ตัวเร่งปฏิกิริยาชนิดของเหลวไอออนิกชนิดกรดซัลโฟนิกในปฏิกิริยาเคมีอินทรีย์

SO_3H - Functionalized Acidic Ionic Liquid Catalysts in Organic Reactions

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บทคัดย่อ

บทความวิจัยนี้ ได้รวบรวมการนำไปใช้ประโยชน์ของของเหลวไอออนิกที่มีหมู่ฟังก์ชั่นเป็นกรดซัลโฟนิก (-SO_3H) ต่ออยู่กับแคตไอออนเป็นชนิด อิมิดาโซเลียม ไพริดิเนียม ฟอสโฟเนียม หรือ แอมโมเนียม และมีเคาน์เตอร์แอนไอออนเป็นกรดชนิดต่างๆ โดยของเหลวไอออนิกชนิดนี้ถูกนำไปใช้ประโยชน์เป็นตัวทำละลาย ตัวเข้าทำปฏิกิริยา และตัวเร่งในปฏิกิริยาเคมีอินทรีย์ต่างๆ อย่างมากมาย โดยบทความวิจัยนี้ได้รวบรวมการนำของเหลวไอออนิกชนิดกรดบรอนสเตดไปใช้ในปฏิกิริยาเคมีอินทรีย์บางปฏิกิริยาที่สำคัญ ได้แก่ ปฏิกิริยาเอสเทอริฟิเคชัน ปฏิกิริยาแมนนิช ปฏิกิริยาฟรีเดล-คราฟท์ ปฏิกิริยาไนเตรชัน ปฏิกิริยาการจัดตัวแบบแบ็คแมน ปฏิกิริยาฟิวแลนเดอร์ ปฏิกิริยาการเพิ่มแบบไมเคล ปฏิกิริยาแบบหลายองค์ประกอบ และปฏิกิริยาการสังเคราะหสารประกอบอินโดล เป็นต้น ซึ่งของเหลวไอออนิกชนิดกรดบรอนสเตรตเหล่านี้สามารถช่วยให้ปฏิกิริยาเกิดอย่างมีประสิทธิภาพ ให้ร้อยละของผลิตภัณฑ์ที่สูง และยังสามารถนำกลับมาใช้ใหม่ได้โดยไม่สูญเสียประสิทธิภาพ

คำสำคัญ : ของเหลวไอออนิกชนิดกรด ปฏิกิริยาเคมีอินทรีย์ ตัวเร่งปฏิกิริยาชนิดกรดบรอนสเตด

Abstract

This review concluded the utilization of SO_3H-functionalized ionic liquids bearing imidazolium, pyridinium, phosphonium or ammonium cations and various acids couteranions in numerous organic reactions as efficient solvents, reagents and catalysts. Some of the versatile organic reactions are described in this review, including esterification, Mannich reaction, Friedel-Crafts reaction, nitration, Beckmann rearrangement, Friedlander reaction, Michael addition, multicomponent reaction and Fisher indole synthesis. Advantages of these SO_3H-functionalized ionic liquids can promote the reactions efficiently, providing the products in high yields and can be reused in several times without significant loss of catalytic activity.

Keywords : acidic ionic liquid, organic reaction, Brönsted acidic catalyst

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Introduction

Ionic liquids (ILs) are organic salts usually existing in liquid form at and below room temperature, called “room temperature ionic liquids (RTILs)”. ILs have received attention in many years as solvents, reagents and catalysts for numerous organic syntheses due to their unique properties including non-volatility, non-flammable, high thermal stability, high solubility for a wide range of inorganic and organic materials and recyclability. In addition they could be suitable and environmental-friendly catalysts for toxic-free reactions especially the processes that able to take place in water media because of ILs could be miscible in water and water-tolerant. To date, a variety of ILs are designed and synthesized with different cations, anions and substituted to accommodate functional groups that possess of catalytic properties. Among them, Brönsted acidic ionic liquids (BAILs) (Amarasekara, 2016), especially SO_3H-functionalized ionic liquid (Figure 1), are important acidic ionic liquids that exhibit great potential in replacement of conventional homogeneous and heterogeneous acid catalysts such as sulfuric acid (H_2SO_4) and hydrochloric acid (HCl).

Cation $^{(+)}$ —**Linker**—SO_3H

Figure 1 Brönsted acid SO_3H-functionalized ionic liquids

The syntheses of SO_3H-functionalized ionic liquids were first reported by Forbes and co-workers in 2002. Their research applied these ionic liquids as efficient catalyst for Fischer esterification, alcohol dehydrodimerization and pinacol/benzopinacol rearrangement (Cole et al., 2002). To date, there are many reports on the use of BAILs as solvents, reagents and catalysts in synthetic organic reactions. Therefore, the aim of this review is to conclude the utilization of BAILs in such some of versatile organic reactions including esterification, Mannich reaction, Friedel-Crafts reaction, nitration, Beckmann rearrangement, Friedlander reaction, Michael addition, multicomponent reaction and Fisher indole synthesis (Figure 2).

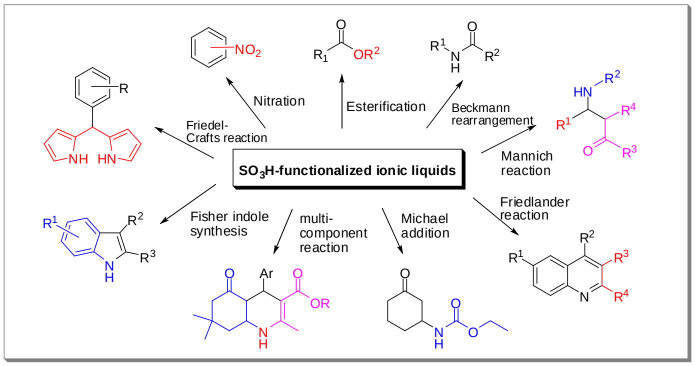
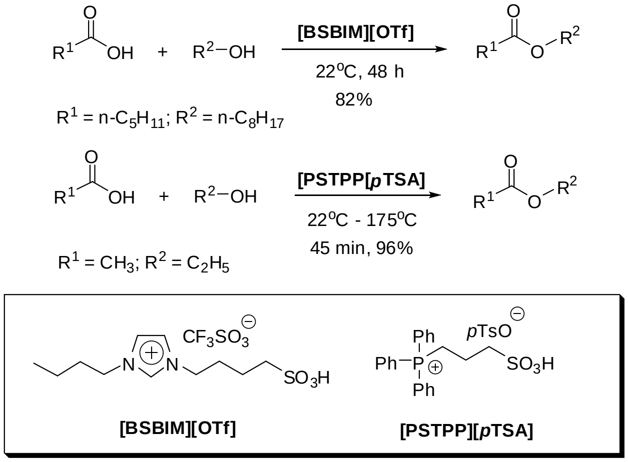


Figure 2 Brönsted acid SO_3H-functionalized ionic liquids catalyzed organic reactions

