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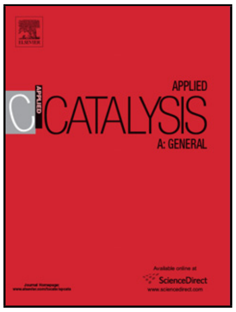

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Brönsted acid ionic liquids catalyzed Friedel-Crafts Alkylations of electron-rich arenes with aldehydes

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Abstract

Triarylmethanes (TRAMs) and diarylalkanes (DIAAs) are valuable intermediates with wide applications in many fields. TRAMs are usually obtained from the acid-catalysed bisarylation of activated aryl aldehydes. However, the synthesis poses many problems, such as harsh reaction conditions, and the disposal of the excess solvents and/or toxic metal waste etc. In this study, some functionalized ionic liquids including Brönsted acid ionic liquids (BAILs) and traditional ionic liquids were designed and synthesized. BAILs catalyzed Friedel-Crafts (F-C) alkylation was applied in this specific reaction for the first time. And the BAILs showed bifountional properties acting as catalyst and solvent. Research shows that BAILs can be used for catalyzing F-C alkylations of electron-rich arenes with aromatic or aliphatic aldehydes successfully under mild reaction conditions. Furthermore, BAILs containing triflic anion has higher activity than other BAILs and traditional ionic liquids. [HSO_3-pmim][OTf] gets the highest yields in the presence of 20 mol % of BAILs at 40 ºC to give the corresponding TRAMs derivatives. After five cycles, the yields remains about 93%～97%. Finally, according to IR spectrum and the experimental validation, the aromatic electrophilic substitution reaction was considered to be the possible catalysis mechanisms.

Keywords: Triarylmethane; Functionalized ionic liquids; Friedel-Crafts; alkylation; Aldehydes.

1. Introduction

Triarylmethanes (TRAMs) and diarylalkanes (DIAAs) have been extensively applied as key intermediates in synthesis, medicine, and industrial chemistry [1], including photochromic agents [2], dyes [3], protective groups [4], and building blocks for dendrimers and NLOs [5,6]. Ring-hydroxylated TRAMs were also reported to exhibit antioxidant, antitumor, antitubercular, antiviral, antifungal and anti-inflammatory activities [7].

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Due to their interesting chemical properties, synthesis process of TRAMs and DIAAs have received more and more attention mainly about Friedel-Crafts (F-C) alkylation of electron-rich arenes with aldehydes and their imines [8-10]. The process involves a multistep F-C alkylation promoted by Lewis or Bronsted acids such as $AuCl_3$ [11], $[Ir(COD)Cl]_2$-$SnCl_4$ [12], $ZnBr_2/SiO_2$ [13], $FeCl_3/Ac_2O$ [14], $Bi_2(SO_4)_3$/TMSCl [15], molecular iodine [16], TfOH [17,18], silica gel-supported $NaHSO_4$ [19], *o*-benzenedisulfonimide [20], polystyrene-supported sulfonic acid [21], perfluorinated sulfonic acid resin (Nafion-H) [22], montmorillonite [23, 24] and so on. However these methods encounter with many problems, such as longer reaction time, low yield of products, harsh reaction conditions, and generation of acidic waste, especially the use of hazardous and expensive catalysts, and volatile organic solvents. So, the development of green catalysts and non-volatile solvents can be of great significance.

The emergence of ionic liquids (ILs) has provided new option to solve the above problems. Over the past few years, ILs have attracted considerable attention as an environmentally benign alternative for organic synthesis procedures [25-31]. Compared with traditional Brönsted acid catalysts, Brönsted acid ionic liquids (BAILs) have more advantages such as, non-volatility, non-flammability, good chemical and thermal stability over a wide temperature range, and good solubility with many organic compounds. Recently, some research have focused on the synthesis of strong BAILs and applied as dual solvent–catalyst for esterification [32,33], Fischer indole synthesis [34,35], Mannich Reaction [36], dehydration [37], Beckmann rearrangement [38] and so on [39-47]. However, to the best of our knowledge, the BAILs were not used as both environmentally friendly novel catalysts and green solvents to catalyze F-C alkylation. Here, we report BAILs catalyzed F-C alkylation using electron-rich arenes with aromatic or aliphatic aldehydes to generate either TRAMs or DIAAs respectively without any solvents, especially under mild reaction conditions.

