Supplementary Material

Figure 1S: Dependence of the ln (*endo/exo*) selectivity for the reaction of cyclopentadiene with acrolein in different solvents with different solvent parameters: a) E_T^N, b) β, c) δ^2 and d) V_M

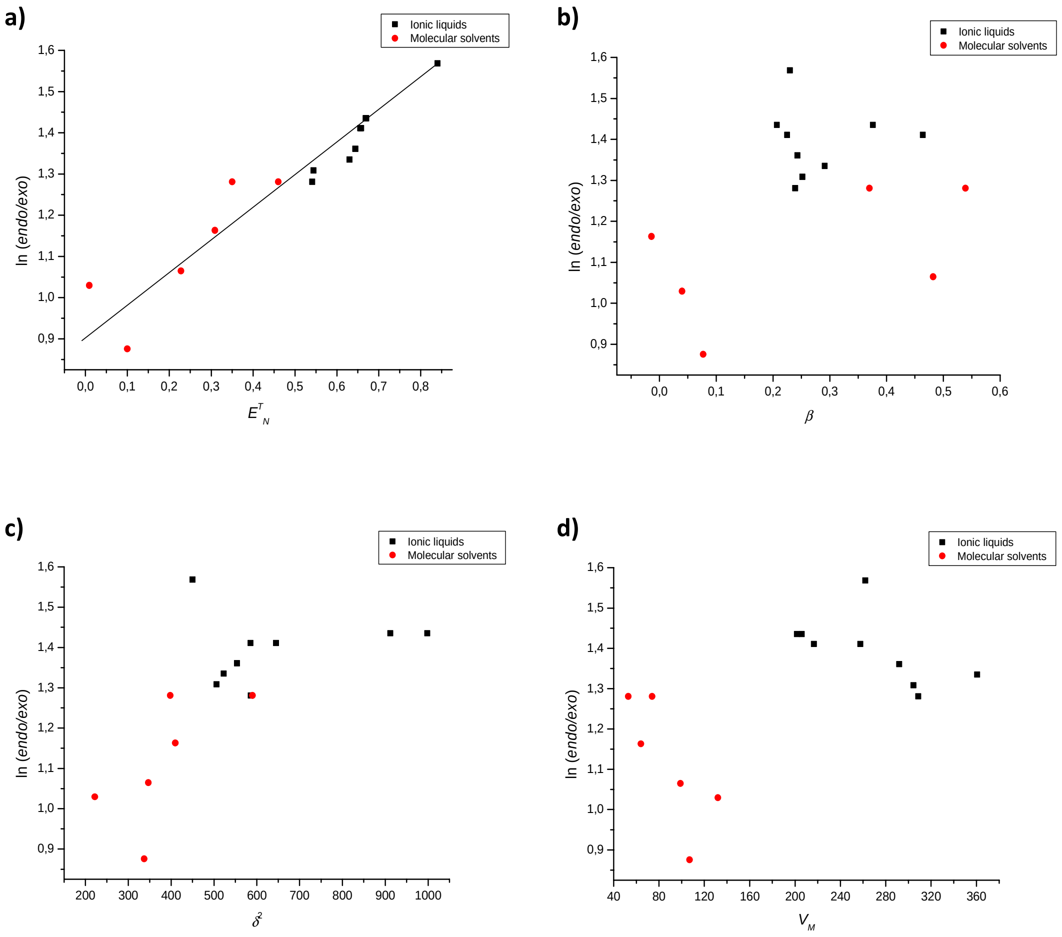


Figure 2S: Single relationships of ln (*endo/exo*) for the reaction of cyclopentadiene with methyl acrilate in different solvents with different solvent parameters: a) π*, b) E_T^N, c) β, d) δ^2 and e) ΔU

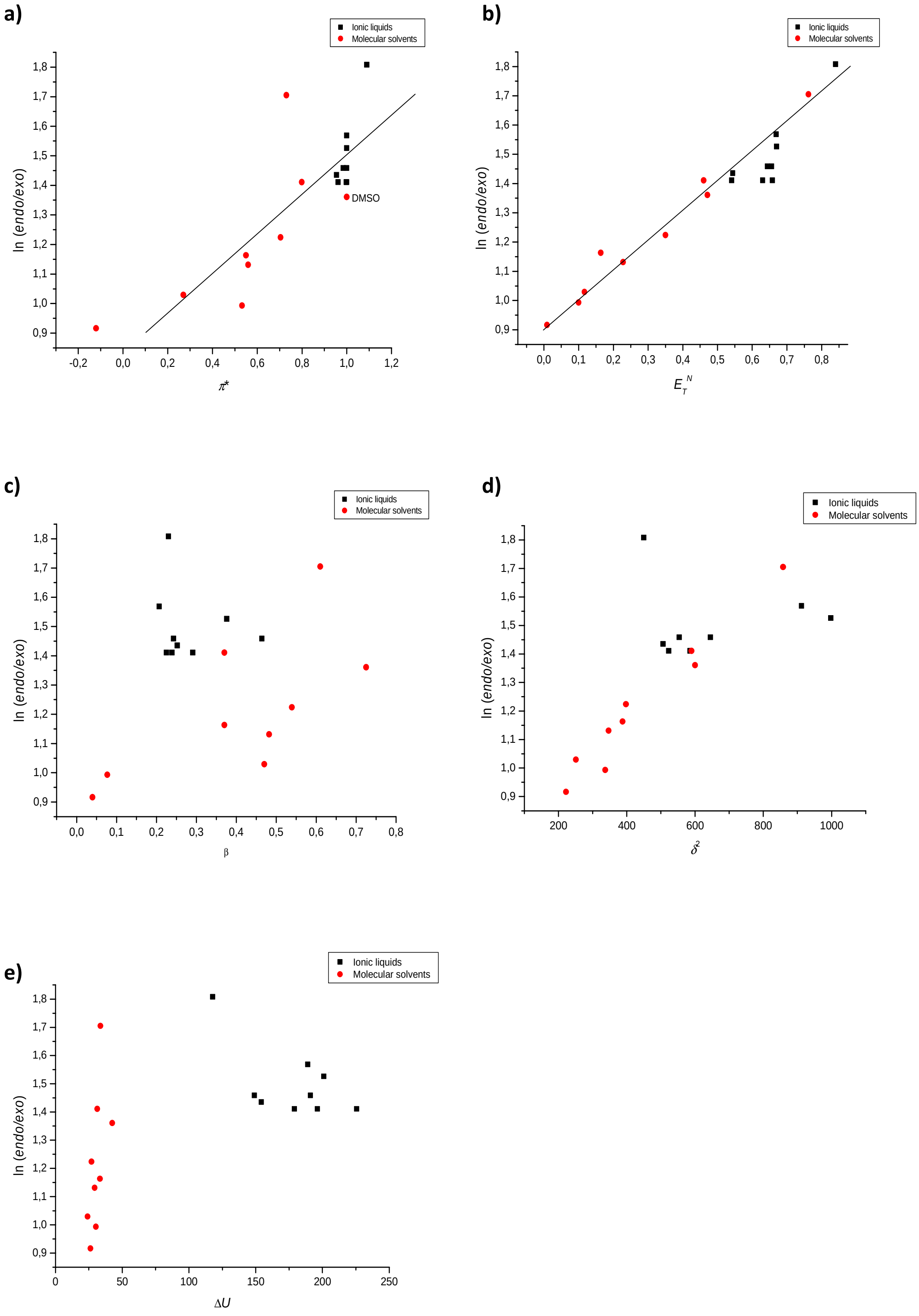
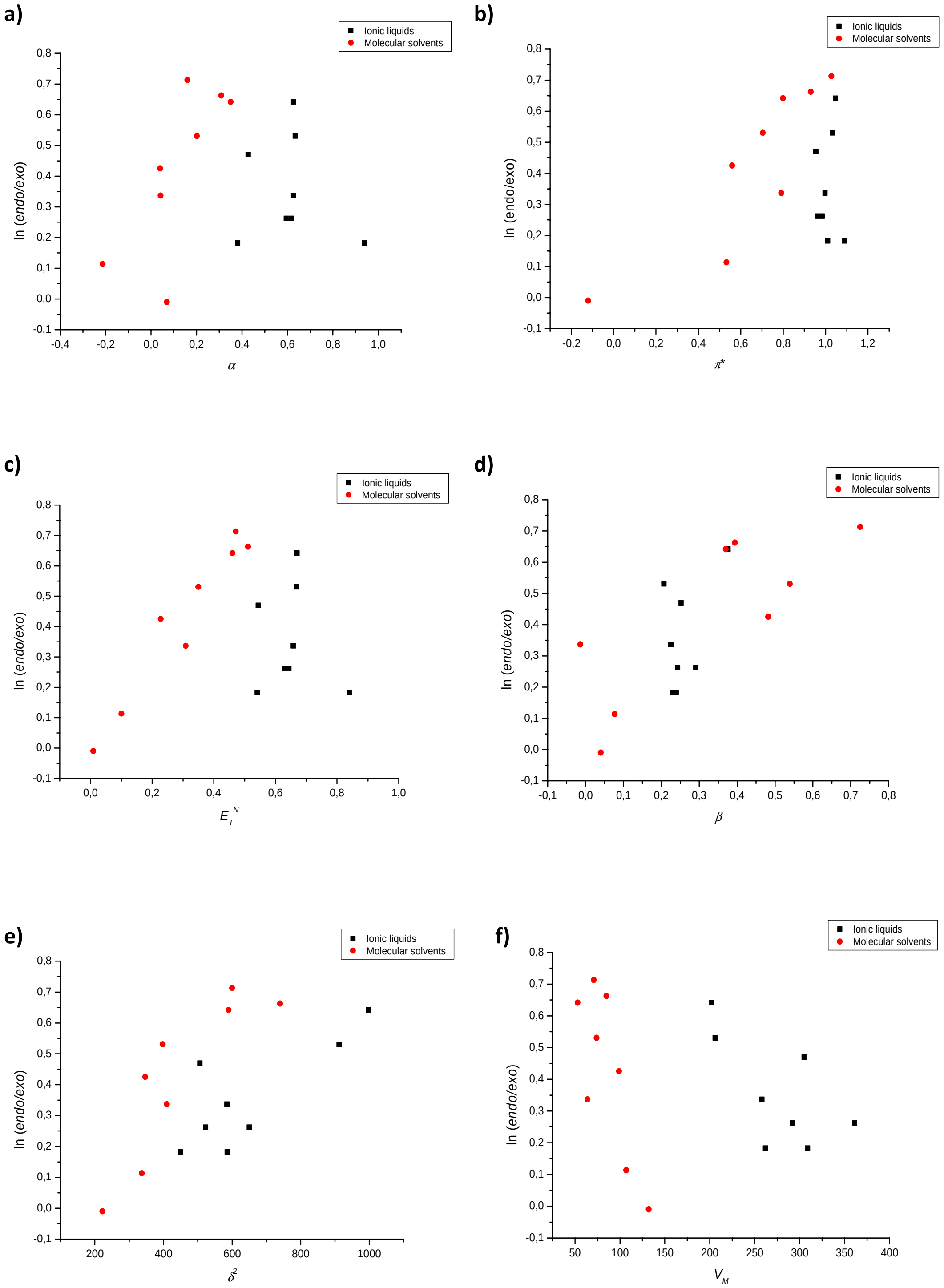
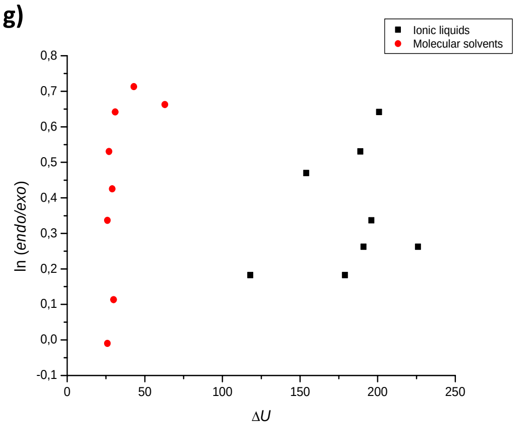


