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ORIGINAL PAPER

Synthesis of task-specific imidazolium ionic liquid as an efficient catalyst in acetylation of alcohols, phenols, and amines

Snehkrishn A. Chaubey[1] · **Roli Mishra**[1]

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Abstract

Herein, we report the synthesis of task-specific amino-functionalized imidazolium ionic liquid, acetate1-(2-tert-butoxy-carbonylamino-ethyl)-3-methyl-3H-imidazol-1-ium; (Boc-NH-EMIM.OAc), as an efficient catalyst for the acetylation of alcohols, phenols, and amines in the presence of acetic anhydride (acetylating reagent). Remarkably, acetic anhydride in the presence of 10 mol% of catalyst (Boc-NH-EMIM.OAc) under solvent-free conditions showed excellent acetylation activity in shorter duration of time. On the basis of this, a general procedure for acetylation of alcohols, phenols, and amines has been developed. The ionic liquid (Boc-NH-EMIM.OAc) can be readily recovered and reused successfully up to four consecutive cycles without any significant loss of its catalytic activity. We have been able to show that this acetylating method has many advantages. It gives high yields, takes shorter time, and develops the possibility of benign environmental-friendly process.

Keywords Amino-functional imidazolium ionic liquids · Acetylation · Catalyst · Acetic anhydride · Solvent-free condition · Boc-NH-EMIM.OAc

Introduction

The acetylation/acylation reactions are very versatile reactions, and acetylated alcohols, phenols, and amines are important building blocks in organic synthesis during oxidation, peptide coupling, and glycosidation reactions for peptide synthesis, nucleotides, oligonucleotides, steroids, and other natural products. Significantly, the protection of alcohols, phenols, thiols, and amino groups attracts attention of the scientific community from both academic and industrial fields (Von Larock 1989). Numerous methodologies have been developed for the acetylation of alcohols, which involves the use of bases such as pyridine, triethyl amine and dimethylamino pyridine (Höfle et al. 1978; Scriven 1983). Several Lewis acids such as $ZnCl_2$ (Baker and Ammerman 1995), $CoCl_2$ (Iqbal and Srivastava 1992), and metal (Sc, Bi, Cu and Sn) triflates (Ishihara et al. 1996; Orita et al. 2001; Chandra et al. 2002) have been also found to be effective catalysts for acetylation. In spite of the accomplishment in the above-stated acetylation procedures, there are numerous drawbacks in them because some of the catalysts utilized are complex, costly, and toxic. The word "complex" refers to metal complexes. Thus, there is an urgent need to overcome the above constraints in the acetylation procedures.

To avoid the use of toxic substance and the generation of waste in chemical reactions, the use of green procedure of synthesis is a good choice. From both environmental and economical point of view, using ionic liquids as media for organic reactions has attracted significant interests as ionic liquids are considered to be environmentally acceptable and safe. Recently, there are a lot of reports on the value of ILs as solvents and catalysts (Song et al. 2013; Jiang et al. 2008). This class of compounds has huge scope in chemical synthesis due to their diverse properties like low melting point (< 100 °C) salts, typically liquid at room temperature, solvation of wide range of both organic and inorganic compounds, high thermal stability, low vapor pressure, recyclability, and ease of handling (Tan et al. 2009; Armand et al. 2009; Liu et al. 2008; Jutz et al. 2011). Along with these properties, ILs are also known as designer solvents (MacFarlane and Forsyth 2003) because their properties can be altered according

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✉ Roli Mishra
rolimishra2@gmail.com; roli.mishra@iar.ac.in

[1] Department of Physical Sciences, Institute of Advanced Research, Gandhinagar, Gujarat 382426, India

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to the need of applications by simple tuning of cations and/or anions. These entire properties make ILs very appropriate candidates for the development of environmentally benign chemical processes and greener substitutes to traditional volatile organic solvents in chemical transformations.

The literature illustrates only a few reports on acetylation reactions involving the ionic liquids as solvents or/and catalysts or both (Liu et al. 2008; Shen and Ji 2009; Wang et al. 2009; López et al. 2011). Recently, in the search of new environment friendly method, Lewis acid based ionic liquids (Wang et al. 2008; Abbott et al. 2005), and Brönsted acidic ionic liquids (Wuts and Greene 2007; Hajipour et al. 2009) have been successfully used as the catalysts for the acetylation of alcohols and phenols. Previously, our group has reported Lewis Acid-Based Ionic Liquid (EMIM·$AlCl_4$) as mild and efficient catalyst for tritylation of alcohols with triphenyl methyl alcohol (Tr-OH) and 4-monomethoxyl trityl alcohol (MMTr-OH) (Chaubey et al. 2018). Moreover, acyl imidazolium derivatives have been used as acetylating agents in protection of alcohols (Leclercq et al. 2010; Connors and Pandit 1978; Saha et al. 1989; Pandit and Connors 1982; Kamijo et al. 1983; Nakatsuji et al. 2006). There have also been reports on the acylation of alcohols (Yang et al. 2007) and cellulose (Abe et al. 2016) using acetic anhydride, catalyzed by task-oriented ionic liquid, 1-ethyl 3-methyl-imidazolium acetate [EMIM.OAc]. Acetylation of alcohols, phenols, and amines with acetic anhydride by using the succinimide-*N*-sulphonic acid catalyst at room temperature under solvent-free conditions has been reported by Shirini and Khaligh (2013). Though these available methods furnished good results, they drawbacks like long reaction time, formation of by-product, and being expensive. Therefore, there is still a great need for simple, mild, easy-to-handle, and environment-friendly catalysts to produce acetyl esters. Several toxicity studies of ionic liquids have been previously reported (Mena et al. 2020; Bubalo et al. 2017; Zanoni et.al. 2019; Mishra et.al. 2019).

The activities of various ionic liquids in acetylation reaction and the effects of process constraints like reaction time, temperature, catalyst-to-reactant ratio, and catalyst recyclability are investigated. The application of the ionic liquids with an amino-functional group (NH_2-EMIM.X^-; X = Br, BF_4, PF_6) has been explored as a medium to absorb CO_2 from natural gas, catalyst for Knoevenagel reactions, and stable dispersion of multiwalled carbon nanotubes. Considering aforementioned discussion and our unrelenting efforts for developing proficient ionic liquid-based catalyst (Chaubey et al. 2018), we have investigated the present amino-functional imidazolium ionic liquid-catalyzed acetylation of alcohol, phenol, and amine in the presence of acetic anhydride as an acetylating reagent to the corresponding acetates. In order to demonstrate the advantages of this process, Table 1 compares the results obtained from the O-acetyl protection of benzyl alcohol by our method with some of those reported in the literature (Cai et al. 2006; Song et al. 2005; Zhou et al. 2009; Kurnia et al. 2011).

