

## Synthesis of Quinoxaline Derivatives using Sulfonic Acid Functionalized Imidazolium Salts as Highly Efficient and Reusable Brønsted Acidic Ionic Liquids Catalysts under Solvent-free Conditions

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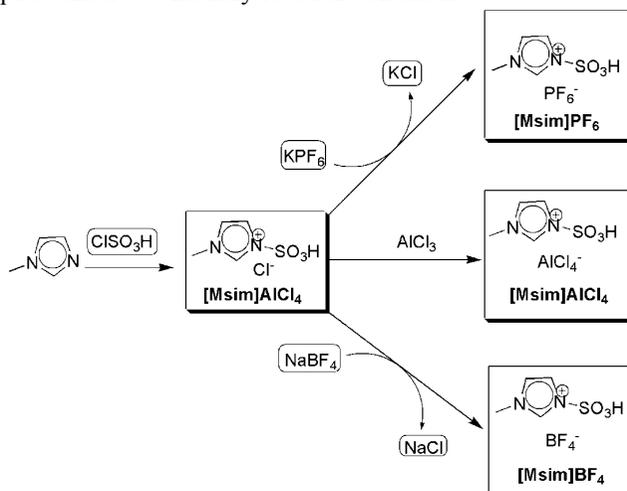
**Abstract:** A simple, highly efficient and green procedure for the condensation of aryl and alkyl 1,2-diamines with  $\alpha$ -diketones in the presence of catalytic amount of sulfonic acid functionalized imidazolium salts (SAFIS) is described. Using this method, quinoxaline derivatives as biologically interesting compounds are produced in high to excellent yields and short reaction times. Environmentally benign, simple methodologies, easy workup procedure, clean reaction, short reaction time, high yield and easy preparation of the catalysts are some advantages of this work. In this work, some sulfonic acid functionalized imidazolium salts (SAFIS), as a new category of ionic liquids, are synthesized by eco-friendly and simple procedures, and used as highly efficient and reusable catalysts to promote the following one-pot organic transformations under solvent-free conditions.

**Keywords:** Quinoxalines synthesis, Sulfonic acid functionalized imidazolium salts, Acidic ionic liquids, Green chemistry

### Introduction

Ionic liquids (based imidazolium or other organic cations) have received considerable interest as eco-friendly solvents, catalysts and reagents in organic synthesis because of their unique properties, such as low volatility, non-flammability, high thermal stability, negligible vapor pressure and ability to dissolve a wide range of materials<sup>1-9</sup>. Among them, Brønsted acidic ionic liquids, with the useful characteristics of solid acids and mineral liquid acids, have designed to replace the traditional mineral liquid acids like sulfuric acid and hydrochloric acid in chemical procedures<sup>10-14</sup>. Considering the unique properties of imidazolium salts with Brønsted acidic property and their successful applications in organic transformations<sup>6-9</sup>, more recently, we have synthesized some sulfonic acid functionalized imidazolium salts, with Brønsted acidic property, including ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}<sup>10-13</sup>, ionic liquid 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl} and 3-methyl-1-sulfonic acid imidazolium tetrachloroaluminate {[Msim]

$\text{AlCl}_4\}$  (as a solid)<sup>13</sup> and successfully applied them as highly efficient catalysts and reagents in organic synthesis<sup>10-13</sup>. Along this line, in this presented work, we have reported the preparation of two sulfonic acid functionalized imidazolium salts (SAFIS), 3-methyl-1-sulfonic acid imidazolium hexafluorophosphate(V)  $\{[\text{Msim}]\text{PF}_6\}$  and 3-methyl-1-sulfonic acid imidazolium tetrafluoroborate  $\{[\text{Msim}]\text{BF}_4\}$  as new ionic liquids (Scheme 1). We wish to use them as effective catalysts for different organic transformations. Herein, we have found that the preparation of quinoxalines derivatives can be efficiently performed in the presence of these ionic liquids under eco-friendly reaction conditions.

