Electronic Supplementary Material (ESI) for RSC Advances.


**Supporting Information**

## Experimental

### Molecular Dynamics Simulations

Molecular dynamics simulations of the candidate systems were performed using the DL_POLY software. Forcefield parameters for the selected ionic liquids were taken from the forcefield of Canongia Lopes and Padua [*J. Phys. Chem. B*, **108**, 11250 (2004); *J. Phys. Chem. B*, 108, 16893 (2004)]. For tobramycin, suitable Lennard-Jones and intramolecular parameters were taken from OPLS-AA [*J. Am. Chem. Soc.*, **118**, 11225 (1996)], while atomic charges were generated through fitting of the molecular electrostatic potential to individual rings of the tobramycin molecule (owing to its size, a quantum mechanics treatment of the whole molecule was unfeasible).

Cubic boxes of 200 ion pairs of the ionic liquids and one tobramycin molecule were randomly generated at the experimental pure ionic liquid density. These were then allowed to relax in the NPT ensemble for several nanoseconds, before main production runs were performed. All presented calculated quantities are averages over the final 5 ns of the simulations.

### General Experimental Methods

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Solutions or liquids were introduced to the round bottom flask using oven dried Hamilton syringes through rubber septa. Reactions performed using magnetic stirring were performed using Teflon-coated stirrer bars. Removal of solvents was achieved using a rotary evaporator at water aspirator pressure or under high vacuum (0.01 mm Hg).

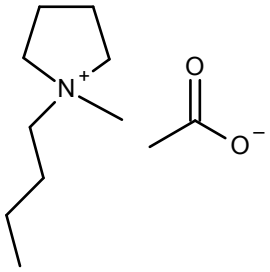
Chemicals were purchased from Sigma-Aldrich Chemical Company. Solvents for extractions and chromatography were of technical grade. Purification was carried out *via* flash chromatography using the Biotage purification system. Analytical TLC was performed with Merck Silica gel 60 $F_{254}$ plates. Visualisation was accomplished by UV-light (λ= 254 nm) and/or staining with an anisaldehyde or ninhydrin solution, followed by heating. $^{1}H$, $^{13}C$, $^{31}P$ and 2D (H-COSY, HMQC) NMR spectra were recorded on Brüker advance DPX 400. TMS (0 ppm, $^{1}H$

NMR) and $CDCl_3$ (77 ppm, $^{13}C$ NMR) were used as internal references. The chemical shifts (δ) are reported in p.p.m (parts per million). High resolution mass spectrometry (HRMS) was recorded on a VG Quattro Triple Quadropole Mass Spectrometer (ES). The names of the compounds have been named according to standard IUPAC. Solubility study of tobramycin **1** was performed by the addition of 1-5 mg portions of tobramycin to 1000mg of the corresponding ionic liquid in a sealed glass vial. The suspensions were initially vortexed for 30s to aid dispersion through the ionic liquid media. The samples were then stirred vigorously at room temperature until reaching saturation which was determined by qualitative visual observation. Each sample was performed in triplicate and the average quantity of tobramycin **1** solubilized and recorded as the weight percentage (wt %).

**Solubility procedure**

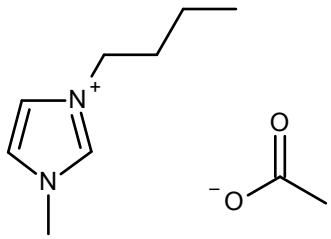
The solubility study of tobramycin **1** was performed by the addition of 1-5 mg portions of tobramycin to 1000mg of the corresponding ionic liquid in a sealed glass vial. The suspensions were initially vortexed for 30s to aid dispersion through the ionic liquid media. The samples were then stirred vigorously at room temperature until reaching saturation which was determined by qualitative visual observation. Each sample was performed in triplicate and the average quantity of tobramycin **1** solubilized and recorded as the weight percentage (wt %).

