Understanding the Polarity of Ionic Liquids

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Synthetic Methods.

General

Unless otherwise stated ALL reactions were conducted in an anaerobic atmosphere of nitrogen. Solvents were distilled from the relevant drying agents prior to use. Toluene was stood over Na and distilled (benzophenone was used as a moisture indicator). Ethylacetate was distilled from fresh CaH_2. Dichloromethane was used directly after passing HPLC grade solvent through an activated zeolite drying column. 1-methylimidazole and 1,2-dimethylimidazole were distilled from KOH. Halogenoalkanes were distilled from P_2O_5.

Chloride content of the ionic liquids was determined by a $AgNO_3$ test. AgCl has a solubility of 1.4 mgl^{-1} in water, hence all of the ionic liquids synthesised will have a chloride content below this value.

1-butyl-3-methylimidazolium chloride, [C_4C_1im]Cl

1-methylimidazole (200 ml, 2.53 mol) was added dropwise to 1-chlorobutane (288 ml, 2.87 mol) in ethyl acetate (200 ml). The mixture was stirred at 45 °C for 14 days. The two-phase mixture was cooled to -14 °C until the product crystallised. The liquid was removed, the crystals were washed with ethyl acetate and recrystallised from acetonitrile. [C_4C_1im]Cl was recovered as a white crystalline solid and dried under vacuum (55.9% yield).

δ_H (400 MHz, $CDCl_3$)/ppm: 10.58(s, 1H, NC*H*N), 7.60 (s, 1H, NC*H*CHN), 7.43 (s, 1H, NCHC*H*N), 4.23 (t, J = 7.4, 2H, $NC\mathit{H}_2CH_2$), 4.03 (s, 3H, $NC\mathit{H}_3$), 1.90 – 1.73 (m, 2H, $CH_2C\mathit{H}_2CH_2$), 1.26 (m, 2H, $CH_2C\mathit{H}_2CH_3$), 0.86 (t, J = 7.4, 3H, $CH_2C\mathit{H}_3$).

δ_C (101 MHz, CDCl3)/ppm: 137.83 (s, N*C*HN), 123.67 (s, N*C*HCHN), 121.98 (s, NCH*C*HN), 49.69 (s, $N\mathit{C}H_2CH_2$), 36.47 (s, $N\mathit{C}H_3$), 32.11 (s, $CH_2\mathit{C}H_2CH_2$), 19.38 (s, $CH_2\mathit{C}H_2CH_3$), 13.37 (s, $CH_2\mathit{C}H_3$).

m/z ($LSIMS^+$): 139 ($[C_4C_1im]^+$, 100%), 313 ($[(C_4C_1im)_2Cl]^+$, 10%)

m/z ($LSIMS^-$): 35 (Cl^-, 80%), 209 ($[(C_4C_1im)Cl_2]^+$, 65%)

Elemental analysis (calc.): %C = 54.87 (55.01), %H = 8.79 (8.66), %N = 15.95 (16.04).

1-butyl-3-methylimidazolium tetrafluoroborate, $[C_4C_1im][BF_4]$

To a flask containing a stirred solution of $[C_4C_1im]Cl$ (197 g, 1.13 mol) in CH_2Cl_2 (200 cm^3) was added sodium tetrafluoroborate under N_2 (128 g, 1.16 mol). The mixture was stirred for 24 h and the white precipitate was allowed to settle. Cannula filtration and subsequent washing of the NaCl residue with CH_2Cl_2 (2 × 50 cm^3) gave a colourless liquid, which was further diluted with CH_2Cl_2 (100 cm^3) and washed with aliquots of water until halide free, as indicated by the $AgNO_3$ test of the water washings. The liquid was dried *in vacuo* for 3 h at 50 °C then filtered through a short pad (1−1.5 cm) of acidic and then basic alumina and thoroughly dried *in vacuo* at 50°C for a further 8 h to afford $[C_4C_1im][BF_4]$ (75.9% yield) as a free-flowing colourless liquid

δ_H (270 MHz, DMSO-d^6)/ppm: 8.96 (1H, s, NC*H*N), 7.68 (2H, m, NC*H*CHN), 7.61 (2H, m, NCHC*H*N), 4.16 (2H, t, ^3J = 7.2 Hz, $NC\mathit{H}_2CH_2$), 3.85 (3H, s, $NC\mathit{H}_3$), 1.77 (2H, m, $CH_2C\mathit{H}_2CH_2$), 1.26 (2H, m, $CH_2C\mathit{H}_2CH_3$), 0.88 (3H, t, J = 7.3 Hz, $CH_2C\mathit{H}_3$)

δ_C: (68 MHz, DMSO-d^6)/ppm 136.52 (s, N*C*HN), 123.58 (s, N*C*HCHN), 122.26 (s, NCH*C*HN), 48.68 (s, $N\mathit{C}H_2CH_2$), 35.66 (s, $N\mathit{C}H_3$), 31.43 (s, $CH_2\mathit{C}H_2CH_2$), 18.83 (s, $\mathit{C}H_2CH_3$), 13.16 (s, $CH_2\mathit{C}H_3$).

m/z (FAB^+): 139 ($[C_4C_1im]^+$, 100), 365 ($[(C_4C_1im)_2(BF_4)]^+$, 57%)

m/z (FAB^-): 19 (F^-, 59), 87 ($[BF_4]^-$, 100), 313 ($[(C_4C_1im)(BF_4)_2]^-$, 12%)

Elemental analysis (calc.): %C = 42.45 (42.51), %H = 6.71 (6.79), %N = 12.26 (12.39).

1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4C_1im][PF_6]$

As for the preparation of $[C_4C_1im][BF_4]$ except, $[C_4C_1im]Cl$ (62.3 g, 0.356 mol) in CH_2Cl_2 (80 cm^3) and sodium hexafluorophosphate (61.8 g, 0.367 mmol) were employed to afford $[C_4C_1im][PF_6]$ (83.7% yield) as a colourless viscous liquid.

δ_H (270 MHz, DMSO-d^6)/ppm: 9.03 (1H, s, NC*H*N), 7.68 (1H, m, NC*H*CHN), 7.63 (1H, m, NCHC*H*N), 4.16 (2H, t, J = 7.2 Hz, NCH_2CH$_2$), 3.85 (3H, s, NCH$_3$), 1.78 (2H, m, CH$_2$CH_2CH$_2$), 1.27 (2H, m, CH_2CH$_3$), 0.90 (3H, t, J = 7.3 Hz, CH$_2$CH_3)

δ_C (68 MHz, DMSO-d^6)/ppm: 136.51 (s, N*C*HN), 123.57 (s, N*C*HCHN), 122.22 (s, NCH*C*HN), 48.65 (s, N*C*H$_2$CH$_2$), 35.66 (s, N*C*H$_3$), 31.36 (s, CH$_2$*C*H$_2$CH$_2$), 18.79 (s, *C*H$_2$CH$_3$), 13.14 (s, CH$_2$*C*H$_3$)

m/z (FAB$^+$): 139 ($[C_4C_1im]^+$, 100), 423 ($[(C_4C_1im)_2PF_6]^+$, 56%)

m/z (FAB$^-$): 19 (F^-, 20), 145 ($[PF_6]^-$, 100%)

Elemental analysis (calc.): %C = 33.95 (33.81), %H = 5.31 (5.31), %N = 9.68 (9.86).

1-butyl-3-methylimidazolium hexafluoroantimonate, $[C_4C_1im][SbF_6]$

As for the preparation of $[C_4C_1im][BF_4]$ except, $[C_4C_1im]Cl$ (62.3m g, 0.357mol) in CH_2Cl_2 (80 cm^3) and sodium hexafluoroantimonate (94.9g, 0.368mmol) were employed to afford $[C_4C_1im][SbF_6]$ (83.7% yield) as a colourless free-flowing liquid.

δ_H (270 MHz, DMSO-d^6)/ppm: 9.03 (1H, s, NC*H*N), 7.66 (1H, m, NC*H*CHN), 7.60 (1H, m, NCHC*H*N), 4.16 (2H, t, J = 7.2 Hz, NCH_2CH$_2$), 3.86 (3H, s, NCH$_3$), 1.79 (2H, m, CH$_2$CH_2CH$_2$), 1.28 (2H, m, CH_2CH$_3$), 0.90 (3H, t, J = 7.3 Hz, CH$_2$CH_3)

δ_C (68 MHz, DMSO-d^6)/ppm: 136.54 (s, N*C*HN), 123.57 (s, N*C*HCHN), 122.21 (s, NCH*C*HN), 48.77 (s, N*C*H$_2$CH$_2$), 35.64 (s, NCH$_3$), 31.43 (s, CH$_2$*C*H$_2$CH$_2$), 18.85 (s, *C*H$_2$CH$_3$), 13.09 (s, CH$_2$*C*H$_3$)

m/z (FAB$^+$): 139 ($[C_4C_1im]^+$, 100), 513 ($[(C_4C_1im)_2(SbF_6)]^+$, 14%)

m/z (FAB$^-$): 19 (F^-, 67), 235 ($[SbF_6]^-$, 100%)

Elemental analysis (calc.): %C = 25.60 (25.62), %H = 4.14 (4.03), %N = 7.34 (7.47).

1-butyl-3-methylimidazolium trifluoromethanesulfonate, [C_4C_1im][OTf]

As for the preparation of [C_4C_1im][BF_4] except, [C_4C_1im]Cl (55.7 g, 0.319 mol) in CH_2Cl_2 (60 cm^3) and lithium trifluoromethanesulfonate (33.5 g, 0.329 mmol) were employed to afford [C_4C_1im][OTf] (61.2% yield) as a colourless free-flowing liquid.

δ_H (400 MHz, $CDCl_3$)/ppm: 8.77 (s, 1H, NC*H*N), 7.27 (m, 2H, NC*H*CHN), 3.98 (t, J = 7.3, 2H, N$CH_2$$CH_2$), 3.74 (s, 3H, N$CH_3$), 1.63 (m, 2H, $CH_2CH_2CH_2$), 1.11 (m, 2H, $CH_2CH_2CH_3$), 0.70 (t, J = 6.0, 3H, CH_2CH_3).

δ_C (101 MHz, $CDCl_3$)/ppm: 135.94 (s, N*C*HN), 123.47 (s, N*C*HCHN), 122.21 (s, NCH*C*HN), 120.38 (q, J = 320.1, [CF_3SO_3]), 49.35 (s, NCH_2CH_2), 35.82 (s, NCH_3), 31.55 (s, $CH_2CH_2CH_2$), 18.91 (s, $CH_2CH_2CH_3$), 12.87 (s, CH_2CH_3).

m/z (ESI$^+$): 139 ([C_4C_1im]$^+$, 100%), 427 ([(C_4C_1im)$_2$(OTf)]$^+$, 40%)

m/z (ESI$^-$): 149 ([OTf] $^-$, 85%), 437 ([(C_4C_1im)(OTf)$_2$]$^-$, 100%), 725 ([(C_4C_1im)$_2$(OTf)$_3$]$^-$, 20%)

Elemental analysis (calc.): %C = 37.35 (37.50), %H = 5.24 (5.24), %N = 9.60 (9.72).

1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide, [C_4C_1im][NTf_2]

As for the preparation of [C_4C_1im][BF_4] except, [C_4C_1im]Cl (84.5 g, 0.484 mol) in CH_2Cl_2 (100 cm^3) and lithium bis(trifluoromethanesulfonyl)imide (144 g, 0.499 mmol) were employed to afford [C_4C_1im][NTf_2] (91.9 % yield) as a colourless free-flowing liquid.

δ_H (400 MHz, DMSO-d^6)/ppm: 9.06 (1H, s, NC*H*N), 7.68 (1H, s, NC*H*CHN), 7.62 (1H, s, NCHC*H*N), 4.17 (2H, t, J = 8.0 Hz, NCH_2CH_2), 3.86 (3H, s, NCH_3), 1.79 (2H, m, $CH_2CH_2CH_2$), 1.29 (2H, m, CH_2CH_3), 0.91(3H, t, J = 6 Hz, CH_2CH_3).

