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Ionic liquid triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl} as a novel, highly efficient and homogeneous catalyst for the synthesis of β-acetamido ketones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes

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ABSTRACT

In this work, the efficiency, generality and applicability of novel Brønsted acidic ionic liquid triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl, *N*,*N*-diethyl-*N*-sulfoethanammonium chloride} as homogeneous and green catalyst for organic transformations under various conditions are studied. Herein, the following one-pot multi-component reactions in the presence of {[Et_3N–SO_3H]Cl are investigated: (i) the synthesis of β-acetamido ketones from acetophenones, aldehydes, acetonitrile and acetyl chloride in solution and under extremely mild conditions (room temperature), (ii) the preparation of 1,8-dioxo-octahydroxanthenes from dimedone (5,5-dimethyl-1,3-cyclohexanedione) (2 equiv.) and aldehydes (1 equiv.) under solvent-free conditions at moderate temperature (80 °C), and (iii) the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes from β-naphthol (2 equiv.) and aldehydes (1 equiv.) in harsh conditions (120 °C) in the absence of solvent. High yields, relatively short reaction times, efficiency, generality, clean process, simple methodology, low cost, easy work-up, ease of preparation and regeneration of the catalyst and green conditions (in the synthesis of the xanthene derivatives) are advantages of the application of [Et_3N–SO_3H]Cl as catalyst in the above organic reactions. This work is the first report of the ionic liquid.

1. Introduction

Ionic liquids (ILs) are defined as pure compounds, consisting only of cations and anions (i.e., salts), which melt at or below 100 °C [1–3]. These salts have attracted rising interest in the last decades for chemists because of their unique properties such as high thermal and chemical stability, non-flammability, non-volatility, wide liquid-state temperature range, large electrochemical window and favorable salvation behavior [3,4]. This increased interest led to an exponential growth of papers reporting on various aspects of ILs, including synthesis of a vast number of new ILs, and their application in synthetic transformations (as solvent, catalyst and reagent) [1–15], electrochemistry [3,16], spectroscopy and extraction and separation processes [3]. Among the different kinds of ionic liquids, Brønsted acidic ones have designed to replace solid acids and traditional mineral liquid acids like sulfuric acid and hydrochloric acid to catalyze chemical transformations [17–23]. Along this line, more recently, we have synthesized some Brønsted acidic ionic liquids in which a SO_3H group has bonded with a positive nitrogen (N^+) in organic compound, and successfully applied them as catalysts and regents in organic transformations [17–20]. In continuation of our studies on the preparation of acidic ILs, and their applications as catalyst and reagent in organic transformations [17–20], we have synthesized Brønsted acidic ionic liquid triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl, *N*,*N*-diethyl-*N*-sulfoethanammonium chloride} (Fig. 1) as a new, homogeneous and green catalyst, from the simple reaction of triethylamine with chlorosulfonic acid. According to the high efficacy of our previous acidic ILs to catalyze organic reactions [17–20], we predict that our new catalyst, [Et_3N–SO_3H]Cl, can also promote different organic transformations. Moreover, a lot of ILs do not solve in organic solvents; [Et_3N–SO_3H]Cl solves in most of organic solvents. This matter is an important factor to catalyze reactions successfully in organic media. Herein, we have found that the one-pot multi-component synthesis of β-acetamido ketones, 1,8-dioxo-

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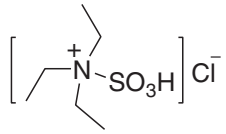


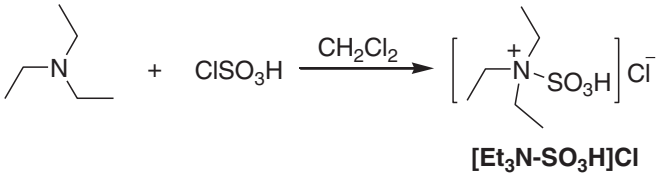
Fig. 1. The structure of triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl}.

octahydroxanthenes and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes can be efficiently performed in the presence of this novel catalyst.

Multi-component reactions (MCRs) have drawn great interest enjoying an outstanding status in modern organic synthesis and medicinal chemistry because they are one-pot processes bringing together three or more components and show high atom economy and high selectivity [17,24–29]. Moreover, MCRs offer the advantage of simplicity and synthetic efficiency over conventional chemical reactions [17,24–29].

β-Acetamido ketones are of importance as they have been used as the precursor of 1,3-amino alcohols [30], β-amino acids [31], and γ-lactams [32], as well as various bioactive molecules such as antibiotic nikkomycins or neopolyoxines [33,34]. These compounds have been also applied as aglucosidase inhibitors [35]. Thus, the synthesis of β-acetamido ketones has attracted much attention in organic synthesis. The one-pot multi-component condensation of acetophenones with aromatic aldehydes, acetonitrile and acetyl chloride has been used as the most common synthetic route towards β-acetamido ketones [35–46]. Some catalysts have been utilized for this transformation, such as $La(OTf)_3$ [35], $CoCl_2$ [36], $Zr(HSO_4)_4$ [37], ZnO nanoparticles [38], heteropoly acids [39], silica sulfuric acid [40], $Sc(OTf)_3$ [41], 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane-bis(tetrafluoroborate) [42], polyaniline-supported salts [43], $CeCl_3{\cdot}7H_2O$ [44], $ZrOCl_2{\cdot}8H_2O$ [45], and $AlCl_3$ [46].

There has been significant attention in recent years in the synthesis of xanthenes and their related derivatives such as 1,8-dioxo-octahydroxanthens and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes due to their useful spectroscopic properties and applications in industry as dyes in laser technology [47], and as pH sensitive fluorescent materials for visualization of biomolecules [48]. Moreover, xanthene based compounds exhibit extensive activities in biological and pharmaceutical aspects such as anti-inflammatory [49], antiviral [50], antibacterial [51], antitumor [52], and neuropharmacological [53], and they have been applied in photodynamic therapy (PDT) [54]. Xanthene derivatives have been also utilized as inflexible carbon skeletons for the assembly of chiral bidentate phosphine ligands with potential applications in catalytic processes [55,56]. The usual method for the synthesis of 1,8-dioxo-octahydroxanthenes involves the one-pot multi-component condensation between dimedone (5,5-dimethyl-1,3-cyclohexanedione) (2 equiv.) and aldehydes (1 equiv.), by utilizing a number of catalysts, e. g. amberlyst-15 [57], $NaHSO_4$-SiO_2 [58], $SbCl_3/SiO_2$ [58], silica-supported $H_{14}[NaP_5W_{30}O_{110}]$ nanoparticles [59], SiO_2-R-SO_3H [60], $H_3PW_{12}O_{40}$ supported MCM-41 [61], DABCO-bromine [62], cyanuric chloride [63], TMSCl [64], and $ZrO(OTf)_2$ [65]. The best and most interesting protocol for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes is the one-pot multi-component reaction of β-naphthol (2 equiv.) with aldehydes (1 equiv.) in the presence of some catalysts, such as $ZrO(OTf)_2$ [65], heteropolyacids [66], Dowex-50 W [67], 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) [68], $KAl(SO_4)_2{\cdot}12H_2O$ [69], nano-TiO_2 [70], $Yb(OTf)_3$ [71], $Sc[N(SO_2C_8F_{17})_2]_3$ [72], $InCl_3$ [73], $TaCl_5$ [74], and $HClO_4$-SiO_2 [75].