**2**) 1-butyl-1-methyl-pyrrolidinium acetate



Procedure: To 1-butyl-1-methyl-pyrrolidinium methyl carbonate (5.0 g, 0.02 mol, 1.0eq) was added acetic acid (1.38 g, 1.32mL, 0.02 mol, 1.0eq) and left stirring for 1 hour or until $CO_2$ no longer evolved. The sample was then left under high vacuum with stirring for 24 hours to give 4.6g of 1-butyl-1-methyl-pyrrolidinium acetate as a slightly viscous hygroscopic oil in quantitative yield.[1]H NMR ($D_2O$, 400 MHz): δ ppm 3.42-3.31 (4H, m, $NC\underline{H}_2CH_2CH_2C\underline{H}_2N$), 3.16 (2H, t, *J*= 8.3Hz, $NC\underline{H}_2CH_2CH_2CH_3$), 2.89 (3H, s, $NC\underline{H}_3$), 2.12-2.01 (4H, m, $NCH_2C\underline{H}_2C\underline{H}_2CH_2N$), 1.78 (3H, s, $O(C=O)C\underline{H}_3$), 1.63 (2H, quin, *J*= 7.8Hz, $NCH_2C\underline{H}_2CH_2CH_3$), 1.28-1.22 (2H, m, $NCH_2CH_2C\underline{H}_2CH_3$), 0.81 (3H, t, *J*= 7.5Hz, $NCH_2CH_2CH_2C\underline{H}_3$). [13]C-NMR (125MHz): δ ppm 160.8 ($O(\underline{C}=O)CH_3$). 64.2 ($N\underline{C}H_2CH_2CH_2\underline{C}H_2N$), 48.1 ($N\underline{C}H_2CH_2CH_2CH_3$ and $N\underline{C}H_3$), 25.0 ($NCH_2\underline{C}H_2\underline{C}H_2CH_2N$), 23.0 ($O(C=O)\underline{C}H_3$), 21.3 ($NCH_2\underline{C}H_2CH_2CH_3$), 19.2 ($NCH_2CH_2\underline{C}H_2CH_3$), 12.7 ($NCH_2CH_2CH_2\underline{C}H_3$).

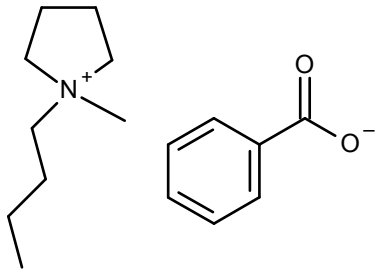
**3**) 1-butyl-3-methyl-imidazolium acetate



Procedure: To 1-butyl-3-methyl-imidazolium methyl carbonate (5.0g, 0.02 mol, 1.0eq) in methanol (10mL) was added acetic acid (1.4g, 0.02mol, 1.0eq) and left stirring for one hour at room temperature. After which, excess methanol was removed under reduced pressure and the concentrated solution left under high vacuum over night to yield 4.6g (99%) of 1-butyl-3-methyl-imidazolium acetate as a brown viscous oil.[1]H NMR ($D_2O$, 400 MHz): δ ppm

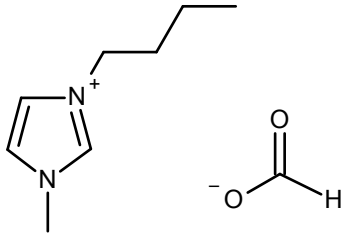
8.49 (1H, s, NC<u>H</u>=N), 7.23 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 7.18 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 3.93 (2H, t, *J*= 7.5Hz, NC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$), 3.62 (3H, s, NC<u>H</u>$_3$), 1.64 (3H, s, C<u>H</u>$_3$COO), 1.58 (2H, quin, *J*= 7.0Hz, NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 1.04 (2H, sxt, *J*= 7.6Hz, NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 0.65 (3H, t, *J*= 7.5Hz, NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$), $^{13}$C-NMR (125MHz): δ ppm 180.1 (CH$_3$<u>C</u>OO), 135.8 (N<u>C</u>H=N), 123.5 (N<u>C</u>H=CHN or NCH=<u>C</u>HN), 122.2 (N<u>C</u>H=CHN or NCH=<u>C</u>HN), 49.2 (N<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$), 35.7 (N<u>C</u>H$_3$), 31.2 (NCH$_2$<u>C</u>H$_2$CH$_2$CH$_3$), 23.2 (<u>C</u>H$_3$COO), 18.7 (NCH$_2$CH$_2$<u>C</u>H$_2$CH$_3$), 12.7 (NCH$_2$CH$_2$CH$_2$<u>C</u>H$_3$).

