Res Chem Intermed
DOI 10.1007/s11164-013-1043-1

Brønsted acidic ionic liquids catalyzed the preparation of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14 (13*H*)-tetraones and 3,4-dihydro-1*H*-benzo[*b*] xanthene-1,6,11(2*H*,12*H*)-triones

Hamid Reza Shaterian · Marziyeh Sedghipour · Ebrahim Mollashahi

Received: 13 December 2012 / Accepted: 11 January 2013

Abstract An environmentally green method for the synthesis of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone and 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-trione derivatives using Brønsted acidic ionic liquids, 3-methyl-1-sulfonic acid imidazolium chloride, 1-*H*-3-methyl-imidazolium hydrogensulfate, triethylamine-bonded sulfonic acid, and triethylammonium hydrogensulfate as reusable catalysts under thermal solvent-free conditions is described.

Keywords Ionic liquids · Aldehydes · Green chemistry · Domino reactions · Catalyst

Introduction

The development of cleaner technologies is a major subject in green chemistry [1]. Among the several aspects of green chemistry, the reduction or replacement of volatile organic solvents from the reaction medium is of greatest concern [2]. Ionic liquids (ILs) have received considerable interest as ecofriendly solvents, catalysts, and reagents in the context of green synthesis because of their unique properties such as low volatility, nonflammability, high thermal stability, negligible vapor pressure, and ability to dissolve a wide range of materials [3]. 2-Hydroxy-1, 4-naphthoquinone (HNQ; Lawsone) is the principal natural dye (1.0–1.4 %) in the leaves of henna, *Lawsonia inermis*. Henna has been used for more than 4,000 years, not only as a hair dye but also as a body paint and tattoo dye. Today, semi-permanent hair dyes containing henna as well as its pure dye ingredient, HNQ, are widely used and have become increasingly popular due to their natural origin [4, 5].

H. R. Shaterian (✉) · M. Sedghipour · E. Mollashahi
Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, PO Box 98135-674, Zahedan, Iran
e-mail: hrshaterian@chem.usb.ac.ir

Published online: 26 January 2013

Naphthoquinones have been the subject of much interest for a number of years due to their various biological activities, their industrial applications, and their potential as intermediates in the synthesis of heterocycles [6]. Xanthenes and benzoxanthenes have been reported to possess diverse biological and therapeutic properties, such as antibacterial [7], antiviral [8], and anti-inflammatory activity [9], as well as photodynamic therapy [10]. The other useful applications of this heterocycles are as dyes [11], fluorescent materials for visualization of biomolecules [12], and in laser technologies [13]. Some procedures have been developed for the synthesis of aryl-5*H*-dibenzo[*b,i*] xanthene-5,7,12,14 (13*H*)-tetraone and 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-triones such as *p*-toluene sulfonic acid (*p*-TSA) [14, 15], pyrrolidonium hydrogensulfate [16], (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogensulfate [16]. In continuation our research on ILs as catalysts [17]), we would like to report new applications of the ILs, 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}, 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^-, triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl}, and triethylammonium hydrogensulfate [Et_3NH][HSO_4] as catalysts (Fig. 1).

These reusable catalysts were applied in the present research for the preparation of (1) 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones from 2-hydroxy-1,4-naphthoquinone, and arylaldehydes, and (2) 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-triones from 2-hydroxy-1,4-naphthoquinone, arylaldehydes and dimedone under thermal solvent-free conditions (Scheme 1).

Experimental

Materials and methods

All reagents were purchased from Merck and Aldrich and used without further purification. 3-Methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} [18], 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim][HSO_4] [19], triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl} [20], and triethylammonium hydrogensulfate [Et_3NH][HSO_4] [21] were prepared according to the reported procedure. All yields refer to isolated products after purification. The NMR spectra were recorded on a