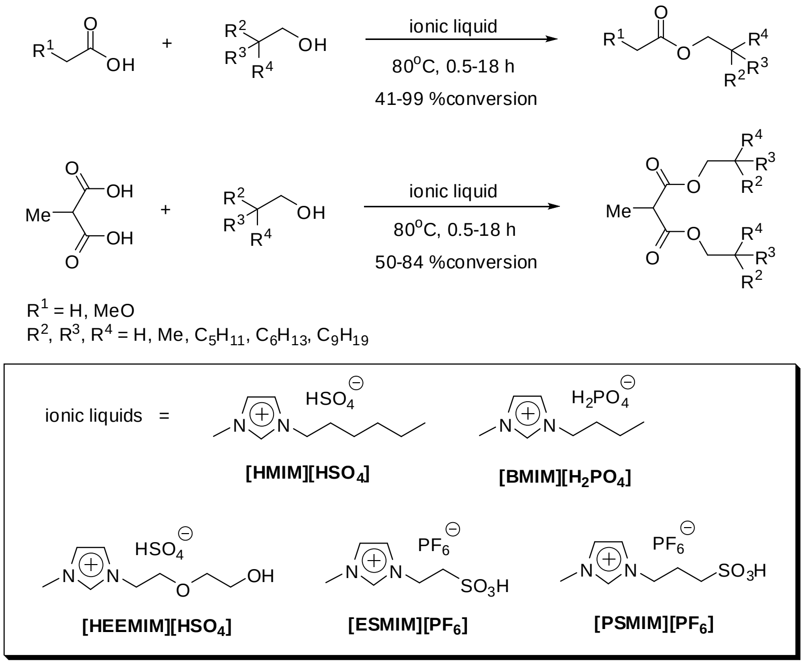
1. Esterification Reaction

The first utilization of SO_3H-functionalized ionic liquid was described in 2002 by Cole's group. Two ionic liquids, named 1-butylsulfonic-3-butylimidazolium trifluoromethanesulfonate ([BSBIM][OTf]) and propylsulfonic triphenylphosphonium *p*-toluenesulfonate ([PSTPP][*p*TSA]), were investigated as dual solvent-catalysts in several classical acid-promoted organic reaction, particularly Fisher esterification. The results showed that both catalysts could provide the ester products in good yields with 82 and 96% for [BSBIM][OTf] and [PSTPP][*p*TSA] respectively (Scheme 1) (Cole et al., 2002).



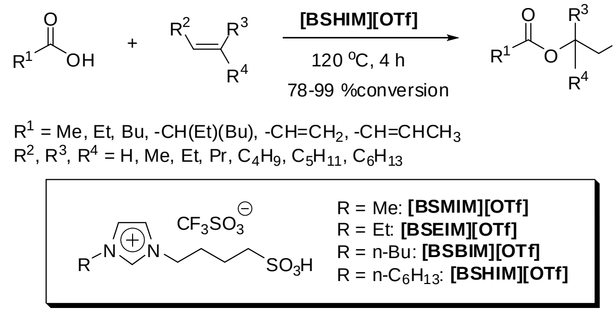
Scheme 1

In 2002, Bazureau and co-workers studied a series of imidazolium ionic liquids with various acids counteranion, such as hydrogen sulfate (HSO_4), dihydrogen phosphate (H_2PO_4) and hexafluorophosphate (PF_6), as recyclable catalysts for the esterification of carboxylic acids and aliphatic alcohols under mild reaction conditions. This research showed good yields up to 99% and high selectivity of desired products in all cases, although ionic liquid that consisted H_2PO_4 anion showed a low reaction rate rather than that HSO_4 anion due to lower acidity of H_2PO_4 counteranion. Especially, 1-propylsulfonic-3-methylimidazolium hexafluorophosphate ([PSMIM][PF_6]) was found to be the most effective for less active carboxylic acids, such as methylmalonic acid and methoxyacetic acid, comparing to other ionic liquid catalysts (Scheme 2) (Fraga-Dubreuil, Bourahla, Rahmouni, Bazureau, & Hamelin, 2002).



Scheme 2

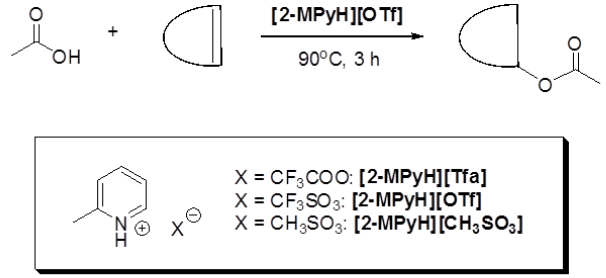
Esterification of aliphatic acids with olefins using SO_3H-functionalized imidazolium ionic liquid as catalyst was investigated by Deng's group in 2004. Various ionic liquids with different alkyl side chains were tested in the reaction of aliphatic acids and olefins in 1:3 mole ratio at 120°C for 4 h and the result showed that high lipophilicity of 1-butylsulfonic-3-hexylimidazolium trifluoromethanesulfonate ([BSHIM][OTf]) gave the highest %conversion yield of the ester products compared to other three ionic liquid catalysts (Scheme 3). In addition, the catalyst [BSHIM][OTf] could be reused after a treatment in vacuum (5-12 mmHg) at 80°C and found that slight decreasing in activity after four times in consecutive runs (Gu, Shi, & Deng, 2004).



Scheme 3

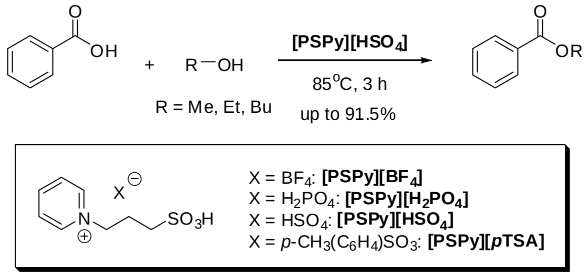
Continually, in 2006, Deng's group also found that 2-methylpyridinium-based acidic ionic liquids could work well as catalysts for the esterification of cyclic olefin with acetic acid. The reactions were performed at

90°C for 3 h to successfully afford the ester products >99% conversion yield in the presence of 20 mol% of 2-methylpyridinium trifluoromethanesulfonate ([2-MPyH][OTf]), less active in the presence of 2-methylpyridinium methanesulfonate ([2-MPyH][CH_3SO_3]) and no reaction in the presence of 2-methylpyridinium trifluoroacetate ([2-MPyH][Tfa]) (Scheme 4). (Duan, Gu, Zhang, Zhu, & Deng, 2006).



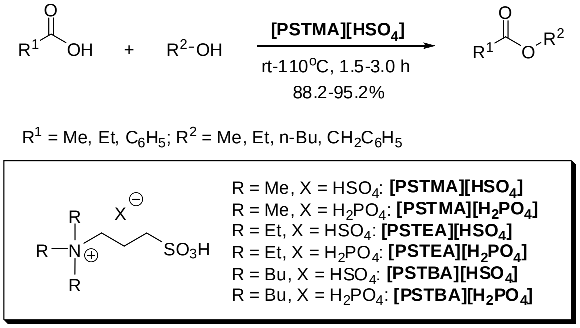
Scheme 4

In 2005, Wang and co-worker reported the use of SO_3H-functionalized pyridinium ionic liquids as catalysts for esterification of benzoic acid with three common alcohols such as methanol, ethanol and butanol (Scheme 5). The result showed that all ionic liquids exhibited good catalytic activity toward esterification. Especially, propylsulfonic pyridinium hydrogen sulfate ([PSPy][HSO_4]) that consisted HSO_4 anion could give the ester products in highest yield (up to 91.5%). This result indicated that the catalytic activity of ionic liquid is depending on anion, in which HSO_4 anion showed higher efficiency than other anions. Furthermore, this method could easily separate the ester products by decantation, and the catalyst could be then reused for several times after removed of water (Xing, Wang, Zhou, & Dai, 2005).



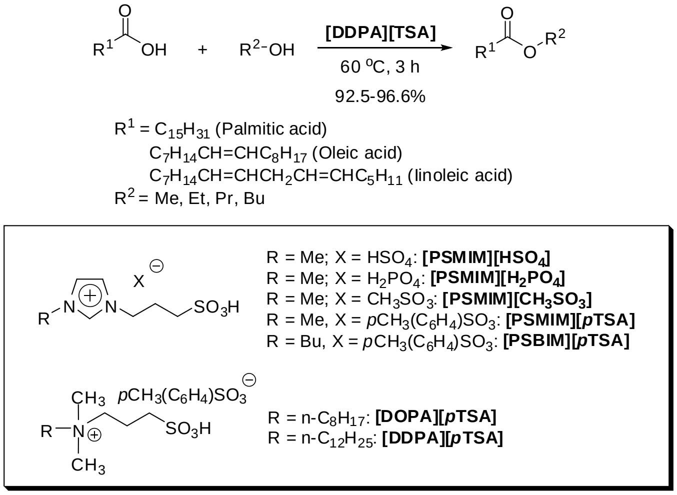
Scheme 5

In 2006, Liu and co-worker used SO_3H-functionalized trialkanylammonium ionic liquid as dual solvent and catalyst for Fischer esterification. The reactions were performed at room temperature to 110°C for 1.5-3.0 h to afford the ester products in good yields (88-95%). In which the highest yield of ester was found when using propylsulfonic trimethylammonium hydrogen sulfate ([PSTMA][HSO_4]) as solvent and catalyst (Scheme 6). This procedure could easily separate ester products by decantation and the catalyst could be reused without decreasing of catalytic activity (Fang, Zhou, Ye, & Liu, 2006).



