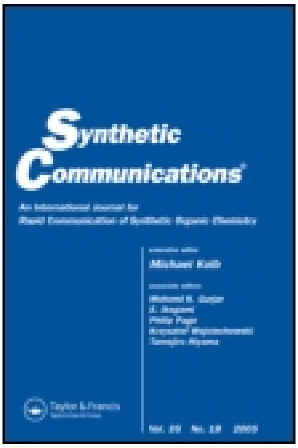

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Brønsted Acidic Ionic Liquids as Efficient Catalysts for the Synthesis of Amidoalkyl Naphthols

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BRØNSTED ACIDIC IONIC LIQUIDS AS EFFICIENT CATALYSTS FOR THE SYNTHESIS OF AMIDOALKYL NAPHTHOLS

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A simple, clean, and environmentally benign three-component process for the synthesis of amidoalkyl naphthols using Brønsted acidic ionic liquids as efficient catalysts in solution and under solvent-free conditions is described.

Keywords: Amidoalkyl naphthols; Brønsted acidic ionic liquids; multicomponent reactions

INTRODUCTION

Multicomponent reactions (MCRs) have attracted considerable attention because they are performed without need to isolate any intermediate during the processes, which reduces time and saves both energy and raw materials.[1] They have merits over two-component reactions in several aspects including the simplicity of a one-pot procedure, possible structural variations, and potential to build up complex molecules. Bigenilli,[2] Ugi,[3] Passerini,[4] and Mannich[5] reactions are some examples of MCRs. Development of new MCRs and improvement and modification of known MCRs are still popular areas of research in current organic chemistry. One such reaction is the synthesis of amidoalkyl naphthols. These compounds are generally synthesized in a three-component reaction of aldehydes, urea or an amide, and β-naphthol in the presence of various catalysts such as iodine,[6] montmorillonite K_{10},[7] $HClO_4 \cdot SiO_2$,[8] $K_5CoW_{12}O_{40} \cdot 3H_2O$,[9] $FeCl_3 \cdot SiO_2$,[10] and sulfamic acid (H_2NSO_3H).[11] However, some of the reported methods require prolonged reaction time, reagents in stoichiometric amounts, or toxic solvents and generate only moderate yields of the product. The increasing attention during the past decades to environmental protection has led both academic and industrial groups to develop chemical processes with maximum yield and minimum cost while using nontoxic reagents, solvents, and catalysts or solvent-free conditions. For these reasons, the development of simple, efficient, clean, high-yielding, and environmentally benign

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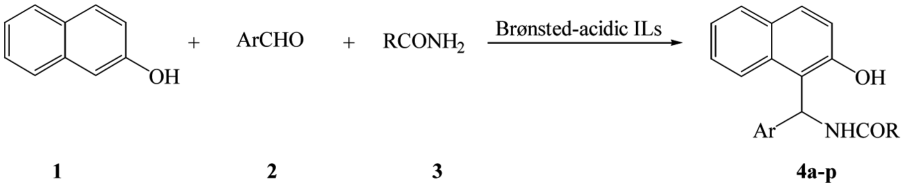
approaches using new catalysts for the synthesis of these compounds is an important task for organic chemists.

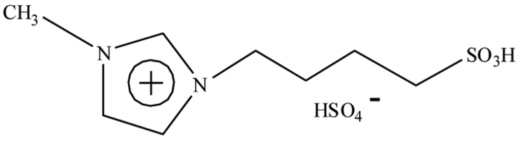
Ionic liquids (ILs), recognized as environmentally benign media, have been widely applied in many reactions as catalysts or dual catalyst–solvents because of their low vapor pressure, reusability, and high thermal and chemical stability.[12,13] The introduction of Brønsted acidic functional groups into cations or anions of the ILs, especially the SO_3H functional groups, obviously enhanced their acidities and water solubilities.[14–17] Because of these properties, Brønsted acidic ILs can be used as highly efficient acid catalysts. Moreover, their polar nature makes them useful under solvent-free conditions because polar media decrease energy of the transition state and therefore increase the reaction rate. In fact, the use of Brønsted acidic ILs as catalysts is an area of ongoing activity; however, development and exploration of Brønsted acidic ILs are currently in the preliminary stage. To the best of our knowledge, there are no examples of the use of Brønsted acidic ILs as catalyst for the synthesis of amidoalkyl naphthols.