Recently, ionic liquids have gained recognition as environmentally friendly. Keeping this rationale in mind, we have designed and synthesized ionic liquids Boc-NH-EMIM.OAc as a catalyst. To the best of our knowledge, there is no evidence of using the ionic liquid Boc-NH-EMIM.OAc as organocatalyst for the acetylation reaction of alcohols, phenols, and amines using acetic anhydride. Through this communication, we report a fast, simpler, and efficient procedure for the acetylation of alcohols, phenols, and amines with acetic anhydride in the presence of ionic liquid Boc-NH-EMIM.OAc under solvent-free conditions. Our catalyst is recyclable up to four cycles without any loss of catalytic activity. It is pertinent to indicate that in this report we have not attempted to evaluate the toxicity issues.

Table 1 Comparisons of the publish procedure for the acetylation of alcohols (imidazolium ionic liquid) with the present method

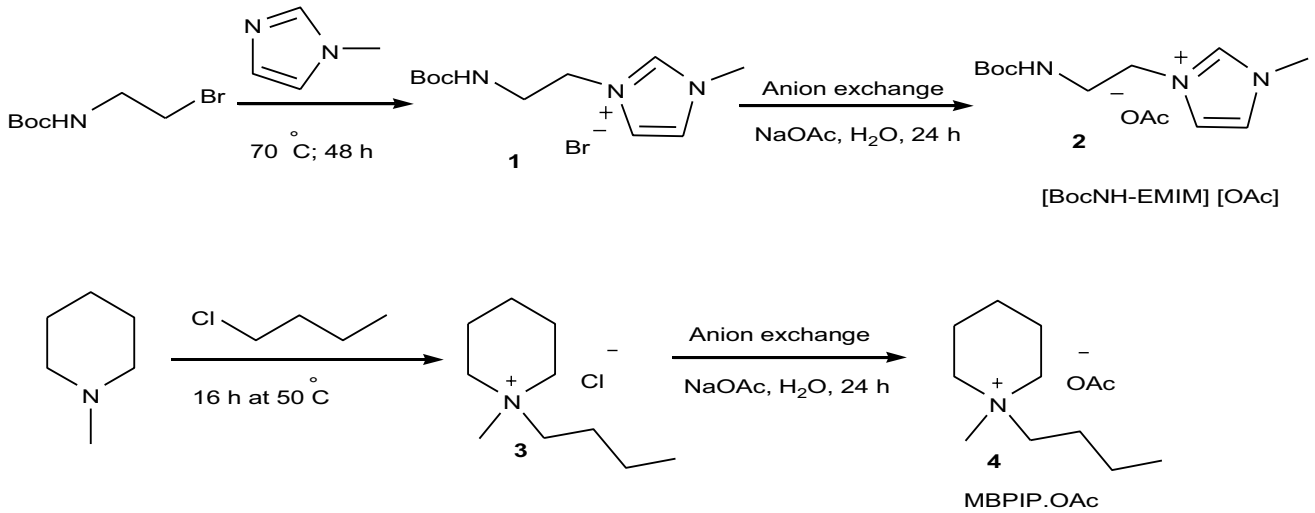
Entry	Imidazolium ILs	Time (min)/Temp (°C)/Yield	References
1	[BMIM] [OTs] + [BMIM][BF4]^{S}	5/50/99	Cai et al. (2006)
2	[BMIM] [BS] + [BMIM][BF4]^{S}	5/50/99	
3	[BMIM][p-CBS] + [BMIM][BF4]^{S}	5/50/99	
4	[BMIM][m-NBS] + [BMIM][BF4]^{S}	5/50/99	
5	[BMIM][BF4]$^{C–S}$	1140/RT/99	Song et al. (2005)
6	[BMIM][FeCl4]$^{C–S}$	20–200/RT/88–94	Zhou et al. (2009)
7	[EMIM][OAc]$^{C–S}$	5/RT/93	Kurnia et al. (2011)
8	[EMIM][HSO4]$^{C–S}$	5/RT/99	
9	[BocNH-EMIM][OAc]^{C}	5/RT/99	Present work

S, ionic liquid used as solvent only; C, ionic liquid used as catalyst only; C–S, ionic liquid used as solvent and catalyst both

Results and discussion

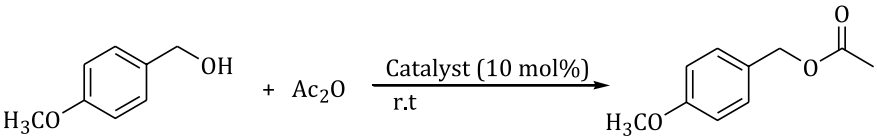
Ionic liquid 1-(N-Boc-2-ethylamine)-3-methylimidazolium acetate (Boc-NH-EMIM.OAc) was prepared by reaction of N-methylimidazole with N-boc-bromoethylamine followed by anion exchange with sodium acetate (NaOAc) as a viscous dark brown liquid (Scheme 1). *N*-butyl-N-methylpiperidinium acetate (MBPIP.OAc) was prepared by treating to a solution of N-methylpiperidine with chlorobutane. The reaction mixture was refluxed under a nitrogen atmosphere at 70 °C, and after completion of reaction, white solid precipitate of desired product was formed. The product was purified by washing with ethyl acetate. Chloride ion was exchanged with sodium acetate (NaOAc). The structure was confirmed by IR, ^{1}HNMR, ^{13}CNMR, and MS (ESI).

A number of experiments were carried out to optimize the reaction conditions for acetylation, viz. the effects of solvents, kinds of ionic liquid, mol% of ionic liquid, and types of substrate. In the beginning of this study, 4-methoxy benzyl alcohol (1 mmol) as model substrate was treated with acetic anhydride (1.5 mmol) in the presence and the absence of base/catalyst for duration of time at room temperature to compare the catalytic performance of the NaOAc, [BMIM] BF_4, [BMIM] PF_6, and [BMIM]



Scheme 1. Synthesis of [Boc-NH-EMIM][OAc] and *N*-butyl-N-methylpiperidinium acetate (MBPIP.OAc) catalyst

Table 2 Optimization of catalyst for acetylation reaction of *p*-methoxy benzyl alcohol



Entry	Catalyst	Catalyst (mmol %)	Time (min)	Yield (%)
1	No catalyst	–	120	–
2	NaOAc	10	120	20
3	[BMIM]BF_4	10	120	35
4	BMIM]PF_6	10	120	40
5	[BMIM]Br	10	120	25
6	[BMIM]OAc	10	90	35
7	[Boc-NH-EMIM]Br	10	120	45
8	[Boc-NH-EMIM].OAc	10	5	98
9	4MBP.OAc	10	30	50
10	MBPIP.OAc	10	30	45

Br. It was observed that without catalyst no acetylated product was detected (Table 2, entry 1). In the presence of CH_3COONa the acetylation reaction occurs slowly (Table 2, entry 2). It is, further, observed that [BMIM] BF_4, [BMIM] PF_6 and [BMIM] Br also demonstrated poor yields of acetylated product (Table 2, entries 3, 4, and 5). On the other hand, the reaction was accelerated obviously when BMIM.OAc was used for the acetylation reaction (Table 2, entries 6). It may be due to the catalytic nature of ionic liquids. Based on the observed results in Table 2, a suitable mechanism is proposed for the acetylation of alcohols in Fig. 1 (benzyl alcohol as a model substrate).