**4**) 1-butyl-1-methyl-pyrrolidinium benzoate



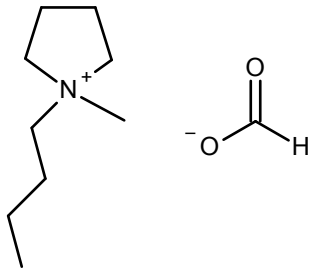

<u>Procedure</u>: To 1-butyl-1-methyl-pyrrolidin-1-ium; methyl carbonate (5.0 g, 0.02 mol, 1.0eq) in methanol (10mL), was added benzoic acid (2.81 g, 0.02 mol, 1.0eq) and left stirring for 1 hour or until $CO_2$ was no longer evolved. The mixture was concentrated under reduced pressure, and then left under high vacuum with stirring for 24 hours to give 6.0 g (99%) of 1-butyl-1-methyl-pyrrolidinium benzoate as a slightly viscous hygroscopic brown oil.$^{1}$H-NMR ($CDCl_3$, 400MHz): δ ppm 7.76-7.73 (2H, m, Ar), 7.43 (1H, m, Ar), 7.34-7.33 (2H, m, Ar), 3.27-3.11 (4H, m, NC<u>H</u>$_2$CH$_2$CH$_2$C<u>H</u>$_2$N), 3.08-2.98 (2H, m , NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 2.74 (3H, s, NC<u>H</u>$_3$), 2.04-1.90 (4H, m, NCH$_2$C<u>H</u>$_2$C<u>H</u>$_2$CH$_2$N), 1.57-1.44 (2H, m, NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 1.22-1.11 (2H, m, NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 0.75 (3H, t, *J*= 7.6Hz, NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$), $^{13}$C-NMR (125MHz): δ ppm 174.65 (O(<u>C</u>=O)Ar), 135.6 (Ar), 131.6 (Ar), 129.0 (Ar), 128.4 (Ar), 64.1 (NC<u>H</u>$_2$CH$_2$CH$_2$C<u>H</u>$_2$N), 64.0(N<u>C</u>H$_3$), 47.9 (N<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$), 25.0 (NCH$_2$<u>C</u>H$_2$CH$_2$CH$_3$), 21.2 (NCH$_2$<u>C</u>H$_2$<u>C</u>H$_2$CH$_2$N), 19.2 (NCH$_2$CH$_2$<u>C</u>H$_2$CH$_3$), 12.8 (NCH$_2$CH$_2$CH$_2$<u>C</u>H$_3$).

**5**) 1-butyl-3-methyl-imidazolium formate



Procedure: To 1-butyl-3-methyl-imidazolium methyl carbonate (5.0 g, 0.02 mol, 1.0eq) in methanol (10mL) was added formic acid (0.97 mL, 0.03 mol, 1.0eq) and left stirring for one hour. Excess methanol was removed under reduced pressure and the concentrated solution left under high vacuum with stirring over night to give 4.3 g of 1-butyl-3-methyl-imidazolium formate as a brown semi viscous oil in quantitative yield. $^{1}$H NMR ($D_2O$, 400 MHz): δ ppm 8.51 (1H, s, NC<u>H</u>=N), 8.16 (1H, s, <u>H</u>(C=O)), 7.25 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 7.19 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 3.94 (2H, t, *J*= 7.0Hz, NC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$), 3.57 (3H, s, NC<u>H</u>$_3$), 1.59 (2H, quin, *J*= 7.5Hz, NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 1.09-1.03 (2H, m, NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 0.65 (3H, t, *J*= 7.0Hz, NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$), $^{13}$C-NMR (125MHz): δ ppm 170.4 (H<u>C</u>(C=O)), 135.8 (N<u>C</u>H=N), 123.5 (N<u>C</u>H=CHN or NCH=<u>C</u>HN), 122.2 (N<u>C</u>H=CHN or NCH=<u>C</u>HN), 49.2 (N<u>C</u>H$_3$), 35.7 (N<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$), 31.2 (NCH$_2$<u>C</u>H$_2$<u>C</u>H$_2$CH$_3$), 18.7 (NCH$_2$CH$_2$CH$_2$<u>C</u>H$_3$).

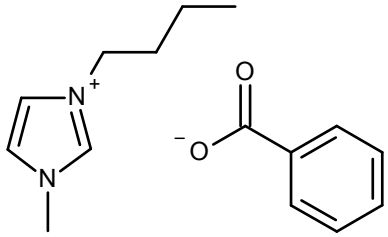
**6**) 1-butyl-1-methyl-pyrrolidinium formate



Procedure: To 1-butyl-1-methyl-pyrrolidinium methyl carbonate (5.0 g, 0.02 mol, 1.0eq) in methanol (10mL) was added formic acid (0.95 mL, 0.03 mol, 1.0eq) and left stirring for 1 hour. Excess methanol was removed under reduced pressure and the mixture left stirring overnight under high vacuum to give 4.25 g (98%) of 1-butyl-1-methyl-pyrrolidinium formate a as pale yellow oil. $^{1}$H-NMR ($CDCl_3$, 400MHz): δ ppm 8.32 (1H, s, <u>H</u>(C=O)), 3.43-3.31 (4H, m,

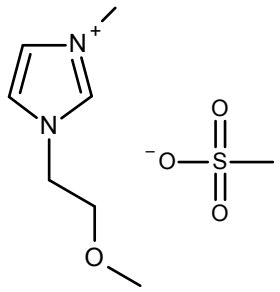
$NC\underline{H}_2CH_2CH_2C\underline{H}_2N$), 3.19 (2H, t, *J*= 8.6Hz, $NC\underline{H}_2CH_2CH_2CH_3$), 2.90 (3H, s, $NC\underline{H}_3$), 2.14-2.03 (4H, m, $NCH_2C\underline{H}_2C\underline{H}_2CH_3$), 1.65 (2H, qt, *J*= 16.0Hz, 7.9Hz, $NCH_2C\underline{H}_2CH_2CH_3$), 1.26 (2H, dt, *J*= 14.8Hz, 7.4Hz, $NCH_2CH_2C\underline{H}_2CH_3$), 0.82 (3H, t, *J*= 7.4Hz, $NCH_2CH_2CH_2C\underline{H}_3$) $^{13}$C-NMR (125MHz): δ ppm 170.9 (H($\underline{C}$=O)), 64.2 ($N\underline{C}H_2CH_2CH_2\underline{C}H_2N$), 64.1 ($N\underline{C}H_2CH_2CH_2CH_3$), 48.1 ($N\underline{C}H_3$), 25.1 ($NCH_2\underline{C}H_2CH_2CH_3$), 21.3 ($NCH_2\underline{C}H_2\underline{C}H_2CH_2N$), 19.3 ($NCH_2CH_2\underline{C}H_2CH_3$), 12.8 ($NCH_2CH_2CH_2\underline{C}H_3$).