Figure 3S: Dependence of the ln (*endo/exo*) for the reaction of cyclopendiene with acrylonitrile in different solvents with different solvent parameters: a) α, b) π^*, c) E_T^N, d) β, e) δ^2, f) V_M and g) ΔU.



g)



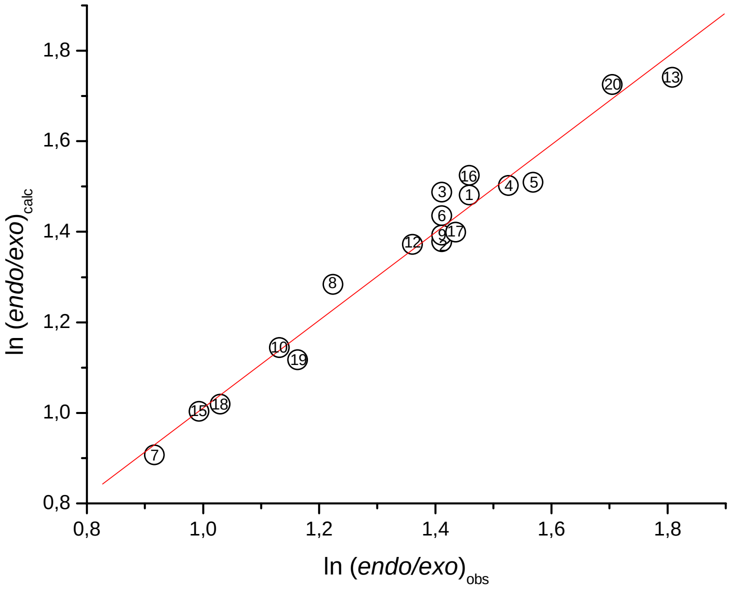


Figure 4S: Plot of the calculated values *versus* the observed values of ln (*endo/exo*) for cyclopentadiene and methyl acrylate in the 18 solvents. 1:[bmim][N(Tf)$_2$]; 2:[bm$_2$im][N(Tf)$_2$]; 3:[emim][N(Tf)$_2$]; 4:[bmim][BF$_4$]; 5:[bmim][PF$_6$]; 6:[omim][N(Tf)$_2$]; 7:hexane; 8:acetone; 9:acetonitrile; 10:ethyl acetate: 12: dimethyl sulfoxide, 13:[Hbim][N(Tf)$_2$]; 15:toluene; 16:[bmim][OTf]; 17:[bmpy][N(Tf)$_2$]; 18:ether; 19:1,4-dioxane; 20:methanol. Employed equation: ln (*endo/exo*) = 0.94 + 0.51 α + 0.37 π^* – 7.42 x 10^{-4} ΔU

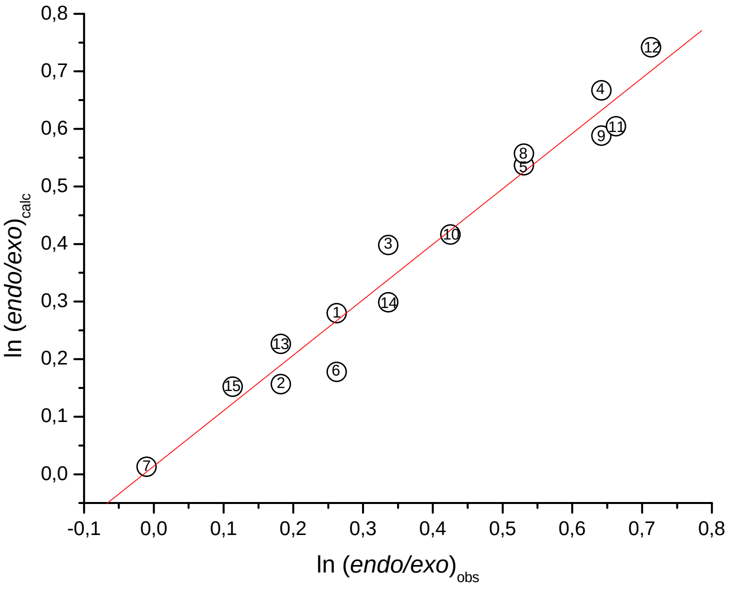


Figure 5S: Plot of the calculated values *versus* the observed values of ln (*endo/exo*) for cyclopentadiene and acrylonitrile in 16 solvents. 1:[bmim][N(Tf)$_2$]; 2:[bm$_2$im][N(Tf)$_2$]; 3:[emim][N(Tf)$_2$]; 4:[bmim][BF$_4$]; 5:[bmim][PF$_6$]; 6:[omim][N(Tf)$_2$]; 7:hexane; 8:acetone; 9:acetonitrile; 10:ethyl acetate; 11:propylene carbonate; 12: dimethyl sulfoxide, 13:[Hbim][N(Tf)$_2$]; 14:dichloromethane; 15:toluene. Employed equation: ln (*endo/exo*)= 0.33 + 0.33 E_T^N + 0.49 β + 2.82 x 10^{-3} ΔU – 3.17 x 10^{-3} V_M

Figure 6S. Single relationships of lnk_2 for the reaction of cyclopentadiene with acrolein versus some solvent solvent parameters: a) π^*, b) E_T^N, c) β, d) δ^2 and e) ΔU