Scheme 1. The synthesis of [Et_3N–SO_3H]Cl.

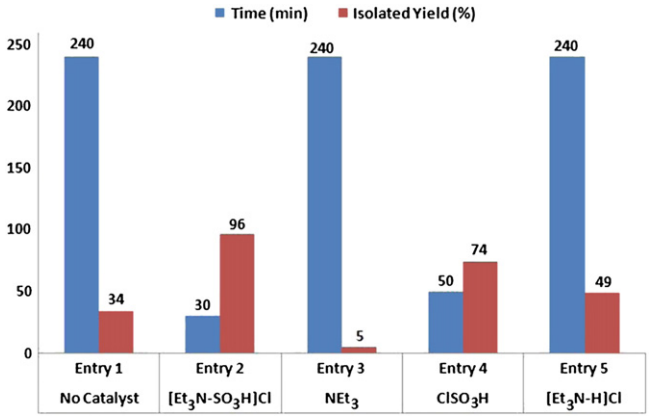


Fig. 2. The solvent-free reaction between β-naphthol and benzaldehyde using 15 mol% of [Et_3N–SO_3H]Cl, NEt_3, $ClSO_3H$ or [Et_3N–H]Cl at 120 °C.

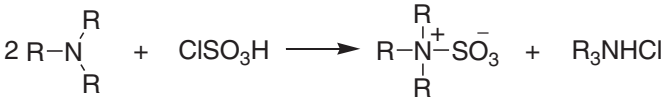
Although some catalysts for the synthesis of β-acetamido ketones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes are known, newer catalysts continue to attract attention for their difference with the others, novelty and effectiveness. Furthermore, most of the reported methods for the synthesis of the title compounds are associated with one or more of the following drawbacks: (i) low yields, (ii) long reaction times, (iii) the use of large amount of catalyst, and (iv) the use of expensive, non-available or toxic catalysts, (v) tedious work-up procedure, (vi) performances under certain special conditions, and (vii) poor agreement with the green chemistry protocols.

Having the above subjects in mind, and also in continuation of ongoing program to prepare Brønsted acidic ILs and apply them as catalysts in organic synthesis [17–20], we, in this paper, introduce ionic liquid triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl} as a novel, highly efficient, homogeneous, regenerable and green catalyst for organic reactions. Herein, we report the first applications of this interesting catalyst for some on-pot multi-component organic transformations including: (i) the synthesis of β-acetamido ketones by the reaction of acetophenones with aldehydes, acetonitrile and acetyl chloride, (ii) the preparation of 1,8-dioxo-octahydroxanthenes *via* the condensation of 2 equiv. of dimedone with 1 equiv. of aldehydes, and (iii) the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes by the reaction between 2 equiv. of β-naphthol and 1 equiv. of aldehydes. Interestingly, our protocols have none of the above-mentioned disadvantages at all.

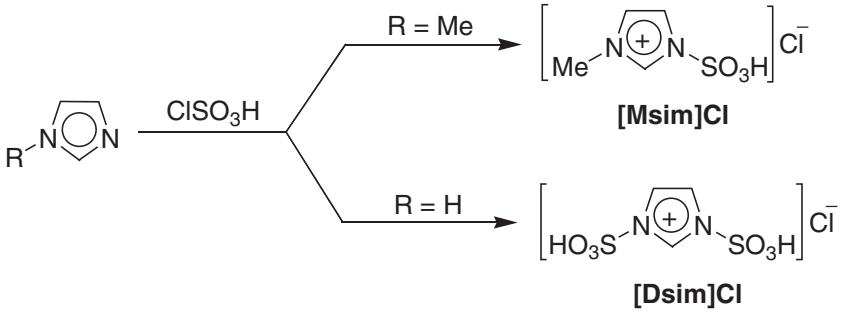
2. Experimental

2.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. Acetonitrile and dichloromethane were dried, distilled and stored over molecular sieves. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by thin layer chromatography (TLC) using silica gel SIL G/UV 254 plates.



Scheme 2. The preparation of R_3N^+–SO_3^- by the reaction of tertiary amines (2 equiv.) with chlorosulfonic acid (1 equiv.).



Scheme 3. The nucleophilic reaction of 1-methylimidazole or imidazole with chlorosulfonic acid.

The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The ^{1}H NMR (300, 400 or 500 MHz) and ^{13}C NMR (75, 100 or 125 MHz) were run on a Bruker Avance DPX, FT-NMR spectrometers. Mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model.

2.2. Procedure for the preparation of ionic liquid [Et_3N–SO_3H]Cl

A solution of triethylamine (0.50 g, 5 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a stirring solution of chlorosulfonic acid (0.58 g, 5 mmol) in dry CH_2Cl_2 (40 mL) over a period of 10 min at 10 °C. Afterward, the reaction mixture was allowed to heat to room temperature (accompanied with stirring), and stirred for another 4 h. The solvent was evaporated, and the liquid residue was triturated with *t*-butylmethyl ether (3 × 10 mL) and dried under powerful vacuum at 90 °C to give [Et_3N–SO_3H]Cl as a viscous pale yellow oil in 93% yield.

2.3. General procedure for the synthesis of β-acetamido ketone derivatives **1a–o**

To a mixture of compounds consisting of acetophenone (1 mmol), aldehyde (1 mmol), acetonitrile (3 mL) and acetyl chloride (0.3 mL) in a 10 mL round-bottomed flask was added [Et_3N–SO_3H]Cl (0.033 g, 0.15 mmol), and the resulting mixture was stirred at room temperature. After completion of the reaction, as monitored by TLC, crushed ice (10 mL) was added to the reaction mixture and stirred thoroughly. On solidification, the crude product (solid) was filtered, dried, and purified by short column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/4).