δ_C: (100 MHz, DMSO-d^6)/ppm: 136.61 (s, N*C*HN), 123.61 (s, N*C*HCHN), 122.27 (s, NCH*C*HN), 119.68 (q, J_{C-F} = 320 Hz, [N(SO_2CF_3)$_2$]$^-$), 48.80 (s, NCH_2CH_2), 35.63 (s, NCH_3), 31.48 (s, $CH_2CH_2CH_2$), 18.83 (s, CH_2CH_3), 12.92 (s, CH_2CH_3).

m/z (ESI$^+$): 139, ([C_4C_1im]$^+$, 100%), 558, [(C_4C_1im)$_2$(NTf_2)]$^+$

m/z (ESI$^-$): 280, ([NTf_2]$^-$, 100%), 699, [(C_4C_1im)(NTf_2)$_2$]$^-$

Elemental Analysis (calc) : %C = 28.75 (28.64), %H = 3.68 (3.61), %N = 10.02

1-butyl-3-methylimidazolium acetate, [C_4C_1im][$MeCO_2$]

[C_4C_1im]Br (130.2 g, 0.594 mol) and of silver acetate (99.7 g, 0.597 mol) were combined with water (250 ml) in a 500 ml conical flask covered with aluminium foil to reduce photo degradation. The solution was stirred overnight. The slightly yellow precipitate was removed and the filtrate tested for the presence of silver and bromide. An aqueous 2M solution of [C_4C_1im]Br was added dropwise until precipitate formation ceased and a subsequent test for silver ions with dilute HCl was negative. The ionic liquid was dried to completion *in vacuo* at 60 °C (yield 84.8%).

δ_H (400 MHz, DMSO-d_6)/ppm : 10.17 (1H, s, NC*H*N), 7.91 (1H, s, NC*H*CHN), 7.83 (1H, s, NCHC*H*N), 4.20 (2H, t, NCH_2CH_2), 3.88 (3H, s, NCH_3), 1.75 (2H, m, $CH_2CH_2CH_2$), 1.58 (3H, m, $CH_3CO_2^-$), 1.22 (2H, m, CH_2CH_3), 0.87 (3H, t, CH_2CH_3).

δ_C (100 MHz, DMSO-d_6)/ppm : 173.59 (s, [CH_3CO_2]$^-$),137.04 (s, N*C*HN), 124.02 (s, N*C*HCHN), 122.27 (s, NCH*C*HN), 48.41 (s, NCH_2CH_2), 35.76 (s, NCH_3), 31.33 (s, $CH_2CH_2CH_2$), 18.74 (s, CH_2CH_3), 13.27 (s, CH_2CH_3) ppm.

m/z (LSIMS$^+$): 139 (100%) [C_4C_1im]$^+$, 337 (14%) [(C_4C_1im)$_2$(CH_3CO_2)]$^+$

m/z (LSIMS$^-$): 59 (100%) [CH_3CO_2]$^-$, 119 (61%) [$(CH_3CO_2)_2H$]$^-$, 257 (68%), [$(CH_3CO_2)_2$(C_4C_1im)]$^-$, 455 (28%) [(C_4C_1im)$_2$$(CH_3CO_2)_3$]$^-$

Elemental analysis (calc.): %C = 60.63 (60.58), %H = 9.13 (9.15), %N = 13.96 (14.13).

1-butyl-3-methylimidazolium dicyanamide, [C_4C_1im][$N(CN)_2$]

Silver nitrate (71.3 g, 0.42 mol) in water (150 ml) was added dropwise to a solution of sodium dicyanamide (39.2 g, 0.44 mol) in water (150 ml). The solution was stirred for one hour before filtering and washing to produce silver dicyanamide. The solid was dried at 80 °C.

[C_4C_1im]Br (76.4 g. 0.349 mol) was dissolved in water (50 ml). The [C_4C_1im]Br solution was added to a stirred suspension of 63.9 g (0.367 mol) silver dicyanamide in water (100 ml). The suspension was stirred for 12 h in the dark and the precipitate was removed by filtration. A sample was taken and a drop of dilute HCl solution added. The absence of precipitate indicated that the concentration of silver ions was below detection limit. The crude product was purified by continuous extraction of the ionic liquid from an aqueous phase into dichloromethane. The dichloromethane phase was isolated and the ionic liquid dried to completion *in vacuo* at 40°C. $[C_4C_1im][N(CN)_2]$ was a clear, slightly yellow/green liquid (71.6% yield).

δ_H (400 MHz, DMSO-d$_6$)/ppm: 9.10 (1H, s, NC*H*N), 7.75 (1H, s, NC*H*CHN), 7.68 (1H, s, NCHC*H*N), 4.17 (2H, t, NCH_2CH_2), 3.85 (3H, s, NCH_3), 1.77 (2H, m, $CH_2CH_2CH_2$), 1.26 (2H, m, CH_2CH_3), 0.89 (3H, t, CH_2CH_3) ppm.

δ_C (100 MHz, DMSO-d$_6$)/ppm: 199.55 (s, $[N(CN)_2]^-$) 136.96 (s, N*C*HN), 124.02 (s, N*C*HCHN), 122.68 (s, NCH*C*HN), 49.00 (s, NCH_2CH_2), 36.17 (s, NCH_3), 31.80 (s, $CH_2CH_2CH_2$), 19.32 (s, CH_2CH_3), 13.65 (s, CH_2CH_3) ppm.

m/z (LSIMS$^+$): 139 (100%) $[C_4C_1im]^+$, 344 (8%) $[(C_4C_1im)_2(N(CN)_2)]^+$

m/z (LSIMS$^-$): 66 (100%) $[N(CN)_2]^-$.

Elemental analysis (calc.): %C = 56.06 (58.51), %H = 7.21 (7.37), %N = 31.36 (34.12).

1-butyl-3-methylimidazolium dimethylphosphate, $[C_4C_1im][Me_2PO_4]$

To a solution of 1-butylimidazole (105.27 g, 848 mmol) in toluene (100 ml), trimethylphosphate (113.19 g, 808 mmol) was added drop-wise. The resulting mixture was stirred at 80 °C for 22 h and subsequently cooled to -14 °C for 2.5 h. As the clear colorless liquid remained as one phase, it was stirred at 90 °C for 64 h. The resultant yellow liquid was put into the freezer at -14 °C for 2.5 h. As no phase separation occurred, the liquid was diluted with toluene (400 ml), upon which phase separation occurred. The toluene phase was separated and the ionic liquid phase washed with toluene. The remaining solvent was removed under vacuum and $[C_4C_1im][Me_2PO_4]$ was obtained as a light yellow free flowing liquid (94% yield).

δ_H (400 MHz, DMSO)/ppm: 9.64 (s, 1H, NC*H*N), 7.88 (m, 1H, NC*H*CHN), 7.80 (m, 1H, NCHC*H*N), 4.18 (t, $^3J = 7.2$, 2H, NCH_2CH_2), 3.87 (s, 3H, NCH_3), 3.27 (d, 6H, $[(CH_3)_2PO_4]^-$), 1.76 (m, 2H, $CH_2CH_2CH_2$), 1.25 (m, 2H, CH_2CH_3), 0.88 (t, J = 7.4, 3H, CH_2CH_3).

δ_C (101MHz, DMSO)/ppm: 137.27 (s, N*C*HN), 123.61 (s, N*C*HCHN), 122.32 (s, NCH*C*HN), 51.24 (d, J = 5.6, $[(CH_3)_2PO_4]^-$), 48.36 (s, NCH_2CH_2), 35.56 (s, NCH_3), 31.43 (s, $CH_2CH_2CH_2$), 18.77 (s, CH_2CH_3), 13.25 (s, CH_2CH_3).

δ_P: (162 MHz, DMSO)/ppm: 1.51 (s, $[(CH_3)_2 PO_4]^-$).

m/z (ESI$^+$): 139 ($[C_4C_1im]^+$, 100%), 403 ($[(C_4C_1im)_2(Me_2PO_4)]^+$, 40%)

m/z (ESI$^-$): 125 ([Me_2PO_4]$^-$, 100%)

Elemental analysis (calculated): % = 28.75 (28.64), % H = 3.66 (3.61), % N 9.89 (10.02).

1-butyl-3-methylimidazolium methylsulfate, [C_4C_1im][$MeSO_4$]

1-butylimidazole (135 g, 143 ml, 1.09 mol) in toluene (200 ml) was cooled to 0 °C and dimethylsulfate (103 ml, 1.09 mol) was added drop-wise with stirring, with a further 1 hour of stirring at room temperature. The top phase was decanted and the lower phase was washed with toluene. After removal of the toluene, the ionic liquid was dried *in vacuo* at 40 °C. [C_4C_1im][$MeSO_4$] was recovered as a colourless, viscous liquid (70.8% yield).

δ_H (400 MHz, DMSO-d$_6$)/ppm: 9.12 (1H, s, NC*H*N), 7.79 (H, s, NC*H*CHN), 7.71 (H, s, NCHC*H*N), 4.17 (2H, t, NCH_2CH$_2$), 3.86 (3H, s, NCH_3), 3.41 (3H, s, [H_3COSO$_3$]$^-$), 1.76 (2H, m, CH$_2$CH_2CH$_2$), 1.24 (2H, m, CH_2CH$_3$), 0.87 (3H, t, CH$_2$CH_3).

δ_C (100 MHz, DMSO-d$_6$)/ppm: 137.04 (s, N*C*HN), 124.02 (s, N*C*HCHN), 122.72 (s, NCH*C*HN), 53.41 (s, [H$_3$COSO$_3$]$^-$) 48.92 (s, N*C*H$_2$CH$_2$), 36.09 (s, N*C*H$_3$), 31.84 (s, CH$_2$*C*H$_2$CH$_2$), 19.20 (s, *C*H$_2$CH$_3$), 13.66 (s, CH$_2$*C*H$_3$).

m/z (LSIMS$^+$): 139 (100%) [C_4C_1im]$^+$, 389 (4%) [(C_4C_1im)$_2$($MeSO_4$)]$^+$

m/z (LSIMS$^-$): 111 (100%) [$MeSO_4$]$^-$, 361 (3%) [(C_4C_1im)($MeSO_4$)$_2$]$^-$

Elemental analysis (calc.): %C = 43.22 (43.18), %H = 7.29 (7.25), %N = 11.19 (11.27).

1-butyl-3-methylimidazolium methylsulfonate, [C_4C_1im][$MeSO_3$]

Methanesulfonic acid (33.73 g, 351 mmol) was added with stirring to a solution of 1-butyl-3-methylimidazolium methylcarbonate (351 mmol). Vigorous gas formation was observed. The solution warmed only slightly on addition. The ionic liquid was dried *in vacuo* until crystallisation was observed. The salt was recrystallised twice from acetonitrile. The solid was washed with ethyl acetate and in dried vacuum. [C_4C_1im][$MeSO_3$] was recovered as a white solid (yield = 70%).

δ_H (400 MHz, DMSO-d$_6$)/ppm: 9.28 (1H, s, NC*H*N), 7.82 (1H, s, NC*H*CHN), 7.75 (1H, s, NCHC*H*N), 4.18 (2H, t, NCH_2CH$_2$), 3.87 (3H, s, NCH_3), 2.34 (3H, s, [*H*$_3$CSO$_3$]$^-$), 1.77 (2H, m, CH$_2$C*H*$_2$CH$_2$), 1.26 (2H, m, C*H*$_2$CH$_3$), 0.90 (3H, t, N-CH$_2$C*H*$_3$).

δ$_C$ (100 MHz, DMSO-d$_6$)/ppm: 137.15 (N*C*HN), 124.08 (N*C*HCHN), 122.74 (NCH*C*HN), 48.88 (N*C*H$_2$CH$_2$), 40.25 ([H$_3$*C*SO$_3$]$^-$) 36.14 (N*C*H$_3$), 31.83 (CH$_2$*C*H$_2$CH$_2$), 19.22 (*C*H$_2$CH$_3$), 13.72 (CH$_2$*C*H$_3$).

m/z (LSIMS$^+$): 139 (100%) [C$_4$C$_1$im]$^+$, 373 (5%) [(C$_4$C$_1$im)$_2$(MeSO$_3$)]$^+$

m/z (LSIMS$^-$): 95 (100%) [MeSO$_3$]$^-$, 329 (10%) [(C$_4$C$_1$im)(MeSO$_3$)$_2$]$^-$, 563 (4%) [(C$_4$C$_1$im)$_2$(MeSO$_3$)$_3$]$^-$.

MP: 72°C

Elemental analysis (calc.): %C = 45.96 (46.13), %H = 7.92 (7.74), %N = 11.84 (11.86).

1-pentyl-3-methylimidazolium chloride, [C$_5$C$_1$im]Cl.

1-methylimidazole (55 ml, 0.7 mol) was added dropwise under N$_2$ to a mixture of 1-chloropentane (100 ml, 0.83 mol) in acetonitrile (150 ml). The solution was heated to 75 °C and stirred for five days. The mixture was cooled at room temperature and further cooled to -14 °C for three days. A biphasic solution formed and the top layer was decanted. The bottom layer was washed with ethyl acetate, before drying *in vacuo* for 24 hours at 45°C, affording [C$_5$C$_1$im]Cl (72% yield) as a yellowish viscous liquid.

