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Bicyclic imidazolium-based ionic liquids: synthesis and characterization

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Abstract—We previously reported the use of imidazole as starting compound for preparing a bicyclic imidazolium ionic liquid, [b-3C-im][NTf_2], with an overall 29% isolated yield in four synthetic steps. This new room temperature ionic liquid was shown to be far more chemically stable than commonly used [bmim][PF_6], [bdmim][PF_6], and [bdmim][NTf_2]. Because of this intriguing chemical stability, it prompted us to develop a more generalized and high yielding synthesis so that molecular diversity of bicyclic ionic liquids may be explored. In this work, we amended the previous synthetic route by employing 4-chlorobutyronitrile or 5-chlorovaleronitrile as starting materials and successfully developed a five-step synthesis of a series of novel bicyclic imidazolium-based ionic liquids in 40–53% overall isolated yields. We investigated intrinsic reactivity of all bicyclic ionic liquids prepared and found that, under strongly basic conditions, among all tested ionic liquids the 5,5-membered [R-3C-im][NTf_2] ionic liquids were most stable to solvent deuterium isotope exchange while the previously reported [bdmim][NTf_2] ionic liquid was 50% deuterium exchanged at its C-2 methyl in 30 min at ambient temperature. Under identical condition, the commonly used [bmim][NTf_2] ionic liquid was deuterium exchanged instantaneously at its C-2 hydrogen. In the absence of bases, only [bmim][PF_6] was deuterium exchanged (50% within 1 h) and all other ionic liquids gave no detectable exchanges even after 25 days at ambient temperature. Moreover, both [bmim][NTf_2] and [bdmim][NTf_2] ionic liquids were readily methylated at C-2 position with methyl iodide under basic condition at room temperature. Under the same condition, [R-3C-im][NTf_2] and [R-4C-im][NTf_2] ionic liquids were completely stable and chemically inert. We envisioned that [R-3C-im][NTf_2] should be well suited as solvents for organic synthesis.

1. Introduction

Ionic liquids are a class of polar solvents that are entirely constituted of ions.[1] They are typically liquid at low temperatures (<100 °C). Owing to its high thermal stability, low volatility, and co-solvent miscibility, ionic liquids have recently attracted a great deal of attention as environmentally benign and useful solvents in diverse applications such as organic synthesis, chemical catalysis, separation technology, and novel electrolytes for batteries.[1]

Today, the ionic liquid research continues to be much dominated by 1,3-dialkylimidazolium salts with fluorine-containing anions.[1] These ionic liquids serve well as excellent alternatives to classical organic solvents.[2] Recently, we reported the synthesis of a new bicyclic imidazolium ionic liquid, [b-3C-im][NTf_2], that carries superior chemical and hydrolytic stability.[3] This room temperature ionic liquid was demonstrated to be far more chemically stable than commonly used [bmim][PF_6], [bdmim][PF_6], and [bdmim]-[NTf_2].[3] Because of the intriguing property, it prompted us to develop a more generalized and high yielding synthesis so that molecular diversity of bicyclic ionic liquids may be explored.

In this report, we aimed at demonstrating that the bicyclic [b-3C-im][NTf_2] and its analogous [R-3C-im][NTf_2] and [R-4C-im][NTf_2] (R=Me, Et, Pr, and Bu) ionic liquids can be reliably prepared by an alternative, more generalized synthetic route starting from simple chemical reagents. This new synthesis was advantageous because the common structural core of fused dihydropyrroloimidazole (for [R-3C-im][NTf_2]) or tetrahydroimidazopyridine (for [R-4C-im][NTf_2]) was established so that derivatives of bicyclic ionic liquids could be readily prepared and characterized. Also, because it is known that the C-2 hydrogen on imidazolium salts is acidic and chemically reactive,[4,5] we purposely designed and constructed ring structure between N-1 nitrogen and C-2 carbon so that potential side reactions under basic conditions could be conveniently prevented or minimized. These bicyclic ionic liquids should therefore be more chemically stable than other known C-2 unsubstituted

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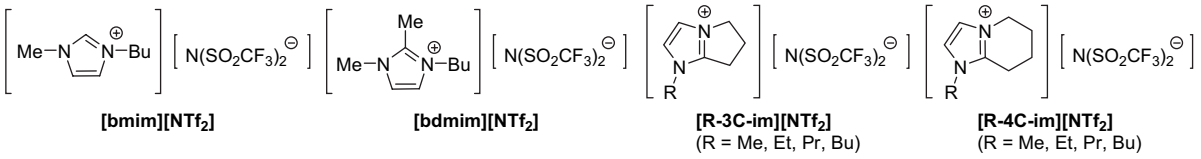
imidazolium ionic liquids.[3,6] Moreover, we illustrated the usefulness of bicyclic ionic liquids, [R-3C-im][NTf_2] in particular, as valuable solvents for organic synthesis by testing their chemical stability and inertness for experiments of solvent deuterium isotope exchange reactions as well as chemical methylations.

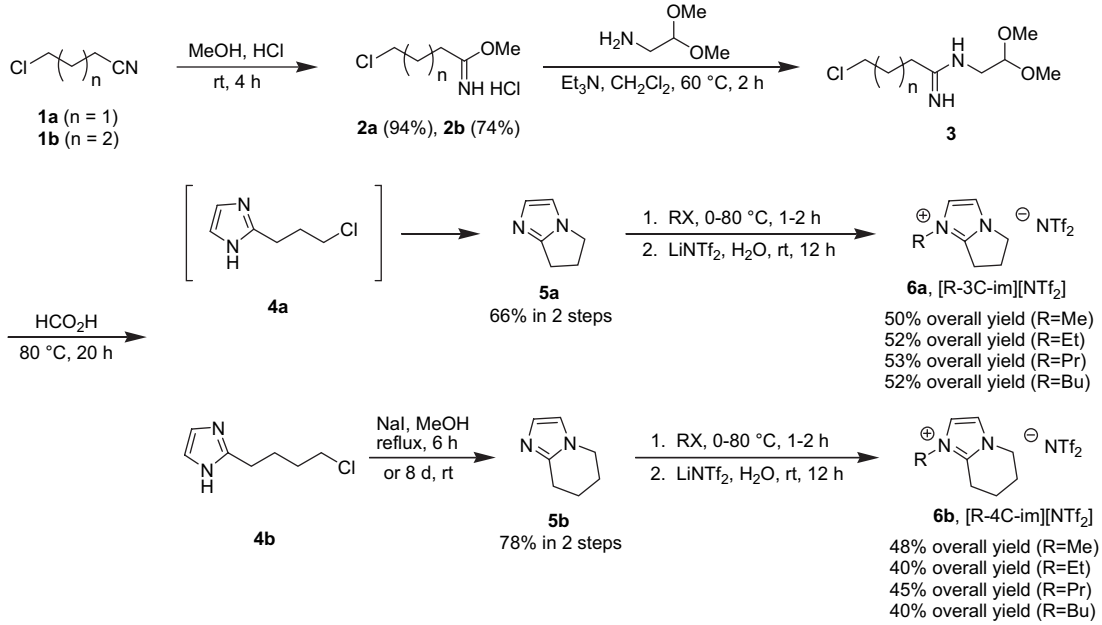


2. Results and discussion

Most 1,3-dialkylimidazolium ionic liquids are stable toward many organic as well as inorganic reaction conditions. However, these properties are not completely ubiquitous and in fact, under certain experimental conditions, the cation or anion of ionic liquids could undergo undesirable or unexpected chemical transformations.[5] For example, the PF_6 anion of imidazolium ionic liquids has been known to steadily undergo hydrolysis to produce phosphate and HF.[7] In addition, ionic liquids containing Lewis base anions such as dicyanamide anion greatly facilitate the O-acetylation of alcohols, including carbohydrates.[8] In this case, the ionic liquid used ([bmim[$N(CN)_2$]) was served as an effective solvent as well as an active base catalyst. For cations, stemming from its known acidity at C-2 hydrogen of the imidazolium nucleus, the apparent reactivity of imidazolium cation to organic electrophiles, such as aldehydes in the Baylis–Hillman reaction or *o*-fluoronitrobenzene in nucleophilic aromatic substitution, has been documented in the literature.[9,10] All these obviously limited or complicated the usefulness of ionic liquids served as solvents in synthetic reactions. The development of novel ionic liquids with much improved chemical and hydrolytic stability is therefore of an urgent need.

