



Task specific dicationic acidic ionic liquids catalyzed efficient and rapid synthesis of benzoxanthenones derivatives



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ABSTRACT

A rapid and straightforward approach to the synthesis of dibenzo[a,j]xanthenes and 1,8-dioxo-octahydroxanthenes using task specific dicationic acidic ionic liquids as a highly efficient and readily available catalyst under solvent-free condition have been developed. A series of Brønsted–Lewis acidic ionic liquid were prepared and investigated their catalytic activity for synthesis of various xanthenes derivatives from aldehydes and 2-naphthol or dimedone. The ease of the product separation without organic solvent and column chromatography and reusability of acidic ionic liquid catalyst makes this method economically affordable for large-scale synthesis.

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1. Introduction

Multicomponent reactions (MCRs) under catalytic solvent-free conditions not only a powerful tool in organic synthesis; they also represent an ideal protocol for the construction of different heterocycles and natural products [1]. Multicomponent reaction is a very significant tool for atom economic synthesis of highly valuable products with good to excellent yields from cheap and readily available starting materials in organic chemistry [2]. Furthermore, MCRs have to be a benefit of time saving, environmental friendly, cost-effectiveness and the important source of molecular diversity for academic and industrial synthetic chemists [3–6].

A new emerging type of greener solvents and catalysts that have received widespread attention as an eco-friendly reaction medium is ionic liquids (ILs) [7]. ILs are an emerging class of advanced materials due to their particular properties such as negligible vapor pressure, wide liquid range, excellent solubility, and good selectivity [8]. The unusual properties of ILs have made a variety of applications such as solvent, catalysts, gas adsorbents, and chromatography stationary phases in recent years [9–13]. Acidic ionic liquids; ionic liquids with acidic properties (Brønsted-type and Lewis-type) is an important ionic liquid derivatives that are replaced with the most common acids used in labs and in industry [14–18]. Furthermore, acidic ILs possesses the advantages of both liquid acid and solid acid catalysts such as water solubility, recyclable,

high acid density, easy separation, and reusability [19]. In this context, acidic ILs is now widely acknowledged as a new class of advanced acidic catalyst for many organic transformations [20].

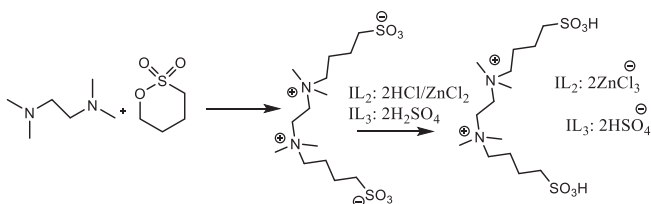
Benzoxanthenones and its derivatives have a great deal of importance due to their numerous biological activities, including their anti-bacterial and anti-inflammatory in medicinal chemistry and biology [21]. They are used as fluorescent compounds in laser technology and widely used as building blocks in dye chemistry [22]. The simplest and practical preparation of benzoxanthenones and its derivatives, involve the construction of the C–O bond via condensation reaction of carbonyl compounds with naphthol derivatives in the presence of acidic catalysts [23]. In light of their wide range of industrial applications, numerous protocols have been reported in the preparation of biologically important 14-aryl-14H -dibenzo[a,j]xanthenes [24–33] and 1,8-dioxo-octahydro-xanthene [34–38] using a variety of catalysts or promoter in the literature. However, the majority of acid catalysts are highly corrosive and are not easy to recover for reuse. Therefore, it is still necessary to develop green and reusable catalysts for environmentally benign synthesis of benzoxanthenone derivatives using simple starting materials.

2. Experimental

2.1. General

All starting materials and task specific dicationic acidic ionic liquids components such as aldehydes, dimedone, β -naphthols, H_2SO_4 , $ZnCl_2$,

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Scheme 1. Preparation of acidic ionic liquid.

tetramethylethylenediamine TMEDA and 1,4-butane sultone were commercially available. Melting points were determined on Buchi 535 melting point apparatus. ^1H and ^{13}C NMR spectra was recorded on 500 MHz NMR spectrometer using DMSO-d_6 as solvent. Chemical shifts were expressed in (ppm) downfield from TMS. All the reactions were monitored by thin layer chromatography (TLC) with UV light as detecting agents.

2.2. Acidic ionic liquid preparations

IL1 and IL4–IL8 were prepared according to our previous paper [39].