In this study, a series of functionalized ionic liquids (FILs) including Brönsted acid ionic liquids and traditional ionic liquids were designed and synthesized shown in Scheme **1**. Then the above ILs was applied to catalyze F-C alkylation reaction of 1,2,4-trimethoxybenzene (**1a**) with benzaldehyde (**2a**) , which was chosen as model reaction to investigate the synthesis of bis(2,4,5-trimethoxyphenyl)phenylmethane (**3a**). After optimization, the catalysis process with FILs $[HSO_3$-pmim][OTf] was investigated. Some important factors, such as system temperature, reaction time and the amount of catalyst, different kinds of aldehydes and electron-rich arenes were investigated. Moreover, the recycling and reuse of $[HSO_3$-pmim][OTf] was investigated. Finally, the possible catalysis mechanisms were probed.

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2. Experimental

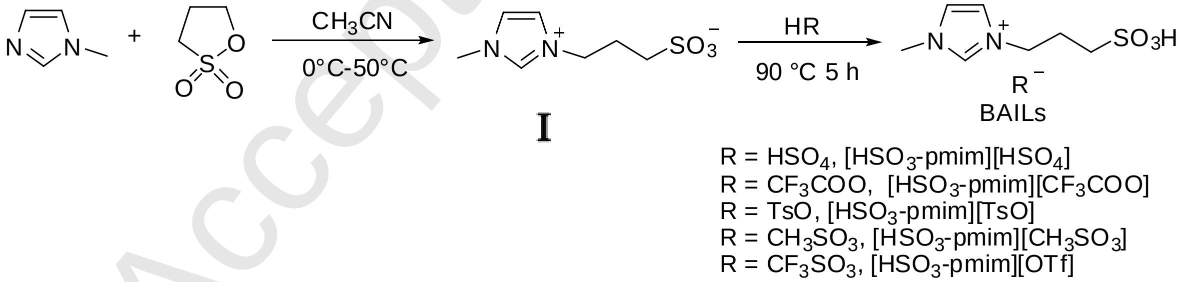
2.1. Materials and methods

Reagents used in the study were purchased as the analytical reagent grade and used without further purification. TLC analyses were performed using percolated TLC silica gel F_{254} plates. Melting points were recorded on X - 4 digital microscopic melting point apparatus. NMR spectra were recorded on an Avance III-400 (Bruker) NMR spectrometer.

2.2. BAILs Preparation

BAILs were prepared according to reference [46]. A stoichiometric amount of 1,3-propane sultone was added dropwise to a solution of *N*-methylimid-azole or triethylamine in acetonitrile at 0 ºC, and then the mixture was stirred at 50 °C for 3 h. The obtained white powder was filtered, washed with diethyl ether for 3 times and dried in vacuo to afford pure 1-alkyl-3-(alkyl-3-sulfonate) imidazolium zwitterions ( ). The precursor of BAILs ( ) was characterized by ^{1}H NMR.

After the synthesis of zwitterionic precursor (I), a stoichiometric amount of acid aqueous solution was added into it and stirred at 90 °C for 5 h. The BAILs were obtained by rotary distillation and vacuum drying. The synthesis routes were summarized in Scheme **1**.



Scheme 1. Synthesis of BAILs

2.3. General procedure for triarylmethanes and diarylalkanes synthesis

A mixture of aldehyde **2** (1.0 mmol), aromatic compound **1** (2.0 mmol) and BAILs (0.2 mmol) was stirred at 40 °C for the desired time. The reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, 1 ml of water was added into the reaction mixture, and the target compound

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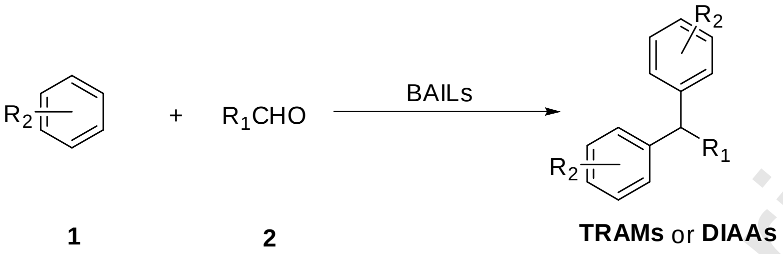
was obtained though simple filtration. The pure ionic liquids got by drying the filtrate were reused for another cycle. Synthesis route is listed in Scheme **2**.



