

## *Chapter 2*

**Investigation of 1, 3-disulfonic acid imidazolium carboxylate ionic liquids as task-specific Brønsted acidic catalysts for one-pot synthesis of 1,8-dioxo-decahydroacridine and 14-substituted-14*H*-dibenzo[a,j]xanthene derivatives**

**Published with small modification:**

**Dutta, A.K.,** Gogoi, P. and Borah, R. “Synthesis of dibenzoxanthene and acridine derivatives catalysed by 1,3-disulfonic acid imidazolium carboxylate ionic liquids” *RSC. Adv.* **4**, 41287--41291, 2014.

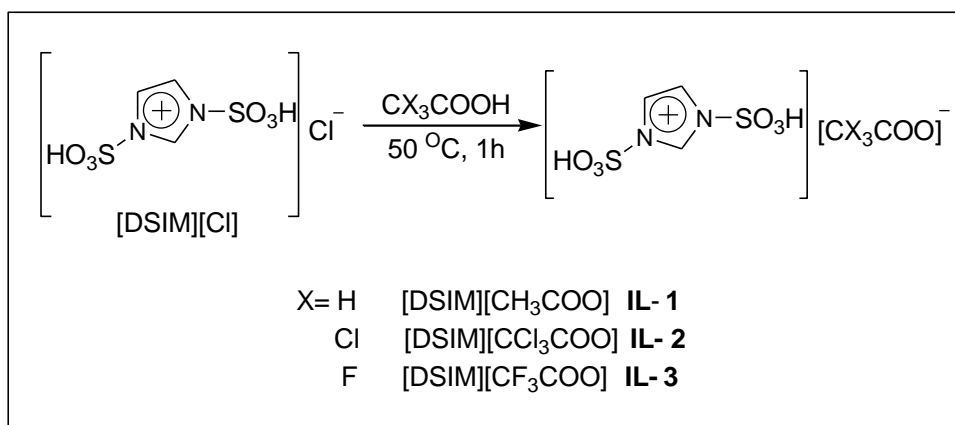
## 2.1. Introduction

The dual solvent-catalytic uses of task-specific ionic liquids with special functions, offer a new and environmentally benign approach toward modern chemical processes [1]. By virtue of the incorporated functional groups, these unique salts can act not only as solvents but also as catalysts in an array of synthetic, separations and electrochemical applications [2]. Their solubility can also be tuned readily depending on the nature of cations and anions so that they can phase separate from organic as well as aqueous media [3]. The preparation and application of such dual nature of acidic ionic liquids in organic reactions overcomes the common problems of conventional molecular solvents and acid catalysts [4]. The work of this chapter concerns on the synthesis and characterization of three new members of task-specific Brønsted acidic 1,3-disulfonic acid imidazolium carboxylate ionic liquids (ILs) [DSIM][X] where X = [CH<sub>3</sub>COO]<sup>-</sup>, [CCl<sub>3</sub>COO]<sup>-</sup>, [CF<sub>3</sub>COO]<sup>-</sup> with various analytical techniques such as <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, elemental analysis, acidity measurement and thermogravimetric analysis [5-6]. After observing their acidities and thermal stabilities, these ILs were investigated as reusable homogeneous acidic catalysts for one-pot preparation of dibenzoxanthene and 1,8-dioxo-decahydroacridine derivatives under environmentally benign methods such as solvent-free medium and aqueous phases. The limitations of conventional Brønsted or Lewis acid catalyzed methods for these two types of heterocycles have been discussed in **Chapter-1 (Section-1.2d)**. The use of ionic liquids simplified the reaction conditions in terms of product selectivity, reaction time, recycling of catalyst and isolation of product for both classes of the heterocycles [7-8].

## 2.2. Results and Discussion

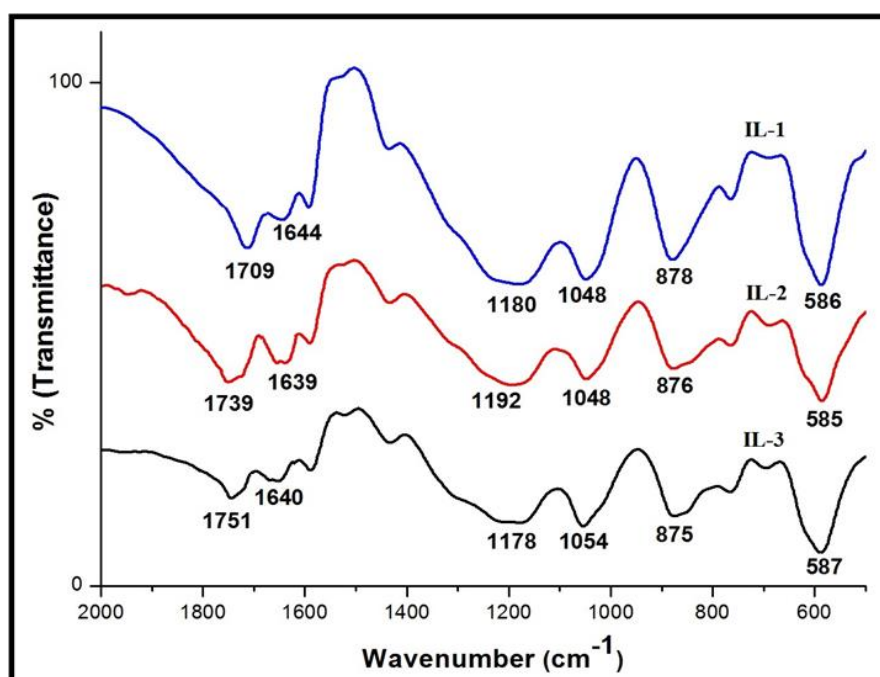
### 2.2.1. Synthesis and characterization of 1, 3-disulfonic acid imidazolium carboxylate ILs

To fulfil the above objectives, initially the three 1, 3-disulfonic imidazolium carboxylate ionic liquids [DSIM][X] where X = [CH<sub>3</sub>COO] (**IL-1**), [CCl<sub>3</sub>COO] (**IL-2**), [CF<sub>3</sub>COO] (**IL-3**) were synthesized from the reactions of 1,3-disulfonic acid imidazolium chloride ([DSIM][Cl]) and three different carboxylic acids (AcOH, CCl<sub>3</sub>COOH and CF<sub>3</sub>COOH) at room temperature stirring [9] (**Scheme-2.1**).