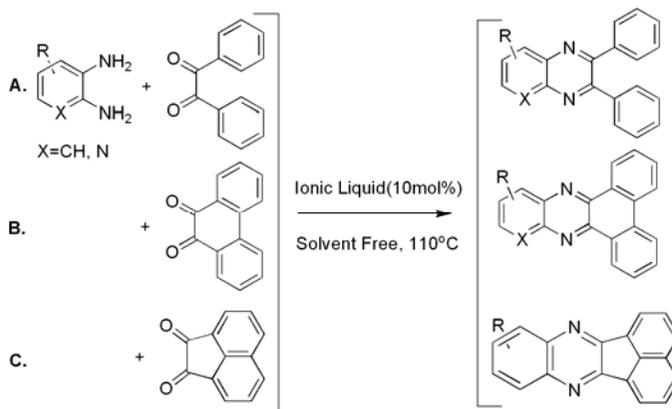


**Scheme 1.** The preparation of the sulfonic acid functionalized imidazolium salts  $\{[\text{Msim}]\text{X}\}$

Design of highly efficient chemical reactions, which provide maximum structural complexity and diversity with a minimum number of synthetic steps to assemble compounds, is a major challenge of modern drug discovery<sup>14</sup>. Recently, multicomponent reactions have emerged as a highly valuable synthetic tool in the context of modern drug discovery. Atom economy and convergent character, simplicity of a one-pot procedure, possible structural variations, accessible complexity of molecules and very large number of accessible compounds are among the described advantages of multicomponent reactions<sup>15</sup>. Thus, they are perfectly amenable to automation for combinatorial synthesis<sup>16,17</sup>. Quinoxaline derivatives are a very important class of nitrogen-containing compounds and have been widely used in dyes<sup>18</sup> pharmaceuticals<sup>19,20</sup> and electrical/photochemical materials<sup>21-26</sup>. Quinoxaline ring moiety constitute part of the chemical structures of various antibiotics such as Echinomycin, Levomycin and Actinoleutin<sup>27-28</sup>, that are known to inhibit growth of gram positive bacteria and are active against various transplantable tumors. A number of synthetic strategies have been developed for the preparation of substituted quinoxalines<sup>29-31</sup>. By far, the most common method relies on the condensation of an aryl 1,2-diamine with a 1,2-dicarbonyl compound in refluxing ethanol or acetic acid for 2–12 h giving 34–85% yields<sup>32</sup>. Recently, Heravi *et al.*<sup>33</sup>, and More *et al.*<sup>34</sup>, reported greener methods for the synthesis of quinoxaline derivatives in green solvents (EtOH/H<sub>2</sub>O), using copper sulphate pentahydrate and cerium (IV) ammonium nitrate as catalysts, respectively. 2,3-Disubstituted quinoxalines have also been prepared by Suzuki–Miyaura coupling reaction<sup>35</sup>, condensation of *o*-phenylenediamines and 1,2-dicarbonyl compounds in MeOH/AcOH under microwave irradiation<sup>36</sup>, iodine catalyzed cyclocondensation of 1,2-dicarbonyl compounds and substituted *o*-phenylene diamines in

DMSO<sup>37</sup> and CH<sub>3</sub>CN<sup>38</sup>. Different catalysts used for quinoxaline synthesis such as IBX<sup>39</sup>, Oxalic Acid<sup>40</sup>, SBSSA<sup>41</sup>, Microwave/I<sub>2</sub><sup>42</sup>, SnCl<sub>2</sub>/SiO<sub>2</sub><sup>43</sup>, I<sub>2</sub><sup>44</sup>, Ultrasound Irradiation<sup>45</sup>, NH<sub>4</sub>Cl<sup>46</sup>, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O<sup>47</sup>, Citric acid<sup>48</sup>, ionic liquid<sup>49</sup>, Bentonit Clay K-10<sup>50</sup>, AcOH<sup>51</sup> and BSA<sup>52</sup>. Nevertheless, many of the reported methods are associated with one or more of the following drawbacks: low yields, long reaction times, the use of large amount of catalyst, the use of toxic or expensive catalysts and inefficiency of method.