We recently reported a four-step synthesis of a new, bicyclic [b-3C-im][NTf_2] room temperature ionic liquid that exhibits excellent chemical stability.[3] This preliminary preparation of [b-3C-im][NTf_2] used imidazole as the starting compound and was, however, of poor total isolated yield (29%). In order to produce bicyclic ionic liquids with substantial amount and to enlarge the molecular diversity so that best possible bicyclic ionic liquids for organic synthesis can be screened and identified, we required a generalized, more expedient, and high yielding synthesis to prepare [b-3C-im][NTf_2] and its analogous ionic liquids.

Our new synthesis of bicyclic imidazolium ionic liquids (**6a** and **6b**) is outlined in Scheme 1. The fused imidazoles **5a** (6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole) and **5b** (5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine) served as key intermediates and the common structural cores for the synthesis of both bicyclic ionic liquids. The compounds **5a** and **5b** could be prepared in a straightforward manner by two intramolecular cyclizations of the corresponding amidines **3**, which accordingly should be obtainable from the condensation reactions of α-aminoacetaldehyde dimethyl acetal with the imidate hydrochlorides (**2a** and **2b**) derived from commercially available 4-chlorobutyronitrile **1a** and 5-chlorovaleronitrile **1b**, respectively.



Scheme 1. Synthesis of bicyclic imidazolium-based ionic liquids, [R-3C-im][NTf_2] (**6a**) and [R-4C-im][NTf_2] (**6b**) (R=Me, Et, Pr, and Bu).

Despite apparent structural simplicity of fused imidazoles **5a** and **5b**,[11] we were surprised to find no general and established methodologies for the facile synthesis of these heterocycles in the literature. Hua and co-workers previously used 2-pyrrolidinone and δ-valerolactam to condense with aminoacetaldehyde diethyl acetal in the presence of tine tetrachloride or titanium tetrachloride catalysts to conveniently prepare the corresponding bicyclic imidazoles **5a** and **5b**, respectively.[11] In spite of good yielding (61–80%), the preparation, however, took long reaction hours (51–74 h) and required high reaction temperatures (140–155 °C).[11] As another example, having an intramolecular heteroaromatic radical cyclization as the key reaction step, Bowman and co-workers used imidazole as the starting reagent to successfully develop a six-step synthesis of **5a** and **5b**.[12] The overall isolated yields for **5a** and **5b** were quite poor (4% and 3%, respectively). We initially investigated the synthesis of **5a** and **5b** from 4-chlorobutyronitrile **1a** and 5-chlorovaleronitrile **1b**, respectively, following the method developed by Muchowski and co-workers.[13] However, unsatisfactory results were obtained after several trials primarily due to disappointing isolated yields of the imidates that were hygroscopic, unstable, and prone to decomposition. Change of solvents apparently did not improve the yields. We then turned our attention to carry out imidate forming reaction under acidic conditions and found that the isolated yields of corresponding imidates **2a** and **2b** were greatly increased (94% for **2a** and 74% for **2b**). This approach therefore gave us quick access to the required bicyclic imidazoles (Scheme 1).[14] As the second step in the synthesis, a mixture of the imidates **2** and aminoacetaldehyde dimethyl acetal under basic condition was refluxed to readily afford the crude amidines **3** that were used directly for the next reaction. The amidine **3a**, upon heating at 80 °C in formic acid solution and subsequent aqueous hydrolysis, was conveniently converted into the desired 1,2-fused imidazole **5a** in essentially quantitative yield (66% yield in two steps). The corresponding 2-substituted imidazole intermediate **4a** was not observed and isolated under the experimental condition. This is an efficient and convenient synthesis of **5a**, an important structural core for bicyclic ionic liquid synthesis (Scheme 1). Using identical condition, the amidine **3b** was, however, cyclized smoothly into the stable 2-substituted imidazole **4b**. We found that, upon standing at ambient temperature for 8 days, this 2-(4-chlorobutyl)imidazole **4b** slowly and cleanly cyclized to afford **5b** with quantitative yield (78% yield in two steps). When the condition of the Finkelstein cyclization (NaI in refluxed methanol) was employed, the conversion of **4b** to **5b** could be accelerated to completion in 6 h with an excellent 97% isolated yield. This structural core **5b** is the basis of the library preparation of ionic liquids **6b**. Finally, the desired ionic liquids, [R-3C-im][NTf_2] (**6a**) and [R-4C-im][NTf_2] (**6b**) (R=Me, Et, Pr, and Bu), were prepared by direct alkylation of **5a** and **5b** with appropriate alkyl halides followed by halide exchange with potassium bis(trifluoromethylsulfonyl)imide, $KNTf_2$. The overall isolated yields of syntheses of bicyclic ionic liquids **6a** and **6b** were 50–53% and 40–48%, respectively. In comparison with our previous synthesis of [b-3C-im][NTf_2],[3] the synthetic strategy shown in Scheme 1 uses commercially available, inexpensive starting compounds and reagents as well as mild reaction conditions to efficiently produce key structural cores of **5a** and **5b** so that various bicyclic imidazolium ionic liquids **6a** and **6b** can therefore be conveniently accomplished.

Besides [m-3C-im][NTf_2] (**6a**, R=Me) and [m-4C-im][NTf_2] (**6b**, R=Me), all bicyclic imidazolium ionic liquids prepared are liquid at room temperature. In this work, we were interested in the [NTf_2]-based bicyclic imidazolium ionic liquids because these water-insoluble and hydrophobic [NTf_2]-based ionic liquids were mainly developed as valuable and reusable solvents for green organic synthesis, known to be poorly associated with water, and of unusual low melting points.[15] We have also previously demonstrated that the anion in ionic liquids played minimal role in the experiments of solvent deuterium isotope exchange.[3] The conformationally constrained and non-planar structure of bicyclic ionic liquids may additionally contribute to low melting points. For physical properties, [R-3C-im][NTf_2] and [R-4C-im][NTf_2] (R=Me, Et, Pr, and Bu) are readily miscible with polar organic solvents such as methanol, ethanol, acetone, dichloromethane, chloroform, tetrahydrofuran, ethyl acetate, acetonitrile, and dimethylforamide, but practically insoluble in less polar solvents including diethyl ether, *n*-hexane, dioxane, cyclohexane, benzene, and toluene. The ionic liquids **6a** and **6b** (R=Me, Et, Pr, and Bu) are all immiscible with water.