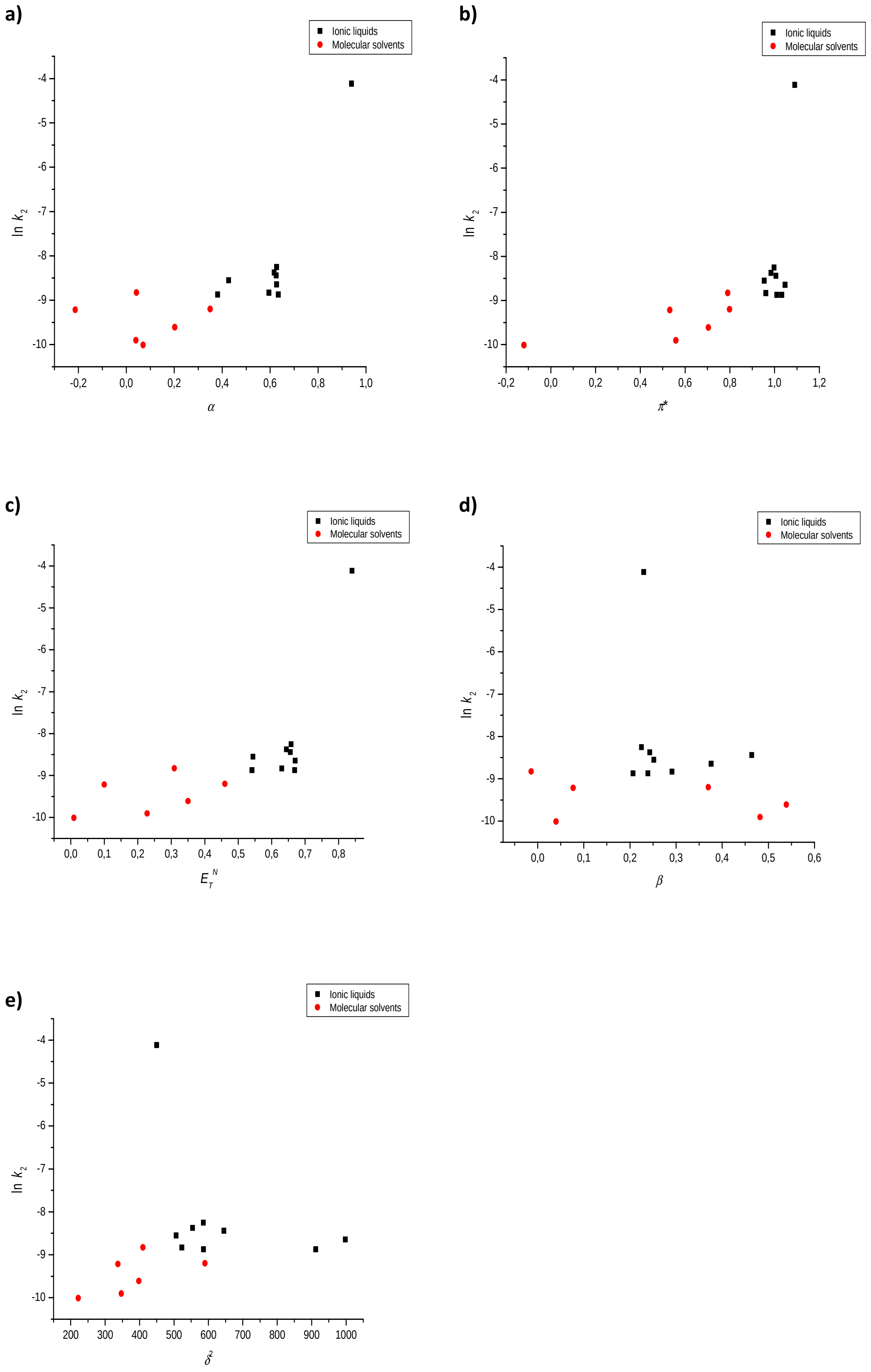


Figure 7S. Single relationships of lnk_2 for the reaction of cyclopentadiene with methyl acrylate versus some solvent parameters: a) π^*, b) E_T^N, c) β, d) δ^2 and e) ΔU

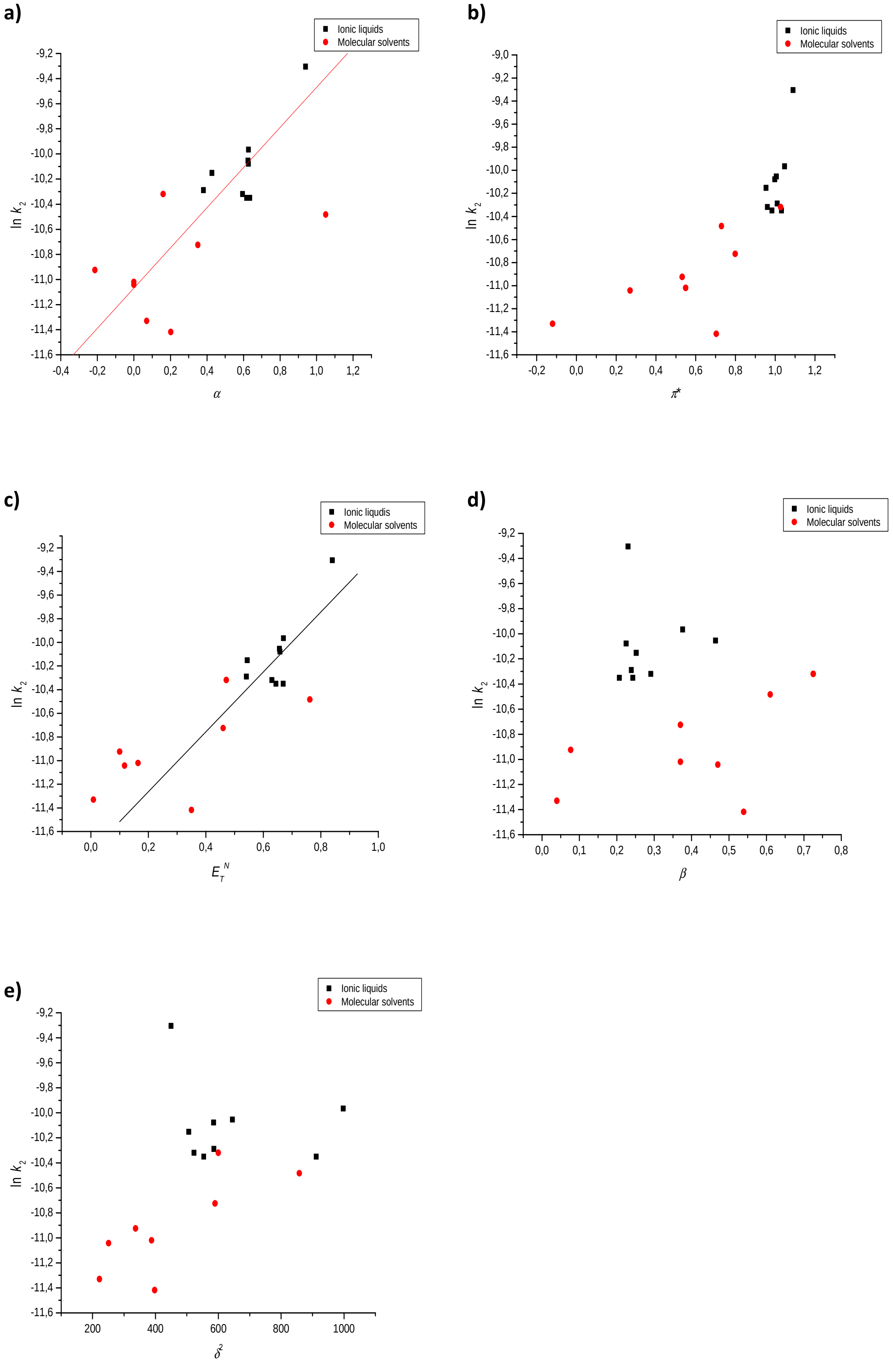
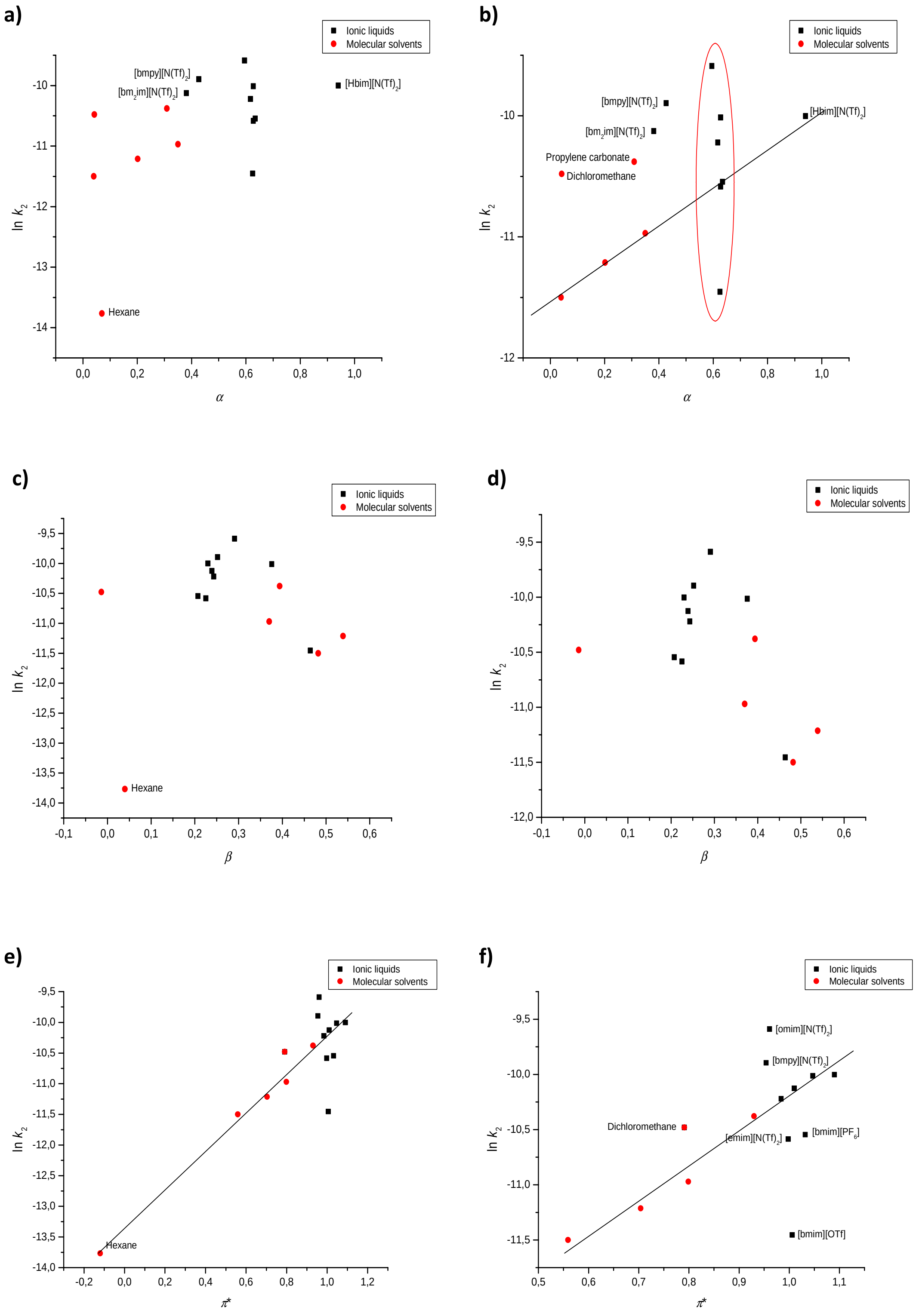


