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Acidic ionic liquids catalyzed three-component synthesis of 12-aryl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione and 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one derivatives

Hamid Reza Shaterian *, Majid Mohammadnia, Farzaneh Moradi

Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, PO Box 98135-674, Zahedan, Iran

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A B S T R A C T

Synthesis of 12-aryl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione derivatives by the three component reaction of 2-hydroxynaphthalene-1,4-dione, aldehydes, and 2*H*-indene-1,3-dione under solvent-free conditions at 70 °C in the presence of catalytic amount of acidic ionic liquids such as triethylammonium hydrogensulfate ([Et_3NH][HSO_4]), triethylamine-bonded sulfonic acid ([Et_3N–SO_3H]Cl), 2-pyrrolidonium hydrogensulfate ([Hnhp][HSO_4]), 3-methyl-1-sulfonic acid imidazolium chloride ([Msim]Cl), and 1-methylimidazolium hydrogensulfate ([Hmim][HSO_4]) is described. In addition, 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one derivatives from the reaction of β-naphthol, aldehydes, and 2*H*-indene-1,3-dione under thermal solvent-free conditions in the presence of mentioned catalysts is reported.

1. Introduction

Ionic liquids (ILs), because of their low volatility, nonflammability, capability to dissolve various organic and inorganic compounds, and potentially recyclable properties, have attracted considerable attention as environmentally friendly reaction media in the green organic synthesis [1–5]. ILs could effectively drive the development of green and chemical industries. As is known to all, discovering a new ionic liquid is relatively easy, but determining its usefulness as a solvent and catalyst requires a much more substantial investment [1–9]. With the fast development of green chemistry and our tireless efforts, herein, we applied some acidic ionic liquids such as triethylammonium hydrogensulfate ([Et_3NH][HSO_4]), triethylamine-bonded sulfonic acid ([Et_3N–SO_3H]Cl), 2-pyrrolidonium hydrogensulfate ([Hnhp][HSO_4]), 3-methyl-1-sulfonic acid imidazolium chloride ([Msim]Cl), and 1-methylimidazolium hydrogensulfate ([Hmim][HSO_4]) as catalysts (Scheme 1) in the synthesis of 12-aryl-12*H*-indeno[1,2-b]naphtho[3,2-e]pyran-5,11,13-trione and 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13*H*)-one derivatives (Scheme 2).

Triethylammonium hydrogensulfate [10] was used in the iodination of alcohols [11], triethylamine-bonded sulfonic acid [12] was applied in the preparation of β-acetamido ketones, 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[a,j]xanthenes [12], 2-pyrrolidonium hydrogensulfate [13] can catalyzed synthesis of benzoxanthene derivatives [13], 3-methyl-1-sulfonic acid imidazolium chloride [14] was used in preparation of 1-amidoalkyl-2-naphthols [15], benzimidazoles [16], and 1-methylimidazolium hydrogensulfate [17] was applied in the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones [18] and 1,1-diacetates [17].

2. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. The acidic ionic liquids such as triethylammonium hydrogensulfate [10], triethylamine-bonded sulfonic acid [12], 2-pyrrolidonium hydrogensulfate [13], 3-methyl-1-sulfonic acid imidazolium chloride [14], and 1-methylimidazolium hydrogensulfate [17] were prepared according to literature [10,12–14,17]. All yields refer to isolated products after purification. The NMR spectra were recorded on a Bruker Avance DPX 300 MHz instrument. The spectra were measured in DMSO-d_6 relative to TMS (0.00 ppm). 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.

2.1. Synthesis of 12-aryl-12H-indeno[1,2-b]naphtho[3,2-e]pyran-5,11,13-trione under solvent-free conditions

The mixture of the aldehydes (10 mmol), 2*H*-indene-1,3-dione (11 mmol), 2-hydroxynaphthalene-1,4-dione (10 mmol) and ionic

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* Corresponding author. Tel.: +98 541 2446565; fax: +98 541 2431067.
E-mail address: hrshaterian@chem.usb.ac.ir (H.R. Shaterian).