This outcome encourages us to design more acetate based ionic liquids viz. Boc-NH-EMIM.OAc and MBPIP.OAc. Positive charge is delocalized over the aromatic ring in imidazolium ILs, while it is localized in piperidinium ILs. This charge distribution of the cations plays a major role in the acidity of ILs. Due to high acidity of imidazolium-based ILs compared to piperidinium-based ILs nucleophilic behavior of anion will be weaker in imidazolium. Keeping this rationale in mind, we have explored *N*-butyl-N-methylpiperidinium acetate (MBPIP.OAc).

It was found that Boc-NH-EMIM.OAc demonstrated outstanding catalytic activities, gave yields of 98% at room temperature in shorter time (Table 2, entry 8) compared to other acetate ILs viz. 4MBP.OAc (1-butyl-4-methylpyridinium acetate, *N*-butyl-N-methylpiperidinium acetate (MBPIP.OAc), [BMIM] BF_4, [BMIM] PF_6, and [BMIM] Br. The other ILs ([BMIM] BF_4, [BMIM] PF_6, [BMIM] Br) furnished lower yields of acetylated products. Thus Boc-NH-EMIM.OAc was used as model ionic liquid-based catalyst for acetylation reactions.

In order to determine the effects of solvents on acetylation reactions, we investigated the acetylation reactions in different solvent systems (DCM, chloroform, toluene, CH_3CN, and DMF) and the results are presented in (Table 3). It was observed that under neat condition (in the absence of solvents) acetylation reactions worked extremely well and furnished good yields of acetylated products (Table 3).

Boc-NH-EMIM.OAc catalyst amount varied up to 20 mol% to examine its effects on acetylation yields. The results clearly show that the decrease in the loading of Boc-NH-EMIM.OAc from 10 to 5 mol% resulted in lower yields of the products (Table 3, entry 7 vs 6), whereas on increasing the amount of Boc-NH-EMIM.OAc from 10 to 15 mol%, there was no effect on the yields of the products (Table 3, entry 7 vs 8). The highest yield of acetylated product was accomplished at 10 mol% catalysts (Table 3, entry 4). Further enhancement in the catalyst amount did not improve the yield of the acetylated product as it is evident from Table 3 (entry 9). This is accredited to the increased viscosity of the solution, leading to the reduced interaction among the reactants and the ILs.

This is also important to explore the reusability of the Boc-NH-EMIM.OAc as the catalyst since it may have possibly considerable impact on the overall economy of catalyst. We have also found that the catalyst used for the acetylation was easily regenerated by washing with diethyl ether. The entire acetylated products went into the organic layer, but the ionic liquid catalyst which was left at the bottom was dried

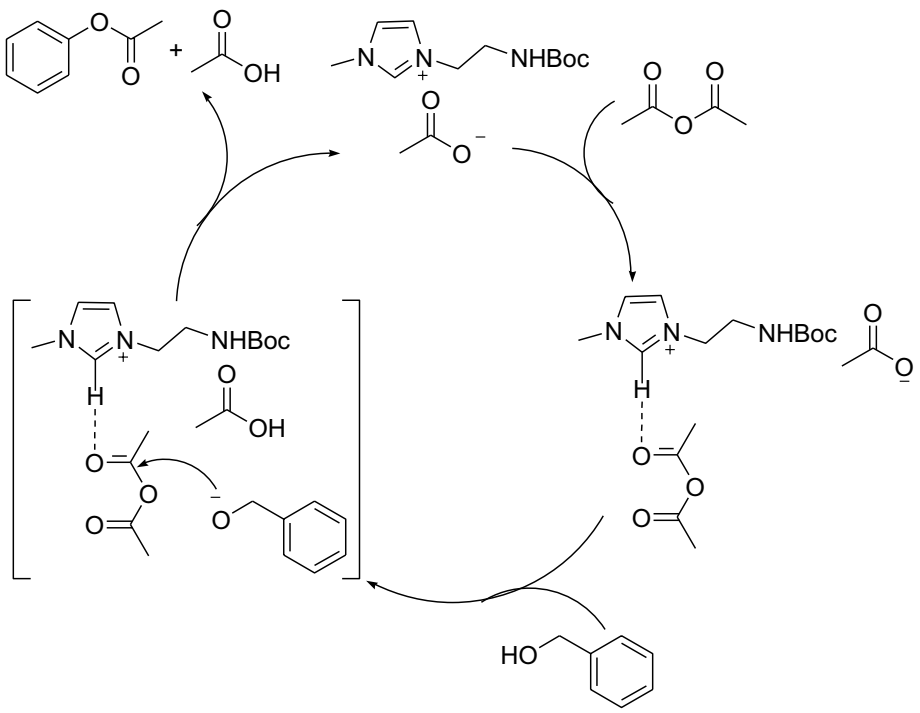
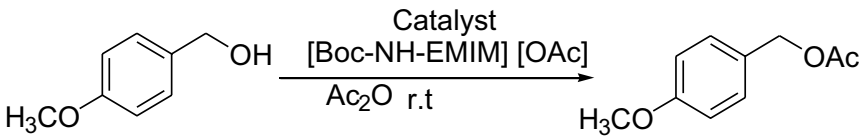


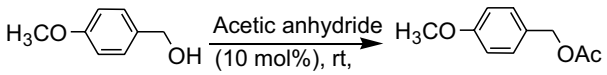
Fig. 1 Proposed mechanism for the acetylation of alcohols (benzyl alcohol as a model substrate)

Table 3 Optimization of the reaction conditions (solvent and mol% of catalyst)



Entry	Solvent	Catalyst (mol%)	Time (min)	Yield (%)
1	DCM	10	40	30
2	CHCl3	10	40	35
3	CH3CN	10	60	45
4	Toluene	10	90	10
5	DMF	10	60	55
6	No solvent	10	5	98
7	No solvent	05	5	65
8	No solvent	15	5	96
9	No solvent	20	5	96

Table 4 Recycling of [Boc-NH-EMIM][OAc] during the acetylation of alcohol



Cycle (Reuse)	Time (min)	Yield (%)
1	5	98
2	5	95
	7	97
3	5	92
	10	95
4	5	85
	20	90
5	5	20
	120	75

at 50 °C for 4 h to get recycled catalyst. No aqueous workup was required. Experiments were run with recycled catalyst to test whether this catalyst can be reused. The result showed that catalyst could be reused up to four cycles without significant loss of activities (Table 4).