**7**) 1-butyl-3-methyl-imidazolium benzoate



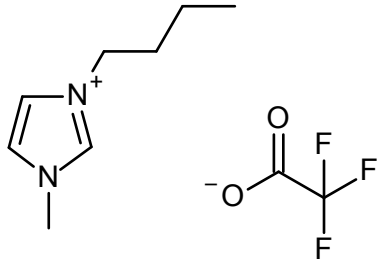

Procedure: To 1-butyl-3-methyl-imidazolium methyl carbonate (5.0 g, 0.02 mol, 1.0eq) in methanol (10mL) was added benzoic acid (2.85 g, 0.02 mol, 1.0eq) and left stirring for one hour, after which excess methanol was removed under reduced pressure and concentrated. The oil was then left under high vac over night with stirring to give 6.08 g of 1-butyl-3-methyl-imidazol-1-ium benzoate as a hygroscopic viscous brown oil in quantitative yield.$^{1}$H NMR ($D_2O$, 400 MHz): δ ppm 8.38 (1H, s, $NC\underline{H}$=N), 7.56 (2H, d, *J*= 7.8Hz, Ar), 7.28-7.22 (1H, m, Ar), 7.24-7.20 (2H, m, Ar), 7.15 (1H, s, $NC\underline{H}$=CHN or NCH=C$\underline{H}$N), 7.10 (1H, s, $NC\underline{H}$=CHN or NCH=C$\underline{H}$N), 3.85 (2H, t, *J*= 7.5Hz, $NC\underline{H}_2CH_2CH_2CH_3$), 3.57 (3H, s, $NC\underline{H}_3$), 1.53 (2H quin, *J*= 7.5Hz, $NCH_2CH_2C\underline{H}_2CH_3$), 1.10-1.06 (2H, m, $NCH_2CH_2C\underline{H}_2CH_3$) 0.64 (3H, t, *J*= 7.5Hz, $NCH_2CH_2CH_2C\underline{H}_3$) $^{13}$C-NMR (125MHz): δ ppm 174.9 ($\underline{C}$=O), 136.2 ($N\underline{C}$H=N), 135.6 (Ar), 131.1 (Ar), 128.8 (Ar), 128.2 (Ar), 123.4 (Ar), 122.1(Ar), 49.2($N\underline{C}H_3$), 35.6($NC\underline{H}_2CH_2CH_2CH_3$), 31.2 ($NCH_2\underline{C}H_2CH_2CH_3$), 18.7 ($NCH_2CH_2\underline{C}H_2CH_3$), 12.6 ($NCH_2CH_2CH_2\underline{C}H_3$).

**8**) 1-methoxyethyl-3methyl imidazolium methane sulphonate[1]



Procedure: A mixture of methyl-imidazole (12.1g, 0.147mol, 1.0eq) and 2-methoxyethyl methanesulfonate was heated at reflux in dry toluene (100mL) for 24 hours with stirring under $N_2$, to give the ionic liquid which formed a distinct immiscible layer at the bottom of the reaction mixture. The organic layer was decanted off, and the aqueous layer was washed with ethyl acetate and concentrated under reduced pressure to give 1-methoxyethyl-3-methyl imidazolium methane sulphonate as a brown semi viscous oil in 85% yield.[1] $^1$H NMR ($D_2O$, 400 MHz): δ ppm 8.60 (1H, s, NC<u>H</u>=N), 7.36 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 7.30 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 4.24 (2H, t, *J*=4.8Hz, NC<u>H</u>$_2$CH$_2$OCH$_3$), 3.75 (3H,s, NCH$_3$), 3.69 (2H, t, *J*= 4.5Hz, NCH$_2$C<u>H</u>$_2$OCH$_3$), 3.23 (3H, s, NCH$_2$CH$_2$OC<u>H</u>$_3$), 2.63 (3H, s, SC<u>H</u>$_3$), $^{13}$C-NMR (125MHz): δ ppm 138.3 (N<u>C</u>H=N), 123.5 (N<u>C</u>H=CHN or NCH=<u>C</u>HN), 122.5 (N<u>C</u>H=CHN or NCH=<u>C</u>HN), 69.8 (N<u>C</u>H$_3$), 58.1 (NCH$_2$<u>C</u>H$_2$OCH$_3$), 48.8 (N<u>C</u>H$_2$CH$_2$OCH$_3$), 38.5 (S<u>C</u>H$_3$), 35.6 (NCH$_2$CH$_2$O<u>C</u>H$_3$).