δ$_H$ (400 MHz, DMSO-d^6)/ppm 9.36 (1H, s, NC*H*N), 7.83 (1H, s, NC*H*CHN), 7.76 (1H, s, NCHC*H*N), 4.17 (2H, t, J = 8.0 Hz, NC*H*$_2$CH$_2$), 3.86 (3H, s, NC*H*$_3$), 1.78 (2H, m, NCH$_2$C*H*$_2$CH$_2$), 1.25 (4H, m, N(CH$_2$)$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.86 (3H, t, J = 8 Hz, CH$_2$C*H*$_3$)

δ$_C$ (100 MHz, DMSO-d^6)/ppm: 136.64 (s, N*C*HN), 123.57 (s, N*C*HCHN), 122.25 (s, NCH*C*HN), 48.65 (s, N*C*H$_2$CH$_2$), 35.69 (s, N*C*H$_3$), 29.05 (s, NCH$_2$*C*H$_2$CH$_2$), 27.59 (s, *C*H$_2$CH$_2$CH$_3$), 21.47 (s, C*H*$_2$CH$_3$), 13.72 (s, CH$_2$C*H*$_3$).

m/z (ESI$^+$): 153, ([C$_5$C$_1$im]$^+$, 100%, 341, [(C$_5$C$_1$im)$_2$Cl]$^+$

m/z (FAB$^-$): 35, [Cl]$^-$, 30%, 223, [(C$_5$C$_1$im)Cl$_2$]$^-$

Elemental Analysis (calc) : %C = 57.27 (57.29), %H = 8.89 (9.08), %N = 14.81 (14.85)

1-pentyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_5C_1im][N(Tf)_2]$

As for the preparation of $[C_4C_1im][BF_4]$ except, lithium bis(trifluoromethanesulfonyl)imide (114.83 g, 0.4 mol) and 1-pentyl-3-methylimidazolium chloride (68.39 g, 0.36 mol) were used to afford $[C_5C_1im][N(Tf)_2]$ (62% yield) as a colourless liquid.

δ_H (400 MHz, DMSO-d^6)/ppm: 9.08 (1H, s, NC*H*N), 7.71 (1H, s, NC*H*CHN), 7.64 (1H, s, NCHC*H*N), 4.15 (2H, t, J = 8.0 Hz, $NC\mathit{H}_2CH_2$), 3.85 (3H, s, $NC\mathit{H}_3$), 1.80 (2H, m, $NCH_2CH_2C\mathit{H}_2$), 1.25 (4H, m, $C\mathit{H}_2C\mathit{H}_2CH_3$), 0.86 (3H, t, J = 8 Hz, $CH_2C\mathit{H}_3$)

δ_C (100 MHz, DMSO-d^6)/ppm: 136.60 (s, N*C*HN), 119.65 (q, $J_{C\text{-}F}$ = 320 Hz, $[N(SO_2\mathit{C}F_3)_2]^-$), 123.65 (s, N*C*HCHN), 122.29 (s, NCH*C*HN), 48.98 (s, $N\mathit{C}H_2CH_2$), 35.70 (s, $N\mathit{C}H_3$), 29.20 (s, $NCH_2\mathit{C}H_2CH_2$), 27.71 (s, $NCH_2CH_2\mathit{C}H_2$), 21.57 (s, $\mathit{C}H_2CH_3$), 13.51 (s, $CH_2\mathit{C}H_3$).

m/z (ESI$^+$): 153, $[C_5C_1im]^+$, 100%, 341, $[(C_5C_1im)_2(NTf_2)]^+$

m/z (ESI-): 280, $[NTf_2]^-$, 100%, 713, $[(C_5C_1im)(NTf_2)_2]^-$

Elemental Analysis (calc): %C = 30.66 (30.48), %H = 3.79 (3.95), %N = 9.64 (9.70)

1-ethyl-3-methylimidazolium bromide, $[C_2C_1im]Br$

The same procedure was used as indicated for $[C_4C_1im]Cl$ with the exception of the use of 1-bromoethane (100 ml, 1.34 mol) and 1-methylimidazole (106 ml, 1.34 mol) in toluene (75 ml) and stirred for 45 h at 30-35 ºC to give a bright white crystalline solid (87.0 % yield).

δ_H (270 MHz, DMSO-d^6)/ppm: 9.50 (1H, s, NC*H*N), 7.95(1H, s, NC*H*CHN) 7.84 (1H, s, NCHC*H*N), 4.23 (2H, q, J = 7.3 Hz, $NC\mathit{H}_2CH_3$), 3.88 (3H, s, $NC\mathit{H}_3$), 1.37 (3H, t, 3J = 7.3 Hz, $NCH_2C\mathit{H}_3$).

δ_C (68 MHz, DMSO-d^6)/ppm: 136.18 (s, N*C*HN), 123.31 (s, N*C*HCHN), 121.83 (s, NCH*C*HN), 43.96 (s, $N\mathit{C}H_2CH_3$), 35.70 (s, $N\mathit{C}H_3$) and 15.13 (s, $NCH_2\mathit{C}H_3$).

m/z FAB$^+$: 111, $[C_2C_1im]^+$, 100 %, 301, $[(C_2C_1im)_2Br]^+$, 11 %

m/z FAB$^-$: 6 %; 79, $[Br]^-$, 100 %, 269, $[(C_2C_1im)Br_2]^-$

Elemental analysis (calc): %H = 5.81 (5.84), %C = 37.75 (37.84), %N = 14.67 (16.04)

1-ethyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl) imide, $[C_2C_1im][NTf_2]$

As for the preparation of $[C_4C_1im][BF_4]$, except $[C_2C_1im]Br$ (50 g, 0.26 mol) in CH_2Cl_2 (60 ml) and lithium *bis*(trifluoromethanesulfonyl)imide (80.4 g, 0.28 mol) to give $[C_2C_1im][NTf_2]$ as a colourless liquid (89% yield).

δ_H (400 MHz, $CDCl_3$)/ppm: 8.48 (1H, s, $NC\mathit{H}N$), 7.30 (1H, s, $NC\mathit{H}CHN$), 7.25 (1H, s, $NCHC\mathit{H}N$), 4.12 (2H, q, J = 7.3 Hz, $NC\mathit{H}_2CH_3$), 3.81 (3H, s, $NC\mathit{H}_3$) and 1.42 (3H, t, J = 7.4 Hz, $NCH_2C\mathit{H}_3$).

δ_C (400 MHz, $CDCl_3$)/ppm: 135.25 (s, $N\mathit{C}HN$), 123.64 (s, $N\mathit{C}HCHN$), 121.99 (s, $NCH\mathit{C}HN$), 119.67 (q, $J_{13C\text{-}19F}$ = 320.9 Hz, $[N(SO_2\mathit{C}F_3)_2]^-$), 45.01 (s, $N\mathit{C}H_2CH_3$), 35.91 (s, $N\mathit{C}H_3$) and 14.71 (s, $NCH_2\mathit{C}H_3$).

m/z (FAB^+): 111, ($[(C_2C_1im)]^+$, 100 %), 502, ($[(C_2C_1im)_2(N(Tf)_2)]^+$, 43 %)

m/z (FAB^-): 280, ($[N(Tf)_2]^-$, 100 %), 671, ($[(C_2C_1im)(N(Tf)_2)_2)]^-$ 77 %)

Elemental analysis (calc): %H = 2.83 (2.18), %C = 24.56 (24.65), %N = 10.74 (10.65)

1-hexyl-3-methylimidazolium bromide, $[C_6C_1im]Br$

A solution of 1-bromohexane (193 ml, 1.37 mol) and 1-methylimidazole (109 ml, 1.37 mol) were heated in toluene at 55-60 ºC for 72 h to give a slightly yellow liquid. The liquid was washed repeatedly with ethyl acetate to give $[C_6C_1im]Br$ as a white crystalline solid, which was filtered and subsequently dried *in vacuo* for 24 h at 60 ºC (91 % yield).

δ_H (400 MHz, $CDCl_3$)/ppm: 10.0 (1H, s, $NC\mathit{H}N$), 7.53 (1H, s, $NC\mathit{H}CHN$),7.37 (1H, s, $2NCHC\mathit{H}N$), 4.07 (2H, t, J = 7.4 Hz, $NC\mathit{H}_2CH_2$), 3.87 (3H, s, $NC\mathit{H}_3$), 1.64 (2H, m, $NCH_2C\mathit{H}_2CH_2$ 1.02 (6H, m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$), 0.58 (3H, t, J = 7.0 Hz $CH_2C\mathit{H}_3$).

δ_C (400 MHz, $CDCl_3$)/ppm: 136.74 (s, $N\mathit{C}HN$), 123.73 (s, $N\mathit{C}HCHN$), 122.08 (s, $NCH\mathit{C}HN$), 49.76 (s, $N\mathit{C}H_2CH_2$), 36.43 (s, $N\mathit{C}H_3$), 30.80 (s, $NCH_2\mathit{C}H_2CH_2$), 30.03 (s, $NCH_2CH_2\mathit{C}H_2$), 25.58 (s, $\mathit{C}H_2CH_2CH_3$), 22.10 (s, $\mathit{C}H_2CH_3$) 13.72 (s, $CH_2\mathit{C}H_3$).

m/z FAB^+: 167, ($[C_6C_1im]^+$, 100 %), 413, ($[(C_6C_1im)_2Br]^+$, 45 %)

m/z FAB^-: 79, $[Br]^-$, 81, $[Br]^-$, 85 %, 100 %, (138, $[Br_2]^-$, 2 %)

Elemental analysis (calc): %H = 7.75 (7.73), %C = 48.62 (48.75), %N = 11.34 (11.22).

1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[\mathrm{C_6C_1im}][\mathrm{NTf_2}]$

As for the preparation of $[\mathrm{C_4C_1im}][\mathrm{BF_4}]$ except, lithium bis(trifluoromethylsulfonyl)imide (120.6 g, 0.42 mol) and $[\mathrm{C_6C_1im}]\mathrm{Cl}$ (100 g, 0.39 mol) were used to afford $[\mathrm{C_6C_1im}][\mathrm{NTf_2}]$. The ionic liquid was washed repeatedly with hexane and treated with activated charcoal passing through a column with acidic and then basic alumina. This afforded $[\mathrm{C_6C_1im}][\mathrm{NTf_2}]$ as a colourless liquid, free-flowing liquid (84 % yield).

δ_{H} (400 MHz, $\mathrm{CDCl_3}$)/ppm: 8.63 (1H, s, $\mathrm{NC}H\mathrm{N}$), 7.70 (2H, s, $\mathrm{NC}H\mathrm{CHN}$), 7.64 (2H, s, $\mathrm{NCHC}H\mathrm{N}$), 4.17 (2H, t, J = 7.2 Hz, $\mathrm{NC}H_2\mathrm{CH_2}$), 3.86 (3H, s, $\mathrm{NC}H_3$), 1.79 (2H, M, $\mathrm{NCH_2C}H_2\mathrm{CH_2}$), 1.28 (2H, m , $\mathrm{NCH_2CH_2C}H_2$) 0.91 (3H, t, J = 7.3 Hz, $\mathrm{CH_2CH_2C}H_3$).

δ_{C} (400 MHz, $\mathrm{CDCl_3}$)/ppm: 135.71 (s, $\mathrm{N}C\mathrm{HN}$), 123.75 (s, $\mathrm{N}C\mathrm{HCHN}$) 122.35 (s, $\mathrm{NCH}C\mathrm{HN}$), 119.77 (q, $J_{\mathrm{13C\text{-}19F}}$ = 321 Hz, $[\mathrm{N(SO_2}C\mathrm{F_3)_2}]^-$), 50.06 (s, $\mathrm{N}C\mathrm{H_2CH_2}$), 36.12 (s, $\mathrm{N}C\mathrm{H_3}$), 30.85 (s, $\mathrm{NCH_2}C\mathrm{H_2}$), 29.92 (s, $\mathrm{NCH_2CH_2}C\mathrm{H_2}$), 25.6 (s, $C\mathrm{H_2CH_2CH_3}$), 22.19 (s, $C\mathrm{H_2CH_3}$) 13.70 (s, $\mathrm{CH_2}C\mathrm{H_3}$).

m/z ($\mathrm{FAB^+}$): 167,($[(\mathrm{C_6C_1im})]^+$, 100 %), 614, ($[(\mathrm{C_6C_1im})_2(\mathrm{NTf_2})]^+$, 14 %)

m/z ($\mathrm{FAB^-}$): 280, $[\mathrm{NTf_2}]^-$, 100 %.

Elemental analysis (calc): %H = 4.28 (4.23), %C = 32.22 (32.27), %N = 9.39 (9.32%)

1-methyl-3-octylimidazolium bromide, $[\mathrm{C_8C_1im}]\mathrm{Br}$

The same procedure as as indicated for $[\mathrm{C_4C_1im}]\mathrm{Cl}$ except 1-bromooctane (200 ml, 1.16 mol) and 1-methylimidazole (93 ml, 1.16 mol) were heated in toluene at 40 ºC for 3 days to give a slightly yellow liquid. The liquid was washed with diethylether and dried *in vacuo* for 24 h to give $[\mathrm{C_8C_1im}]\mathrm{Br}$ (90 % yield).