Figure 8S: Single relationships between the ln k_2 of the Diels-Alder reaction between cyclopentadiene and acrylonitrile versus some solvent parameters (with and without hexane).



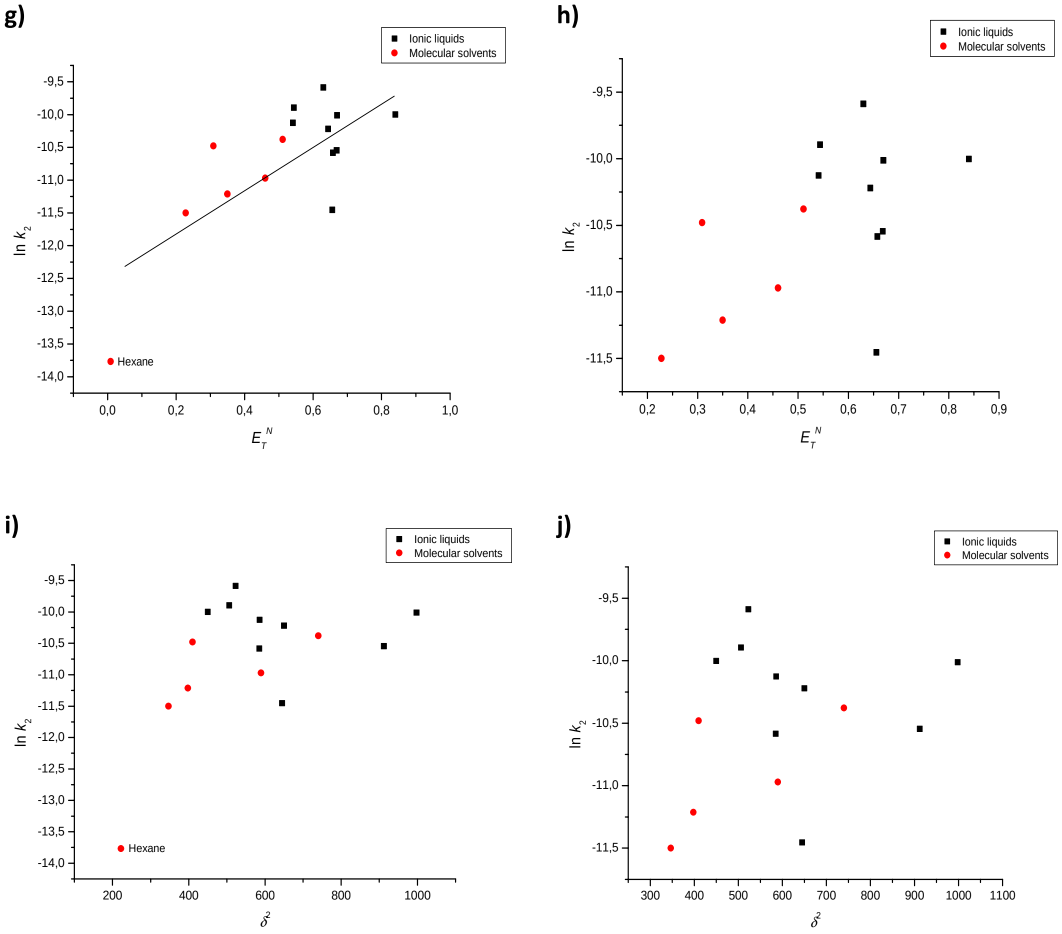

g)
Ionic liquids
Molecular solvents
ln k_2
-9,5
-10,0
-10,5
-11,0
-11,5
-12,0
-12,5
-13,0
-13,5
-14,0
Hexane
0,0
0,2
0,4
0,6
0,8
1,0
E_T^N
h)
Ionic liquids
Molecular solvents
ln k_2
-9,5
-10,0
-10,5
-11,0
-11,5
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
E_T^N
i)
Ionic liquids
Molecular solvents
ln k_2
-9,5
-10,0
-10,5
-11,0
-11,5
-12,0
-12,5
-13,0
-13,5
-14,0
Hexane
200
400
600
800
1000
δ^2
j)
Ionic liquids
Molecular solvents
ln k_2
-9,5
-10,0
-10,5
-11,0
-11,5
300
400
500
600
700
800
900
1000
1100
δ^2

Figure 9S: Calculated *versus* observed second order rate constants of the Diels-alder between acrolein and cyclopentadiene for several solvents. 1: [bmim][N(Tf)$_2$]; 2: [bm$_2$im][N(Tf)$_2$]; 3:[emim][N(Tf)$_2$]; 4:[bmim][BF$_4$]; 5:[bmim][PF$_6$]; 6: [omim][N(Tf)$_2$]; 7:hexane; 8:acetone; 9: acetonitrile; 10:ethyl acetate; 13:[Hbim][N(Tf)$_2$]; 14:dichloromethane; 15:toluene; 16:[bmim][OTf]; 17: [bmpy][N(Tf)$_2$].

Used Equation: $\ln k_2 = -9.86 + 0.99\,\alpha - 1.53\,\beta + 1.34\,\pi^* - 0.002\,\eta$

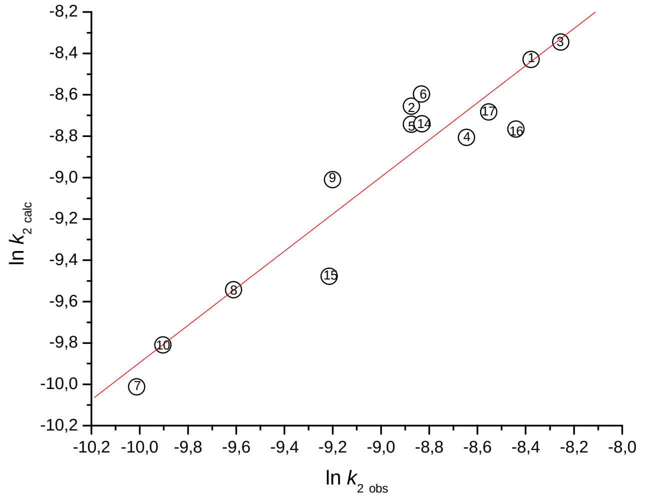
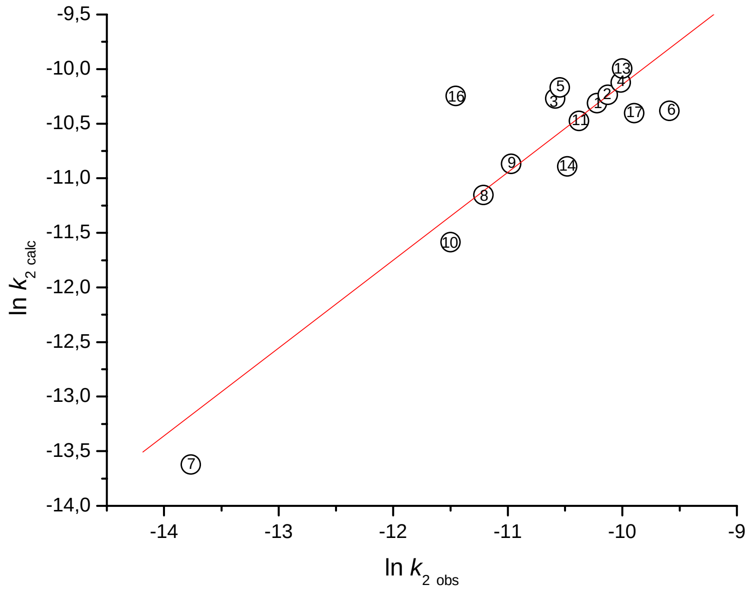