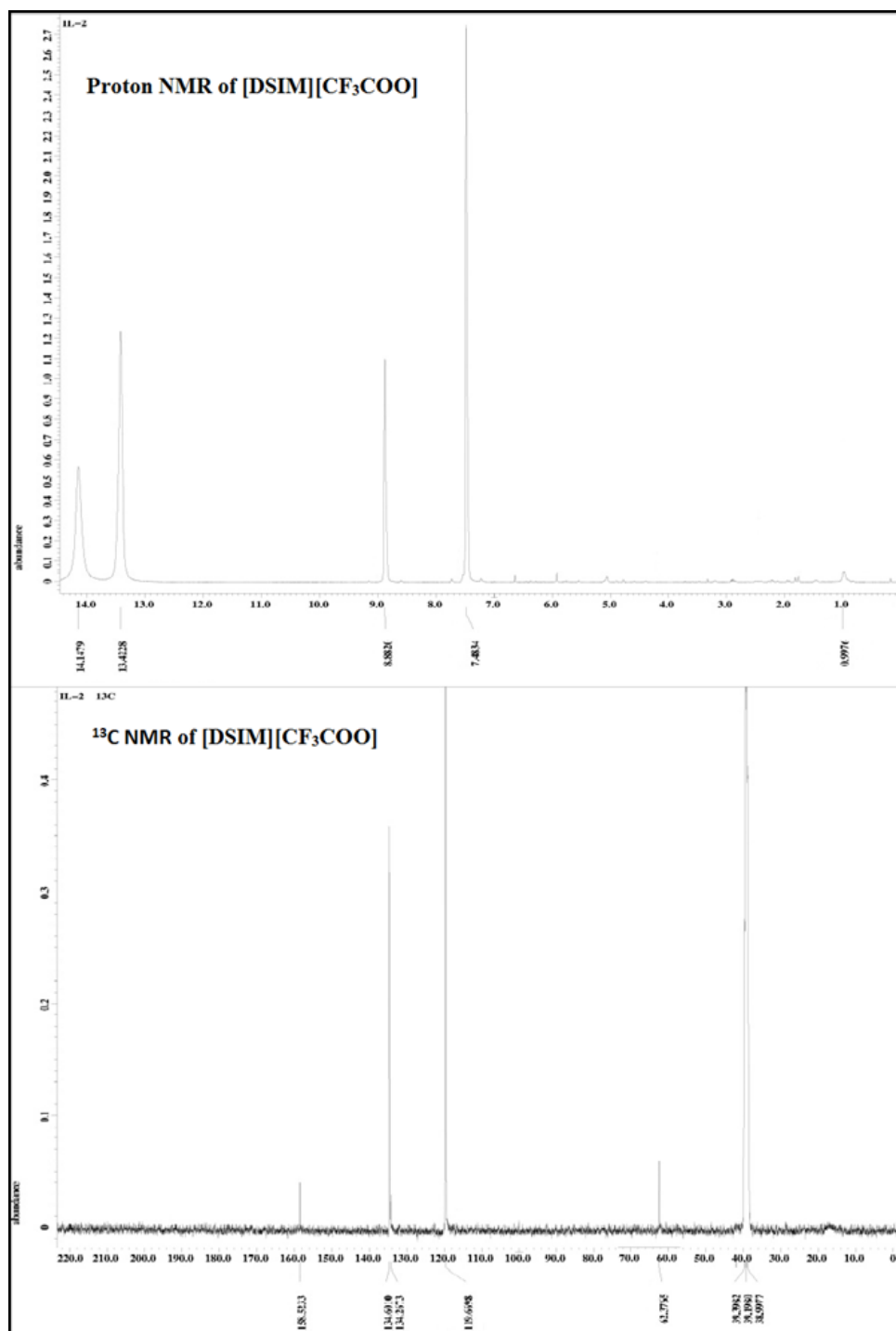
**Scheme-2.1:** Synthesis of 1,3-disulfonic acid imidazolium carboxylate ILs

### 2.2.1.1. Spectral analysis



**Fig.2.1:** FT-IR spectra of three ILs

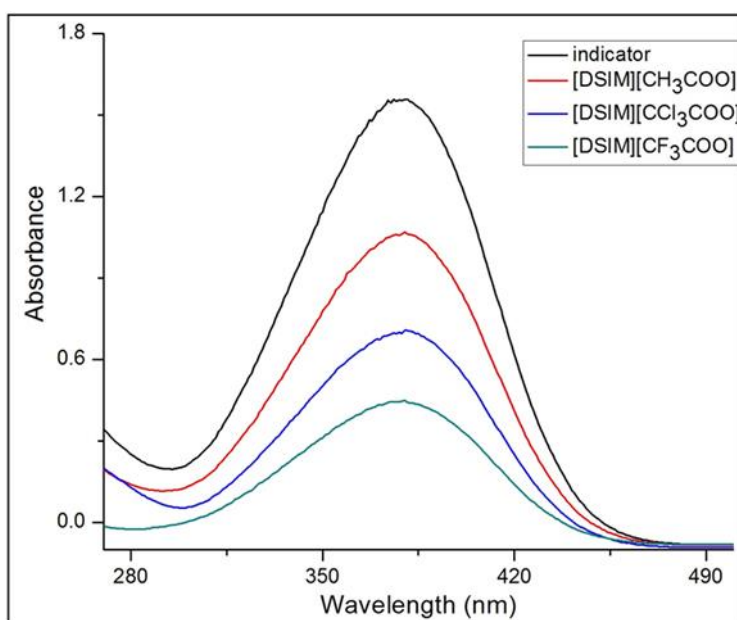
The FT-IR spectra (**Fig.2.1**) of these ILs showed three strong absorption bands at 1178-1192, 1048-1054 and 586-587  $\text{cm}^{-1}$  corresponding to S-O asymmetric and symmetric stretching and bending vibration of  $-\text{SO}_3\text{H}$  groups. The peaks around 875-878  $\text{cm}^{-1}$  expressed the N-S stretching vibration. The carboxylate anions gave strong asymmetric bands around 1709-1751  $\text{cm}^{-1}$  in the same region of imidazolium ions. The  $-\text{OH}$  groups of the ionic liquids indicated broad and strong peaks at 3000-3660  $\text{cm}^{-1}$ .



**Fig.2.2:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of [DSIM][CF<sub>3</sub>COO]

In <sup>1</sup>H NMR spectra the characteristic acidic protons of two -SO<sub>3</sub>H groups of the ILs appeared in 14.2 and 11.3-13.4 ppm respectively (**Fig.2.2**). The presence of carbonyl signal at 158.6 -172 ppm in <sup>13</sup>C NMR spectra confirmed the existence of carboxylate anions in these ionic liquids (**Fig.2.2**). The structures were further supported by the elemental analysis data.

### 2.2.1.2. UV-Visible acidity study



**Fig.2.3:** Hammett plot of ionic liquids using basic indicator 4-nitroaniline

The acidity of the ILs was determined on an UV-Visible spectrophotometer using 4-nitroaniline as basic indicator by following the Hammett equation that already reported in literature [10]. The absorbance of the basic indicator [I] was determined in ionic liquid solution which decreases with increasing the acidity of ionic liquid. The protonated form [IH]<sup>+</sup> of the indicator never appeared because of low molar absorptivity. The Hammett function H<sup>o</sup> for each ionic liquid was calculated using equation-1 by measuring the absorption differences [I]/[IH]<sup>+</sup>.

$$H^o = pK(I)_{aq} + \log [I]/[IH]^+ \quad (1)$$

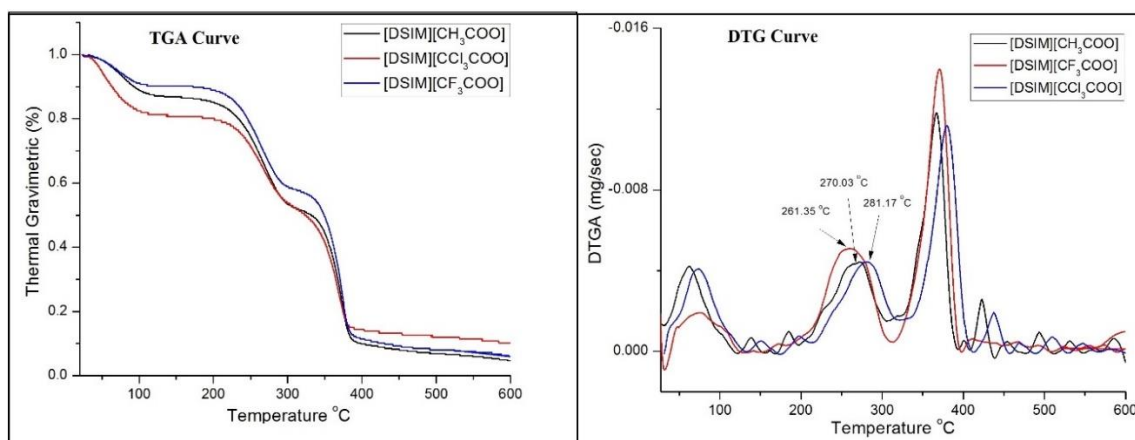
Where pK(I)<sub>aq</sub> is the pK<sub>a</sub> value of the basic indicator in aqueous solution. The relative acidity of the ILs can be obtained by determining the values of H<sup>o</sup> (table-2.1). The typical procedure involved the mixing of indicator 4-nitroaniline (5 mg/L, pK<sub>a</sub>=0.99) and ionic liquid (5 mmol/L) in ethanol with equal concentration. The maximum absorbance observed at 382 nm in ethanol. The order of acidities of these ionic liquids were found from the Hammett plot (**Fig.2.3**) in the decreasing order as follows: [DSIM][CF<sub>3</sub>COO]> [DSIM][CCl<sub>3</sub>COO]> [DSIM][CH<sub>3</sub>COO] which was also supported by the corresponding H<sup>o</sup> values included in **table-2.1**.