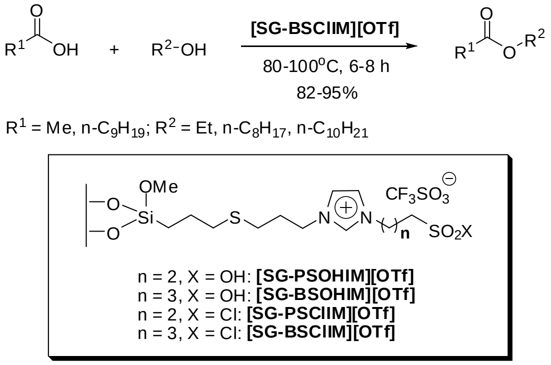
Scheme 6

Recently, Qin and co-worker reported biodiesel synthesis *via* esterification of free fatty acids and alcohols using long-chain Brönsted acidic ionic liquid as catalyst. They compared the catalytic activity of various ionic liquids in the reaction of oleic acid and methanol at 60°C for 3 h to the results that long alkyl chain ionic liquid, 3-(*N*,*N*-dimethyldodecylammonium)propanesulfonic acid *p*-toluenesulfonate ([DDPA][*p*TSA]) exhibited more efficiency than short alkyl chain ionic liquids with higher yield and shorter reaction time. Furthermore, they found that TSA anion plays an essential role for acceleration of the reaction, leading to the better conversion yield than other anions. Furthermore, this method could provide the derivative products in 92.5 to 96.5% yield (Scheme 7) with possibility in reuse for nine runs to yield remaining unchanged. The products could be separated from catalytic system by decantation (He, Qin, Chang, Sun, & Gao, 2013).



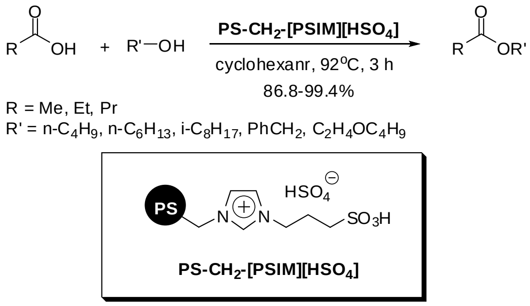
Scheme 7

While, esterification reaction promoted by heterogeneous catalyst bearing imidazolium ionic liquid was reported by Yokoyama and co-worker in 2006. Silica gel was used to be supporter for a variety of imidazolium ionic liquids. The results showed that these heterogeneous ionic liquids could promote the esterification reaction at 80-100°C for 6-8 h, leading to ester products in high yields (82-95%). Especially [SG-BSCIIM][OTf] was found to give the best result (Scheme 8). Moreover, this protocol could easily separate the ester products by decantation and the catalyst could be reused in several times with no any significant loss of catalytic performance (Qiao, Hagiwara, & Yokoyama, 2006).



Scheme 8

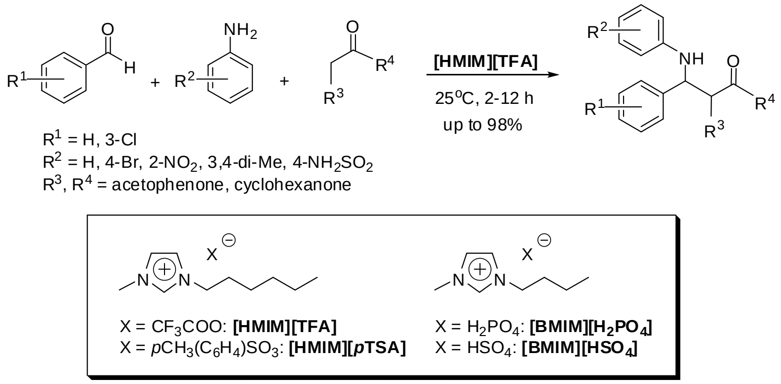
In 2010, Xu and co-worker developed the heterogeneous ionic liquid catalyst for esterification by using polystyrene (PS) as supporter. The results showed that catalytic activity of PS-supported 1-propylsulfonic imidazolium hydrogen sulfate (PS-CH_2-[PSIM][HSO_4]) was almost the same of common acid-ionic liquid, [PSIM][HSO_4], however, the heterogeneous catalyst facilitated the separation of the product and found to exhibit an efficient catalytic activity with thermal stability (Scheme 9). Interestingly, the reusability of this catalyst was tested until 13 times and found that slight decreased in yield (7.3%) (Xu *et al.,* 2010).



Scheme 9

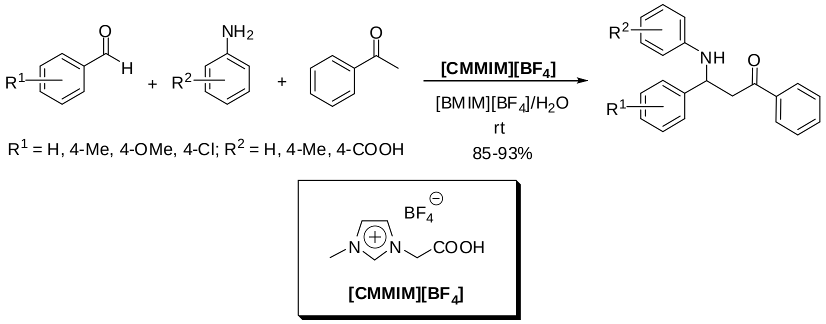
2. Mannich-type Reaction

In 2004, Jiang and co-worker used Brönsted acidic ionic liquids having acid anions as solvent and catalyst for one-pot three components Mannich reaction of aldehydes, amines and ketones (Scheme 10). Several imidazolium ionic liquids were compared their catalytic activity in this work at 25°C for 2-12 h, leading to highest yield of the desired product in the presence of 1-hexyl-3-methylimidazolium trifluoroacetate ([HMIM][TFA]). No reaction in the presence of [BMIM][HSO_4] due to strong acidity of HSO_4 that readily reacts with amine. Using optimization, the derivative products were successfully obtained in good yield (up to 98%). In addition, the catalyst could be reused four times without any loss of catalytic activity (Zhao *et al*., 2004).