**11**) 1-butyl-3-methyl-imidazol-1-ium trifluoroacetate

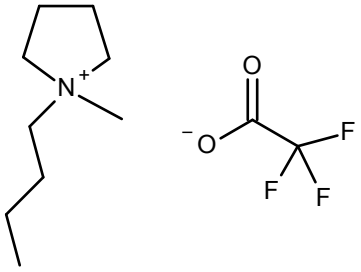


Procedure: To 1-butyl-3-methyl-imidazolium methyl carbonate (5.0g, 0.02 mol, 1.0eq) in methanol (10mL) was added trifluoroacetate (1.79mL, 0.02 mol, 1.0eq) and left stirring for one hour. Excess methanol was removed under reduced pressure and the concentrated solution left under high vacuum with stirring over night to give 5.8g of 1-butyl-3-methyl-

[1] M. C. Uzagare, Y. S. Sanghvib, M. M. Salunkhe, *Green Chemistry*., 2003, **5**, 370

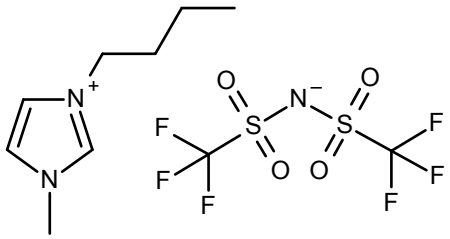
imidazolium trifluoroacetate in quantitative yield.[1]H NMR ($D_2O$, 400 MHz): δ ppm 8.52 (1H, s, NC<u>H</u>=N), 7.26 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 7.21 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 3.98 (2H, t, *J*= 7.3Hz, NC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$), 3.68 (3H, s, NC<u>H</u>$_3$), 1.63 (2H, quin, *J*= 7.3Hz, NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 1.12-1.09 (2H, m, NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 0.71 (3H, t, *J*=7.3Hz, NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$), $^{13}$C-NMR (125MHz): δ ppm 162.9 (q, $^1J^{13}_{C\text{-}}{}^{19}_{F}$ =44.7Hz, CF$_3$(<u>C</u>=O)), 135.8 (N<u>C</u>H=N), 123.5(N<u>C</u>H=CHN or NCH=<u>C</u>HN), 122.2 (N<u>C</u>H=CHN or NCH=<u>C</u>HN), 116.3 (q, $^1J^{13}_{C\text{-}}{}^{19}_{F}$ =362.7Hz, <u>C</u>F$_3$(C=O)), 49.2 (N<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$), 35.6 (N<u>C</u>H$_3$), 31.2 (NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 18.7 (NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 12.6 (NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$).

**12**) 1-butyl-1-methyl-pyrrolidinium trifluoroacetate




<u>Procedure</u>: To 1-butyl-1-methyl-pyrrolidinium methyl carbonate (5.0g, 0.02 mol, 1.0eq) in methanol (10mL) was added trifluoroacetate (1.76 mL, 0.02 mol, 1.0eq) and left stirring for 1 hour. Excess methanol was then removed under reduced pressure, and then left stirring under high vacuum overnight to give 5.4g (91%) of 1-butyl-1-methyl-pyrrolidinium trifluoroacetate as a pale brown hygroscopic oil.[1]H-NMR ($CDCl_3$, 400MHz): δ ppm 3.43-3.31 (4H, m, NC<u>H</u>$_2$CH$_2$CH$_2$C<u>H</u>$_2$N), 3.21-3.16 (2H, m, NC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$), 2.91 (3H, s. NC<u>H</u>$_3$), 2.14-2.04 (4H, m, NCH$_2$C<u>H</u>$_2$C<u>H</u>$_2$CH$_2$N), 1.71-1.60 (2H, m, NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 1.27 (2H, sxt, *J*= 7.4Hz, NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 0.83 (3H, t, *J*= 7.4Hz, NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$), $^{13}$C-NMR (125MHz): δ ppm 162.7 (q, $^1J^{13}_{C\text{-}}{}^{19}$F= 43.8Hz, (O(<u>C</u>=O)C<u>F</u>$_3$)), 116.4 (q, $^1J^{13}_{C\text{-}}{}^{19}$F= 363.5Hz, (O(C=O)CF$_3$)), 64.3 (N<u>C</u>H$_2$CH$_2$CH$_2$<u>C</u>H$_2$N), 64.1 (N<u>C</u>H$_3$), 48.1 (N<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$), 25.1 (NCH$_2$<u>C</u>H$_2$CH$_2$CH$_3$), 21.4 (NCH$_2$<u>C</u>H$_2$<u>C</u>H$_2$CH$_2$N), 19.3 (NCH$_2$CH$_2$<u>C</u>H$_2$CH$_3$), 12.8 (NCH$_2$CH$_2$CH$_2$<u>C</u>H$_3$).