**Table-2.1:** Values of Hammett function ( $H^\circ$ ) for ionic liquids

Entry	IL	$\lambda_{\max}$	[I]%	[IH]%	$H^\circ$
1	Blank	1.558	100.0	0	-
2	[DSIM][CH <sub>3</sub> COO]	1.07	73.9	26.1	1.44
3	[DSIM][CCl <sub>3</sub> COO]	0.71	45.6	54.4	0.91
4	[DSIM][CF <sub>3</sub> COO]	0.448	28.8	71.2	0.60

### 2.2.1.3. Thermogravimetric analysis

The thermo gravimetric analysis of the three ionic liquids showed (**Fig.2.4**) slight weight loss below 100 °C due to absorbed moisture. All these ionic liquids were thermally stable in the temperature range of 260-281 °C



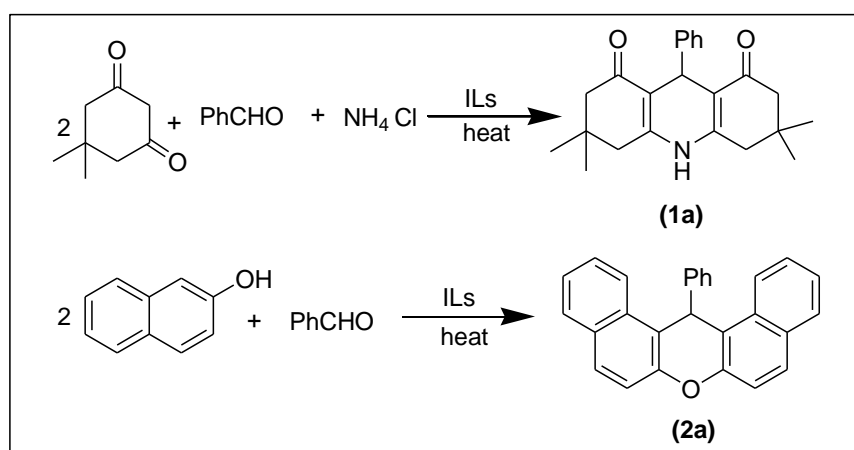
**Fig.2.4:** The TG/DTG diagrams of ILs

### 2.2.2. Catalytic activity of the three acidic ILs

After calculating the acidity of each IL, their amounts were optimized as acidic catalysts for the model synthesis of 1, 8-dioxo-decahydroacridine (**1a**) and dibenzoxanthene (**2a**) in various conditions (table-2.2). As a reaction medium the three ionic liquids didn't yield any product at ambient temperature for 4 hour. But at 100 °C the above reactions produced excellent yields within 10-15 minutes in [DSIM][CF<sub>3</sub>COO] and [DSIM][CCl<sub>3</sub>COO] ILs as reaction medium (table-2.2, entries 2,4,10,12) while [DSIM][CH<sub>3</sub>COO] ionic liquid showed less amount of product (table-2.2, entries 1, 9). In next step, the synthesis of (**1a**) and (**2a**) were performed at various temperatures for determining the optimized amount of two acidic IL catalysts (**IL-2** and **IL-3**). For dibenzoxanthene, the best catalytic activity of

**IL-2** and **IL-3** was observed with 25 mol % at 100 °C and 90 °C respectively in solvent-free medium (table-2.2, entries 11, 14). Likewise, the optimized temperature for 1,8-dioxo-decahydroacridine were found at 100 °C for **IL-2** and at 80 °C for **IL-3** in presence of 25 mol% of each IL under neat condition (table-2.2, entries 3, 6). Both ILs were also capable to produce reasonable amount of the 1, 8-dioxo-decahydroacridine in water at 90 °C within short time using the optimized amount of catalyst (table-2.2, entry 8). The solubility of dimedone in hot water with NH<sub>4</sub>Cl might attribute to the formation of decahydroacridine derivatives in water.

**Table-2.2:** Ionic liquids catalyzed optimization of the reaction conditions for the synthesis of (**1a**) and (**2a**)



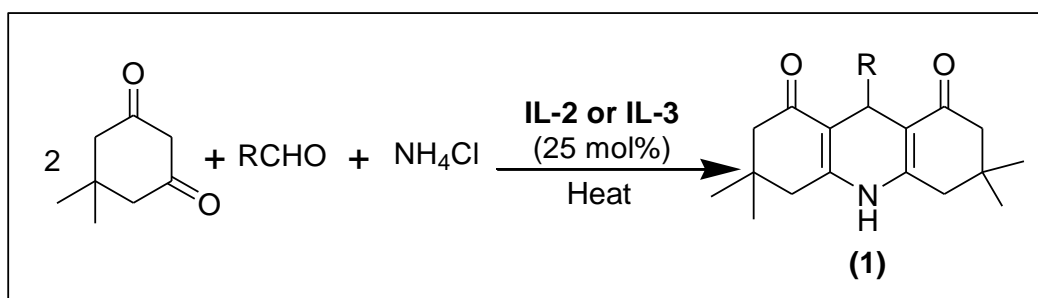
Entry	IL(mol%)	Temp (°C)	Time (min)	% of yield <sup>a</sup>
For 1,8-dioxo-decahydroacridine derivatives ( <b>1a</b> )				
1	<b>IL-1</b> (100)	100	25	65
2	<b>IL-2</b> (100/50)	100	10/10	98/98
3	<b>IL-2</b> (25/10)	100	10/45	96/65
4	<b>IL-3</b> (100/50)	100	10/10	100/100
5	<b>IL-3</b> (25/10)	100	10/45	100/82
6	<b>IL-3</b> (25)	90/80/70	10/10/25	100/100/70
7	<b>IL-2</b> (25)	80/90	20	70
8	<b>IL-2/IL-3</b> (25)	90	30	93 <sup>b</sup> /98 <sup>b</sup>
For dibenzoxanthene derivatives ( <b>2a</b> )				
9	<b>IL-1</b> (100)	100	30	70
10	<b>IL-2</b> (100/50)	100	15/30	95/93
11	<b>IL-2</b> (25/10)	100	20/45	92/44

12	<b>IL-3</b> (100/50)	100	15/15	96/98
13	<b>IL-3</b> (25/10)	100	15/45	97/70
14	<b>IL-3</b> (25)	90/80/70	15/25/40	95/80/65
15	<b>IL-2</b> (25)	80/90	45	55
16	<b>IL-2/IL-3</b> (25)	100	1 h	48 <sup>b</sup> /60 <sup>b</sup>

<sup>a</sup> Isolated yields; <sup>b</sup> Using 1 ml of water

However, the synthesis of (**1a**) was possible only up to 48-60 % yields in water at 100 °C along with unreacted 2-naphthol and aldehyde (table-2.2, entry 16). It may be due to heterogeneous phases of 2-naphthol in water medium. The standardized conditions were extended with various types of aldehydes using **IL-2** and **IL-3** as catalyst for the synthesis of other derivatives of these heterocyclic compounds. All these results were included in **table-2.3** and **table-2.4**. The results were observed to be satisfactory irrespective of the nature of aldehydes except with cinnamaldehyde and furfuraldehyde in both cases.