Figure 10S: Plot of the calculated values *versus* the observed values of ln k_2 of Diels Alder reaction of acrylonitrile and cyclopentadiene for the 15 solvents. 1:[bmim][N(Tf)$_2$]; 2:[bm$_2$im][N(Tf)$_2$]; 3:[emim][N(Tf)$_2$]; 4:[bmim][BF$_4$]; 5:[bmim][PF$_6$]; 6:[omim][N(Tf)$_2$]; 7:hexane; 8:acetone; 9:acetonitrile; 10:ethyl acetate; 11:propylene carbonate; 12: dimethyl sulfoxide, 13:[Hbim][N(Tf)$_2$]; 14:dichloromethane; 15:toluene; 16:[bmim][OTf]; 17:[bmpy][N(Tf)$_2$]. Used eq.: $-13.26 + 3.00\,\pi^*$



Synthesis of Ionic Liquids

Synthesis of 1-butyl-1-methylpyrrolidinium salts

Synthesis of 1-butyl-1-methylpyrrolidinium chloride, [bmpy]Cl

In a Schlenk flask, 1-chlorobutane (221 ml, 2.05 mol) was added slowly, with cooling, to 1-methylpyrrolidine (200 ml, 1.92 mol) in propan-2-ol (200 ml). After this addition, the mixture was brought to reflux for 24 h. The yellow coloured solution was allowed to cool to room temperature and then placed in a freezer (-14 ºC) for 24 h. The yellow mother liquor was removed by cannula filtration to leave transparent crystals, which were re-crystallized with propan-2-ol (2 × 50 ml), washed with ethyl acetate (50 ml) and then dried in *vacuo* to yield a white crystalline solid (314 g, 1.76 mol, 92 %).

δ_H (270 MHz, DMSO-d_6)/ppm: 3.69-3.40 (6H, m, N(CH_2)$_2$(CH$_2$)$_2$ and NCH_2(CH$_2$)$_2$CH$_3$), 3.02 (3H, s, NCH_3), 2.06 (4H, m, N(CH$_2$)$_2$(CH_2)$_2$), 1.66 (2H, m, J = 7.2 Hz, NCH$_2$CH_2CH$_2$CH$_3$), 1.29 (2H, sextet, ^3J = 7.3 Hz, N(CH$_2$)$_2$CH_2CH$_3$) and 0.91 (3H, t, ^3J = 7.3 Hz, N(CH$_2$)$_3$CH_3).

δ_C (68 MHz, DMSO-d_6)/ppm: 62.83 (s, NCH$_2$), 62.11 (s, NCH$_2$(CH$_2$)$_2$CH$_3$), 46.97 (s, NCH$_3$), 24.85 (s, NCH$_2$(CH$_2$)$_2$), 20.82 (s, NCH$_2$$CH_2CH_2CH_3$), 19.19 (s, N(CH$_2$)$_2$$CH_2CH_3$) and 13.39 (s, N(CH$_2$)$_3$$CH_3$).

m/z (FAB+) MS: 319 ([(bmpy)$_2$Cl]$^+$, 15 %); 142 ([bmpy]$^+$, 100 %).

m/z (FAB-) MS: 212 ([(bmpy)Cl$_2$)]$^-$, 100 %); 37 ([^{37}Cl]$^-$, 34 %); 35 ([^{35}Cl]$^-$, 40 %).

Elemental analysis: Calc: H 11.34%, C 60.83%, N 7.88%; Found: H 11.44%, C 60.62%, N 7.92%.

Synthesis of 1-alkyl-3-methylimidazolium salts

Synthesis of 1-butyl-3-methylimidazolium chloride, [bmim]Cl

In a Schlenk flask, 1-chlorobutane (150 ml, 1.44 mol) was added slowly, with cooling, to 1-methylimidazole (100 ml, 1.25 mol) in toluene (75 ml) and stirred. The resulting mixture was heated to at 45 ºC for 48 h. After cooling to room temperature, the upper organic phase was decanted and the lower phase was allowed to crystallise. The product was purified by crystallisation from acetonitrile/ethyl acetate and dried under *vacuo* to give the title compound (185 g, 1.06 mol, 85 %) as white crystals.

δ_H (270 MHz, DMSO-d_6)/ppm: 9.80 (1H, s, N$_2$CH), 8.01 and 7.92 (2H, 2 s, 2NCH), 4.23 (2H, t, ^3J = 7.1 Hz, NCH_2(CH$_2$)$_2$CH$_3$), 3.90 (3H, s, NCH_3), 1.74 (2H, quintet, ^3J = 7.4 Hz, , NCH$_2$CH_2CH$_2$CH$_3$), 1.19 (2H, sextet, ^3J = 7.3 Hz, , NCH$_2$CH$_2$CH_2CH$_3$) and 0.83 (3H, t, ^3J = 7.3 Hz, N(CH$_2$)$_3$CH_3).

δ_C (68 MHz, DMSO-d_6)/ppm: 136.76 (s, N_2C), 123.42 and 122.20 (s, 2N*C*H), 48.20 (s, N*C*$H_2(CH_2)_2CH_3$), 35.57 (s, N*C*H_3), 31.33 (s, $NCH_2CH_2CH_2CH_3$), 18.63 (s, $N(CH_2)_2CH_2CH_3$) and 13.15 (s, $N(CH_2)_3CH_3$).

m/z FAB+ MS: 313, $[(bmim)_2Cl]^+$, 20 %; 139, $[bmim]^+$, 100 %.

m/z FAB- MS: 383, $[(bmim)_2Cl_3]^-$, 20 %; 209, $[(bmim)Cl_2]^-$, 100 %; 35, $[Cl]^-$, 50 %.

Elemental analysis: Calc: H 8.66 %, C 55.01%, N 16.04%; Found: H 8.74%, C 55.14%, N 15.72%.

Synthesis of 1-ethyl-3-methylimidazolium bromide, [emim]Br

The same procedure was used as indicated for [bmim]Cl with the exception of the use of bromoethane instead of chlorobutane. 1-bromoethane (100 ml, 1.34 mol) was added slowly, with cooling, to 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 (223.8 g , 87.0 %).

δ_H (270 MHz, DMSO-d_6)/ppm: 9.50 (1H, s, N_2CH), 7.95 and 7.84 (2H, 2 s, 2NC*H*), 4.23 (2H, q, ^3J = 7.3 Hz, NCH_2CH_3), 3.88 (3H, s, NCH_3) and 1.37 (3H, t, ^3J = 7.3 Hz, NCH_2CH_3).

δ_C (68 MHz, DMSO-d_6)/ppm: 136.18 (s, N_2C), 123.31 and 121.83 (s, 2N*C*H), 43.96 (s, NCH_2CH_3), 35.70 (s, NCH_3) and 15.13 (s, NCH_2CH_3).

m/z FAB+ MS: 301, $[(emim)_2Br]^+$, 11 %; 111, $[emim]^+$, 100 %.

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

Elemental analysis: Calc: H 5.84%, C 37.84%, N 16.04%; Found: H 5.81%, C 37.75%, N 14.67%.

Synthesis of 1-hexyl-3-methylimidazolium bromide, [hmim]Br

The same procedure as indicated for [emim]Br except 1-bromohexane (193 ml, 1.37 mol) and 1-methylimidazole (109 ml, 1.37 mol) were heated in toluene at 30-35 ºC for 48 h to give a slightly yellow liquid. The liquid was washed with ethyl acetate/ether and dried in *vacuo* for 24 h at 60 ºC (321 g, 91 %).

δ_H/ ppm (400 MHz, $CDCl_3$): 10.0 (1H, s, N_2CH), 7.53 and 7.37 (2H, s, 2NC*H*), 4.07 (2H, t, ^3J = 7.4 Hz, $NCH_2(CH_2)_4CH_3$), 3.87 (3H, s, NCH_3), 1.64 (2H, m, $NCH_2CH_2(CH_2)_3CH_3$), 1.02 (6H, m, $N(CH_2)_2(CH_2)_3CH_3$) and 0.58 (3H, t, ^3J = 7.0 Hz $N(CH_2)_5CH_3$).

δ_C/ ppm (400 MHz, $CDCl_3$): 136.74 (s, N_2C), 123.73 and 122.08 (s, 2NCH), 49.76 (s, $NCH_2(CH_2)_4CH_3$), 36.43 (s, NCH_3), 30.80 (s, $NCH_2CH_2(CH_2)_3CH_3$), 30.03 (s, $N(CH_2)_2CH_2(CH_2)_2CH_3$), 25.58 (s, $N(CH_2)_3CH_2CH_2CH_3$), 22.10 (s, $N(CH_2)_4CH_2CH_3$) and 13.72 (s, $N(CH_2)_5CH_3$).

m/z FAB+ MS: 413, $[(hmim)_2Br]^+$, 45 %; 167, $[hmim]^+$, 100 %.

m/z FAB- MS: 81, $[Br]^-$, 85 %; 79, $[Br]^-$, 100 %.

Elemental analysis: Calc: H 7.73%, C 48.75%, N 11.22%; Found: H 7.75%, C 48.62%, N 11.34%.

Synthesis of 1-methyl-3-octylimidazolium bromide, [omim]Br

The same procedure as indicated for [bmim]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 ether and dried in *vacuo* for 24 h (288 g, 90 %).