In order to generalize the use of Boc-NH-EMIM.OAc as an efficient catalyst for acetylation of structurally different alcohols, phenols, and amines with acetic anhydride, 10 mol% of Boc-NH-EMIM.OAc was treated at room temperature. The results obtained are shown in Table 5. In all cases, the acetylated products were obtained in good to excellent yields.

Regarding acetylation of the benzylic alcohols, an electron-donating group at the aromatic nucleus accelerated the reaction and afforded the corresponding acetylated products in high yields (Table 5, entries 1, 8–10). The acetylation of benzylic alcohols, phenols, and aromatic amines with electron-withdrawing groups, viz. nitro, chloro, fluoro, and aldehyde and ketone substituents, was also scrutinized. However, electron-withdrawing groups impeded the reactions and the yields of the acetylated products were 85 to 92% (Table 5, entries 2–3, 14–16, 18). Satirically hindered alcohols furnished corresponding acetylated products relatively in lower yields (Table 5, entries 4, 7). Substrate 11 was selectively converted to the corresponding acetylated products without affecting the base-labile-protecting Fmoc group (Table 5, entry 11).

The acetylation of lithocholic and deoxycholic acid was performed in the presence of 5 mol% ionic liquid; the desired acetylated products 3α-12α-diacetoxy-5β-cholan-24-oic acid methyl ester (12) and 3α-Acetoxy-5β-cholan-24-oic acid methyl ester (13) were obtained in 65–75% yield in 90 min. Indeed, the yields of 3α-12α-diacetoxy-5β-cholan-24-oic acid methyl ester (12) and 3α-acetoxy-5β-cholan-24-oic acid methyl ester (13) were increased to 80–85%, using 10 mol% ILs with full conversion in a relatively shorter time of 15 min (Table 5; entry 12, 13). This catalyst was not only applicable to primary alcohols but also underwent smoothly in case of secondary alcohols (Table 5; entries 5–7, 10, 12–13). The alcohols were transformed into the corresponding acetates in excellent yields without any difficulty in shorter times (Table 5; 1–13). Phenols and amines were also acetylated in good to excellent yields (Table 5; 14–20). As a result of our investigations, we have demonstrated [Boc-NH-EMIM] [OAc] as an efficient catalyst for the acetylation of alcohols, phenols, and amines. It is apparent the current procedure is more proficient than the compared procedures with reference to

Table 5 Acetylation of primary and secondary alcohol, phenol and amine

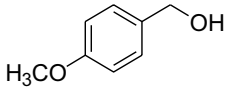
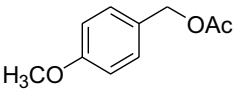
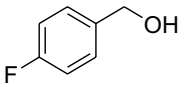
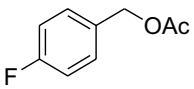
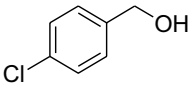
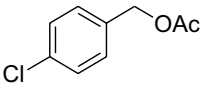
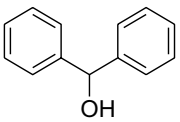
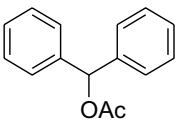
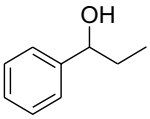
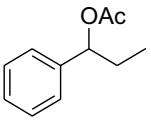
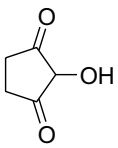
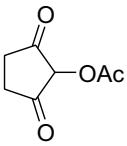
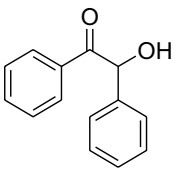
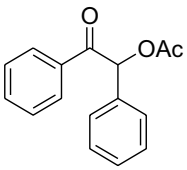
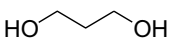
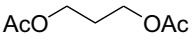
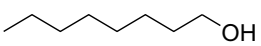
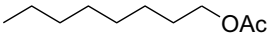
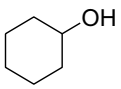
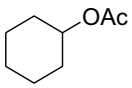
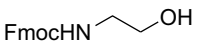
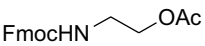
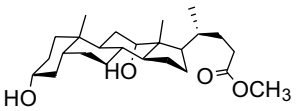
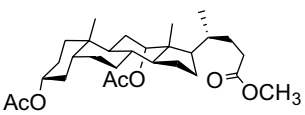
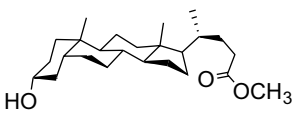
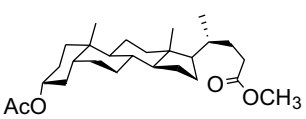
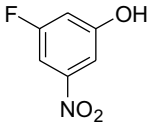
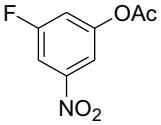
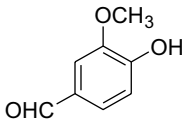
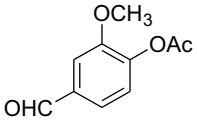
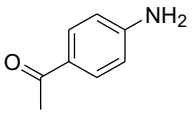
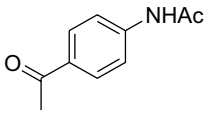
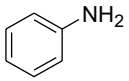
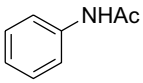
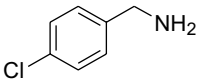
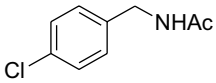
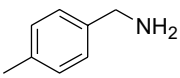
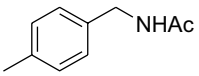
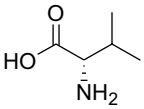
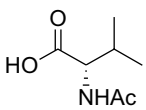
Entry	Substrate	Product	Time (min)	Yield (%)
1			5	98
2			8	89
3			8	86
4			10	85
5			10	92
6			5	92
7			10	80
8			5	94
9			8	95
10			7	96
11			5	95
12			15	80
13			15	85

Table 5 (continued)

Entry	Substrate	Product	Time (min)	Yield (%)
14			2	78
15			3	86
16			5	85
17			5	95
18			5	87
19			5	96
20			20	88

conditions, recyclability of catalyst, reaction times, and/or the products' yields.