In continuation of application of Bronsted acidic ionic liquid (BAIL) and solid acid<sup>55-62</sup>, we report here our results on the efficient solvent-free synthesis of 2,3-diarylquinoxalines, dibenzo[a,c]phenazines and acenaphto[1,2-b] quinoxalines in the presence of a catalytic amount of ionic liquids 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl}, 3-methyl-1-sulfonic acid imidazolium hexafluorophosphate(V) {[Msim]PF<sub>6</sub>} or 3-methyl-1-sulfonic acid imidazolium tetrafluoroborate {[Msim]BF<sub>4</sub>} under solvent-free conditions (Scheme 2). Interestingly, these methods for the preparation of the quinoxalines derivatives have none of the above-mentioned drawbacks at all.



**Scheme 2.** Quinoxalines synthesis by the sulfonic acid functionalized imidazolium salts (SAFIS)

## Experimental

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. The <sup>1</sup>H NMR (500 or 300 MHz) and <sup>13</sup>C NMR (125 or 75 MHz) were run on a Bruker Avance DPX. FT-NMR spectrometer ( $\delta$  in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Optical rotations were measured in spectral grade solvents using a Perkin–Elmer 341 polarimeter.

### Preparation of ionic liquid [Dsim]Cl

To a round-bottomed flask (100 mL) containing imidazole (0.340 g, 5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL), was added chlorosulfonic acid (1.177 g, 10.2 mmol) drop wise over a period of 20 min at room temperature. After the addition was completed, the reaction mixture was stirred for 12 h under pressure of nitrogen (to remove the produced HCl) and allowed to stand for 5 min and the CH<sub>2</sub>Cl<sub>2</sub> was decanted. The residue was washed with dry CH<sub>2</sub>Cl<sub>2</sub> (3×50 mL) and dried under vacuum to give [Dsim]Cl as a viscous pale yellow oil in 95% yield, 1.257 g<sup>13</sup>.

### Preparation of ionic liquid [Msim]Cl

A round-bottomed flask (100 mL) was charged with 1-methylimidazole (0.410 g, 5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (50 mL) and then chlorosulfonic acid (0.583 g, 5 mmol) was added drop wise over a period of 5 min at room temperature. After the addition was completed, the reaction mixture was stirred for 20 min and allowed to stand for 5 min and the  $\text{CH}_2\text{Cl}_2$  was decanted. The residue was washed with dry  $\text{CH}_2\text{Cl}_2$  (3×50 mL) and dried under vacuum to give [Msim]Cl as a viscous colorless oil in 97% yield, 0.964 g<sup>13</sup>.

### Preparation of ionic liquids [Msim]PF<sub>6</sub> and [Msim]BF<sub>4</sub>

A mixture of [Msim]Cl (0.993 g, 5 mmol) and KPF<sub>6</sub> (0.92 g, 5 mmol) or NaBF<sub>4</sub> (0.548 g, 5 mmol) in a round-bottomed flask (100 mL) was stirred for 12 h at 60 °C. Then to separate produced ionic liquid from KCl or NaCl, absolute ethanol (25 mL) was added to the reaction mixture, stirred for 2 min and filtered (KCl and NaCl are insoluble in absolute ethanol). The solvent of the filtrate was evaporated under vacuum to give [Msim]PF<sub>6</sub> or [Msim]BF<sub>4</sub> in 92% (1.421 g) and 94% (1.173 g) yields, respectively.