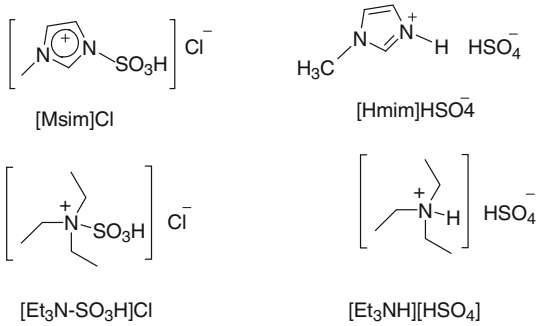
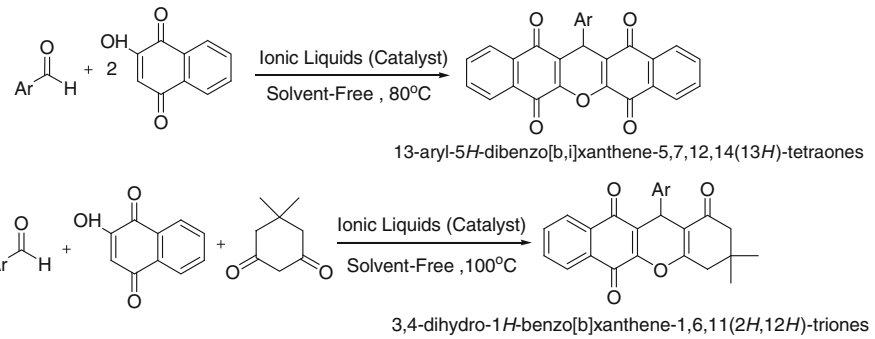


Fig. 1 The structures of 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}, 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^-, triethylamine-bonded sulfonic acid {[Et_3 N–SO_3H]Cl}, and triethylammonium hydrogensulfate [Et_3NH][HSO_4]



Ionic Liquids: 3-methyl-1-sulfonic acid imidazolium chloride,1-*H*-3-methyl-imidazolium hydrogensulfate, triethylamine-bonded sulfonic acid, triethylammonium hydrogensulfate

Scheme 1 The preparation of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones and 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-triones

Bruker Avance DPX 300 MHz instrument. The spectra were measured in DMSO-d_6 relative to TMS (0.00 ppm). Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. TLC was performed on silica–gel Poly Gram SIL G/UV 254 plates.

General procedure for preparation of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones

A mixture of aromatic aldehydes (1 mmol), 2-hydroxy-1,4-naphthoquinone (2 mmol) and ILs 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} (13 mol%, 0.13 mmol, 0.026 g), 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^- (11 mol%, 0.11 mmol, 0.018 g), triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl} (13 mol%, 0.13 mmol, 0.028 g) and triethylammonium hydrogensulfate [Et_3NH][HSO_4] (9 mol%, 0.09 mmol, 0.018 g) was heated at 80 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, water was added to the mixture and the solid crude product was filtered off. The pure product was obtained by recrystallization from the hot EtOH. For recycling the catalyst, after washing solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and IL was recovered and reused.

Selected spectroscopic data for two known products are given below.

13-Phenyl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (Table 2, entry 1)

Red powder, mp: 304–306 °C; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 5.09$ (1H, s, CH), 7.16–8.08 (13H, m, arom.) ppm; IR (KBr) (υ_{max}, cm^{-1}): 3,035, 1,660, 1,569.

13-(4-Bromophenyl)-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (Table 2, entry 5)

Yellow powder, mp: 334–336 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.17 (1H, s, CH), 7.43–8.16 (12H, m, arom.) ppm; IR (KBr) (υ_{max}, cm^{-1}): 3,088, 1,663, 1,657, 1,608.

General procedure for preparation of 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-triones

A mixture of aromatic aldehydes (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol) and dimedone (1 mmol) and ILs 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} (13 mol%, 0.13 mmol, 0.026 g), 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^- (12 mol%, 0.12 mmol, 0.020 g), triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl} (11 mol%, 0.11 mmol, 0.024 g) and triethylammonium hydrogensulfate [Et_3NH][HSO_4] (13 mol%, 0.13 mmol, 0.026 g) was heated at 100 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, water was added to the mixture and the catalyst was filtered off. The pure product was obtained by recrystallization from the hot EtOH. For recycling the catalyst, after completely washing the solid products with water, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and IL was recovered and reused.

Selected spectroscopic data for two known products are given below.