δ_{H} (400 MHz, $\mathrm{CDCl_3}$): 9.73 (1H, s, $\mathrm{NC}H\mathrm{N}$), 7.36 (1H, s, $\mathrm{NC}H\mathrm{CHN}$), 7.22 (1H, s, $\mathrm{NCHC}H\mathrm{N}$), 3.85 (2H, t, ^3J = 7.4 Hz, $\mathrm{NC}H_2\mathrm{CH_2}$), 3.64 (3H, s, $\mathrm{NC}H_3$), 1.42 (2H, m, $\mathrm{NCH_2C}H_2$), 0.76 (10H, m, $\mathrm{NCH_2CH_2C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 0.33 (3H, t, ^3J = 6.9 Hz $\mathrm{CH_2C}H_3$).

δ_{C} (400 MHz, $\mathrm{CDCl_3}$): 136.38 (s, $\mathrm{N}C\mathrm{HN}$), 123.55 (s, $\mathrm{N}C\mathrm{HCHN}$), 122.00 (s, $\mathrm{NCH}C\mathrm{HN}$), 49.52 (s, $\mathrm{N}C\mathrm{H_2CH}$), 36.20 (s, $\mathrm{N}C\mathrm{H_3}$), 31.15 (s, $\mathrm{NCH_2}C\mathrm{H_2}$), 29.88 (s, $\mathrm{NCH_2CH_2}C\mathrm{H_2}$), 28.51 (s, $\mathrm{NCH_2CH_2CH_2}C\mathrm{H_2}$), 28.45 (s, $C\mathrm{H_2CH_2CH_2CH_3}$), 25.71 $C\mathrm{H_2CH_2CH_3}$), 22.06 (s, $C\mathrm{H_2CH_3}$), 13.63 (s, $\mathrm{CH_2}C\mathrm{H_3}$).

m/z FAB$^+$: 195, ([C_8C_1im]$^+$, 100 %), 469, ([(C_8C_1im)$_2$Br]$^+$, 18 %)

m/z FAB$^-$: 79, [Br]$^-$, 81, [Br]$^-$, 85 %, 100 %, 162, ([Br_2]$^-$, 4 %)

Elemental analysis (calc): %H = 8.42 (8.72), %C = 52.37 (51.59), %N = 10.18 (10.21)

1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl) imide, [C_8C_1im][NTf_2]

As for the preparation of [C_4C_1im][NTf_2], except [C_4C_1im]Br (150 g, 0.54 mol) in CH_2Cl_2 (200 ml) and lithium *bis*(trifluoromethanesulfonyl)imide (160.8 g, 0.56 mol) to give [C_8C_1im][NTf_2] as a colourless liquid (81 % yield).

δ_H (400 MHz, $CDCl_3$)/ppm: 8.70 (1H, s, NC*H*N), 7.35 (1H, m, NC*H*CHN), 7.33 (1H, m, NCHC*H*N), 4.15 (2H, t, J = 7.4 Hz, NCH_2CH$_2$), 3.92 (3H, s, NCH_3), 1.85 (2H, m, $NCH_2CH_2CH_2$), 1.28 (10H, m, $NCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 0.86 (3H, t, J = 6.9 Hz CH_2CH_3).

δ_C (400 MHz, $CDCl_3$)/ppm: 135.84 (s, N*C*HN), 123.78 (s, NCH*C*HN), 122.32 (s, N*C*HCHN), 119.8 (q, $J_{13C-19F}$ = 321 Hz, [$N(SO_2CF_3)_2$]$^-$), 50.15 (s, NCH_2CH_2), 36.21 (s, NCH_3), 31.58 (s, NCH_2CH_2), 30.03 (s, $NCH_2CH_2CH_2$), 28.89 (s, NCH_2 $CH_2CH_2CH_2$), 28.76 (s, $CH_2CH_2CH_2CH_3$), 26.04 $CH_2CH_2CH_3$), 22.51 (s, CH_2CH_3), 13.95 (s, NCH_2CH_3).

m/z (FAB$^+$): 195, ([(C_8C_1im)]$^+$, 100 %), 670, ([(C_8C_1im)$_2$(NTf_2))]$^+$, 17 %)

m/z (FAB$^-$): 280, ([NTf_2]$^-$, 100 %).

Elemental analysis (calc): %H = 4.88 (4.76), %C = 35.39 (35.50), %N = 8.84 (8.72)

1-butyl-2,3-dimethylimidazolium chloride, [$C_4C_1C_1$im]Cl

As for the preparation of [C_4C_1im]Cl except, 1-chlorobutane (65.0ml, 0.620 mol) and 1,2-dimethylimidazole (50ml, 0.564 mol) used to afford [$C_4C_1C_1$im]Cl (83.8% yield) as a white crystalline solid.

δ_H (270 MHz, DMSO-d^6)/ppm: 7.78 (1H, s, NC*H*CHN), 7.53 (1H, s, NCHC*H*N), 4.12 (2H, t, J = 7.3 Hz, NCH_2CH$_2$), 3.73 (3H, s, NCH_3), 2.60 (3H, s, N_2CCH_3), 1.74 (2H, m $NCH_2CH_2CH_2$), 1.28 (2H, m, $CH_2CH_2CH_3$), 0.88 (3H, t, J = 7.3 Hz, NCH_2CH_3)

δ_C (68 MHz, DMSO-d^6)/ppm: 144.36 (s, N*C*N), 122.21 (s, N*C*HCHN), 120.76 (s, NCH*C*HN), 47.37 (s, N*C*H$_2$CH$_2$), 34.50 (s, N*C*H$_3$), 31.19 (s, NCH$_2$*C*H$_2$), 18.88 (s, *C*H$_2$CH$_3$), 13.31 (s, CH$_2$*C*H$_3$), 8.90 (s, N$_2$C*C*H$_3$)

m/z (FAB$^+$): 153 ([C$_4$C$_1$C$_1$im]$^+$, 100%), 342 ([(C$_4$C$_1$C$_1$im)$_2$Cl]$^+$, 41%)

m/z (FAB$^-$): 188 ([matrix + Cl]$^-$, 100%)

Elemental analysis: %C = 57.28 (57.29), %H = 9.26 (9.08), %N = 14.72 (14.85).

1-butyl-2,3-dimethylimidazolium tetrafluoroborate, [C$_4$C$_1$C$_1$im][BF$_4$]

As for the preparation of [C$_4$C$_1$im][BF$_4$] except, [C$_4$C$_1$C$_1$im]Cl (77.2 g, 0.410 mol) and sodium tetrafluoroborate (46.4 g, 0.422 mmol) were employed to afford [C$_4$C$_1$C$_1$im][BF$_4$] (69.0 g, 70.2%) as a viscous colourless liquid, which often crystallised upon agitation at room temperature.

δ_H (270 MHz, DMSO-d^6)/ppm: 7.57 (2H, m, NC*H*C*H*N), 4.11 (2H, t, J = 7.3 Hz, NC*H*$_2$CH$_2$), 3.76 (3H, s, NC*H*$_3$), 2.58 (3H, s, N$_2$CC*H*$_3$), 1.71 (2H, m, NCH$_2$C*H*$_2$), 1.30 (2H, m, C*H*$_2$CH$_3$), 0.90 (3H, t, J = 7.3 Hz, CH$_2$C*H*$_3$)

δ_C (68 MHz, DMSO-d^6)/ppm: 144.32 (s, N*C*CH$_3$N), 122.20 (s, N*C*HCHN), 120.78 (s, NCH*C*HN), 47.34 (s, N*C*H$_2$CH$_2$), 34.49 (s, N*C*H$_3$), 31.19 (s, NCH$_2$*C*H$_2$), 18.86 (s, *C*H$_2$CH$_3$), 13.29 (s, CH$_2$*C*H$_3$), 8.87 (s, N$_2$C*C*H$_3$)

m/z (FAB$^+$): 153 ([C$_4$C$_1$C$_1$im]$^+$, 100), 393 ([(C$_4$C$_1$C$_1$im)$_2$(BF$_4$)]$^+$, 19%)

m/z (FAB$^-$): 19 (F$^-$, 30), 87 ([BF$_4$]$^-$, 100%)

Elemental analysis (calc): %C = 44.83 (45.03), %H = 7.11 (7.14), %N 11.53 (11.67).

1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide, [C$_4$C$_1$C$_1$im][NTf$_2$]

As for the preparation of [C$_4$C$_1$im][BF$_4$] except, [C$_4$C$_1$C$_1$im]Cl (30.9 g, 0.164 mol) in CH$_2$Cl$_2$ (50ml) and lithium bis(trifluoromethanesulfonyl)imide (48.8 g, 0.169 mmol) were employed to afford [C$_4$C$_1$C$_1$im][NTf$_2$] (89.0% yield) as a colourless free-flowing liquid.

δ_H (270 MHz, CD_2Cl_2)/ppm: 7.58 (2H, m, NC*H*C*H*N), 4.12 (2H, t, J = 7.3 Hz, $NC\mathit{H}_2CH_2$), 3.77 (3H, s, $NC\mathit{H}_3$), 2.59 (3H, s, $N_2CC\mathit{H}_3$), 1.73 (2H, m, $NCH_2C\mathit{H}_2$), 1.32 (2H, m, $C\mathit{H}_2CH_3$), 0.92 (3H, t, J = 7.3 Hz, $CH_2C\mathit{H}_3$)

δ_C (68 MHz, DMSO-d^6)/ppm: 144.17 (s, $N\mathit{C}CH_3N$), 122.26 (s, N*C*HCHN), 120.80 (s, NCH*C*HN), 119.57 (q, $J_{13C-19F}$ = 321.6 Hz, $[N(SO_2\mathit{C}F_3)]^-$), 47.44 (s, $N\mathit{C}H_2CH_2$), 34.51 (s, $N\mathit{C}H_3$), 31.16 (s, $NCH_2\mathit{C}H_2$), 18.85 (s, $\mathit{C}H_2CH_3$), 13.06 (s, $CH_2\mathit{C}H_3$) and 8.92 (s, $NC\mathit{C}H_3N$)

m/z (FAB$^+$): 153 ($[C_4C_1C_1im]^+$, 100%), 586 ($[(C_4C_1C_1im)_2(NTf_2)_2]^+$, 20%)

m/z (FAB$^-$): 280 ($[NTf_2]^-$, 100%)

Elemental analysis (calc): %C = 30.52 (30.69), %H = 4.00 (3.95), %N = 9.51 (9.70).

1-(2-ethoxy-ethyl)-1-methylimidazolium chloride, $[C_2OC_2C_1im]Cl$

2-chloroethyl ethyl ether (62 ml, 0.58 mol) was added under N_2 to a mixture of 1-methylimidazole (23 ml, 0.3 mol) and acetonitrile (100 ml) and the solution was stirred at 75°C for five days. Upon cooling to -14 °C for 24 hours, two layers were formed and the top acetonitrile layer was decanted. The product was washed with ethylacetate and dried *in vacuo* for 24 hour at 45 °C, affording $[C_2OC_2C_1im]Cl$ (68% yield) as a pale yellow liquid.

δ_H (400 MHz, DMSO-d^6)/ppm: 9.16 (1H, s, NC*H*N), 7.75 (1H, s, NC*H*CHN), 7.72 (1H, s, NCHC*H*N), 4.35 (2H, t, J = 8 Hz, $NC\mathit{H}_2CH_2O$), 3.87 (3H, s, $NC\mathit{H}_3$), 3.71 (2H, t, J = 8 Hz, $NCH_2C\mathit{H}_2O$), 3.45 (2H, q, J = 8 Hz, $OC\mathit{H}_2CH_3$), 1.08 (3H, t, J = 8 Hz, $OCH_2C\mathit{H}_3$).

δ_C (100 MHz, DMSO-d^6)/ppm: 136.93 (s, N*C*HN), 123.39 (s, N*C*HCHN), 122.61 (s, NCH*C*HN), 67.52 (s, $N\mathit{C}H_2CH_2O$), 65.45 (s, $O\mathit{C}H_2CH_3$), 48.72 (s, $NCH_2\mathit{C}H_2O$), 35.69 (s, $N\mathit{C}H_3$), 14.84 (s, $OCH_2\mathit{C}H_3$).

m/z (ESI$^+$): 155, ($[C_2OC_2C_1im]^+$, 100%), 345, ($[(C_2OC_2C_1im)_2Cl]^+$)

m/z (FAB$^-$): 35 ($[Cl]^-$, 100%), 225, $[(C_2OC_2C_1im)Cl_2]^-$)

Elemental analysis (calc) : %C = 50.48 (50.39), %H = 8.03 (7.93), %N = 14.53 (14.69)

1-(2-ethoxy-ethyl)-1-methylimidazolium bis(trifluoromethanesulfonyl)imide, [$C_2OC_2C_1$im][NTf_2]

As for the preparation of [C_4C_1im][BF_4] except, lithium bis(trifluoromethanesulfonyl)imide (57.4 g, 0.2 mol) and [$C_2OC_2C_1$im]Cl (33.88 g, 0.17 mol) were used to afford [$C_2OC_2C_1$im][NTf_2] (81% yield) as a colourless liquid.