δ_H/ ppm (400 MHz, $CDCl_3$): 9.73 (1H, s, N_2CH), 7.36 and 7.22 (2H, s, 2NCH), 3.85 (2H, t, ^3J = 7.4 Hz, $NCH_2(CH_2)_6CH_3$), 3.64 (3H, s, NCH_3), 1.42 (2H, m, $NCH_2CH_2(CH_2)_5CH_3$), 0.76 (10H, m, $N(CH_2)_2(CH_2)_5CH_3$) and 0.33 (3H, t, ^3J = 6.9 Hz $N(CH_2)_7CH_3$).

δ_C/ ppm (400 MHz, $CDCl_3$): 136.38 (s, N_2C), 123.55 and 122.00 (s, 2NCH), 49.52 (s, $NCH_2(CH_2)_6CH_3$), 36.20 (s, NCH_3), 31.15 (s, $NCH_2CH_2(CH_2)_5CH_3$), 29.88 (s, $N(CH_2)_2CH_2(CH_2)_4CH_3$), 28.51 (s, $N(CH_2)_3CH_2(CH_2)_3CH_3$), 28.45 (s, $N(CH_2)_4CH_2(CH_2)_2CH_3$), 25.71 $N(CH_2)_5CH_2CH_2CH_3$), 22.06 (s, $N(CH_2)_6CH_2CH_3$) and 13.63 (s, $N(CH_2)_7CH_3$).

m/z FAB+ MS: 469, $[(omim)_2Br]^+$, 18 %; 195, $[omim]^+$, 100 %.

m/z FAB- MS: 162, $[Br_2]^-$, 4 %; 81, $[Br]^-$, 100 %; 79, $[Br]^-$, 100 %.

Elemental analysis: Calc: H 8.72%, C 51.59%, N 10.21%; Found: H 8.42%, C 52.37%, N 10.18%.

Synthesis of 1-butyl-2,3-dimethylimidazolium salts

Synthesis of 1-butyl-2,3-dimethylimidazolium chloride, $[bm_2im]Cl$

In a Schlenk flask, 1-chlorobutane (65 ml, 0.620 mol) was added slowly, with cooling, to 1,2-dimethylimidazole (50 ml, 0.564 mol) in toluene (75 ml) and stirred. The resulting mixture was heated to reflux for 24 h. After cooling, the upper organic phase was decanted and the lower phase was allowed to crystallise. The product was purified by washing with ethyl acetate/acetonitrile (4 by 20 ml) to give the product as a white crystalline solid (89.1 g, 83.8 %).

δ_H (270 MHz, DMSO-d_6)/ppm: 7.78 and 7.53 (2H, s, 2NC*H*), 4.12 (2H, t, ^3J = 7.3 Hz, $NC\mathit{H_2}(CH_2)_2CH_3$), 3.73 (3H, s, $NC\mathit{H_3}$), 2.60 (3H, s, $N_2CC\mathit{H_3}$), 1.74 (2H, quintet, ^3J = 7.4 Hz, $NCH_2C\mathit{H_2}CH_2CH_3$), 1.28 (2H, sextet, ^3J = 7.5 Hz, $N(CH_2)_2C\mathit{H_2}CH_3$) and 0.88 (3H, t, ^3J = 7.3 Hz, $N(CH_2)_3C\mathit{H_3}$).

δ_C (68 MHz, DMSO-d_6)/ppm: 144.36 (s, $N_2\mathit{C}$), 122.21 and 120.76 (s, 2N*C*H), 47.37 (s, $N\mathit{C}H_2(CH_2)_2CH_3$), 34.50 (s, $N\mathit{C}H_3$), 31.19 (s, $NCH_2\mathit{C}H_2CH_2CH_3$), 18.88 (s, $N(CH_2)_2\mathit{C}H_2CH_3$), 13.15 (s, $N(CH_2)_3\mathit{C}H_3$) and 8.90 (s, $N_2C\mathit{C}H_3$).

m/z (FAB+): 342 ($[(bm_2im)_2Cl]^+$, 41 %), 153 ($[bm_2im]^+$, 100 %).

m/z (FAB-): 223 ($[(bm_2im)Cl_2]^-$, 100 %), 35 ($[Cl]^-$, 40 %).

Elemental analysis: Calc: H 9.08%, C 57.29%, N 14.85%; Found: H 9.26%, C 57.28%, N 14.72%.

Synthesis of 1-alkylimidazolium salts

Synthesis of 1-butylimidazolium chloride, [Hbim]Cl

In a Schlenk flask, 2M hydrogen chloride solution in diethyl ether (402 ml, 0.8 mol) was added slowly, with cooling, to a solution of 1-butylimidazole (106 ml, 0.8 mol) in diethyl ether and stirred for 48h under nitrogen to give a white solid (96 g, 75 %)

δ_H/ ppm (400 MHz, $CDCl_3$): 10.11 (1H, br. s, N*H*), 9.34 (1H, s, $N_2C\mathit{H}$), 7.35 and 7.13 (2H, s, 2NC*H*), 4.29 (2H, t, ^3J = 7.3 Hz, $NC\mathit{H_2}(CH_2)_4CH_3$), 1.88 (2H, m, $NCH_2C\mathit{H_2}CH_2CH_3$), 1.38 (2H, m, $N(CH_2)_2C\mathit{H_2}CH_3$) and 0.97 (3H, t, ^3J = 7.4 Hz $N(CH_2)_3C\mathit{H_3}$).

δ_C/ ppm (400 MHz, $CDCl_3$): 135.66(s, $N_2\mathit{C}$), 121.31 and 120.10 (s, 2N*C*H), 49.03 (s, $N\mathit{C}H_2(CH_2)_2CH_3$), 32.39 (s, $NCH_2\mathit{C}H_2CH_2CH_3$), 19.45 (s, $N(CH_2)_2\mathit{C}H_2CH_3$) and 13.44 (s, $N(CH_2)_3CH_3$).

m/z FAB+ MS: 285, $[(Hbim)_2Cl]^+$, 12 %; 125, $[Hbim]^+$, 100 %.

m/z FAB- MS: 71, $[Cl_2]^-$, 14 %; 37, $[^{37}Cl]^-$, 27 %; 35, $[Cl]^-$, 100%

Elemental analysis: Calc: H 8.16%, C 52.40%, N 17.33%; Found: H 8.17%, C 52.40%, N 17.45%.

Synthesis of ionic liquids via metathesis

Synthesis of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide, [bmpy][N(Tf)$_2$]

In a Schlenk flask, a solution of [bmpy]Cl (35.8 g, 0.202 mol) in dichloromethane (50 ml) was added to lithium *bis*(trifluoromethanesulfonyl)imide (57.4 g, 0.200 mol). The resulting suspension was stirred for 72 h, then filtered. The residual salt was washed with aliquots of dichloromethane and the combined organic extracts were washed with water until the aqueous phase was halide free (by silver nitrate test), after which the solvent was removed *in vacuo*. The resulting liquid was treated with activated charcoal and filtered through a pad of acidic alumina to give a colourless liquid (73 g, 86 %).

δ_H (270 MHz, DMSO-d_6)/ppm: 3.56-3.36 (4H, m, $N(CH_2)_2$), 3.34-3.24 (2H, m, $NCH_2(CH_2)_2CH_3$), 2.99 (3H, s, NCH_3), 2.10 (4H, m, $NCH_2(CH_2)_2CH_3$), 1.70 (2H, m, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.33 (2H, sextet, ^3J = 7.4 Hz, $N(CH_2)_2CH_2CH_3$) and 0.94 (3H, t, ^3J = 7.1 Hz, $N(CH_2)_3CH_3$).

δ_C (68 MHz, DMSO-d_6)/ppm: 119.53 (q, $^1J_{13C\text{-}19F}$ = 321.6 Hz, $[N(SO_2CF_3)_2]^-$), 63.48 (s, NCH_2), 63.08 (s, $NCH_2(CH_2)_2CH_3$), 47.52 (s, NCH_3), 24.91 (s, $NCH_2(CH_2)_2CH_3$), 21.03 (s, $NCH_2CH_2CH_2CH_3$), 19.22 (s, $N(CH_2)_2CH_2CH_3$) and 13.16 (s, $N(CH_2)_3CH_3$).

m/z (FAB+) MS: 564, $[(bmpy)_2(N(Tf)_2)]^+$, 1 %; 142, $[(bmpy)]^+$, 100 %.

m/z (FAB-) MS: 702, $[(bmpy)(N(Tf)_2)_2]^-$, 5 %; 280, $[N(Tf)_2)]^-$,100 %.

Elemental analysis: Calc: H 4.77%, C 31.28%, N 6.63%; Found: H 4.86%, C 31.38%, N 6.51%.

Synthesis of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide, [bmim][N(Tf)₂]

In a two-neck flask, lithium *bis*(trifluoromethanesulfonyl)imide (144 g, 0.499 mol) was added to a solution of [bmim]Cl (84.5 g, 0.484 mol) in dichloromethane (100 ml). The resulting suspension was stirred for 48 h, then filtered. The residual salt was washed with dichloromethane (2 x 10 ml) and the combined organic extracts were washed with water until the aqueous phase was halide free (by silver nitrate test), after which the solvent was removed *in vacuo*. The resulting liquid was filtered through a pad of acidic alumina to give a colourless liquid (186 g, 91.9 %).

