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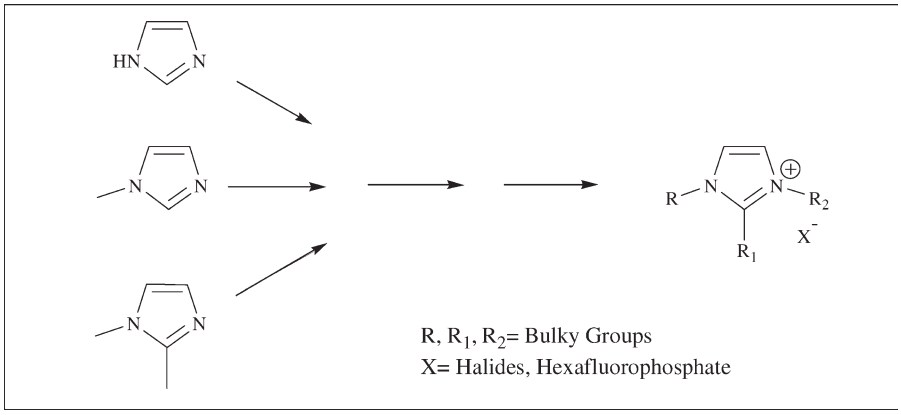

We report syntheses of bulky group containing imidazolium based ionic liquids. The bulky groups were introduced at N-1, C-2, and N-3 positions of the imidazole ring using convenient methodologies.

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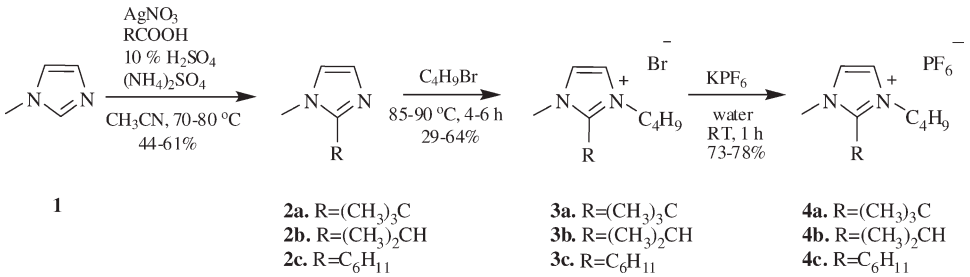
INTRODUCTION

Ionic liquids are receiving an upsurge of interest as green solvents primarily as replacements for conventional reaction media in chemical processes [1]. The imidazolium based ionic liquids are the extensively used and best investigated class of ionic liquids. It was recognized as early as 1964 that the C-2 proton of the 1,3-dialkylimidazolium cation is acidic and can be exchanged under weakly basic conditions [2]. The deprotonation of the 1,3-dialkylimidazolium cation causes the formation of a stable carbene strongly stabilized by two adjacent nitrogen atoms, which has desirable effects on some reactions like those involving organometallic catalysts [3]. On the other hand, it produces detrimental effects in many reactions carried out under basic conditions [4]. In addition to this, another problem associated with imidazolium based ionic liquids is hygroscopicity [5]. Syntheses of some ionic liquids with a methyl group at the 2-position were reported and these were found stable as compared to unsubstituted ionic liquids. The added stability is satisfactorily efficient to avoid some of unwanted competing reactions frequently occurring in their unsubstituted counterparts [6,7]. Although, this replacement of hydrogen with methyl group at the 2-position rendered the imidazole ring less acidic but later on it was established that even this methyl group is not completely inert and could behave acidic and undergo proton exchange even under surprisingly mild conditions. In presence of weak bases, the 1-butyl-2,3-dimethylimidazolium based ionic liquid was found to undergo exchange of proton with deuterium [8]. To overcome these shortcomings of known ionic liquids, we incorporated some even larger alkyl and aryl groups at positions C-2, in addition at N-1 and N-3 positions of the imidazole ring.

RESULTS AND DISCUSSION

Four series of such bulky group containing ionic liquids were synthesized. The first series describes the syntheses of C-2 modified ionic liquids [9]. 1-Methylimidazole **1** upon reaction with various alkyl carboxylic acids in the presence of silver nitrate, and ammonium persulfate in sulfuric acid (10%) readily provided 1-methyl-2-subtituted imidazoles **2a-c**, which upon reaction with *n*-butyl bromide followed by anion exchange with potassium hexafluorophosphate provided the desired ionic liquid **4a-c** in good yields (Scheme 1). For synthesizing the second series of the ionic liquids **8a-c** having bulky groups at N-1 position, the direct