**13**) 1-butyl-3-methyl-imidazolium bistriflamide[2]



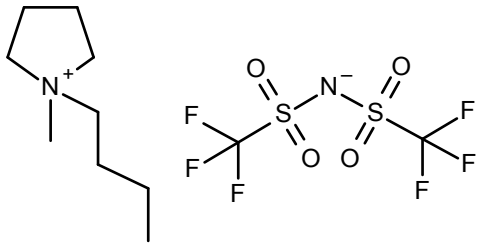
*Procedure*: To a solution of 1-butyl-3-methyl imidazolium bromide (200.0g, 0.91mol, 1.0eq) in distilled water (300mL) was added a solution of lithium bistriflimide (393.0g, 1.37mol, 1.5eq) in distilled water (300mL) and left stirring for 24 hours at room temperature. The lower ionic liquid layer that had formed was separated and the remaining aqueous layer was washed with DCM (3x40mL). The organic extracts were combined and washed with distilled water until the aqueous washes no longer tested positive for halide content by the addition of a silver nitrate solution. The solution was then passed through a column consisting of alternating layers of silica-alumina and charcoal, and then washed with a further addition of DCM (~300mL). The solution was concentrated under reduced pressure to give the desired product as colourless and slightly viscous colourless oil in 81% yield.[1] $^{1}$H NMR ($CDCl_3$, 400 MHz): δ ppm 8.62 (1H, s, NC<u>H</u>=N), 7.37 (s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 7.36 (s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 4.16 (2H, t, *J*= 7.5Hz, $NC\underline{H}_2CH_2CH_2CH_3$), 3.92 (3H, s, $NC\underline{H}_3$), 1.85 (2H, quin, *J*= 7.5Hz, $NCH_2C\underline{H}_2CH_2CH_3$), 1.36-1.32 (2H, m, $NCH_2CH_2C\underline{H}_2CH_3$), 0.95 (3H, t, *J*= 7.3Hz, $NCH_2CH_2CH_2C\underline{H}_3$), $^{13}$C-NMR (125MHz): δ ppm 135.7 (N<u>C</u>H=N), 123.7 (NCH=<u>C</u>HN or N<u>C</u>H=CHN), 122.3 (NCH=<u>C</u>HN or N<u>C</u>H=CHN), 120.5 (q, $^{1}J^{13}_{C}\text{-}^{19}_{F}$ = 321.1 Hz, S<u>C</u>$F_3$) 49.3 (N<u>C</u>$H_3$), 35.9 (N<u>C</u>$H_2CH_2CH_2CH_3$), 31.8 ($NCH_2\underline{C}H_2CH_2CH_3$), 19.1 ($NCH_2CH_2\underline{C}H_2CH_3$), 12.8 ($NCH_2CH_2CH_2\underline{C}H_3$).

**14**) 1-Butyl-1-methylpyrrolidinium bistriflimide:[3]

---

[2] M. Lombardo, M. Chiarucci, C. Trombini, ***Green Chem.***, 2009,**11**, 574

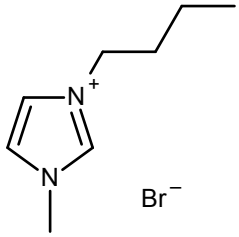
[3] M. Lombardo, M. Chiarucci, C. Trombini, ***Green Chem.***, 2009,**11**, 574



Procedure: To a solution of 1-butyl-1-methyl pyrrolidinium bromide (75.0g, 0.34mol, 1.0eq) in distilled water (150mL) was added a solution of lithium bistriflimide (147.0g, 0.51mol, 1.5eq) in distilled water (150mL) and left stirring for 24 hours at room temperature. The lower ionic liquid layer that had formed was separated and the remaining aqueous layer was washed with DCM (3x20mL). The organic extracts were combined and washed with distilled water until the aqueous washes no longer tested positive for halide content by the addition of a silver nitrate solution. The solution was then passed through a column consisting of alternating layers of silica-alumina and charcoal, and then washed through with a further addition of DCM (150mL). The solution was concentrated under reduced pressure to give 107.0g of the desired product as colourless and slightly viscous oil in 83% yield.$^{1}$H NMR (DMSO-d6, 400 MHz): δ ppm 3.65-3.32 (4H, m, $NC\underline{H}_2CH_2CH_2C\underline{H}_2N$), 3.30-3.23 (2H, m, $NC\underline{H}_2CH_2CH_2CH_3$), 2.96 (3H, s, $NC\underline{H}_3$), 2.08 (4H, br, $NCH_2C\underline{H}_2C\underline{H}_2CH_2N$), 1.65 (2H, quin, *J*= 7.4Hz, $NCH_2C\underline{H}_2CH_2CH_3$), 1.30 (2H, septet, *J*= 7.4Hz, $NCH_2CH_2C\underline{H}_2CH_3$), 0.92 (3H, t, *J*= 7.4Hz, $NCH_2CH_2CH_2C\underline{H}_3$), $^{13}$C-NMR (125MHz): δ ppm 119.5 (q, $^{1}J^{13}_{C\text{-}}{}^{19}_{F}$ = 321.6Hz, 2 x $\underline{C}F_3S$), 63.5 ($N\underline{C}H_2CH_2CH_2\underline{C}H_2N$), 63.1 ($N\underline{C}H_3$), 47.5 ($N\underline{C}H_2CH_2CH_2\underline{C}H_2N$), 24.9 ($N\underline{C}H_2CH_2CH_2CH_3$), 21.0 ($NCH_2\underline{C}H_2CH_2CH_3$), 19.2 ($NCH_2CH_2\underline{C}H_2CH_3$), 13.2 ($NCH_2CH_2CH_2\underline{C}H_3$).