12-Phenyl-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-trione (Table 4, entry 1)

Orange powder, mp: 264–266 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.94 (3H, s, CH_3), 1.07 (3H, s, CH_3), 2.15 and 2.31 (2H, AB system, J = 16.2 Hz, CH_2), 2.67 (2H, s, CH_2), 4.88 (1H, s, CH), 7.10–7.15 (1H, m, H–Ar), 7.21–7.32 (2H, m, H–Ar), 7.43–7.46 (2H, m, H–Ar). 7.80–7.91 (3H, m, H–Ar) 7.99–8.07 (1H, m, H–Ar) ppm; IR (KBr) (υ_{max}, cm^{-1}): 2,926, 1,678, 1,606.

12-(4-Bromophenyl)-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*b*]xanthenes-1,6,11(2*H*,12*H*)-trione (Table 4, entry 5)

Yellow powder.; mp: 267–269 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.94 (3H, s, CH_3),1.07 (3H, s, CH_3), 2.15 and 2.31 (2H, AB system, J = 15.9 Hz, CH_2), 2.67 (2H, s, CH_2), 4.88 (1H, s, CH), 7.107.12(2H, d, J = 8.4 Hz, H–Ar), 7.42–7.45 (2H, m, H–Ar), 7.83–7.90 (3H, m, H–Ar), 8.03–8.06 (1H, m, H–Ar) ppm; IR (KBr) (υ_{max}, cm^{-1}): 2,957, 1,660, 1,616, 1,579.

Results and discussion

To choose optimum conditions, first we tried to prepare 13-(4-chlorophenyl)-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone from the reaction of 4-chlorobenzaldehyde (1 mmol) and 2-hydroxy-1,4-naphthoquinone (2 mmol) as a model under solvent-free conditions at different temperatures (60, 70, 80 °C) in the presence of A: 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} (29, 14, 20, 10, 13, 15 mmol%), B: 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^- (28, 10, 15, 9, 11, 14 mmol%), C: triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl} (29, 15, 20, 9, 13, 16 mmol%), D: triethylammonium hydrogensulfate [Et_3NH][HSO_4] (29, 12, 18, 5, 9, 13 mmol%). The amount of the catalysts with highest yield and short reaction time were chosen as A: 13, B: 11, C: 13, and D: 9 mol% under thermal (80 °C) solvent-free conditions (Table 1).

Using these optimized reaction conditions, the scope and efficiency of this procedure was explored for the synthesis of a wide variety of substituted 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones derivatives. Interestingly, a variety of aldehydes including substituted arylaldehydes participated well in this reaction and gave the desired product in good to excellent yields (Table 2). As seen from Table 2, both aromatic aldehydes carrying electron-donating or electron-withdrawing substituents act well in these reaction conditions. Aliphatic aldehydes such as *n*-heptanal and *n*-octanal were intact in this reaction.

In continuation of this work, we tried to synthesize 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-triones. To choose optimum conditions, first we tried to prepare 12-(4-chlorophenyl)-3,3-dimethyl-3,4-dihydro-2*H*-benzo[*b*]xanthene-1,6,11(12*H*)-trione from the reaction of 4-chlorobenzaldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol) and dimedone (1 mmol) as a model under solvent-free conditions at different temperatures (80, 90, 100 °C) in the presence of A: 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} (30, 11, 22, 8, 13, 15 mmol%), B: 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^- (29, 10, 20, 10, 12, 16 mmol%), C: triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl} (28, 11, 15, 10, 11, 13 mmol%),

Table 1 Optimization the amount of the ionic liquids as catalyst A: {[Msim]Cl}, B: [Hmim]HSO_4^-, C: {[Et_3N–SO_3H]Cl}, D: [Et_3NH][HSO_4] at different temperature under solvent-free conditions

Entry	Catalyst (mol%)				Temperature (°C)	Time (min)				Yield (%)[a]			
	A	B	C	D		A	B	C	D	A	B	C	D
1	29	28	29	29	60	–	–	–	–	Trace	Trace	Trace	Trace
2	14	10	15	12	70	20	18	17	20	69	70	68	62
3	20	15	20	18	70	14	12	12	13	79	79	76	71
4	10	9	9	5	80	10	8	10	7	87	85	83	87
5	13	11	13	9	80	5	4	4	4	97	95	98	95
6	15	14	16	13	80	3	4	3	3	98	95	97	96