Scheme 1



1

2a. R=$(CH_3)_3C$
2b. R=$(CH_3)_2CH$
2c. R=C_6H_{11}

3a. R=$(CH_3)_3C$
3b. R=$(CH_3)_2CH$
3c. R=C_6H_{11}

4a. R=$(CH_3)_3C$
4b. R=$(CH_3)_2CH$
4c. R=C_6H_{11}

Scheme 2

5

6a. R=CH_3CH_2
6b. R=$(CH_3)_3C$
6c. R=$C_6H_5CH_2$

7a. R=CH_3CH_2
7b. R=$(CH_3)_3C$
7c. R=$C_6H_5CH_2$

8a. R=CH_3CH_2
8b. R=$(CH_3)_3C$
8c. R=$C_6H_5CH_2$

alkylation was achieved using a method developed earlier involving reaction of various alkyl and aryl halides with **5** in the presence of sodium hydride as a base in DMF at −15°C [10]. The ionic liquids were obtained after quaternization of 1-alkylimidazoles **6a-c** followed by anion exchange with potassium hexafluorophosphate (Scheme 2).

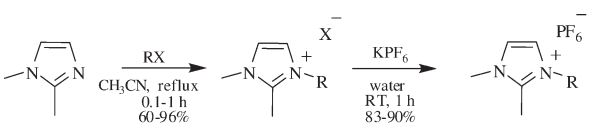
The third series involved alterations at the N-3 position of the imidazole ring. 1,2-Dimethylimidazole **9** upon reaction with various alkyl and aryl halides under reflux conditions yielded 1,2-dimethylimidazolium halides **10a-f**, which after being subjected to anion exchange provided the desired ionic liquids **11a-f** (Scheme 3). The fourth series illustrates ionic liquids with similar bulky groups attached at the N-1 and the N-3 positions. Herein, reaction of imidazole **5** with alkyl halides in the presence of potassium carbonate yielded 1,3-dialkylimidazolium halides **12a-c**, and anion exchange with potassium hexafluorophosphate in water at ambient temperature yielded the desired ionic liquids **13a-c** (Scheme 4).

To summarize, we have successfully synthesized four series of new ionic liquids with bulky groups placed at the various positions of the imidazole ring. These ionic liquids are expected to offer ideal physicochemical properties, including low hygroscopicity as compared to their unsubstituted counterparts and better stability, when used under basic conditions. Our efforts in the direction of utility of the newly synthesized ionic liquids will be reported in due course of time.

EXPERIMENTAL

Compounds were checked for their purity on precoated silica gel G_{254} TLC plates (Merck) and the spots were visualized under UV spectrophotometer and then by exposing them to iodine vapors. Column chromatographic purification was carried out on Merck silica gel (100–200 mesh). Melting points were recorded on capillary melting point apparatus as well as DSC. NMR spectra were recorded on 300 MHz Bruker FT-NMR (Advance DPX 300) spectrometer using tetramethylsilane as internal standard and the chemical shifts are reported in δ units. Mass spectra were recorded on a Finnigan Mat LCQ spectrometer (Xcaliber software) using APCI/ESI mode.

Scheme 3

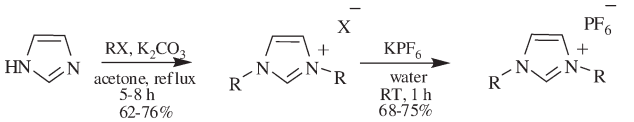


9

10a. R=CH_3, X=I
10b. R=CH_3CH_2, X=I
10c. R=$CH_3CH_2CH_2$, X=I
10d. R=$(CH_3)_2CH$, X=I
10e. R=*c*-C_5H_9, X=Br
10f. R=$C_6H_5CH_2$, X=Br

11a. R=CH_3
11b. R=CH_3CH_2
11c. R=$CH_3CH_2CH_2$
11d. R=$(CH_3)_2CH$
11e. R=*c*-C_5H_9
11f. R=$C_6H_5CH_2$

Scheme 4



5

12a. R=$(CH_3)_2CH$, X=I
12b. R=$C_6H_5CH_2$, X=Br
12c. R=*c*-C_5H_9, X=Br

13a. R=$(CH_3)_2CH$
13b. R=$C_6H_5CH_2$
13c. R=*c*-C_5H_9

Typical procedure for the synthesis of 2-alkylimidazoles 2a–c. A solution of 1-methylimidazole (1 mmol) in CH_3CN (5 mL) was added to a mixture of silver nitrate (0.6 mmol) and alkylcaboxylic acid (3.0 mmol) in 10% H_2SO_4 (10 mL), and the reaction mixture was heated at 70°C. A freshly prepared solution of ammonium persulfate (3 mmol) in water (10 mL) was added drop wise over 15 min. The heating source was then removed and reaction proceeded with the evolution of carbon dioxide. After 15 min, reaction mixture was poured onto ice, and made alkaline by adding 30% NH_4OH solution and extracted with EtOAc (4 × 50 mL). The combined extracts were washed with brine (2 × 10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford oil, which upon column chromatography over silica gel (100–200 mesh) afforded **2a-c**.