δ_H (270 MHz, DMSO-d_6)/ppm: 9.08 (1H, s, N_2CH), 7.70 and 7.64 (2H, 2 s, 2NCH), 4.17 (2H, t, ^3J = 7.2 Hz, $NCH_2(CH_2)_2CH_3$), 3.86 (3H, s, NCH_3), 1.79 (2H, quintet, ^3J = 7.3 Hz, , $NCH_2CH_2CH_2CH_3$), 1.28 (2H, sextet, ^3J = 7.4 Hz, , $NCH_2CH_2CH_2CH_3$) and 0.91 (3H, t, ^3J = 7.3 Hz, $N(CH_2)_3CH_3$).

δ_C (68 MHz, DMSO-d_6)/ppm: 136.54 (s, N_2CH), 126.68 and 122.21 (s, 2NCH), 119.57 (q, $^1J_{13C\text{-}19F}$ = 321.8 Hz, $[N(SO_2CF_3)_2]^-$), 48.67 (s, $NCH_2(CH_2)_2CH_3$), 35.60 (s, NCH_3), 31.38 (s, $NCH_2CH_2CH_2CH_3$), 18.75 (s, $N(CH_2)_2CH_2CH_3$) and 12.93 (s, $N(CH_2)_3CH_3$).

m/z (FAB+) MS: 558, $[(bmim)_2(N(Tf)_2)]^+$, 1 %; 139, $[(bmim)]^+$, 100 %.

m/z (FAB-) MS: 699, $[(bmim)(N(Tf)_2)_2)]^-$, 8 %; 280, $[N(Tf)_2]^-$, 92 %.

Elemental analysis: Calc: H 3.61%, C 28.60%, N 10.02%; Found: H 3.49%, C 28.65%, N 9.85%.

Synthesis of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide, [emim][N(Tf)$_2$]

The same procedure as indicated for the preparation of [bmim][N(Tf)$_2$], except [emim]Br (50 g, 0.26 mol) in CH_2Cl_2 (60 ml) and lithium *bis*(trifluoromethanesulfonyl)imide (80.4 g, 0.28 mol) were mixed to give a colourless liquid (90.5 g, 89 %).

δ_H (400 MHz, $CDCl_3$)/ppm: 8.48 (1H, s, N$_2$C*H*), 7.30 and 7.25 (2H, 2 s, 2NC*H*), 4.12 (2H, q, ^3J = 7.3 Hz, NC*H*$_2$CH$_3$), 3.81 (3H, s, NC*H*$_3$) and 1.42 (3H, t, ^3J = 7.4 Hz, NCH$_2$C*H*$_3$).

δ_C (400 MHz, $CDCl_3$)/ppm: 135.25 (s, N$_2$*C*), 123.64 and 121.99 (s, 2N*C*H), 119.67 (q, $^1J_{13C\text{-}19F}$ = 320.9 Hz, $[N(SO_2CF_3)_2]^-$), 45.01 (s, N*C*H$_2$CH$_3$), 35.91 (s, N*C*H$_3$) and 14.71 (s, NCH$_2$*C*H$_3$).

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

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

Elemental analysis: Calc: H 2.18%, C 24.65%, N 10.65%; Found: H 2.83%, C 24.56%, N 10.74%.

Synthesis of 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide, [hmim][N(Tf)$_2$]

As for the preparation of [bmim][N(Tf)$_2$], except [hmim]Br (100 g, 0.39 mol) in CH_2Cl_2 (150 ml) and lithium *bis*(trifluoromethanesulfonyl)imide (120.6 g, 0.42 mol) were mixed to give a colourless liquid (149.7 g, 84 %).

δ_H (400 MHz, $CDCl_3$)/ppm: 8.63 (1H, s, N$_2$C*H*), 7.70 and 7.64 (2H, 2 s, 2NC*H*), 4.17 (2H, t, ^3J = 7.2 Hz, NC*H*$_2$(CH$_2$)$_2$CH$_3$), 3.86 (3H, s, NC*H*$_3$), 1.79 (2H, quintet, ^3J = 7.3 Hz, , NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.28 (2H, sextet, ^3J = 7.4 Hz, , NCH$_2$CH$_2$C*H*$_2$CH$_3$) and 0.91 (3H, t, ^3J = 7.3 Hz, N(CH$_2$)$_3$C*H*$_3$).

δ_C (400 MHz, $CDCl_3$)/ppm: 135.71 (s, N$_2$CH), 123.75 and 122.35 (s, 2N*C*H), 119.77 (q, $^1J_{13C\text{-}19F}$ = 321 Hz, $[N(SO_2CF_3)_2]^-$), 50.06 (s, N*C*H$_2$(CH$_2$)$_4$CH$_3$), 36.12 (s, N*C*H$_3$), 30.85 (s, NCH$_2$*C*H$_2$(CH$_2$)$_3$CH$_3$), 29.92 (s, N(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$CH$_3$), 25.6 (s, N(CH$_2$)$_3$*C*H$_2$CH$_2$CH$_3$), 22.19 (s, N(CH$_2$)$_4$*C*H$_2$CH$_3$) and 13.70 (s, N(CH$_2$)$_5$*C*H$_3$).

m/z (FAB+) MS: 614, $[(hmim)_2(N(Tf)_2)]^+$, 14 %; 167, $[(hmim)]^+$, 100 %.

m/z (FAB-) MS: 280, $[N(Tf)_2]^-$, 100 %.

Elemental analysis: Calc: H 4.23%, C 32.27%, N 9.32%; Found: H 4.28%, C 32.22%, N 9.39%.

Synthesis of 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl) imide, [omim][N(Tf)$_2$]

As for the preparation of [bmim][N(Tf)$_2$], except [omim]Br (150 g, 0.54 mol) in CH_2Cl_2 (200 ml) and lithium *bis*(trifluoromethanesulfonyl)imide (160.8 g, 0.56 mol) were mixed to give a colourless liquid (207.8 g, 81 %).

δ_H/ ppm (400 MHz, $CDCl_3$): 8.70 (1H, s, N_2CH), 7.35 and 7.33 (2H, m, 2NCH), 4.15 (2H, t, ^3J = 7.4 Hz, $NCH_2(CH_2)_6CH_3$), 3.92 (3H, s, NCH_3), 1.85 (2H, m, $NCH_2CH_2(CH_2)_5CH_3$), 1.28 (10H, m, $N(CH_2)_2(CH_2)_5CH_3$) and 0.86 (3H, t, ^3J = 6.9 Hz $N(CH_2)_7CH_3$).

δ_C/ ppm (400 MHz, $CDCl_3$): 135.84 (s, N_2C), 123.78 and 122.32 (s, 2NCH), 119.8 (q, $^1J_{13C-19F}$ = 321 Hz, $[N(SO_2CF_3)_2]^-$), 50.15 (s, $NCH_2(CH_2)_6CH_3$), 36.21 (s, NCH_3), 31.58 (s, $NCH_2CH_2(CH_2)_5CH_3$), 30.03 (s, $N(CH_2)_2CH_2(CH_2)_4CH_3$), 28.89 (s, $N(CH_2)_3CH_2(CH_2)_3CH_3$), 28.76 (s, $N(CH_2)_4CH_2(CH_2)_2CH_3$), 26.04 $N(CH_2)_5CH_2CH_2CH_3$), 22.51 (s, $N(CH_2)_6CH_2CH_3$) and 13.95 (s, $N(CH_2)_7CH_3$).

m/z (FAB+) MS: 670, $[(omim)_2(N(Tf)_2)]^+$, 17 %; 195, $[(omim)]^+$, 100 %.

m/z (FAB-) MS: 280, $[N(Tf)_2]^-$, 100 %.

Elemental analysis: Calc: H 4.76%, C 35.50%, N 8.72%; Found: H 4.88%, C 35.39%, N 8.84%.

Synthesis of 1-butyl-1-methylimidazolium trifluoromethylsulfonate, [bmim][OTf]

The same procedure used as [bmim][N(Tf)$_2$] except, lithium trifluoromethylsulfonate (33.5 g, 0.329 mol) and [bmim]Cl (55.7 g, 0.319 mol) in CH_2Cl_2 (60 ml) were mixed to give a colourless liquid (74.7 g, 61.2 %).

δ_H (270 MHz, DMSO-d_6)/ppm: 9.08 (1H, s, N_2CH), 7.70 and 7.64 (2H, m, 2NCH), 4.17 (2H, t, ^3J = 7.2 Hz, $NCH_2(CH_2)_2CH_3$), 3.86 (3H, s, NCH_3), 1.79 (2H, quintet, ^3J = 7.3 Hz, , $NCH_2CH_2CH_2CH_3$), 1.28 (2H, sextet, ^3J = 7.4 Hz, , $NCH_2CH_2CH_2CH_3$) and 0.91 (3H, t, ^3J = 7.3 Hz, $N(CH_2)_3CH_3$).