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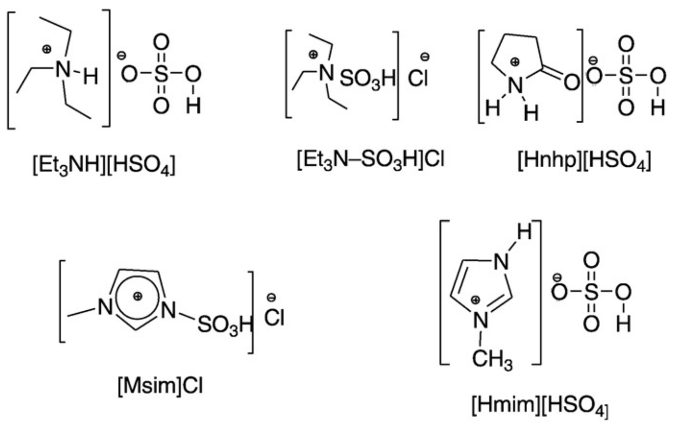


Scheme 1. The structure of acidic Brønsted ionic liquids: $[Et_3NH][HSO_4]$, $[Et_3N–SO_3H]Cl$, $[Hnhp][HSO_4]$, $[Msim]Cl$, $[Hmim][HSO_4]$.

liquids containing $[Et_3NH][HSO_4]$ (15 mol%), $[Et_3N–SO_3H]Cl$ (16 mol%), $[Hnhp][HSO_4]$ (14 mol%), [Msim]Cl (17 mol%), and $[Hmim][HSO_4]$ (15 mol%) as acidic catalysts was stirred at 70 °C for the specific time. The reaction mixture changed from liquid phase to soft-solid phase during the reaction. After completion of the reaction, it was cooled to room temperature. Then, 5 mL of water was added to the mixture and heated again. The ionic liquid was dissolved in water, and filtered for separation of the crude product. The separated product was washed twice with water (2 × 5 mL). The solid product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. All of the desired product(s) were characterized by comparison of their physical data with those of known compounds. For recycling the catalysts, after washing solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused.

Selected spectra for two known products are given below:

12-Phenyl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione (Table 2, entry 1): yellow powder, mp 312–313 °C.; IR (KBr): ν_{max} = 3032, 1667, 1635, 1660 cm^{-1}.; ^1H NMR (300 MHz, DMSO-d_6): δ = 5.49 (s, 1H, CH), 7.16–7.54 (m, 6H, ArH), 7.64–7.92 (m, 4H, ArH), 7.99 (d, *J* = 8.4 Hz, 1H, ArH), 8.12 (d, *J* = 7.6 Hz, 1H, ArH), 8.17 (d, *J* = 7.6 Hz, 1H, ArH) ppm.

12-(4-Nitrophenyl)-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione (Table 2, entry 4): Yellow powder, mp > 330 °C.; IR (KBr): ν_{max} = 3076, 1664, 1636, 1590 cm^{-1}.; ^1H NMR (300 MHz, DMSO-d_6): δ = 6.06 (s, 1H, CH), 7.46–7.68 (m, 6H, ArH), 7.79–7.96 (m, 4H, ArH), 8.06 (d, *J* = 8.8 Hz, 1H, ArH), 8.12 (d, *J* = 7.6 Hz, 1H, ArH) ppm.

2.2. General procedure for the synthesis of 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-one derivatives under solvent-free conditions