**Table-2.3:** Synthesis of 1,8-dioxo-decahydroacridines (**1a-h**) using ionic liquids **IL-2** and **IL-3** as catalysts



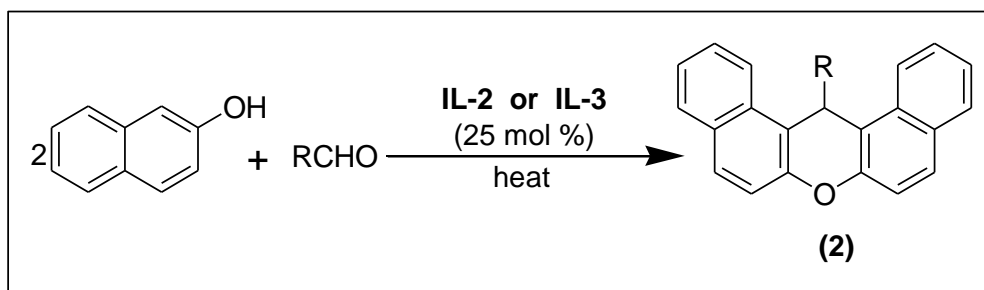
Entry	R	Solvent Free		Water	
		Time (min)	% yield <sup>a</sup> (A/B)	Time (min)	% yield <sup>a,b</sup> (C/D)
1	Ph	10	96/100 ( <b>1a</b> )	25	93/98 ( <b>1a</b> )
2	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	10	96/100 ( <b>1b</b> )	30	92/96 ( <b>1b</b> )
3	4-MeC <sub>6</sub> H <sub>4</sub>	15	94/98 ( <b>1c</b> )	35	90/94 ( <b>1c</b> )
4	4-ClC <sub>6</sub> H <sub>4</sub>	15	96/97 ( <b>1d</b> )	35	93/94 ( <b>1d</b> )
5	4-MeO-C <sub>6</sub> H <sub>4</sub>	15	95/99 ( <b>1e</b> )	35	90/96 ( <b>1e</b> )
6	-H	20	83/85 ( <b>1f</b> )	40	80/83 ( <b>1f</b> )
7	2-Naphthyl	15	95/97 ( <b>1g</b> )	40	92/93 ( <b>1g</b> )



8	PhCH=CH-	15	94/97 ( <b>1h</b> )	35	90/94 ( <b>1h</b> )
---	----------	----	---------------------	----	---------------------

<sup>a</sup> Isolated yields ; <sup>b</sup> Methods- A: using 25 mol % of ionic liquid **IL-2** at 100 °C ; B : Using 25 mol % of ionic liquid **IL-3** at 80 °C; C : Using 25 mol % of ionic liquids **IL-2** at 90 °C; D : Using 25 mol % of ionic liquid **IL-3** at 90 °C;

**Table-2.4:** Synthesis of dibenzoxanthene derivatives (**2a-h**) using ionic liquids **IL-2** and **IL-3** as catalysts

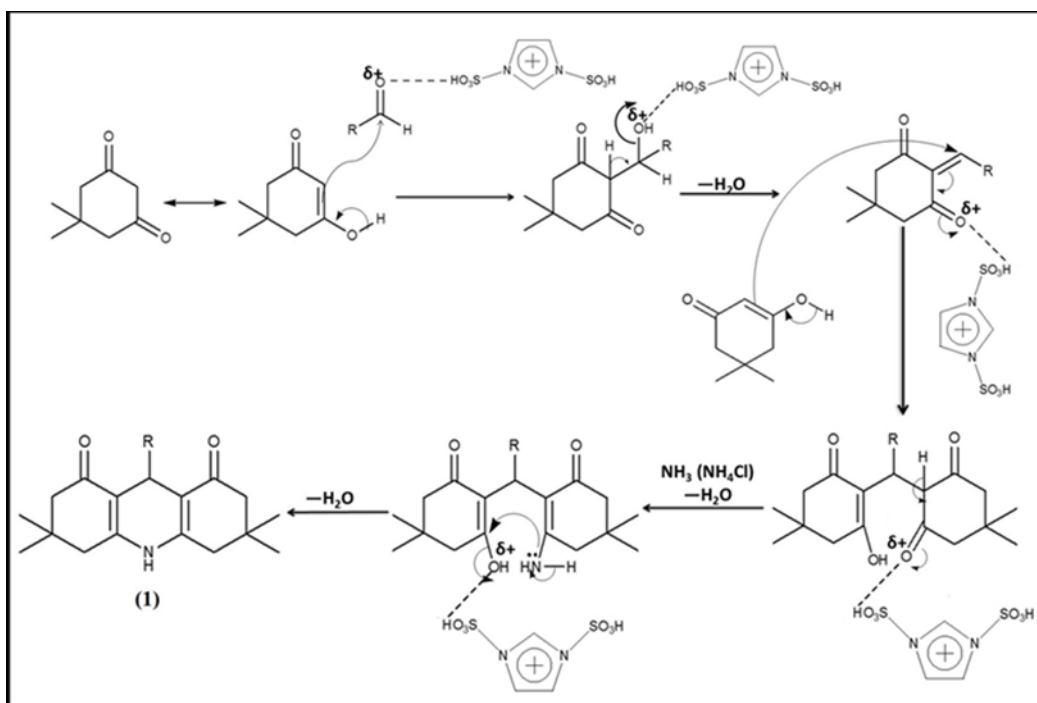


Entry	R	Time(min) (A/B)	% yield <sup>a, b</sup> (A/B)
1	Ph	20/15	92/97 ( <b>2a</b> )
2	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	25/20	88/94 ( <b>2b</b> )
3	4-MeC <sub>6</sub> H <sub>4</sub>	20/15	90/93 ( <b>2c</b> )
4	4-ClC <sub>6</sub> H <sub>4</sub>	25/20	85/94 ( <b>2d</b> )
5	4-MeOC <sub>6</sub> H <sub>4</sub>	20/15	92/97 ( <b>2e</b> )
6	H-	30/35	78/85 ( <b>2f</b> )
7	2-Naphthyl	20/15	90/96 ( <b>2g</b> )
8	PhCH=CH-	25/20	91/97 ( <b>2h</b> )

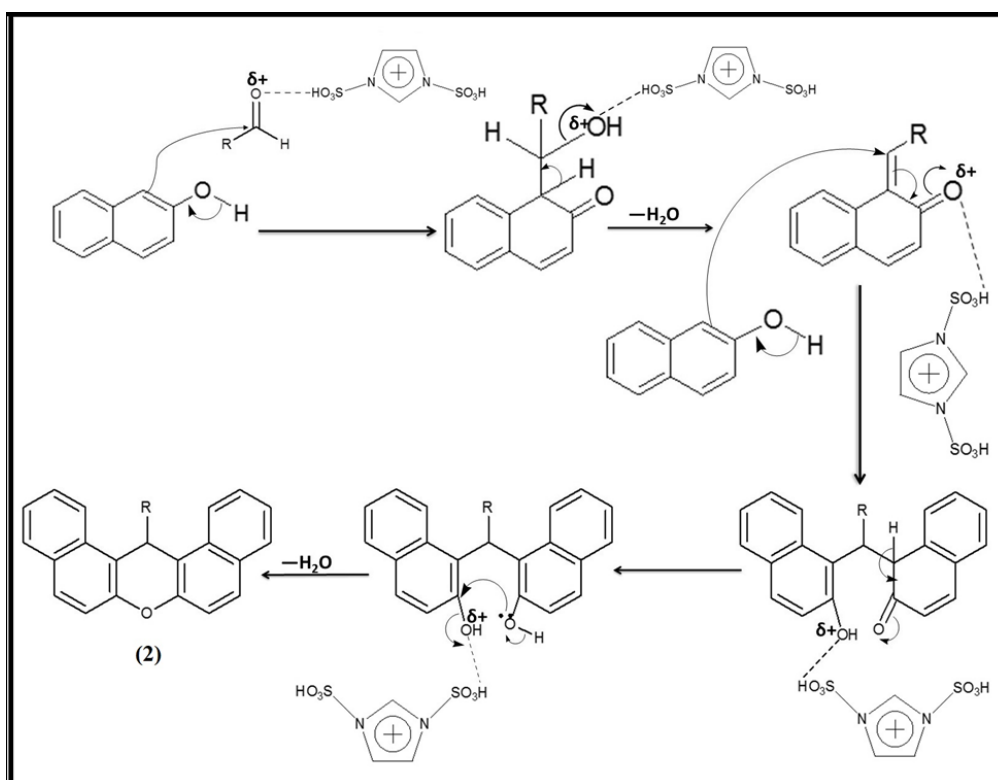
<sup>a</sup> Isolated yields ; <sup>b</sup> Methods A : using 25 mol % of ionic liquid **IL-2** at 100 °C ; B : Using 25 mol % of ionic liquid **IL-3** at 90 °C;

### 2.2.3. Plausible Mechanism

The plausible mechanism for the synthesis of 1,8-dioxo-decahydroacridine and dibenzoxanthene catalysed by IL was shown below (**Scheme-2.2a** and **Scheme-2.2b**).



