



## Short Communication

# Efficient production of 2-amino-4*H*-chromenes and 14-aryl-14*H*-dibenzo[*a, j*]xanthenes catalyzed by *N, N*-diethyl-*N*-sulfoethanaminium hydrogen sulfate

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### KEYWORDS

Acidic ionic liquid

*N, N*-Diethyl-*N*-sulfoethanaminium  
hydrogen sulfate {[Et<sub>3</sub>N-SO<sub>3</sub>H]HSO<sub>4</sub>}

2-Amino-4*H*-chromene

14-Aryl-14*H*-dibenzo[*a, j*]xanthene

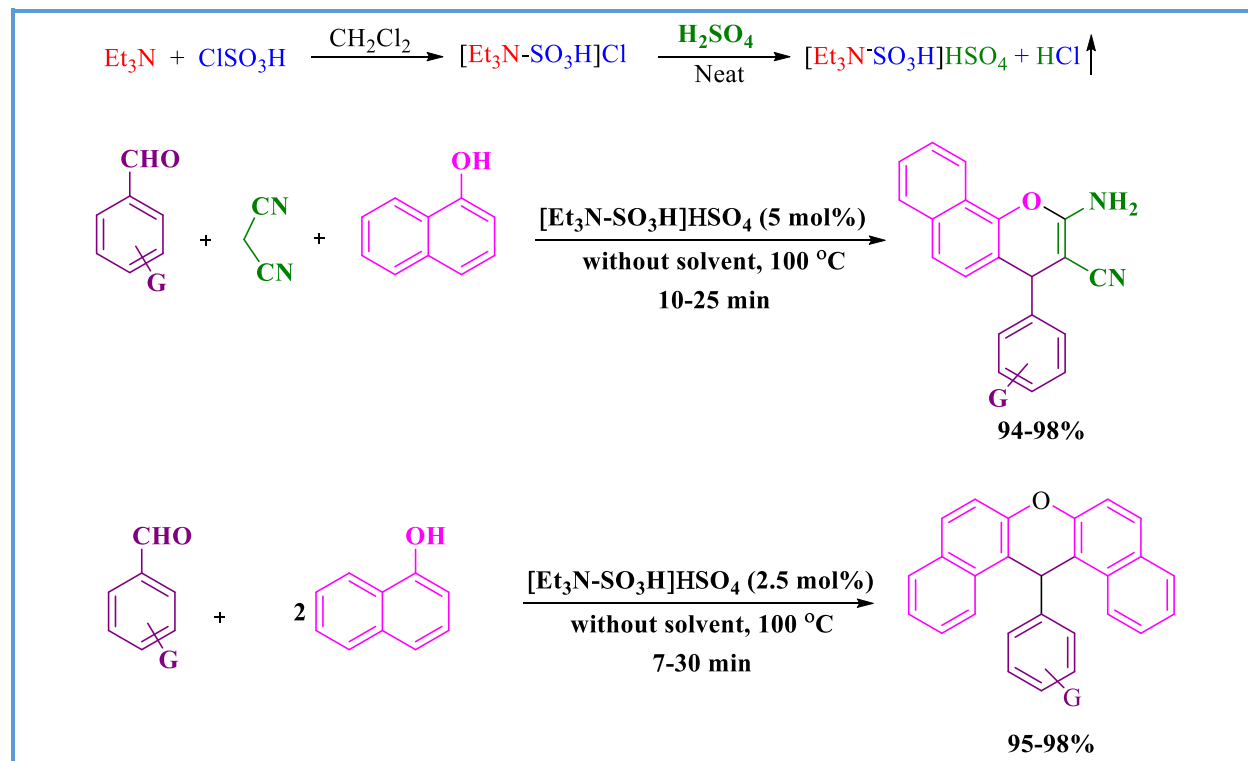
Solvent-free

### ABSTRACT

In this study, acidic ionic liquid *N, N*-diethyl-*N*-sulfoethanaminium hydrogen sulfate {[Et<sub>3</sub>N-SO<sub>3</sub>H]HSO<sub>4</sub>} was utilized to promote two classes of useful organic transformations under solvent-free conditions including, *i*) the condensation of arylaldehydes with malononitrile and 1-naphthol, leading to 2-amino-4*H*-chromenes, and *ii*) the condensation reaction of arylaldehydes with 2-naphthol to give 14-aryl-14*H*-dibenzo[*a, j*]xanthenes. The ionic liquid efficiently catalyzed the reactions, and the products were obtained in excellent yields (94-98%) within short reaction times (8-30 min).