Scheme 2. Synthesis route of TRAMs and DIAAs catalyzed by BAILs

3. Results and discussion

3.1 Selection of BAILs

The designable property makes it possible the diversity of functionalized ILs. So the proper chosen of ILs is very important for the F-C alkylation reaction process. The selection of ILs including traditional ionic liquids (in Table **1** entries **1-2**) and Brönsted acid ionic liquids (BAILs) was probed. The result was shown in Table **1**. Seven types of BAILs were used for catalyzing F-C alkylations of electron-rich 1,2,4-trimethoxybenzene (**1a**) with benzaldehyde (**2a**). The corresponding TRAM bis(2,4,5-trimethoxyphenyl) phenylmethane (**3a**) at 40°C (Scheme **3**) were obtained. There is no other extra solvent added during the reaction process. Results show that [HSO_3-pmim][OTf] was chosen as catalyst, the yields 99% was achieved in 30 minutes. Furthermore, the reaction can be realized free of traditional volatile organic solvent. However, traditional ionic liquids were not efficient for the reaction (Table **1**, entries **1** and **2**). To be noted, it can be observed that the BAILs containing triflic anion get higher yields than other BAILs. At the same time, it can be observed that there is no relationship between the catalytic capability and acidic strength, which was also reported by previous literatures [46,48].

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Table 1. Friedel-Crafts Alkylation reaction of **1a** and **2a** in the presence of ILs

Entry	IL	Time/h	Yield^b/%
1	[BMIM][BF_4]	12	0
2	[BMIM][PF_6]	12	0
3	[HSO_3-pmim][OTf]	0.5	99
4	[HSO_3-pmim][CF_3COO]	6	86

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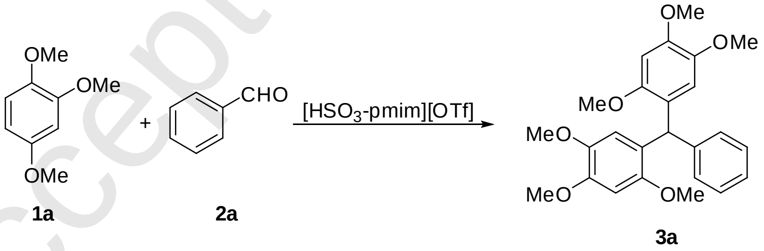
5	$[HSO_3\text{-pmim}][CH_3SO_3]$	8	83
6	$[HSO_3\text{-pmim}][HSO_4]$	5	80
7	$[HSO_3\text{-pmim}][TsO]$	6	78

[a] Reaction conditions: 1,2,4-trimethoxybenzene (**1a**, 2.00 mmol), benzaldehyde (**2a**, 1.00 mmol), catalysts (0.2 mmol), 40 °C, solvent free. [b] Isolated yield.

3.2 Optimization of the reaction conditions

In this section, the reaction of arene (**1a**) with aldehyde (**2a**) was also chosen as typical one for the synthesis of **3a**. $[HSO_3\text{-pmim}][OTf]$, was chosen as catalyst and solvent. Some factors including the effect of system temperature, reaction time, ratio of IL (mol%) were investigated in detail (Table **2**). Results show that the reaction cannot realized without addition of $[HSO_3\text{-pmim}][OTf]$ (Table **2**, entry **1**). However, 1 mol % of $[HSO_3\text{-pmim}][OTf]$ was introduced into the system, the yield of 65% can be got in 5 h (Table **2**, entry **2**). With the increase of the amount of IL to 20 mol %, the reaction activity was strengthened and the reaction time was shortened obviously only in 0.5 h. At the same time, effect of system temperature was shown in table **2** entries **2**, **3**, **4**, **5** and **6**. Results show that higher temperature is not beneficial for the reaction process. So 40 °C was chosen as operation temperature throughout the investigation. At this temperature, the initial material was almost completely converted by TLC monitoring and the yield reach up to 99 % (Table **2**, entry **9**).