Handy and Okello were first to investigate solvent deuterium isotope exchange with fructose-derived imidazolium ionic liquids by ^{1}H MMR.[16] They confirmed that the C-2 hydrogen on C-2 unsubstituted ionic liquid was chemically reactive and rapidly exchanged with D_2O solvent. They further established that, under basic conditions, the C-2-methyl-substituted ionic liquid was not completely inert and could proceed deuterium exchange.[16] Their results had previously led us to synthesize the conformationally constrained [b-3C-im][NTf_2] ionic liquid and investigate its susceptibility to solvent deuterium exchange.[3] Our preliminary study of solvent deuterium isotope exchanges with [bmim][NTf_2], [bdmim][NTf_2], and [b-3C-im][NTf_2] ionic liquids indicated that, as expected, both [bmim][NTf_2] and [bdmim][NTf_2] were chemically reactive and exchanged with deuterium solvents; [b-3C-im][NTf_2], however, was completely resistant to deuterium isotope exchange within the study time period (5 h) at ambient temperature.[3] In this report, we systematically investigate chemical reactivity of [b-3C-im][NTf_2] and its bicyclic analogous ionic liquids, **6a** and **6b** (R=Me, Et, Pr, and Bu). We envisaged that the constrained fused rings, their non-planar overall structures, and the likely high pK_a values at C-2's CH_2 group of [R-3C-im][NTf_2] and [R-4C-im][NTf_2] ionic liquids should contribute significantly to their resistance to solvent deuterium exchanges.

The time-dependent exchange rate profile shown in Figure 1 correlates well with the rates reported in our previous communication.[3] The solvent exchange rates were measured in two (neutral and strongly basic) experimental conditions by observing the changes in the ^{1}H NMR integrals of the C-2 position hydrogens (i.e., H, CH_2, or CH_3 at C-2 position) to that of the terminal methyl hydrogens (a non-exchangeable position) on the butyl group (for [bmim][NTf_2] and [bdmim][NTf_2]) or on the alkyl (R) group (for **6a** and **6b**). Results from Figure 1 showed that, under strongly basic conditions (0.1 M KOD in the 1:1 mixture of CD_3OD and D_2O),

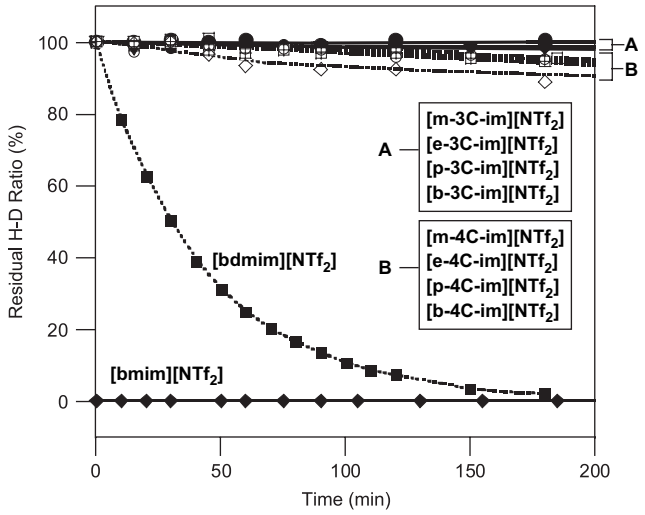


Figure 1. Solvent deuterium isotope exchange at C-2 of [R-3C-im][NTf_2] (**6a**, R=Me, Et, Pr, and Bu), [R-4C-im][NTf_2] (**6b**, R=Me, Et, Pr, and Bu), [bdmim][NTf_2], and [bmim][NTf_2] ionic liquids (0.1 M each) in CD_3OD/D_2O (1:1, v/v; 0.5 mL) containing 0.1 M KOD. The initial progress of deuterium exchange (t=0–200 min) could readily be monitored by ^1H NMR.

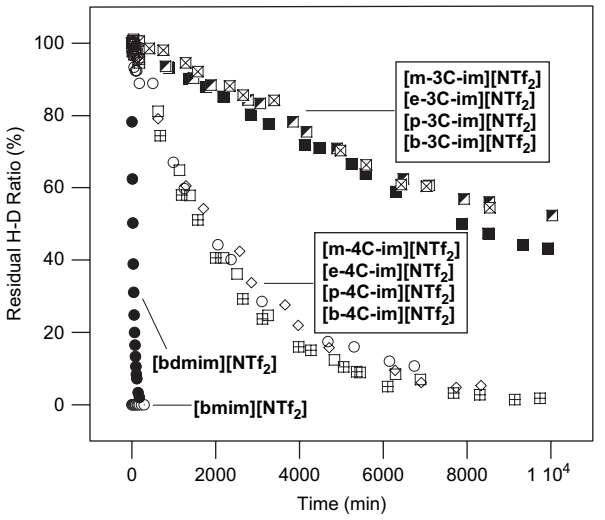


Figure 2. Solvent deuterium isotope exchange at C-2 of [R-3C-im][NTf_2] (**6a**, R=Me, Et, Pr, and Bu), [R-4C-im][NTf_2] (**6b**, R=Me, Et, Pr, and Bu), [bdmim][NTf_2], and [bmim][NTf_2] ionic liquids (0.1 M each) in CD_3OD/D_2O (1:1, v/v; 0.5 mL) containing 0.1 M KOD. The complete progress of deuterium exchange (t=0–10,000 min) could be monitored by ^1H NMR.

the [R-3C-im][NTf_2] ionic liquids (R=Me, Et, Pr, and Bu) proceeded essentially no deuterium isotope exchanges at C-2's CH_2 group for up to 3 h while the [bdmim][NTf_2] ionic liquid was 50% deuterium exchanged at C-2 methyl position in 30 min at ambient temperature. As expected, the [bmim][NTf_2] ionic liquid was deuterium exchanged instantaneously at the acidic C-2 hydrogen. This 1-butyl-3-methylimidazolium cation likely undergoes base-mediated abstraction of the C-2 proton to form the ylide intermediate stabilized by a carbene-like resonance structure. Results also demonstrated that bicyclic [R-4C-im][NTf_2] ionic liquids (**6b**) were less stable than [R-3C-im][NTf_2] (**6a**) in solvent deuterium isotope exchanges.

Upon incubating in deuterium solvent for long time (up to 7 days), we found that, under strongly basic condition, all bicyclic **6a** and **6b** (R=Me, Et, Pr, and Bu) ionic liquids studied underwent very slow but measurable exchanges at the C-2 methylene groups with the solvent (Fig. 2). The constrained, non-planar dihydropyrroloimidazolium ring structure in [R-3C-im][NTf_2] ionic liquids appears to make the CH_2 hydrogens at C-2 less accessible than that of the tetrahydroimidazopyridinium ring in [R-4C-im][NTf_2] ionic liquids for solvent exchange. Under the experimental condition, the times required at 50% deuterium exchange ($t_{1/2}$) for [R-3C-im][NTf_2] (**6a**, R=Me, Et, Pr, and Bu) and [R-4C-im][NTf_2] (**6b**, R=Me, Et, Pr, and Bu) ionic liquids were approximately 140 and 28 h, respectively; that is, [R-3C-im][NTf_2] ionic liquids are far more chemically stable than [R-4C-im][NTf_2] ionic liquids in basic reaction condition. The nature of alkyl R group in both bicyclic ionic liquids apparently plays minimal role in solvent deuterium isotope exchanges.

