ESI

SUPPLEMENTARY MATERIALS

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Figure S1: Biotransformation of chlorobenzene by *P. putida* UV4 in the presence of [C_8mpyrrol][NTf_2].

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General procedure for synthesis of bromide salts:

A solution of 1-methylimidazole or 1,2-dimethylimidazole (1 eq) in acetonitrile (25 cm^3) was prepared and cooled in an ice/water bath. To this solution was added a bromo-alkane of choice drop wise (1.1 eq) (2 to 8 linear carbons). The resulting solution was then stirred and allowed to warm to room temperature. It was then heated at reflux overnight. After evaporation of the solvent, the viscous solution was either washed and decanted or crystallised by addition of ethyl acetate (3 x 25 cm^3) and resulting crystals were filtered. If a solid was obtained, the crude product was recrystallised from a reduced volume of acetonitrile before the addition of ethyl acetate. If a viscous liquid was obtained, the solvent was removed *in vacuo* at 60 ºC and excess starting material was extracted from the product with ethyl acetate.

3-Butyl-1-methylimidazolium bromide, $[C_4mim]Br$
White crystalline solid is obtained (99% yield).
^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.91 (t, J = 7.3 Hz, 3H, butyl-CH_3); 1.34 (m, 2H, butyl-CH_2); 1.86 (m, 2H, butyl-CH_2); 4.08 (s, 3H, N^+CH_3); 4.30 (t, J = 7.32 Hz, 2H, N^+CH_2); [7.45 (s, 1H); 7.57 (s, 1H)] (4,5-H); 10.33 (s, 1H, 2-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.3 (butyl-CH_3); 19.3 (butyl-CH_2); 32.0 (butyl-CH_2); 36.6 (N^+CH_3); 49.7 (N^+CH_2); 121.9, 123.5 (C-4 and C-5); 137.3 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 139 ($[C_4mim]^+$, 100%), 357 ($\{[C_4mim]_2Br\}^+$, 10%).

3-Hexyl-1-methylimidazolium bromide, $[C_6mim]Br$
Colourless viscous liquid is obtained (95 % yield).
^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.76 (t, J = 7.2 Hz, 3H, hexyl-CH_3); 1.20 (m, 6H, hexyl-$(CH_2)_3$); 1.81 (q, J = 7.2 Hz, 2H, hexyl-CH_2); 4.02 (s, 3H, N^+CH_3); 4.22 (t, J = 7.3 Hz, 2H, N^+CH_2); [7.43 (s, 1H); 7.59 (s, 1H)] (4,5-H); 10.13 (s, 1H, 2-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.7 (hexyl-CH_3); 22.1, 25.6, 30.0, 30.8 (hexyl-CH_2); 36.5 (N^+CH_3); 49.9 (N^+CH_2); 121.9, 123.6 (C-4 and C-5); 136.9 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 167 ($[C_6mim]^+$, 100%), ES^- *m/z* (% rel. intensity): 79 (Br^-, 100%).

3-Octyl-1-methylimidazolium bromide, $[C_8mim]Br$
Colourless viscous liquid is obtained (99.9% yield).
^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.79 (t, J = 6.7 Hz, 3H, octyl-CH_3); 1.17-1.25 (m, 10H, octyl-$(CH_2)_5$); 1.84 (m, 2H, octyl-CH_2); 4.06 (s, 3H, N^+CH_3); 4.25 (t, J = 7.4, 2H, N^+CH_2); [7.42 (s, 1H); 7.60 (s, 1H)] (4,5-H); 10.27 (s, 1H, 2-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.8 (octyl-CH_3); 22.3,

26.0, 28.7, 28.8, 30.1, 31.4 (octyl-CH_2); 36.5 (N^+CH_3); 49.9 (N^+CH_2); 121.8, 123.6 (C-4 and C-5); 137.1 (C-2). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 195.1 ($[C_8min]^+$, 100), 471 ($\{[C_8mim]_2Br\}^+$, 10).

3-Decyl-1-methylimidazolium bromide, $[C_{10}mim]Br$

Colourless viscous liquid is obtained (90% yield).