1-Methyl-2-tert-butylimidazole (2a). Yield 44%; amber color liquid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.49 (s, 9H, 3× CH_3), 3.77 (s, 3H, N—CH_3), 6.77 (s, 1H 4-Ar—H), 6.94 (s, 1H, 5-Ar—H); MS (APCI): 139.1(M+1). Anal. Calcd. for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.23; H, 9.93; N, 20.43.

1-Methyl-2-isopropylimidazole (2b). Yield 29%; amber color liquid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.15 (d, 3H, CH_3, J = 2.3 Hz), 1.17 (d, 3H, CH_3, J = 2.7 Hz), 2.97 (m, 1H, CH), 3.53 (s, 3H, N—CH_3), 6.71 (d, 1H, 5-Ar—H, J = 1.1 Hz), 6.81 (d, 1H, 4-Ar—H, J = 0.9 Hz); MS (APCI): 125.5(M+1). Anal. Calcd. for $C_7H_{12}N_2$: C, 67.70; H, 9.74; N, 22.56. Found: C, 67.56; H, 10.07; N, 22.83.

1-Methyl-2-cyclohexylimidazole (2c). Yield 61%; amber color liquid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.24–1.83 (m, 10H, 5x CH_2), 2.55 (t, 1H, CH J = 3.25), 3.51 (s, 3H, N—CH_3), 6.67 (d, 1H, 5-Ar—H, J = 1.1), 6.85 (d, 1H, 4-Ar—H J = 0.9); MS (APCI): 165.8(M+1). Anal. Calcd. for $C_{10}H_{16}N_2$: C, 73.13; H, 9.82; N, 17.06. Found: C, 73.45; H, 9.65; N, 17.34.

Typical procedure for synthesis of 1-alkylimidazoles 6a–c. Sodium hydride (60% suspension, 4.41 mmol) was placed in a two-necked flask and imidazole (1.47 mmol) in DMF (10 mL) was added under nitrogen atmosphere at −15°C. The reaction mixture was stirred for another 30 min at −15°C, and then alkyl halide (1.17 mmol) was added. The temperature of the reaction was raised to −5°C and the reaction mixture was stirred for another 3 hours under N_2. After completion, reaction was quenched with methanol (5 mL) and solvent was evaporated to give the crude product which was purified using silica gel (100–200 mesh) column chromatography to obtain 6a–c.

1-Ethylimidazole (6a). Yield 78%; light brown liquid; ^{1}H NMR($CDCl_3$, 300 MHz): δ 1.42–1.46 (t, 3H, CH_3, J = 7.40 Hz), 3.96–4.01 (q, 2H, N—CH_2, J = 7.36 Hz), 6.92 (s, 1H, Ar—H), 7.04 (s, 1H, Ar—H), 7.48 (s, 1H Ar—H); MS (APCI): 97.2(M+1). Anal. Calcd. for $C_5H_8N_2$: C, 62.47; H, 8.39; N, 29.14. Found: C, 62.73; H, 8.10; N, 29.36.

1-Isopropylimidazole (6b). Yield 75%; light brown liquid; ^{1}H NMR($CDCl_3$, 300 MHz): δ 1.47–1.49 (d, 6H, 2x CH_3, J = 6.74 Hz), 4.30–4.37 (m, H, N—CH), 6.96 (s, 1H, Ar—H), 7.05 (s, 1H, Ar—H), 7.53 (s, 1H Ar—H); MS (APCI): 111.1(M+1). Anal. Calcd. for $C_7H_{12}N_2$: C, 67.70; H, 9.74; N, 22.56. Found: C, 67.64; H, 9.49; N, 22.22.

1-Benzylimidazole (6c). Yield 70%; light brown liquid; ^{1}H NMR($CDCl_3$, 300 MHz): δ 5.11 (s, 2H, CH_2), 6.89 (s, 1H, Im—H), 7.08 (s, 1H, Im-H), 7.13–7.16 (m, 2H, Ar—H), 7.29–7.37 (m, 3H, Ar—H), 7.54 (s, 1H Ar—H); MS (APCI): 159.2(M+1). Anal. Calcd. for $C_9H_8N_2$: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.57; H, 5.91; N, 19.29.

Typical procedure for synthesis of alkyl imidazolium bromides 3a-c and 7a-c. Bromobutane (3 mmol) was added to alkylated compounds **2a-c** or **6a-c** (1 mmol) and the reaction was stirred for 4–6 hours at 85–90°C. The reaction mixture was dried under reduced pressure and column chromatography over silica gel (100–200 mesh) provided the quaternized compounds.

