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An imidazolium tosylate salt as efficient and recyclable catalyst for acetylation in an ionic liquid

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Abstract A novel non-metallic salt, 1-butyl-3-methylimidazolium tosylate ([*bmim*][O*Ts*]) dissolved in the ambient temperature ionic liquid of 1-butyl-3-methylimidazolium tetrafluoroborate ([*bmim*][BF_4]), was found to be the efficient catalyst for acetylation with the advantages of good recyclability, avoidance of metal contamination, mild reaction conditions, and wide availability for substrates (alcohols, phenols, and amines), could completely replace organic bases, metal *Lewis* acids, or metallic triflates to fulfill acetylation by a nucleophilic catalytic mechanism, which was supported by ^{13}C NMR analysis.

Keywords Acetylation; Ionic liquids; Ionic catalysts; Imidazolium tosylate.

Introduction

The acylation of alcohols, phenols, or amines with acid anhydrides is one of the most frequently used processes in organic synthesis [1], which can be catalyzed by bases such as pyridine, 4-(dimethylamino)-pyridine (*DMAP*) or 4-pyrrolidinopyridine (*PPY*) [2]. In addition, protonic acids such as *p*-toluene sulfonic acid [3] and *Lewis* acids, such as $ZnCl_2$ [4], $CoCl_2$ [5], $TaCl_5$ [6], $ZrCl_4$ [7], $InCl_3$ [8], $MgBr_2$ [9], SmI_2 [10], and *TMS*Cl [11], are also well known to catalyze the acylation of alcohols if the substrates preclude the acid-sensitive groups. Recently, various metallic triflates like Cu(O*Tf*)$_2$ [12], Sc(O*Tf*)$_3$ [13], Yb(O*Tf*)$_3$ [14], In(O*Tf*)$_3$ [15], Bi(O*Tf*)$_3$ [16], Ce(O*Tf*)$_3$ [17], and Gd(O*Tf*)$_3$ [18] etc., have been reported to be very effective catalysts for acetylation using *Ac*OH or Ac_2O as inexpensive acylating agents with the attractive advantage of recyclability, but suffering from the drawbacks of high cost, toxicity, and metal contamination for organic products. Up to date, a number of acetylation catalyzed by (*Lewis*) acids and bases is known, however, many of them are limited in their applications due to the instability of reactants or products under the (acidic or basic) reaction conditions, tedious work-up procedures, or non-recyclability of catalysts [18]. In viewpoint of today's environmental consciousness, chemists have shown considerable interests in the uses of environmentally benign reaction media and catalysts. Consequently, it would be desirable to develop neutral, reusable, and metal-free catalysts for acetylation. The uses of organic ionic salts as catalysts are inspired by the research of ionic liquids (ILs), which are characteristic of unique properties, such as organic composition without involvement of metal ions, recyclability due to non-volatility, flexible cation/anion combination, excellent solvents for polar compounds, and versatile modifications by functional units [19–24].

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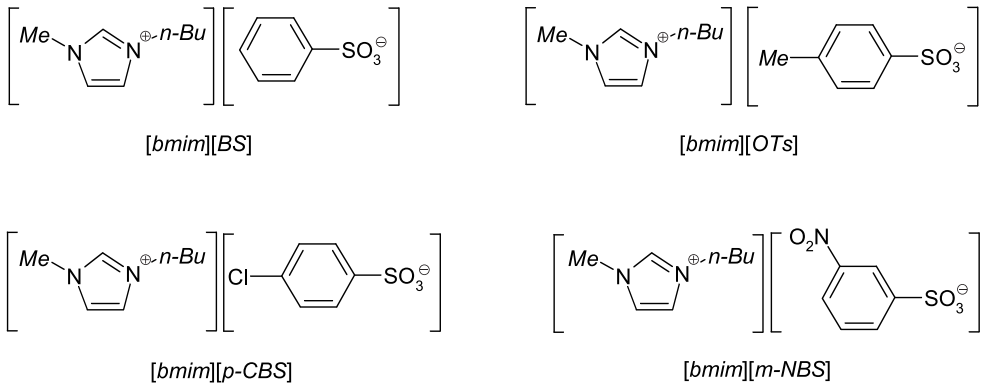