2.2.1. Preparation of IL3

Acidic ionic liquids (IL3) were synthesized by known methods reported on the literature [40] with little modification (Scheme 1). The obtained acidic ILs were characterized by ^1H NMR and FTIR spectrum the results were compared to the literature data. A 25 mL round-bottom flask with a magnet was vacuum dried and cooled under argon and charged with tetramethylethylenediamine TMEDA (14.9 mL, 100 mmol) and 1,4-butane sultone (30 mL, 300 mmol) and stirred under 80°C for 6 h until white zwitterion solid was obtained. This zwitterion salt was washed with ethyl acetate and dried under vacuum to obtain the pure zwitterion solid in a good yield (90%). Then two equimolar concentrated sulfuric acid (98%) was added dropwise to the zwitterion and the mixture was stirred magnetically for 10 h at 60°C to form the honey like viscous liquid. The resulting liquid was washed repeatedly with ethyl acetate and dried in a high vacuum at 120°C for 8 h until pure ionic liquid were obtained.

^1H NMR (500 MHz, D_2O): δ 1.74–1.76 (m, 4H), 1.90–1.92 (m, 4H), 2.93 (t, $J = 7.2$ Hz, 4H), 3.20 (s, 12H), 3.41 (t, $J = 8.1$ Hz, 4H), 3.85 (s, 4H), 4.48 (OH), FTIR KBr, cm^{-1} : 1050 and 930 ($-\text{SO}_3\text{H}$), 1160 (C–N), 3379 (O–H).

IL2 was synthesized according to the same procedure, only instead of H_2SO_4 , HCl and ZnCl_2 were added (Scheme 1).

2.3. Typical experimental procedure

To a mixture of aldehyde (0.5 mmol) and β -naphthol (1 mmol) or dimedone (1 mmol) was added acidic ionic liquid (1 mol%) and this reaction mixture were heated at 110°C with vigorously stirring for 10–40 min. After completion of the reaction, the mixtures were cooled to room temperature and washed with water to get the crude product. The crude product was recrystallized from ethanol to afford the pure product which required no further purification. All compounds were characterized as the basis of their spectroscopic data (NMR) and melting point by comparison with those reported on the literature.

2.3.1. Selected spectral data

3a: ^1H NMR (500 MHz, DMSO-d_6): δ = 8.20 (d, $J = 7.8$ Hz, 2H), 7.82–7.58 (m, 6H), 7.53–7.00 (m, 7H), 6.32 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 147.9, 144.2, 130.9, 130.1, 127.9, 127.1.2, 126.8, 126.2, 125.8, 125.3, 124.7121.8, 116.4, 116.2, 39.8.

3c: ^1H NMR (500 MHz, DMSO-d_6): δ = 8.40 (d, $J = 7.8$ Hz, 2H), 7.72–6.71 (m, 14H), 6.12 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 157.9, 148.6, 136.4, 133.8, 130.9, 130.1, 129.4, 129.2, 127.2, 123.8, 123.2, 117.8, 117.1, 113.8, 53.8, 37.1.

3e: ^1H NMR (500 MHz, DMSO-d_6): δ = 8.39 (d, $J = 7.8$ Hz, 2H), 8.01–7.46 (m, 14H), 6.46 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 154.9, 146.8, 131.9, 130.8, 128.9, 128.1, 127.8, 127.1, 125.9, 125.3, 123.8, 118.7, 117.7, 116.9, 32.8.

5a: ^1H NMR (500 MHz, DMSO-d_6): δ = 7.24–7.11 (m, 5H), 4.40 (s, 1H), 2.42–2.6 (m, 8H), 1.01 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 196.2, 161.8, 136.1, 128.9, 127.8, 113.4, 53.8, 50.8, 48.7, 32.0, 31.8, 28.1, 25.6.

5b: ^1H NMR (500 MHz, DMSO-d_6): δ = 7.10 (d, $J = 7.2$ Hz, 2H), 6.82 (d, $J = 7.2$ Hz, 2H), 4.62 (s, 1H), 3.70 (s, 3H), 2.42–2.17 (m, 8H), 0.98–1.05 (m, 12H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 195.8, 160.9, 157.1, 128.6, 128.1, 113.8, 55.2, 50.2, 40.1, 37.4, 34.2, 31.9, 30.2, 27.5, 26.9.

Table 1
Optimization of reaction condition.

entry	IL (1 mol%)	Temp. ($^\circ\text{C}$)	Yields (%) ^a
1	IL1	110	45
2	IL2	110	93
3	IL3	110	95
4	IL4	110	90
5	IL5	110	75
6	IL6	110	64
7	IL7	110	81
8	IL8	25	72
9	IL3	40	20
10	IL3	60	58
11	IL3	80	82
12	IL3	100	90
13	–	25	00
14	–	110	28

^a Isolated yields.

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