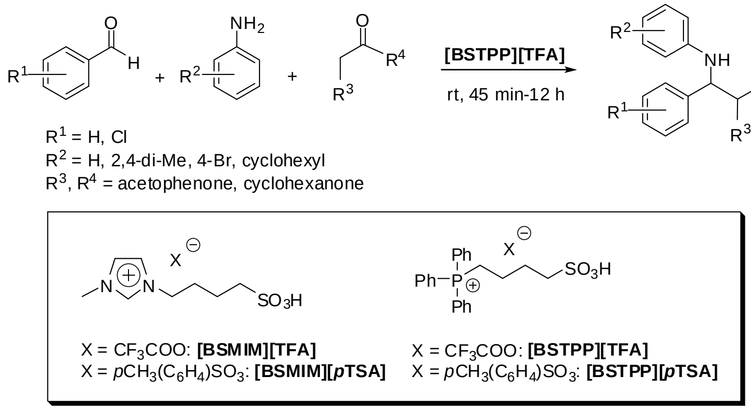
Scheme 10

In 2005, Song's group reported the use of carboxyl-functionalized imidazolium ionic liquid as catalyst for one-pot three components Mannich reaction of aromatic aldehydes, anilines and acetophenone (Scheme 11). The reactions were successfully achieved at room temperature in the presence of 5 mol% of 1-carboxymethyl-3-methylimidazolium tetrafluoroborate ([CMMIM][BF_4]) in aqueous of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) to afford the corresponding products in high yields (85-93%) (Li, Peng, & Song, 2005). For comparison, it was found that this catalyst could give the better yield than previous reported acid catalysts such as HCl (Akiyama, Takaya, & Kagoshima, 2002), AcOH, PS-SO_3H (Limura, Nobutou, Manable, & Kobayashi, 2003) and [Hmim][TFA] (Zhao et al, 2004). More advantage, this catalyst could be recycled for six times without significant loss of activity compared to other catalysts.



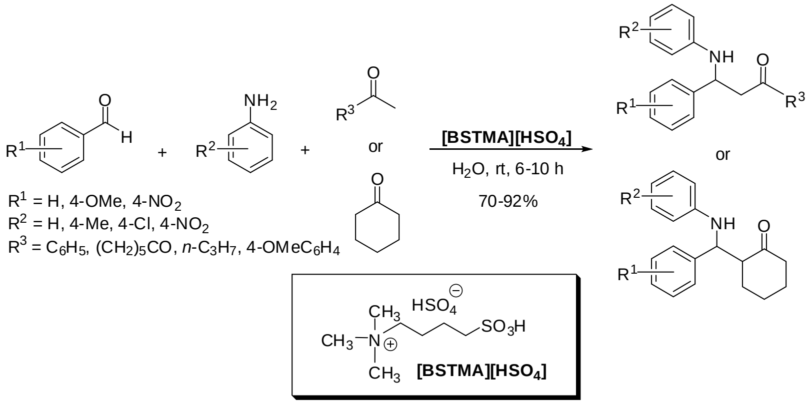
Scheme 11

In 2006, Joseph's group used SO_3H-functionalized ionic liquids as solvent and catalysts for one-pot three components Mannich reaction of aldehydes, amines and ketone (1:1:1 mole ratio) at room temperature (Scheme 12). A series of SO_3H-functionalized ionic liquids bearing triphenylphosphonium and immidazolium as cations with TFA and PTSA as anions was investigated. It was found that triphenylphosphonium with *p*TSA anion, [TPBSP][TFA], gave the best yield of desired product (96.7%) than other ionic liquid catalysts. Moreover, the ionic liquid catalyst could be recycled for four times without any loss in activity (Sahoo, Joseph, & Halligudi, 2006).



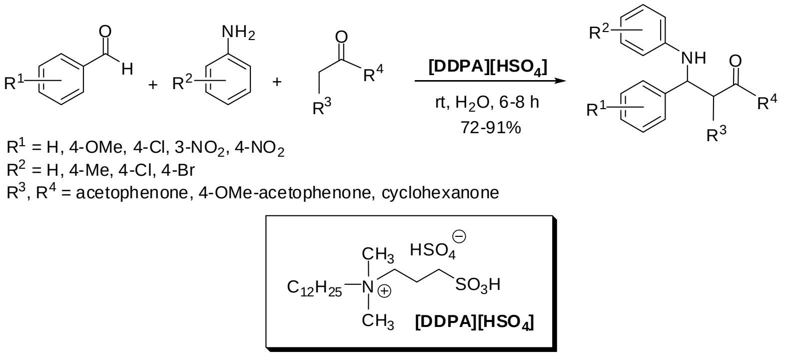
Scheme 12

Fang's group reported various kinds of SO_3H-functionalized trialkanylammonium ionic liquids catalyzed one-pot three components Mannich reaction. First work, in 2007, they started with short alkyl chain of SO_3H-functionalized trialkanylammonium ionic liquid, butylsulfonic trimethylammonium hydrogen sulfate ([BSTMA][HSO_4]), at room temperature in various solvents (Scheme 13). Their research showed that water solvent provided the desired product in slightly lower yield (90%) than ethanol (94%) and methanol (92%), however, water was chose as suitable solvent due to environmental and economic reasons. By employing this protocol, the derivative products were obtained in high yields (70-92%) in the presence of 10 mol% of [BSTMA][HSO_4]. And the catalytic system could be reused for seven times without any loss of activity (Fang, Luo, Zhou, & Liu, 2007).



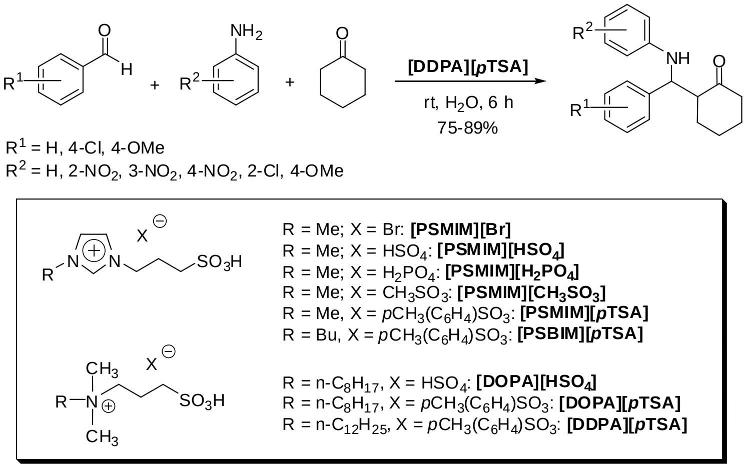
Scheme 13

In the other work, in 2009, Fang's group found that long alkyl chain bearing SO_3H-functionalized ammonium ionic liquid also showed good catalytic performance for one-pot three components Mannich reaction of aromatic aldehydes, aromatic amines and ketone (1:1:1 mole ratio) in several solvents (Scheme 14) (Fang, Fei, & Liu, 2009). Water was selected as solvent because it is offer as green and cheap solvent, although provided slightly lower yield than polar solvents. They performed the reaction by using 10 mol% of [DDPA][HSO_4] in water at 25°C for 6-8 h, and the corresponding products were obtained in high yields (72-91%) as well as their previous report (Fang *et al.*, 2007). Furthermore, the catalyst could be also reused for six times without noticeably decreasing the catalytic activity.



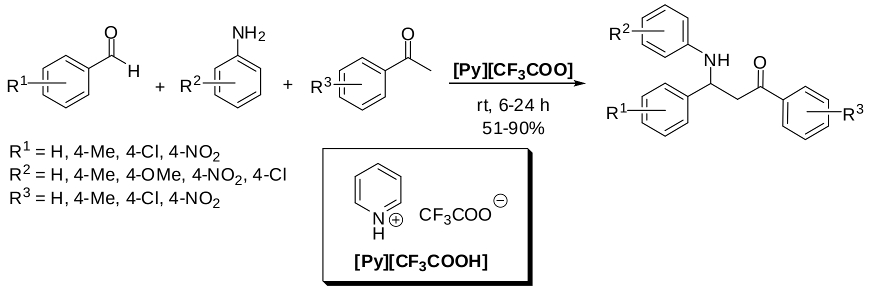
Scheme 14

Similar to Fang's research (Fang et al., 2009), Chang's group investigated the catalytic performance of SO_3H-functionalized ionic liquids with different acid anions toward one-pot three components Mannich reaction of aromatic aldehydes, aromatic anilines and cyclohexanone (1:1:1 mole ration) in 2014 (Scheme 15). The reactions were smoothly carried out by using various Brönsted acidic ionic liquids in water media at 25°C. In this study, they found that the catalytic activity of ionic liquids consist of *p*-toluenesulfonate anion (*p*TSA) was greater than other anions and showed the highest yield in case of [DOPA][*p*TSA]. By using optimized condition, corresponding products were obtained in high yields (75-89%) by using 10 mol% of [DOPA][*p*TSA]. Furthermore, [DOPA][pTSA] could be reused for nine times with remaining unchanged in yield (Chang *et al.,* 2014).