Scheme 1

Highlighted by the unique features of ILs and the outstanding catalytic behavior of metallic triflates for acetylation [12, 15, 17, 18], herein we synthesized a series of imidazolium based salts with the substituted benzenesulphonates as counterions, which were dissolved in the ambient temperature IL of [*bmim*][BF_4] (1-butyl-3-methylimidazolium tetrafluoroborate) in considerations of their ionic nature and miscibility, to catalyze acetylation of alcohols, amines, and phenols. The selection of benzenesulphonates as anions was due to their similar nature to that of O*Tf*- as a good nucleophile (*Lewis* base).

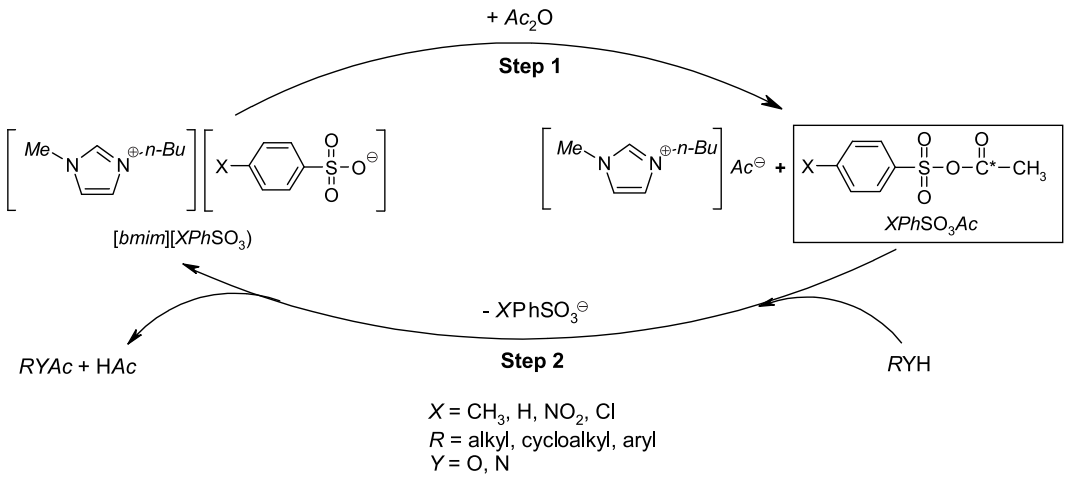
Results and discussion

A series of neutral imidazolium-benzenesulphonate salts with different electro-withdrawing and electron-donating groups were synthesized (Scheme 1), which were used to catalyze acetylation in the IL of [*bmim*][BF_4]. BF_4^- was selected as the anion because of its inertness to hydrolysis compared to PF_6^-, eliminating the possibility of HF formation if the traces of water were present in the reaction systems as reported in Ref. [25].

Table 1 Comparison of acetylation of benzyl alcohol or cyclohexanol catalyzed by different imidazolium salts[a]

Entry	Substrate	Catalyst	Time/min[b]	Yield/%[c]
1	benzyl alcohol	[*bmim*][*BS*]	5	>99
2	benzyl alcohol	[*bmim*][O*Ts*]	5	>99
3	benzyl alcohol	[*bmim*][*p-CBS*]	5	>99
4	benzyl alcohol	[*bmim*][*m-NBS*]	5	>99
5	cyclohexanol	[*bmim*][*BS*]	100	98
6	cyclohexanol	[*bmim*][O*Ts*]	40	99
7	cyclohexanol	[*bmim*][*p-CBS*]	150	98
8	cyclohexanol	[*bmim*][*m-NBS*]	180	96

