



**SYNTHESIS, CHARACTERIZATION AND APPLICATION OF TWO NOVEL  
SULFONIC ACID FUNCTIONALIZED IONIC LIQUIDS AS EFFICIENT  
CATALYSTS IN THE SYNTHESIS OF 1,8-DIOXO-OCTAHYDROXANTHENES**

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**Abstract:** In this work, two novel sulfonic acid functionalized ionic liquids, 1-methyl-1-sulfonic acid pyrrolidinium chloride [MPyrSO<sub>3</sub>H]Cl (IL<sub>1</sub>) and 4-methyl-4-sulfonic acid morpholinium chloride [MMorSO<sub>3</sub>H]Cl (IL<sub>2</sub>), were simply prepared, characterized and used as highly efficient and reusable homogeneous catalysts to promote the synthesis of 1,8-dioxo-octahydroxanthenes by reaction of dimedone with aldehydes under solvent-free conditions.

**Keywords:** Sulfonic acid functionalized ionic liquids; 1,8-Dioxo-octahydroxanthenes; Solvent-free conditions.

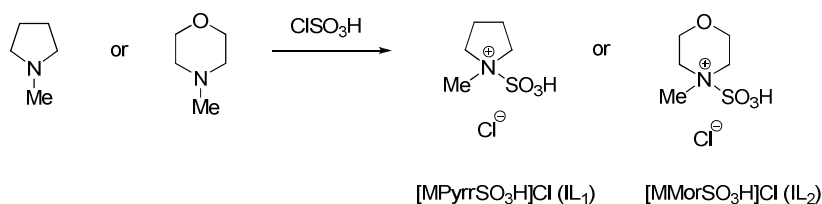
### **Introduction**

The development of environmentally benign, efficient and economical methods for the synthesis of organic compounds remains a significant challenge in synthetic chemistry. Green chemistry emphasizes the need for environmentally clean synthesis, which involves improvement in selectivity, high atom efficiency, elimination of hazardous solvents and reagents, and easy separation with recovery and reuse of catalysts.<sup>1,2</sup> As a result, volatile organic solvents are being replaced by non-toxic, nonvolatile media such as ionic liquids (ILs).<sup>3</sup> ILs, have attracted rising interest in the last decade in a variety of organic transformations as catalysts or dual catalyst-solvents.<sup>4</sup> The introduction of the SO<sub>3</sub>H functional group into the cationic or anionic part of the ILs, obviously enhanced their acidities and water solubilities and has made it possible to design new ILs with specific properties. Such ILs can be used as highly efficient acid catalysts and have been receiving extensive interest as green substitute for H<sub>2</sub>SO<sub>4</sub>, HCl, HF and AlCl<sub>3</sub> catalysts in chemical processes.<sup>5</sup>

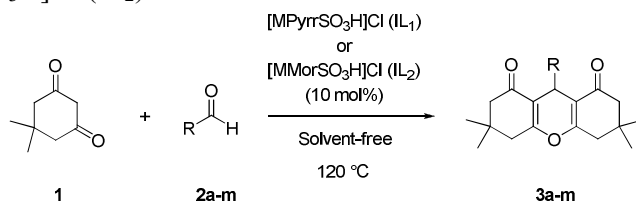
Xanthenes have received great attention because of their wide range of therapeutic and biological properties, such as antibacterial,<sup>6</sup> antiviral,<sup>7</sup> and anti-inflammatory activities.<sup>8</sup> In particular, xanthenediones constitute a structural unit in a number of natural products<sup>9</sup> and have been used as versatile synthons because of the inherent reactivity of the inbuilt pyran ring.<sup>10</sup> The most straightforward procedure for the synthesis of xanthenediones involves the condensation of aldehydes with 1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione (dimedone) in the presence of a variety of catalysts such as ZnO nanoparticles,<sup>11</sup> ceric

ammonium nitrate,<sup>12</sup> cellulose sulfonic acid,<sup>13</sup> trimethylsilyl chloride,<sup>14</sup> SbCl<sub>3</sub>/SiO<sub>2</sub>,<sup>15</sup> Fe<sup>3+</sup>-montmorillonite,<sup>16</sup> *p*-dodecylbenzenesulfonic acid,<sup>17</sup> hydrotrope,<sup>18</sup> polyaniline-*p*-toluenesulfonate salt,<sup>19</sup> Dowex-50W,<sup>20</sup> alumina supported acidic ionic liquid,<sup>21</sup> SmCl<sub>3</sub>,<sup>22</sup> L-proline,<sup>23</sup> and polyvinylpolypyrrolidone-supported boron trifluoride.<sup>24</sup> While each of these methods has its own advantage, many suffer from limitations such as prolonged reaction times, the use of relatively expensive catalysts, required use of organic solvents, unsatisfactory yields, and tedious isolation procedures. Thus the discovery of a new and efficient catalyst with high catalytic activity, short reaction times, recyclability, and simple reaction work-up for the preparation of 1,8-dioxo-octahydroxanthenes is of great interest.