## Graphical Abstract

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## Introduction

Currently, ionic liquids (ILs) are receiving considerable global attention as solvent, reagent, and catalyst in organic synthesis. These extensive applications of ILs are attributed to their unique properties including, low vapor pressure, non-flammability, wide liquid-state temperature range, high thermal and chemical stability, favorable solvating capability, large electrochemical window, and ability to catalyze different kinds of organic reactions. In particular, acidic ILs possess useful characteristics of solid acids and mineral liquid acids, and have been designed to replace conventional mineral liquid acids like sulfuric acid and hydrochloric acid to catalyze chemical transformations [1–12].

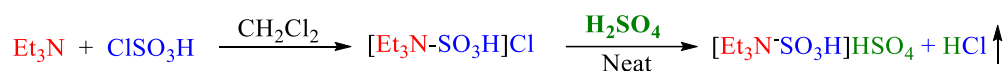
The reaction of arylaldehydes with malononitrile and 1-naphthol has been utilized for the preparation of 2-amino-4*H*-chromenes; some acidic and basic catalysts have been applied for this reaction [13–20]. Some

biological activities of this class of chromene derivatives include antimicrobial [21], antitumor [22], antiviral [23], and sex pheromone [24] properties. They have also been employed as potent biodegradable agrochemicals [25], cosmetics, and pigments [26]. Condensation of the arylaldehydes with 2-naphthol, using Bronsted or Lewis acidic catalysts has been applied as the most useful protocol for synthesis of the 14-aryl-14*H*-dibenzo[*a*, *j*]xanthenes as an important class of benzoxanthenes [27–35]. Xanthene derivatives, especially benzoxanthenes are of importance since they have various biological activities such as antibacterial [36], anti-cancer [37], and anti-inflammatory [38] properties. Furthermore, some other benzoxanthenes have found applications in industries, such as fluorescent materials for visualization of biomolecules [39], and as dyes in laser technology [40].

In the presented work, we evaluated the applications of the *N*, *N*-diethyl-*N*-

sulfoethanaminium hydrogen sulfate {[Et<sub>3</sub>N-SO<sub>3</sub>H]HSO<sub>4</sub>} as a homogeneous and highly effective ionic-liquid catalyst for the following organic transformations: (i) the solvent-free reaction of arylaldehydes with malononitrile and 1-naphthol to afford 2-amino-4*H*-chromenes, and (ii) the solventless reaction of arylaldehydes with 2-naphthol to produce 14-aryl-14*H*-dibenzo[*a, j*]xanthenes.

### Materials and methods



**Scheme 1.** The production of [Et<sub>3</sub>N-SO<sub>3</sub>H]HSO<sub>4</sub>

### Experimental

#### General procedure for the preparation of 2-amino-4*H*-chromenes

A mixture of aldehyde (1 mmol), malononitrile (1 mmol, 0.066 g), 1-naphthol (1 mmol, 0.144 g) and [Et<sub>3</sub>N-SO<sub>3</sub>H]HSO<sub>4</sub> (0.05 mmol, 0.014 g) (in a test tube) was initially stirred magnetically at 110 °C, and after solidification of the reaction mixture, it was strongly stirred by a small rod at the same temperature. After completion of the transformation, as indicated by TLC {eluted by *n*-hexane/ethyl acetate (3/1)}, and cooling the reaction mixture to room temperature, the resulted solid was powdered. Then, the water (2 mL) was added to it, stirred for 1 min, and filtered. The resulting precipitate (crude product) was recrystallized from EtOH (96%) to afford the pure product.

#### General procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a, j*]xanthenes

A mixture of arylaldehyde (1 mmol), 2-naphthol (2 mmol, 0.288 g) and [Et<sub>3</sub>N-

All chemicals were purchased from Merck or Fluka Chemical Companies. [Et<sub>3</sub>N-SO<sub>3</sub>H]HSO<sub>4</sub> was prepared according to the literature [9] (Scheme 1). The known products were identified by comparing their melting points and spectral data with the reported data. Progress of the reactions was monitored by thin layer chromatography (TLC). A Büchi B-545 instrument was used to measure the melting points. The <sup>1</sup>H NMR (250 or 300 MHz) and <sup>13</sup>C NMR (62.5 or 75) were recorded on a Bruker Avance DPX, FT-NMR spectrometers.

SO<sub>3</sub>H]HSO<sub>4</sub> (0.025 mmol, 0.007 g,) in a test tube was firstly stirred magnetically at 120 °C. After solidification of the reaction mixture, it was stirred with a small rod at same temperature. After the reaction was completed, as indicated by TLC {eluted by *n*-hexane/ethyl acetate (4/1)}, it was cooled down to room temperature, and the resulted solid was powdered, water (2 mL) was added to it, stirred for 1 min, and filtered. The resulting precipitate (crude product) was recrystallized from EtOH (96%) to afford the pure product.