Under neutral conditions (CD_3OD/D_2O=1:1, v/v), only [bmim][NTf_2] exchanged with deuterium solvent ($t_{1/2}$=1 h) and all other ionic liquids studied in this work gave no detectable exchanges for up to 25 days at ambient temperature (Fig. 3). We reasoned that the likely higher pK_a values at

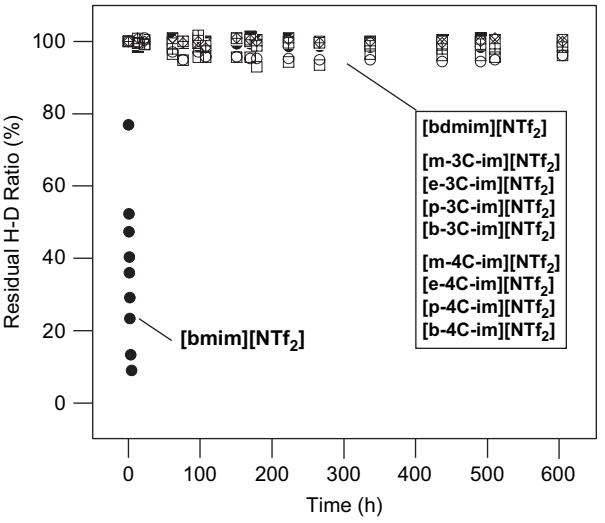
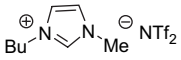
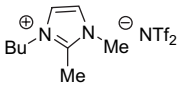
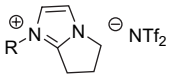
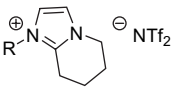


Figure 3. Solvent deuterium isotope exchange at C-2 of [R-3C-im][NTf_2] (**6a**, R=Me, Et, Pr, and Bu), [R-4C-im][NTf_2] (**6b**, R=Me, Et, Pr, and Bu), [bdmim][NTf_2], and [bmim][NTf_2] ionic liquids (0.1 M each) in CD_3OD/D_2O (1:1, v/v; 0.5 mL). The complete progress of deuterium exchange (t=0–600 h) could be readily monitored by ^1H NMR.

C-2 CH_3 or CH_2 groups of [bdmim][NTf_2], [R-3C-im][NTf_2], and [R-4C-im][NTf_2] ionic liquids prevent them from being deuterium exchanged with solvent.[16] The result of these studies indicates that the C-2 position of imidazolium ionic liquids can be made less acidic by simply replacing the hydrogen with an alkyl group. Table 1 summarizes exchange rates of all ionic liquids studied in deuterium solvents under neutral and basic conditions.

The fact that the alkyl substitution at C-2 position in bicyclic [R-3C-im][NTf_2] ionic liquids (**6a**, R=Me, Et, Pr, and Bu) provides additional chemical stability could be further supported from a series of alkylation reactions on imidazolium ionic liquids (Figs. 4 and 5). Treatment of the commonly

Table 1. Chemical stability of [bmim][NTf_2], [bdmim][NTf_2], [R-3C-im][NTf_2], and [R-4C-im][NTf_2] room temperature ionic liquids under both neutral and basic conditions

Entry	Ionic liquid		Approximate $t_{1/2}$ (h)[a]	
			Neutral condition[b]	Basic condition[c]
1	[bmim][NTf_2]		1	0
2	[bdmim][NTf_2]		>600	0.5
3	[R-3C-im][NTf_2] (R=Me, ET, Pr, and Bu)		>600	140
4	[R-4C-im][NTf_2] (R=Me, Et, Pr, and Bu)		>600	28

[a] Determined by ^{1}H NMR (for detail, see Section 4).
[b] The experimental condition: ionic liquid (0.1 M); CD_3OD/D_2O (1:1, v/v; 0.5 mL).
[c] The experimental condition: ionic liquid (0.1 M); CD_3OD/D_2O (1:1, v/v; 0.5 mL); KOD (0.1 M).

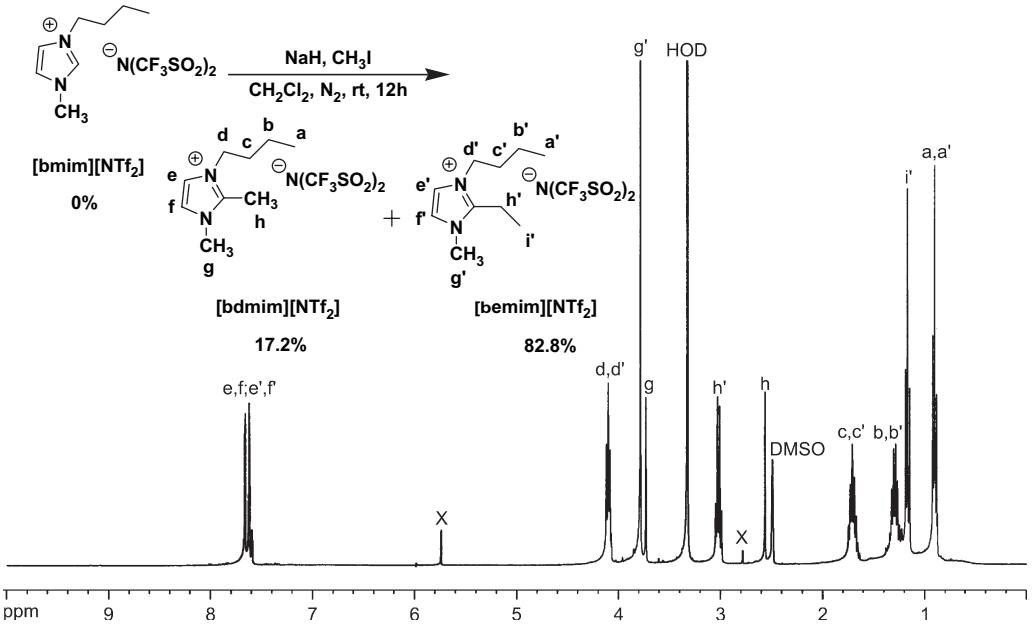


Figure 4. ^{1}H NMR spectrum of a mixture of mono- and doubly methylated [bmim][NTf_2] room temperature ionic liquids (17.2% and 82.8%, respectively) in DMSO-d_6. For detail, see Section 4.

used [bmim][NTf_2] ionic liquid with excessive sodium hydride and methyl iodide clearly resulted in the formation of both 1-butyl-2-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bemim][NTf_2]) and [bdmim][NTf_2] products (Fig. 4). Under our reaction condition, the doubly methylated [bemim][NTf_2] ionic liquid was a major product (83%). A similar result was obtained starting with [bdmim][NTf_2] ionic liquid; the [bemim][NTf_2] was the sole reaction product and no 1-butyl-2-isopropyl-3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide was observed or isolated. In cases of [R-3C-im][NTf_2] (**6a**) and [R-4C-im][NTf_2] (**6b**) ionic liquids (R=Me, Et, Pr, and Bu), treatment with excessive sodium hydride and methyl iodide results in full recovery of starting material and methylated adducts were not observed, indicating that these constrained, bicyclic ionic liquids (**6a** and **6b**) are chemically inert and much more stable than the C-2 unsubstituted and methyl-substituted imidazolium ionic liquids ([bmim][NTf_2] and [bdmim][NTf_2]). A representative example ([e-3C-im][NTf_2]) is given in Figure 5.