## Results and Discussion

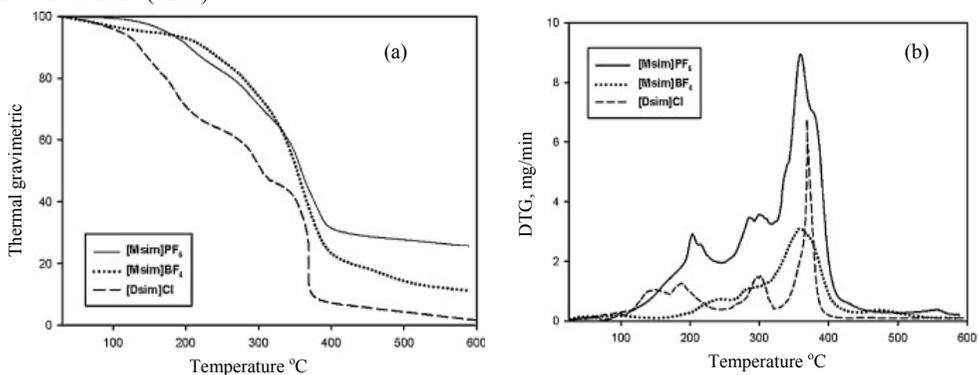
At first, ionic liquid 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl} was prepared by the reaction of imidazole (1 eq.) with chlorosulfonic acid (2 eq.) in  $\text{CH}_2\text{Cl}_2$  (Scheme 1)<sup>13</sup>. In the next step, 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} was prepared by the reaction of 1-methylimidazole with chlorosulfonic acid in  $\text{CH}_2\text{Cl}_2$  with almost 100% atom economy<sup>10-13</sup>. Then, the other SAFIS, 3-methyl-1-sulfonic acid imidazolium hexafluorophosphate(V) {[Msim]PF<sub>6</sub>} and 3-methyl-1-sulfonic acid imidazolium tetrafluoroborate {[Msim]BF<sub>4</sub>}, were prepared by anion exchange procedure (Scheme 1). As it is shown in Scheme 1, [Msim]Cl was reacted with Lewis acids KPF<sub>6</sub> and NaBF<sub>4</sub> to afford ionic liquids [Msim]PF<sub>6</sub> and [Msim]BF<sub>4</sub>, respectively. The structures of the SAFIS were identified by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR as well as mass spectra. The corresponding spectral data are reported in the Experimental section.

In another study, to confirm that [Msim]Cl was completely converted to [Msim]BF<sub>4</sub>, a solution of AgNO<sub>3</sub> in distilled water was added to a solution of [Msim]BF<sub>4</sub> in distilled water. The absence of AgCl precipitate indicates complete conversion of the [Msim]Cl to [Msim]BF<sub>4</sub>.

Thermal gravimetric analysis (TGA) of the sulfonic acid functionalized imidazolium salts were also studied (Figure 1). As thermal gravimetry (TG) and differential thermal gravimetric (DTG) diagrams indicate, weight losses of [Dsim]Cl happened in four steps after 150 °C and [Msim]PF<sub>6</sub> and [Msim]BF<sub>4</sub> were decomposed after 200 °C and 230 °C, respectively. The TG pattern of [Msim]PF<sub>6</sub> and [Msim]BF<sub>4</sub> is similar to single stage decomposition in which no intermediate was exactly identified. But, we observed multistage decomposition pattern in [Dsim]Cl. Some weight losses were observed about 10%, 30%, 15% and 44% which can be related to loss of  $\text{CH}_2 = \text{CH}_2$  or HCl, SO<sub>3</sub>, CH<sub>3</sub>CN and ClSO<sub>3</sub>H, correspondingly. Therefore, [Msim]PF<sub>6</sub>, [Msim]BF<sub>4</sub> and [Dsim]Cl could be applied as catalysts under 200 °C, 230 °C and 150 °C.

In our initial study on the applicability of the SAFIS in organic synthesis, we investigated the preparation of 2,3-diarylquinoxalines from benzene-1,2-diamines and 1,2-dicarbonyl compounds in the presence of them (Scheme 1). For this purpose, the condensation of 2,3-diphenylquinoxaline (1 mmol) with benzil (1 mmol) was examined using different amounts of [Dsim]Cl, [Msim]PF<sub>6</sub> or [Msim]BF<sub>4</sub> at various temperatures

under solvent-free conditions. The results are summarized in Table 1. Interestingly, the three SAFIS were highly efficient, and 10 mol% of them was sufficient to afford the product in excellent yields and in very short reaction times at 110 °C (Table 1, entry 4). No improvement in the reaction results was observed by increasing the amount of the catalysts and the temperature. Optimization of  $[H^+]$  is very important. When  $[H^+]$  increased, activities of phenyldiamine for attaching to carbonyl group decreased and it needs more time for cyclization and quinoxaline synthesis. The solvent-free condensation was also tested at 110 °C without catalyst in which the reaction did not significantly progress even after long reaction time (12 h).