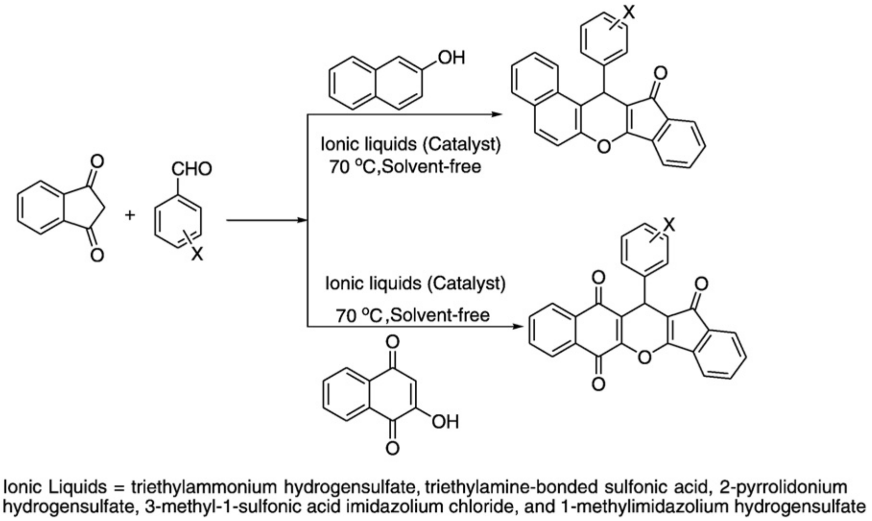
The mixture of β-naphthol (10 mmol), benzaldehydes (10 mmol) and 2*H*-indene-1,3-dione (10 mmol) and ionic liquids containing $[Et_3NH][HSO_4]$ (14 mol%), $[Et_3N–SO_3H]Cl$ (16 mol%), $[Hnhp][HSO_4]$ (15 mol%), [Msim]Cl (17 mol%), and $[Hmim][HSO_4]$ (16 mol%) as acidic catalysts was stirred at 70 °C for the specific time. The reaction mixture changed from liquid phase to soft-solid phase during the reaction. After completion of the reaction, it was cooled to room temperature. Then, 5 mL of water was added to the mixture and heated again. The ionic liquid was dissolved in water, and filtered for separation of the crude product. The separated product was washed twice with water (2 × 5 mL). The solid product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. All of the desired product(s) were characterized by comparison of their physical data with those of known compounds. For recycling the catalysts, after washing solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused.

Selected spectra for two known products are given below:

13-(4-Methylphenyl)-indeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one (Table 4, entry 6):

Yellow solid, mp 194 °C.; IR (KBr): ν_{max} = 2950, 1649, 1597, 1372, 1228, 1185 cm^{-1}.; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 5.61 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 2H, ArH), 7.21 (d, *J* = 8.0 Hz, 2H, ArH), 7.43–7.28 (m, 6H, ArH), 7.50 (d, *J* = 9.2 Hz, 1H, ArH), 7.88–7.82 (m, 3H, ArH) ppm.

13-(4-Chlorophenyl)-indeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one (Table 4, entry 2): Yellow solid, mp 227 °C.; IR (KBr): ν_{max} = 2952, 1649, 1594, 1375, 1225, 1189 cm^{-1}.; ^1H NMR (300 MHz, $CDCl_3$): δ = 5.63 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 2H, ArH), 7.45–7.25 (m, 8H, ArH), 7.51 (d, *J* = 8.8 Hz, 1H, ArH), 7.75 (t, *J* = 9.2 Hz, 1H, ArH), 7.88–7.84 (m, 2H, ArH) ppm.



Scheme 2. Synthesis of 12-aryl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione and 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one derivatives.

Table 1

Optimization conditions for preparation 12-(4-chlorophenyl)-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione from 4-chlorobenzaldehyde, 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione in the presence of different amount of ionic liquids, A: triethylammonium hydrogensulfate, B: triethylamine-bonded sulfonic acid, C: 2-pyrrolidonium hydrogensulfate, D: 3-methyl-1-sulfonic acid imidazolium chloride, and E: 1-methylimidazolium hydrogensulfate, as catalyst under varieties temperature.

Entry	Catalyst (mol%)					Temperature (°C)	Time (min)					Yield (%)[a]				
	A	B	C	D	E		A	B	C	D	E	A	B	C	D	E
1	20	21	20	20	18	25	30	28	28	35	30	44	40	49	49	40
2	35	32	30	34	32	25	30	30	30	38	32	56	55	60	60	54
3	20	18	19	20	19	50	22	20	24	30	26	60	58	62	62	60
4	30	31	30	30	31	50	15	12	10	15	15	70	69	70	70	72
5	10	10	8	10	10	70	13	10	8	11	10	81	80	82	81	81
6	15	16	14	17	15	70	12	9	7	10	9	94	93	93	92	91
7	20	20	20	23	19	70	12	9	7	10	9	95	94	94	93	92

[a] Yields refer to pure isolated products.