3. Conclusion

In this report, we synthesized and characterized a new class of room temperature ionic liquids [R-3C-im][NTf_2] (**6a**, R=Et, Pr, and Bu) that appear to fulfill practical requirement as an inert solvent for chemical reactions and these ionic liquids may open exciting perspectives of use in various synthetic applications of natural and non-natural products of biological significance. The synthesis was general and advantageous primarily, because all bicyclic ionic liquids

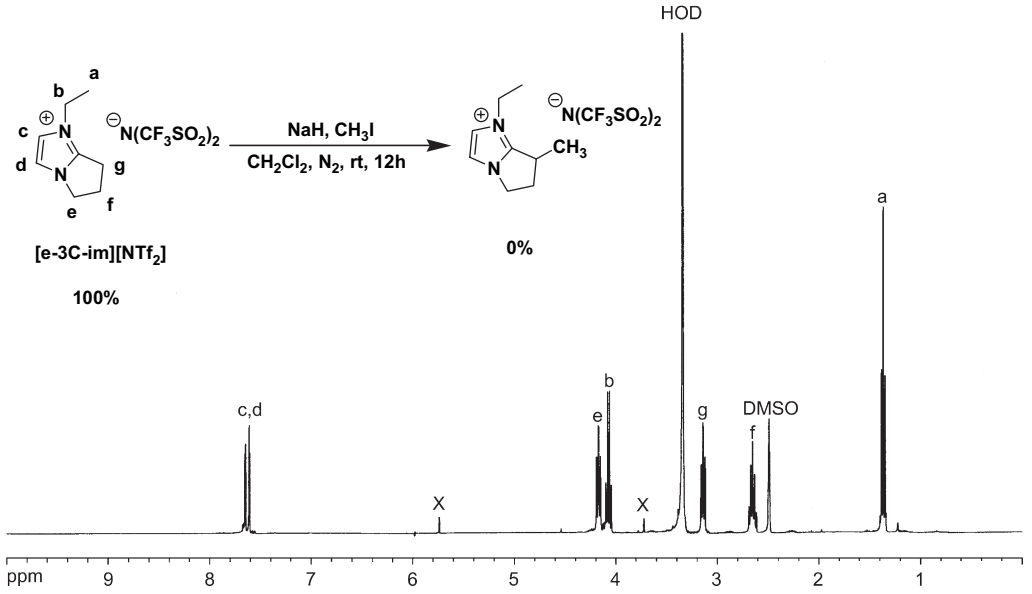


Figure 5. ^{1}H NMR spectrum of CH_3I-treated [e-3C-im][NTf_2] room temperature ionic liquid in DMSO-d_6. Under experimental condition (excessive NaH and CH_3I in CH_2Cl_2 for 12 h at ambient temperature), [e-3C-im][NTf_2] was totally inert to methylation reaction. For detail, see Section 4.

were prepared from common structural cores of the fused dihydropyrroloimidazole **5a** (for [R-3C-im][NTf_2]) or tetrahydroimidazopyridine **5b** (for [R-4C-im][NTf_2]) so that derivatives, or even molecular libraries, of ionic liquids could be readily accomplished and characterized. The results presented in this research clearly demonstrated that the C-2 unsubstituted ionic liquids such as [bmim][NTf_2] were evidently reactive and participated in chemical reactions; the replacement of the C-2 hydrogen with an alkyl ring structure to produce constrained, non-planar bicyclic ionic liquids added additional stability (as well as decreased melting points) and was much resistant to solvent deuterium exchanges and methylation reactions. Even the room temperature ionic liquids [R-3C-im][NTf_2] (**6a**, R=Et, Pr, and Bu) are not completely inert and still can be subject to very slow deprotonation ($t_{1/2}$~6 days) under strongly basic conditions, the added stability and robustness nevertheless provide sufficient chemical tolerance to avoid some of the competing side reactions that are so common in the simple imidazolium-based ionic liquids. The [R-3C-im][NTf_2] (**6a**, R=Et, Pr, and Bu) are the most chemically stable imidazolium-based room temperature ionic liquids available today.

4. Experimental

4.1. General experimental section

Flash chromatography was performed on silica gel (230–400 mesh). TLC was carried out on aluminum-backed silica plates precoated with silica (0.2 mm), which were developed using standard visualizing agents such as UV fluorescence and iodine. Unless otherwise indicated, all reactions were carried out without the aid of dry nitrogen or argon. NMR spectra were recorded on a Varian Gemini 200 at 200 MHz (^{1}H) and a Bruker AVANCE DPX 400 at 100 MHz (^{13}C) in CD_3OD unless otherwise stated. Chemical shifts were quoted in parts per million (ppm). Melting points were determined on a Fargo MP-2D apparatus (Taiwan, ROC) and are uncorrected. Solvents and reagents were obtained from commercial sources and were used without further purification.

4.2. Synthesis of 1-alkyl-2,3-trimethyleneimidazolium bis(trifluoromethanesulfonyl)imide [R-3C-im][NTf_2] ionic liquids (6a)

4.2.1. 6,7-Dihydro-5*H*-pyrrolo[1,2-*a*]imidazole 5a. Hydrogen chloride was slowly bubbled into a solution of 1 mL (10 mmol) of 4-chlorobutyronitrile (**1a**) and 0.47 mL (11.6 mmol) of methanol in ether (5 mL) at ambient temperature for 4 h under nitrogen. After the solution was saturated, it was allowed to stand at −20 °C for another 24 h. The solvent and excess HCl were removed under reduced pressure to give a white salt. The salt was successively washed with ether and dried in vacuo to give 3-chloropropanimidate hydrochloride (**2a**) (1.69 g, 94% yield); ^{1}H NMR (200 MHz, CD_3Cl) δ 2.24–2.28 (m, CCH_2C, 2H), 2.99 (t, J=7.8 Hz, CH_2, 2H), 3.64 (t, J=6.2 Hz, CH_2, 2H), 4.33 (s, CH_3, 3H).

To the solution of imidate **2a** (1.69 g, 9.8 mmol) in dichloromethane (10 mL) were added aminoacetaldehyde dimethyl acetal (0.86 mL, 7.8 mmol) and triethylamine (4.1 mL, 29.6 mmol). The reaction mixture was heated to reflux at 60 °C for 2 h. After the reaction, the solvent and excess triethylamine were removed under reduced pressure to afford the desired amidine product (**3**). This crude product **3** was used directly for the next reaction.

A solution of crude amidine **3** in formic acid (5 mL) was heated at 80 °C for 20 h. Formic acid was removed in vacuo, benzene was added to the residue, and the mixture was evaporated to dryness. Water (2 mL) and solid sodium bicarbonate were added to the residue to raise the pH of the solution to 10. The solution was extracted three times with dichloromethane (3×15 mL). The extracts were dried over anhydrous Na_2SO_4. Filtration and evaporation under reduced pressure afforded pure yellowish solid **5a** (564 mg, 66% yield in two steps); mp 72–73.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$)

δ 2.60 (p, J=7.2 Hz, CCH_2C, 2H), 2.86 (t, J=7.4 Hz, N=CCH_2, 2H), 3.97 (t, J=7.0 Hz, NCH_2, 2H), 6.90 (s, C=CH, 1H), 7.03 (s, C=CH, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 22.9, 25.2, 44.5, 114.3, 132.9, 154.6.

4.2.2. 1-Methyl-2,3-trimethyleneimidazolium bis(trifluoromethanesulfonyl)imide [m-3C-im][NTf$_2$] ionic liquid (6a, R=Me). To an ice-cooled round-bottomed flask containing 6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole **5a** (100 mg, 0.93 mmol) was added methyl iodide (145 mg, 1.0 mmol). The alkylation reaction was carried out at 0 °C for 1 h. The reaction mixture was mixed with water (4 mL) and washed three times with ethyl acetate (3×2 mL). The residual ethyl acetate present in aqueous solution was removed in vacuo. Lyophilization of the aqueous solution afforded the yellow solid, 1-methyl-2,3-trimethyleneimidazolium iodide, with excellent isolated yield (213 mg, 92%).