Scheme 15

In 2009, Yue and co-worker reported the use of pyridinium trifluoroacetate ([Py][CF_3COO]) as solvent and catalyst for one-pot three components Mannich reaction under organic solvent-free condition. The reaction of aromatic aldehydes, aromatic amines and aromatic ketone (1:1:1 mole ratio) was carried out at room temperature for 6-24 h in the presence of 130 mol% of [Py][CF_3COO] to afford the good yields of β–amino carbonyl compounds (51-90%) (Scheme 16). The catalyst could be reused for four times without any loss of catalytic activity (Yue, Feng, Zhu, & Liu, 2009).

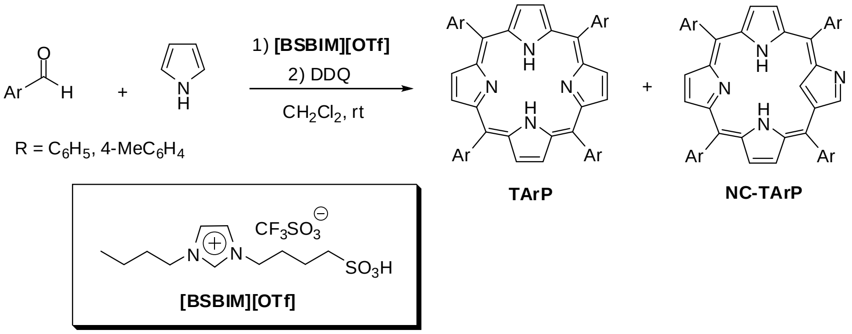


Scheme 16

3. Friedel-Crafts Reaction

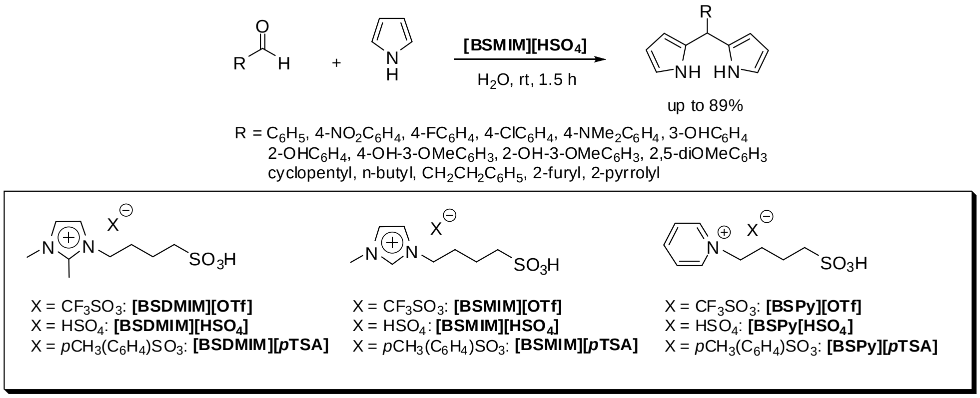
The BAIL-catalyzed reaction is also applicable for Friedel-Crafts reactions. In 2004, Ishikawa and co-worker first reported the synthesis of symmetric porphyrin from aromatic aldehyde and pyrrole (1:1 mole ratio) at room temperature by using [BSBIM][OTf] as catalyst in dichloromethane (CH_2Cl_2) solvent with ratio 3:10 mL of

[BSBIM][OTf] and CH_2Cl_2 for 20 min, then following by addition of DDQ powder (1 equivalent) to afford the porphyrine TArP in 43% and prophyrinNC-TArP in 10% yield (Scheme 17). Reusability of the catalyst was investigated at least ten times to result no loss of catalytic activity (Kitaoka, Nobuoka, & Ishikawa, 2004).



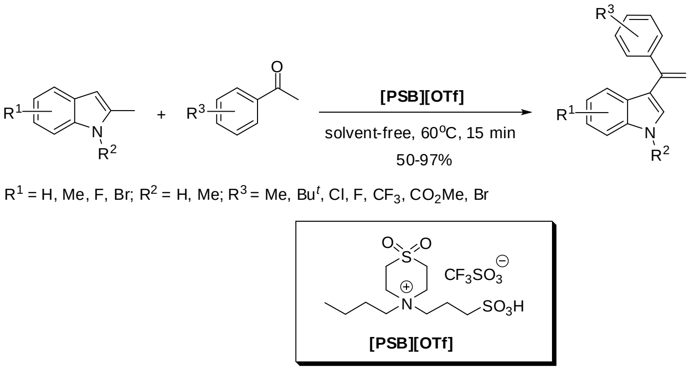
Scheme 17

In recently, our group reported the use of SO_3H-functionnalized ionic liquids as efficient catalysts for green synthesis of dipyrromethanes *via* double Friedel-Crafts reaction from aldehydes and pyrrole under aqueous media at room temperature (Scheme 18). Different cations and anions on the structure of ionic liquids were screened and It was found that [BSMIM][HSO_4] could provide the highest yield of products in good yields (up to 89%). And the catalyst in aqueous phase can be recycled after separation of the organic product without significant loss of activity (Senapak, Saeeng, Jaratjaroonphong, Kasemsuk, & Sirion, 2016).



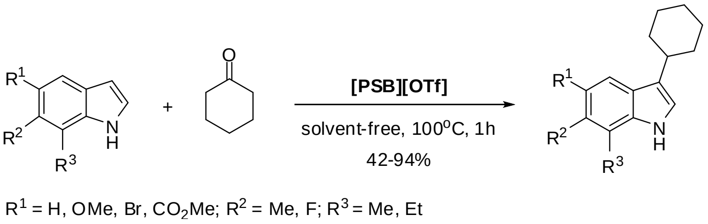
Scheme 18

Novel SO_3H-functionalized ionic liquid, [PSB][OTf], was reported by Gu and co-work in 2014. They used this kind of acidic ionic liquid as catalyst for the synthesis of 3-vinylindoles from indoles and ketones (Scheme 19). The reaction was proceeded smoothly in the presence of 3 mol% of [PSB][OTf] at 60°C for 15 min under solvent-free condition, and the corresponding products were obtained in moderate to high yields (50-97%). In addition, this protocol showed that the [PSB][OTf] exhibited more efficient than [PSMIM][OTf] and other the other acid-catalysts including TsOH, TfOH, $FeCl_3$ and $Sc(OTf)_3$ (Taheri et al., 2014).



Scheme 19

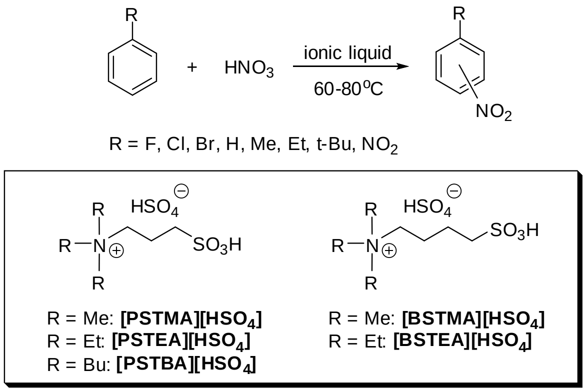
Subsequently, Gu's group employed the ionic liquid [PSB][OTf] as a catalyst for reductive Friedel-Crafts alkylation of indoles and cyclic ketones (Scheme 20). The reaction was conducted without using an external reductant under solvent-free condition at 100°C for 1 h in the presence of various acid-catalysts. This research showed that [PSB][OTf] proved to be most efficient catalyst, especially, more active than [PSMIM][OTf]. Using just 10 mol% of this catalyst, corresponding C3-cycloalkylindoles could be produced in yields of between 42 and 92%. And ionic liquid [PSB][OTf] could be recycled until six times without loss of activity (90% at sixth time) (Taheri, Lai, Cheng, & Gu, 2015).