3. Results and discussions

To study the effect of catalyst loading and temperature on the three component condensation reactions for the synthesis of 12-(4-chlorophenyl)-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione, the solvent-free reaction of 4-chlorobenzaldehyde, 2*H*-indene-1,3-dione, 2-hydroxynaphthalene-1,4-dione in the presence of the ionic liquid, triethylammonium hydrogensulfate ([Et_3NH][HSO_4]), as catalyst was selected as a model (Table 1). The reaction was carried out with different amount of triethylammonium hydrogensulfate as catalyst (10, 15, 20, 30, 35, mol%) and varieties temperature (25, 50, 70 °C) (Table 1). As it was shown from Table 1, 15 mol% of [Et_3NH][HSO_4] as catalyst at 70 °C afforded the corresponding product in 12 min with 94% of yield. In continuation of our study, optimization conditions of ionic liquids, [Et_3N–SO_3H]Cl, [Hnhp][HSO_4], [Msim]Cl, and [Hmim][HSO_4], as catalysts in the model were investigated. According to Table 1 and its general optimization procedure, 16 mol% of [Et_3N–SO_3H]Cl, 15 mol% of [Hnhp][HSO_4], 17 mol% of [Msim]Cl, and 16 mol% of [Hmim][HSO_4] as catalysts under solvent-free conditions at 70 °C was chosen (Table 1). In addition, we used concentrated H_2SO_4 (98%) as catalyst in the selected model. Thus, H_2SO_4 (7 mol%) was used instead of acidic ionic liquids at room temperature and in an ice bath. We observed that all of starting materials were decomposed in the exothermic reaction accompanied by the release of heat. These results confirm that reusable acidic ionic liquids act better than non recyclable H_2SO_4.

Next, three-component condensation reaction of aromatic aldehydes, 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione, under optimized conditions for preparation of 12-aryl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione was investigated (Table 2). The wide ranges of substituted and structurally diverse aldehydes synthesize the corresponding products in high to excellent yields using the five acidic ionic liquids as catalysts (Table 2). Then, we examined aliphatic aldehyde such as heptanal instead of benzaldehyde in the reaction. The all starting materials in the reaction almost were intact, only trace product was formed without any side products after 24 h (Table 2, Entry 12).

We also investigated the recycling of the ionic liquids under solvent-free conditions using the model reaction of 4-chlorobenzaldehyde, 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione in the presence of [Et_3NH][HSO_4] (15 mol%),[Et_3N–SO_3H]Cl (16 mol%), [Hnhp][HSO_4] (14 mol%), [Msim]Cl (17 mol%), and [Hmim][HSO_4] (15 mol%) (Table 2, Entry 2). After completion of the reaction, water was added and the precipitated mixture was filtered off for separation of crude products. After washing the solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused (Fig. 1). The recovered catalysts were reused four runs without any loss of its activities.

In order to show the accessibility of the present work in comparison with only one reported results in the literature, we summarized some of the results for the preparation of 12-(4-chlorophenyl)-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione in Table 3. The results show that acidic ionic liquids such as [Et_3NH][HSO_4] (15 mol%),[Et_3N–SO_3H]Cl (16 mol%), [Hnhp][HSO_4] (14 mol%), [Msim]Cl (17 mol%), and [Hmim][HSO_4] (15 mol%) under solvent-free conditions relative to poly(4-vinylpyridinium) hydrogensulfate (P(4-VPH)HSO_4) (20 mg) at 100 °C [19], are the most efficient catalysts with respect to the reaction time and exhibits broad applicability in terms of yields. If we compare the catalytic activity of the acidic ionic liquids together in the present work (Table 3), we will observe that the 2-pyrrolidonium hydrogensulfate, ([Hnhp][HSO_4]), show much higher activities and

Table 2

Three component synthesis of 12-aryl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione derivatives from the reaction of 2-hydroxynaphthalene-1,4-dione, 2*H*-indene-1,3-dione, and aldehydes in the presence of A: [Et_3NH][HSO_4] (15 mol%), B: [Et_3N-SO_3H]Cl (16 mol%), C: [Hnhp][HSO_4] (14 mol%), D: [Msim]Cl (17 mol%), and E: [Hmim][HSO_4] (15 mol%) as catalysts.