[a] Yields refer to the isolated pure products. The preparation of 13-(4-chlorophenyl)-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone from the reaction of 4-chlorobenzaldehyde (1 mmol) and 2-hydroxy-1,4-naphthoquinone (2 mmol) was studied

Table 2 The preparation of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones using A: {[Msim]Cl} (13 mol%), B: $[Hmim]HSO_4^-$ (11 mol%), C: $\{[Et_3N–SO_3H]Cl\}$ (13 mol%), D: $[Et_3NH][HSO_4]$ (9 mol%) under Thermal (80 °C) solvent-free conditions

Entry	ArCHO	Time (min)				Yield (%)[a]				References to the known products
		A	B	C	D	A	B	C	D	
1	C_6H_5CHO	7	7	6	8	96	94	95	98	[14], [15], [16], [22]
2	$4\text{-}ClC_6H_4CHO$	5	4	5	4	95	92	98	93	[14], [15], [16], [22]
3	$4\text{-}NO_2C_6H_4CHO$	6	6	5	7	90	91	93	90	[14], [15], [16], [22]
4	$4\text{-}CH_3C_6H_4CHO$	7	7	8	9	88	90	90	89	[14], [15], [16], [22]
5	$4\text{-}BrC_6H_4CHO$	4	4	5	4	96	94	95	94	[14], [15], [16], [22]
6	$4\text{-}FC_6H_4CHO$	5	5	6	4	89	91	90	90	[14], [15], [16], [22]
7	$3\text{-}NO_2C_6H_4CHO$	5	4	5	6	95	93	95	96	[14], [15], [16], [22]

[a] Based on the reaction of arylaldehydes (1 mmol) and 2-hydroxy-1,4-naphthoquinone (2 mmol), Yields refer to the isolated pure products. All known products were compared with authentic samples in the literature

D: triethylammonium hydrogensulfate $[Et_3NH][HSO_4]$ (30, 10, 20, 7, 13, 16 mmol%). The best result with the highest yield and short reaction time was obtained at 100 °C and catalytic amounts of A: 13, B: 12, C: 11, D: 13 mol% of the ILs as catalyst (Table 3).

Using these optimized reaction conditions, the scope and efficiency of these procedures were explored for the synthesis of a wide variety of substituted 3, 4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-triones (Table 4). Aliphatic aldehydes such as *n*-heptanal and *n*-octanal were intact in this reaction.

The proposed mechanism is described according to the literature [16] for preparation of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones in the presence of Brønsted acidic IL such as 3-methyl-1-sulfonic acid imidazolium chloride (Scheme 2). Brønsted acidic IL with hydrogen bonding can activate the carbonyl groups of aldehyde (1) to decrease the energy of transition state. Then, nucleophilic attack of 2-hydroxy-1,4-naphthoquinone to the (1) causes to the

Table 3 Optimization the amount of the ionic liquids as catalyst A: {[Msim]Cl}, B: $[Hmim]HSO_4^-$, C: $\{[Et_3N–SO_3H]Cl\}$, D: $[Et_3NH][HSO_4]$ for preparation of 12-(4-chlorophenyl)-3,3-dimethyl-3,4-dihydro-2*H*-benzo[*b*]xanthene-1,6,11(12*H*)-trione at different temperature under solvent-free conditions

Entry	Catalyst (mol%)				Temperature (°C)	Time (min)				Yield (%)[a]			
	A	B	C	D		A	B	C	D	A	B	C	D
1	30	29	28	30	80	–	–	–	–	Trace	Trace	Trace	Trace
2	11	10	11	10	90	15	20	12	13	68	67	65	63
3	22	20	15	20	90	14	17	10	12	73	70	70	69
4	8	10	10	7	100	9	10	8	9	81	80	85	80
5	13	12	11	13	100	5	7	4	6	93	92	95	94
6	15	16	13	16	100	4	5	4	4	93	92	96	95

[a] Based on the reaction of 4-chlorobenzaldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol) and dimedone (1 mmol). Yields refer to the isolated pure product