In continuation of our previous work on the applications of reusable acid catalysts in the synthesis of organic compounds,[18–21] herein we report a simple and green method for the synthesis of amidoalkyl naphthols in excellent yields using Brønsted acidic ILs (Scheme 1).

For our investigations, two Brønsted acidic ILs, 3-methyl-1-(4-sulfonic acid)-butylimidazolium hydrogen sulfate $[(CH_2)_4SO_3HMIM][HSO_4]$ (IL_1) (Fig. 1) and

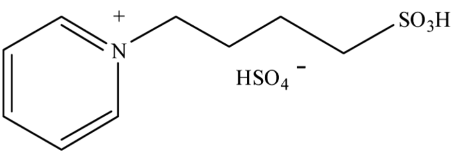


Scheme 1. Synthesis of amidoalkyl naphthols.



$[(CH_2)_4SO_3HMIM][HSO_4]$

Figure 1. Brønsted-acidic IL_1 structure.



$[(CH_2)_4SO_3HPY][HSO_4]$

Figure 2. Brønsted-acidic IL_2 structure.

N-(4-sulfonic acid)butylpyridinium hydrogen sulfate $[(CH_2)_4SO_3HPY][HSO_4]$ (IL_2) (Fig. 2) were prepared, according to the literature procedure.[22,23]

RESULTS AND DISCUSSION

Initially benzaldehyde was selected as a representative aldehyde. To optimize the reaction conditions, it was reacted with β-naphthol and acetamide in the presence of Brønsted acidic ILs in 1,2-dichloroethane (method A) or under neat conditions (method B). In 1,2-dichloroethane as solvent, excellent yield of the product was obtained at room temperature. Increasing the reaction temperature up to the boiling point of the solvent did not decrease the reaction time noticeably. Therefore, room temperature was selected as the optimum temperature and 1,2-dichloroethane as solvent (method A). In a different approach, under solvent-free conditions, the effect of temperature was also investigated by carrying out the same model reaction at various temperatures. It was observed that yield is a function of temperature, so the yield increased as the reaction temperature was raised to 90 °C. The product was obtained in excellent yield in a short reaction time at 90 °C. Higher temperatures did not increase the yield noticeably, and therefore 90 °C was selected as the optimum temperature under solvent-free conditions (method B).

The efficiency of the reaction is mainly affected by the amount of the catalyst (Table 1). No product could be detected in the absence of the catalyst, whereas good results were obtained in the presence of the catalyst. The optimal amounts of the catalysts were 5 mol% IL_1 and 10 mol% IL_2 for both conditions (entries 3 and 8). As can be seen in Table 1, the reaction in the presence of ILs needs less reaction time under solvent-free conditions at 90 °C.

Encouraged by the results obtained from IL-catalyzed reaction of β-naphthol with benzaldehyde and acetamide, a series of amidoalkyl naphthols were prepared in good yields using various aldehydes and urea or amides in the presence of the optimal amounts of the catalysts. The results are summarized in Table 2. All reactions

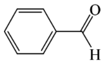
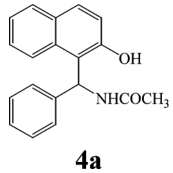
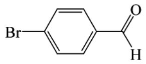
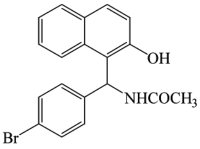
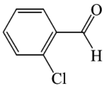
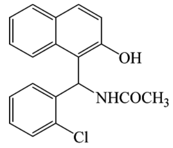
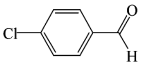
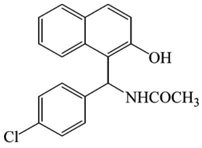
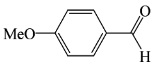
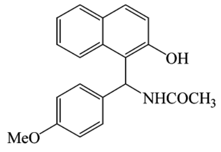
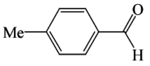
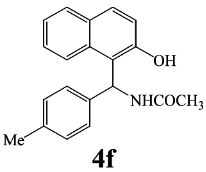
Table 1. Optimizing the reaction conditions[a]