1-Butyl-3-methyl-2-tert-butylimidazolium bromide (3a). Yield 64%; pale brown solid; m.p. 154°C; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.01(t, 3H, CH_3, J = 11.5 Hz), 1.43 (m, 2H, CH_2, J = 4.21 Hz), 1.66 (s, 9H, 3x CH_3), 1.85 (m, 2H, CH_2), 4.05 (s, 3H, N—CH_3), 4.3 (t, 2H, CH_2, J = 8.30 Hz), 7.42 (d, 1H, 4-Ar—H, J = 1.94 Hz), 7.52 (d, 1H, 5-Ar—H J = 2.05); MS (APCI): 195.5(M+1). Anal. Calcd. for $C_{14}H_{25}N_2Br$: C, 52.37; H, 8.42; N, 10.18; Br, 8.46. Found: C, 52.75; H, 8.01; N, 10.38; Br, 8.21.

1-Butyl-3-methyl-2-isopropylimidazolium bromide (3b). Yield 61%; brown semisolid; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.90 (t, 3H, CH_3, J = 7.22 Hz), 1.24–1.39 (m, 8H, 2x CH_3, CH_2), 1.67–1.77 (m, 2H, CH_2), 3.53–3.68 (m, H, CH), 3.83 (s, 3H, N—CH_3), 4.09–4.14 (t, 2H, CH_2, J = 7.43 Hz), 7.35 (s, 1H, 4-Ar—H), 7.41 (s, 1H, 5-Ar—H); MS (APCI): 181.1(M+1). Anal. Calcd. for $C_{11}H_{21}N_2Br$: C, 50.58; H, 8.10; N, 10.72; Br, 30.59. Found: C, 50.82; H, 8.32; N, 10.53; Br, 30.41.

1-Butyl-3-methyl-2-cyclohexylimidazolium bromide (3c). Yield 57%; light yellow solid; m.p. 194.8; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.97 (t, 3H, CH_3, J = 7.32 Hz), 1.21 (m, 2H, CH_2), 1.78–2.00 (m, 10H, 5x CH_2), 3.95 (s, 3H, N—CH_3), 4.21 (t, 2H, CH_2, J = 7.52 Hz), 7.44 (d, 1H, 5-Ar—H, J = 1.05 Hz), 7.88 (d, 1H 4-Ar—H J = 4.70 Hz); MS (APCI): 221.6(M+1). Anal. Calcd. for $C_{14}H_{25}N_2Br$: C, 55.81; H, 8.36; N, 9.30; Br, 26.52. Found: C, 55.68; H, 8.69; N, 9.08; Br, 26.42.

1-Butyl-3-ethylimidazolium bromide (7a). Yield 80%; light brown liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.98–1.02 (t, 3H, CH_3, J = 7.41 Hz), 1.35–1.44 (m, 2H, CH_2), 1.53–1.57 (t, 3H, CH_3, J = 7.37), 7.67 (s, 1H, Ar—H), 7.68 (s, 1H Ar—H), 9.06 (s, 1H Ar—H); MS (APCI): 153.4(M+1). Anal. Calcd. for $C_9H_{17}N_2Br$: C, 46.36; H, 7.35; N, 12.02; Br, 34.27. Found: C, 46.02; H, 7.64; N, 12.29; Br, 34.35.

1-Butyl-3-isopropylimidazolium bromide (7b). Yield 78%; light brown liquid; ^{1}H NMR (CD_3OD, 300 MHz): δ 0.97–1.01 (t, 3H, CH_3, J = 7.45 Hz), 1.35–1.41 (m, 2H, CH_2), 1.57–1.59 (d, 6H, 2x CH_3, J = 6.22 Hz), 1.85–1.93 (m, 2H, CH_2), 4.22–4.26 (t, 2H, N—CH_2), 4.67–4.70 (m, H, CH), 7.67 (s, 1H, Ar—H), 7.75 (s, 1H, Ar—H), 9.15 (s, 1H Ar—H); MS (APCI): 167.4(M+1). Anal. Calcd. for $C_{11}H_{21}N_2Br$: C, 50.58; H, 8.10; N, 10.72; Br, 30.59. Found: C, 50.82; H, 8.42; N, 10.43; Br, 30.71.

1-Butyl-3-benzylimidazole bromide (7c). Yield 70%; light brown liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.95–0.99 (t, 3H, CH_3, J = 7.36 Hz), 1.33–1.39 (m, 2H, CH_2), 1.84–1.91 (m, 2H, CH_2), 4.22–4.26 (t, 2H, CH_2, J = 7.38), 5.44 (s, 2H, N—CH_2), 7.40–7.64 (m, 5x Ar—H), 7.66 (s, H, Im—H), 7.68 (s, H, Im—H), 9.18 (s, 1H Ar—H)); MS (APCI): 215.2(M+1). Anal. Calcd. for $C_{13}H_{17}N_2Br$: C, 55.53; H, 6.09; N, 9.96; Br, 28.42. Found: C, 55.21; H, 6.32; N, 9.68; Br, 28.24.