Table 4 The preparation of 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-triones using A: {[Msim]Cl} (13 mol%), B: [Hmim][HSO_4] (12 mol%), C: {[Et_3N–SO_3H]Cl} (11 mol%), D: [Et_3NH][HSO_4] (13 mol%) under thermal (100 °C) solvent-free conditions

Entry	Aldehydes	Time (min)				Yield (%)[a]				References to the known products
		A	B	C	D	A	B	C	D	
1	C_6H_5CHO	5	7	9	6	94	93	95	97	[16], [23]
2	4-ClC_6H_4CHO	5	7	4	6	93	92	95	94	[16], [23]
3	4-$NO_2C_6H_4CHO$	6	7	8	7	86	90	91	96	[16], [23]
4	4-$CH_3C_6H_4CHO$	9	7	10	12	90	91	90	87	[16], [23]
5	4-BrC_6H_4CHO	8	4	5	10	90	89	91	93	[16], [23]
6	4-FC_6H_4CHO	7	9	9	13	96	92	97	95	[16], [23]
7	3-$NO_2C_6H_4CHO$	9	7	7	4	91	92	90	92	[16], [23]
8	3-BrC_6H_4CHO	10	5	6	13	90	89	92	87	[16], [23]
9	3-ClC_6H_4CHO	10	7	12	8	92	93	89	93	[16], [23]

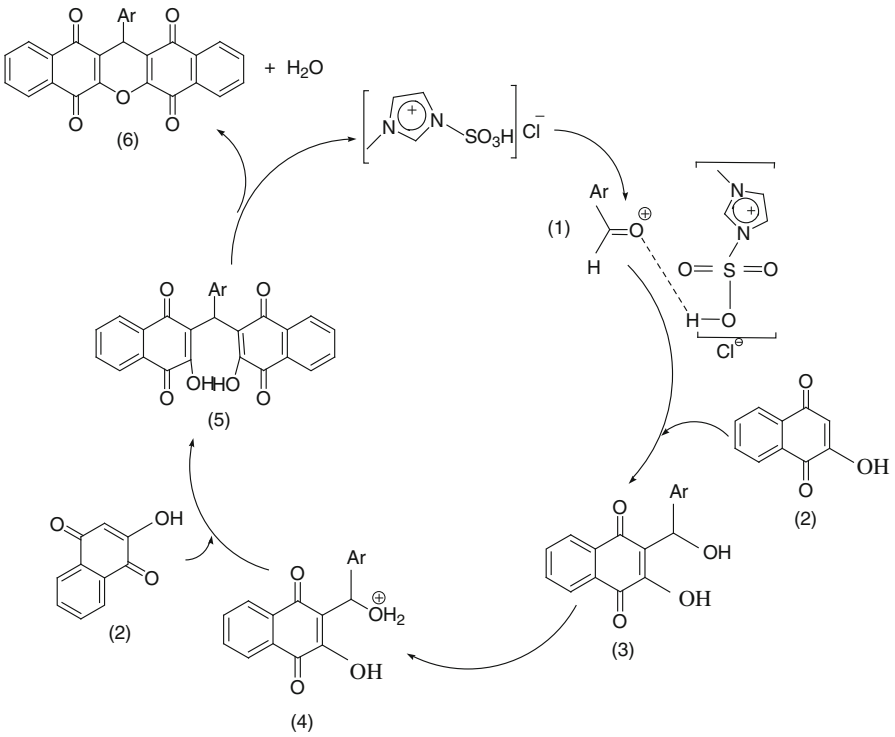
[a] Based on the reaction of arylaldehydes (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol) and dimedone (1 mmol). Yields refer to the isolated pure products. All know products were compared with authentic samples in the literature

formation of intermediate (3) which followed by the protonation and nucleophilic attack of 2-hydroxy-1,4-naphthoquinone giving the intermediate (5). Their subsequent intramolecular cyclization and dehydration give the 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones (6).

The suggested cyclic catalytic mechanism for the preparation of 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-triones is explained in Scheme 3. Brønsted acidic ILs act as catalyst. Initially, the Knoevenagel condensation of arylaldehydes (7) with dimedone (8) provide 2-arylidene-5,5-dimethylcyclohexane-1,3-dione (9) in the presence of the catalyst. Then, nucleophilic attack of 2-hydroxy-1,4-naphthoquinone to the activated of (9) causes the formation of the intermediate (11) which followed intramolecular cyclization and dehydration to give 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-trione (Scheme 3).