Entry	Aldehydes	Time (min)					Yield (%)[a]					Melting point m.p (°C)/lit. m.p (°C) [ref]
		A	B	C	D	E	A	B	C	D	E	
1	C_6H_5	12	10	8	10	9	91	91	92	90	89	313/(311–314) [19]
2	4-BrC_6H_4	12	10	8	10	9	92	92	91	91	90	>330/(>330) [19]
3	4-MeC_6H_4	13	10	9	11	10	90	91	90	90	89	317/(314–316) [19]
4	4-ClC_6H_4	12	9	7	10	9	94	93	93	92	91	>330 /(>330) [19]
5	2-ClC_6H_4	12	9	7	10	9	92	91	91	91	90	317/(316–318) [19]
6	3,4-$Cl_2C_6H_3$	12	9	7	10	9	93	91	92	91	91	304/(302–305) [19]
7	4-$MeOC_6H_4$	13	10	8	11	10	90	91	90	90	91	310/(309–311) [19]
8	4-FC_6H_4	12	10	8	10	9	90	91	90	91	89	291/(290–292) [19]
9	4-$NO_2C_6H_4$	12	9	7	10	9	91	91	90	92	90	>330 /(>330) [19]
10	3-$NO_2C_6H_4$	12	9	7	10	9	90	90	90	91	89	>330/(>330) [19]
12	*n*-Heptanal	24 h	–	–	–	–	Trace	–	–	–	–	–

[a] Yields refer to the isolated pure products. The desired known pure products were characterized by comparison of their physical data (melting points, IR, ^1H NMR) with those of known compounds.

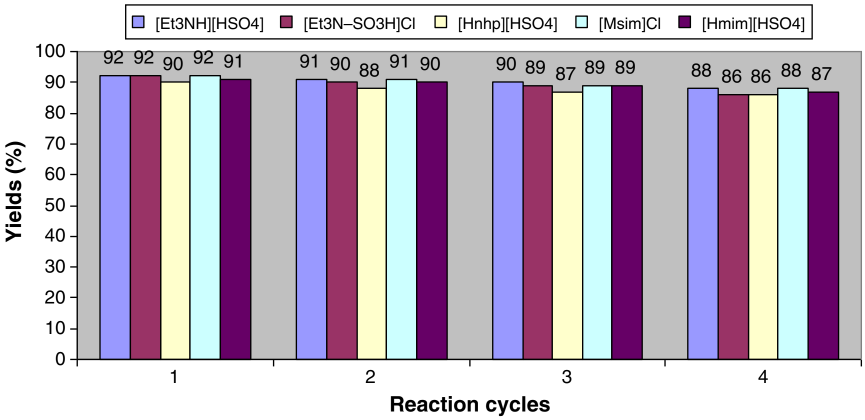


Fig. 1. Investigation the recycling of the ionic liquids in the synthesis of 12-(4-chlorophenyl)-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-trione.

better results than [Et_3NH][HSO_4], [$Et_3N–SO_3H$]Cl, [Msim]Cl, and [Hmim][HSO_4].

We also applied [Et_3NH][HSO_4], [$Et_3N–SO_3H$]Cl, [Hnhp][HSO_4], [Msim]Cl, and [Hmim][HSO_4] in condensation reaction of β-naphthol, aldehydes, and 2*H*-indene-1,3-dione under solvent-free conditions for preparation of 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one derivatives under (Scheme 1). As, we described optimization procedure, the reaction of 4-chlorobenzaldehyde, β-naphthol, 2*H*-indene-1,3-dione was selected as model. The reaction was carried out in the presence different amount of catalysts, [Et_3NH][HSO_4] (9, 14, 20, 21, 22, 28, 35 mol%), [$Et_3N–SO_3H$]Cl (11, 16, 19, 20, 22, 30, 32 mol%), [Hnhp][HSO_4] (9, 15, 18, 20, 21, 30, 32 mol%), [Msim]Cl (11, 17, 20, 21, 23, 31, 34 mol%), and [Hmim][HSO_4] (10, 16, 18, 19, 20, 30, 32 mol%), and varieties temperature (25, 50, 70 °C) under solvent-free conditions. The best results were obtained when the amount of catalysts were chosen as [Et_3NH][HSO_4] (14 mol%), [$Et_3N–SO_3H$]Cl (16 mol%), [Hnhp][HSO_4] (15 mol%), [Msim]Cl (17 mol%), and [Hmim][HSO_4] (16 mol%) at 70 °C for both of them. Then, three-component condensation reaction of aromatic aldehydes, β-naphthol, and 2*H*-indene-1,3-dione under optimized conditions for preparation of 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one derivatives was investigated (Table 4). A wide range of substituted and structurally diverse aldehydes were used and the corresponding products were synthesized in high to excellent yields, which demonstrated that this method tolerates both electron-withdrawing and electron-donating constituents (Table 4). Then, we examined aliphatic aldehyde such as *n*-heptanal instead of benzaldehyde in the reaction. The all starting materials in the reaction almost were intact, only trace product was formed without any side products after 24 h (Table 4, Entry 10).