In this view and in line with our interest on the development of environmentally friendly methods in organic transformations using green catalysts,<sup>25-35</sup> herein firstly we report the preparation of two new sulfonic acid functionalized ILs, 1-methyl-1-sulfonic acid pyrrolidinium chloride [MPyrrSO<sub>3</sub>H]Cl (IL<sub>1</sub>) and 4-methyl-4-sulfonic acid morpholinium chloride [MMorSO<sub>3</sub>H]Cl (IL<sub>2</sub>) (Scheme 1), and then investigate their catalytic activity as homogeneous and green catalysts in the synthesis of 1,8-dioxo-octahydroxanthenes by reaction of dimedone with aldehydes under solvent-free conditions (Scheme 2). Moreover, we have also investigated the recyclability of the prepared ILs as one of the most important factors of their environmental fate.



**Scheme 1.** The preparation of sulfonic acid functionalized ionic liquids, [MPyrrSO<sub>3</sub>H]Cl (IL<sub>1</sub>) and [MMorSO<sub>3</sub>H]Cl (IL<sub>2</sub>)



**Scheme 2.** Synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by sulfonic acid functionalized ionic liquids, [MPyrrSO<sub>3</sub>H]Cl (IL<sub>1</sub>) or [MMorSO<sub>3</sub>H]Cl (IL<sub>2</sub>)

## Experimental

All chemicals were available commercially and used without additional purification. Melting points were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Bruker 250, 400 and 500 FT spectrometers.

### Synthesis of ionic liquids [MPyrrSO<sub>3</sub>H]Cl (IL<sub>1</sub>) and [MMorSO<sub>3</sub>H]Cl (IL<sub>2</sub>)

To a solution of 1-methylpyrrolidine or 4-methylmorpholine (5 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL), chlorosulfonic acid (5 mmol) was added dropwise over a period of 10 min at 10 °C. Afterward, the reaction mixture was allowed to heat to room temperature with stirring, and stirred for another 4 h. The solvent was evaporated *in vacuo*, and the liquid residue was washed with diethyl ether (2×10 ml) and dried *in vacuo* at 70 °C to give [MPyrrSO<sub>3</sub>H]Cl (IL<sub>1</sub>) or [MMorSO<sub>3</sub>H]Cl (IL<sub>2</sub>) as viscous pale yellow oils in high yields.

1-Methyl-1-sulfonic acid pyrrolidinium chloride [MPyrrSO<sub>3</sub>H]Cl (**IL**<sub>1</sub>): Pale yellow oil, Yield 93%. IR (KBr disc):  $\nu$  3600-2400, 1645, 1463, 1185, 1112, 1047, 865, 582 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO):  $\delta$  1.85-1.92 (m, 4H, 2CH<sub>2</sub>), 2.64 (s, 3H, CH<sub>3</sub>), 3.00-3.04 (m, 4H, 2CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, d<sub>6</sub>-DMSO):  $\delta$  23.9, 41.2, 55.5.

4-Methyl-4-sulfonic acid morpholinium chloride [MMorSO<sub>3</sub>H]Cl (**IL**<sub>2</sub>): Pale yellow oil, Yield 91%. IR (KBr disc):  $\nu$  3600-2400, 1645, 1463, 1186, 1113, 1043, 865, 575 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO):  $\delta$  2.77 (s, 3H, CH<sub>3</sub>), 3.10-3.20 (m, 4H, 2CH<sub>2</sub>), 3.75-3.85 (m, 4H, 2CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, d<sub>6</sub>-DMSO):  $\delta$  43.5, 53.5, 64.3.