We also investigated the recycling of the catalysts under solvent-free conditions for the synthesis of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (benzaldehyde and 2-hydroxy-1,4-naphthoquinone, Table 2, entry 1) and 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-trione (benzaldehyde, 2-hydroxy-1,4-naphthoquinone, and dimedone; Table 4, entry 1) using 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}, 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^-, triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl}, and triethylammonium hydrogensulfate [Et_3NH][HSO_4] as catalysts. After completion of the reaction, the reaction mixture was cooled to room temperature, and the IL was dissolved in water. For recycling the catalyst, after completely washing the solid products with water, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and IL was recovered and reused. The recovered catalysts were reused five times without any loss of their activities (Figs. 2, 3).

To show the merit of the present work in comparison with the reported results in the literature, we compared the results of 3-methyl-1-sulfonic acid imidazolium

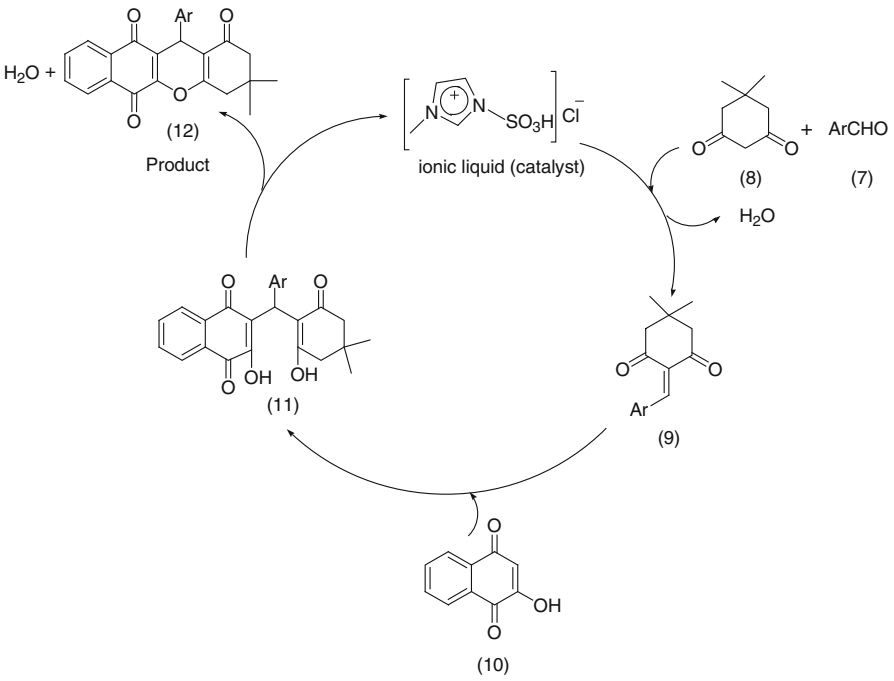


Scheme 2 The proposed mechanism for the preparation of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones

chloride {[Msim]Cl}, 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^-, triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl}, and triethylammonium hydrogensulfate [Et_3NH][HSO_4] as catalysts with *p*-TSA [14, 15], trifluoroacetic acid (TFA) with 1,1,3,3-*N,N,N′,N′*-tetramethylguanidinium trifluoroacetate (TMGT) IL [24], 2-pyrrolidonium hydrogensulfate [16], and (4-sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogensulfate [16] in the synthesis 13-phenyl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone from benzaldehyde, 2-hydroxy-1,4-naphthoquinone. As shown in Table 5, the present ILs can act as suitable catalysts with respect to reaction times and yields of the products.