**Scheme-2.2a:** Plausible mechanism of synthesis of 1,8-dioxo-decahydroacridine

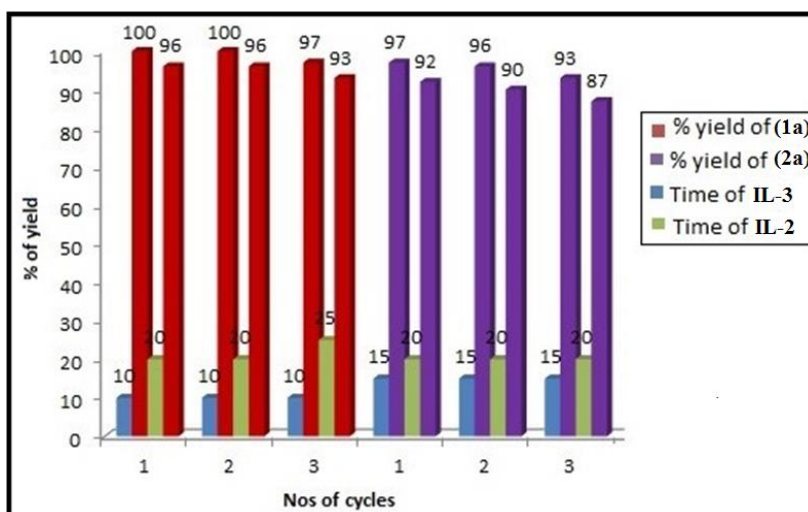


**Scheme-2.2b:** Plausible mechanism of synthesis of dibenzoxanthene

#### 2.2.4. Reusability test

The reusability of the ionic liquids **IL-2** and **IL-3** were expressed by using bar diagram (**Fig.2.5**) for three consecutive runs for the synthesis of 1, 8-dioxo-

decahydroacridine (**1a**) and dibenzoxanthene (**2a**) under the optimized reaction conditions in solvent-free medium. Recyclability study indicated the high catalytic activity of the two ILs even after the third run with slight increasing reaction time.



**Fig.2.5:** Reusability curve of **IL-2** and **IL-3**

## 2.3. Conclusion

In summary, a new group of 1, 3- disulfonic acid imidazolium carboxylate ionic liquids was prepared and characterized by different analytical techniques. The acidity order of these ionic liquids in Hammett plot was identical with their catalytic activity for the one-pot synthesis of 1,8-dioxodecahydroacridine (**1**) in solvent-free or aqueous medium and dibenzoxanthene (**2**) derivatives in solvent-free condition under thermal treatment in good to excellent yields.

## 2.4. Experimental Section

### 2.4.1. General information

All chemicals were purchased from chemical suppliers and used without any purification. Thin layer chromatography was monitored on glass plate using Merck silica gel. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were run on a JEOL 400 MHz spectrometer ( $\delta$  in ppm) in DMSO- $d_6$  and  $\text{CDCl}_3$  solvents. FT-IR spectra were recorded on a Nicolet Impact-410 spectrometer. The Hammett plot of the ILs was measured on an UV 2550 spectrophotometer using 4-nitroaniline as basic indicator. The thermal stability of the three ionic liquids was performed on Shimadzu TGA 50. Perkin Elmer 20 analyzer was utilized for elemental

analysis of all compounds. Melting points were recorded on a Buchi-545 apparatus and compared with the literature data for known derivatives of both this heterocycle [11-14]. All the products were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR and CHN analysis.

#### **2.4.2. Experimental procedure**

##### **(a) Preparation of 1, 3 di-sulfonic acid imidazolium carboxylate ionic liquid [DSIM][X] where X= [CH<sub>3</sub>COO], [CCl<sub>3</sub>COO], [CF<sub>3</sub>COO]**

All these ionic liquids were prepared by mixing of equal amount of (5 mmol) [DSIM][Cl] ionic liquids and carboxylic acids ( CH<sub>3</sub>COOH, CCl<sub>3</sub>COOH, CF<sub>3</sub>COOH) in dry dichloromethane (12 ml) in a 50 ml two necked round bottom flask at room temperature within 30 mins. The HCl gas outlet was connected to a vacuum system through water and an alkali trap. The mixture was continued to stirring for one hour to complete the elimination of produced HCl gas and then diluted with 10 ml of dry CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> layer was decanted and washed the residue by more of it (3 x 10 mL). The ionic liquid residue was dried under vacuum to get [DSIM][X] as reddish colored viscous liquids with 98-100 % yields.

##### **(b) General procedure for the synthesis of 1,8-dioxo-decahydroacrdine derivatives (1)**

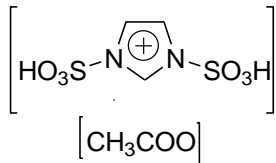
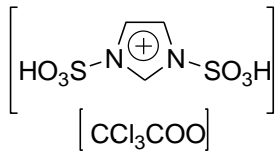
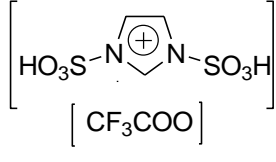
A mixture of dimedone (2 mmol), aldehydes (1 mmol), ammonium chloride (1 mmol) and ionic liquid (25 mol %) was heated in an oil bath for the specified temperature in absence of any solvent (or in 1 mL of water). After completion of the reaction as monitored by TLC, the product was extracted from the ionic liquid phases using dry dichloromethane (3 x 3 mL) as solvent. The product was isolated through distillation of dichloromethane solution under reduced pressure and the ionic liquid medium was again used for next cycle of reaction. The solid product was purified by recrystallization in aqueous ethanol (15 %) to get analytically pure product.

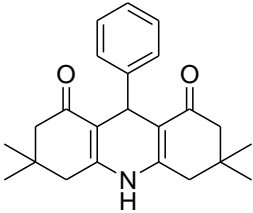
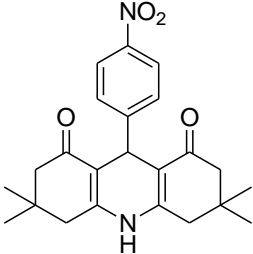
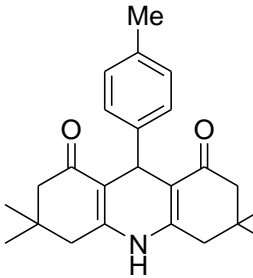
##### **(c) General procedure for the synthesis of dibenzoxanthene derivatives (2)**

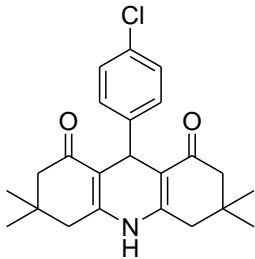
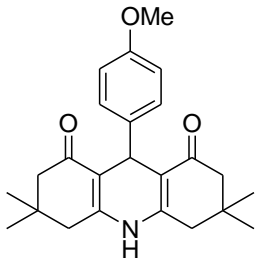
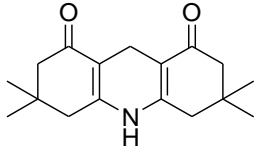
A mixture of 2-naphthol (2 mmol), aldehyde (1mmol) and ionic liquid (25 mol %) was heated in an oil bath for the specified temperature in absence of any solvent. After completion of the reaction as monitored by TLC, the product was extracted from the ionic liquid phases using dry dichloromethane (3 x 3 mL) as solvent. The product was isolated through distillation of dichloromethane solution under reduced pressure and the ionic liquid medium was again used for next cycle of reaction. The crude product, thus isolated

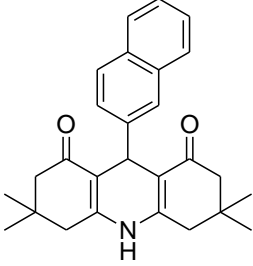
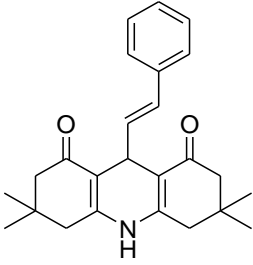
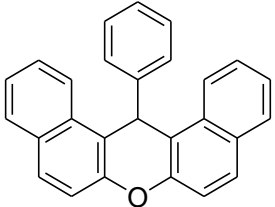
was subjected to further purification by recrystallization in aqueous ethanol (15%) to get analytically pure product.