**Note:** Selected spectroscopic data of the synthesized 2-amino-4*H*-chromenes and 14-aryl-14*H*-dibenzo[*a, j*]xanthenes were given in supplementary materials.

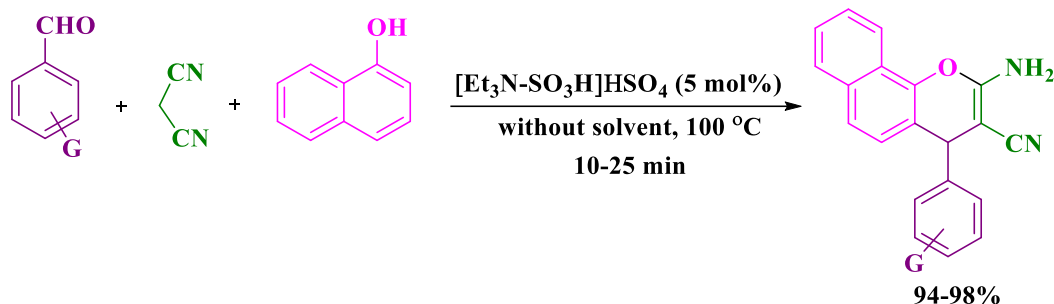
### Results and Discussion

#### Preparation of 2-amino-4*H*-chromenes

At first, as a model reaction, the solventless condensation of *m*-nitrobenzaldehyde (1 mmol) with malononitrile (1 mmol) and 1-naphthol (1 mmol) (Scheme 2) was studied using different amounts of [Et<sub>3</sub>N-SO<sub>3</sub>H]HSO<sub>4</sub> at various

temperatures. The related results are summarized in Table 1. As seen in Table 1, the best results were observed when 5 mol% of the

ionic liquid was used at 110 °C (entry 2). Increasing the catalyst amount and the temperature did not give better results.



**Scheme 2.** The production of 2-amino-4H-chromenes using  $[\text{Et}_3\text{N-SO}_3\text{H}]\text{HSO}_4$

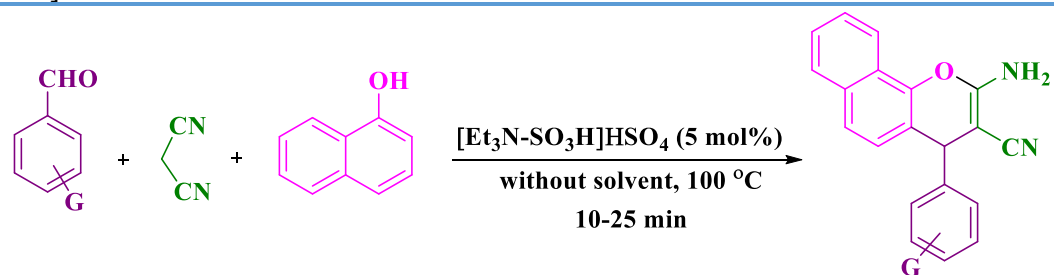
**Table 1.** The reaction of *m*-nitrobenzaldehyde with malononitrile and 1-naphthol using  $[\text{Et}_3\text{N-SO}_3\text{H}]\text{HSO}_4$  at different temperatures

Entry	Mol%	Temp. (°C)	Time (min)	Yield <sup>a</sup> (%)
1	2.5	110	40	71
2	5	110	10	98
3	7.5	110	10	98
4	5	100	15	90
5	5	115	10	98

<sup>a</sup> Isolated yield

After the reaction was optimized in terms of the catalyst amount and temperature, various arylaldehydes were reacted with malononitrile and 1-naphthol at the presence of  $[\text{Et}_3\text{N-SO}_3\text{H}]\text{HSO}_4$  (Table 2). As seen in Table 2,  $[\text{Et}_3\text{N-SO}_3\text{H}]\text{HSO}_4$  was a highly efficient catalyst for the synthesis of 2-amino-4H-chromenes; because all arylaldehydes (bearing electron-withdrawing, halogen and electron-releasing substituents) afforded the respective of 2-amino-4H-chromene derivatives in excellent yields and in short reaction times.

