—C—CH₂—SO₃), 1.99 (m, 2H, N—C—CH₂—C—SO₃). ¹³C NMR (75.5 MHz, D₂O): δ 65.00, 52.51, 47.89, 18.85. MS (m/z): 279.05 (M⁺), 182.14(100).

N,N,N-triethyl-*N*-propanesulfonic acid ammonium hydrogen sulfate [TEPSA][HSO₄]. ¹H NMR (300 MHz, D₂O): δ 3.22–3.05 (m, 8H, (6H + 2H), N—CH₂—CH₃, N—CH₂—C—SO₃), 2.85 (t, J = 7.2 Hz 2H, N—C—C—CH₂—SO₃), 1.97 (m, 2H, N—C—CH₂—C—SO₃), 1.12 (t, 9H, N—C—CH₃). ¹³C NMR (75.5 MHz, D₂O): δ 56.00, 52.95, 48.34, 18.93, 8.04. MS (m/z): 321.05 (M⁺), 322.05, 320.15, 194.05(100).

N,N,N-tributyl-*N*-propanesulfonic acid ammonium hydrogen sulfate [TBPSA][HSO₄]. ¹H NMR (500 MHz, D₂O): δ 3.28(t, 2H, J = 4.0 Hz, N—CH₂—C—SO₃), 3.13(t, 6H, J = 8.5 Hz, N—CH₂—C—CH₃), 2.85(t, 2H, J = 7.0 Hz, N—C—C—CH₂—SO₃), 2.03 (m, 2H, N—C—CH₂—C—SO₃), 1.56 (m, 6H, N—C—CH₂—C—CH₃), 1.27 (m, 6H, N—C—C—CH₂—CH₃), 0.84 (t, 9H, J = 7.5 Hz, N—C—C—CH₃).

Scheme 2



^{13}C NMR (75.5 MHz, D_2O): δ 58.49, 50.66, 48.42, 23.93, 20.36, 19.16, 14.46. MS (m/z): 405.29 (M^+), 406.28, 404.28(100).

N,N,N-trimethyl-N-butanefulfonic acid ammonium hydrogen sulfate [TMBSA]/[HSO₄]. ^1H NMR (300 MHz, D_2O): δ 3.24 (t, J = 8.4 Hz, 2H, $\text{N}-\text{CH}_2-\text{C}-\text{C}-\text{SO}_3$), 2.99 (s, 9H, $\text{N}-\text{CH}_3$), 2.85 (t, J = 7.5 Hz, 2H, $\text{N}-\text{C}-\text{C}-\text{CH}_2-\text{SO}_3$), 1.82 (m, 2H, $\text{N}-\text{C}-\text{CH}_2-\text{C}-\text{C}-\text{SO}_3$), 1.70 (m, 2H, $\text{N}-\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{SO}_3$). ^{13}C NMR (75.5 MHz, D_2O): δ 66.15, 53.16, 50.31, 21.46, 19.93. MS (m/z): 293.36 (M^+), 196.39(100).

N,N,N-triethyl-N-butanefulfonic acid ammonium hydrogen sulfate [TEBSA]/[HSO₄]. ^1H NMR (300 MHz, D_2O): δ 3.15 (q, J = 7.2 Hz, 6H, $\text{N}-\text{CH}_2-\text{CH}_3$), 3.07 (t, J = 8.4 Hz, 2H, $\text{N}-\text{CH}_2-\text{C}-\text{C}-\text{SO}_3$), 2.82 (t, J = 7.2 Hz, 2H, $\text{N}-\text{C}-\text{C}-\text{CH}_2-\text{SO}_3$), 1.68 (m, 4H, $\text{N}-\text{C}-\text{C}_2\text{H}_4-\text{C}-\text{SO}_3$), 1.11 (m, J = 7.2 Hz, 9H, $\text{N}-\text{CH}_2-\text{CH}_3$). ^{13}C NMR (75.5 MHz, D_2O): δ 56.21, 52.85, 50.32, 21.50, 20.20, 6.90. MS (m/z): 335.35 (M^+), 208.36(100).

General procedure for the synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthenes derivatives. In a typical experiment, to a round-bottomed flask charged with β -naphthol (10 mmol) **1**, aldehyde (**5** mmol) **2** in 5 mL of water was added to acidic ionic liquid (0.25 mmol) under stirring. The mixture was then stirred for a certain time at 100°C (Scheme 2). On completion (monitored by TLC), the precipitated crude product was collected by filtration and recrystallized from ethanol (95%) to afford pure 14-aryl-14H-dibenzo[*a,j*]xanthenes **3**. The filtrate containing ionic liquid could be reused directly in the next run without further purification. The products were identified by IR, ^1H NMR, and physical data (m.p.) with those reported in the literatures.

The selected data for chalcone 3a. 14-Phenyl-14H-dibenzo[*a,j*]xanthene (3a, $\text{C}_{27}\text{H}_{18}\text{O}$). Colorless crystals; m.p. 184–185°C; IR (KBr, cm^{-1}): 3074, 3020, 2886, 1622, 1591, 1513, 1455, 1430, 1401, 1251, 1152, 1078, 1028, 962, 857, 827, 743, 700. ^1H NMR (300 MHz, CDCl_3): δ 6.46 (s, 1H, CH), 6.96 (t, J = 7.2 Hz, 1H, Ar-H), 7.12 (t, J = 7.2 Hz, 2H, Ar-H), 7.36–7.58 (m, 8H, Ar-H), 7.74–7.81 (m, 4H, Ar-H), 8.37 (d, J = 8.4 Hz, 2H, Ar-H).

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