		Method A		Method B	
Entry	Catalyst (mol%)	Time	Yield[b] (%)	Time (min)	Yield[b] (%)
1	None	4 h,30 min	0	120	0
2	IL_1 (2)	4 h	65	15	58
3	IL_1 (5)	2 h,30 min	96	<1	90
4	IL_1 (10)	2 h,45 min	96	1	91
5	IL_1 (15)	2 h,45 min	95	2	89
6	IL_2 (2)	5 h	49	25	21
7	IL_2 (5)	4 h,30 min	67	10	65
8	IL_2 (10)	3 h	94	3	86
9	IL_2 (15)	3 h,50 min	95	4	86
10	IL_2 (20)	3 h,50 min	92	5	85

[a] β-Naphthol/benzaldehyde/acetamide/IL_1 or IL_2 1:1:1.3:0.05 or 0.10.

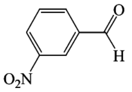
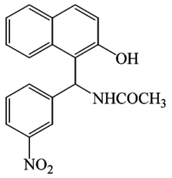
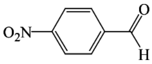
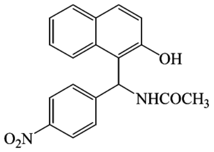
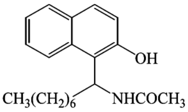
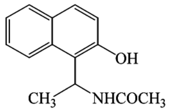
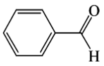
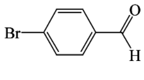
[b] Isolated yields.

Table 2. Brønsted acidic IL–catalyzed synthesis of amidoalkyl naphthols[a]

				Method A		Method B	
Entry	Aldehyde	Urea or amide	Products	Time IL_1/IL_2	Yield[b] (%) IL_1/IL_2	Time (min) IL_1/IL_2	Yield[b] (%) IL_1/IL_2
1		H_3CCONH_2	 **4a**	2 h,30 min/ 3 h	96/94	<1/3	90/86
2		H_3CCONH_2	 **4b**	2 h,30 min/ 3 h,15 min	96/95	<1/3	91/88
3		H_3CCONH_2	 **4c**	2 h,30 min/ 3 h,30 min	93/92	2/3	88/80
4		H_3CCONH_2	 **4d**	2 h,15 min/ 3 h,15 min	95/94	1/3	90/86
5		H_3CCONH_2	 **4e**	3 h,15 min/ 4 h	86/83	3/6	78/76
6		H_3CCONH_2	 **4f**	2 h,50 min/ 3 h,40 min	88/84	4/7	80/78

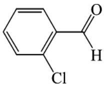
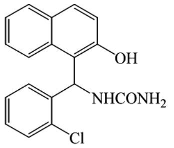
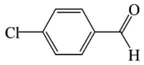
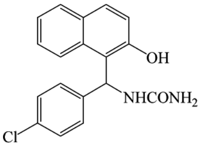
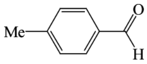
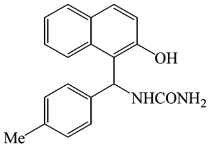
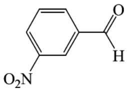
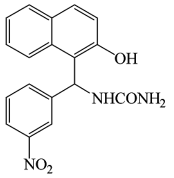
(*Continued*)

Table 2. Continued

				Method A		Method B	
Entry	Aldehyde	Urea or amide	Products	Time IL_1/IL_2	Yield[b] (%) IL_1/IL_2	Time (min) IL_1/IL_2	Yield[b] (%) IL_1/IL_2
7		H_3CCONH_2	 **4g**	2 h,50 min/ 3 h	92/91	2/4	87/83
8		H_3CCONH_2	 **4h**	2 h,40 min/ 3 h	97/94	1/3	90/85
9	$CH_3(CH_2)_6CHO$	H_3CCONH_2	 **4i**	3 h/4 h	Trace	15	Trace
10	CH_3CHO	H_3CCONH_2	 **4j**	3 h/4 h	Trace	15	Trace
11		H_2NCONH_2	 **4k**	3 h,30 min/ 3 h,40 min	90/88	7/9	82/77
12		H_2NCONH_2	 **4l**	3 h,50 min/ 4 h	94/90	6/8	85/82

(*Continued*)