Scheme 3 Reaction of **1a** with **2a**

Table 2. $[HSO_3\text{-pmim}][OTf]$ catalyzed Friedel-Crafts Alkylation reaction of **1a** with **2a** in different conditions

Entry	IL (mol%)	Temp./ °C	Time/h	Yield[b]/%
1	0	rt	24	0
2	1	rt	5	65

3	1	40	0.5	77
4	1	50	0.5	77
5	1	60	0.5	76
6	1	70	0.5	76
7	10	40	0.5	85
8	15	40	0.5	91
9	20	40	0.5	99

[a] Reaction conditions: 1,2,4-trimethoxybenzene (**1a**) (2.00 mmol), benzaldehyde (**2a**) (1.00 mmol), solvent free ; [b] Isolated yield.

In order to prove the universality of F-C Alkylation reaction catalyzed by BAILs further, different substrates (**1** and **2**, in Scheme **2**) were chosen under the optimal conditions, which were shown in Table **3**. Eleven kinds of aldehydes including aromatic aldehyde and aliphatic aldehyde were chosen as electrophil reagent. There are different functional groups in aromatic ring of aromatic aldehydes including electron-donating group (Table **3**, entries **2-4**, and **8**) and electron-withdrawing group (Table **3,** entries **5-7**, and **9**). From results, BAILs can catalyze Friedel-Crafts Alkylation reaction of 1,2,4-Trimethoxybenzene with all kinds of aromatic aldehydes to get the corresponding symmetric TRAMs **3b-v** with high yields. Aromatic aldehyde including Electron-withdrawing group is beneficial for improving the yield of F-C Alkylation reaction. Then, different aliphatic aldehydes were chosen as substrates with electron-rich arene (**1a**) to get the DIAAs derivatives **3h** and **3i** (Table **3,** entries **10-11**). Interestingly, benzaldehyde (Table **3,** entry **10**) without any substituent group in aromatic ring achieve high yield about 99%. From the above investigation, it can be concluded that the Friedel-Crafts Alkylation reaction catalyzed by BAILs is suitable for different aldehydes including aromatic aldehydes (4-R_1CHO or 2-R_1CHO) and aliphatic aldehydes. And most of the reaction yields were more than 90%.

Table 3. [HSO_3-pmim][OTf] catalyzed Friedel-Crafts Alkylation reaction of electron-rich arene (**1a**) with various aldehydes[a]

Entry	R_1	Product	Time/h	Yield[b]/%
1	C_6H_5	**3a**	0.5	99
2	4-$CH_3OC_6H_4$	**3b**	4	83[c]

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3	4-$CH_3C_6H_4$	**3c**	3	90
4	2-OHC_6H_4	**3d**[c]	8	74[c]
5	4-$NO_2C_6H_4$	**3e**	0.5	94
6	4-ClC_6H_4	**3f**	0.5	91
7	4-FC_6H_4	**3g**	1	92
8	2-$CH_3OC_6H_4$	**3u**	0.5	92
9	2,6-$Cl_2C_6H_3$	**3v**	0.5	93
10	H	**3h**	0.5	99
11	C_5H_{11}	**3i**[c]	3	90[c]

[a] Reaction conditions: 1,2,4-trimethoxybenzene (2.00 mmol), aldehydes (1.00 mmol), [HSO_3-pmim][OTf] (0.2 mmol), 40 °C, solvent free. [b] Isolated yield. [c] The products were purified by chromatogram after filtration.