### 2.4.3. Spectral data of ionic liquids, 1,8-dioxodecahydroacridinone (1) and 14-substituted-14*H*-dibenzo[*a,j*]xanthenes (2)

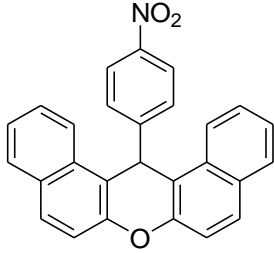
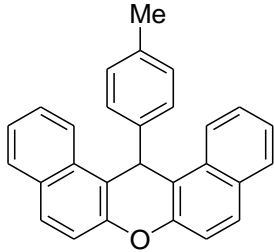
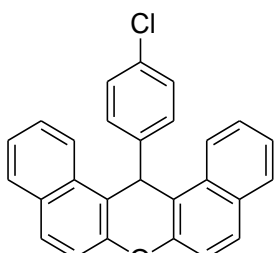
Products	Spectral data
	<p><b>1,3-Di-sulfonic-acid-imidazoliumacetate, [DISM][CH<sub>3</sub>COO] (IL-1):</b> Light reddish oil, 98% yield; FT-IR (KBr): 3556, 3453, 3217, 1709, 1644, 1592, 1435, 1180, 1048, 878, 764, 586 cm<sup>-1</sup>; <sup>1</sup>HNMR (400 MHz, DMSO-d<sub>6</sub>): δ 1.79 (s, 3H), 7.53 (s, 2H), 8.91 (s, 1H), 11.30 (s, 1H), 14.17 (s, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ 21.5, 119.8, 134.7, 172.6; CHN analysis (%): C<sub>5</sub>H<sub>8</sub>O<sub>8</sub>S<sub>2</sub>N<sub>2</sub>, Cal. C 20.83, H 2.80, N 9.70; Found C 20.91, H 2.84, N 9.73.</p>
	<p><b>1,3-Di-sulfonic-acid-imidazoliumtrichloroacetate, [DISM][CCl<sub>3</sub>COO] (IL-2):</b> Dark reddish oil, 100% yield; FT-IR (KBr): 3416, 3316, 1748, 1639, 1591, 1433, 1192, 1048, 876, 764, 688, 585 cm<sup>-1</sup>; <sup>1</sup>HNMR (400 MHz, DMSO-d<sub>6</sub>): δ 7.46 (s, 2H), 8.87 (s, 1H), 12.77 (s, 1H), 14.2 (s, 1H); <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>6</sub>): δ 79.6, 120.0, 134.5, 163.0; CHN analysis (%): C<sub>5</sub>H<sub>5</sub>O<sub>8</sub>S<sub>2</sub>N<sub>2</sub>Cl<sub>3</sub>, Cal. C 15.35; H 1.27, N 7.15; Found C 15.38, H 1.30, N 7.19.</p>
	<p><b>1,3-Di-sulfonic-acid-imidazoliumtrifluoroacetate, [DISM][CF<sub>3</sub>COO] (IL-3):</b> Reddish oil, 100 % yield; FT-IR (KBr): 3531, 3420, 1751, 1640, 1588, 1432, 1178, 1054, 875, 765, 694, 587 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>): δ 7.48 (s, 2H), 8.89 (s, 1H), 13.42 (s, 1H), 14.14 (s, 1H); <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>6</sub>): δ 62.4, 119.7, 134.2, 134.6 158.6; CHN analysis (%): C<sub>5</sub>H<sub>5</sub>O<sub>8</sub>S<sub>2</sub>N<sub>2</sub>F<sub>3</sub>, Cal. C 17.69, H 1.51, N 8.16; Found C 17.72, H 1.54, N 8.19.</p>

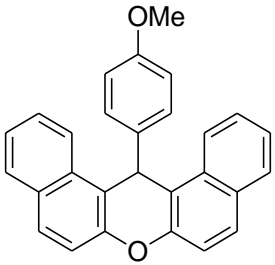
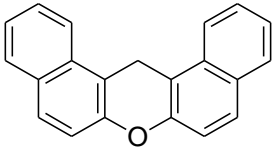
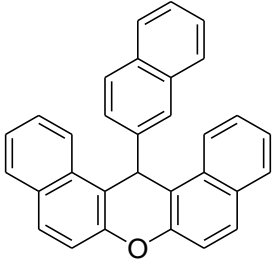
	<p><b>3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-phenylacridine-1,8(2<i>H</i>,5<i>H</i>,9<i>H</i>,10<i>H</i>)-dione (1a) (table-2.3, entry 1):</b> White solid; m.p. 287 °C; FT-IR (KBr): 3446, 3001, 2858, 1675, 1605, 1375, 1244, 1221, 1111, 1077, 1032, 882, 799 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.99 (s, 6H), 1.09 (s, 6H), 2.18(s, 2H), 2.20(s, 2H), 2.46 (s, 4 H), 4.75 (s, 1 H), 7.09 (m, 1H), 7.18-7.23 (m, 2H), 7.27-7.29 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 27.4, 29.3, 31.9, 32.3, 40.9, 50.8, 115.8, 126.4, 128.1, 128.5, 144.2, 162.3, 196.4; CHN analysis: Calculated for C<sub>23</sub>H<sub>27</sub>NO<sub>2</sub> (%): C 79.05, H 7.79, N 4.01; Found C 79.10, H 7.82, N 4.05.</p>
	<p><b>3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(4-nitrophenyl)acridine-1,8(2<i>H</i>,5<i>H</i>,9<i>H</i>,10<i>H</i>)-dione (1b) (table-2.3, entry 2):</b> Yellow solid; m.p. 286 °C; FT-IR (KBr): 3421, 2983, 2888, 1629, 1384, 1245, 1201, 1143, 1089, 1032, 866, 804 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.99 (s, 6H), 1.12 (s, 6H), 2.18(s, 2H), 2.23(s, 2H), 2.50 (s, 4 H) 4.83 (s, 1 H), 7.47 (d, 2H, <i>J</i>=8.7 Hz), 8.09 (d, <i>J</i>=8.7 Hz, 2H,); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 27.3, 29.3, 32.3, 32.4, 40.9, 50.7, 114.6, 123.5, 129.4, 146.6, 151.6, 163.0, 196.3; CHN analysis: Calculated for C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> (%): C 70.03, H 6.64 ,N 7.10; Found C 70.06, H 6.68, N 7.15.</p>
	<p><b>3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-p-tolylacridine-1,8(2<i>H</i>,5<i>H</i>,9<i>H</i>,10<i>H</i>)-dione (1c) (table-2.3, entry 3):</b> Pale white solid; m.p. 279 °C; FT-IR (KBr): 3418, 2993, 2865, 1605, 1575, 1370, 11243, 1206, 1147, 1078, 1024, 909, 826, 780 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.99 (s, 6H), 1.09 (s, 6H), 2.18(s, 2H), 2.21(s, 2H), 2.25(s, 4H), 2.45(s, 3H), 4.71 (s, 1H), 7.02(d, 2H, <i>J</i>= 7.8 Hz), 7.18 (d, 2H, <i>J</i>=7.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.1, 27.5, 29.4, 31.5, 32.3, 40.9, 50.8, 115.8, 128.3, 128.9, 135.9, 141.3, 162.2, 196.5; CHN analysis: Calculated for C<sub>24</sub>H<sub>29</sub>NO<sub>2</sub> (%): C 79.30, H 8.04, N 3.85; Found C 79.27, H 8.08, N 3.88.</p>

