Supplementary Information Figure S1a: Effect of the skimmer 1 voltage (sk_1) on the ESI (+) mass spectra of [BuMeIm][Tf₂N] in acetonitrile–water solution.

Supplementary Information Figure S1b: Effect of the skimmer 1 voltage (sk_1) on the ESI (–) mass spectra of [BuMeIm][Tf₂N] in acetonitrile–water solution.

Supplementary Information Figure S2: MS^2 spectra of BuMeIm⁺ (m/z = 139.1) of [BuMeIm][Tf₂N] solution in acetonitrile-water.

Supplementary Information Figure S3: MS^2 spectra of Tf_2N^- (*m*/*z* = 279.7) of [BuMeIm][Tf_2N] solution in acetonitrile-water.

Supplementary Information Figure S4: ESI (–) mass spectra of [BuMeIm]Cl in acetonitrile-water solution. Skimmer 1 voltage = –45V. M = [BuMeIm]Cl.



Supplementary Information Figure S1a



Supplementary Information Figure S1b



Supplementary Information Figure S2



Supplementary Information Figure S3



Supplementary Information Figure S4