*General procedure for the synthesis of 1,8-dioxo-octahydroxanthenes 3a-m catalyzed by [MPyrrSO<sub>3</sub>H]Cl (**IL**<sub>1</sub>) or [MMorSO<sub>3</sub>H]Cl (**IL**<sub>2</sub>)*

To a mixture of dimedone (**1**) (2 mmol), and an aldehyde **2a-m** (1 mmol), in a round bottom flask, IL<sub>1</sub> or IL<sub>2</sub> (10 mol% based on aldehyde) was added. The mixture was heated in the oil bath at 120 °C for 6-14 min and the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and warm water (10 mL) was added to it, stirred for 5 min and filtered. The solid residue was collected and recrystallized from ethanol (96%) to give the pure products **3a-m** in high yields.

9-(4-Chlorophenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (**3b**): IR (KBr disc):  $\nu$  3050, 2952, 1661, 1626, 1489, 1469, 1361, 1198, 1166, 1140, 853 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.99 (s, 6H, 2CH<sub>3</sub>), 1.10 (s, 6H, 2CH<sub>3</sub>), 2.20 (AB<sub>q</sub>,  $\Delta\nu$  = 30.0 Hz,  $J_{AB}$  = 16.3 Hz, 4H, 2CH<sub>2</sub>), 2.46 (s, 4H, 2CH<sub>2</sub>), 4.71 (s, 1H, CH), 7.21 (AB<sub>q</sub>,  $\Delta\nu$  = 18.0 Hz,  $J$  = 8.5 Hz, 4H, arom-H).

9-(3-Bromophenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (**3e**): IR (KBr disc):  $\nu$  3079, 2957, 1676, 1626, 1472, 1428, 1359, 1199, 1164, 1137, 999, 806 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.01 (s, 6H, 2CH<sub>3</sub>), 1.11 (s, 6H, 2CH<sub>3</sub>), 2.21 (AB<sub>q</sub>,  $\Delta\nu$  = 24.0 Hz,  $J_{AB}$  = 16.3 Hz, 4H, 2CH<sub>2</sub>), 2.48 (s, 4H, 2CH<sub>2</sub>), 4.71 (s, 1H, CH), 7.09 (t,  $J$  = 7.8 Hz, 1H, arom-H), 7.24 (d,  $J$  = 8.5 Hz, 1H, arom-H), 7.30 (d,  $J$  = 7.7 Hz, 1H, arom-H), 7.35 (s, 1H, arom-H).

9-(4-Fluorophenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (**3f**): IR (KBr disc):  $\nu$  3062, 2958, 1661, 1627, 1508, 1468, 1363, 1223, 1199, 1167, 1141, 851 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.99 (s, 6H, 2CH<sub>3</sub>), 1.10 (s, 6H, 2CH<sub>3</sub>), 2.20 (AB<sub>q</sub>,  $\Delta\nu$  = 29.0 Hz,  $J_{AB}$  = 16.3 Hz, 4H, 2CH<sub>2</sub>), 2.46 (s, 4H, 2CH<sub>2</sub>), 4.72 (s, 1H, CH), 6.90 (t,  $J$  = 8.7 Hz, 2H, arom-H), 7.23-7.28 (m, 2H, arom-H).

9-(4-Nitrophenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (**3g**): IR (KBr disc):  $\nu$  3015, 2959, 1663, 1516, 1471, 1362, 1344, 1201, 1167, 1139, 851 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.00 (s, 6H, 2CH<sub>3</sub>), 1.13 (s, 6H, 2CH<sub>3</sub>), 2.22 (AB<sub>q</sub>,  $\Delta\nu$  = 36.0 Hz,  $J_{AB}$  = 16.4 Hz, 4H, 2CH<sub>2</sub>), 2.50 (s, 4H, 2CH<sub>2</sub>), 4.83 (s, 1H, CH), 7.48 (d,  $J$  = 8.4 Hz, 2H, arom-H), 8.10 (d,  $J$  = 8.4 Hz, 2H, arom-H).

9-(4-Methoxyphenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (**3i**): IR (KBr disc):  $\nu$  3012, 2959, 1667, 1626, 1511, 1463, 1359, 1261, 1195, 1165, 1138, 842 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.02 (s, 6H, 2CH<sub>3</sub>), 1.13 (s, 6H, 2CH<sub>3</sub>), 2.22 (AB<sub>q</sub>,  $\Delta\nu$  = 31.3 Hz,  $J_{AB}$  = 16.2 Hz, 4H, 2CH<sub>2</sub>), 2.48 (s, 4H, 2CH<sub>2</sub>), 3.76 (s, 3H, OCH<sub>3</sub>), 4.73 (s, 1H, CH), 6.78 (d,  $J$  = 8.6 Hz, 2H, arom-H), 7.22 (d,  $J$  = 8.6 Hz, 2H, arom-H).