To a solution of 1-methyl-2,3-trimethyleneimidazolium iodide (100 mg, 0.4 mmol) in water (1 mL) was added the bistrifluoromethanesulfonimide lithium salt (114 mg, 0.4 mmol). The mixture was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was diluted with dichloromethane (6 mL) and then washed three times with water (3×2 mL). Removal of the solvent under reduced pressure afforded the 1-methyl-2,3-trimethyleneimidazolium bis(trifluoromethylsulfonyl)imide [m-3C-im][NTf$_2$] (**6a**, R=Me) as a white solid (140 mg, 87%); mp 83–85 °C; ^{1}H NMR (200 MHz, CD_3OD) δ 2.79 (p, J=7.4 Hz, CH_2, 2H), 3.17 (t, J=7.5 Hz, N=CCH_2, 2H), 3.79 (s, NCH_3, 3H), 4.26 (t, J=7.3 Hz, NCH_2, 2H), 7.42 (s, HC=CH, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 23.3, 26.8, 35.4, 49.3, 118.7, 121.1 (q, J_{CF}=318 Hz, CF_3) 127.9, 154.5; FAB-HRMS m/z [M]$^+$ calcd for $C_7H_{11}N_2$ 123.0922, found 123.0919.

4.2.3. 1-Ethyl-2,3-trimethyleneimidazolium bis(trifluoromethanesulfonyl)imide [e-3C-im][NTf$_2$] ionic liquid (6a, R=Et). To a round-bottomed flask containing 6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole **5a** (100 mg, 0.93 mmol) was added bromoethane (111 mg, 1.0 mmol). The alkylation reaction was allowed to proceed at 60 °C for 2 h. After the reaction, the solution was mixed with water (4 mL) and washed three times with ethyl acetate (3×2 mL). The residual ethyl acetate present and the solvent were removed in vacuo to finally afford a yellow liquid, 1-ethyl-2,3-trimethyleneimidazolium bromide, with excellent isolated yield (219 mg, 97%).

To a solution of 1-ethyl-2,3-trimethyleneimidazolium bromide (100 mg, 0.46 mmol) in water (1 mL) was added the bistrifluoromethanesulfonimide lithium salt (132 mg, 0.46 mmol). The mixture was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was diluted with dichloromethane (6 mL) and then washed three times with water (3×2 mL). Removal of the solvent under reduced pressure afforded the 1-ethyl-2,3-trimethyleneimidazolium bis(trifluoromethylsulfonyl)imide [e-3C-im][NTf$_2$] (**6a**, R=Et) as a yellow liquid (165 mg, 86%); ^{1}H NMR (200 MHz, CD_3OD) δ 1.48 (t, J=7.4 Hz, CH_3, 3H), 2.79 (p, J=8.2 Hz, CH_2, 2H), 3.20 (t, J=7.6 Hz, N=CCH_2, 2H), 4.13 (q, J=7.4 Hz, C=NCH_2, 2H), 4.26 (t, J=7.4 Hz, NCH_2, 2H), 7.44 (d, J=2.0 Hz, C=CH, 1H), 7.50 (d, J=2.0 Hz, C=CH, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 15.0, 23.5, 26.7, 45.1, 49.0, 118.9, 121.1 (q, J_{CF}=318 Hz, CF_3) 126.2, 153.7; FAB-HRMS m/z [M]$^+$ calcd for $C_8H_{13}N_2$ 137.1079, found 137.1082.

4.2.4. 1-Propyl-2,3-trimethyleneimidazolium bis(trifluoromethanesulfonyl)imide [p-3C-im][NTf$_2$] ionic liquid (6a, R=Pr). To a round-bottomed flask containing 6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole **5a** (100 mg, 0.93 mmol) was added bromopropane (125 mg, 1.0 mmol). The alkylation reaction was allowed to proceed at 80 °C for 2 h. After the reaction, the solution was mixed with water (4 mL) and washed three times with ethyl acetate (3×2 mL). The residual ethyl acetate present and the solvent were removed in vacuo to finally afford a yellow liquid, 1-propyl-2,3-trimethyleneimidazolium bromide, with excellent isolated yield (207 mg, 97%).

To a solution of 1-propyl-2,3-trimethyleneimidazolium bromide (100 mg, 0.43 mmol) in water (1 mL) was added the bistrifluoromethanesulfonimide lithium salt (125 mg, 0.44 mmol). The mixture was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was diluted with dichloromethane (6 mL) and then washed three times with water (3×2 mL). Removal of the solvent under reduced pressure afforded the 1-propyl-2,3-trimethyleneimidazolium bis(trifluoromethylsulfonyl)imide [p-3C-im][NTf$_2$] (**6a**, R=Pr) as a yellow liquid (163 mg, 88%); ^{1}H NMR (200 MHz, CD_3OD) δ 0.97 (t, J=7.4 Hz, CH_3, 3H), 1.78–1.98 (m, CH_2, 2H), 2.80 (p, J=8.2 Hz, CH_2, 2H), 3.19 (t, J=7.6 Hz, N=CCH_2, 2H), 4.06 (t, J=7.3 Hz, C=NCH_2, 2H), 4.27 (t, J=7.3 Hz, NCH_2, 2H), 7.45 (d, J=2 Hz, C=CH, 1H), 7.50 (d, J=1.8 Hz, C=CH, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 10.9, 23.5, 23.9, 26.7, 49.1, 51.4, 118.9, 121.1 (q, J_{CF}=318 Hz, CF_3) 126.8, 153.8; FAB-HRMS m/z [M]$^+$ calcd for $C_9H_{15}N_2$ 151.1235, found 151.1235.

4.2.5. 1-Butyl-2,3-trimethyleneimidazolium bis(trifluoromethanesulfonyl)imide [b-3C-im][NTf$_2$] ionic liquid (6a, R=Bu). To a round-bottomed flask containing 6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole **5a** (100 mg, 0.93 mmol) was added bromobutane (140 mg, 1.0 mmol). The alkylation reaction was allowed to proceed at 80 °C for 2 h. After the reaction, the solution was mixed with water (4 mL) and washed three times with ethyl acetate (3×2 mL). The residual ethyl acetate present and the solvent were removed in vacuo to finally afford a yellow liquid, 1-butyl-2,3-trimethyleneimidazolium bromide, with excellent isolated yield (219 mg, 97%).

To a solution of 1-butyl-2,3-trimethyleneimidazolium bromide (100 mg, 0.41 mmol) in water (1 mL) was added the bistrifluoromethanesulfonimide lithium salt (118 mg, 0.41 mmol). The mixture was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was diluted with dichloromethane (6 mL) and then washed three times with water (3×2 mL). Removal of the solvent under reduced pressure afforded the 1-butyl-2,3-trimethyleneimidazolium bis(trifluoromethylsulfonyl)imide [b-3C-im][NTf$_2$] (**6a**, R=Bu) as a yellow liquid (158 mg, 87%); ^{1}H NMR (200 MHz, CD_3OD) δ 0.98 (t, J=7.2 Hz, CH_3, 3H), 1.28–1.48 (m, CH_2, 2H), 1.83 (p, J=7.6 Hz, CH_2,

2H), 2.82 (p, J=8.0 Hz, CH_2, 2H), 3.19 (t, J=7.6 Hz, N=CCH_2, 2H), 4.09 (t, J=7.3 Hz, C=NCH_2, 2H), 4.26 (t, J=7.4 Hz, NCH_2, 2H), 7.44 (d, J=2.0 Hz, C=CH, 1H), 7.49 (d, J=2.0 Hz, C=CH, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 13.7, 20.4, 23.5, 26.7, 32.5, 49.0, 49.7, 118.9, 121.1 (q, J_{CF}=318 Hz, CF_3) 126.7, 153.8; FAB-HRMS m/z $[M]^+$ calcd for $C_{10}H_{17}N_2$ 165.1392, found 165.1391.