To probe if arenes have influence on F-C Alkylation reaction catalyzed by BAILs, various arenes as nucleophiles with 4-nitrobenzaldehyde or benzaldehyde were investigated at 40 °C, with 20 mol% [HSO_3-pmim][OTf] which was shown in Table **4**. With the decrease of methoxy group in quality (compounds **3a**, **3j**, **3l**), the electron cloud density on the benzene ring of nucleophiles is reduced correspondingly. At the same time, the activity of Friedel-Crafts Alkylation reaction gradually decrease, which can be reflected in the end time of reaction in turn (0.5h, 2h, 6h) and in the corresponding yields (99%, 86%, 45%). Moreover, the catalytic synthesis of compounds (for example, **3e**, **3k**, **3n**) is consistent with the above change rules. According to the theory of nucleophile reaction, when the aromatic ring of nucleophile is connected with weaker electron donor group such as methyl (**3q**) or withdrawing electron group such as nitryl (**3r**), the electron cloud density on the aromatic ring of nucleophile is lower. So F-C Alkylation reaction cannot be catalyzed by BAILs. It can be concluded that not all arenes is suitable for the F-C Alkylation reaction catalyzed by BAILs. Only electron-rich arenes can be chosen as all kinds of aldehydes.

Table 4. [HSO_3-pmim][OTf] catalyzed Friedel-Crafts Alkylation reaction of aromatic aldehydes with nucleophiles

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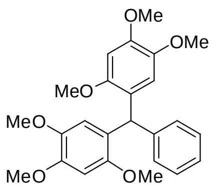
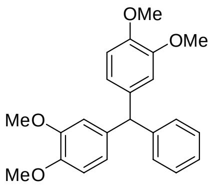
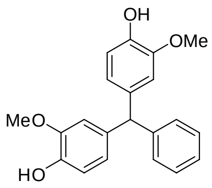


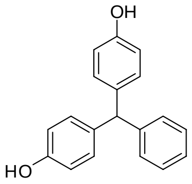
3a 0.5 h^{d}, (99%)



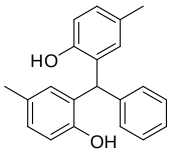
3j 2 h^{d}, (86%)



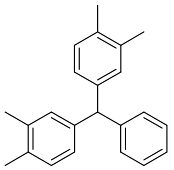
3l 6 h^{d}, (45%)^{c}



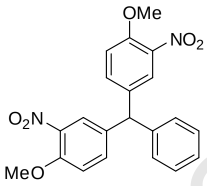
3o 7 h^{d}, (63%)



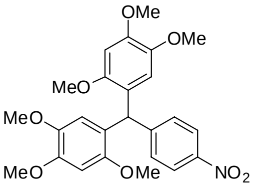
3p 6 h^{d,} (40%)^{c}



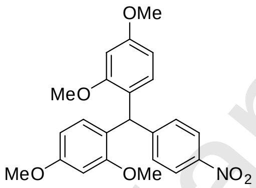
3q 12 h^{d}, (0%)



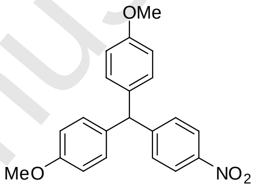
3r 12 h^{d}, (0%)



3e 0.5 h^{d}, (94%)



3k 2 h^{d}, (87%)



3n 3 h^{d}, (61%)

[a] Reaction conditions: nucleophiles (2.00 mmol), aromatic aldehydes (1.00 mmol), [HSO_3-pmim][OTf] (0.2 mmol), 40 °C, solvent free.

[b] Isolated yields after column chromatography. [c] 50 mol % [HSO_3-pmim][OTf] was used.

[d] The time reaction was completed.

3.3 Reuse of [HSO_3-pmim][OTf]

Reuse of BAILs was also carried out by using [HSO_3-pmim][OTf] (0.2 mmol) to catalyze model reaction of substitution **1a** (2.00 mmol) with **2a** (1.00 mmol) at 40 °C. After the completion of the reaction, 1 ml of water was added into the reaction mixture, and the target compound was got though simple filtration. The pure ILs was obtained by drying the filtrate. Then the recycled ILs can be reused for another cycles. The results are summarized in Fig **1**.The yields of 93%-99% were obtained during the five recycling cycles. This result shows that the BAILs based catalyst was stable. It is worth noting that the catalyst was recycled simply by evaporation of water.