**Figure 1.** (a) Thermal gravimetry and (b) differential thermal gravimetry of the [Dsim]Cl, [Msim]PF<sub>6</sub> and [Msim]BF<sub>4</sub>

**Table 1.** Effect of amounts of the catalysts and temperature on the condensation of phenylenediamine (1 mmol) with benzil (1 mmol)

Entry	Catalyst amount, mol%	Temp. °C	[Dsim]Cl		[Msim]PF <sub>6</sub>		[Msim]BF <sub>4</sub>	
			Time min	Yield <sup>a</sup> %	Time min	Yield <sup>a</sup> %	Time min	Yield <sup>a</sup> %
1	–	110	600	32	600	29	600	30
2	5	110	8	88	14	89	17	91
3	7.5	110	5	90	9	93	10	90
4	10	110	2	98	3	98	5	97
5	10	120	3	97	6	99	6	95
6	10	100	5	92	8	90	11	91
7	10	90	9	93	11	91	12	92
8	10	80	14	90	15	89	18	87
9	15	110	3	98	6	98	7	98

<sup>a</sup>Isolated yield

1,2-Diamines was condensed with benzyl, phenanthrene-9,10-dione and acenaphthylene-1,2-dione using [Dsim]Cl, [Msim]PF<sub>6</sub> or [Msim]BF<sub>4</sub> (results summarized in Table 2). As it can be seen in Table 2, all catalysts were highly efficient and general, and gave the desired quinoxalines in high yields and short reaction times.

**Table 2.** The solvent-free synthesis of quinoxalines using the sulfonic acid functionalized imidazolium salts (SAFIS)

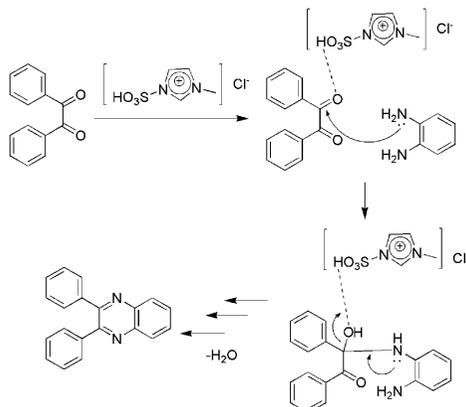
Entry	Product <sup>b</sup> (Q)	[Dsim]Cl		[Msim]PF <sub>6</sub>		[Msim]BF <sub>4</sub>		M.P °C[Found] [Lit.]
		Time min	Yield %	Time min	Yield %	Time min	Yield %	
1		2	98	3	98	5	97	125 -126 128 -129[37]
2		2	94	3	92	4	90	113 -115 116 -117[38]
3		20	95	25	93	30	90	127 -128
4		15	95	18	95	30	92	140 -142 139-140[45]
5		25	92	30	92	30	90	185 -186 185 -187[38]
6		45	89	50	87	50	82	143 -145
7		50	92	50	91	50	90	134 -137 141 -142[54]
8		20	91	25	89	25	89	134 -136 148 -150[39]
9		30	90	35	89	35	90	188 -189 ----[43]
10		55	88	60	85	45	86	124 -126
11		40	90	35	90	45	84	120 -122
12		40	90	40	88	50	85	131 -134

Contd...