δ_H (400 MHz, DMSO-d^6)/ppm: 9.07 (1H, s, NC*H*N), 7.72 (1H, s, NC*H*CHN), 7.68 (1H, s, NCHC*H*N), 4.33 (2H, t, J = 8 Hz, NC*H*$_2$CH$_2$O), 3.87 (3H, s, NC*H*$_3$), 3.71 (2H, t, J = 8 Hz, NCH$_2$C*H*$_2$O), 3.45 (2H, q, J = 8 Hz, OC*H*$_2$CH$_3$), 1.08 (3H, t, J = 8 Hz, OCH$_2$C*H*$_3$).

δ_C (100 MHz, DMSO-d^6)/ppm: 136.81 (s, N*C*HN), 123.44 (s, N*C*HCHN), 122.66 (s, NCH*C*HN), 119.52 (q, $^1J_{C\text{-}F}$ = 320 Hz, [N(SO$_2$*C*F$_3$)$_2$]$^-$), 67.52 (s, N*C*H$_2$CH$_2$O), 65.55 (s, N(CH$_2$)$_2$O*C*H$_2$CH$_3$), 48.90 (s, NCH$_2$*C*H$_2$OCH$_2$CH$_3$), 35.72 (s, N*C*H$_3$), 14.77 (s, OCH$_2$*C*H$_3$).

m/z (ESI$^+$): 155, ([$C_2OC_2C_1$im]$^+$, 80%), 590, ([($C_2OC_2C_1$im)$_2$(NTf$_2$)]$^+$, 100%)

m/z (ESI$^-$): 280, ([N(Tf)$_2$]$^-$, 100%), 715, ([($C_2OC_2C_1$im)[(NTf$_2$]$_2$)]$^-$)

Elemental analysis (calc) : %C = 27.65 (27.59), %H = 3.53 (3.47), %N = 9.44 (9.56)

1-methyl-3-pentamethyldisiloxymethylimidazolium chloride, [(SiOSi)C_1C_1im]Cl

Pentamethyldisiloxymethyl chloride (20 ml, 0.098 mol) was added dropwise under N_2 to 1-methylimidazole (7.0 ml, 0.09 mol) in acetonitrile (20 ml. The solution was heated at 85 °C for 3 days and after cooling at 4°C for two days, a biphasic solution had formed. Acetonitrile was carefully decanted from the white solid product, which was then washed with ethyacetate and dried *in vacuo* for 24 hours, affording [(SiOSi)C_1C_1im]Cl (85% yield) as a white crystalline solid.

δ_H (400 MHz, DMSO-d^6)/ppm: 8.93 (1H, s, NC*H*N), 7.71 (1H, s, NC*H*CHN), 7.55 (1H, s, NCHC*H*N), 3.86 (2H, s, NC*H*$_2$Si(CH$_3$)$_2$), 3.85 (3H, s, NC*H*$_3$), 0.17 (6H, s, NCH$_2$Si(C*H*$_3$)$_2$OSi(CH$_3$)$_3$) and 0.04 (9H, s, NCH$_2$Si(CH$_3$)$_2$OSi(C*H*$_3$)$_3$).

δ_C: (100 MHz, DMSO-d^6)/ppm: 135.88 (s, N*C*HN), 123.59 (s, N*C*HCHN), 123.13 (s, NCH*C*HN), 41.06 (s, N*C*H$_2$Si(CH$_3$)$_2$, 35.68 (s, N*C*H$_3$), 1.73 (s, NCH$_2$Si(*C*H$_3$)$_2$OSi(CH$_3$)$_3$), -0.97 (s, NCH$_2$Si(CH$_3$)$_2$OSi(*C*H$_3$)$_3$).

δ_{Si}: (79 MHz, DMSO-d^6)/ppm: 10.47 (s, *S*i(CH$_3$)$_3$), 2.33 (s, NCH$_2$*Si*(CH$_3$)$_2$)

m/z (ESI$^+$): 243, ([(SiOSi)C_1C_1im]$^+$, 100%)

m/z (FAB-): 35 (Cl$^-$, 90%), 313, ([(SiOSiC_1C_1im)Cl$_2$]$^-$, 20%)

MP: 140°C

Elemental analysis (predicted) : %C = 43.13 (43.06), %H = 8.25 (8.31), %N = 9.97 (10.04)

1-methyl-3-pentamethyldisiloxymethylimidazolium bis(trifluoromethanesulfonyl)imide, [(SiOSi)C_1C_1im][N(Tf)$_2$]

As for the preparation of [C_4C_1im][BF_4] except, lithium bis(trifluoromethanesulfonyl)imide (20 g, 0.07 mol) and [(SiOSi)C_1C_1im]Cl (18.2g, 0.065 mol) were used to afford [(SiOSi)C_1C_1im][N(Tf)$_2$] (72% yield) as a colourless liquid.

δ_H (400 MHz, DMSO-d^6)/ppm: 8.91 (1H, s, NC*H*N), 7.69 (1H, s, NC*H*CHN), 7.54 (1H, s, NCHC*H*N), 3.86 (5H, s, NC*H*$_2$Si(CH$_3$)$_2$ and NC*H*$_3$), 0.17 (6H, s, NCH$_2$Si(C*H*$_3$)$_2$OSi(CH$_3$)$_3$), 0.05 (9H, s, NCH$_2$Si(CH$_3$)$_2$OSi(C*H*$_3$)$_3$).

δ_C (100 MHz, DMSO-d^6)/ppm: 135.82 (s, N*C*HN), 124.33 (q, $J_{C\text{-}F}$ = 320 Hz, [N(SO$_2$*C*F$_3$)$_2$]$^-$), 123.57 (s, N*C*HCHN), 123.13 (s, NCH*C*HN), 41.13 (s, N*C*H$_2$Si(CH$_3$)$_2$), 35.62 (s, N*C*H$_3$), 1.47 (s, NCH$_2$Si(*C*H$_3$)$_2$), -1.23 (s, OSi(*C*H$_3$)$_3$).

δ_{Si} (79 MHz, DMSO-d^6)/ppm: 10.56 (s, O*Si*(CH$_3$)$_3$) and 2.20 (s, NCH$_2$*Si*(CH$_3$)$_2$)

m/z (ESI$^+$): 243, [SiOSiC_1C_1im]$^+$, 100%, 766, [(SiOSiC_1C_1im)$_2$(NTf$_2$)]$^+$

m/z (ESI$^-$): 280, [NTf$_2$]$^-$, 100%, 803, [(SiOSiC_1C_1im)(NTf$_2$)$_2$]$^-$

Elemental analysis (calc) : %C = 27.64 (27.53), %H = 4.55 (4.43), %N = 7.92 (8.03)

1-methyl-3-heptamethyltrisiloxymethylimidazolium chloride, [(SiO)$_2$SiC_1C_1im]Cl

3-(chloromethyl)heptamethyl trisiloxane (59 ml, 0.2 mol) was added dropwise under N$_2$ to 1-methylimidazole (13.47 ml, 0.17 mol) in acetonitrile (50 ml), before heating at 75 °C for 10 days with stirring. After cooling the acetonitrile was removed by evaporation affording yellowish solid. The solid was washed with ethylacetate and dried *in vacuo* for 24 hours, affording [(SiO)$_2$SiC_1C_1im]Cl as a white crystalline solid (66.8 % yield).

δ_H (400 MHz, DMSO-d^6)/ppm: 9.01 (1H, s, NC*H*N), 7.74 (1H, s, NC*H*CHN), 7.53 (1H, s, NCHC*H*N), 3.87 (3H, s, NC*H*$_3$), 3.81 (2H, s, NC*H*$_2$Si), 0.17 (3H, s, NCH$_2$SiC*H*$_3$), 0.08 (18H, s, OSi(C*H*$_3$)$_6$).

δ_C (100 MHz, $CDCl_3$)/ppm: 139.21 (s, N*C*HN), 122.66 (s, N*C*HCHN), 122.34 (s, NCH*C*HN), 41.35 (s, $\mathrm{N}\mathit{C}\mathrm{H_2Si}$), 36.80 (s, $\mathrm{N}\mathit{C}\mathrm{H_3}$), 1.94 (s, $\mathrm{NCH_2Si(}\mathit{C}\mathrm{H_3))}$), -1.16 (s, $\mathrm{OSi(}\mathit{C}\mathrm{H_3)_3}$).

δ_{Si} (79 MHz, DMSO-d^6)/ppm: 10.49 (s, $\mathrm{NCH_2}\mathit{Si}\mathrm{CH_3}$), -32.04 (s, $\mathrm{(O}\mathit{Si}\mathrm{(CH_3)_3)}$

m/z (ESI^+): 317, $[(SiO)_2SiC_1C_1im]^+$, 100%

m/z (FAB^-): 35, $[Cl]^-$, 100%, 387, $[((SiO)_2SiC_1C_1im)(Cl)_2)]^-$

MP: 80 °C

Elemental analysis (predicted): %C = 40.9 (40.82), %H = 8.36 (8.28), %N = 7.90 (7.93)

1-methyl-3-heptamethyltrisiloxymethylimidazolium bis(trifluoromethanesulfonyl)imide, $[(SiO)_2SiC_1C_1im][NTf_2]$

As for the preparation of $[C_4C_1im][BF_4]$ except, lithium bis(trifluoromethanesulfonyl)imide (28.7 g, 0.1 mol) and $[(SiO)_2SiC_1C_1im]Cl$ (32 g, 0.09 mol) were used to afford $[(SiO)_2SiC_1C_1im][NTf_2]$ (95.4% yield) as a colourless liquid.

δ_H (400 MHz, DMSO-d^6)/ppm: 8.91 (1H, s, NC*H*N), 7.71 (1H, s, NC*H*CHN), 7.51 (1H, s, NCHC*H*N), 3.86 (3H, s, $\mathrm{NC}\mathit{H}\mathrm{_3}$), 3.80 (2H, s, $\mathrm{NC}\mathit{H}\mathrm{_2Si}$), 0.17 (3H, s, $\mathrm{NCH_2SiC}\mathit{H}\mathrm{_3}$), 0.08 (18H, s, $\mathrm{Si(C}\mathit{H}\mathrm{_3)_6}$).

δ_C (100 MHz, $CDCl_3$-d)/ppm: 135.94 (s, N*C*HN), 124.70 (q, $J_{C\text{-}F}$ = 319 Hz, $[\mathrm{N(SO_2}\mathit{C}\mathrm{F_3)_2]^-}$), 123.73 (s, N*C*HCHN), 123.14 (s, NCH*C*HN), 41.12 (s, $\mathrm{N}\mathit{C}\mathrm{H_2Si(CH_3)(OSi(CH_3)_3)_2}$), 36.12 (s, $\mathrm{N}\mathit{C}\mathrm{H_3}$), 1.52 (s, $\mathrm{NCH_2Si(}\mathit{C}\mathrm{H_3)OSi}$), -1.83 (s, $\mathrm{(OSi(}\mathit{C}\mathrm{H_3)_3)_2}$).

δ_{Si} (79 MHz, DMSO-d^6)/ppm 11.02 (s, $\mathrm{NCH_2}\mathit{Si}\mathrm{CH_3[(OSi(CH_3)_3]_2}$), 2.6 (s, $\mathrm{NCH_2SiCH_3((O}\mathit{Si}\mathrm{(CH_3)_3)_2}$)

m/z (ESI^+): 317, $[(SiO)_2SiC_1C_1im]^+$, 100%

m/z (ESI^-): 280, $[NTf_2]^-$, 100%, 877, $[(SiO)_2SiC_1C_1im)((NTf_2)_2)]^-$

Elemental analysis (calc) : %C = 28.24 (28.13), %H = 4.93 (4.89), %N = 6.95 (7.03)

1-butyl-1-methylpyrrolidinium chloride, $[C_4C_1pyrr]Cl$

1-chlorobutane (77 ml, 0.73 mol) was added dropwise under N_2, to a mixture of 1-methylpyrrolidine (72 ml, 0.7 mol) in acetonitrile (50 ml). The mixture was heated at

75 °C for 36 hours. The solution was cooled at room temperature then further cooled at 4 °C for 1 day. The acetonitrile was decanted, leaving a white solid. The white solid was washed with ethylacetate and dried *in vacuo* for 24 hours, affording [C_4C_1pyrr]Cl as a white crystalline solid (77.9% yield).