[a] Substrate 0.01 mol, Ac_2O 0.02 mol, catalyst 0.001 mol (10%), solvent ([*bmim*][BF_4]) 1 cm^3, reaction temperature 50°C
[b] The reaction was monitored by TLC
[c] GC yield of acetylated product



Scheme 2

When benzyl alcohol was applied as the model substrate, due to less steric hindrance and good stability as a primary alcohol, the acetylation was virtually complete in 5 min in each system (Table 1, entries 1–4). So, cyclohexanol with bulky steric hindrance as a secondary alcohol was used to investigate the activity difference. As shown in Table 1 (entries 5–8), the acetylation catalyzed by different salts occurred at varying reaction rates in the ranking of [*bmim*][O*Ts*] > [*bmim*][*BS*] > [*bmim*][*p-CBS*] > [*bmim*][*m-NBS*]. These results suggested that the electron-donating substitute ($-CH_3$) in benzenesulfonate like [*bmim*][O*Ts*] favorably improves the catalytic activity, and that the electron-drawing substituents ($-NO_2$ and –Cl) in benzenesulfonate like [*bmim*][*p-CBS*] and [*bmim*][*m-NBS*] deteriorate the activity.

These results are in coincidence with nucleophilic acetylation catalyzed by metal triflates [12, 15, 17, 18]. Similarly, in our work the $XPhSO_3^-$ anion ($X = -CH_3$, –H, $-NO_2$, and –Cl) as a nucleophile reacts with Ac_2O to form intermediate $XPhSO_3Ac$ (Step 1 in Scheme 2), which is attacked by *RY*H (*R* = alkyl, cycloalkyl, aryl; *Y* = O, N) to give the acylated product due to the easily cleavable feature of bulky group $XPhSO_3$. Whenever *X* is an electron-donating group such as $-CH_3$, the increased nucleophilicity favors the attack of OTs^- to Ac_2O, facilitating the formation of *OTs-Ac*. This proposed mechanism was supported

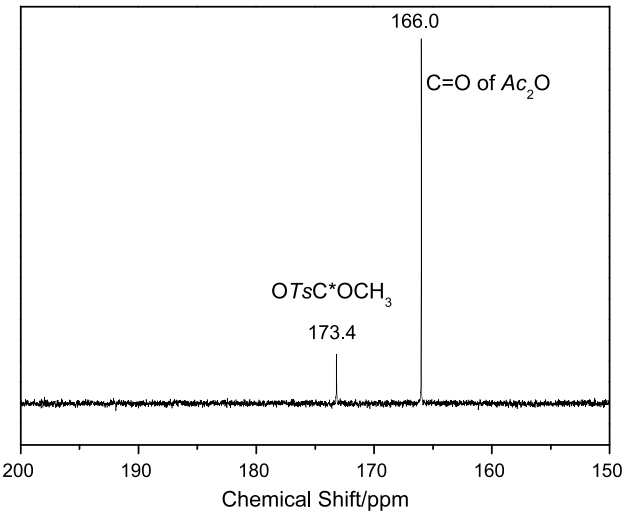
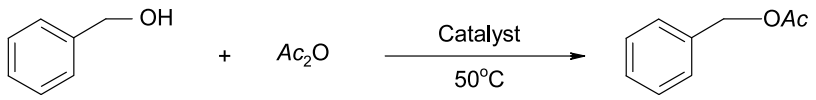


Fig. 1 ^{13}C NMR spectrum obtained upon mixing [*bmim*][O*Ts*] with Ac_2O (1:10 mol ratio, $CDCl_3$, room temperature)

Table 2 Comparison of acetylation of benzyl alcohol catalyzed by [*bmim*][O*Ts*] to those of conventional catalysts in ionic liquids and organic solvents[a]