Table 2. Continued

				Method A		Method B	
Entry	Aldehyde	Urea or amide	Products	Time IL_1/IL_2	Yield[b] (%) IL_1/IL_2	Time (min) IL_1/IL_2	Yield[b] (%) IL_1/IL_2
13		H_2NCONH_2	 **4m**	3 h,40 min/ 4 h	92/90	8/9	80/79
14		H_2NCONH_2	 **4n**	3 h/ 3 h,15 min	95/93	7/8	87/85
15		H_2NCONH_2	 **4o**	4 h/ 4 h,20 min	91/85	8/10	78/75
16		H_2NCONH_2	 **4p**	4 h/ 4 h,30 min	90/85	8/8	85/82

[a] All the products were characterized by ^1H NMR and IR spectral data and comparison of their melting points with those of authentic samples.[6,8,10]

[b] Isolated yields.

were conducted in 1,2-dichloroethane at room temperature or under neat conditions at 90 °C. The yields of the products were greater in the first case (method A), but the conversion times were shorter in the second case (method B). Aromatic aldehydes underwent facile conversions but aliphatic aldehydes afforded the products in very poor yields (trace). In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the products in good yields. It was found that the aromatic aldehydes with electron-withdrawing groups reacted faster than the aromatic aldehydes with electron-donating groups.

Reusability of the catalysts were also investigated. For this purpose, the model reaction was again studied in the optimized conditions in method B. After the completion of the reaction, the catalysts were recovered and reused for similar reactions. IL_1 and IL_2 in a second run resulted in 88% and 85% yields, respectively.

CONCLUSION

In conclusion, we have reported a new catalytic method for the synthesis of amidoalkyl naphthols using aromatic aldehydes, urea or amides, and β-naphthol in the presence of Brønsted acidic ILs as efficient, reusable, and ecofriendly homogeneous catalysts. The catalysts can be reused after a simple workup, with a gradual decline of their activity being observed. Good yields, short reaction times, simplicity of operation, and easy workup are some advantages of this protocol.

EXPERIMENTAL

All compounds were known, and their physical and spectroscopic data were compared with those of authentic samples and found to be identical. Melting points were recorded on an Electrothermal 9100 melting-point apparatus. The infrared (IR) spectra were obtained on a 4300 Shimadzu spectrophotometer as KBr disks. The ^1H NMR (100-MHz) spectra were recorded on a Bruker AC 100 spectrometer.

General Procedure for the Prepration of Amidoalkyl Naphthols

Method A. To a mixture of β-naphthol (1 mmol), aromatic aldehyde (1 mmol), and urea or amide (1.3 mmol) in 1,2-dicholoroethane (5 ml), Brønsted acidic ILs (5 mol% IL_1 or 10 mol% IL_2) were added. The mixture was stirred at room temperature, and the reaction was monitored by thin-layer chromotography (TLC). After completion of the reaction, the precipitate was filtered off and recrystallized from ethanol to give pure amidoalkyl naphthols (Table 2).

Method B. A mixture of β-naphthol (1 mmol), aromatic aldehyde (1 mmol), and urea or amide (1.3 mmol), in the presence of Brønsted acidic ILs (5 mol% IL_1 or 10 mol% IL_2), was heated at 90 °C. After completion of the reaction, the reaction mixture was cooled to room temperature and cold ethanol was added. The precipitate was filtered off and recrystallized from ethanol to obtain pure amidoalkyl naphthols (Table 2).

Recycling of the Catalyst

The catalysts are soluble in ethanol and therefore could be recycled from the filtrate. The catalysts were recovered by evaporation of the ethanol, washed with diethyl ether, and dried at 50 °C under vacuum for 1 h.

REFERENCES

1. (a) Devi, I.; Bhuyan, P. J. Sodium bromide–catalysed one-pot synthesis of tetrahydrobenzo[b]pyrans via a three-component cyclocondensation under microwave irradiation and

solvent-free conditions. *Tetrahedron Lett.* **2004**, *45*, 8625–8627; (b) Mashraqui, S. H.; Patil, M. B.; Mistry, H. D.; Ghadigaonkar, S.; Meetsma, A. A three-component reaction of phenol, aldehyde, and active methylene substrate under Lewis acid catalysis: Successful trapping of o-quinone methide to afford benzopyran systems. *Chem. Lett.* **2004**, *33*, 1058–1059; (c) Chetia, A.; Saikia, C. J.; Lekhok, K. C.; Boruah, R. C. A facile synthesis of 1,7-dicarbonyl compounds via three-component Michael addition reactions. *Tetrahedron Lett.* **2004**, *45*, 2649–2651; (d) Wang, L. M.; Xia, J.; Qin, F.; Qian, C.; Sun, J. Yb(OTf)(3)-catalyzed one-pot synthesis of quinazolin-4(3H)-ones from anthranilic acid, amines, and ortho esters (or formic acid) in solvent-free conditions. *Synthesis* **2003**, 1241–1247.