The recycling of the ionic liquids was studied such as above procedure in selected model. The recovered catalysts were reused four runs without any loss of its activities (Fig. 2).

In order to show the accessibility of the present work in comparison with only one reported results in the literature such as silica chloride [20], we summarized some of the results for the preparation of 13-(4-chlorophenyl)-indeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one in Table 5. The results show that acidic ionic liquids such as [Et_3NH][HSO_4] (14 mol%), [$Et_3N–SO_3H$]Cl (16 mol%), [Hnhp][HSO_4] (15 mol%), [Msim] Cl (17 mol%), and [Hmim][HSO_4] (16 mol% are the most efficient catalysts with respect to the reaction time and yields of the products. As it was shown from Table 5, [Hnhp][HSO_4] show much higher activities and

Table 3
Comparison the results of [Et_3NH][HSO_4], [Et_3N-SO_3H]Cl, [Hnhp][HSO_4], [Msim]Cl, and [Hmim][HSO_4] with P(4-VPH)HSO_4 in the synthesis 12-(4-chlorophenyl)-12*H*-indeno [1,2-b]naphtho[3,2-e]pyran-5,11,13-trione.

Entry	Catalyst (mol%)	Conditions	Time	Yield (%)[a] [ref]
1	P(4-VPH)HSO_4 (20 mg)	Solvent-free, 100 °C	90 min	92 [19]
2	[Et_3NH][HSO_4] (15 mol%)	Solvent-free, 70 °C	12 min	94 (present work)
3	[Et_3N-SO_3H]Cl (16 mol%)	Solvent-free, 70 °C	9 min	93 (present work)
4	[Hnhp][HSO_4] (14 mol%)	Solvent-free, 70 °C	7 min	93 (present work)
5	[Msim]Cl (17 mol%)	Solvent-free, 70 °C	10 min	92 (present work)
6	[Hmim][HSO_4] (15 mol%)	Solvent-free, 70 °C	9 min	91 (present work)

[a] Yields refer to isolated pure products and based on the reaction of 4-chlorobenzaldehyde, 2-hydroxynaphthalene-1,4-dione, and 2*H*-indene-1,3-dione.

Table 4
Three component synthesis of 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one derivatives from the reaction of β-naphthol, 2*H*-indene-1,3-dione, and aldehydes in the presence of A: [Et_3NH][HSO_4] (14 mol%), B: [Et_3N-SO_3H]Cl (16 mol%), C: [Hnhp][HSO_4] (15 mol%), D: [Msim]Cl (17 mol%), and E: [Hmim][HSO_4] (16 mol%) as catalysts.

Entry	Aldehydes	Time (min)					Yield (%)[a]					Melting point m.p (°C)/lit. m.p (°C) [ref]
		A	B	C	D	E	A	B	C	D	E	
1	C_6H_5	10	10	9	9	10	89	90	92	90	91	201/(202–03) [20]
2	4-ClC_6H_4	10	9	8	9	10	93	93	92	92	91	227/(225–226) [20]
3	2,4-$Cl_2C_6H_3$	10	9	8	9	10	91	92	91	92	92	254/(252–253) [20]
4	3-$NO_2C_6H_4$	11	9	9	10	11	91	91	91	92	92	242/(240–241) [20]
5	2-ClC_6H_4	12	10	10	11	12	92	91	91	90	92	241/(240–241) [20]
6	4-MeC_6H_4	12	10	11	10	11	90	91	91	90	92	194/(192–193) [20]
7	4-$MeOC_6H_4$	12	10	11	10	9	91	90	91	91	89	227/(225–226) [20]
8	4-FC_6H_4	12	11	10	9	10	90	91	91	90	91	209/(208–209) [20]
9	3,4-$Cl_2C_6H_3$	10	10	9	11	10	90	91	91	90	89	246/(245–246) [20]
10	*n*-Heptanal	24 h	–	–	–	–	Trace	–	–	–	–	–