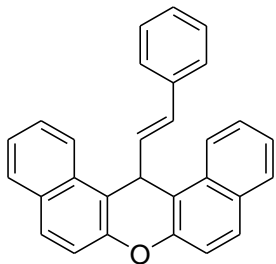
	<p><b>9-(4-Chlorophenyl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethylacridine-1,8(2<i>H</i>,5<i>H</i>,9<i>H</i>,10<i>H</i>)-dione (1d) (table-2.3, entry 4):</b> Brown solid; m.p. 300 °C; FT-IR (KBr): 3277, 2961, 2816, 1647, 1398, 1256, 1225, 1144, 1029, 1004, 977, 880, 730 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.94 (s, 6H), 1.06 (s, 6H), 2.12(s, 2H), 2.22 (s, 2H), 2.31 (s, 4H), 5.01 (s, 1H), 7.20 (d, 2H, <i>J</i>= 7.7 Hz), 7.34 (d, 2H, <i>J</i>=7.7 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 27.2, 29.6, 32.7, 33.7, 40.7, 51.0, 113.2, 126.0, 128.1, 146.7, 149.6, 196.1; CHN analysis: Calculated for C<sub>23</sub>H<sub>26</sub>ClNO<sub>2</sub> (%): C 71.96, H 6.83, N 3.65; Found C 72.01, H 6.86, N 3.68.</p>
	<p><b>3,4,6,7-Tetrahydro-9-(4-methoxyphenyl)-3,3,6,6-tetramethylacridine-1,8(2<i>H</i>,5<i>H</i>,9<i>H</i>,10<i>H</i>)-dione (1e) (table-2.3, entry 5) :</b> Pale white solid; m.p. 280 °C; FT-IR (KBr): 3293, 2956, 2845, 1628, 1484, 1393, 1295, 1257, 1161, 1063, 1009, 828 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.99 (s, 6H), 1.09 (s, 6H), 2.18(s, 2H), 2.21 (s, 2H), 2.45 (s, 4H), 3.73(s, 3H), 4.69 (s, 1 H), 6.76 (d, 2H, <i>J</i>= 7.8Hz), 7.21 (d, 2H, <i>J</i>=7.8Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 27.4, 29.4, 31.0, 32.3, 40.9, 47.1, 50.8, 55.3, 113.5, 115.9, 129.4, 136.6, 157.9, 162.2, 196.7; CHN analysis: Calculated for C<sub>23</sub>H<sub>29</sub>NO<sub>3</sub> (%): C 75.96, H 7.70, N 3.69; Found C 75.98, H 7.74, N 3.68.</p>
	<p><b>3,4,6,7-Tetrahydro-3,3,6,6-tetramethylacridine-1,8(2<i>H</i>,5<i>H</i>,9<i>H</i>,10<i>H</i>)-dione (1f) (table-2.3, entry 6):</b> White solid; m.p. 156 °C; FT-IR (KBr): 3432, 2962, 2880, 1609, 1376, 1246, 1239, 1151, 1083, 1026, 873, 809 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.05 (s, 12 H), 2.29(s, 8H), 3.16 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 15.9, 27.1, 29.5, 31.8, 46.0, 113.5, 189.5; CHN analysis: Calculated for C<sub>17</sub>H<sub>23</sub>NO<sub>2</sub> (%): C 74.73, H 8.42 ,N 5.13; Found C 74.71, H 8.44, N 5.15.</p>

	<p><b>3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(naphthalen-2-yl)acridine-1,8(2H,5H,9H,10H)-dione (1g) (table-2.3, entry 7):</b> Grey solid; m.p. 204 °C; FT-IR (KBr): 3768, 2956, 2875, 1666, 1462, 1361, 1195, 1144, 999, 928, 800, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.95 (s, 6H), 1.19(s, 6H), 2.06-2.22(m, 4H), 2.5(s, 4H), 5.52(s, 1H), 7.20(s, 1H), 7.30 (m,1H), 7.44(m, 1H), 7.60-7.62(m, 2H), 7.75(d, 1H, <i>J</i>=8.2 Hz), 8.81(s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 27.4, 29.4, 32.3, 41.0, 50.7, 116.9, 124.9, 125.7, 125.9, 127.5, 128.2, 131.7, 133.6, 162.2 196.7; CHN analysis: Calculated for C<sub>27</sub>H<sub>29</sub>NO<sub>2</sub> (%): C 81.2, H 7.27, N 3.51; Found C 81.18, H 7.30, N 3.50.</p>
	<p><b>3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-styrylacridine-1,8(2H,5H,9H,10H)-dione (1h) (table-2.3, entry 8):</b> Grey solid; m.p. 215 °C ; FT-IR (KBr): 3429, 2934, 1640, 1628, 1540, 1392, 1078, 1026, 874, 773 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.12(s, 12H), 2.29(s, 4H), 2.44(s, 4H), 4.41(d, 1H, <i>J</i>= 5.5 Hz), 6.27-6.31(m, 2H), 7.22-7.27 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 27.6, 27.9, 29.2, 32.2, 40.9, 50.8, 126.3, 127.1, 128.3, 130.4, 131.3, 137.2, 163.1, 196.5; CHN analysis: Calculated for C<sub>25</sub>H<sub>29</sub>NO<sub>2</sub> (%): C 80, H 7.73 , N 3.73; Found C 80.12 , H 7.76 , N 3.75.</p>
	<p><b>14-Phenyl-14H-dibenzo[a,j]xanthene (2a) (table-2.4, entry 1):</b> Pale yellow solid, m.p. 186 °C; FT-IR (KBr): 3061, 3020, 1624, 1592, 1513, 1458, 1409, 1249, 1077, 963, 804, 743 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.45 (s, 1H), 6.96 (t, 1H, <i>J</i>= 7.7 Hz), 7.12 (t, 2H, <i>J</i>= 7.7 Hz), 7.39 (t, 2H, <i>J</i>= 7.4 Hz), 7.45-7.47 (m, 4H), 7.52 (t, 2H, <i>J</i>= 7.3 Hz), 7.77 (d, 2H, <i>J</i>= 8.7 Hz), 7.80 (d, 2H, <i>J</i>= 8.0 Hz), 8.38 (d, 2H, <i>J</i>= 8.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 38.1, 118.0, 118.4, 122.7, 124.2, 126.8, 128.2, 128.5, 128.7, 128.8, 131.1, 131.4, 145.0, 148.8; CHN analysis: Calculated for C<sub>27</sub>H<sub>18</sub>O (%): C 90.50, H 5.02; Found: C 90.45, H 5.08.</p>