Entry	Catalyst	Solvent	Time/min[b]	Yield/%[c]
1	–	–	72	98
2	[*bmim*][O*Ts*] (fresh)	[*bmim*][BF_4]	5	99
3	[*bmim*][O*Ts*] (2nd run)	[*bmim*][BF_4]	5	99
4	[*bmim*][OTs] (3rd run)	[*bmim*][BF_4]	5	99
5	[*bmim*][O*Ts*] (4th run)	[*bmim*][BF_4]	5	99
6	[*bmim*][O*Ts*] (5th run)	[*bmim*][BF_4]	5	99
7	[*bmim*][O*Ts*] (6th run)	[*bmim*][BF_4]	5	99
8	[*bmim*][O*Ts*] (7th run)	[*bmim*][BF_4]	5	99
9	[*bmim*][O*Ts*] (8th run)	[*bmim*][BF_4]	5	99
10	[*bmim*][O*Ts*] (9th run)	[*bmim*][BF_4]	5	99
11	[*bmim*][O*Ts*] (10th run)	[*bmim*][BF_4]	5	99
12	pyridine	[*bmim*][BF_4]	8	99
13	pyridine	1,4-dioxane	10	98
14	*DMAP*	[*bmim*][BF_4]	2	98
15	*DMAP*	1,4-dioxane	3	99
16[d]	Na[O*Ts*]	[*bmim*][BF_4]	10	98
17[d]	Na[O*Ts*]	1,4-dioxane	20	97

[a] Catalyst 0.001 mol (10%), *Ph*CH_2OH 0.01 mol, Ac_2O 0.02 mol, solvent 1 cm^3, reaction temperature 50°C
[b] The reaction was monitored by *TLC*
[c] GC yield of *Ph*CH_2OAc
[d] Inhomogeneous reaction system

by ^{13}C NMR analysis monitoring the mixed solution of [*bmim*][O*Ts*] and Ac_2O (1:10 mol ratio, $CDCl_3$, room temperature) (Fig. 1). In addition to a signal at $\delta = 166.0$ ppm ascribed to carbonyl (C=O) of Ac_2O, a small signal at 173.4 ppm was assigned to the formed active intermediate O*Ts*-C*OCH$_3$ as the reactive acylating agent, which had also been observed in Refs. [12, 15].

To further examine the catalytic performance of screened [*bmim*][O*Ts*], comparison of the activity of [*bmim*][O*Ts*] in [*bmim*][BF_4] to that of pyridine or *DMAP* in 1,4-dioxane was conducted as shown in Table 2. Obviously, the activity of [*bmim*][O*Ts*]-[*bmim*][BF_4] system was competitive to those of the conventional systems (entries 12–15) with impressive advantage of recyclability (entries 2–11). After 10 recycling uses, the activity of [*bmim*][O*Ts*]–[*bmim*][BF_4] perfectly maintained without any loss, indicating that this system did not undergo deactivation or decomposition at all by the formed by-product of acetic acid (*Ac*OH) [26]. The pure product of *Ph*CH$_2$O*Ac* was obtained simply by extraction with cyclohexane from the IL phase, washing with saturated sodium hydrocarbonate solution and brine separately (to remove Ac_2O and *Ac*OH) before drying. When pyridine or *DMAP* in 1,4-dioxane was applied as catalyst, which is one of the most effective catalysts for acetylation [2], the separation of substrates/product/catalyst was tedious and these base catalysts were prone to be deactivated by the by-product of *Ac*OH [12, 26]. Whenever pyridine (or *DMAP*) was neutralized by HO*Ac*, the formed organic salt could not be reused as the base catalyst anymore. Hence, the recycling uses of pyridine or *DMAP* were not simply feasible.