Synthesis of 1-(N-Boc-2-ethylamine)-3-methylimidazolium acetate (2) *N*-methyl imidazole (0.782 ml, 9.82 mmol, 1.1 eq.) was added to N-Boc-2-bromoethylamine (2.720 g, 8.92 mmol) in CH_3CN and was stirred at 70 ºC for 48 h. The progress of reactions was monitored by TLC and taken to completion. Bromide salt (3) was washed with ethyl acetate and dichloromethane. The solvent was removed by decantation, and the residue was purified by column chromatography method on silica gel, using acetone and methanol as eluent to give desired 1-(N-Boc-2-ethylamine)-3-methylimidazolium bromide Boc-NH-EMIM.Br (1) as yellowish colour viscous liquid in 84% (2.32 g) yield (Scheme 1, Compound 3). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.30 (s, 1H, Im), 8.20 (s, 1H, Im), 7.75 (s, 2H, Im), 7.34–7.33 (s, 1H, Im-NH), 7.15–7.14 (d, 1H, NH), 4.28–4.20 (m, 2H, CH_2), 3.85 (s, 3H, Im-CH_3), 3.72 (s, 2H, CH_2), 3.44–3.33 (m, 2H), 1.57 (s, 1H), 1.31 (s, 9H, Boc). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 155.6, 136.9, 124.7, 123.0, 121.4, 78.0, 64.0, 48.9, 38.9, 35.6, 33.7, 29.0, 28.0. ESI-MS calcd for [$C_{11}H_{20}N_3O_2^+$] 226.155, found 226.283.

The ionic liquid [Boc-NH-EMIM] [OAc] was prepared by metathesis of [Boc-NH-EMIM] [Br] with sodium acetate. [Boc-NH-EMIM] [Br] salt was dissolved in deionized water and aqueous CH_3COONa (equimolar) was added drop-wise under stirring at RT for 18 h and water was removed under vacuum. To the viscous crude ionic liquid Boc-NH-EMIM. OAc, acetonitrile was added and filtered to remove NaBr. Acetonitrile potion was removed under reduced pressure to get desired product and washed once with diethyl ether to remove organic impurities. This was, then, dried under high vacuum (with heating at 40 °C) for at least 2–3 h to minimize the moisture content. FTIR (ATR, νcm^{-1}): 3287, 2360, 2131, 1598, 1448, 1357, 1175, 1096, 979, 926, 814, 657, 545, 445, 414; ^{1}H NMR (400 MHz, $DMSOd_6$): δ 9.11 (s, 1H), 7.70 (s, 1H), 7.55 (s, 1H), 6.86 (s, 1H), 4.17–4.29 (t, 2H), 3.84 (s, 1H), 3.63 (s, 1H), 3.15–3.3 (s, 1H), 2.07 (s, 1H), 1.89 (s, 2H), 1.56 (s, 1H), 1.32 (S, 9H); ^{13}C NMR (100 MHz, $DMSOd_6$): δ = 155.6, 137.3, 128.3, 123.1, 120.4, 78.2, 64.1, 49.1, 39.5, 38.9, 35.6, 32.7, 28.5, 21.0; ESI-MS calcd for [$C_{11}H_{20}N_3O_2^+$] 226.1550, found 226.1498.

Synthesis of N-butyl-N-methylpiperidinium acetate (MBPIP.OAc) To *N*-methyl piperidine (1.21 ml, 10 mmol) in

pressure tube, bromobutane (1.180 ml, 11 mmol) was added slowly with continuous stirring at 25 °C. Mixture was stirred for 16 h at 50 °C in nitrogen atmosphere. The solution was washed with dry diethyl ether and remaining residue evaporated on a rotavapour. MBPIP.Br was treated with sodium acetate in similar fashion as described compound 2. A solid precipitate of NaCl was removed by filtration. White liquid product was kept under high vaccum at 50 °C for 3 h (yield; 95%). The product *N-butyl-N-methylpiperidinium acetate (4)* was confirmed by ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 3.39–3.32$ (m, 6H), 3.09 (s, 3H), 2.05 (s, 3H), 1.78 (s, br, 3H), 1.67–1.45 (m, 4H), 1.33–1.24 (m, 2H), 0.91 (t, 3H. $J = 7.2$ Hz). FTIR (ATR, νcm^{-1}): 2959, 2874, 1474, 1353, 1225, 1050, 940, 673, 576, cm^{-1}.

General procedure for Acetylation of alcohols To mixture of an alcohols (10.0 mmol), acetic anhydride (Ac_2O) (15 mmol; 1.5 equivalent) and 10 mol % of catalyst [Boc-$NHCH_2CH_2MIM$] [OAc] was stirred at room temperature. Completion of reactions was monitored through TLC. After completion of the reactions, the reaction mixture evaporated under vacuum till dryness. The residue was extracted with diethyl ether and concentrated. The crude products were purified by column chromatography on neutral alumina using hexanes/ethyl acetate as the eluent to give corresponding products. *Acetic acid 4-methoxy-benzyl ester (entry 1)* FTIR (ATR, νcm^{-1}): 2956, 2838, 2360, 1733, 1612, 1515, 1221, 1024, 958, 813, 756, 607, 561, 518, 431, 408; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.30–7.25$ (m, 2H), 6.90–6.87 (m, 2H), 5.04 (s, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 159.6, 130.1, 128.1, 113.9, 113.8, 66.1, 55.3, 29.7, 21.0

Acetic acid 4-fluoro-benzyl ester (entry 2) FTIR (ATR, νcm^{-1}): 2360, 1737, 1605, 1511, 1379, 1221, 1158, 1027, 822, 766, 607, 551; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.32–7.07$ (m, 2H), 7.06–7.02 (m, 2H), 5.06 (s, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 163.9, 161.4, 131.8, 130.3, 130.2, 115.6, 115.3, 65.5,20.9.

Acetic acid 4-chloro-benzyl ester (entry 3) FTIR (ATR, νcm^{-1}): 2359, 1735, 1599, 1493, 1377, 1222, 1092, 1014, 803, 530; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.34–7.32$ (m, 2H), 7.29–7.25 (m, 2H), 5.06 (s, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 134.4, 134.1, 129.6, 128.7, 65.4, 29.7, 20.9.