Typical procedure for the synthesis of 1-alkyl-2,3-dimethylimidazolium halides 10a–f. To a solution of 1,2-dimethylimidazole (2.08 mmol) in CH_3CN was added alkyl halide (6.24 mmol) and reaction was stirred for a time ranging from 6 minutes to 1 hour at a temperature ranging from 25 to 65°C. The reaction mixture was then washed with diethyl ether and dried under reduced pressure and purified by column chromatography.

1,2,3-Trimethylimidazolium iodide (10a). Yield 80%; white solid; m.p. 45°C; ^{1}H NMR(CD_3OD, 300 MHz): δ 2.60 (s, 3H, CH_3), 3.81 (s, 6H, 2x N—CH_3), 7.44 (s, 2H, 4,5-Ar—H); MS (APCI): 111.1(M+1). Anal. Calcd. for $C_6H_{11}N_2I$: C, 30.27; H, 4.66; N, 11.77; I, 53.31. Found: C, 30.44; H, 4.80; N, 11.30; I, 53.62.

1-Ethyl-2,3-dimethylimidazolium iodide (10b). Yield 88%; white solid; m.p. 92°C; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.43 (t, 3H, CH_3, J = 7.31 Hz), 2.63 (s, 3H, CH_3), 3.81 (s, 3H, N—CH_3), 4.15–4.23 (m, 2H, N—CH_2), 7.46 (s, 1H, 5-Ar—H), 7.52 (s, 1H 4-Ar—H); MS (APCI): 125.1(M+1). Anal. Calcd. for $C_7H_{13}N_2I$: C, 33.35; H, 5.20; N, 11.11; I, 50.34. Found: C, 33.51; H, 5.60; N, 11.40; I, 50.14.

2,3-Dimethyl-1-propylimidazolium iodide (10c). Yield 81%; light brown semisolid; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.86 (t, 3H, CH_3, J = 7.38 Hz), 1.72 (m, 2H, CH_2), 2.53 (s, 3H, CH_3), 3.72 (s, 3H, N—CH_3), 3.99 (t, 2H, N—CH_2, J = 7.35 Hz), 7.36 (s, 1H, 5-Ar—H), 7.40 (s, 1H 4-Ar—H); MS (APCI): 139.1(M+1). Anal. Calcd. for $C_8H_{15}N_2I$: C, 36.11; H, 5.68; N, 10.53; I, 47.69. Found: C, 36.52; H, 5.81; N, 10.25; I, 47.91.

1-Isopropyl-2,3-dimethylimidazolium iodide (10d). Yield 77%; light yellow solid; m.p. 136°C; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.50 (d, 3H, CH_3, J = 7.30 Hz), 1.56 (d, 3H, CH_3, J = 6.76 Hz), 2.46 (s, 3H, CH_3), 3.69 (s, 3H, N—CH_3), 4.65–4.79 (m, 2H, N—CH), 7.49 (s, 1H, 5-Ar—H), 7.63 (s, 1H 4-Ar—H); MS (APCI): 139.1(M+1). Anal. Calcd. for $C_8H_{15}N_2I$: C, 36.11; H, 5.68; N, 10.53; I, 47.69. Found: C, 36.24; H, 5.69; N, 10.33; I, 47.85.

1-Cyclopentyl-2,3-dimethylimidazolium bromide (10e). Yield 60%; brown semisolid; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.78–1.95 (m, 8H, CH_2), 2.63 (s, 3H, CH_3), 3.83 (s, 3H, N—CH_3), 4.73 (m, 1H, N—CH), 7.46 (s, 1H, 5-Ar—H), 7.52 (s, 1H 4-Ar—H); MS (APCI): 165.1(M+1). Anal. Calcd. for $C_{10}H_{17}N_2Br$: C, 48.99; H, 6.99; N, 11.43; Br, 32.59. Found: C, 48.65; H, 7.11; N, 11.03; Br, 32.25.

1-Benzyl-2,3-dimethylimidazolium bromide (10f). Yield 96%; brown semisolid; ^{1}H NMR(CD_3OD, 300 MHz): δ 2.62 (s, 3H, CH_3), 3.83 (s, 3H, N—CH_3), 5.40 (s, 2H, Ph—CH_2), 7.32 (d, 2H, J = 6.03 Hz), 7.38 (m, 3H, J = 6.10), 7.51 (s, 2H 2x Ar—H); MS (APCI): 187.1(M+1). Anal. Calcd. for $C_{12}H_{15}N_2Br$: C, 53.95; H, 5.66; N, 10.49; Br, 29.91. Found: C, 54.22; H, 5.29; N, 10.19; Br, 30.19.