δ_H (400 MHz, DMSO-d^6)/ppm: 3.49 (6H, m, ring (CH_2)N(CH_2) and chain N$CH_2$$CH_2$), 3.02 (3H, s, N$CH_3$), 2.05 (4H, s, ring $NCH_2$$CH_2$), 1.65 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.27 (2H, m, $CH_2CH_2CH_3$), 0.89 (3H, t, J = 8 Hz, CH_2CH_3).

δ_C (100 MHz, DMSO-d^6)/ppm: 63.14 (s, ring CH_2NCH_2), 62.51 (s, chain NCH_2CH_2), 47.25 (s, NCH_3), 24.95 (s, ring NCH_2CH_2), 20.97 (s, chain NCH_2CH_2), 19.29 (s, CH_2CH_3), 13.51 (s, CH_2CH_3)

m/z (ESI$^+$): 142, ([C_4C_1py]$^+$, 100%), 319, [(C_4C_1py)$_2$Cl]$^+$

m/z (FAB$^-$): 35, [Cl]$^-$, 10%) , 212, [(C_4C_1py)Cl_2, 40%]$^-$

MP: 124 °C

Elemental analysis (calc) : %C = 60.70 (60.83), %H = 11.20 (11.34), %N = 7.94 (7.88)

1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, [C_4C_1pyrr][NTf_2]

As for the preparation of [C_4C_1im][BF_4] except [C_4C_1pyrr]Cl (34.0 g, 0.191 mol) in CH_2Cl_2 (50 cm^3) and lithium bis(trifluoromethanesulfonyl)imide (54.94 g, 0.191 mol) were employed to afford [C_4C_1pyrr][NTf_2], as a colourless liquid (91% yield)

δ_H (500 MHz, d^6-DMSO in capillary)/ppm: 2.94 (4H, m, CH_2NCH_2), 2.74 (m, 2H, NCH_2CH_2), 2.44 (s, 3H, NCH_3), 1.63 (4H, m, ring NCH_2CH_2), 1.19 (2H, m, $NCH_2CH_2CH_2$), 0.82 (2H, m, CH_2CH_3), 0.40 (t, J = 7.4, 3H, $NCH_2CH_2CH_2CH_3$).

δ_C (126 MHz, d6-DMSO in capillary) /ppm: 118.86 (q, J = 320.9, [$N(SO_2CF_3)_2$]$^-$), 63.07 (s, CH_2NCH_2), 63.02 (s, ring NCH_2CH_2, 46.69 (s, NCH_3), 24.18 (s, $NCH_2CH_2CH_2$), 20.04 (s, $NCH_2CH_2CH_2$), 18.14 (s, CH_2CH_3), 11.56 (s, CH_2CH_3).

m/z (ESI$^+$): 142 ([C_4C_1pyrr]$^+$, 45%), 564 ([(C_4C_1pyrr)$_2$ (NTf_2)]$^+$, 100%)

m/z (ESI-): 280 [NTf_2]$^-$, 100%), 702 ([(C_4C_1pyrr)(NTf_2)$_2$]$^-$, 10%)

Elemental analysis (calc): C 31.38% (31.28%), H 4.69% (4.77%), N 6.55% (6.63%).

1-butyl-1-methylpyrrolidinium dimethylphosphate, [$\mathrm{C_4C_1}$pyrr][$\mathrm{Me_2PO_4}$]

To a solution of 1-butylpyrrolidine (90.95 g, 715 mmol) in toluene (100 mL), trimethylphosphate (72.0 g, 616 mmol) was added drop-wise. The resulting mixture was stirred at 80 °C for 24 h. The resulting liquid was diluted with toluene (400 mL), upon which phase separation occurred. The toluene phase was separated off and the IL phase washed with toluene. The remaining solvent was evaporated under vacuum and [$\mathrm{C_4C_1}$pyrr][$\mathrm{Me_2PO_4}$] was obtained as a lightly yellow solid (74% yield).

δ_H (400 MHz, DMSO-d^6)/ppm: 3.51 (4H, m, $\mathrm{C}H_2\mathrm{NC}H_2$), 3.37 (2H, m, $\mathrm{NC}H_2$), 3.24 (6H, d, J = 10.3, $[(\mathrm{C}H_3)_2\mathrm{PO_4}]^-$), 3.01 (3H, s, $\mathrm{NC}H_3$), 2.06 (4H, m, ring $\mathrm{NCH_2C}H_2$) , 1.66 (2H, m, $\mathrm{NCH_2C}H_2\mathrm{CH_2}$), 1.30 (2H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 0.91 (3H, t, J = 7.4, $\mathrm{CH_2C}H_3$).

δ_C (101 MHz, DMSO-d^6)/ppm: 63.09 (s, $C\mathrm{H_2N}C\mathrm{H_2}$), 62.55 (s, ring $\mathrm{NCH_2}C\mathrm{H_2}$), 51.16 (d, J = 6.0, $[(C\mathrm{H_3})_2\mathrm{PO_4}]^-$), 47.13 (s, $\mathrm{N}C\mathrm{H_3}$), 24.97 (s, $\mathrm{N}C\mathrm{H_2CH_2}$), 20.98 (s, $\mathrm{NCH_2}C\mathrm{H_2}$), 19.30 (s, $C\mathrm{H_2CH_3}$), 13.49 (s, $\mathrm{CH_2}C\mathrm{H_3}$).

δ_P (162 MHz, DMSO-d^6)/ppm:1.39 (s, $[(\mathrm{CH_3})_2P\mathrm{O_4}]^-$).

m/z (ESI$^+$): 142 ([$\mathrm{C_4C_1}$pyrr]$^+$, 100%), 409 ([($\mathrm{C_4C_1}$pyrr)$_2$($\mathrm{Me_2PO_4}$)]$^+$, 10%)

m/z (ESI$^-$): 125 ([$\mathrm{Me_2PO_4}$]$^-$, 20%), 392 ([($\mathrm{C_4C_1}$pyrr)($\mathrm{Me_2PO_4}$)$_2$]$^+$, 10%)

Elemental analysis (calc): %C = 49.29 (49.43), %H = 11.34 (9.80), %N = 4.61 (5.24).

8-Methyl-1,8-diazabicycloundecene trifluoromethylsulfate , [$\mathrm{C_1}$DBU][OTf]

A solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (62.39 g, 410 mmol) in toluene (70 ml) was cooled to -78 °C and methyltriflate (50.00 g, 305 mmol) was slowly distilled in directly. The resulting solution was allowed to come to room temperature and stirred over night, after which the solution had separated into two phases. The toluene phase was removed and the IL phase washed with toluene. The solvent was removed *in vacuo*, and yellow free-flowing liquid obtained. The measured Kamlet-Taft values with $\alpha = 0.7$ indicated the presence of residual [H−DBU]. The product was diluted with dichloromethane (700 mL) and washed with aqueous KOH solution (0.01 mol/L, 1 mL) and then washed with water (1 mL) until base free. The solvent was removed and the product filtered through a double layer of basic (top) and acidic (bottom) alumina. These steps were repeated until the Kamlet-Taft α value had stabilized. The product was obtained as a pale yellow free-flowing liquid (64% yield).

δ_H (400 MHz, DMSO-d^6) /ppm: 3.62 (m, 2H, $\mathrm{NC}H_2\mathrm{C_4H_8N}$), 3.45 (t, J = 5.9, 2H, $\mathrm{NC}H_2\mathrm{C_2H_4N}$), 3.41 (t, J = 5.8, 2H, $\mathrm{NC}H_2\mathrm{C_2H_4N}$), 3.20 (s, 3H, $\mathrm{NC}H_3$), 2.84 (m, 2H, Cq $CH_2C_4H_8N$), 1.97 (m, 2H, $NCH_2CH_2CH_2N$), 1.65 (m, 6H, $CH_2C_3H_6CH_2N$).

δ_C (101 MHz, DMSO-d^6)/ppm: 166.05 (s, Cq), 120.70 (q, J = 323.2, [CF_3SO3]$^-$), 53.87 (s, $NCH_2C_4H_8$), 48.18 (s, $NCH_2C_2H_4N$), 48.11 (s, $NCH_2C_2H_4N$), 40.56 (s, NCH_3), 27.80 (s, $CH_2C_3H_6CH_2$), 27.47 (s, Cq$CH_2C_4H_8N$), 25.66 (s, $CH_2C_3H_6CH_2$), 21.75 (s, $CH_2C_3H_6CH_2$), 19.41 (s, $NCH_2CH_2CH_2N$).

m/z (ESI$^+$): 167 ([C_1DBU]$^+$, 100%), 483 ([(C_1DBU)$_2$(OTf)], 10%)

m/z (ESI$^-$): 149 ([OTf]$^-$, 100%), 465 ([(C_1DBU)(OTf)$_2$]$^-$, 55%)

Elemental analysis (calc): C 41.80% (41.76%), H 5.92% (6.05%), N 8.75% (8.86%).

1-Methyl-1,8-diazabicycloundecene methylsulphate, [C_1DBU][$MeSO_4$]

To an ice cooled solution of DBU (98.34 g, 646 mmol) in toluene (120 ml), dimethylsulphate (78.77 g, 625 mmol) was slowly added dropwise. The resulting mixture was stirred 17 h, after which the solution had separated into two phases.

The toluene phase was separated and the ionic liquid phase washed with toluene. The remaining solvent was removed *in vacuo*, and a light yellow, free-flowing liquid obtained. This liquid solidified upon repeated extraction with toluene, to give [C_1DBU][$MeSO_4$] as a white solid (98% yield).

δ_H (400 MHz, DMSO-d^6)/ppm: 3.63 (m, 2H, $NCH_2C_4H_8N$), 3.47 (t, J = 5.9, 2H, $NCH_2C_2H_4N$), 3.42 (t, J = 5.8, 2H, $NCH_2C_2H_4N$), 3.37 (s, 3H, [CH_3SO_4]$^-$), 3.20 (s, 3H, NCH_3), 2.84 (m, 2H, Cq$CH_2C_4H_8N$), 1.97 (m, 2H, $NCH_2CH_2CH_2N$), 1.64 (m, 6H, $CH_2C_3H_6CH_2N$).

δ_C (101 MHz, DMSO-d^6)/ppm: 166.03 (s, Cq), 53.84 (s, $NCH_2C_4H_8$), 52.81 (s, [CH_3SO_4]$^-$), 48.13 (s, $NCH_2C_2H_4N$), 48.08 (s, $NCH_2C_2H_4N$), 40.55 (s, NCH_3), 27.83 (s, $CH_2C_3H_6CH_2$), 27.46 (s, Cq $CH_2C_4H_8N$), 25.65 (s, $CH_2C_3H_6CH_2$), 21.73 (s, $CH_2C_3H_6CH_2$), 19.43 (s, $NCH_2CH_2CH_2N$).

m/z (ESI$^+$): 167 ([C_1DBU]$^+$, 100%), 445 ([(C_1DBU)$_2$($MeSO_4$)]$^+$, 10%)

m/z (ESI$^-$): 111 ([$MeSO_4$]$^-$, 100%)

Elemental analysis (calc): C% 47.63 (47.46), H% 7.86 (7.97), N% 9.99 (10.06).

1-pentyl-1-methylpyrrolidium chloride, [C_5C_1pyrr]Cl.

1-methylpyrrolidine (80 ml, 0.9 mol) was added under N_2 to a mixture of 1-chloropentane (120 ml, 1 mol) and acetonitrile (100 ml) and heated at 75 °C for five days. The reaction mixture was cooled at room temperature for a day. 100 ml ethylacetate was added to the flask, precipitating a white solid. The solvent was removed and the white solid was washed with ethylacetate and dried *in vacuo* for 24 hours at 45 °C, affording [C_5C_1pyrr]Cl as a white crystalline solid.

δ_H (400 MHz, DMSO-d^6)/ppm: 3.50 (4H, m, CH_2NCH_2), 3.33 (2H, m, chain NCH_2CH_2), 2.99 (3H, s, NCH_3), 2.07 (4H, s, ring $N(CH_2)_2(CH_2)_2$), 1.68 (2H, m, $NCH_2CH_2CH_2$), 1.28 (4H, m, chain $NCH_2CH_2CH_2CH_2CH_3$) and 0.89 (3H, t, J = 8 Hz, CH_2CH_3).