**16**) 1-butyl-3-methyl-imidazolium bromide[4]

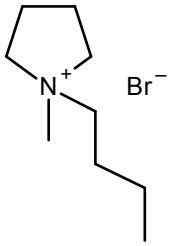
[4] A. K. Burrell, R. E. Del Sesto, S. N. Baker, T. M. McCleskeya, G. A. Baker, ***Green Chem***., 2007,**9** , 449




Procedure: To a rbf was added 1-methyl imidazole (50.0g, 0.61mol, 1.0eq) and bromobutane (102.0g, 0.74mol, 1.2eq) with stirring and heated at 55°C under an atmosphere of $N_2$ for 24 hours. To the resulting solution was added ethyl acetate (300mL) and thoroughly mixed, then decanted off. The mixture was concentrated under reduced pressure and a white solid precipitated out. The solid was washed with ethyl acetate (3 x 30mL) under suction, and then dried under high vacuum, to yield 141.0g of 1-butyl-3-methyl-imidazolium bromide in 84% yield as a white hygroscopic solid.[1]H NMR ($CDCl_3$, 400 MHz) δ ppm 10.3 (1H, s, NC<u>H</u>=N), 7.77 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 7.64, (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 4.37 (2H, t, *J*= 7.3Hz, NC<u>$H_2$</u>$CH_2CH_2CH_3$), 4.15 (3H, s, NC<u>$H_3$</u>), 1.92 (2H, m, $NCH_2C$<u>$H_2$</u>$CH_2CH_3$), 1.38 (2H, m, $NCH_2CH_2C$<u>$H_2$</u>$CH_3$), 0.97 (3H, t, *J*= 7.0Hz, $NCH_2CH_2CH_2C$<u>$H_3$</u>), [13]C NMR (125MHz): δ ppm 134.9 (N<u>C</u>H=N), 121.8 (NCH=<u>C</u>HN or N<u>C</u>H=CHN), 120.3 (NCH=<u>C</u>HN or N<u>C</u>H=CHN), 47.7 (N<u>C</u>$H_3$), 34.6 (N<u>C</u>$H_2CH_2CH_2CH_3$), 30.1 ($NCH_2$<u>C</u>$H_2CH_2CH_3$), 17.3 ($NCH_2CH_2$<u>C</u>$H_2CH_3$), 11.3 ($NCH_2CH_2CH_2$<u>C</u>$H_3$).

**17**) 1-butyl-1-methyl-pyrrolidinium bromide[5]

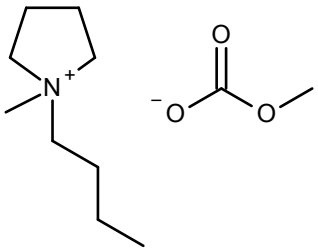
[5] M. Lombardo, M. Chiarucci, C. Trombini, *Green Chem*., 2009,**11**, 574




Procedure: To a rbf containing a solution of 1-methylpyrollidine (58.0g, 0.7mol, 1.0eq) in acetonitrile (100mL) was added 1-bromobutane (110.0g, 0.8mol, 1.1eq), then left stirring at 75°C under an atmosphere of $N_2$ for 18 hours. The mixture was allowed to cool to room temperature and the residual solvent was removed under reduced pressure, which was then recrystalised from ethyl acetate to give 155.2g of an off white hygroscopic solid in 75% yield.[1]H NMR ($CDCl_3$, 400 MHz) δ 3.88-3.79 (4H, m, $NC\underline{H}_2CH_2CH_2C\underline{H}_2N$), 3.67 (2H, t, *J*= 8.9Hz, $NC\underline{H}_2CH_2CH_2CH_3$), 3.03 (3H, s, $NC\underline{H}_3$), 2.37-2.28 (4H, m, $NCH_2C\underline{H}_2C\underline{H}_2CH_2N$), 1.83-1.75 (2H, m, $NCH_2C\underline{H}_2CH_2CH_3$), 1.46 (2H, dq, *J*= 15.0Hz, 7.4Hz, $NCH_2CH_2C\underline{H}_2CH_3$), 1.00 (3H, t, *J*= 7.4Hz, $NCH_2CH_2CH_2C\underline{H}_3$).[13]C-NMR (125MHz): δ ppm 64.4 ($N\underline{C}H_2CH_2CH_2\underline{C}H_2N$), 64.0 ($N\underline{C}H_3$), 48.6 ($NCH_2\underline{C}H_2\underline{C}H_2CH_2N$), 25.9 ($N\underline{C}H_2CH_2CH_2CH_3$), 21.7 ($NCH_2\underline{C}H_2CH_2CH_3$), 19.7 ($NCH_2CH_2\underline{C}H_2CH_3$), 13.7 ($NCH_2CH_2CH_2\underline{C}H_3$).