Note: For the synthesis of tris(β-acetamido ketone) **1p**, the amounts of *p*-bromoacetophenone, tris(aldehyde), acetonitrile, acetyl chloride and [Et_3N–SO_3H]Cl were 3.3 mmol, 1 mmol, 9 mL, 0.9 mL and 0.25 mmol, respectively.

2.4. General procedure for the synthesis of 1,8-dioxo-octahydroxanthene derivatives **2a–n**

To a mixture of dimedone (0.28 g, 2 mmol) and aldehyde (1 mmol) in a test tube, [Et_3N–SO_3H]Cl (0.055 g, 0.25 mmol) was added. The resulting mixture was firstly stirred magnetically, and after solidification of the reaction mixture with a small rod at 80 °C, and the reaction progress was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature, H_2O (5 mL) was added to it, stirred for 3 min and filtered. The solid residue was recrystallized from EtOH (95%) to give the pure product.

2.5. General procedure for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes **3a–j**

A mixture of β-naphthol (0.42 g, 2 mmol), aldehyde (1 mmol) and [Et_3N–SO_3H]Cl (0.033 g, 0.15 mmol) in a test tube, was firstly stirred magnetically, and after solidification of the reaction mixture with a small rod, at 120 °C. After completion of the reaction, as monitored with TLC, the reaction mixture was cooled to room temperature, H_2O (5 mL) was added to it, stirred for 3 min, and filtered. Then, the solid residue was recrystallized from EtOH (95%) to give the pure product.

3. Results and discussion

3.1. Studies to confirm the structure of triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl}

To prepare ionic liquid triethylamine-bonded sulfonic acid (Scheme 1), firstly, triethylamine (in dry CH_2Cl_2) was added dropwise to a stirring solution of chlorosulfonic acid in dry CH_2Cl_2 over a period of 10 min at room temperature, and the resulting mixture was stirred at room temperature for 3 h. Afterward, the solvent was evaporated, and the liquid residue was triturated with dry *t*-butylmethyl ether (three times) and dried under vacuum to give [Et_3N–SO_3H]Cl as a viscous pale yellow oil in about 90% purity; we could not be separated [Et_3N–SO_3H]Cl from the by-product. We thought that the by-product was [Et_3N–H][$ClSO_3$] which formed besides the catalyst in about 10% by the acid–base reaction between triethylamine and chlorosulfonic acid; the small peak observed in 11.75 ppm of ^{1}H NMR spectra of the catalyst is related to the acidic hydrogen of [Et_3N–H][$ClSO_3$]. In another procedure, chlorosulfonic acid (in dry CH_2Cl_2) was added dropwise to a stirring solution of triethylamine in dry CH_2Cl_2 over a period of 10 min at room temperature, and the resulting mixture was stirred at room temperature for 3 h. In these conditions, [Et_3N–H][$ClSO_3$] was also produced, accompanied with [Et_3N–SO_3H]Cl, more than the previous method. Increasing the reaction times in both procedures did not improve the results. In order to synthesize [Et_3N–SO_3H]Cl purely, in the next step, triethylamine (in dry CH_2Cl_2) was added dropwise to a stirring solution of chlorosulfonic acid (in dry CH_2Cl_2) over a period of 10 min at 10 °C, and the resulting mixture was stirred at room temperature for 4 h. Then, the solvent was evaporated, and the liquid residue was triturated with dry *t*-butylmethyl ether (three times) and dried under powerful vacuum to afford pure [Et_3N–SO_3H]Cl as a viscous pale yellow oil. In this procedure, the by-product {[Et_3N–H][$ClSO_3$]} was not obtained (the peak related to the acidic hydrogen of the by-product (11.75 ppm) was not observed in the ^{1}H NMR spectra of the catalyst). The complete explanations on the identification of the structure of the catalyst are given below:

The structure of [Et_3N–SO_3H]Cl was identified by ^{1}H and ^{13}C NMR and mass spectra. The corresponding spectral data have been reported in Section 2. Here, we study ^{1}H NMR data of [Et_3N–SO_3H]Cl. The important peak of ^{1}H NMR spectra of [Et_3N–SO_3H]Cl is related to the acidic hydrogen (SO_3H) which was observed in 7.43 ppm. To confirm that this peak (7.43) is really related to the hydrogen of SO_3H in [Et_3N–SO_3H]Cl, not the hydrogen of $ClSO_3H$ (its unreacted starting material) or another possible product formed from the