Scheme 20

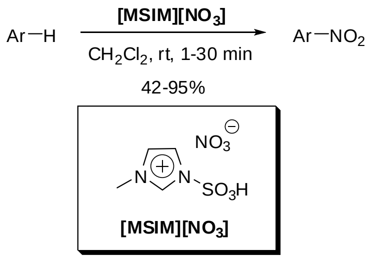
4. Nitration

In 2008, Fang's group used a series of SO_3H-functionalized trialkanylammonium ionic liquids with hydrogen sulfate anion (HSO_4) catalyzed regioselective mononitration of aromatic compounds (Scheme 21). The reactions were successfully carried out at 60-80°C, the results showed that all ionic liquid catalysts could provide the good yields and improved para-selectivity for halogenbenzenes compared to those in the absence of the catalyst. Particularly, [PSTBA][HSO_4] gave the higher rate enhancement than others because the lipophilicity of ionic liquid could increase rate of nitration reaction. In addition, [PSTBA][HSO_4] could be recovered and reused without decreasing of catalytic activity (Fang, Shi, Cheng, Gong, & Liu, 2008).



Scheme 21

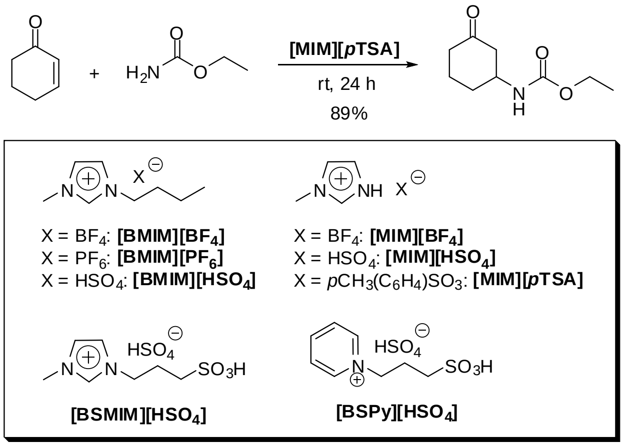
In 2012, Zolfigol et al. reported the use of 3-methyl-1-sulfonic acid imidazolium nitrate ([MSIM][NO_3]) as nitrating agent and Brönsted acidic ionic liquid for nitration of aromatic compounds (Scheme 22). The reactions were processed smoothly at room temperature in CH_2Cl_2 solvent, giving the corresponding products fair to good yields (42-95%) (Zolfigol et al., 2012).



Scheme 22

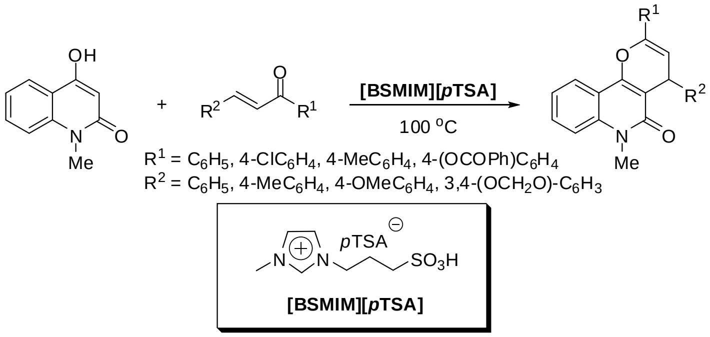
5. Michael Addition

Two applications of Michael addition using acidic ionic liquid catalysts were presented in this review. First, in 2012, Han et al. reported the use of several types of acidic-functionalized ionic liquids as catalyst for hetero-Michael addition under solvent-free condition at room temperature (Scheme 23). This research showed that, with 1-methylimidazolium *p*-toluenesulfonic ([MIM][*p*TSA]), the reaction proceeded more efficiently than other ionic liquid to afford the derivative products in good to excellent yields (up to 99%) and the catalyst could be reused at least five times (Han, Yang, Li, & Xia, 2012).



Scheme 23

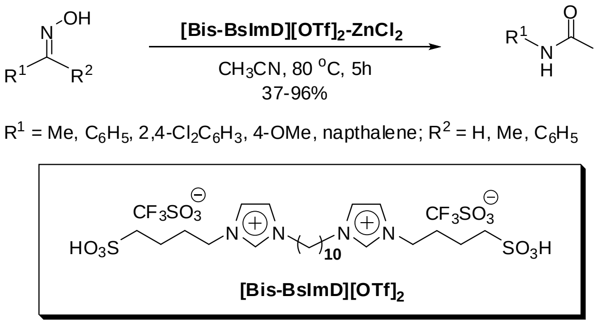
In the other work, Hajra et al. showed that the reactivity of a catalytic amount of acidic ionic liquid, 1-methyl-3-(4-sulfobutyl)imidazolium-4-methylbenzenesulfonate ([BSMIM][pTSA]) in Michael addition of 4-hydroxy-1-methyl-2-quinolone with chalcones for the synthesis of pyrano[3,2-c]quinolin-2-one derivatives under solvent- and metal-free condition at 110°C (Scheme 24). The reaction was achieved in a variety of chalcones through Michael addition followed by cyclization to afford the corresponding products in 70-86% yields (Bagdi, & Hajra, 2014).



Scheme 24

6. Beckmann Rearrangement

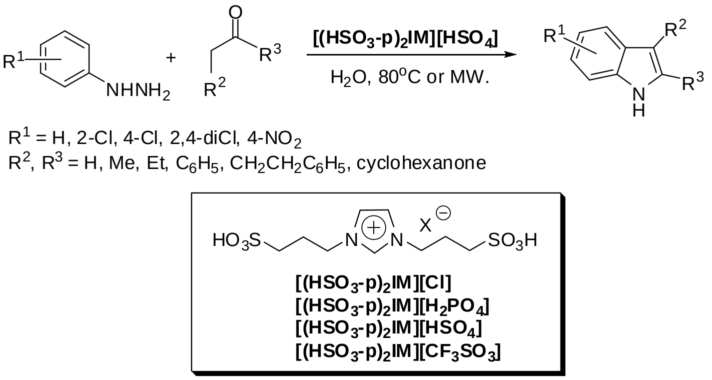
In 2009, Liu et al. reported a series of Brönsted acidic ionic liquids bearing double alkyl sulfonic acid groups mediated zinc chloride as catalyst for Beckmann rearrangement of oxime (Scheme 25). The reactions was successfully carried out using 5 mol% of [Bis-BslmD]$[CF_3SO_3]_2$-$ZnCl_2$ in CH_3CN at 80°C for 5 h to yield of the desired products in 37-96%. The catalytic system could be recycled for three times (Lui *et al.,* 2009).



Scheme 25

7. Fisher Indole Synthesis

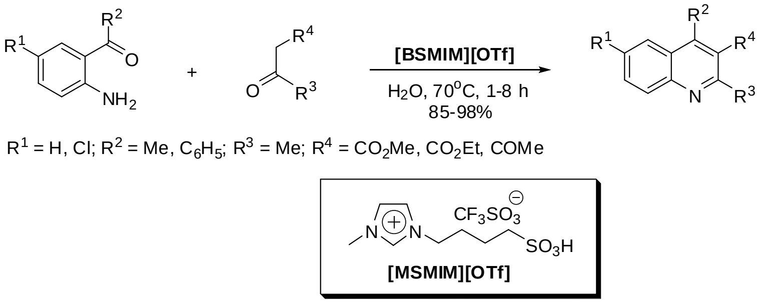
Li and Xu et al. reported the novel SO_3H-functionalized ionic liquids bearing two alkyl sulfonic acid groups in the imidazolium cations and applied as catalysts for the one-pot Fisher indole synthesis in water medium (Scheme 26). First work in 2009, they performed the reactions at 80°C for 0.5 h to successfully afforded the indole products in good yields (68-96%) in the presence of 50 mol% of $[HSO_3\text{-P})_2IM][HSO_4]$ (Xu et al., 2009). In other work, they performed the reactions under microwave irradiation in water medium, providing the indole products more efficiently in good yields (86-96%) with small amount of catalyst (5 mol%) and shorter reaction time compared to their previous attempts (Xu et al., 2012). In addition, the catalytic system could be reused at least twelve times without an obvious decrease in catalytic activity in both cases.



