

# 1-Methylimidazolium trifluoroacetate ([Hmim]TFA): An efficient reusable acidic ionic liquid for the synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines

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## Abstract

Brønsted acidic ionic liquid, 1-methylimidazolium trifluoroacetate ([Hmim]TFA) catalyzed synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines in excellent yields and short period of times at 80 °C. Anions effects of the ionic liquid on the reaction rate have been investigated. The ionic liquid was easily separated from the reaction mixture by water extraction and was recycled four times without any loss in activity.

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## 1. Introduction

Ionic liquids (ILs) are now well known as salts with melting points below 100 °C, and typically have broad liquid ranges, low vapor pressures, and may be both non-coordinating, but highly polar. They are receiving considerable global attention because they offer a unique environment for chemistry, biocatalysis, separation science, material synthesis, and electrochemistry [1]. The implementation of task specific ionic liquids (TSILs) further enhances the versatility of classical ionic liquids where both reagent and medium are coupled [2–5]. The union of reagent with medium has been found to be a viable alternative approach toward modern synthetic chemistry especially when considering the growing environmental demands being placed on chemical processes.

Xanthene derivatives are parent compounds of a large number of naturally occurring, as well as synthetic deriva-

tives, and occupy a prominent position in medicinal chemistry [6–8]. In particular, xanthenediones constitute a structural unit in a number of natural products [9], and have been used as versatile synthons because of the inherent reactivity of the inbuilt pyran ring [10]. The synthesis of xanthenediones usually condenses appropriate active methylene carbonyl compounds with aldehydes catalyzed by sulfuric acid or hydrochloric acid [11]. Recently, Van Vranken et al. described two-step synthesis of 9-aryl-6-hydroxy-3*H*-xanthen-3-one fluorophores by condensation of aryl aldehydes and fluororesorcinol [12]. Singh et al. [13] reported another method for the preparation of xanthenediones through carbon transfer reactions of 1,3-oxazinanes and oxazolidines with carbon nucleophiles. Regarding the availability and the economic viability of starting materials, the first method is far superior to the second method. Therefore, many alternative catalysts, such as *p*-toluenesulfonic acid [14], *p*-dodecylbenzenesulphonic acid [15], InCl<sub>3</sub>/ionic liquid [16], Fe<sup>3+</sup>-montmorillonite [17], NaHSO<sub>4</sub>-SiO<sub>2</sub> or silica chloride [18], amberlyst-15 [19], and silica sulfuric acid [20] have been reported for the synthesis xanthenedione derivatives. However, some of them often involve the use of expensive reagents, hazard

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organic solvents, and tedious workup. Hence, a more realistic catalyzed condensation between active methylene carbonyl compound and aldehyde is needed for contemporary chemical synthesis with less waste and more facile isolation of products, perhaps with reuse of the catalysts as well.

## 2. Experimental

### 2.1. General

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz, respectively. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer.

### 2.2. Synthesis of ionic liquid

The synthesis of ionic liquid has been carried out using a similar method reported in the literature [21]. 1-Methylimidazole was placed in a two-necked flask, which was equipped with a magnetic stirrer and cooled in an ice-water bath. A small amount of water was added and then the trifluoroacetic acid (1 equiv.) was added slowly with stirring. The reaction mixture was stirred for an additional period of 2 h. Then water in the crude product was evaporated with a rotary evaporator at 70 °C and thus a colorless liquid product was obtained. The ionic liquid was formed quantitatively and in high purity as assessed by NMR.

### 2.3. General procedure for the synthesis of 1,8-dioxo-octahydroanthene derivatives

To a mixture of an aromatic aldehyde (1 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) in a round bottom flask [Hmim]TFA (100 mg) was added. The mixture was heated at 80 °C and the reaction was monitored by TLC. After completion of the reaction, water added to the mixture and filtered. The solid residue was recrystallized from ethanol.

### 2.4. General procedure for the synthesis of 1,8-dioxo-decahydroacridine derivatives

A primary amine (1.2 mmol) was added to the mixture of an aromatic aldehyde (1 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) in [Hmim]TFA (100 mg). The reaction was conducted under the conditions as above. After completion of the reaction, water added to the mixture and filtered. The solid residue was recrystallized from ethanol.

## 3. Results and discussion

In our continued interest in the development of a highly expedient methodology [22–27] for the synthesis of fine chemicals and heterocyclic compounds of biological importance, we report here the synthesis of 1,8-dioxo-octahydroanthenes, and 1,8-dioxo-decahydroacridines in the presence of 1-methylimidazolium trifluoroacetate ([Hmim]TFA) as an acidic IL.

We first studied a reaction between 5,5-dimethyl-1,3-cyclohexanedione (**1**) and 4-chlorobenzaldehyde by screening the reaction conditions. In order to determine the optimum conditions, we examined the influence of the reaction temperature, the reaction time, the amounts of IL, and the type IL (Table 1). In all reaction the conditions were optimized for a 100% conversion. It could be seen that the best result was obtained with 0.1 g of [Hmim]TFA at 80 °C (Table 1, entry 7).

After optimizing the conditions, we next examined the generality of these conditions to other substrates using several aromatic aldehydes (Scheme 1). The results are summarized in Table 2. It could be seen that [Hmim]TFA as environmentally benign acidic IL catalyzed the condensation of dimedone, and a wide range of aromatic aldehydes at 80 °C. As indicated in Table 2, in all cases the reaction gives the products in good yields and prevents problems which many associate with solvent use such as cost, handling, safety and pollution.

Table 1  
Optimization of the reaction condition

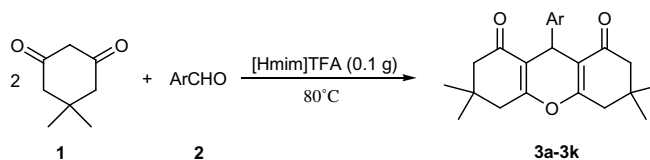
Entry <sup>a</sup>	IL <sup>b</sup>	Temperature (°C)	Yield (%) <sup>c</sup>	Time (h)
1	[Hmim]TFA	25	Trace	12
2	[Hmim]TFA	35	Trace	12
3	[Hmim]TFA	45	15	12
4	[Hmim]TFA	50	40	12
5	[Hmim]TFA	60	70	10
6	[Hmim]TFA	70	75	6
7	[Hmim]TFA	80	90	3
8	[Hmim]TFA	90	91	3
9	[Hmim]TFA	100	90	2.5
10	[Hmim]HClO <sub>4</sub>	80	50	3
11	[Hmim]HSO <sub>4</sub>	80	55	3
12	[Hmim]BF <sub>4</sub>	80	70	3
13	– <sup>d</sup>	80	40	12

<sup>a</sup> In all reaction the conditions were optimized for a 100% conversion.

<sup>b</sup> The reactions were run in the presence of 0.1 g of IL.

<sup>c</sup> Isolated yield.

<sup>d</sup> The reaction was run under neat condition.



Scheme 1.

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