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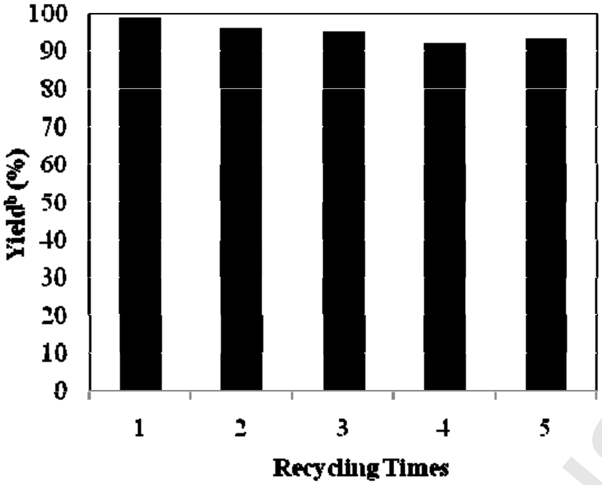

Fig 1. Recycling of [HSO_3-pmim][OTf]

^{a} Reaction conditions: substitution **1a** (2.00 mmol), **2a** (1.00 mmol), [HSO_3-pmim][OTf] (0.2 mmol), 40 °C, solvent free. ^{b} Isolated yield.

3.4 Alkylation mechanism catalyzed by Brönsted acid [HSO_3-pmim][OTf]

The possible mechanism is discussed as follows (Fig **2**). In general, it is a multistep Friedel–Crafts alkylation catalyzed by Brönsted acid [HSO_3-pmim][OTf]. Aromatic nucleophilic addition reaction was taken place for benzaldehyde at the very beginning; however, the reaction did not stop at this step. The compound diarylmethanol(Ⅱ) immediately reacts with a second molecule of the arene-rich compound and TRAMs were got following a typical aromatic electrophilic substitution mechanism. So, the above mechanism also proves the greenness of this process because only one molecule of water is produced as by-product during bisarylation (TRAMs or DIAAs) synthesis process.

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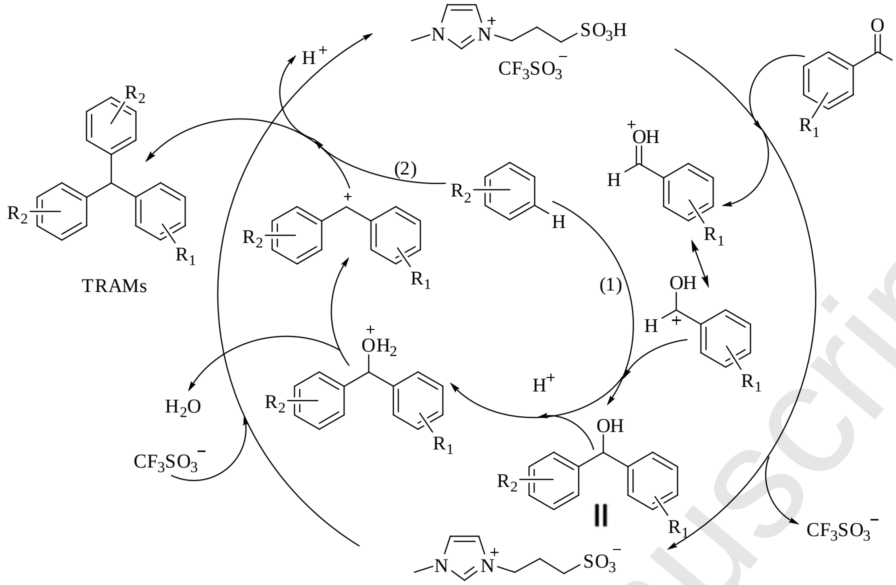

Fig 2. Mechanism of Friedel-Crafts Alkylation reaction catalyzed by [HSO_3-pmim][OTf].