13		2	92	4	92	5	88	123 -125 129 -131[38]
14		15	87	18	86	25	81	145 -147 [44]
15		2	99	3	96	3	97	225 -226 223 -225[38]
16		5	96	7	93	8	95	218 -220 208 -210[38]
17		10	98	15	91	20	94	245 -246
18		40	86	45	91	55	84	215 -216
19		20	94	20	90	35	89	259 -260
20		35	91	35	90	45	90	221 -223
21		30	94	45	93	50	90	159 -162
22		25	93	40	90	35	91	321-323
23		2	97	4	98	5	95	228 -229 300[38]
24		30	93	35	90	45	88	229 -231
25		5	91	10	90	18	90	235-236 238-240[38]
26		30	94	45	88	50	91	224-226

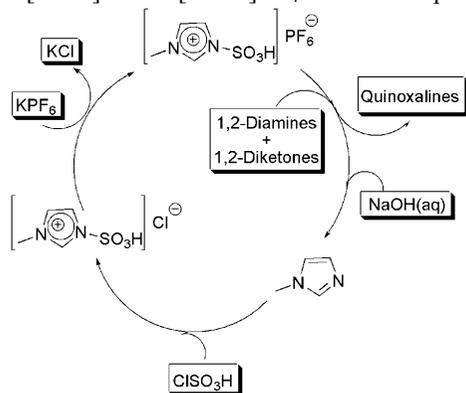
In a plausible mechanism (Scheme 3), at first, 1,2-diketone compounds is activated by the acidic group of [Dsim]Cl (or the other SAFIS). Then, benzene-1,2-diamines attacks to

the carbonyl group of the activated 1,2-diketones. Next, by removing H<sub>2</sub>O, quinoxaline is prepared. [Dsim]Cl again activates intermediate, afterward, by removing H<sub>2</sub>O, 2,3-diphenyl-quinoxaline forms.



**Scheme 3.** The plausible mechanism for the condensation reaction of benzene-1,2-diamine with benzil using the SAFIS

As previously showed, [Dsim]Cl, [Msim]PF<sub>6</sub> and [Msim]BF<sub>4</sub> were highly efficient and general for the synthesis of the quinoxaline derivatives. To raise the catalysts worth, their recoverability and reusability were studied. For this purpose, the reaction of benzene-1,2-diamine with benzil using [Msim]PF<sub>6</sub> was carried out several times, and the reaction mixtures were combined. Afterward, H<sub>2</sub>O was added to the combined reaction mixtures, stirred for 5 min, and filtered [Msim]PF<sub>6</sub> is soluble in H<sub>2</sub>O; however, the reaction mixture is not soluble in H<sub>2</sub>O. In the aqueous media, a quantity of [Msim]PF<sub>6</sub> hydrolyzed to 1-methylimidazole (as monitored on TLC) and H<sub>2</sub>SO<sub>4</sub>. To complete hydrolysis of [Msim]PF<sub>6</sub>, and consequently formation of 1-methylimidazole, a solution of NaOH (10%) was added to the filtrate, and stirred for 5 min. The solution was extracted with *t*-butylmethyl ether, washed with H<sub>2</sub>O and dried. Evaporation of the solvent gave 1-methylimidazole. The recovered 1-methylimidazole was reacted with chlorosulfonic acid to give [Msim]Cl. [Msim]Cl was reacted with NaPF<sub>6</sub> to produce [Msim]PF<sub>6</sub>. The catalytic activity of the reproduced [Msim]PF<sub>6</sub> was as same as the first one. The regeneration of this catalyst is summarized in Scheme 4. [Dsim]Cl and [Msim]BF<sub>4</sub> were also reproduced accordingly.



**Scheme 4.** The regeneration of [Msim]PF<sub>6</sub>

It should be mentioned that [Msim]Cl and [Msim]AlCl<sub>4</sub> were also successfully employed in the synthesis of the quinoxaline derivatives and the results were similar to [Dsim]Cl, [Msim]PF<sub>6</sub> and [Msim]BF<sub>4</sub>.

## Conclusion

We have introduced some novel sulfonic acid functionalized imidazolium salts including [Dsim]Cl, [Msim]PF<sub>6</sub> and [Msim]BF<sub>4</sub> as highly efficient, regenerable catalysts for organic transformations. For instance, in this work, the synthesis of quinoxalines derivatives by the one-pot condensation reaction, were efficiently catalyzed by these imidazolium salts. The promising points for the presented methodology are efficiency, generality, high yields, very short reaction times, cleaner reaction profile, simplicity, ease of preparation of the catalyst.

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