Acetic acid benzhydryl ester (entry 4) FTIR (ATR, νcm^{-1}): 3033, 2360, 1737, 1495, 1370, 1227, 1020, 743, 697, 549; ^{1}H NMR (400 MHz, CDCl3): $\delta = 7.34–7.25$ (m, 10H), 6.82 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.0, 140.2, 127.8, 77.3, 30.0, 22.0, 14.1

Acetic acid 1-phenyl-propyl ester (entry 5) FTIR (ATR, νcm^{-1}): 3385, 3152, 2975, 2365, 1701, 1518, 1370, 1247, 1164, 1011, 849, 755; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.34–7.30$ (m, 2H), 7.39–7.25 (m, 2H), 5.66 (t, 1H), 2.08 (s, 3H), 1.97–1.77 (q, 2H), 0.87 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 140.5, 128.3, 127.8, 126.5, 29.7, 29.2, 21.2, 19.1, 9.8.

Acetic acid 2,5-dioxo-cyclopentyl ester (entry 6) FTIR (ATR, νcm^{-1}): 2986, 2371, 1714, 1374, 1163, 1051, 824, 644, 507; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.83$ (s, 4H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 169.0, 165.6, 29.7, 25.6, 17.6.

Acetic acid 2-oxo-1,2-diphenyl-ethyl ester (entry 7) FTIR (ATR, νcm^{-1}): 3062, 2360, 1693, 1597, 1448, 1372, 1225, 1055, 971, 862, 755, 695, 582, 526; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, $J = 4.0$ Hz, 2H), 7.45–7.40 (m, 2H), 7.39–7.33 (m, 4H), 6.86 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 193.8, 170.5, 134.7, 133.6, 128.9, 77.7, 29.5, 21.7, 14.2.

Acetic acid 2-acetoxymethyl-ethyl ester (entry 8) FTIR (ATR, νcm^{-1}): 2963, 2289, 1738, 1371, 1212, 1045, 957, 847; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.27–5.22 (m, 2H), 4.31–4.27 (m, 1H), 4.18–4.13 (m, 1H), 2.09 (s, 9H); ^{13}CNMR (100 MHz, $CDCl_3$): 170.2, 69.0, 62.2, 29.6, 20.7.

Acetic acid octyl ester (entry 9) FTIR (ATR, νcm^{-1}): 2926, 2860, 1739, 1462, 1369, 1234, 1038, 960, 724, 640; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (t, $J = 6.8$ Hz, 2H), 2.04 (s, 3H), 1.65–1.60 (m, 2H), 1.58–1.27 (m, 10H), 0.90 (t, J = 6.8, Hz, m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.2, 64.6, 31.9, 31.7, 29.7, 29.3, 29.2, 29.1, 28.6, 25.9, 22.6, 21.0, 14.0.

Acetic acid cyclohexyl ester (entry 10) ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.76–4.70 (m, 1H), 2.02 (s, 3H), 1.86–180 (m, 4H), 174–1.70 (m, 6H), 1.57–1.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.6, 72.7, 35.5, 31.6, 29.7, 25.4, 23.8, 22.6, 21.4.

Acetic acid 2-(9H-fluoren-9-ylmethoxycarbonylamino)-ethyl ester (entry 11) FTIR (ATR, νcm^{-1}): 3319, 2930, 2364, 1720, 1550, 1441, 1258, 1157, 1055, 956, 613, 471; ^{1}H NMR (400 MHz, $CDCl_3$): 7.77–7.26 (m, 8H); 4.474.42 (m, 3H), 4.23–4.00 (m, 2H), 3.78–3.32 (m, 2H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 143.8, 141.4, 127.7, 127.1, 125.0, 120.1, 47.4, 40.2, 20.9.

3α-12α-Diacetoxy-5β-cholan-24-oic Acid methyl ester (12) ^{1}H NMR (400 MHz, $CDCl_3$): 5.07 (d, 1H, $J = 2.8$ Hz), 4.70 (m, 1H), 3.66 (s, 3H), 2.34–2.31 (m, 1H), 2.22–2.20 (m, 1H),2.10 (s, 3H), 2.03 (s, 3H), 1.88–1.10 (m, 24H), 0.90 (s, 3H), 0.81 (s, 3H), 0.79 (s, 3H): ^{13}C NMR (100 MHz, $CDCl_3$): 174.6, 170.5, 170.4, 75.9, 74.2, 51.5, 49.4, 47.6, 45.0, 41.8, 35.7, 34.7, 3.4.4, 34.0, 32.2, 31.0, 30.8, 27.3, 26.9, 26.6, 25.8, 25.6, 23.4, 23.0, 21.4, 21.3, 17.5.

3α-Acetoxy-5β-cholan-24-oic acid methyl ester (13) ^{1}H NMR (400 MHz, $CDCl_3$): 4.71 (d, 1H, $J = 4.8$ Hz), 2.40–2.36 (m, 1H), 2.30–2.26 (m, 1H), 2.17 (s, 3H), 2.02 (s, 3H), 1.98–0.90 (m, 32H), 0.64 (s, 3H): ^{13}C NMR (100 MHz, $CDCl_3$): 178.0, 76.7, 74.4, 56.5, 56.0, 42.7, 41.9, 40.4, 40.1, 35.8, 35.3, 35.0, 34.6, 32.2, 30.8, 30.6, 28.1, 27.0, 26.6, 26.3, 24.2, 23.3, 21.4, 20.8, 18.2.

Acetic acid 3-fluoro-5-nitro-phenyl ester (entry 14) FTIR (ATR, νcm^{-1}): 3092, 2349, 1775, 1597, 1529, 1345, 1274, 1149, 1085, 1011, 891, 826, 689, 620; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.79 (s, 1H), 8.19–7.47 (m, 2H), 7.46- 7.21 (m, 1H), 3.99 (s, 3H) 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 193.8, 170.5, 134.7, 133.6, 128.9, 29.5, 21.7, 14.2.

Acetic acid 4-formyl-2-methoxy-phenyl ester (entry 15) FTIR (ATR, νcm^{-1}): 3028, 3028, 2626, 2359, 1706, 1506, 1384, 1278, 1193, 1147, 1014, 897, 735, 603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.50–7.47 (m, 2H), 7.46–7.21 (m, 1H), 3.99 (s, 3H) 2.08 (s, 3H); ^{13}CNMR (100 MHz,$CDCl_3$): 191.3, 177.2, 168.5, 166.5, 152.0, 145.0, 138.5, 137.9, 135.3,134.3, 131.2, 124.7, 123.0, 118.9, 111.4, 89.4, 60.5, 56.1, 49.5, 40.1, 36.8, 29.3, 21.2, 14.2.