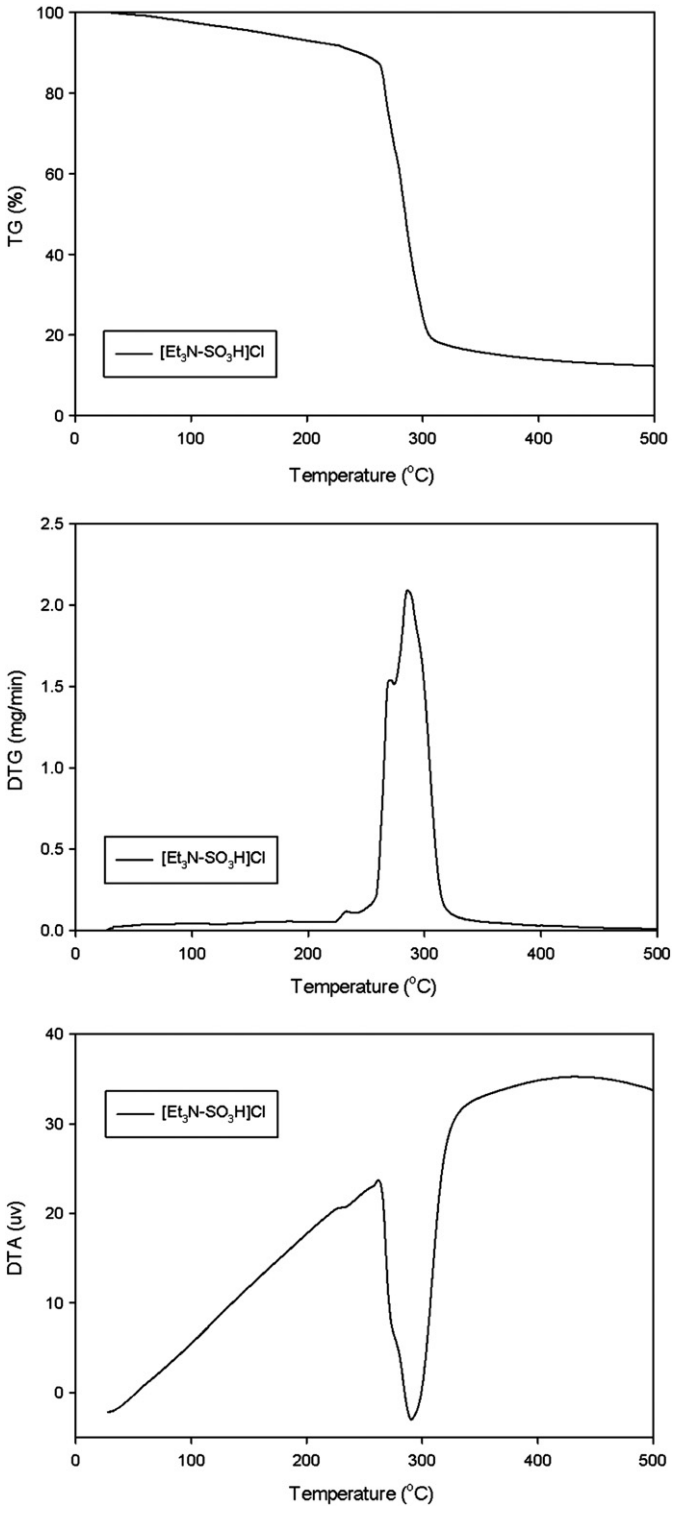


Fig. 3. The thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) diagrams of $[Et_3N–SO_3H]Cl$.

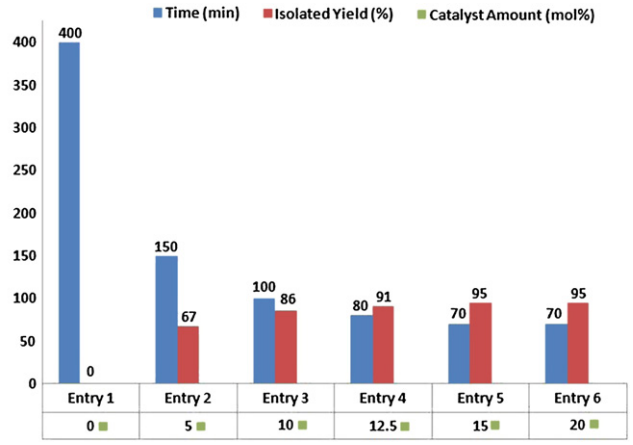
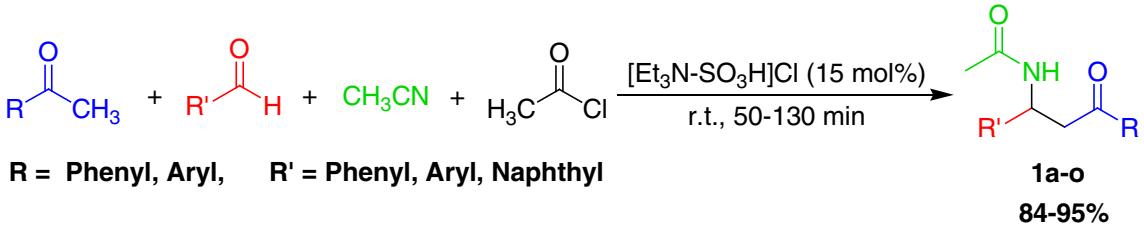


Fig. 4. Effect of different amounts of $[Et_3N–SO_3H]Cl$ on the reaction of acetophenone with benzaldehyde, acetonitrile and acetyl chloride at room temperature.

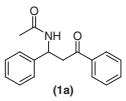
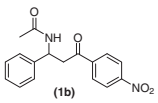
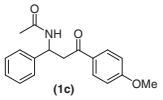
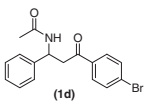
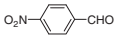
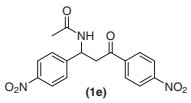
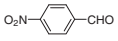
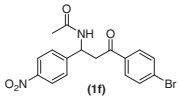
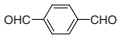
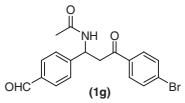
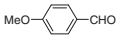
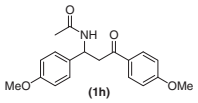
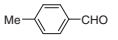
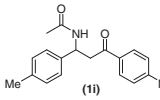
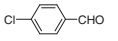
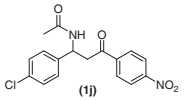
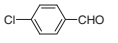
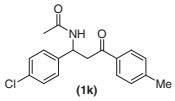
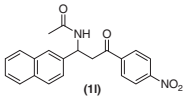
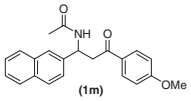
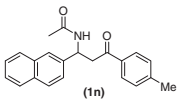
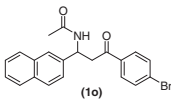
reaction of NEt_3 with $ClSO_3H$ {i.e. $[Et_3N–H][ClSO_3]$}, we also run ^1H NMR spectra of $ClSO_3H$ as well as $[Et_3N–H]Cl$ in $CDCl_3$ {the acidic hydrogens of $[Et_3N–H][ClSO_3]$ and $[Et_3N–H]Cl$ are same. There was no $[Et_3N–H][ClSO_3]$ in the Chemical Companies catalogs. Thus, we used $[Et_3N–H]Cl$ instead of $[Et_3N–H][ClSO_3]$}. In these spectra, the peaks of the acidic hydrogens of $[Et_3N–SO_3H]Cl$, $ClSO_3H$ and $[Et_3N–H]Cl$ were observed in 7.43, 10.75 and 11.59 ppm, respectively. The difference between the peaks of the acidic hydrogens in the compounds confirmed that the peak observed in 7.43 ppm of the ^1H NMR spectra of $[Et_3N–SO_3H]Cl$ is correctly related to the hydrogen of the SO_3H group of this compound.