When Na[O*Ts*] was used to replace [*bmim*][O*Ts*] in consideration of the same O*Ts*$^-$ anion (entries 16, 17), its activity was obviously lower than that of [*bmim*][BF_4] maybe due to insolubility of NaO*Ts* in [*bmim*][BF_4] or in 1,4-dioxane, thus limiting the mass transfer. In the [*bmim*][O*Ts*]–[*bmim*][BF_4] system, the cation endowed with slight acidity corresponding to the C2 proton in [*bmim*]$^+$ [19] could be regarded as the source of acid catalytic effects, leading to the dual activation coming from the [*bmim*]$^+$ cation and the O*Ts*$^-$ anion (nucleophile, *Lewis* base) [12, 19]. The synergistic effect from the [*bmim*]$^+$ cation and the O*Ts*$^-$ anion imparts advantageous catalytic properties to [*bmim*][O*Ts*]–[*bmim*]-[BF_4] system, accounting for the efficient acetylation.

Table 3 Generality of [*bmim*][O*Ts*]–[*bmim*][BF_4] for acetylation of alcohols, phenols, or amines[a]

Entry	Substrate	Time/min[b]	Yield/%[c]
1	benzyl alcohol	5	99
2	1-butanol	10	99
3	1-octanol	10	98
4	1-decanol	20	98
5	2-octanol	60	96
6	cyclohexanol	40	99
7	1-phenyl-ethanol	20	98
8[d]	propane-1,2-diol	20	99
9	*tert*-butanol	300	79[e] (2[f])
10	citric acid tributyl ester	480	19[e] (–[f])
11	phenol	10	97
12	4-methyl-phenol	20	96
13	2-methyl-phenol	40	95
14[d]	benzene-1,2-diol	20	98
15	4-nitro-phenyl	120	98
16	salicylic acid methyl ester	480	13
17	1-naphthalenol	60	97
18	phenylamine	5	96
19	benzylamine	5	97

[a] Substrate 0.01 mol, Ac_2O 0.02 mol, [*bmim*][BF_4] 1 cm^3, [*bmim*][O*Ts*] 0.001 mol, reaction temperature 50°C
[b] The reaction was monitored by *TLC*
[c] GC yield to product of acetylation
[d] Only di-acetylated product was obtained
[e] Isolated yield
[f] The yield obtained with pyridine as the catalyst was indicated in parenthesis

The generality of the [*bmim*][O*Ts*]–[*bmim*][BF_4] system for acetylation was demonstrated in Table 3 in which a wide array of substrates with different electronic/steric character and reactivity was selected. The results showed that the [*bmi*m][O*Ts*]–[*bmim*]-[BF_4] system was generally efficient for the acetylation of (primary, secondary) alcohols, phenols, and amines. As to tertiary alcohols of *tert*-butanol and citric acid tributyl ester with high reactivity for dehydration (entries 9 and 10), the acylated products obtained without formation of the elimination products, which were confirmed by calculative balance between substrate conversions and isolated yields of the acylated products. Due to bulky hindrance of the tertiary alcohols, the reaction rate was much lower compared to those with the primary and secondary alcohols as the substrates (entries 1–8). On doing the same reactions with pyridine as a catalyst, no reactions (acetylation and dehydration) occurred at all. As to a substrate with two hydroxyl groups, like propane-1,2-diol or benzene-1,4-diol (entries 8, 14),

the di-acylated products were obtained without mono-acetylation. The acetylation of amines (sensitive to acid catalysts) and phenols (sensitive to base catalysts) could also be carried out smoothly in [*bmim*][O*Ts*]–[*bmim*][BF_4] (entries 11–19). Hence, due to the neutral feature of the [*bmim*][O*Ts*]–[*bmim*][BF_4] system, this method could be widely applicable for acetylation involving reactants or products instable under acidic or basic reaction conditions [26].

Conclusively, we developed an ionic catalytic system of [*bmim*][O*Ts*]–[*bmim*][BF_4], which can efficiently catalyze the acetylation with the advantages of wide scope of substrates (alcohols, phenols, and amines) under neutral conditions, excellent recyclability, non-metal contamination, facile separation work-up, and insensitivity to air and water. The acceleration of acetylation catalyzed by [*bmim*][O*Ts*]–[*bmim*][BF_4] could be explained by the synergistic effects from the $[bmim]^+$ cation as a weak acid catalyst and the OTs^- anion as a nucleophilic (*Lewis* base) catalyst.