Conclusions

We have developed a green and straightforward protocol for the synthesis of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones and 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-trione using ILs 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}, 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^-, triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl}, and triethylammonium hydrogensulfate [Et_3NH][HSO_4] as efficient catalysts under thermal solvent-free conditions. This procedure provides several advantages such as cleaner



Scheme 3 The proposed mechanism for the preparation of 3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*, 12*H*)-triones

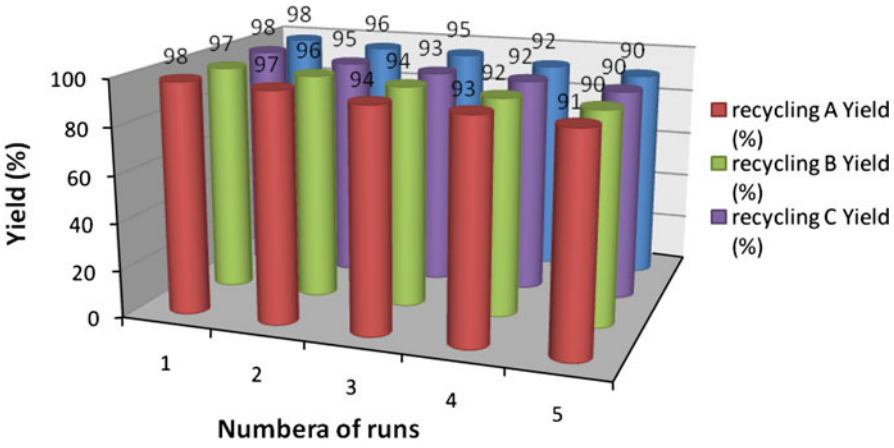


Fig. 2 Reusability of the ionic liquids in the preparation of 13-phenyl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone

reactions, easier work-up, reduced reaction times, reusable catalyst, and an eco-friendly promising strategy. This methodology offers significant improvements with regard to the scope of this transformation, simplicity in operation, and green aspects by avoiding expensive or corrosive catalysts.

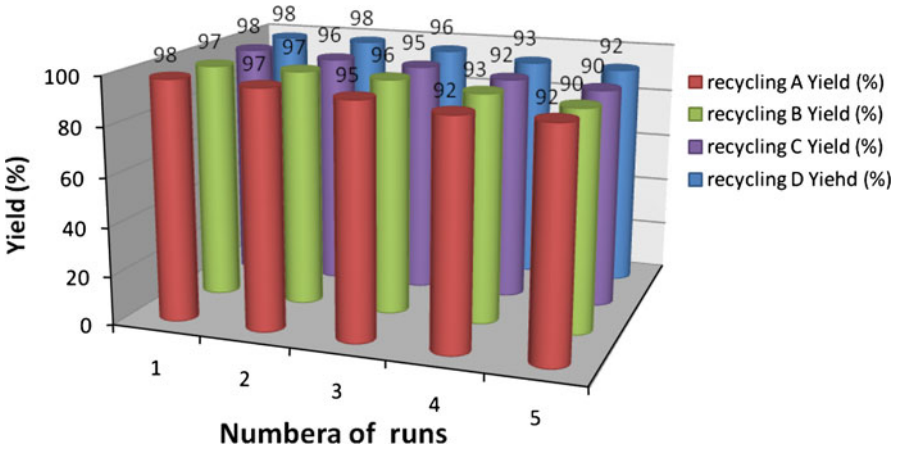


Fig. 3 Reusability of the ionic liquids in the preparation of 12-phenyl-3,4-dihydro-1*H*-benzo[*b*]xanthene-1,6,11(2*H*,12*H*)-trione

Table 5 Comparison the results of 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}, 1-*H*-3-methyl-imidazolium hydrogensulfate [Hmim]HSO_4^-, triethylamine-bonded sulfonic acid {[Et_3N–SO_3H]Cl}, and triethylammonium hydrogensulfate [Et_3NH][HSO_4] as catalysts with other catalysts in the literature