**18**)1-butyl-1-methyl-pyrrolidinium methyl carbonate[6]

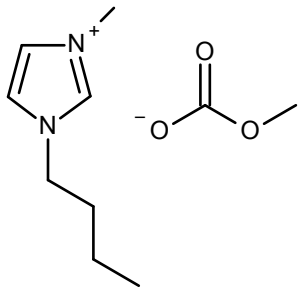
[6]J. D. Holbrey, R. D. Rogers, S. Shuklaa, C. D. Wilfred, *Green Chem*., 2010, **12**, 407



Procedure: To a pressurised reaction vessel was added 1-butyl-pyrrolidine (56.6g, 0.4mol, 1.0eq), dimethylcarbonate (164.0g, 1.2mol, 4.0eq) and methanol (40mL). The reaction vessel was sealed and heated to 130°C and left stirring for 12hours. The solution was concentrated then recrystalised from a solution of methanol-ethyl acetate to give 85.4g of an off white solid in 88% yield. $^{1}$H NMR (DMSO-d6, 400 MHz): δ ppm 3.59-3.47 (4H, m, $NC\underline{H}_2CH_2CH_2C\underline{H}_2N$), 3.43 (5H, m, $NC\underline{H}_2CH_2CH_2CH_3$ and $NC\underline{H}_3$), 3.10 (3H, s, $OC\underline{H}_3$), 2.18-2.13 (4H, m, $NCH_2C\underline{H}_2C\underline{H}_2CH_2N$), 1.77-1.72 (2H, m, $NCH_2C\underline{H}_2CH_2CH_3$), 1.38-1.34 (2H, m, $NCH_2CH_2C\underline{H}_2CH_3$), 0.97 (3H, t, *J*= 7.4Hz, $NCH_2CH_2CH_2C\underline{H}_3$) $^{13}$C NMR (125 MHz): δ ppm 156.2 ($O(\underline{C}{=}O)OCH_3$), 63.5 ($N\underline{C}H_2CH_2CH_2\underline{C}H_2N$), 53.9 ($O(C{=}O)O\underline{C}H_3$), 51.5 ($N\underline{C}H_3$), 47.3 ($N\underline{C}H_2CH_2CH_2CH_3$), 25.2 ($NCH_2\underline{C}H_2\underline{C}H_2CH_2N$), 21.2 ($NCH_2\underline{C}H_2CH_2CH_3$), 19.4 ($NCH_2CH_2\underline{C}H_2CH_3$), 12.5 ($NCH_2CH_2CH_2\underline{C}H_3$).

**19**) 1-butyl-3-methyl-imidazolium methyl carbonate[7]

[7] J. D. Holbrey, R. D. Rogers, S. Shuklaa, C. D. Wilfred, *Green Chem*., 2010, **12**, 407



Procedure: To a pressurised reaction vessel was added 1-butyl-imidazole (61.0g, 0.5mol, 1.0eq), dimethylcarbonate (177.0g, 2.0mol, 4.0eq) and methanol (40mL). The reaction vessel was sealed and heated to 130°C and left stirring for 12 hours. The solution was concentrated under reduced pressure then recrystalised from a solution of methanol-ethyl acetate to give 101.7g of an off white solid in 96% yield. $^{1}$H NMR (DMSO-d6, 400 MHz): δ ppm 9.39 (1H, s, NC<u>H</u>=N), 7.82 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 7.73 (1H, s, NC<u>H</u>=CHN or NCH=C<u>H</u>N), 4.18 (2H, t, *J* = 7.4Hz, NC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$), 3.94 (3H, s, NC<u>H</u>$_3$), 3.11 (3H, s, C(O)OC<u>H</u>$_3$), 1.85 (2H, m, NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 1.35 (2H, t, *J*= 7.4Hz, NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$) $^{13}$C-NMR (125MHz): δ ppm 156.3 ((<u>C</u>=O)O), 136.0 (N<u>C</u>H=N), 123.9 (N<u>C</u>H=CHN or NCH=<u>C</u>HN), 122.4 (N<u>C</u>H=CHN or NCH=<u>C</u>HN), 63.6 ((C=O)O<u>C</u>H$_3$), 49.4 (N<u>C</u>H$_3$), 36.0(N<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$), 32.0(NCH$_2$<u>C</u>H$_2$CH$_2$CH$_3$), 19.4(NCH$_2$CH$_2$<u>C</u>H$_2$CH$_3$), 12.9 (NCH$_2$CH$_2$CH$_2$<u>C</u>H$_3$).