Experimental

N-Methylimidazole was dried with 5 Å molecular sieve overnight and purified by distillation before use. The other chemical reagents were of analytical grade and used as received. The IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. The ^{1}H NMR and ^{13}C NMR (298 K) spectra were recorded on a Bruker Avance 500 spectrometer. All reactions were analysed directly using a SHIMADZU GC-14B Gas Chromatograph equipped with a HP-1 column and a flame ionization detector. Products were identified by GC-MS (Agilent 6890 Series, MS/Agilent 5973 Network). Electrospray ionization mass spectrometry (ESI-MS) analyses were performed on Agilent 1100LC/MSDVL. All reactions were run in an Argonaut Advantage Series 2410 Personal Screening Synthesizer.

Syntheses of imidazolium salts with differently substituted benzenesulfonates as anions

A solution of 17.4 g 1-butyl-3-methylimidazolium chloride [27] (0.1 mol) in 100 cm^3 deionized water was treated with 17.1 g sodium toluene-4-sulfonate (0.1 mol, Na[O*Ts*]). After stirred for 2 h at ambient temperature, the solution was stripped of water by heating *in vacuo*. To the obtained slurry solid 100 cm^3 CH_2Cl_2 were added and the mixture was stirred vigorously at ambient temperature for 6 h. The resultant filtrate was treated with active carbon. After filtration and removal of solvent in *vacuo*, [*bmim*][O*Ts*] was obtained as a waxy yellow solid.

When sodium benzenesulfonate (Na[*BS*]), sodium 3-nitrobenzenesulfonate (Na[*m-NBS*]), and sodium 4-chlorobenzenesulfonate (Na[*p-CBS*]) were applied to react with 1-butyl-3-methylimidazolium chloride for ion exchange, the similar procedures were followed as mentioned above. Finally, [*bmim*][*BS*] and [*bmim*][*m-NBS*] were obtained as pale yellow viscous liquids. [*bmim*][*p-CBS*] was obtained as a waxy yellow solid. [*bmim*][BF_4] was synthesized as reported in Ref. [28].

1-Butyl-3-methylimidazolium tosylate
([*bmim*][O*Ts*], $C_{15}H_{22}N_2O_3S$)
Mp 67°C; ESI-MS: $m/z = 171$ [$bmim^+$], 139 [OTs^-]; ^{1}H NMR (500 MHz, D_2O): $\delta = 0.8$ (m, CH_3), 1.3 (m, N^+CH_2-$CH_2CH_2CH_3$), 1.8 (m, $N^+CH_2CH_2CH_2CH_3$), 2.4 (s, Ar–CH_3), 3.8 (s, N–CH_3), 4.1 (m, N^+CH_2), 7.3 and 7.6 (2d, 2×2H, $J = 8$ Hz, –*Ph*), 7.4 (s, N*CHCH*N^+), 8.6 (s, N*C*HN^+) ppm; IR (KBr disc): $\bar{\nu} = 3149$ (m), 3100 (m), 2960 (m), 2872 (m), 1645 (m), 1570 (m), 1461 (m), 1380 (m), 1192 (s), 1037 (s) cm^{-1}.

1-Butyl-3-methylimidazolium benzenesulfonate
([*bmim*][*BS*], $C_{14}H_{20}N_2O_3S$)
ESI-MS: $m/z = 171$ [$bmim^+$], 125 [BS^-]; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.9$ (m, 3H, CH_3), 1.3 (m, 2H, $N^+CH_2CH_2$-CH_2CH_3), 1.8 (m, 2H, $N^+CH_2CH_2CH_2CH_3$), 4.0 (s, 3H, N–CH_3), 4.2 (m, 2H, N^+CH_2), 7.2, 7.3, 7.9 (m, 2H, 1H, 2H, –*Ph*), 7.3 (m, 2H, N*CHCH*N^+), 10.2 (s, 1H, N*C*HN^+) ppm; IR (KBr disc): $\bar{\nu} = 3149$ (m), 3112 (m), 2961 (m), 2872 (m), 1655 (m), 1570 (m), 1471 (m), 1379 (m), 1192 (s), 1037 (s) cm^{-1}.