Scheme 26

8. Friedlander Quinoline Synthesis

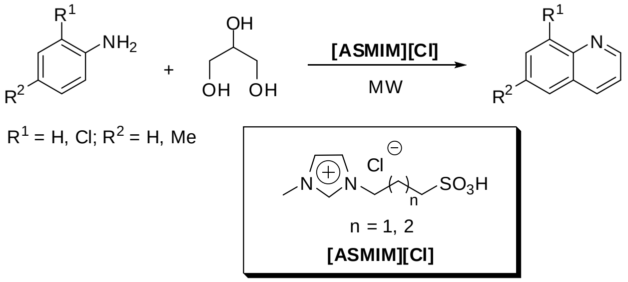
SO_3H-functionalized imidazolium ionic liquid ([BSMIM][OTf]) was used successfully as a catalyst for the synthesis of quinoline derivatives *via* Friedlander reaction by Akbari et al. in 2010 (Scheme 27). The reaction was carried out by using 2-aminoaryl ketones and β-ketoester or ketone (1:1 mole ratio) in the presence of 5 mol% of [BSMIM][OTf] under water media at 70 °C for 1-8 h, leading to the products in good yields (85-98%). And [BSMIM][OTf] can be reused for six times without loss of activity (Akbari, Heydari, Kalhor, & Kohan, 2010).



R^1 = H, Cl; R^2 = Me, C_6H_5; R^3 = Me; R^4 = CO_2Me, CO_2Et, COMe

Scheme 27

In recently, the synthesis of quinolones was described by Amarasekara *et al.* in 2014. In the presence of Brönsted acidic ionic liquids, naming 1-(1-alkylsulfonic)-3methylimidazolium chloride ([ASMIM][Cl]), the reaction was successfully performed under microwave condition in short reaction time without oxidant and metal catalyst (Scheme 28). The corresponding products were obtained in good yields (70-78%) (Amarasekara, & Hasan, 2014).

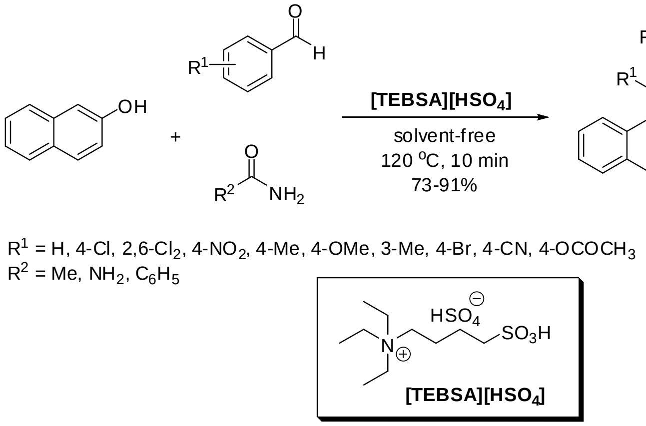


R^1 = H, Cl; R^2 = H, Me

Scheme 28

9. Multi-component Reaction

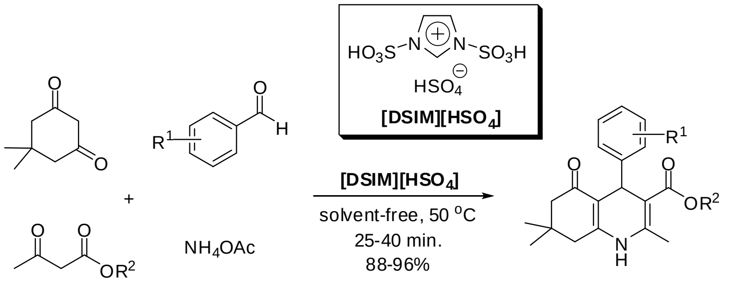
Multi-component reaction of aldehydes, amides, and 2-naphthol for the synthesis of aminoalkylnapthols was reported by Hajipour and co-workers in 2009 (Scheme 29). The reaction was achieved in the presence of Brönsted acidic ionic liquid, [TEBSA][HSO_4] under solvent-free condition at 120°C for 10 min, resulting in 73-91% yields of the corresponding products. The catalytic activity of this acidic ionic liquid was compared with $Fe(HSO_4)_3$, iodine, sulfamic acid and $K_5CoW_{12}O_{40}{\cdot}3H_2O$ catalysts, and the result showed that exhibited more efficient than that the other catalysts. In addition, the [TEBSA][HSO_4] can be reused for four times without loss of activity (Hajipour, Ghayeb, Sheikhan, & Ruoho, 2009).



R^1 = H, 4-Cl, 2,6-Cl_2, 4-NO_2, 4-Me, 4-OMe, 3-Me, 4-Br, 4-CN, 4-$OCOCH_3$
R^2 = Me, NH_2, C_6H_5

Scheme 29

The one-pot four components of hexahydroquinolines synthesis catalyzed by 1,3-disulfonic acid imidazolium hydrogen sulfate ([Dsim][HSO_4]) under solvent-free condition was described by Zare et al. in 2013 (Scheme 30). The reaction of aromatic aldehydes, dimedone, β-ketoesters and ammonium acetate (1:1:1:1.2 mole ratio) were successfully reacted in the presence of 3 mol% of [Dsim][HSO_4] at 50 °C for 25-40 minutes to afford the desired products in high yields (88-96%). The catalyst can be reused for four times without loss of activity (Zare, Abi, Moosavi-Zare, Beyzavi, & Zolfigol, 2013).



R^1 = H, 4-NO_2, 3-NO_2, 4-OMe, 4-Me, 4-OH, 4-Br, 3-Br, 4-Cl; R^2 = OEt, OMe

Scheme 30

Conclusions

In summary, this review provides an introductory overview of the use of Brönsted acidic ionic liquids (BAILs) in versatile organic reactions. The utility of BAILs is now well recognized as solvents, reagent and catalyst for acid-promoted organic reactions in recent years. Due to BAILs are suitable for environmentally friendly benign processes including metal-free and solvent-free conditions and they can play a distinguished role in reactivity. Especially, they are suitable for reactions that need to proceed in water and can be reused allowing products to be easily separated by simple extraction or filtration. To date, the types of organic reactions catalyzed by BAILs are now much more attention than that of the reactions used metal catalysts. The wide applications of BAILs catalyst in organic reactions will provide a driving force for future development of green chemistry.

References

Akbari, J., Heydari, A., Kalhor, H. R. & Kohan, S. A. (2010). Sulfonic acid functionalized ionic liquid in combinatorial approach, a recyclable and water tolerant-acidic catalyst for one-pot Friedlander quinoline synthesis. *J. Comb. Chem., 12,* 137-140.

Akiyama, T., Takaya, J., Kagoshima, H. (2002). Brönsted acid-catalyzed Mannich-type reactions in aqueous media. *Adv. Synth. Catal., 344*, 338-347.

Amarasekara, A. S. & Hasan, M. A. (2014). 1-(1-Alkylsulfonic)-3-methylimidazolium chloride Brönsted acidic ionic liquid catalyzed Skraup synthesis of quinolones under microwave heating. *Tetrahedron Lett.*, *55*, 3319-3321.

Amarasekara, A. S. (2016). Acidic ionic liquids. *Chem. Rev.*, *116*, 6133-6183.