δ_C (68 MHz, DMSO-d_6)/ppm: 136.54 (s, N_2C), 126.68 and 122.21 (s, 2NCH), 119.57 (q, $^1J_{13C-19F}$ = 321.8 Hz, $[N(SO_2CF_3)_2]^-$), 48.67 (s, $NCH_2(CH_2)_2CH_3$), 35.60 (s, NCH_3), 31.38 (s, $NCH_2CH_2CH_2CH_3$), 18.75 (s, $N(CH_2)_2CH_2CH_3$) and 12.93 (s, $N(CH_2)_3CH_3$).

m/z (FAB+) MS: 427, $[(bmim)_2(OTf)]^+$, 17 %; 139, $[(bmim)]^+$, 100 %.

m/z (FAB-) MS: 437, $[(bmim)(OTf)_2]^-$, 17 %; 149, $[OTf]^-$, 100 %.

Elemental analysis: Calc: H 5.24%, C 37.50%, N 9.72%; Found: H 5.22%, C 37.33%, N 9.54%.

Synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF$_4$]

In a Schlenk flask, sodium tetrafluoroborate (197 g, 1.13 mol) was added to a solution of [bmim]Cl (128 g, 1.16 mol) in dichloromethane (200 ml). The resulting suspension was stirred for 48 h, then filtered. The residual salt was washed with dichloromethane (2 x 10 ml) and the combined organic fractions were washed with water until the aqueous phase was halide free (by silver nitrate test), after which the solvent was removed *in vacuo*, giving a colourless liquid (193 g, 75.9 %).

δ_H (270 MHz, DMSO-d_6)/ppm: 8.96 (1H, s, N_2CH), 7.68 and 7.61 (2H, m, 2NC*H*), 4.16 (2H, t, ^3J = 7.2 Hz, $NCH_2(CH_2)_2CH_3$), 3.85 (3H, s, NCH_3), 1.77 (2H, quintet, ^3J = 7.3 Hz, , $NCH_2CH_2CH_2CH_3$), 1.26 (2H, sextet, ^3J = 7.4 Hz, , $NCH_2CH_2CH_2CH_3$) and 0.88 (3H, t, ^3J = 7.3 Hz, $N(CH_2)_3CH_3$).

δ_C (68 MHz, DMSO-d_6)/ppm: 136.52 (s, N_2C), 123.58 and 122.26 (s, 2NCH), 48.68 (s, $NCH_2(CH_2)_2CH_3$), 35.66 (s, NCH_3), 31.43 (s, $NCH_2CH_2CH_2CH_3$), 18.83 (s, $N(CH_2)_2CH_2CH_3$) and 13.16 (s, $N(CH_2)_3CH_3$).

m/z (FAB+) MS: 365, $[(bmim)(BF_4)]^+$, 12 %; 139, $[(bmim)]^+$, 100 %.

m/z (FAB-) MS: 313, $[(bmim)(BF_4)_2)]^-$, 8 %; 87, $[BF_4]^-$, 92 %; 19, F^-, 100%.

Elemental analysis: Calc: H 6.79%, C 42.51%, N 12.39%; Found: H 6.71%, C 42.45%, N 12.26%.

2.2.3.7.8 Synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF$_6$]

The same procedure as described for [bmim][BF$_4$] but using sodium hexafluorophosphate (61.8 g, 0.367 mol) and [bmim]Cl (62.3 g, 0.356 mol). The reaction gave a colourless liquid (84.9 g, 83.7 %) that it was confirmed by ^{1}H NMR, FAB MS and elemental analysis.

δ_H (270 MHz, DMSO-d_6)/ppm: 9.03 (1H, s, N_2CH), 7.68 and 7.63 (2H, m, 2NC*H*), 4.16 (2H, t, ^3J = 7.2 Hz, $NCH_2(CH_2)_2CH_3$), 3.85 (3H, s, NCH_3), 1.78 (2H, quintet, ^3J = 7.3 Hz, , $NCH_2CH_2CH_2CH_3$), 1.27 (2H, sextet, ^3J = 7.4 Hz, , $NCH_2CH_2CH_2CH_3$) and 0.90 (3H, t, ^3J = 7.3 Hz, $N(CH_2)_3CH_3$).

δ_C (68 MHz, DMSO-d_6)/ppm: 136.51 (s, N_2C), 123.57 and 122.22 (s, 2NCH), 48.65 (s, $NCH_2(CH_2)_2CH_3$), 35.66 (s, NCH_3), 31.36 (s, $NCH_2CH_2CH_2CH_3$), 18.79 (s, $N(CH_2)_2CH_2CH_3$) and 13.14 (s, $N(CH_2)_3CH_3$).

m/z (FAB+) MS: 423, $[(\text{bmim})(PF_6)]^+$, 1 %; 139, $[(\text{bmim})]^+$, 100 %.

m/z (FAB-) MS: 145, $[PF_6)]^-$, 100 %; 19, F^-, 23%.

Elemental analysis: Calc: H 5.31%, C 33.81%, N 9.86%; Found: H 5.31%, C 33.95%, N 9.68%.

Synthesis of 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl) imide, $[bm_2im][N(Tf)_2]$

In a Schlenk flask, lithium *bis*(trifluoromethanesulfonyl)imide (48.8 g, 0.169 mol) was added to a solution of $[bm_2im]Cl$ (30.9 g, 0.164 mol) in dichloromethane (50 ml). The resulting suspension was stirred for 48 h, then filtered. The residual salt was washed with dichloromethane (2 x 10 ml) and the combined organic extracts were washed with water until the aqueous phase was halide free (by silver nitrate test), after which the solvent was removed *in vacuo*. The resulting liquid was filtered through a pad of acidic alumina to give a colourless liquid (71.1 g, 89 %).

δ_H (270 MHz, DMSO-d_6)/ppm: 7.58 (2H, ^3J = 1.97 Hz, 2NCH), 4.12 (2H, t, ^3J = 7.3 Hz, $NCH_2(CH_2)_2CH_3$), 3.77 (3H, s, NCH_3), 2.59 (3H, s, N_2CCH_3), 1.73 (2H, quintet, ^3J = 7.5 Hz, $NCH_2CH_2CH_2CH_3$), 1.32 (2H, sextet, ^3J = 7.5 Hz, $NCH_2CH_2CH_2CH_3$) and 0.92 (3H, t, ^3J = 7.3 Hz, $N(CH_2)_3CH_3$).

δ_C (68 MHz, DMSO-d_6)/ppm: 144.17 (s, N_2C), 122.26 and 120.80 (s, 2NCH), 119.57 (q, $^1J_{13C-19F}$ = 321.6 Hz, $[N(SO_2CF_3)_2]^-$), 47.44 (s, $NCH_2(CH_2)_2CH_3$), 34.51 (s, NCH_3), 31.16 (s, $NCH_2CH_2CH_2CH_3$), 18.85 (s, $N(CH_2)_2CH_2CH_3$) and 13.06 (s, $N(CH_2)_3CH_3$) and 8.92 N_2CCH_3).

m/z (FAB+) MS: 586, $[(bm_2im)_2(N(Tf)_2)]^+$, 1 %; 153, $[(bm_2im)]^+$, 100 %.

m/z (FAB-) MS: 280, $[N(Tf)_2)]^-$,100 %.

Elemental analysis: Calc: H 3.95%, C 30.69%, N 9.70%; Found: H 4.00%, C 30.52%, N 9.51%.

Synthesis of 1-butylimidazolium bis(trifluoromethanesulfonyl)imide, $[Hbim][N(Tf)_2]$

In a Schlenk flask, lithium *bis*(trifluoromethanesulfonyl)imide (57.2 g, 0.2 mol) was added to a solution of [Hbim]Cl (32.0 g, 0.2 mol) in dichloromethane (50 ml). The resulting suspension was stirred for 48 h, then filtered. The residual salt was washed with dichloromethane (2 x 10 ml) and the combined organic extracts were washed with water until the aqueous phase was halide free (by silver nitrate test), after which the solvent was removed *in vacuo*. The resulting liquid was filtered through a pad of acidic alumina to give a colourless liquid (72.9 g, 90 %).

δ_H/ ppm (400 MHz, $CDCl_3$): 12.00 (1H, s, NH), 8.40 (1H, s, N_2CH), 7.31 (2H, m, 2NCH), 4.16 (2H, t, ^3J = 7.4 Hz, $NCH_2(CH_2)_4CH_3$), 1.83 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.33 (2H, m, $N(CH_2)_2CH_2CH_3$) and 0.92 (3H, t, ^3J = 7.4 Hz $N(CH_2)_3CH_3$).

δ_C/ ppm (400 MHz, $CDCl_3$): 135.19(s, N_2C), 121.90 and 120.00 (s, 2NCH), 119,5 (q, $^1J_{13C\text{-}19F}$ = 321.8 Hz, $[N(SO_2CF_3)_2]^-$), 48.31 (s, $NCH_2(CH_2)_2CH_3$), 31.44 (s, $NCH_2CH_2CH_2CH_3$), 18.82 (s, $N(CH_2)_2CH_2CH_3$) and 13.11 (s, $N(CH_2)_3CH_3$).

m/z (FAB+) MS: 530, $[(Hbim)_2(N(Tf)_2)]^+$, 45 %; 125, $[(Hbim)]^+$, 100 %.

m/z (FAB-) MS: 280, $[N(Tf)_2)]^-$,100 %.

Elemental analysis: Calc: H 3.35%, C 26.77%, N 10.40%; Found: H 3.24%, C 26.68%, N 10.37%.