In another study, to prove that $[Et_3N–SO_3H]Cl$ was correctly synthesized, and this is responsible of the catalytic results, as a model, the condensation of β-naphthol with benzaldehyde, leading to 14-aryl-14*H*-dibenzo[*a,j*]xanthenes **3a**, was examined in the presence of 15 mol% of the starting materials used for the preparation of the catalyst (i.e. NEt_3 and $ClSO_3H$) as well as the possible product formed by the reaction of NEt_3 with $ClSO_3H$ {this possible product is $[Et_3N–H][ClSO_3]$; however, there was not this compound in the Chemical Companies catalogs. Moreover, the acidic hydrogen of the cation of $[Et_3N–H][ClSO_3]$ can catalyze the reaction, not its anion. Thus, we used $[Et_3N–H]Cl$ instead of it} at 120 °C under solvent-free conditions. The results are presented in Fig. 2. As Fig. 2 indicates, $[Et_3N–SO_3H]Cl$ efficiently catalyzed the reaction; NEt_3 could not catalyze the reaction; and $ClSO_3H$ as well as $[Et_3N–H]Cl$ and also catalyst-free conditions gave low yields of the product in long reaction times (when $ClSO_3H$ was used as catalyst, by-products were produced besides the main product; however, in the case of $[Et_3N–H]Cl$, a large amount of the starting materials remained). It should be mentioned that because of the low boiling point of NEt_3, the reaction was carried out at 85 °C when this catalyst was applied. The model reaction was also checked using 15 mol% of the impure catalyst formed by the above-mentioned procedure {$[Et_3N–SO_3H]Cl$ accompanied with about 10% of $[Et_3N–H][ClSO_3]$}, at 120 °C in the absence of solvent in



Scheme 4. The synthesis of β-acetamido ketones from acetophenones, arylaldehydes, acetonitrile and acetyl chloride using $[Et_3N–SO_3H]Cl$.

Table 1
The triethylamine-bonded sulfonic acid catalyzed synthesis of β-acetamido ketones *via* the reaction of acetophenones with aldehydes, acetonitrile and acetyl chloride at room temperature.

Aldehyde	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
	 (1a)	70	95	100–102 (104–106) [37]
	 (1b)	90	93	77–79 (74–76) [45]
	 (1c)	60	92	126–128 (130–132) [45]
	 (1d)	60	91	102–104 (98–101) [43]
	 (1e)	130	84	185–188 (187–188) [37]
	 (1f)	120	87	162–163 (162–163) [46]
	 (1g)	75	86	104–106 (104–105) [46]
	 (1h)	60	91	124–127 (124–127) [46]
	 (1i)	50		117–119 (118–119) [46]
	 (1j)	120	87	114–116 (116–118) [39]
	 (1k)	75	89	130–132 (130–132) [46]
	 (1l)	110	87	164–165 (165–166) [46]
	 (1m)	80	90	108–110 (108–110) [46]
	 (1n)	90	85	110–112 (112–114) [46]
	 (1o)	90	88	139–141 (138–140) [46]

[a] Isolated yield.

which the product was obtained in lower yield and longer reaction time with respect to the pure catalyst. These results also confirmed that the catalyst has been correctly synthesized, and its structure is $[Et_3N–SO_3H]Cl$, not $[Et_3N–H][ClSO_3]$.

Moreover, it is well known that tertiary amine–sulfur trioxide ($R_3N^+–SO_3^-$) produces by the dropwise addition of chlorosulfonic acid (1 equiv.) to tertiary amines (2 equiv.) dissolved in dichloroethane at low temperature (Scheme 2) [76,77]. In these conditions, in each time, there are excess amount of Et_3N besides $ClSO_3H$ in the reaction mixture; thus, 1 equiv. of tertiary amine (as a nucleophile) attacks to the sulfur of $ClSO_3H$ to give $[R_3N–SO_3H]Cl$, and another 1 equiv. of amine acts as a base and abstracts the acidic hydrogen of $[R_3N–SO_3H]Cl$ to afford R_3N^+-SO_3^- and R_3NHCl. In the synthesis of $[Et_3N–SO_3H]Cl$, we add 1 equiv. of triethylamine dropwise to 1 equiv. of chlorosulfonic acid at low temperature. In these conditions, in each time, there are excess amount of $ClSO_3H$ besides Et_3N in the reaction mixture; thus, when NEt_3 reacts with $ClSO_3H$, and $[Et_3N–SO_3H]Cl$ forms, there is no base in the reaction media to abstract the acidic hydrogen of the compound to afford Et_3N^+-SO_3^- and Et_3NHCl. Also, according to the literature [76,77], in the reaction of tertiary amines with chlorosulfonic acid at low temperature, the reaction route is the nucleophilic substitution (substitution of Cl of $ClSO_3H$ by the nitrogen of tertiary amine), not the acid–base reaction (abstraction of the hydrogen of $ClSO_3H$ by tertiary amine to give $[R_3N–H][ClSO_3]$. The solvent-free reaction of β-naphthol with benzaldehyde was also examined using 15 mol% of $Et_3N^+–SO_3^-$ at 120 °C in which the product was obtained in 27% within 240 min. Considering this subject as well as the above procedures for the preparation of $R_3N^+–SO_3^-$ and $[Et_3N–SO_3H]Cl$, it is logical that our procedure must give $[Et_3N–SO_3H]Cl$, not $[R_3N–H][ClSO_3]$ or $Et_3N^+–SO_3^-$. The peak with integral 1, observed in 7.43 ppm of the ^1H NMR spectra of the catalyst, also confirmed existence a SO_3H group in the catalyst, and consequently its structure $\{[Et_3N–SO_3H]Cl\}$.