Bagdi, A. K. & Hajra, A. (2014). Brönsted acidic ionic liquid catalyzed tandem reaction of 4-hydroxy-1-methyl-2-quinolone with chalcone: regioselective synthesis of pyrano[3,2-c]quinolin-2-ones. *RSC. Adv.*, *4*, 23287-23291.

Chang, T., He, L., Bian, L., Han, H., Yuan, M. & Gao, X. (2014). Brönsted acid-surfactant-combined catalyst for the Mannich reaction in water. *RSC Adv., 4*, 727-731.

Cole, A. C., Jensen, J. L., Ntai, I., Tran, K. L. T., Weaver, K. J., Forbes, D.C. & Davis, J. H. Jr. (2002). Novel Brönsted acidic ionic liquids and their use as dual solvent-catalysts. *J. Am. Chem. Soc.,124*, 5962-5963.

Duan, Z., Gu, Y., Zhang, J., Zhu, L. & Deng, Y. (2006). Protic pyridinium ionic liquids: synthesis, activity determination and their performances for acid catalysis. *J. Mol. Catal. A: Chem., 250*, 163-168.

Fang, D., Fei, Z. & Liu, Z. (2009). Functionalized ionic liquid as the recyclable catalyst for Mannich-type reaction in aqueous media. *Catal. Commun., 10,* 1267-1270.

Fang, D., Luo, J., Zhou, X. -L. & Liu, Z .-L. (2007). Mannich reaction in water using acidic ionic liquid as recoverable and reusable catalyst. *Catal. Lett., 116,* 76-80.

Fang, D., Shi, Q. -R., Cheng, J., Gong, K. & Liu, Z. -L. (2008). Regioselective mononitration of aromatic compounds using Brönsted acidic ionic liquids as recoverable catalysts. *Appl. Catal. A: Gen., 345*, 158-163.

Fang, D., Zhou, X. -L., Ye, Z. -W. & Liu, Z. -L. (2006). Brönsted acidic ionic liquid and their use as dual solvent-catalysts for Fischer esterification. *Ind. Eng. Chem. Res., 45,* 7982-7984.

Fraga-Dubreuil, J., Bourahla, K., Rahmouni, M., Bazureau, J. P. & Hamelin, J. (2002). Catalysed esterifications in room temperature ionic liquids with acidic counteranion as recyclable reaction media. *Catal. Commun., 3*, 185-190.

Gu, Y., Shi, F. & Deng, Y. (2004). Esterification of aliphatic acids with olefin promoted by Brönsted acidic ionic liquids. *J. Mol. Catal. A: Chem.*, 212, 71-75.

Hajipour, A. R., Ghayeb, Y., Sheikhan, N. & Ruoho, A. E. (2009). Brönsted acidic ionic liquid as an efficient and reusable catalyst for one-pot synthesis of 1-amidoalkyl 2-naphthols under solvent-free conditions. *Tetrahedron Lett.*, *50*, 5649-5651.

Han, F., Yang, L., Li, Z. & Xia, C. (2012). Acidic-functionalized ionic liquid as an efficient, green and reusable catalyst for hetero-Michael addition of nitrogen, sulfur and oxygen nucleophiles to α,β-unsaturated ketones. *Org. Biomol. Chem., 10,* 346-354.

He, L., Qin, S., Chang, T., Sun, Y. & Gao, X. (2013). Biodiesel synthesis from the esterification of three fatty acids and alcohol catalyzed by long-chain Bronsted acid ionic liquid. *Catal. Sci. Technol., 3*, 1102-1107.

Kitaoka, S., Nobuoka, K. & Ishikawa, Y. (2004). The first utilization of acidic ionic liquid for preparation of tetraarylporphyrins. *Chem. Commun*., 1902-1903.

Li, B. L., Xu, D. –Q., Zhong, A. G. (2012). Novel SO_3H-functionalized ionic liquids catalyzed a simple, green and efficient procedure for Fisher indole synthesis in water under microwave irradiation. J*. Fluorine Chem., 144*, 45-50.

Li, J., Peng, Y. & Song, G. (2005). Mannich reaction catalyzed by carboxyl-functionalized ionic liquid in aqueous media. *Catal. Lett., 102,* 159-162.

Limura, S., Nobutou, D., Manable, K., Kobayashi, S. (2003). Mannich-type reactions in water using a hydrophobic polymer-supported sulfonic acid catalyst. *Chem. Commun*., 1644-1645.

Liu, X., Xiao, L., Wu, H., Li, Z., Chen, J. & Xia, C. (2009). Novel acidic ionic liquids mediated zinc chloride: highly effective catalysts for the Beckmann rearrangement. *Catal. Commun., 10,* 424-427.

Qiao, K., Hagiwara, H. & Yokoyama, C. (2006). Acidic ionic liquid modified silica gel as novel solid catalysts for esterification and nitration reactions. *J. Mol. Catal. A: Chem., 246*, 65-69.

Sahoo, S., Joseph, T. & Halligudi, S. B. (2006). Mannich reaction in Brönsted acidic ionic liquid: A facile synthesis of β-amino carbonyl compounds. *J. Mol. Catal. A: Chem., 244*, 179-182.

Senapak, W., Saeeng, R., Jaratjaroonphong, J., Kasemsuk, T. & Sirion, U. (2016). Green synthesis of dipyrromethanes in aqueous media catalyzed by SO_3H-functionalized ionic liquid. *Org. Biomol. Chem., 14,* 1302-1310.

Taheri, A., Lai, B., Cheng, C. & Gu, Y. (2015). Brönsted acid ionic liquid-catalyzed reductive Friedel-Crafts alkylation of indoles and cyclic ketones without an external reductant. *Green Chem.,* 812-816.

Taheri, A., Liu, C., Lai, B., Cheng, C., Pan, X. & Gu, Y. (2014). Brönsted acidic ionic liquid catalyzed facile synthesis of 3-vinylindoles through direct C3 alkenylation of indoles with simple ketones. *Green Chem*., *16*, 3715-3719.

Xing, H., Wang, T., Zhou, Z. & Dai, Y. (2005). Novel Brönsted-acidic ionic liquids for esterifications. *Ind. Eng. Chem. Res., 44*, 4147-4150.

Xu, D. -Q., Wu, J., Luo, S. -P., Zhang, J. -X., Wu, J. -Y., Du, X. -H. & Xu, Z. -Y. (2009). Fisher indole synthesis catalyzed by novel SO_3H-functionalized ionic liquids in water. *Green Chem., 11*, 1239-1246.

Xu, Z., Wan, H., Miao, J., Han, M., Yang, C. & Guan, G. (2010). Reusable and efficient polystyrene-supported acidic ionic liquid catalyst for esterification. *J. Mol. Catal. A: Chem., 322,* 152-157.

Yue, C. B., Yi, T.F., Zhu, C. B. & Liu, G. (2009). Mannich reaction catalyzed by a novel catalyst under solvent-free conditions. *J. Indust. Eng. Chem., 15*, 653-656.

Zare, A., Abi, F., Moosavi-Zare, A. R., Beyzavi, M.H. & Zolfigol, M. A. (2013). Synthesis, characterization and application of ionic liquid 1,3-disulfonic acid imidazolium hydrogen sulfate as an efficient catalyst for the preparation of hexahydroquinolines. *J. Mol. Liq., 178,* 113-121.

Zhao, G., Jiang, T., Gao, H., Han, B., Huang, J. & Sun, D. (2004). Mannich reaction using acidic ionic liquids as catalysts and solvents. *Green Chem., 6*, 75-77.

Zolfigol, M. A., Khazaei, A., Moosavi-Zare, A. R., Zare, A., Kruger, H. G., Asgari, Z., Khakyzadeh, V. & Kazem[Rostami, M. (2012). Design of ionic liquid 3-methyl-1-sulfonic acid imidazoilum nitrate as reagent for the nitration of aromatic compounds by *in Situ* generation of NO_2 in acidic media. *J. Org. Chem., 77,* 3640-3645.