9-(Thiophene-2-yl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (**3k**): IR (KBr disc):  $\nu$  3073, 2959, 2927, 1664, 1623, 1466, 1426, 1367, 1329, 1196, 1166, 1138, 999, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  1.05 (s, 6H, 2CH<sub>3</sub>), 1.11 (s, 6H, 2CH<sub>3</sub>), 2.26 (s, 4H, 2CH<sub>2</sub>), 2.45 (s, 4H, 2CH<sub>2</sub>), 5.15 (s, 1H, CH), 6.82 (dd,  $J$  = 5.0, 3.5 Hz, 1H, arom-H), 6.96 (d,  $J$  = 2.5 Hz, 1H, arom-H), 7.02 (d,  $J$  = 5.0 Hz, 1H, arom-H).

9-Ethyl-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (**3l**): IR (KBr disc):  $\nu$  2,952, 1,661, 1,361, 1,198, 1,166, 1,140 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  0.66 (t,  $J$  = 7.5 Hz,

3H, CH<sub>3</sub>), 1.11 (s, 12H, 4CH<sub>3</sub>), 1.55-1.62 (m, 2H, CH<sub>2</sub>), 2.27 (s, 4H, 2CH<sub>2</sub>), 2.38 (s, 4H, 2CH<sub>2</sub>), 3.80 (t, *J* = 7.8 Hz, 1H, CH).


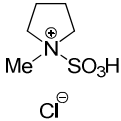
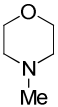
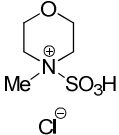
## Results and discussion

### Characterization of the ILs

The structures of IL<sub>1</sub> and IL<sub>2</sub> were deduced from their spectral and microanalytical data. The difference between chemical shifts in <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra of these new ILs and their starting materials, 1-methylpyrrolidine and 4-methylmorpholine, confirmed that these catalysts were exactly synthesized. For example, as shown in Table 1, while two multiplets at  $\delta = 1.65$ -1.70 and 2.32-2.37 ppm and a singlet at  $\delta = 2.22$  ppm were observed in <sup>1</sup>H NMR spectrum for methylene and methyl groups in 1-methylpyrrolidine, [MPyrrSO<sub>3</sub>H]Cl (IL<sub>1</sub>) showed the multiplets at  $\delta = 1.85$ -1.92 and 3.00-3.04 ppm along with a singlet at  $\delta = 2.64$  ppm. Also, the chemical shifts in <sup>13</sup>C NMR spectrum have shifted from  $\delta = 24.5$ , 42.7 and 56.6 ppm for 1-methylpyrrolidine to  $\delta = 23.9$ , 41.2 and 55.5 ppm for [MPyrrSO<sub>3</sub>H]Cl (IL<sub>1</sub>). Because of wide broadening, probably, the signals of OH groups in <sup>1</sup>H NMR spectra were not observed for the ILs. Furthermore, the IR spectra of these ILs showed broad peaks at 2400-3600 cm<sup>-1</sup> related to the OH of SO<sub>3</sub>H groups. Other significant absorption bands in FT-IR spectrum have been reported in experimental section. Further proof came from microanalytical data which showed satisfactory elemental analysis data corresponding to the molecular formula C<sub>5</sub>H<sub>12</sub>ClNO<sub>3</sub>S and C<sub>5</sub>H<sub>12</sub>ClNO<sub>4</sub>S for IL<sub>1</sub> and IL<sub>2</sub>, respectively (Experimental).

**Table 1**

Comparison of chemical shifts in <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra of the ILs, [MPyrrSO<sub>3</sub>H]Cl (IL<sub>1</sub>) and [MMorSO<sub>3</sub>H]Cl (IL<sub>2</sub>), and their starting materials