δ_C (100 MHz, DMSO-d^6) / ppm: 63.29 (s, ring $N(CH_2)_2$), 62.90 (s, $NCH_2(CH_2)_3CH_3$), 47.35 (s, NCH_3), 28.06 (s, ring $N(CH_2)_2(CH_2)_2$), 22.64 (s, $NCH_2CH_2(CH_2)_2CH_3$), 21.68 (s, $N(CH_2)_2CH_2CH_2CH_3$), 21.04 (s, $N(CH_2)_3CH_2CH_3$) and 13.77 (s, CH_2CH_3).

m/z (ESI$^+$): 347, [(C_5C_1pyrr)$_2$Cl]$^+$ and 156, ([C_5C_1pyrr]$^+$, 100%)

Elemental analysis (calc) : %C = 61.12 (62.64), %H = 11.05 (11.56), %N = 7.34 (7.31)

1-pentyl-1-methylpyrrolidium bis(trifluoromethanesulfonyl)imide, [C_5C_1pyrr][NTf_2].

As for the preparation of [C_4C_1im][BF_4] except, lithium bis(trifluoromethanesulfonyl)imide (100 g, 0.35 mol) and [C_5C_1pyrr]Cl (56.44 g, 0.3 mol) were used to afford [C_5C_1pyrr][NTf_2] as a colourless liquid.

δ_H (400 MHz, DMSO-d^6) / ppm: 3.50 (4H, m, ring CH_2NCH_2), 3.30 (2H, m, chain NCH_2CH_2), 2.98 (3H, s, NCH_3), 2.09 (4H, s, ring $N(CH_2)_2(CH_2)_2$), 1.68 (2H, m, $NCH_2CH_2(CH_2)_2CH_3$), 1.30 (4H, m, $N(CH_2)_2CH_2CH_2CH_3$) and 0.89 (3H, t, J = 8 Hz, CH_2CH_3).

δ_C (100 MHz, DMSO-d^6) / ppm: 119.60 (q, $J_{C\text{-}F}$ = 320 Hz, $[N(SO_2CF_3)_2]^-$), 63.51 (s, ring $N(CH_2)_2$), 63.28 (s, chain NCH_2CH_2), 47.51 (s, NCH_3), 28.04 (s, ring $N(CH_2)_2(CH_2)_2$), 22.70 (s, chain $NCH_2CH_2CH_2$), 21.67 (s, chain $N(CH_2)_2CH_2CH_2CH_3$), 21.09 (s, chain $N(CH_2)_3CH_2CH_3$) and 13.58 (s, chain CH_2CH_3).

m/z (ESI$^+$): 156, ([C_5C_1pyrr]$^+$, 100%), 592, ([(C_5C_1pyrr)$_2$$NTf_2$]$^+$)

m/z (ESI$^-$): 280, ([NTf_2]$^-$, 100%), 716, [(C_5C_1pyrr)[(NTf_2)$_2$]$^-$

Elemental analysis (calc) : %C = 33.15 (33.02), %H = 5.15 (5.08), %N = 6.37 (6.42)

1-(2-ethoxyethyl)-1-methylpyrrolidinium chloride, [(C_2OC_2)C_1pyrr]Cl

In a 250 ml flask equipped with reflux condenser 1-methylpyrrolidine (52 ml, 0.5 mol) was added under N_2 to a mixture of 2-chloroethyl ethyl ether (80 ml, 0.73 mol) and acetonitrile (100 ml). The solution was heated at 75 °C for five days while stirring. Then, the flask was cooled at room temperature for a day. 100 ml ethylacetate was added to the flask and white solid precipitated. The solvent was removed via cannula. The white solid was washed with ethylacetate and dried *in vacuo* for 24 hours at 45 °C, affording $[(C_2OC_2)C_1pyrr]Cl$ as a white solid (92% yield)

δ_H (400 MHz, DMSO-d^6)/ppm: 3.78 (2H, s, $NCH_2C\mathit{H}_2OCH_2CH_3$), 3.60 (6H, m, $NC\mathit{H}_2CH_2OCH_2CH_3$ and $N(C\mathit{H}_2)_2$), 3.49 (2H, q, J = 8 Hz, $NCH_2CH_2OC\mathit{H}_2CH_3$), 3.07 (3H, s, $NC\mathit{H}_3$), 2.06 (4H, s, $N(CH_2)_2(C\mathit{H}_2)_2$), 1.12 (3H, t, J = 8 Hz, $N(CH_2)_2OCH_2C\mathit{H}_3$).

δ_C (100 MHz, DMSO-d^6)/ppm: 65.55 (s, $N(CH_2)_2O\mathit{C}H_2CH_3$), 63.96 (s, $NCH_2\mathit{C}H_2OCH_2CH_3$ and $N(\mathit{C}H_2)_2$), 61.87 (s, $N\mathit{C}H_2CH_2OCH_2CH_3$), 47.83 (s, $N\mathit{C}H_3$), 20.80 (s, $N(CH_2)_2(\mathit{C}H_2)_2)$), 14.89 (s, $N(CH_2)_2OCH_2\mathit{C}H_3$).

m/z (ESI$^+$): 158, ($[C_2OC_2C_1pyrr]^+$, 100%), 351, ($[(C_2OC_2C_1pyrr)_2Cl]^+$)

m/z (FAB$^-$): 35, ($[Cl]^-$, 100%), 228, ($[(C_2OC_2C_1pyrr)(Cl)_2]^-$)

MP: 75 °C

Elemental analysis (calc) : %C = 54.56 (55.80), %H = 11.33 (10.41), %N = 7.00 (7.32)

1-(2-ethoxyethyl)-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, $[(C_2OC_2)C_1pyrr][NTf_2]$

As for the preparation of $[C_4C_1im][BF_4]$ except, lithium bis(trifluoromethanesulfonyl)imide (143.54 g, 0.5mol) and $[(C_2OC_2)C_1pyrr]Cl$ (69.28 g, 0.35mol) were used to afford $[(C_2OC_2)C_1pyrr][NTf_2]$ (72 % yield) as a colourless liquid.

δ_H (400 MHz, DMSO-d^6)/ppm : 3.79 (2H, s, $NCH_2C\mathit{H}_2OCH_2CH_3$), 3.53 (8H, m, $NC\mathit{H}_2CH_2OCH_2CH_3$, $N(C\mathit{H}_2)_2$ and $NCH_2CH_2OC\mathit{H}_2CH_3$), 3.04 (3H, s, $NC\mathit{H}_3$), 2.09 (4H, s, $N(CH_2)_2(C\mathit{H}_2)_2$), 1.14 (3H, t, J = 8 Hz, $N(CH_2)_2OCH_2C\mathit{H}_3$).

δ_C (100 MHz, DMSO-d^6)/ppm : 119.56 (q, $J_{C\text{-}F}$ = 320 Hz, $[N(SO_2\mathit{C}F_3)_2]^-$), 65.71 (s, $N(CH_2)_2O\mathit{C}H_2CH_3$), 64.28 (s, $NCH_2\mathit{C}H_2OCH_2CH_3$), 63.94 (s, ring $N(\mathit{C}H_2)_2$), 62.30 (s, $N\mathit{C}H_2CH_2OCH_2CH_3$), 48.06 (s, $N\mathit{C}H_3$), 20.87 (s, ring $N(CH_2)_2(\mathit{C}H_2)_2)$), 14.71 (s, $N(CH_2)_2OCH_2\mathit{C}H_3$).

m/z (ESI$^+$): 158, ($[(C_2OC_2)C_1pyrr]^+$, 100%), 596, ($[((C_2OC_2)C_1pyrr)_2(NTf_2)]^+$)

m/z (ESI$^-$): 280, ($[NTf)_2^-$, 100%, 718), $[((C_2OC_2)C_1pyrr)_2(NTf_2)]^-$)

Elemental Analysis (calc) : %C = 30.27 (30.14), %H = 4.50 (4.60), %N = 6.31 (6.39)

1-methylpentamethyldisiloxy-1-methylpyrrolidinium chloride, $[(SiOSi)C_1C_1pyrr]Cl$.

Pentamethyldisiloxymethyl chloride (56.7 ml, 0.28 mol) was added dropwise under N_2 to 1-methylpyrrolidine (26 ml, 0.25 mol) in acetonitrile (100ml), the mixture was heated at 85°C for 36 hours. The flask was allowed to cool at room temperature and further cooled to -14°C for 2 days. Acetonitrile was carefully decanted from the white solid product which was washed with ethylacetate and dried *in vacuo* for 24 hours, affording $[(SiOSi)C_1C_1pyrr]Cl$ as a white crystalline solid (26% yield).

δ_H (400 MHz, DMSO-d^6)/ppm: 3.50 (4H, m, ring $C\mathit{H}_2NC\mathit{H}_2$), 3.11 (2H, s, $NC\mathit{H}_2Si(CH_3)_2$), 3.07 (3H, s, $NC\mathit{H}_3$), 2.10 (4H, s, ring $NCH_2C\mathit{H}_2$), 0.28 (6H, s, $NCH_2Si(C\mathit{H}_3)_2OSi(CH_3)_3$) and 0.12 (9H, s, $NCH_2Si(CH_3)_2OSi(C\mathit{H}_3)_3$).

δ_C (100 MHz, DMSO-d^6)/ppm: 66.74 (s, $\mathit{C}H_2N\mathit{C}H_2$), 56.25 (s, $N\mathit{C}H_3$), 50.65 (s, $N\mathit{C}H_2Si(CH_3)_2$), 21.16 (s, ring $NCH_2\mathit{C}H$), 1.79 (s, $Si(\mathit{C}H_3)_3$), 1.21 (s, $NCH_2Si(\mathit{C}H_3)_2$).

δ_{Si} (79 MHz, DMSO-d^6) / ppm: 11.04 (s, $NCH_2\mathit{Si}(CH_3)_2$), 0.99 (s, $\mathit{Si}(CH_3)_3$)

m/z (ESI^+): 246, ($[(SiOSi)C_1C_1pyrr]^+$, 100%)

m/z (FAB^-): 35, ($[Cl]^-$, 100%), 316, ($[((SiOSi)C_1C_1pyrr)Cl_2]^-$)

MP: 196 °C.

Elemental analysis (calc): %C = 46.9 (46.86), %H = 10.1 (10.01), %N = 4.85 (4.97)

1-methylpentamethyldisiloxy-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide $[(SiOSi)C_1C_1pyrr][NTf_2]$

As for the preparation of $[C_4C_1im][BF_4]$ except, lithium bis(trifluoromethanesulfonyl)imide (34.45 g, 0.12 mol) and $[(SiOSi)C_1C_1pyrr]Cl$ (18 g, 0.09 mol) were used to afford $[(SiOSi)C_1C_1pyrr][N(Tf)_2]$ (62% yield) as a colourless liquid at 30 °C.

δ_H (400 MHz, DMSO-d^6)/ppm: 3.50 (4H, m, ring $C\mathit{H}_2NC\mathit{H}_2$), 3.08 (2H, s, $NC\mathit{H}_2Si(CH_3)_2$), 3.07 (3H, s, $NC\mathit{H}_3$), 2.11 (4H, s, ring $NCH_2C\mathit{H}_2$), 0.28 (6H, s, $NCH_2Si(C\mathit{H}_3)_2O(CH_3)_3$), 0.12 (9H, s, $OSi(C\mathit{H}_3)_3$).

δ_C (100 MHz, DMSO-d^6)/ppm: 124.29 (q, $J_{C\text{-}F}$ = 320 Hz, $[N(SO_2\mathit{C}F_3)_2]^-$), 66.83 (s, ring $\mathit{C}H_2N\mathit{C}H_2$), 56.37 (s, $N\mathit{C}H_3$), 50.69 (s, $N\mathit{C}H_2Si(CH_3)_2$), 21.13 (s, ring $NCH_2\mathit{C}H_2$), 1.59 (s, $OSi(\mathit{C}H_3)_3$), 1.02 (s, $NCH_2Si(\mathit{C}H_3)_2$).

δ_{Si} (79 MHz, DMSO-d^6)/ppm: 11.17 (s, $NCH_2\mathit{Si}(CH_3)_2$), 0.91 (s, $O\mathit{Si}(CH_3)_3$)

m/z (ESI^+): 246, ($[(SiOSi)C_1C_1pyrr]^+$, 100%), 772, ($[((SiOSi)C_1C_1pyrr)_2(N(Tf)_2)]^+$)

m/z (ESI$^-$): 208, $[N(Tf)_2]^-$, 100%), 806, ($[((SiOSi)C_1C_1pyrr)(NTf_2)_2]^-$)

Elemental analysis (calc) : %C = 29.77 (29.65), % H = 5.42 (5.36), %N = 5.27 (5.32)

Triethanolmethylammonium triflate, $[(HO^2C_2)_3C_1N][OTf]$

To an ice cooled solution of triethanolamine (90.00 g, 603 mmol) in toluene (100 ml), freshly distilled methyl trifluoromethanesulfonate (96.68 g, 589 mmol) was slowly added dropwise. The resulting mixture was stirred for 2 h, after which the solution had separated into two phases. The organic phase was separated off and the ionic liquid phase washed with toluene and the remaining solvent was removed *in vacuo*. Residual triethanolamine was removed from the product by continuous extraction with $CHCl_3$ for 24h. Remaining solvent was removed in vacuo and $[(HO^2C_2)_3C_1N][OTf]$ was obtained as a lightly orange, free-flowing liquid (81% yield).