Typical procedure for the synthesis of 1,3-dialkylimidazolium halides 12a–c. Imidazole (1 mmol) was stirred with alkyl halide (3 mmol) in presence of potassium carbonate (3 mmol) in acetone (5 mL) under reflux conditions for 5–8 hours. Reaction mixture was dried under reduced pressure and column chromatography over silica gel (100:200 mesh) was performed to afford product.

1,3-Diisopropylimidazolium iodide (12a). Yield 76%; brown viscous liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.28 (d, 6H, 2x CH_3, J = 6.70 Hz), 1.57 (d, 6H, 2x CH_3, J = 6.65 Hz), 4.62–4.83 (m, 1H, CH), 7.74 (s, 2H 2x Ar—H), 7.82 (s, 1H, 2-Ar—H); MS (APCI): 153.1(M+1). Anal. Calcd. for $C_9H_{17}N_2I$: C, 38.59; H, 6.12; N, 10.00; I, 45.30. Found: C, 38.21; H, 5.83; N, 9.76; I, 45.03.

1,3-Dibenzylimidazolium bromide (12b). Yield 73%; light brown semisolid; ^{1}H NMR(CD_3OD, 300 MHz): δ 5.46 (s, 4H, 2x CH_2), 7.45 (s, 10x Ar—H), 7.65 (s, 2H, 2x Ar—H), 7.99 (s, 1H, 2-Ar—H); MS (APCI): 294.5(M+1). Anal. Calcd. for $C_{17}H_{17}N_2Br$: C, 62.02; H, 5.20; N, 8.51; Br, 24.27. Found: C, 62.40; H, 5.25; N, 8.22; Br, 23.62.

1,3-Dicyclopentylimidazolium bromide (12c). Yield 62%; pale semisolid; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.80–1.83 (m, 16H, 8x CH_2), 4.75 (m, 2H, 2x CH), 7.19 (s, 2H, 4-Ar—H, 5-Ar—H), 7.98 (s, H, 2-Ar—H); MS (APCI): 206.3(M+1). Anal. Calcd. for $C_{13}H_{21}N_2Br$: C, 54.74; H, 7.42; N, 9.82; Br, 28.01. Found: C, 54.32; H, 7.19; N, 10.07; Br, 27.81.

Typical procedure for synthesis of imidazolium hexafluorophosphate salts 4a–c, 8a–c, 11a–f and 13a–c. To a solutions of the imdazolium halides **3a–c, 7a–c, 10a–f** and **12a–c** (1 mmol) in water (2 mL) was added KPF_6 (1.3 mmol) and the reaction mixture was stirred for 1.5 h at room temperature. Reaction mixture was extracted with dichloromethane (3 × 5 mL) and purified by column chromatography.

1-Butyl-3-methyl-2-tert-butylimidazolium hexafluorophosphate (4a). yield 70%; pale yellow solid; m.p. 84°C; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.98 (t, 3H, CH_3, J = 7.63 Hz), 1.42 (m, 2H, CH_2), 1.65 (s, 9H, 3x CH_3), 1.84 (m, 2H, CH_2), 4.05 (s, 3H, N—CH_3), 4.33 (t, 2H, CH_2, J = 7.91 Hz), 7.40 (d, 1H, 4-Ar—-H, J = 2.02 Hz), 7.50 (d, 1H, 5-Ar—H J = 1.99 Hz); MS (APCI): 195.5(M+1). Anal. Calcd. for $C_{12}H_{23}F_6N_2P$: C, 42.35; H, 6.81; F, 33.50; N, 8.23; P, 9.10. Found: C, 42.60; H, 6.57; F, 33.31; N, 8.47; P, 9.33.

1-Butyl-3-methyl-2-isopropylimidazolium hexafluorophosphate (4b). Yield 73%; brown liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.99 (t, 3H, CH_3, J = 7.22 Hz), 1.28–1.42 (m, 8H, 2x CH_3, CH_2), 1.76–1.86 (m, 2H, CH_2), 3.61–3.71 (m, H, CH), 3.91 (s, 3H, N—CH_3), 4.17–4.22 (t, 2H, CH_2, J = 7.43 Hz), 7.42 (s, 1H, 4-Ar—H), 7.48 (s, 1H, 5-Ar—H); MS (APCI): 181.1(M+1). Anal. Calcd. for $C_{11}H_{21}F_6N_2P$: C, 40.49; H, 6.49; F, 34.94; N, 8.59; P, 9.49. Found: C, 40.60; H, 6.21; F, 34.78; N, 8.38; P, 9.71.