To investigate the mechanism of BAILs catalyzed F-C alkylation reaction, the reaction of arene (**1a**) with aldehyde (**2a**) was chosen as typical substrates to synthesize **3a**. As the reaction with BAILs [HSO_3-pmim][OTf] is so quick, which is not suitable for the investigation of synthesis mechanisms. So its analogues-[HSO_3-pmim][HSO_4] with lower activity was chosen as substitute to prolong reaction time. During the synthesis process, the amount of aldehyde (**2a)** was added excessively. After 5 min or 30 min, samples were removed from the reaction system, respectively. Then water was added to quench the reaction. The corresponding organic layer was determined by IR. Results were listed in Fig**. 3.** In Fig.**3**, the carbonyl characteristic peak of **2a** is about 1698.3cm^{-1}. And the C-O bond stretching vibration peak of **1a** is about 1260 cm^{-1}. From Fig. **3A** (5 min) and Fig. **3B** (30 min), the relative intensity peak of 1698.3 cm^{-1} is decreasing obviously, which indicates that the amount of aldehyde (**2a)** is decreasing and the reaction was proceeding. From IR spectrum, there appears no diarylmethanol (   ) found. However, this transient state would never be avoided during F-C alkylation reaction. In order to verify the reaction may encounter with the above process, another experiment was carried out (Scheme **4**). Arene (**1a**) and diarylmethanol (   ) were chosen as substrates, and [HSO_3-pmim][HSO_4] as the catalyst and solvent. The substrates were converted to **3a** completely within 1 min. That is to say, it is a fast reaction. Diarylmethanol (   ) may be emergent in this specific process. But it is converted into TRAMs quickly. So no Diarylmethanol (   ) can be detected through the IR spectrum. From the above investigations, the proposed mechanism would obey the above scheme.

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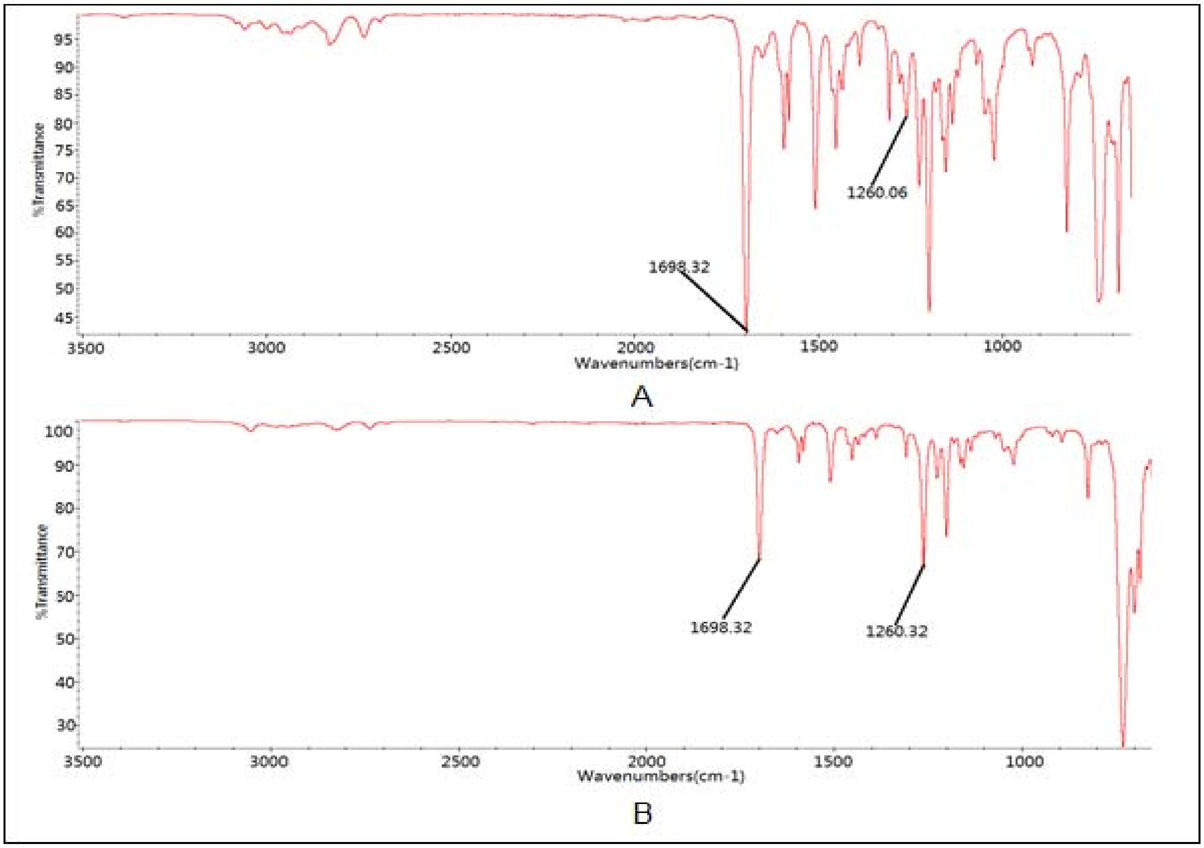
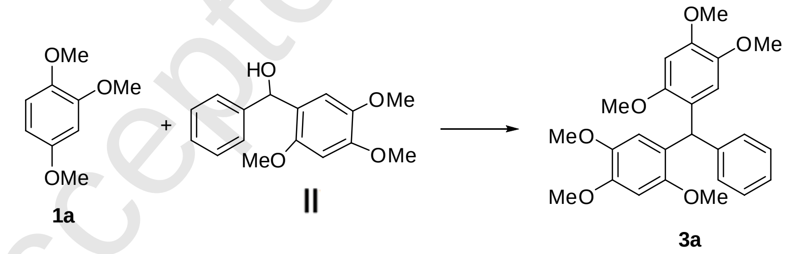