δ_H (400 MHz, DMSO-d^6)/ppm: 5.21 (3H, t, J = 4.9, O*H*), 3.83 (6H, s, CH_2OH), 3.53 (6H, m, NCH_2CH$_2$), 3.12 (3H, s, NCH_3).

δ_C (101 MHz, DMSO-d^6)/ppm: 120.77 (q, J = 322.1, $[CF_3SO_3]^-$), 64.33 (s, N*C*H$_2$CH$_2$), 55.05 (s, *C*H$_2$OH), 49.81 (s, NCH_3).

m/z (ESI$^+$): 164 ($[(HO^2C_2)_3C_1N]+$, 100%).

m/z (ESI$^-$): 149 ($[OTf]^-$, 70%), 462 ($[((HO^2C_2)_3C_1N)(OTf)_2]^-$, 100%).

Elemental analysis (expected): C% 30.74 (30.67), H% 5.63 (5.79), N% 4.39 (4.47).

Triethanolmethylammonium methylsulfate, $[(HO^2C_2)_3C_1N][MeSO_4]$

To an ice cooled biphasic mixture of triethanolamine (74.2 g, 497 mmol) and ethylacetate (210 ml), dimethyl sulfate (63.8 g, 506 mmol) was added drop-wise under vigorous stirring. The liquid was stirred for 2h. The organic phase was separated and the ionic liquid phase extracted with toluene. The remaining solvent was removed in vacuo. Residual triethanolamine was removed from the product by continuous extraction with $CHCl_3$ until no starting material was found. Remaining solvent was removed *in vacuo* and $[(HO^2C_2)_3C_1N][MeSO_4]$ was obtained as a lightly orange, free-flowing liquid (71% yield).

δ_H (400 MHz, DMSO-d^6)/ppm: 5.20 (3H, s, O*H*), 3.83 (6H, s, CH_2OH), 3.52 (6H, m, NCH_2CH$_2$), 3.37 (3H, s, $[CH_3OSO_3]^-$), 3.13 (3H, s, NCH_3).

δ_C (101 MHz, DMSO-d^6)/ppm: 64.24 (s, N*C*H$_2$CH$_2$), 55.01 (s, *C*H$_2$OH), 53.15 (s, [*C*H$_3$OSO$_3$]$^-$), 49.73 (s, N*C*H$_3$).

m/z (LSIMS$^+$): 164 ($[(HO^2C_2)_3C_1N]^+$, 100%).

m/z (LSIMS$^-$): 111 ($[MeSO_4]^-$, 100%), 386 ($[((HO^2C_2)_3C_1N)(MeSO_4)_2]^-$, 10%).

Elemental analysis (calc): C% 35.05 (34.90), H% 7.79 (7.69), N% 5.09 (5.09).

1,2,4-trimethylpyrazolium triflate, [$C_1C_1C_1$pz][OTf]

Methyl trifluoromethanesulfonate (50.00 g, 305 mmol) was distilled directly into an ice cold flask of 1,3-dimethylpyrazole (100.54 g, 1046 mmol) with vigorous stirring. The resulting liquid was stirred for an hour and extracted with toluene first in a separating funnel (6 × 100 ml) and then for 24 h in a continuous extractor. The remaining solvent was removed *in vacuo* and the product filtered through a layer of basic alumina to afford [$C_1C_1C_1$pz][OTf].

δ_H (400 MHz, DMSO-d^6)/ppm: 8.23 (s, 2H, C*H*), 4.05 (s, 6H, NC*H*$_3$), 2.08 (s, 3H, CC*H*$_3$).

δ_C (101 MHz, DMSO)/ppm: 136.38 (s, *C*H), 120.75 (q, J = 322.9, [*C*F$_3$SO$_3$]$^-$), 116.62 (s, *C*CH$_3$), 36.24 (s, N*C*H$_3$), 8.23 (s, C*C*H$_3$).

m/z (ESI$^+$): 111 ($[C_1C_1C_1pz]^+$, 50%), 371 ($[(C_1C_1C_1pz)_2(OTf)]^+$, 100%)

m/z (ESI$^-$): 149 ($[OTf]^-$, 100%), 409 ($[(C_1C_1C_1pz)(OTf)_2]^-$, 30%)

Elemental analysis (calc): C% 32.28 (32.31), H% 4.29 (4.26), N% 10.84 (10.76).

1-methylpyridinium triflate, [C_1pyr][OTf]

Methyl trifluoromethanesulfonate (50.00 g, 305 mmol) was distilled directly into an ice cooled flask of pyridinium (80.63 g, 1019 mmol) under vigorous stirring. The resulting liquid was stirred for an hour and extracted with toluene. The remaining solvent was removed in vacuo and [C_1pyr][OTf] was obtained as a white crystalline solid (62.77g, 85%).

δ_H (400 MHz, DMSO-d^6)/ppm: 8.97 (2H, m, N(C*H*CH)$_2$CH), 8.57 (1H, t, J = 7.8, N(CHCH)$_2$C*H*), 8.12 (2H, m, N(CHC*H*)$_2$CH), 4.34 (3H, s, NC*H*$_3$).

δ_C (101 MHz, DMSO-d^6)/ppm: 145.63 (s, N(*C*HCH)$_2$CH), 145.10 (s, N(CHCH)$_2$*C*H), 127.73 (s, N(CH*C*H)$_2$CH), 47.95 (s, N*C*H$_3$).

m/z (LSIMS$^+$): 94 ($[C_1pyr]^+$, 100%), 337 ($[(C_1pyr)_2(OTf)]^+$, 5%)

m/z (LSIMS$^-$): 149 ($[OTf]^-$, 100%), 392 ($[(C_1pyr)(OTf)_2]^+$, 10%)

Elemental analysis (calc): C% 34.72 (34.57), H% 3.18 (3.32), N% 5.60 (5.76).

Tetrabutylphosphonium Glycinate, [$(C_4)_4P$][Gly]

Sodium glycinate (4.36 g) and tetrabutylphosphonium hydroxide (15 g) were added to water 20 ml) and stirred for 4 hours. The resulting solution was dried in vacuo to give a clear viscous liquid and a white solid. The mixture was dissolved in DCM, the white powder filtered off and the DCM evaporated off. This gave [$(C_4)_4P$][Gly] as a viscous oil with a slight yellow colour (3.02, 20%).

δ_H (400 mHz, DMSO-d^6)/ppm: 3.34 (s, NH_2CH_2COOH), 2.22 (m, PCH_2), 1.58 (m, PCH_2CH_2), 1.4 (m, $PCH_2CH_2CH_2$), 0.9 (m, $PCH_2CH_2CH_2CH_2$).
m/z (LSIMS$^+$) 139 (100%, [$(C_4)_3P$]$^+$), 240 (2%, [$(C_4)_3P$]$^+$), 295 (100%, [$(C_4)_4P$]$^+$).

Kamlet-Taft LSER Method

While the process of interpreting a Kamlet-Taft LSER is rather subtle, the determination of the coefficients in the fit is much more straightforward. Unfortunately, persistent errors occur in the literature due to a basic misunderstanding of the (rather complicated) underlying statistical meaning of the fit parameters.

For example, the coefficient of determination (R^2) is commonly used as a basic means of determining the quality of a 'fit' when a linear correlation is employed. For a single descriptor (the familiar $y = m*x + b$), R^2 is very simple to interpret – the higher the value of R^2 the more closely the points lie to the fit line, and therefore the more likely the fitting parameter is deterministic. For multivariate linear regression, such as an LSER, there is a fundamental difference – the more parameters that are employed, the higher the value of R^2, *regardless of whether those parameters are actually deterministic, physically meaningful or even real*. In the words of Hill, "with six constants you can fit a charging rhinoceros." (Hill Jr., C. G., *An Introduction to Chemical Engineering Kinetics &Reactor Design*, Wiley, New York (1977).

Because of this, R^2 can no longer serve as a catch-all indicator of a parameter's significance. Instead, we have commonly used a set of simple statistical tests to determine the significance of each of our adjustable parameters. In the *simplest* Kamlet-Taft LSER's ($XYZ = XYZ_0 + a*\alpha + b*\beta + s*\pi^*$), there are **four** parameters: a, b, s, and the intercept (XYZ_0). It is important to determine the statistical significance of each individual parameter, but due to co-variance this cannot always be done independently. Therefore, we have chosen to perform these fits using several statistical tests for reference, such as the *p*-value, *t*-value and 95% confidence interval. We analyze for co-variance in larger data sets, but in the smaller data sets more typical of synthetic chemistry ($n < 20$) this is rarely possible.

If we use for example the *p*-value as a test of significance, we must first set a maximum *p*-value which to indicate significance ($p < 0.05$ is typical for our smaller data sets; $p < 0.01$ for larger ones). However, it is still important to determine the significance of each parameter *in the presence and only in the presence of all other statistically significant parameters*. It is further important to note that *this test should include the intercept*.

Our normal procedure is to first perform a multivariate linear regression to determine the coefficients for all 3 variables $\{\alpha, \beta, \pi^*\}$. If all 3 prove statistically significant ($p < 0.01$), then the correlation is accepted. If one or more values reveal a *p*-value of greater than 0.01, then the individual "pairs" must next be investigated. It is very important to note that *one cannot simply reject all parameters with* $p > 0.01$. This is due to possible masking effects between the variables, or other factors such as co-variance. It is quite often the case that variables which are actually statistically significant test as insignificant in the presence of highly uncorrelated variables.

The 3 "pairs" are then tested for significance ($\{\alpha, \beta\}$, $\{\alpha, \pi^*\}$, $\{\beta, \pi^*\}$). If one of these sets provides *p*-values for all parameters less than 0.01, then we accept that set for our correlation. If not, then we next test all three variables individually ($\{\alpha\}$, $\{\beta\}$, $\{\pi^*\}$). Once again, if $p < 0.01$ for all members of one of these sets, then that set is accepted for the correlation. Regardless of which correlation gets accepted (one, two or 3 variables) it is also important to determine the significance of the constant term – if it has a *p*-value greater than 0.01 (or if 0 is contained in the confidence interval) then the correlation should be performed with the constant set to zero. Otherwise it is included.

If no set of variables has proven significant, then there is no existing Kamlet-Taft LSER that describes the phenomenon being observed, and a new set of variables needs to be considered. *It is still possible that one or more members of the Kamlet-Taft variable set is significant*, however, and the new set of variables should include the Kamlet-Taft descriptors once again.

Kamlet-Taft LSER Worked Example. The following rate data are taken from Ranieri, G.; Hallett, J. P.; Welton, T. *Ind. Eng. Chem. Res.* **2008**, *47*, 638.

Solvent	**ln k_2**	**α**	**β**	**π^***
CH_2Cl_2	-2.69	0.1	0.1	0.7
CH_3CN	-4.69	0.2	0.4	0.7
THF	-6.44	0	0.6	0.6
CH_3OH	-7.78	1	0.7	0.6
C_7H_8	-5.01	0	0.1	0.5
[bmpy][$N(CF_3SO_2)_2$]	-2.42	0.4	0.3	1
[bmim][$N(CF_3SO_2)_2$]	-3.69	0.6	0.2	1
[bmpy][CF_3SO_3]	-4.72	0.4	0.5	1
[bmim][CF_3SO_3]	-4.42	0.6	0.5	1

If we perform a linear regression using all variables, we obtain:

$$\ln k_2 = -5.98(\mathit{0.0035}) - 1.02(\mathit{0.36})*\alpha - 5.67(\mathit{0.014})*\beta + 4.82(\mathit{0.016})*\pi^*$$

The numbers in italics represent the *p*-values for each coefficient. Since not all coefficients proved significant, we must then perform a regression using each pair of variables

$$\ln k_2 = -2.30(\mathit{0.041}) + 0.83(\mathit{0.60})*\alpha - 7.41(\mathit{0.025})*\beta$$
$$\ln k_2 = -8.46(\mathit{0.0022}) - 3.11(\mathit{0.078})*\alpha + 6.40(\mathit{0.030})*\pi^*$$
$$\ln k_2 = -5.50(\mathit{0.0020}) - 6.55(\mathit{0.0021})*\beta + 4.12(\mathit{0.012})*\pi^*$$

It is clear that only the third relationship contains all significant parameters. This establishes that our rate constants depend only upon $\{\beta,\pi^*\}$.

It is worth noting that the coefficient of α varies wildly in magnitude and sign across the correlations, further indicating its insignificance. Also, the coefficients for β and π^* are affected by the presence of the insignificant variable, as their *p*-values are increased by the presence of α in the correlation, falsely decreasing their apparent significance.