1-Butyl-3-methyl-2-cyclohexylimidazolium hexafluorophosphate (4c). Yield 78%; pale yellow solid; m.p. 123.6 °C; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.96 (t, 3H, CH_3, J = 7.28 Hz), 1.37 (m, 2H, CH_2), 1.71–2.17 (m, 10H, 5x CH_2), 3.92 (s, 3H, N—CH_3), 4.10 (t, 2H, CH_2, J = 7.76 Hz), 7.19 (s, 1H, 5-Ar—H), 7.24 (s, 1H 4-Ar—H); MS (APCI): 221.6 (M+1). Anal. Calcd. for $C_{14}H_{25}F_6N_2P$: C, 45.95; H, 6.88; F, 31.12; N, 7.65, P; 8.46. Found: C, 45.66; H, 6.96; F, 30.98; N, 7.34, P; 8.67.

1-Butyl-3-ethylimidazolium hexafluorophosphate (8a). Yield 78%; light brown liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.98–1.02 (t, 3H, CH_3, J = 7.41 Hz), 1.35–1.44 (m, 2H, CH_2), 1.53–1.57 (t, 3H, CH_3, J = 7.37), 7.67 (s, 1H, Ar—H), 7.68 (s, 1H Ar—H), 9.06 (s, 1H Ar—H); MS (APCI): 153.4(M+1). Anal. Calcd. for $C_9H_{17}F_6N_2P$: C, 36.25; H, 5.75; F, 38.23; N, 9.39; P, 10.39. Found: C, 35.97; H, 5.61; F, 38.58; N, 9.59; P, 10.63.

1-Butyl-3-isopropylimidazolium hexafluorophosphate (8b). Yield 80%; light brown liquid; ^{1}H NMR (CD_3OD, 300 MHz): δ 0.94–0.99 (t, 3H, CH_3, J = 7.45 Hz), 1.33–1.40 (m, 2H, CH_2), 1.54–1.56 (d, 6H, 2x CH_3, J = 6.22 Hz), 1.83–1.89 (m, 2H, CH_2), 4.20–4.24 (t, 2H, N—CH_2), 4.62–4.67 (m, H, CH),

7.62 (s, 1H, Ar—H), 7.73 (s, 1H, Ar—H), 9.12 (s, 1H Ar—H); MS (APCI): 167.4(M+1). Anal. Calcd. for $C_{11}H_{21}F_6N_2P$: C, 40.49; H, 6.49; F, 34.94; N, 8.59; P, 9.49. Found: C, 40.19; H, 6.44; F, 34.77; N, 8.82; P, 9.63.

1-Butyl-3-benzylimidazole hexafluorophosphate (8c). Yield 85%; light brown liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.96–1.00 (t, 3H, CH_3, J = 7.36 Hz), 1.32–1.41 (m, 2H, CH_2), 1.84–1.91 (m, 2H, CH_2), 4.21–4.25 (t, 2H, CH_2, J = 7.38), 5.43 (s, 2H, N—CH_2), 7.39–7.47 (m, 5x Ar-H), 7.63 (s, H, Im—H), 7.67 (s, H, Im—H), 9.18 (s, 1H Ar—H)); MS (APCI): 215.2(M+1). Anal. Calcd. for $C_{13}H_{17}F_6N_2P$: C, 45.09; H, 4.95; F, 32.92; N, 8.09; P, 8.95. Found: C, 45.31; H, 4.88; F, 32.75; N, 8.32; P, 8.92.

1,2,3-Trimethylimidazolium hexafluorophosphate (11a). Yield 86%; pale yellow solid; m.p. 251°C; ^{1}H NMR(CD_3OD, 300 MHz): δ 2.61 (s, 3H, CH_3), 3.82 (s, 6H, 2x N—CH_3), 7.45 (s, 2H, 4,5-Ar—H); MS (APCI): 111.1(M+1). Anal. Calcd. for $C_6H_{11}F_6N_2P$: C, 28.14; H, 4.33; F, 44.51; N, 10.94; P, 12.09. Found: C, 28.45; H, 4.56; F, 44.62; N, 10.79; P, 12.22.

1-Ethyl-2,3-dimethylimidazolium hexafluorophosphate (11b). Yield 88%; colorless solid; m.p. 92°C; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.43 (t, 3H, CH_3, J = 7.31 Hz), 2.63 (s, 3H, CH_3), 3.81 (s, 3H, N—CH_3), 4.15–4.23 (m, 2H, N—CH_2), 7.46 (s, 1H, 5-Ar—H), 7.52 (s, 1H 4-Ar—H); MS (APCI): 125.1(M+1). Anal. Calcd. for $C_7H_{13}F_6N_2P$: C, 31.12; H, 4.85; F, 42.19; N, 10.37; P, 11.47. Found: C, 31.39; H, 4.62; F, 42.37; N, 10.41; P, 11.61.