	<p><b>14-(4-Nitrophenyl)-14H-dibenzo[a,j]xanthene (2b) (table-2.4, entry 2):</b> Light yellow solid, m.p. 312 °C; FT-IR (KBr): 3418, 2924, 2853, 2372, 2188, 1719, 1591, 1509, 1397, 1335, 1240, 1099, 952, 810, 741 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.95 (s, 1H), 7.40-7.43 (m, 2H), 7.52 (d, 2H, <i>J</i>= 9.2 Hz), 7.58 (t, 2H, <i>J</i>= 7.8 Hz), 7.66 (d, 2H, <i>J</i>= 8.2 Hz), 7.81-7.86 (m, 4H), 7.98 (d, 2H, <i>J</i>= 8.2 Hz), 8.28 (d, 2H, <i>J</i>= 8.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 37.9, 116, 118.2, 122.2, 123.9, 124.8, 127.4, 129.0, 129.2, 129.8, 131.1, 146.5, 148.9, 152; CHN analysis: Calculated for C<sub>27</sub>H<sub>17</sub>O<sub>3</sub>N (%): C 80.39, H 4.21, N 3.47; Found C 80.45, H 4.26, N 3.53.</p>
	<p><b>14-(4-Methylphenyl)-14H-dibenzo[a,j]xanthene (2c) (table-2.4, entry 3):</b> Yellow solid, m.p. 228 °C; FT-IR (KBr): 3068, 2917, 1626, 1597, 1515, 1466, 1437, 1404, 1258, 1125, 1088, 966, 840, 816, 785, 746 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.31 (s, 3H), 6.15 (s, 1H), 6.77 (d, 2H, <i>J</i>= 7.8 Hz), 6.92 (t, 1H, <i>J</i>= 7.4 Hz), 7.13-7.17 (m, 6H), 7.28 (t, 1H, <i>J</i>= 6.9 Hz), 7.36 (d, 3H, <i>J</i>= 7.8 Hz), 7.69-7.79 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.1, 62.8, 111.8, 116.4, 121.4, 122.7, 126.8, 127.8, 128.9, 129.2, 129.4, 129.8, 130, 138.5, 146.6, 156, 199.8; CHN analysis: Calculated for C<sub>28</sub>H<sub>20</sub>O (%): C 90.32, H 5.37; Found C 90.36, H 5.43.</p>
	<p><b>14-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthene (2d) (table-2.4, entry 4):</b> White solid, m.p. 288 °C; FT-IR (KBr): 2926, 1590, 1485, 1243, 1083, 806 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.45 (s, 1H), 7.08 (d, 2H, <i>J</i>= 8.8 Hz), 7.37-7.44 (m, 5H), 7.48 (d, 1H, <i>J</i>= 8.7 Hz), 7.55 (t, 2H, <i>J</i>= 6.9 Hz), 7.77 (d, 2H, <i>J</i>= 8.7 Hz), 7.83 (d, 2H, <i>J</i>= 7.8 Hz), 8.31 (d, 2H, <i>J</i>= 8.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 37.5, 116.7, 117.8, 122.5, 124.3, 126.8, 128.5, 128.7, 129.0, 129.6, 131.0, 131.2, 143.5, 148.8; CHN analysis: Calculated for C<sub>27</sub>H<sub>17</sub>OCl (%): C 82.54, H 4.32; Found C 82.56, H 4.35.</p>

	<p><b>14-(4-Methoxyphenyl)-14H-dibenzo[a,j]xanthene (2e)</b> (table-2.4, entry 5): White solid, m.p. 204 °C; FT-IR (KBr): 3058, 1591, 1510, 1460, 1396, 1251, 962, 818, 745 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.56 (s, 3H), 6.45 (s, 1H), 6.65 (d, 2H, <i>J</i> = 8.2 Hz), 7.36-7.41 (m, 4H), 7.44 (d, 2H, <i>J</i> = 8.5 Hz), 7.56 (t, 2H, <i>J</i> = 7.6 Hz), 7.78 (d, 2H, <i>J</i> = 8.7 Hz), 7.82 (d, 2H, <i>J</i> = 8.3 Hz), 8.36 (d, 2H, <i>J</i> = 8.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 37.4, 55.5, 113.8, 117.5, 118.2, 122.8, 123.7, 124.2, 126.5, 126.7, 128.7, 129.0, 129.3, 131.2, 131.6, 137.4, 148.8, 157.9; CHN analysis: Calculated for C<sub>28</sub>H<sub>20</sub>O<sub>2</sub> (%): C 86.59, H 5.15; Found: C 86.62, H 5.20.</p>
	<p><b>14-Dihydro-dibenzo[a,j] xanthene (2f)</b> (table-2.4, entry 6): White solid; m.p. 135 °C; FT-IR (KBr): 3057, 1589, 1510, 1455, 1396, 1240, 1171, 1069, 955, 854, 802, 744 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.56 (s, 2H), 7.31 (d, 2H, <i>J</i> = 8.7 Hz), 7.46 (t, 2H, <i>J</i> = 7.3 Hz), 7.63 (m, 2H), 7.76 (d, 2H, <i>J</i> = 9.2 Hz), 7.85 (d, 2H, <i>J</i> = 7.8 Hz), 8.02 (d, 2H, <i>J</i> = 8.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 22.4, 111.0, 117.8, 122.4, 124.2, 126.8, 128.4, 128.5, 130.2, 132.2, 147.9; CHN analysis: Calculated for C<sub>21</sub>H<sub>14</sub>O (%): C 89.36, H 4.97; Found C 89.38, H 5.01.</p>
	<p><b>14-Naphthyl-14H-dibenzo[a,j]xanthene (2g)</b> (table-2.4, entry 7): Brown solid, m.p. 196-197 °C; FT-IR (KBr): 3058, 2378, 1591, 1509, 1398, 1356, 1242, 1158, 1070, 959, 807, 739 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.63 (s, 1H), 7.27-7.37 (m, 4H), 7.48-7.58 (m, 7H), 7.75-7.78 (m, 5H), 8.01 (s, 1H), 8.47 (d, 2H, <i>J</i> = 8.5 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 38.3, 117.0, 117.9, 122.7, 124.2, 126.5, 126.8, 127.4, 127.8, 128.8, 128.9, 131.1, 132.0, 133.0, 142.3, 148.7; CHN analysis: Calculated for C<sub>31</sub>H<sub>20</sub>O (%): C 91.18, H 4.90; Found: C 90.16, H 4.93.</p>

	<p><b>14-Cinnamyl-14H-dibenzo[a,j]xanthene (2h) (table-2.4, entry 8):</b> White solid; m.p. 181 °C; FT-IR (KBr): 2930, 1639, 1583, 1516, 1500, 1421, 1203, 1108, 957 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.33 (d, 1H, <i>J</i>= 5.1 Hz), 6.43-6.56 (m, 2H), 6.87 (d, 2H, <i>J</i>= 8.2 Hz), 7.25-7.27 (m, 5H), 7.32-7.41 (m, 4H), 7.45 (d, 2H, <i>J</i>= 8.7 Hz), 7.80 (d, 2H, <i>J</i>= 8.7 Hz), 8.35 (d, 2H, <i>J</i>= 8.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 40.1, 119.7, 122.8, 123.6, 123.8, 126.3, 127.0, 127.6, 128.0, 128.5, 129.8, 131.8, 134.3, 148.2, 155.7; CHN analysis: Calculated for C<sub>29</sub>H<sub>20</sub>O (%): C 90.62, H 5.20; Found: C 90.51, H 5.24.</p>
---	--

## References

- [1] Wasserscheid, P., & Keim, W. *Angew. Chem. Int. Ed.* **39**, 3773--3789, 2000.
- [2] Bates, E.D., et al. *J. Am. Chem. Soc.* **124**, 926--927, 2002.
- [3] Lee, S. *Chem. Commun.* 1049--1063, 2006.
- [4] Miao, W.S., & Chan, T.H. *Acc. Chem. Res.* **39**, 897--908, 2006.
- [5] Zolfigol, M.A., et al. *J. Org. Chem.* **77**, 3640--3645, 2012.
- [6] Zolfigol, M.A., et al. *Scientia Iranica C.* **19**, 1584--1590, 2012.
- [7] Shi, D.Q., et al. *J. Heterocycl. Chem.* **45**, 653--660, 2008.
- [8] Gong, K., et al. *Dyes Pigm.* **80**, 30--33, 2009.
- [9] Shirini, F., & Khaligh, N.G. *J. Mol. Liq.* **177**, 386--393, 2013.
- [10] Thomazeau, H., et al. *J. Am. Chem. Soc.* **125**, 5264--5265, 2003.
- [11] Vahdat, S.M., & Akbari, M. *Orient. J. Chem.* **27**, 1573--1580, 2011.
- [12] Saeed, C., et al. *Chin. J. Chem.* **27**, 1953--1956, 2009.
- [13] Rajitha, B., et al. *Tetrahedron Lett.* **46**, 8691--8693, 2005.
- [14] Kumar, R., et al. *Tetrahedron Lett.* **51**, 442--445, 2010.