Entry	Catalyst	Catalyst amount (mol%)	Conditions	Time	Yeild (%) [Ref.]
1	*p*-TSA	58 mol%	Solvent-free/ 100 °C	3 h	81 [14]
2	*p*-TSA	58 mol%	Solvent-free/ 80 °C	7 h	74 [15]
3	TMGT/TFA	126 mol%/ 152 mol%	75 °C	1–1.2 h	91 [24]
4	2-Pyrrolidonium hydrogen sulfate	40 mol%	Solvent-free/ 100 °C	30 min	90 [16]
5	(4-Sulfobutyl)tris(4-sulfophenyl)phosphonium hydrogen sulfate	10 mol%	Solvent-free/ 100 °C	10 min	95 [16]
6	[Msim]Cl	13 mol%	Solvent-free/ 80 °C	7 min	96
7	[Hmim]HSO_4^-	11 mol%	Solvent-free/ 80 °C	7 min	94
8	{[Et_3N–SO_3H]Cl}	13 mol%	Solvent-free/ 80 °C	6 min	95
9	[Et_3NH][HSO_4]	9 mol%	Solvent-free/ 80 °C	8 min	98

Acknowledgment We are grateful to the University of Sistan and Baluchestan Research Council for the partial support of this research.

References

1. W. Zhang, B.W. Cue, *Green Techniques for Organic Synthesis and Medicinal Chemistry* (Wiley, Chichester, 2012)
2. A.M. Inamuddin, *Green Solvents I: Properties and Applications in Chemistry* (Springer, London, 2012)
3. A.M. Inamuddin, *Green Solvents II: Properties and Applications in Chemistry* (Springer, London, 2012)
4. B.S. Siddiqui, M.N. Kardar, T. Ali, S. Khan, Helv. Chim. Acta **86**, 2164 (2003)
5. C. Wright, G.V. Ullas, J. Label. Compd. Radiopharm. **45**, 1265 (2002)
6. R.H. Thomson, *Naturally occurring quinines*, 4th edn. (Chapman & Hall, London, 1997)
7. T. Hideo, J. Teruomi, Jpn. Patent 56,005,480 1981
8. R.W. Lamberk, J.A. Martin, J.H. Merrett, K.E.B. Parkes, G.J. Thomas, PCT Int. Appl. WO9,706,178, 1997
9. J.P. Poupelin, G. Saint-Rut, O. Fussard-Blanpin, G. Narcisse, G. Uchida-Ernouf, R. Lakroix, Eur. J. Med. Chem. **13**, 67 (1978)
10. R.-M. Ion, D. Frackowiak, A. Planner, K. Wiktorowicz, Acta Biochim. Pol. **45**, 833 (1998)
11. A. Banerjee, A.K. Mukherjee, Stain Technol. **56**, 83 (1981)
12. C.G. Knight, T. Stephenes, Biochem. J. **258**, 683 (1989)
13. J. Peters, J. Grotemeyer, Rapid Commun Mass Spectrom. **25**, 1169 (2011)
14. Z. Noroozi Tisseh, S.C. Azimi, P. Mirzaei, A. Bazgir, Dye. Pigm. **79**, 273 (2008)
15. A. Bazgir, Z. Noroozi Tisseh, P. Mirzaei, Tetrahedron Lett. **49**, 5165 (2008)
16. H.R. Shaterian, M. Ranjbar, K. Azizi, J. Mol. Liq. **162**, 95 (2011)
17. H.R. Shaterian, M. Arman, F. Rigi, J. Mol. Liq. **158**, 145 (2011)
18. M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, J. Iran Chem. **7**, 646 (2010)
19. A.R. Hajipour, L. Khazdooz, A.E. Ruoho, Catal. Commun. **9**, 89 (2008)
20. A. Zare, A.R. Moosavi-Zare, M. Merajoddin, M.A. Zolfigol, T. Hekmat-Zadeh, A. Hasaninejad, A. Khazaei, M. Mokhlesi, V. Khakyzadeh, F. Derakhshan-Panah, M.H. Beyzavi, E. Rostami, A. Arghoon, R. Roohandeh, J. Mol. Liq. **167**, 69 (2012)
21. J. Weng, C. Wang, H. Li, Y. Wang, Green Chem. **8**, 96 (2006)
22. M. Mohammadpour-Amini, Y. Fazaeli, Z. Yassaee, S. Feizi, A. Bazgir, Open Catal. J. **2**, 40 (2009)
23. M. Dabiri, Z. Noroozi Tisseh, A. Bazgir, J. Heterocycl. Chem. **47**, 1062 (2010)
24. A. Rahmati, Chin. Chem. Lett. **21**, 761 (2010)