2. (a) Jain, S. L.; Joseph, J. K.; Singhal, S.; Sain, B. Metallophthalocyanines (MPCs) as efficient heterogeneous catalysts for Biginelli condensation: Application and comparison in catalytic activity of different MPCs for one-pot synthesis of 3,4-dihydropyrimidin-2-(1H)-ones. *J. Mol. Catal. A: Chem.* **2007**, *268*, 134–138; (b) Zumpe, F. L.; Flüß, M.; Schmitz, K.; Lender, A. Propane phosphonic acid anhydride: A new promoter for the one-pot Biginelli synthesis of 3,4-dihydropyrimidin-2(1H)-ones. *Tetrahedron Lett.* **2007**, *48*, 1421–1423; (c) Kamal, A.; Krishnaji, T.; Azhar, M. A. Copper(II) tetrafluoroborate as a mild and efficient catalyst for the one-pot synthesis of 3,4-dihydropyrimidin-2(H-1)-ones under solvent-free conditions. *Catal. Commun.* **2007**, *8*, 1929–1933.
3. (a) Trifilenkov, A. S.; Ilyin, A. P.; Kysil, V. M.; Sandulenko, Y. B.; Ivachtchenko, A. V. One-pot tandem complexity-generating reaction based on Ugi four-component condensation and intramolecular cyclization. *Tetrahedron Lett.* **2007**, *48*, 2563–2567; (b) Nenajdenko, V. G.; Reznichenko, A. L.; Balenkova, E. S. Diastereoselective Ugi reaction without chiral amines: the synthesis of chiral pyrroloketopiperazines. *Tetrahedron* **2007**, *63*, 3031–3041; (c) Xiang, Z.; Luo, T.; Lu, K.; Cui, J.; Shi, X.; Fathi, R.; Chen, J.; Yang, Z. Concise synthesis of isoquinoline via the Ugi and Heck reactions. *Org. Lett.* **2004**, *6*, 3155–3158.
4. (a) Krishna, P. R.; Dayaker, G.; Narasimha Reddy, P. V. Diastereoselective Passerini reactions using p-toluenesulfonylmethyl isocyanide (TosMIC) as the isonitrile component. *Tetrahedron Lett.* **2006**, *47*, 5977–5980; (b) Andrade, C. K. Z.; Takada, S. C. S.; Suarez, P. A. Z.; Alves, M. B. Revisiting the Passerini reaction under eco-friendly reaction conditions. *Synlett.* **2006**, 1539–1542.
5. (a) Azizi, N.; Torkiyan, L.; Saidi, M. R. Highly efficient one-pot three-component Mannich reaction in water catalyzed by heteropoly acids. *Org. Lett.* **2006**, *8*, 2079–2082; (b) Wu, H.; Shen, Y.; Fan, L.; Wan, Y.; Zhang, P.; Chen, C.; Wang, W. Stereoselective synthesis of β-amino ketones via direct Mannich-type reaction catalyzed with silica sulfuric acid. *Tetrahedron* **2007**, *63*, 2404–2408.
6. Das, B.; Laxminarayana, K.; Ravikanth, B.; Rama Rao, B. Iodine-catalyzed preparation of amidoalkyl naphthols in solution and under solvent-free conditions. *J. Mol. Catal. A: Chem.* **2007**, *261*, 180–183.
7. Kantevari, S.; Vuppalapati, S. V. N.; Nagarapu, L. Montmorillonite K10–catalyzed efficient synthesis of arnidoalkyl naphthols under solvent-free conditions. *Catal. Commun.* **2007**, *8*, 1857–1862.
8. Mahdavinia, G. H.; Bigdeli, M. A.; Heravi, M. M. Silica-supported perchloric acid ($HClO_4$-SiO_2): A mild, reusable, and highly efficient heterogeneous catalyst for the synthesis of amidoalkyl naphthols. *Chin. Chem. Lett.* **2008**, *19*, 1171–1174.
9. Nagarapu, L.; Baseeruddin, M.; Apuri, S.; Kantevari, S. Potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40} \cdot 3H_2O$): A mild and efficient reusable catalyst for the synthesis of amidoalkyl naphthols in solution and under solvent-free conditions. *Catal. Commun.* **2007**, *8*, 1729–1734.