1-Butyl-3-methylimidazolium p-chlorobenzenesulfonate
([*bmim*][*p-CBS*], $C_{14}H_{19}N_2O_3SCl$)
Mp 64°C; ESI-MS: $m/z = 171$ [$bmim^+$], 191 [$p\text{-}CBS^-$]; ^{1}H NMR (500 MHz, D_2O): $\delta = 0.8$ (m, 3H, CH_3), 1.2 (m, 2H, $N^+CH_2CH_2CH_2CH_3$), 1.7 (m, 2H, $N^+CH_2CH_2CH_2CH_3$), 3.8 (s, 3H, N–CH_3), 4.1 (m, 2H, N^+CH_2), 7.3 (s, 2H, N*CH*-*CH*N^+), 7.5 and 7.7 (d, 2×2H, $J = 8$ Hz, –*Ph*) ppm; IR (KBr disc): $\bar{\nu} = 3145$ (m), 3086 (m), 2961 (m), 2871 (m), 1662 (m), 1571 (m), 1473 (m), 1389 (m), 1227 (s), 1186 (s) cm^{-1}.

1-Butyl-3-methylimidazolium m-nitrobenzenesulfonate
([*bmim*][*m-NBS*], $C_{14}H_{19}N_3O_5S$)
ESI-MS: $m/z = 171$ [$bmim^+$], 201.9 [$m\text{-}NBS^-$]; ^{1}H NMR (500 MHz, D_2O): $\delta = 0.8$ (m, 3H, CH_3), 1.2 (m, 2H, N^+CH_2-$CH_2CH_2CH_3$), 1.7 (m, 2H, $N^+CH_2CH_2CH_2CH_3$), 3.8 (s, 3H, N–CH_3), 4.1 (m, 2H, N^+CH_2), 7.3 (s, 2H, N*CHCH*N^+), 7.7, 8.1, 8.3, 8.5 (4×1H, –*Ph*), 8.6 (s, 1H, N*C*HN^+) ppm. IR (KBr disc): $\bar{\nu} = 3145$ (m), 3081 (m), 2961 (m), 2870 (m), 1609 (m), 1569 (m), 1532 (s), 1464 (m), 1349 (s), 1237 (s), 1193 (s) cm^{-1}.

Acetylation procedure and recycling of the [bmim][OTs]–[bmim][BF_4] system

To [*bmim*][O*Ts*] (0.31 g, 0.001 mol) was added 1 cm^3 [*bmim*]-[BF_4]. After stirring for 5 min, the IL solution was mixed with 1.08 g benzyl alcohol (10 mmol) (or other substrates) and 2.04 g acetic anhydride (20 mmol). The resultant homoge-

neous solution was stirred at 50°C monitoring by TLC plate. Whenever the spot of substrate completely disappeared on the TLC plate, the reaction time was determined. Upon completion of the reaction, the organic reactants and products were extracted with $3 \times 8\,cm^3$ cyclohexane and then analyzed by GC to determine the conversions (1-dodecane as internal standard) and the selectivities (normalization method), according to which GC yields were calculated. The structures of the obtained products were further confirmed by GC-MS. The left IL phase was dried *in vacuo* at 60°C (to remove the formed acetic acid and traces of cyclohexane) before the next run. During the recycling uses, only 10 mmol acetic anhydride were needed additionally due to excess acetic anhydride which had been added (2 equiv) in the first run.

Acknowledgements

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