	1-Methylpyrrolidine 	[MPyrrSO <sub>3</sub> H]Cl (IL <sub>1</sub> ) 	4-Methylmorpholine 	[MMorSO <sub>3</sub> H]Cl (IL <sub>2</sub> ) 
<sup>1</sup> H NMR (500 MHz, d <sub>6</sub> -DMSO, 25 °C, TMS), $\delta$	1.65-1.70 (m, 4H, 2CH <sub>2</sub> )	1.85-1.92 (m, 4H, 2CH <sub>2</sub> )	2.14 (s, 3H, CH <sub>3</sub> )	2.77 (s, 3H, CH <sub>3</sub> )
	2.22 (s, 3H, CH <sub>3</sub> )	2.64 (s, 3H, CH <sub>3</sub> )	2.23-2.33 (m, 4H, 2CH <sub>2</sub> )	3.10-3.20 (m, 4H, 2CH <sub>2</sub> )
	2.32-2.37 (m, 4H, 2CH <sub>2</sub> )	3.00-3.04 (m, 4H, 2CH <sub>2</sub> )	3.55-3.58 (m, 4H, 2CH <sub>2</sub> )	3.75-3.85 (m, 4H, 2CH <sub>2</sub> )
<sup>13</sup> C NMR (125 MHz, d <sub>6</sub> -DMSO, 25 °C, TMS), $\delta$	24.5	23.9	46.9	43.5
	42.7	41.2	56.1	53.5
	56.6	55.5	66.8	64.3

### 3.2. Catalytic performance of [MPyrrSO<sub>3</sub>H]Cl IL<sub>1</sub> and [MMorSO<sub>3</sub>H]Cl IL<sub>2</sub> in the synthesis of 1,8-dioxo-octahydroxanthenes

In order to evaluate the catalytic efficiency of the new ILs in the synthesis of 1,8-dioxo-octahydroxanthenes and to determine the most appropriate reaction conditions; initially a model study was carried out on the synthesis of compound **3b** by reaction of dimedone (**1**) (2 mmol), and 4-chlorobenzaldehyde (**2b**) (1 mmol), in different sets of reaction conditions (Table 2). As can be seen, among the tested solvents such as H<sub>2</sub>O, EtOH, EtOAc, CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and also solvent-free conditions and various amounts of the catalyst, the shortest time and best yield was achieved in solvent-free conditions. It was also found that the yield of compound **3b** was strongly affected by the catalyst amount and reaction temperature

in solvent-free conditions. None of the product **3b** was formed in the absence of the catalyst at 120 °C following a 90 min reaction time (entry 1) indicating that the catalyst is necessary for the reaction. Increasing the amount of the catalyst and reaction temperature up to 10 mol% (based on 4-chlorobenzaldehyde) and 120 °C, respectively, increased the yield of the product **3b**, whereas further increase in both catalyst amount and temperature did not improve the product yield and reaction time.

**Table 2**

Optimization of reaction conditions for synthesis of compound **3b** catalyzed by [MPyrrSO<sub>3</sub>H]Cl (**IL**<sub>1</sub>) or [MMorSO<sub>3</sub>H]Cl (**IL**<sub>2</sub>)<sup>a</sup>

Entry	Catalyst (mol%)	Solvent	T (°C)	Time (min)	Isolated Yield (%)
				IL <sub>1</sub> /IL <sub>2</sub>	IL <sub>1</sub> /IL <sub>2</sub>
1	-----	-----	120	90	-----
2	3	-----	90	25/30	23/19
3	3	-----	100	25/30	25/24
4	3	-----	120	15/20	50/47
5	5	-----	90	25/25	27/23
6	5	-----	100	20/25	38/36
7	5	-----	120	15/15	58/57
8	7	-----	90	15/20	31/29
9	7	-----	100	15/20	43/40
10	7	-----	120	12/15	66/64
11	10	-----	90	8/10	47/46
12	10	-----	100	6/8	69/64
13	10	-----	120	6/6	98/93
14	10	-----	140	8/8	96/92
15	12	-----	90	10/10	47/45
16	12	-----	120	8/8	97/93
17	10	H <sub>2</sub> O	Reflux	140/160	54/52
18	10	EtOH	Reflux	90/100	79/78
19	10	EtOAc	Reflux	100/120	67/64
20	10	CH <sub>3</sub> CN	Reflux	100/120	72/71
21	10	CH <sub>2</sub> Cl <sub>2</sub>	Reflux	120/120	60/57
22	10	CHCl <sub>3</sub>	Reflux	120/140	37/33

<sup>a</sup>Reaction conditions: dimedone (**1**) (2 mmol), and 4-chlorobenzaldehyde (**2b**) (1 mmol).

The optimized conditions were used to construct a variety of 1,8-dioxo-octahydroxanthenes. It was found that this method is effective with a variety of aromatic aldehydes independent of the nature of the substituents in the aromatic ring. As illustrated in Table 3, in all cases the expected products were obtained in high yields and short reaction times. Under the same conditions however, moderate yields of the products were obtained using aliphatic aldehydes. Also, as depicted, IL<sub>1</sub> proved to be the better catalyst than IL<sub>2</sub> in terms of yield.