4.3. Synthesis of 1-alkyl-2,3-tetramethyleneimidazolium bis(trifluoromethanesulfonyl)imide [R-4C-im][NTf_2] ionic liquids (6b)

4.3.1. 5,6,7,8-Tetrahydroimidazo[1,2-*a*]pyridine 5b. Hydrogen chloride was slowly bubbled into a solution of 5 mL (44.5 mmol) of 5-chlorovaleronitrile (**1b**) and 1.98 mL (48.9 mmol) of methanol in ether (10 mL) at ambient temperature for 4 h under nitrogen. After the solution was saturated, it was allowed to stand at −20 °C for another 24 h. The solvent and excess HCl were removed under reduced pressure to give a white salt. The salt was successively washed with ether and dried in vacuo to give 4-chlorobutanimidate hydrochloride (**2b**) (6.14 g, 74% yield); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.85–1.92 (m, CH_2CH_2, 4H), 2.81 (t, J=7.2 Hz, N=CCH_2, 2H), 3.56 (t, J=6.0 Hz, $ClCH_2$, 2H), 4.29 (s, OCH_3, 3H).

To the solution of imidate **2b** (6.14 g, 33 mmol) in dichloromethane (10 mL) were added aminoacetaldehyde dimethyl acetal (2.87 mL, 26.4 mmol) and triethylamine (13.7 mL, 99 mmol). The reaction mixture was heated to reflux at 60 °C for 2 h. After the reaction, the solvent and excess triethylamine were removed under reduced pressure to afford the desired amidine product (**3**). This crude product **3** was used directly for the next reaction.

A solution of crude amidine **3** in formic acid (10 mL) was heated at 80 °C for 20 h. Formic acid was removed in vacuo, benzene was added to the residue, and the mixture was evaporated to dryness. Water (5 mL) and solid sodium bicarbonate were added to the residue to raise the pH of the solution to 10. The solution was extracted three times with dichloromethane (3×30 mL). The extracts were dried over anhydrous Na_2SO_4. Filtration and evaporation under reduced pressure afforded pure yellowish liquid **4b**, which slowly and spontaneously converted to **5b** over a period of 8 days at ambient temperature (2.507 g, 78% yield in two steps). If the condition of Finkelstein cyclization (1.1 equiv of sodium iodide in methanol at reflux) was employed, this **4b** conversion to **5b** could be accelerated to completion in only 6 h with an excellent 97% isolated yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.87–2.01 (m, CH_2CH_2, 4H), 2.86 (t, J=6.0 Hz, N=CCH_2, 2H), 3.95 (t, J=5.6 Hz, NCH_2, 2H), 6.77 (d, J=1.2 Hz, C=CH, 1H), 6.95 (d, J=1.2 Hz, C=CH, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 20.6, 22.7, 24.0, 44.5, 117.8, 126.4, 144.4.

4.3.2. 1-Methyl-2,3-tetramethyleneimidazolium bis(trifluoromethanesulfonyl)imide [m-4C-im][NTf_2] ionic liquid (6b, R=Me). Ionic liquid [m-4C-im][NTf_2] (**6b**, R=Me) was prepared from **5b** by essentially the same procedure described for the synthesis of [m-3C-im][NTf_2] ionic liquid (**6a**, R=Me). To an ice-cooled round-bottomed flask containing 5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine **5b** (300 mg, 2.5 mmol) was added methyl iodide (384 mg, 2.7 mmol). The alkylation reaction was carried out at 0 °C for 1 h. The reaction mixture was mixed with water (4 mL) and washed three times with ethyl acetate (3×2 mL). The residual ethyl acetate present in aqueous solution was removed in vacuo. Lyophilization of the aqueous solution afforded the yellow solid, 1-methyl-2,3-tetramethyleneimidazolium iodide, with excellent isolated yield (637 mg, 98%).

To a solution of 1-methyl-2,3-tetramethyleneimidazolium iodide (400 mg, 1.5 mmol) in water (3 mL) was added the bistrifluoromethanesulfonimide lithium salt (435 mg, 1.5 mmol). The mixture was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was diluted with dichloromethane (6 mL) and then washed three times with water (3×2 mL). Removal of the solvent under reduced pressure afforded the 1-methyl-2,3-tetramethyleneimidazolium bis(trifluoromethylsulfonyl)-imide [m-4C-im][NTf_2] (**6a**, R=Me) as a white solid (531 mg, 84%); mp 46–48 °C; ^{1}H NMR (200 MHz, CD_3OD) δ 2.02–2.11 (m, CH_2CH_2, 4H), 2.96–3.01 (m, N=CCH_2, 2H), 3.73 (s, NCH_3, 3H), 4.14 (m, NCH_2, 2H), 7.37 (d, J=2.2 Hz, C=CH, 1H), 7.41 (d, J=2.0 Hz, C=CH, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 19.0, 21.3, 22.1, 34.1, 47.4, 121.1 (q, J_{CF}=318 Hz, CF_3) 121.7, 123.2, 146.0; FAB-HRMS m/z $[M]^+$ calcd for $C_8H_{13}N_2$ 137.1079, found 137.1076.

4.3.3. 1-Ethyl-2,3-tetramethyleneimidazolium bis(trifluoromethanesulfonyl)imide [e-4C-im][NTf_2] ionic liquid (6b, R=Et). Ionic liquid [e-4C-im][NTf_2] (**6b**, R=Et) was prepared from **5b** by essentially the same procedure described for the synthesis of [e-3C-im][NTf_2] ionic liquid (**6a**, R=Et). To a round-bottomed flask containing 5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine **5b** (300 mg, 2.5 mmol) was added bromoethane (295 mg, 2.7 mmol). The alkylation reaction was allowed to proceed at 60 °C for 2 h. After the reaction, the solution was mixed with water (4 mL) and washed three times with ethyl acetate (3×2 mL). The residual ethyl acetate present and the solvent were removed in vacuo to finally afford a yellow solid, 1-ethyl-2,3-tetramethyleneimidazolium bromide, with good isolated yield (486 mg, 86%).

To a solution of 1-ethyl-2,3-tetramethyleneimidazolium bromide (400 mg, 1.7 mmol) in water (3 mL) was added the bistrifluoromethanesulfonimide lithium salt (497 mg, 1.7 mmol). The mixture was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was diluted with dichloromethane (6 mL) and then washed three times with water (3×2 mL). Removal of the solvent under reduced pressure afforded the 1-ethyl-2,3-tetramethyleneimidazolium bis(trifluoromethylsulfonyl)imide [e-4C-im][NTf_2] (**6b**, R=Et) as a yellow liquid (605 mg, 81%); ^{1}H NMR (200 MHz, CD_3OD) δ 1.45 (t, J=7.4 Hz, CH_3, 3H), 2.03–2.09 (m, CH_2CH_2, 4H), 2.98–3.00 (m, N=CCH_2, 2H), 4.05–4.16 (m, CH_2CH_2, 4H), 7.41 (d, J=2.2 Hz, C=CH, 1H), 7.51 (d, J=2.2 Hz, C=CH, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 14.7, 19.1, 21.4, 22.2, 43.4, 47.4, 121.1 (q, J_{CF}=319 Hz, CF_3) 121.4, 122.2, 145.3; FAB-HRMS m/z $[M]^+$ calcd for $C_9H_{15}N_2$ 151.1235, found 151.1235.