Fig 3. IR Spectra of Friedel-Crafts Alkylation reaction mixture (Reaction time: **A** 5 min, **B** 30 min)



Scheme 4 Reaction of **1a** with diarylmethanol (**II)**

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4. Conclusion

Series of functionalized BAILs and traditional ILs were designed and synthesized. BAILs were applied for catalyzing F-C alkylation of electron-rich arenes with aromatic or aliphatic aldehydes successfully. Research shows that [HSO_3-pmim][OTf] as catalyst gets the highest yield. In optimal conditions, the yield of TRAMs or derivatives can reach up to 97% for one cycle, which is much higher than the other BAILs and traditional ILs. After five cycles, the catalytic activity of BAILs remains very high ranging from 93% to 97%. Finally, the possible catalysis mechanisms were investigated. The above study would provide new green catalysts and solvents for the catalysis synthesis of TRAMs and DIAAs.

Acknowledgments

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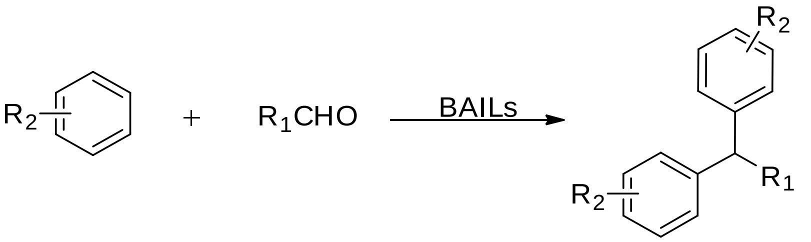

TRAMs or **DIAAs**

In this study, some functionalized ionic liquids including Brönsted acid ionic liquids (BAILs) and traditional ionic liquids were designed and synthesized. BAILs catalyzed Friedel-Crafts(F-C) alkylation was applied in this specific reaction. Research shows that BAILs can be used for catalyzing F-C alkylations of electron-rich arenes with aromatic or aliphatic aldehydes successfully. After five cycles, the yields remains about 93%~97% and without noticeably decreasing the catalytic activity.

Graphical Abstract

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Highlights

- Brönsted acid ionic liquids (BAILs) were designed and synthesized.
- BAILs can be used for catalyzing Friedel-Crafts alkylations successfully.
- $[HSO_3$-pmim][OTf] show higher catalytic activity.
- BAILs can be recycled without noticeably decreasing the catalytic activity

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