N-(4-Acetyl-phenyl)-acetamide (entry 16) FTIR (ATR, νcm^{-1}): 3119, 2359, 1674, 1592, 1407, 1318, 1259, 1013, 838, 759, 592; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, $J = 5.6$ Hz, 2H), 7.92 (d, $J = 2.4$ Hz, 2H), 7.62 (br, s, 1H), 2.57 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 196.9, 168.5, 142.2, 132.9, 129.7, 118.8, 26.4, 24.7.

N-Phenyl-acetamide (entry 17) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.30 (m, 5H, {Benzene}), 6.13 (br, 1H, NH), 4.40–4.39 (d, 2H, CH_2), 2.04–1.99 (s, 3H, Acetate). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 170.2, 138.1, 127.9, 77.0, 43.7, 23.0, 20.7.

N-(4-Chloro-benzyl)-acetamide (entry 18) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30–7.26 (q, 4H, CH {Benzene}), 5.87 (br, 1H, NH), 4.39–4.38 (d, 2H, CH_2), 2.02 (s, 3H, Acetate). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 136.9, 133.4, 129.0, 43.0, 23.2.

N-(4-Methyl-benzyl)-acetamide (entry 19) 1H NMR (400 MHz, CDCl3) δ: 7.19–7.13 (m, 4H, {Benzene}), 5.68 (br, 1H, NH),4.39–4.38 (d, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.00 (s, 3H, Acetate); 13C NMR (100 MHz, $CDCl_3$) δ:169.8, 137.3, 135.2, 129.4, 127.9, 43.6, 23.3, 21.1.

Acetylamino-3-methyl-butyric acid (entry 20) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.2 (d, 1H, NH), 4.54–3.98 (m, 1H, CH), 2.23–2.03 (m, 3H, Acetate), 1.40 (s, 1H, CH), 0.99–0.94 (m, 6H, *Valine*). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.3, 170.8, 57.5, 36.6, 30.9, 28.3, 23.1, 20.6, 19.0, 17.7.

Conclusion

In conclusion, a new amino-functional imidazolium ionic liquid Boc-NH-EMIM.OAc offers a solvent-free efficient catalytic methodology for the acetylation of alcohols, phenols and amine substrate. This method provides several advantages, such as easy workup, excellent yield, mild, simple procedure and does not require special precautions. It can easily be concluded from the outcome that the existing method does not require elevated temperature or use of complex reagents to proceed. Additionally, the reaction takes place rapidly under solvent free systems. It is also important to point out that the ionic liquid could easily be recycled and reused up to four cycles without the loss of activities. These results may offer a wide opportunity to use Boc-NH-EMIM.OAc catalysts within the area of organic transformations. Further study on the application of this kind of catalyst is under progress in our laboratory.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

References

Abbott AP, Bell TJ, Handa S, Stoddart B (2005) O-Acetylation of cellulose and monosaccharides using a zinc based ionic liquid. Green Chem 7:705–707. https://doi.org/10.1039/B511691K

Abe M, Sugimura K, Nishio Y (2016) Regioselectivity in acetylation of cellulose in ionic liquids. ChemistrySelect 1(10):2474–2478. https://doi.org/10.1002/slct.201600520

Armand M, Endres F, MacFarlane DR, Ohno H, Scrosati B (2009) Ionic-liquid materials for the electrochemical challenges of the future. Nat Mater 8(8):621–629. https://doi.org/10.1038/nmat2448

Baker DH, Ammerman CB (1995) Zinc bioavailability. In: Ammerman CB, Baker DH, Lewis AJ (eds) Bioavailability of nutrients for animals: amino acids, minerals, and vitamins. Academic Press, San Diego, pp 367–398. https://doi.org/10.1016/B978-012056250-3/50044-5

Bubalo MC, Radošević K, Redovniković IR, Slivac I, Srček VG (2017) Toxicity mechanisms of ionic liquids. Arh Hig Rada Toksikol 68:171–179. https://doi.org/10.1515/aiht-2017-68-2979

Cai Y, Peng Y, Song G (2006) Amino-functionalized ionic liquid as an efficient and recyclable catalyst for Knoevenagel reactions in water. Catal Lett 109(1–2):61–64. https://doi.org/10.1007/s10562-006-0057-3

Chandra KL, Saravanan P, Singh RK, Singh VK (2002) Lewis acid catalyzed acylation reactions: scope and limitations. Tetrahedron 58(7):1369–1374. https://doi.org/10.1016/S0040-4020(01)01229-7

Chaubey SA, Mishra JS, Mishra R (2018) Efficient approach for the tritylation of alcohols using recyclable Lewis acid-based ionic liquid (EMIM·$AlCl_4$). ACS Omega 3(8):9607–9612. https://doi.org/10.1021/acsomega.8b00691

Connors KA, Pandit NK (1978) N-Methylimidazole as a catalyst for analytical acetylations of hydroxy compounds. Anal Chem 50(11):1542–1545. https://doi.org/10.1021/ac50033a038

Hajipour AR, Khazdooz L, Ruoho AE (2009) Brönsted acidic ionic liquid as an efficient catalyst for acetylation of alcohols and phenols. J Chin Chem Soc 56(2):398–403. https://doi.org/10.1002/jccs.200900058

Höfle G, Steglich W, Vorbrüggen H (1978) 4-Dialkylaminopyridines as highly active acylation catalysts. Angew Chem Int Ed Engl 17(8):569–583. https://doi.org/10.1002/anie.197805691

Iqbal J, Srivastava RR (1992) Cobalt (II) chloride catalyzed acylation of alcohols with acetic anhydride: scope and mechanism. J Org Chem 57(7):2001–2007. https://doi.org/10.1021/jo00033a020

Ishihara K, Kubota M, Kurihara H, Yamamoto H (1996) Scandium trifluoromethanesulfonate as an extremely active Lewis acid catalyst in acylation of alcohols with acid anhydrides and mixed anhydrides. J Org Chem 61(14):4560–4567. https://doi.org/10.1021/jo952237x

Jiang T, Ma S, Zhou Y, Liang S, Zhanga J, Han B (2008) Solvent-free synthesis of substituted ureas from CO_2 and amines with a functional ionic liquid as the catalyst. Green Chem 10:465–469. https://doi.org/10.1039/B717868A

Jutz F, Andanson J-M, Baiker A (2011) Ionic liquids and dense carbon dioxide: a beneficial biphasic system for catalysis. Chem Rev 111(2):322–353. https://doi.org/10.1021/cr100194q

Kamijo T, Yamamoto R, Harada H, Iizuka K (1983) 1-Substituted imidazoles as useful catalysts for acylation of alcohols. Chem Pharm Bull 31(10):3724–3727. https://doi.org/10.1248/cpb.31.3724