[a] Yields refer to the isolated pure products. The desired known pure products were characterized by comparison of their physical data (melting points, IR, ^1H NMR) with those of known compounds.

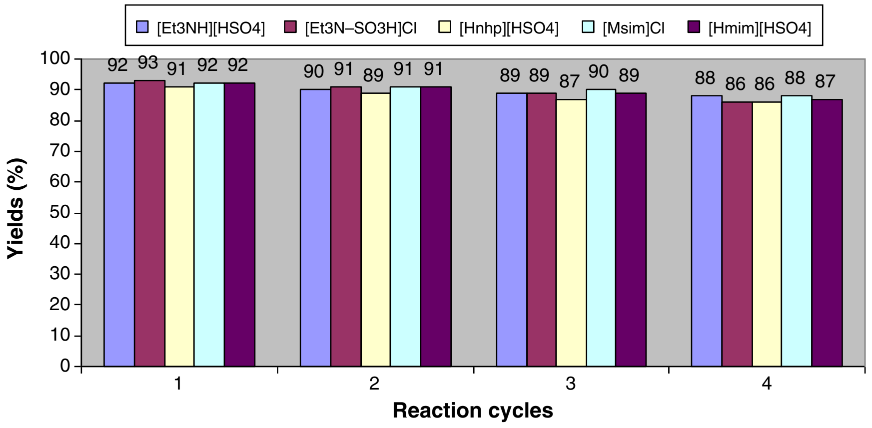


Fig. 2. The recycling of the ionic liquids in the preparation of 13-(4-chlorophenyl)-indeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one.

Table 5
Comparison the results of $[Et_3NH][HSO_4]$, $[Et_3N\text{-}SO_3H]Cl$, $[Hnhp][HSO_4]$, [Msim]Cl, and $[Hmim][HSO_4]$ with SiO_2-Cl in the synthesis 13-(4-chlorophenyl)-indeno[1,2-*b*]naphtho[1,2-*e*]pyran-12(13*H*)-one.

Entry	Catalyst (mol%)	Conditions	Time	Yield (%)[a] [ref]
1	SiO_2–Cl (150 mg)	Solvent-free, 110 °C	1 h	90 [20]
2	$[Et_3NH][HSO_4]$ (14 mol%)	Solvent-free, 70 °C	12 min	93 (present work)
3	$[Et_3N–SO_3H]Cl$ (16 mol%)	Solvent-free, 70 °C	9 min	93 (present work)
4	$[Hnhp][HSO_4]$ (15 mol%)	Solvent-free, 70 °C	7 min	92 (present work)
5	[Msim]Cl (17 mol%)	Solvent-free, 70 °C	10 min	92 (present work)
6	$[Hmim][HSO_4]$ (16 mol%)	Solvent-free, 70 °C	9 min	91 (present work)

[a] Yields refer to isolated pure products and based on the reaction of 4-chlorobenzaldehyde, β-naphthol, and 2*H*-indene-1,3-dione.

better results than $[Et_3NH][HSO_4]$, $[Et_3N–SO_3H]Cl$, [Msim]Cl, and $[Hmim][HSO_4]$ in the present work.

4. Conclusion

We have shown that acidic ionic liquids, which can be prepared from commercially available and inexpensive starting materials, catalyzed efficiently synthesis of 12-aryl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-triones and 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-one derivatives. The simplicity of the procedure, eco-friendly, non-volatile, easy handling, safety and reusability of catalyst are the advantages of these methods. These methods not only afford the products in excellent yields but also avoid the problems associated with catalyst cost, and pollution.

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