**Table 2.** The solventless reaction of arylaldehydes with malononitrile and 1-naphthol catalyzed by  $[\text{Et}_3\text{N-SO}_3\text{H}]\text{HSO}_4$



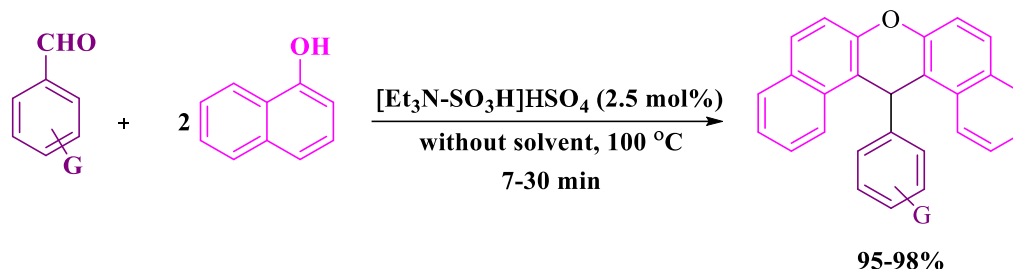
Entry	G	Time (min)	Yield <sup>a</sup> (%)	M.p. °C (Lit.)
1	H	10	95	212-214 (210-211) [20]
2	<i>m</i> -NO <sub>2</sub>	10	98	214-216 (212-214) [20]
3	<i>p</i> -NO <sub>2</sub>	15	98	229-231 (231-234) [14]
4	<i>p</i> -Cl	10	97	228-229 (230-232) [14]
5	<i>o</i> -Cl	15	94	238-240 (236-237) [20]
6	<i>p</i> -CH <sub>3</sub> O	25	96	189-191 (191) [17]

<sup>a</sup> Isolated yield

Producing 14-aryl-14H-dibenzo[*a, j*]xanthenes

In another study, the catalytic activity of  $[\text{Et}_3\text{N-SO}_3\text{H}]\text{HSO}_4$  was tested on the reaction of aromatic aldehydes with 2-naphthol to produce 14-aryl-14H-dibenzo[*a, j*] xanthenes. To optimize the reaction conditions, the reaction of *m*-nitrobenzaldehyde (1 mmol) with 2-

naphthol (1 mmol) (Scheme 3), as a model reaction, was studied in the presence of different molar ratios of the catalyst at range of 90-105 °C. The results are shown in Table 3. As Table 3 shows, higher yield and shorter reaction time were observed when 2.5 mol% of the ionic liquid was utilized at 100 °C.



**Scheme 3.** The synthesis of 14-aryl-14H-dibenzo[*a, j*]xanthenes

**Table 3.** Effect of the catalyst amount and temperature on the reaction of *m*-nitrobenzaldehyde with 2-naphthol

Entry	Mol%	Temp. (°C)	Time (min)	Yield <sup>a</sup> (%)
1	1	100	20	97
2	2.5	100	7	98
3	5	100	7	98
4	2.5	90	22	96
5	2.5	105	7	98

<sup>a</sup> Isolated yield

The efficiency and the generality of the catalyst was evaluated by the reaction of different arylaldehydes (possessing electron-withdrawing substituents, halogens as well as electron-donating substituents) with 2-naphthol. The results are summarized in Table 4. As it can be seen in Table 4, all the reactions were achieved efficiently, and afforded the corresponding 14-aryl-14H-dibenzo[*a, j*] xanthenes in excellent yields in short reaction times. Thus,  $[\text{Et}_3\text{N-SO}_3\text{H}]\text{HSO}_4$  was also efficient and general for this reaction.

**Table 4.** The solvent-free preparation of 14-aryl-14H-dibenzo[*a, j*]xanthenes from aromatic aldehydes and 2-naphthol catalyzed by  $[\text{Et}_3\text{N-SO}_3\text{H}]\text{HSO}_4$

Entry	G	Time (min)	Yield <sup>a</sup> (%)	M.p. °C (Lit.)
1	H	8	95	187-189 (185-187) [33]
2	<i>m</i> -NO <sub>2</sub>	7	98	215-217 (214-216) [33]
3	<i>p</i> -NO <sub>2</sub>	11	98	312-314 (311-312) [30]
4	<i>p</i> -Cl	10	98	291-293 (289-290) [30]
5	<i>m</i> -Cl	12	98	204-206 (207-209) [35]

6	<i>o</i> -Cl	30	97	216-218 (214-216) [30]
7	<i>m</i> -Br	12	98	192-194 (190-191) [30]
8	<i>p</i> -CH <sub>3</sub>	10	97	226-228 (227-229) [35]

<sup>a</sup> Isolated yield

## Conclusions

In this work, we have applied an acidic ionic liquid namely *N,N*-diethyl-*N*-sulfoethanaminium hydrogen sulfate as a highly efficient catalyst to promote two useful organic reactions, i.e. the preparation of 2-amino-4*H*-chromenes from arylaldehydes, malononitrile and 1-naphthol, and the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes from arylaldehydes and 2-naphthol. The promising points for the presented methodology were found to be high yields and efficiency, short reaction times, cleaner reaction profile, simplicity, low cost of the reactants for the catalyst synthesis, ease of the catalyst preparation, and good agreement with the green chemistry protocols.

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## Disclosure Statement

No potential conflict of interest was reported by the authors.

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