10. Shaterian, H. R.; Yarahmadi, H. A modified reaction for the preparation of amidoalkyl naphthols. *Tetrahedron Lett.* **2008**, *49*, 1297–1300.
11. Nagawade, R. R.; Shinde, D. B. Sulfamic acid (H_2NSO_3H)–catalyzed multicomponent reaction of β-naphthol: An expeditious synthesis of amidoalkyl naphthols. *Chin. J. Chem.* **2007**, *25*, 1710–1714.
12. Ranu, B. C.; Banerjee, S. Ionic liquid as catalyst and reaction medium: The dramatic influence of a task-specific ionic liquid, [bmlm]OH, in Michael addition of active methylene compounds to conjugated ketones, carboxylic esters, and nitriles. *Org. Lett.* **2005**, *7*, 3049–3052.
13. Du, D. M.; Chen, X. New advances of organic synthetic reactions and catalytic asymmetric reaction in ionic liquid media. *Chin. J. Org. Chem.* **2003**, *23*, 331–343.
14. Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; James, J.; Davis, H. Novel Brønsted acidic ionic liquids and their use as dual solvent–catalysts. *J. Am. Chem. Soc.* **2002**, *124*, 5962–5963.
15. Arfan, A.; Bazureau, J. P. Efficient combination of recyclable task specific ionic liquid and microwave dielectric heating for the synthesis of lipophilic esters. *Org. Process Res. Dev.* **2005**, *9*, 743–748.
16. Qiao, K.; Yokoyama, C. Koch carbonylation of tertiary alcohols in the presence of acidic ionic liquids. *Catal. Commun.* **2006**, *7*, 450–453.
17. Wasserscheid, P.; Sesing, M.; Korth, W. Hydrogensulfate and tetrakis(hydrogensulfato)-borate ionic liquids: Synthesis and catalytic application in highly Bronsted-acidic systems for Friedel–Crafts alkylation. *Green Chem.* **2002**, *4*, 134–138.
18. Heravi, M. M.; Bakhtiari, K.; Taheri, S.; Oskooie, H. A. A straightforward method for the synthesis of functionalized trisubstituted alkenes through Na_2S/Al_2O_3-catalyzed Knoevenagel condensation. *J. Chin. Chem. Soc.* **2007**, *54*, 1557–1560.
19. Heravi, M. M.; Bakhtiari, K.; Daroogheha, Z.; Bamoharram, F. F. An efficient synthesis of 2,4,6-triarylpyridines catalyzed by heteropolyacid under solvent-free conditions. *Catal. Commun.* **2007**, *8*, 1991–1994.
20. Heravi, M. M.; Motamedi, R.; Bamoharram, F. F.; Seify, N. A catalytic method for synthesis of 6-aryl-1H-pyrazolo[3,4-d]pyrimidin-4[5H]-ones by heteropolyacids: $H_{14}[NaP_5W_{29}MoO_{110}]$ and $H_3PMo_{12}O_{40}$. *Catal. Commun.* **2007**, *8*, 1467–1471.
21. Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Gharib, A.; Jahangir, M. Catalytic method for synthesis of aspirin by a green, efficient, and recyclable solid acid catalyst (Preyssler's anion) at room temperature. *J. Chin. Chem. Soc.* **2007**, *54*, 1017–1022.
22. Wang, W.; Shao, L.; Cheng, W.; Yang, J.; He, M. Brønsted acidic ionic liquids as novel catalysts for Prins reaction. *Catal. Commun.* **2008**, *9*, 337–341.
23. Gui, J.; Cong, X.; Liu, D.; Zhang, X.; Hu, Z.; Sun, Z. Novel Brønsted acidic ionic liquid as efficient and reusable catalyst system for esterification. *Catal. Commun.* **2004**, *5*, 473–477.