4.3.4. 1-Propyl-2,3-tetramethyleneimidazolium bis(trifluoromethanesulfonyl)imide [p-4C-im][NTf$_2$] ionic liquid (6b, R=Pr). Ionic liquid [p-4C-im][NTf$_2$] (**6b**, R=Pr) was prepared from **5b** by essentially the same procedure described for the synthesis of [p-3C-im][NTf$_2$] ionic liquid (**6a**, R=Pr). To a round-bottomed flask containing 5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine **5b** (300 mg, 2.5 mmol) was added bromopropane (333 mg, 2.7 mmol). The alkylation reaction was allowed to proceed at 80 °C for 2 h. After the reaction, the solution was mixed with water (4 mL) and washed three times with ethyl acetate (3×2 mL). The residual ethyl acetate present and the solvent were removed in vacuo to finally afford a yellow solid, 1-propyl-2,3-tetramethyleneimidazolium bromide, with excellent isolated yield (595 mg, 99%).

To a solution of 1-propyl-2,3-trimethyleneimidazolium bromide (400 mg, 1.6 mmol) in water (3 mL) was added the bistrifluoromethanesulfonimide lithium salt (469 mg, 1.6 mmol). The mixture was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was diluted with dichloromethane (6 mL) and then washed three times with water (3×2 mL). Removal of the solvent under reduced pressure afforded the 1-propyl-2,3-tetramethyleneimidazolium bis(trifluoromethylsulfonyl)imide [p-4C-im][NTf$_2$] (**6b**, R=Pr) as a yellow liquid (575 mg, 79%); ^{1}H NMR (200 MHz, CD_3OD) δ 0.98 (t, J=7.3 Hz, CH_3, 3H), 1.78–1.95 (m, CH_2, 2H), 2.05–2.12 (m, CH_2CH_2, 4H), 2.98–3.04 (m, N=CCH_2, 2H), 4.03 (t, J=7.4 Hz, C=NCH_2, 2H), 4.06–4.16 (m, NCH_2, 2H), 7.40 (d, J=2.2 Hz, C=CH, 1H), 7.49 (d, J=2.2 Hz, C=CH, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 10.9, 19.0, 21.5, 22.0, 23.5, 47.3, 49.7, 121.0 (q, J_{CF}=319 Hz, CF_3) 121.9, 122.0, 145.3; FAB-HRMS *m/z* [M]$^+$ calcd for $C_{10}H_{17}N_2$ 165.1392, found 165.1391.

4.3.5. 1-Butyl-2,3-tetramethyleneimidazolium bis(trifluoromethanesulfonyl)imide [b-4C-im][NTf$_2$] ionic liquid (6b, R=Bu). Ionic liquid [b-4C-im][NTf$_2$] (**6b**, R=Bu) was prepared from **5b** by essentially the same procedure described for the synthesis of [b-3C-im][NTf$_2$] ionic liquid (**6a**, R=Bu). To a round-bottomed flask containing 5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine **5b** (300 mg, 2.5 mmol) was added bromobutane (371 mg, 2.7 mmol). The alkylation reaction was allowed to proceed at 80 °C for 2 h. After the reaction, the solution was mixed with water (4 mL) and washed three times with ethyl acetate (3×2 mL). The residual ethyl acetate present and the solvent were removed in vacuo to finally afford a yellow solid, 1-butyl-2,3-tetramethyleneimidazolium bromide, with good isolated yield (519 mg, 82%).

To a solution of 1-butyl-2,3-tetramethyleneimidazolium bromide (400 mg, 1.5 mmol) in water (3 mL) was added the bistrifluoromethanesulfonimide lithium salt (444 mg, 1.5 mmol). The mixture was allowed to proceed the ion exchange for 12 h at room temperature. The resulting solution was diluted with dichloromethane (6 mL) and then washed three times with water (3×2 mL). Removal of the solvent under reduced pressure afforded the 1-butyl-2,3-tetramethyleneimidazolium bis(trifluoromethylsulfonyl)-imide [b-4C-im][NTf$_2$] (**6b**, R=Bu) as a yellow liquid (603 mg, 85%); ^{1}H NMR (200 MHz, CD_3OD) δ 0.98 (t, J=7.2 Hz, CH_3, 3H), 1.30–1.50 (m, CH_2, 2H), 1.80 (p, J=7.6 Hz, CH_2, 2H), 2.03–2.09 (m, CH_2CH_2, 4H), 2.98–3.04 (m, N=CCH_2, 2H), 4.06 (t, J=7.4 Hz, C=NCH_2, 2H), 4.09–4.15 (m, NCH_2, 2H), 7.41 (d, J=2.2 Hz, C=CH, 1H), 7.50 (d, J=2.2 Hz, C=CH, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 13.8, 19.2, 20.5, 21.6, 22.2, 32.3, 47.4, 48.1, 121.1 (q, J_{CF}=319 Hz, CF_3) 122.1, 122.1, 145.4; FAB-HRMS *m/z* [M]$^+$ calcd for $C_{11}H_{19}N_2$ 179.1548, found 179.1546.

4.4. General procedure for deuterium isotope exchange experiments

The ^{1}H NMR of a mixture of CD_3OD/D_2O (1:1, v/v; 0.5 mL) containing 0.1 M ionic liquid was recorded first. An equimolar KOD (0.1 M) was then added to it. The ^{1}H NMR spectrum was therefore collected at regular intervals, ranging from every 10 min for the faster exchanges such as [bmim][NTf$_2$] and [bdmim][NTf$_2$] to every several hours for the slower exchanges such as [R-3C-im][NTf$_2$] and [R-4C-im][NTf$_2$] where R=Me, Et, Pr, and Bu. The ratio of the integrals of the C-2 position hydrogens to that of the terminal methyl hydrogens (a non-exchangeable position) on the butyl group (for [bmim][NTf$_2$] and [bdmim][NTf$_2$]) or the alkyl group (for [R-3C-im][NTf$_2$] and [R-4C-im][NTf$_2$]) was obtained. These values were finally plotted to determine the rate of the exchange reaction.

4.5. General procedure for methylation reaction on [bmim][NTf$_2$], [bdmim][NTf$_2$], [R-3C-im][NTf$_2$], and [R-4C-im][NTf$_2$] ionic liquids

Sodium hydride (1.44 mmol, 60% in oil) was weighed in a dry flask. To this flask was added 2 mL of hexane and the suspension solution was mixed well. The supernatant was removed under reduced pressure. To the resulting flask kept at 0 °C was added a solution of the ionic liquid (0.24 mmol) in anhydrous dichloromethane (3 mL). The solution was stirred under nitrogen and iodomethane (2.4 mmol) was then added dropwise using syringe. The reaction mixture was left to stir for 12 h at ambient temperature. After the methylation reaction, the mixture was diluted with dichloromethane and extracted with water (2×3 mL), dried, and concentrated in vacuo. The resulting crude mixture was finally analyzed by ^{1}H NMR.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.12.003.

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