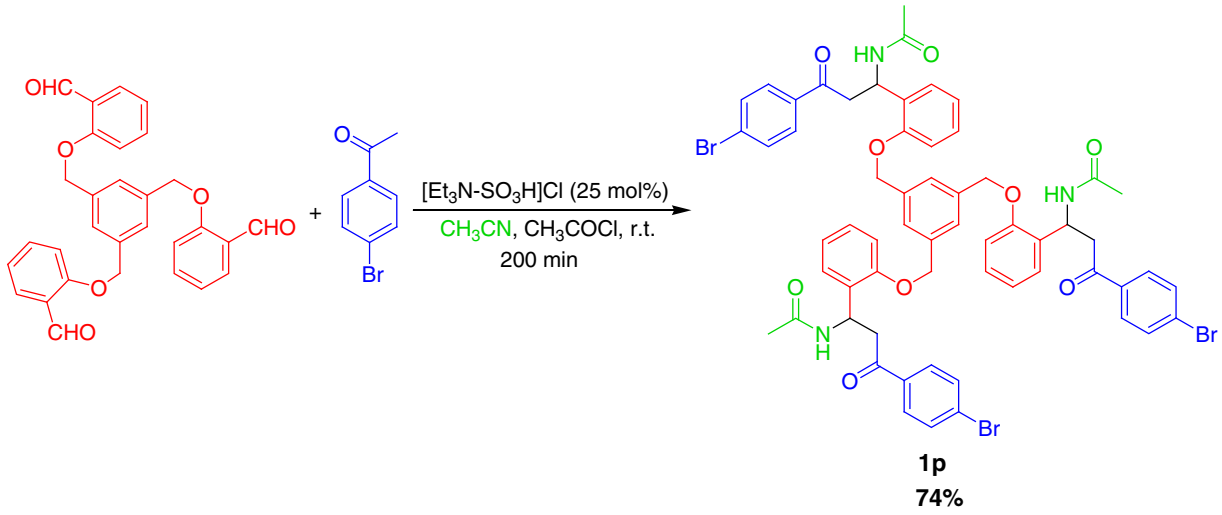
Furthermore, more recently, we [17–20] and also Ghaffari Khaligh [21] showed that when 1-methylimidazole (1 equiv.) or imidazole (2 equiv.) is reacted with chlorosulfonic acid (1 equiv.), the nitrogen atoms of 1-methylimidazole or imidazole act as nucleophile (not base), and attack to the sulfur of $ClSO_3H$ to give 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} or 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl}, correspondingly (Scheme 3). This subject also confirmed that the reaction of triethylamine (1 equiv.) with chlorosulfonic acid (1 equiv.) afforded $[Et_3N–SO_3H]Cl$, not $[Et_3N–H][ClSO_3]$.

Thermal gravimetric analysis (TGA) of $[Et_3N–SO_3H]Cl$ was also studied. The corresponding diagrams are shown in Fig. 3. The thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) diagrams of the catalyst showed weight losses in one step, and decomposition after about 290 °C.

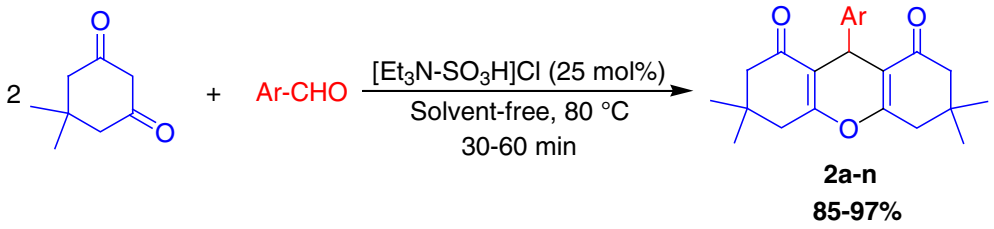
To explore the generality and applicability of the new catalyst, we studied its efficiency to catalyze three types of organic transformations under different conditions and temperatures, including the preparation of β-acetamido ketones in extremely mild (room temperature) and solution conditions, the synthesis of 1,8-dioxo-octahydroxanthenes under relatively mild (80 °C) and solvent-free conditions, and the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes under harsh (120 °C) and solvent-free conditions. Interestingly, $[Et_3N–SO_3H]Cl$ efficiently catalyzed the above reactions under the mentioned conditions to give the desired products in high to excellent yields and in relatively short reaction times.

3.2. Study of the efficiency of triehylamine-bonded sulfonic acid in the synthesis of β-acetamido ketones **1a–p**

Initially, as a model, the condensation of acetophenone (1 mmol) with benzaldehyde (1 mmol), acetonitrile (3 mL) and acetyl chloride (0.3 mL) was examined in the presence of different molar ratios of $[Et_3N–SO_3H]Cl$ at room temperature (Scheme 4). The results are summarized in Fig. 4. As Fig. 4 indicates, 15 mol% of the catalyst was sufficient to catalyze the reaction efficiently; in this case, the corresponding product was obtained in 95% yield within 70 min (Fig. 4, entry 5). No improvement in the reaction results was observed by increasing the amount of $[Et_3N–SO_3H]Cl$ (Fig. 4, entry 6).



Scheme 5. The synthesis of complex compound **1p** using [Et_3N–SO_3H]Cl.



Scheme 6. The condensation of dimedone with aldehydes leading to 1,8-dioxo-octahydroxanthenes using [Et_3N–SO_3H]Cl.

To assess the efficiency and the scope of [Et_3N–SO_3H]Cl in the preparation of β-acetamido ketones, different acetophenones were reacted with structurally and electronically diverse arylaldehydes, acetonitrile and acetyl chloride under the optimal reaction conditions; the respective results are displayed in Table 1. As it can be seen in Table 1, our new catalyst was general and efficient; both acetophenone derivatives and arylaldehydes bearing electron-withdrawing substituents, electron-releasing substituents and halogens on the aromatic ring gave the desired β-acetamido ketones in high to excellent yields (84–95%) and in relatively short reaction times (50–130 min) (Table 1, compounds **1a–k**). [Et_3N–SO_3H]Cl also catalyzed the reaction efficiently when 2-naphthaldehyde instead of benzaldehyde or its derivatives was applied; in these cases, the products were obtained in 85–90% yields after 80–110 min (Table 1, compounds **1l–o**).

Interestingly, the condensation of *p*-bromoacetophenone (3.3 mmol) with a tris(aldehyde) (1 mmol), acetonitrile (9 mL) and acetyl chloride (0.9 mL) in the presence of [Et_3N–SO_3H]Cl (25 mol%) at room temperature afforded tris(β-acetamido ketone) **1p** in 74% yield within 200 min (Scheme 5).

3.3. Study of the efficacy of [Et_3N–SO_3H]Cl in the synthesis of 1,8-dioxo-octahydroxanthenes **2a–n**

Considering the high importance of xanthene derivatives [47–56], in the next step, we examined the efficiency of ionic liquid [Et_3N–SO_3H]Cl in the synthesis of 1,8-dioxo-octahydroxanthenes. To obtain the optimized reaction conditions for the synthesis of this class of compounds, the solvent-free reaction of dimedone (2 mmol) with benzaldehyde (1 mmol) was selected as a model reaction (Scheme 6), and effect of different molar ratios of [Et_3N–SO_3H]Cl and temperature on the reaction was studied (Fig. 5). As it is clear from Fig. 5, higher yield of the product and shorter reaction time were obtained when the reaction was carried our using 25 mol% of the catalyst at 80 °C (Fig. 5, entry 3). Increment the amount of [Et_3N–SO_3H]Cl or the reaction time did not improve the yield (Fig. 5, entries 4 and 7).