2,3-Dimethyl-1-propylimidazolium hexafluorophosphate (11c). Yield 91%; light brown viscous liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 0.86 (t, 3H, CH_3, J = 7.38 Hz), 1.72 (m, 2H, CH_2), 2.53 (s, 3H, CH_3), 3.72 (s, 3H, N—CH_3), 3.99 (t, 2H, N—CH_2, J = 7.35 Hz), 7.36 (s, 1H, 5-Ar—H), 7.40 (s, 1H 4-Ar—H); MS (APCI): 139.1(M+1). Anal. Calcd. for $C_8H_{15}F_6N_2P$: C, 33.81; H, 5.32; F, 40.11; N, 9.86; P, 10.90. Found: C, 33.63; H, 5.12; F, 40.33; N, 9.65; P, 10.71.

1-Isopropyl-2,3-dimethylimidazolium hexafluorophosphate (11d). Yield 89%; light yellow viscous liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.50 (d, 3H, CH_3, J = 7.30 Hz), 1.56 (d, 3H, CH_3, J = 6.76 Hz), 2.46 (s, 3H, CH_3), 3.69 (s, 3H, N-CH_3), 4.65–4.79 (m, 2H, N—CH), 7.49 (s, 1H, 5-Ar—H), 7.63 (s, 1H 4-Ar—H); MS (APCI): 139.1(M+1). Anal. Calcd. for $C_8H_{15}F_6N_2P$: C, 33.81; H, 5.32; F, 40.11; N, 9.86; P, 10.90. Found: C, 34.02; H, 5.18; F, 40.32; N, 9.89; P, 10.75.

1-Cyclopentyl-2,3-dimethylimidazolium hexafluorophosphate (11e). Yield 83%; brown viscous liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.78–1.95 (m, 8H, 4x CH_2), 2.63 (s, 3H, CH_3), 3.83 (s, 3H, N—CH_3), 4.73 (m, 1H, N—CH), 7.46 (s, 1H, 5-Ar—H), 7.52 (s, 1H 4-Ar—H); MS (APCI): 165.1(M+1). Anal. Calcd. for $C_{10}H_{17}F_6N_2P$: C, 38.72; H, 5.52; F, 36.75; N, 9.03; P, 9.98. Found: C, 38.47; H, 5.88; F, 36.39; N, 8.81; P, 9.67.

1-Benzyl-2,3-dimethylimidazolium hexafluorophosphate (11f). Yield 90%; brown viscous liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 2.62 (s, 3H, CH_3), 3.83 (s, 3H, N—CH_3), 5.40 (s, 2H, CH_2), 7.32 (d, 2H, J = 6.03 Hz), 7.38 (m, 3H, J = 6.10), 7.51 (s, 2H 2x Ar—H); MS (APCI): 187.1(M+1). Anal. Calcd. for $C_{12}H_{15}F_6N_2P$: C, 43.38; H, 4.55; F, 34.31; N, 8.43; P, 9.32. Found: C, 43.45; H, 4.31; F, 36.01; N, 8.60; P, 9.53.

1,3-Diisopropylimidazolium hexafluorophosphate (13a). Yield 75%; pale yellow viscous liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.30 (d, 6H, 2x CH_3, J = 6.70 Hz), 1.59 (d, 6H, 2x CH_3, J = 6.65 Hz), 4.64–4.85 (m, 1H, CH), 7.76 (s, 2H 2x Ar—H), 7.84 (s, 1H, 2-Ar—H); MS (APCI): 153.1(M+1). Anal. Calcd. for $C_9H_{17}F_6N_2P$: C, 36.25; H, 5.75; F, 38.23; N, 9.39; P, 10.39. Found: C, 35.94; H, 5.46; F, 38.52; N, 9.47; P, 10.45.

1,3-Dibenzylimidazolium hexafluorophosphate (13b). Yield 80%; light brown viscous liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 5.44 (s, 4H, 2x CH_2), 7.43 (s, 10x Ph—H), 7.63 (s, 2H, 2x Ar—H), 7.95 (s, 1H, 2-Ar—H); MS (APCI): 294.5(M+1). Anal. Calcd. for $C_{17}H_{17}F_6N_2P$: C, 51.78; H, 4.35; F, 28.91; N, 7.10; P, 7.86. Found: C, 51.89; H, 4.48; F, 28.75; N, 7.37; P, 7.92.

1,3-Dicyclopentylimidazolium hexafluorophosphate (13c). Yield 68%; pale yellow viscous liquid; ^{1}H NMR(CD_3OD, 300 MHz): δ 1.77–1.80 (m, 16H, 2x CH_2), 4.72 (m, 2H, 2x CH), 7.14 (s, 2H, 4-Ar—H, 5-Ar-H), 7.93 (s, H, 2-Ar—H); MS (APCI): 206.3(M+1). Anal. Calcd. for $C_{13}H_{21}F_6N_2P$: C, 44.58; H, 6.04; F, 32.54; N, 8.00; P, 8.84. Found: C, 44.33; H, 6.39; F, 32.84; N, 7.88; P, 8.59.

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