**Table 3**

Synthesis of 1,8-dioxo-octahydroxanthenes **3a-m** using [MPyrrSO<sub>3</sub>H]Cl (**IL**<sub>1</sub>) or [MMorSO<sub>3</sub>H]Cl (**IL**<sub>2</sub>)<sup>a</sup>

Entry	R	Product	Time (min)	Isolated Yield (%)	m.p. (°C)		
					IL <sub>1</sub> /IL <sub>2</sub>	IL <sub>1</sub> /IL <sub>2</sub>	Found
1	C <sub>6</sub> H <sub>5</sub>	<b>3a</b>	6/7	91/85	IL <sub>1</sub> /IL <sub>2</sub>	205-206	203-205 [11]
2	4-ClC <sub>6</sub> H <sub>4</sub>	<b>3b</b>	6/6	98/93	IL <sub>1</sub> /IL <sub>2</sub>	233-234	230-232 [14]
3	2-ClC <sub>6</sub> H <sub>4</sub>	<b>3c</b>	8/8	92/89	IL <sub>1</sub> /IL <sub>2</sub>	226-228	225-226 [11]
4	4-BrC <sub>6</sub> H <sub>4</sub>	<b>3d</b>	6/6	95/91	IL <sub>1</sub> /IL <sub>2</sub>	232-234	232-233 [11]
5	3-BrC <sub>6</sub> H <sub>4</sub>	<b>3e</b>	6/7	95/88	IL <sub>1</sub> /IL <sub>2</sub>	188-190	190-192 [24]
6	4-FC <sub>6</sub> H <sub>4</sub>	<b>3f</b>	8/8	91/86	IL <sub>1</sub> /IL <sub>2</sub>	226-228	226-227 [15]
7	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	<b>3g</b>	6/6	95/91	IL <sub>1</sub> /IL <sub>2</sub>	228-230	224-226 [17]
8	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	<b>3h</b>	6/8	90/86	IL <sub>1</sub> /IL <sub>2</sub>	171-173	168-170 [17]
9	4-MeOC <sub>6</sub> H <sub>4</sub>	<b>3i</b>	7/8	93/90	IL <sub>1</sub> /IL <sub>2</sub>	244-245	244-246 [16]

10	4-HOC <sub>6</sub> H <sub>4</sub>	<b>3j</b>	7/8	88/86	246-248	249-251 [16]
11	2-Thienyl	<b>3k</b>	8/8	86/85	162-163	163-165 [11]
12	Et	<b>3l</b>	12/14	55/48	144-146	[23]
13	n-Pr	<b>3m</b>	12/13	76/69	134-136	[23]

<sup>a</sup>Reaction conditions: dimedone (**1**) (2 mmol), aldehyde **2a-m** (1 mmol), [MPyrrSO<sub>3</sub>H]Cl (**IL**<sub>1</sub>) or [MMorSO<sub>3</sub>H]Cl (**IL**<sub>2</sub>) (0.10 mmol, 10 mol% based on aldehyde), 120 °C, solvent-free.

The ability to recycle and reuse of the catalysts, **IL**<sub>1</sub> and **IL**<sub>2</sub>, was studied in this system. For this purpose, after completion of the reaction, the mixture was cooled to room temperature and warm water (40 °C) was added. The precipitated product was collected by filtration, and washed repeatedly with warm water. The combined filtrate was evaporated to dryness under reduced pressure. The residual ionic liquid was repeatedly washed with diethyl ether (3×5 mL) and dried under vacuum at 70 °C before carrying out the next catalytic cycle. We found that the catalyst could be used at least four times with only a slight reduction in activity.

At the end, we believe that these ILs can act as Brønsted acids and therefore promotes the reactions by increasing the electrophilic character of the carbonyl groups in the reactions.

### Conclusion

In conclusion, we have introduced two novel Brønsted acidic ionic liquids, [MPyrrSO<sub>3</sub>H]Cl (**IL**<sub>1</sub>) and [MMorSO<sub>3</sub>H]Cl (**IL**<sub>2</sub>), as highly efficient, green and homogeneous catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes by reaction of dimedone with aldehydes. The method was very fast and the desired products were obtained within a few minutes in good to high yields under solvent-free conditions at 120 °C. The catalyst can be recycled after a simple work-up, and used at least four times without substantial reduction in its catalytic activity. The procedure is also advantageous in the sense that it is a solvent-free reaction and therefore operates under environmentally friendly conditions.

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