After optimization of the reaction conditions, dimedone was reacted with different aldehydes (including aromatic aldehydes possessing electron-withdrawing substituents, electron-donating substituents and halogens on their aromatic ring as well as cinnamaldehyde). The results are reported in Table 2. As it is shown in Table 2, triethylamine-bonded sulfonic acid efficiently catalyzed the reactions to furnish the respective 1,8-dioxo-octahydroxanthenes in high to excellent yields (85–97%) and

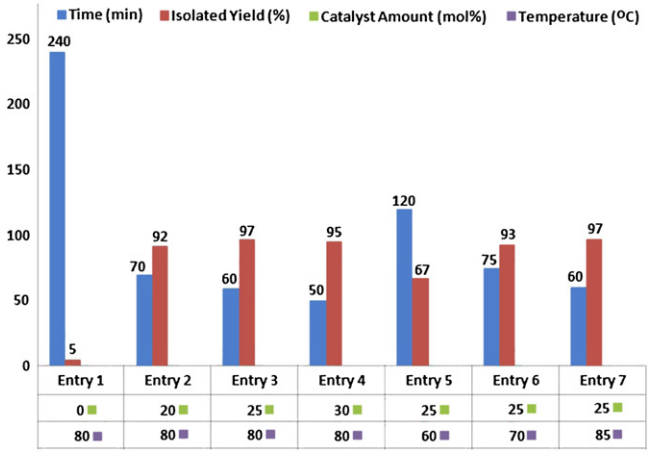
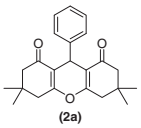
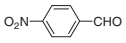
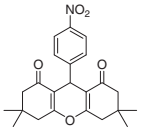
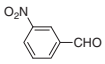
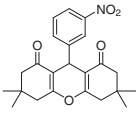
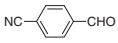
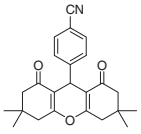
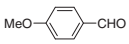
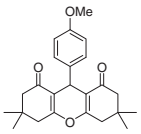
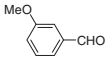
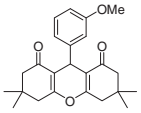
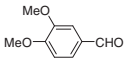
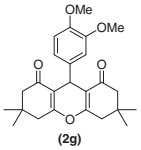
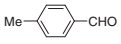
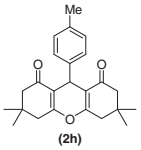
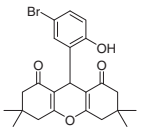
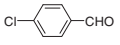
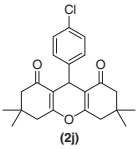
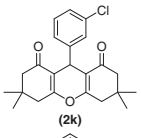
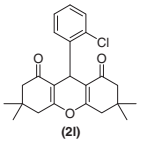
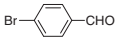
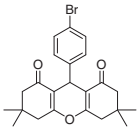
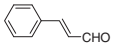
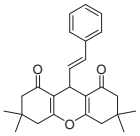


Fig. 5. The solvent-free reaction of dimedone (2 mmol) with benzaldehyde (1 mmol) using different molar ratios of [Et_3N–SO_3H]Cl at range of 60–85 °C.

Table 2
The condensation of dimedone and aldehydes leading to 1,8-dioxo-octahydroxanthenes using $[Et_3N–SO_3H]Cl$ at 80 °C in the absence of solvent.

Aldehyde	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
	 (2a)	60	97	199–201 (201–203) [64]
	 (2b)	35	97	224–226 (228–230) [59]
	 (2c)	40	97	164–166 (168–170) [60]
	 (2d)	40	89	220–222 (217–218) [58]
	 (2e)	55	90	243–245 (248–250) [59]
	 (2f)	55	92	161–163 (161–162) [58]
	 (2g)	45	93	178–180 (175–176) [58]
	 (2h)	50	93	216–218 (219–221) [64]
	 (2i)	60	85	250–252
	 (2j)	40	93	229–231 (230–232) [64]
	 (2k)	40	95	186–187 (183–185) [58]
	 (2l)	30	92	223–225 (226–227) [58]
	 (2m)	40	91	242–244 (240–242) [64]
	 (2n)	60	85	172–174 (177–178) [60]

[a] Isolated yield.

in short reaction times (30–60). Thus, the novel catalyst was general and effective in the preparation of 1,8-dioxo-octahydroxanthene derivatives.

3.4. Study of the efficiency of the catalyst in the preparation of 14-aryl-14H-dibenzo[a,j]xanthenes **3a–j**

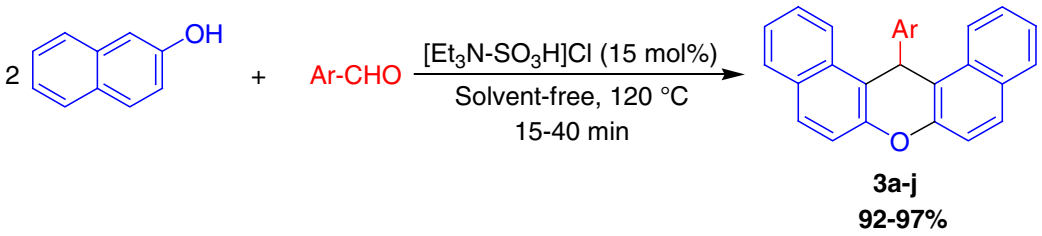
After the successful application of $[Et_3N–SO_3H]Cl$ in the synthesis of β-acetamido ketones and 1,8-dioxo-octahydroxanthenes, we decided to test its efficacy in the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes from β-naphthol and aldehydes (Scheme 7). For this purpose, as a model, the condensation of β-naphthol (2 mmol) with benzaldehyde (1 mmol) was examined using different amounts of the catalyst at range of 100–130 °C under solvent-free conditions (Fig. 6). As Fig. 6 shows, the best results were obtained when the reaction was performed in the presence of 15 mol% of $[Et_3N–SO_3H]Cl$ at 120 °C (Fig. 6, entry 3). Moreover, when the reaction was carried out using the catalyst amount more than 15 mol% or at temperature higher that 120 °C, the results were not considerably modified (Fig. 6, entries 4 and 7).

Under the optimized reaction conditions, β-naphthol was condensed with different aromatic aldehydes (including aldehydes bearing electron-withdrawing substituents, electron-releasing substituents and halogens on their aromatic ring); the corresponding results are summarized in Table 3. As it can be seen in Table 3, $[Et_3N–SO_3H]Cl$ was highly efficient and general in the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes; all reactions proceeded efficiently and the desired products were produced in high yields (92–97%) and short reaction times (15–40 min).