Kurnia KA, Mutalib MIA, Ariwahjoedi B (2011) Estimation of physicochemical properties of ionic liquids [H_2N-C2mim][BF4] and [H2N-C3mim][BF_4]. J Chem Eng Data 56(5):2557–2562. https://doi.org/10.1021/je200068x

Leclercq L, Suisse I, Agbossou-Niedercorn F (2010) Kinetic resolution of racemic secondary alcohols mediated by N-methylimidazole in the presence of optically active acyl chlorides. Eur J Org Chem 14:2696–2700. https://doi.org/10.1002/ejoc.200901075

Liu Y, Liu L, Lu Y, Cai Y-Q (2008) An imidazolium tosylate salt as efficient and recyclable catalystfor acetylation in an ionic liquid. Monatsh Chem 139(6):633–638. https://doi.org/10.1007/s00706-007-0814-z

López I, Bravo JL, Caraballo M, Barnetoc JL, Silvero G (2011) Task-oriented use of ionic liquids: efficient acetylation of alcohols and phenols. Tetrahedron Lett 52(26):3339–3341. https://doi.org/10.1016/j.tetlet.2011.04.079

MacFarlane DR, Forsyth SA (2003) Acids and bases in ionic liquids. ACS Symp Ser 856:264–276. https://doi.org/10.1021/bk-2003-0856.ch022

Mena IF, Diaz E, Palomar J, Rodriguez JJ, Mohedano AF (2020) Cation and anion effect on the biodegradability and toxicity of imidazolium- and choline-based ionic liquids. Chemosphere 240:124947. https://doi.org/10.1016/j.chemosphere.2019.124947

Mishra R, Mishra JS, Chaubey SA (2019) Recent advances on triazolium ionic liquids: synthesis and applications. Curr Org Chem 23(11):1239–1255. https://doi.org/10.2174/1385272823666190627114321

Nakatsuji H, Morita J, Misaki Y, Tanabe Y (2006) Water solvent method for esterification and amide formation between acid chlorides and alcohols promoted by combined catalytic amines: synergy between N-methylimidazole and N,N, N′,N′-tetramethylethylenediamine (TMEDA). Adv Synth Catal 348(15):2057–2062. https://doi.org/10.1002/adsc.200600256

Orita A, Tanahashi C, Kakuda A, Otera J (2001) Highly powerful and practical acylation of alcohols with acid anhydride catalyzed by $Bi(OTf)_3$. J Org Chem 66(26):8926–8934

Pandit NK, Connors KA (1982) Kinetics and mechanism of hydroxy group acetylations catalyzed by N-methylimidazole. J Pharm Sci 71(5):485–491. https://doi.org/10.1002/jps.2600710503

Saha AK, Rapoport H, Schultz P (1989) 1,1'-Carbonylbis(3-methylimidazolium) triflate: an efficient reagent for aminoacylations. J Am Chem Soc 111(13):4856–4859. https://doi.org/10.1021/ja00195a043

Scriven EFV (1983) 4-Dialkylaminopyridines: super acylation and alkylation catalysts. Chem Soc Rev 12:129–161. https://doi.org/10.1039/CS9831200129

Shen Z-L, Ji S-J (2009) Ionic liquid [bmim]BF_4 as an efficient and recyclable reaction medium for the synthesis of O-acetyl cyanohydrin via one-pot condensation of aldehyde, TMSCN, and Ac_2O. Synth Commun 39(5):808–818. https://doi.org/10.1080/00397910802431172

Shirini F, Khaligh NG (2013) A succinimide-N-sulfonic acid catalyst for acetylation reactions in absence of a solvent. Chin J Catal 34(4):695–703. https://doi.org/10.1016/S1872-2067(11)60499-3

Song G, Cai Y, Peng Y (2005) Amino-functionalized ionic liquid as a nucleophilic scavenger in solution phase combinatorial synthesis. J Comb Chem 7(4):561–566. https://doi.org/10.1021/cc049844v

Song J, Fan H, Maa J, Han B (2013) Conversion of glucose and cellulose into value-added products in water and ionic liquids. Green Chem 15:2619–2635. https://doi.org/10.1039/C3GC41141A

Tan SSY, MacFarlane DR, Upfal J, Edye LA, Doherty WOS, Patti AF, Pringle JM, Scott JL (2009) Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid. Green Chem 11:339–345. https://doi.org/10.1039/B815310H

Von Larock RC (1989) Comprehensive organic transformations. VCH Publishers Inc, New York/. https://doi.org/10.1002/ange.19901020837. ISBN ISBN 0-89573-710-8

Wang W, Cheng W, Shao L (2008) [TMBSA] [HSO4] ionic liquid as novel catalyst for the rapid acetylation of alcohols, hydroxy esters and phenols under solvent-free conditions. Catal Lett 121(1–2):77–80. https://doi.org/10.1007/s10562-007-9295-2

Wang D-S, Lib G-Y, Peng Y-Q (2009) Chloroferrate(III) Ionic liquid as recyclable catalyst for the acetylation of alcohols and phenols and for 1,1-diacylation of aldehydes. J Chin Chem Soc 56(4):834–838. https://doi.org/10.1002/jccs.200900123

Wei-Li D, Bi J, Sheng-Lian L, Xu-Biao L, Xin-Man T, Chak-Tonga A (2014) Functionalized phosphonium-based ionic liquids as efficient catalysts for the synthesis of cyclic carbonate from expoxides and carbon dioxide. Appl Catal A Gen 470:183–188. https://doi.org/10.1016/j.apcata.2013.10.060

Wuts PGM, Greene TW (2007) Greene's protective groups in organic synthesis. Wiley, New Jersey. ISBN 978-1-118-05748-3

Yang S-D, Wu L-Y, Yan Z-Y, Pan Z-L, Liang Y-M (2007) A novel ionic liquid supported organocatalyst of pyrrolidine amide: synthesis and catalyzed Claisen–Schmidt reaction. J Mol Catal A Chem 268(1–2):107–111. https://doi.org/10.1016/j.molcata.2006.11.039

Zanoni BV, Brasil Romão G, Andrade RS, Barretto Cicarelli RM, Trovatti E, Chiari-Andrèo BG, Iglesias M (2019) Cytotoxic effect of protic ionic liquids in HepG2 and HaCat human cells: in vitro and in silico studies. Toxicol Res (Camb) 28(3):447–458. https://doi.org/10.1039/c8tx00338f

Zhou X, Wu T, Ding K, Hu B, Hou M, Han B (2009) The dispersion of carbon nanotubes in water with the aid of very small amounts of ionic liquid. Chem Commun 14:1897–1899. https://doi.org/10.1039/B900849G