Considering the high effectiveness of our novel catalyst {$[Et_3N–SO_3H]Cl$} in the synthesis of β-acetamido ketones 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes as important organic compounds, we anticipate that it can be applied as a highly efficient catalyst in organic reactions which need the use of acidic catalysts to speed up.

3.5. Regenerating and reusing the catalyst (Scheme 8)

As previously shown, triethylamine-bonded sulfonic acid was highly efficient and general for the synthesis of three important classes of biologically interesting organic compounds including β-acetamido ketones 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes. To raise the catalyst worth, recoverability (or regenerability) and reusability of it was studied. For this purpose, the reaction of β-naphthol with benzaldehyde using $[Et_3N–SO_3H]Cl$ was carried out several times, and the reaction mixtures were combined. Afterward, H_2O was added to the combined reaction mixtures, stirred for 3 min, and filtered (the catalyst is soluble in H_2O; however, the reaction mixture is not soluble in H_2O). The H_2O of the filtrate (containing the catalyst) was evaporated, and the liquid residue was triturated with *t*-butylmethyl ether (3 times) and dried under powerful vacuum at 90 °C; in this case, a viscous pale yellow oil was obtained. To confirm that the viscous oil is pure [Et_3N–



Scheme 7. The reaction of β-naphthol with arylaldehydes to produce 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes using [Et_3N–SO_3H]Cl.

SO_3H]Cl, we run ^1H NMR spectrum of it. The spectrum showed that the recovered catalyst is not pure; we thought that few amount of [Et_3N–SO_3H]Cl hydrolyzes by H_2O to give [Et_3NH]Cl and H_2SO_4. Thus, we decided to regenerate the catalyst. For this purpose, after the addition of H_2O to the reaction mixture, stirring and filtration, the filtrate (containing the catalyst) was basified by NaOH; in these conditions, [Et_3N–SO_3H]Cl was completely converted to Et_3N and Na_2SO_4. Then, the solution was extracted with CH_2Cl_2, washed with H_2O and dried over Na_2SO_4. The recovered NEt_3 in CH_2Cl_2 was reacted with chlorosulfonic acid according to the mentioned procedure to give [Et_3N–SO_3H]Cl. The catalytic activity of the reproduced catalyst was the same as the first one. The regenerate and reuse cycle of [Et_3N–SO_3H]Cl is summarized in Scheme 8.

4. Conclusions

In summary, we have introduced Brønsted acidic ionic liquid [Et_3N–SO_3H]Cl as a novel, highly efficient, general, homogeneous and green catalyst for organic transformations. For example, in this work, the synthesis of β-acetamido ketones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes efficiently catalyzed by this ionic liquid. The promising points for the presented protocols are efficiency, generality, high yields, short reaction times, cleaner reaction profile, simplicity, low cost, ease of preparation and regeneration of the catalyst, and compliance with the green chemistry protocols (in the case of the xanthene derivatives).

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.molliq.2011.12.012.

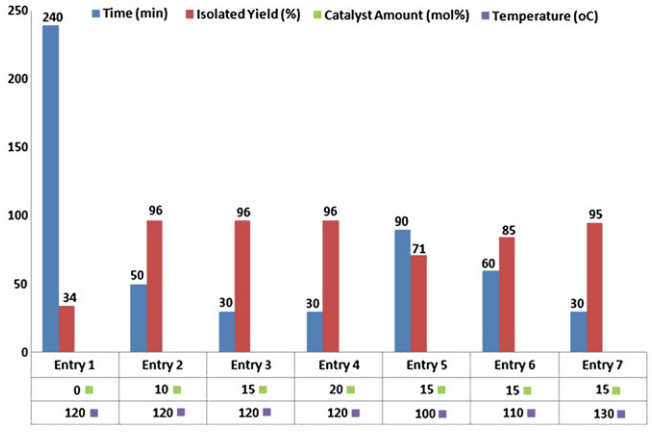
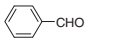
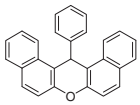
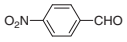
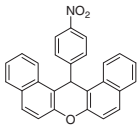
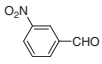
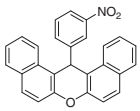
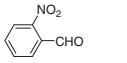
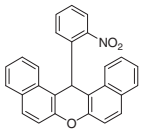
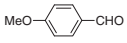
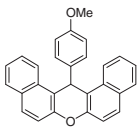
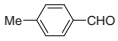
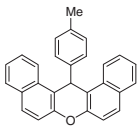
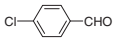
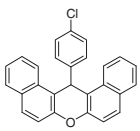
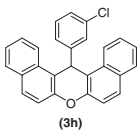
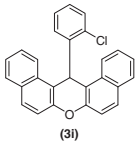
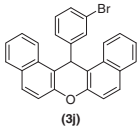
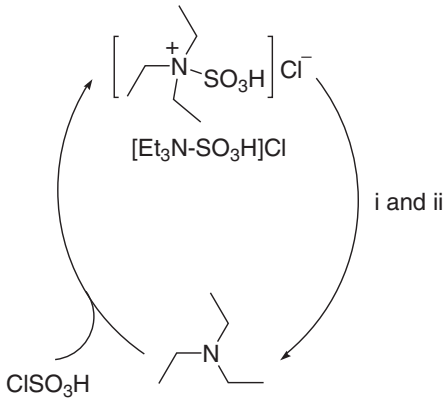


Fig. 6. Effect of amount of the catalyst and temperature on the condensation of β-naphthol (2 mmol) with benzaldehyde (1 mmol) under solvent-free conditions.

Table 3
The [Et_3N–SO_3H]Cl-promoted synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes from β-naphthol and aromatic aldehydes under solvent-free conditions at 120 °C.

Aldehyde	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
	 (3a)	30	96	186–188 (184–185) [70]
	 (3b)	25	97	312–314 (311–312) [68]
	 (3c)	30	97	215–217 (213) [68]
	 (3d)	30	95	212–214 (214–215) [70]
	 (3e)	30	92	200–202 (203–205) [69]
	 (3f)	40	95	225–227 (227–229) [70]
	 (3g)	20	97	284–286 (289–290) [69]
	 (3h)	20	94	207–209 (209–211) [70]
	 (3i)	20	95	209–211 (214–216) [70]
	 (3j)	15	96	186–188 (190–191) [70]

[a] Isolated yield.



Scheme 8. The regenerate and reuse cycle of $[Et_3N–SO_3H]Cl$.

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