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.80 (t, J = 6.7 Hz, 3H, decyl-CH_3); 1.18-1.26 (m, 14H, decyl-$(CH_2)_7$); 1.84 (m, 2H, decyl-CH_2); 4.06 (s, 3H, N^+CH_3); 4.25 (t, J = 7.2 Hz, 2H, N^+CH_2); [7.39 (s, 1H); 7.56 (s, 1H)] (4,5-H); 10.0 (s, 1H, 2-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 22.5 (decyl-CH_3); 26.1, 28.8, 29.1, 29.2, 29.3, 30.1, 31.7 (decyl-CH_2); 36.6 (N^+CH_3); 50.0 (N^+CH_2); 121.8, 123.6 (C-4 and C-5); 137.0 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 223 ($[C_{10}mim]^+$, 100%). ES^- *m/z* (% rel. intensity): 79 (Br^-, 100%).

3-Butyl-1,2-dimethylimidazolium bromide, $[C_4dmim]Br$

White crystalline solid is obtained (95% yield).

^{1}H-NMR (500 MHz, d_1-Chloroform): δ/ppm = 0.97 (t, J = 7.5 Hz, 3H, butyl-CH_3); 1.40 (m, 2H, butyl-CH_2); 1.82 (m, 2H, butyl-CH_2); 2.82 (s, 3H, 2-CH_3), 4.02 (s, 3H, N^+CH_3); 4.19 (t, J = 7.5 Hz, 2H, N^+CH_2); [7.41 (d, J= 1.2 Hz, 1H); 7.65 (d, J= 1.2 Hz, 1H)] (4,5-H). ^{13}C-NMR (125 MHz, d_1-Chloroform): δ/ppm = 11.9 (C-2-CH_3); 19.6 (butyl-CH_3); 13.5, 31.4 (butyl-CH_2); 36.2 (N^+CH_3); 48.8 (N^+CH_2); 120.9, 123.0 (C-4 and C-5). Electrospray MS: ES^+ *m/z* (% rel. intensity): 153 ($[C_4dmim]^+$, 100%). ES^- *m/z* (% rel. intensity): 79 (Br^-, 90%).

3-Hexyl-1,2-dimethylimidazolium bromide, $[C_6dmim]Br$

White crystalline solid is obtained (95% yield).

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.82 (t, J = 6.7 Hz, 3H, hexyl-CH_3); 1.26-1.32 (m, 6H, hexyl-$(CH_2)_3$); 1.76 (m, 2H, hexyl-CH_2); 2.77 (s, 3H, 2-CH_3), 3.98 (s, 3H, N^+CH_3); 4.16 (t, J = 7.5 Hz , 2H, N^+CH_2); [7.45 (d, J= 2.0 Hz, 1H); 7.71 (d, J= 2.0 Hz, 1H)] (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 10.9 (C-2-CH_3); 13.8 (hexyl-CH_3); 22.3, 25.88, 29.7, 31.0 (hexyl-CH_2); 36.1 (N^+CH_3); 48.9 (N^+CH_2); 121.0, 121.0 (C-4 and C-5); 143.6 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 181 ($[C_6dmim]^+$, 100%). ES^- *m/z* (% rel. intensity): 79 (Br^-, 90%).

3-Octyl-1,2-dimethylimidazolium bromide, $[C_8dmim]Br$

White crystalline solid is obtained (98% yield).

^{1}H-NMR (500 MHz, d_1-Chloroform): δ/ppm = 0.87 (t, J = 7 Hz, 3H, octyl-CH_3); 1.28-1.33 (m, 10H, octyl-$(CH_2)_5$); 1.84 (m, 2H, octyl-CH_2); 2.82 (s, 3H, 2-CH_3), 4.01 (s, 3H, N^+CH_3); 4.16 (t, J = 7.5 Hz, 2H,

N^+CH_2); [7.33 (d, J= 1.2 Hz, 1H); 7.58 (d, J= 1.2 Hz, 1H)] (4,5-H). ^{13}C-NMR (125 MHz, d_1-Chloroform): δ/ppm = 11.1 (C-2-CH_3); 14.0 (octyl-CH_3); 22.5, 26.4, 28.9, 29.0, 29.7, 31.6 (octyl-CH_2); 36.3 (N^+CH_3); 49.1 (N^+CH_2); 120.79, 122.9 (C-4 and C-5); 144.1 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 209 ([C_8dmim] $^+$, 100%); ES^- *m/z* (% rel. intensity): 79 (Br^-, 90%).

3-Decyl-1,2-dimethylimidazolium bromide, [C_{10}dmim]Br

White crystalline solid is obtained (96% yield).

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.84 (t, *J* = 6.7 Hz, 3H, decyl-CH_3); 1.24-1.32 (m, 14H, decyl-$(CH_2)_7$); 1.81 (m, 2H, decyl-CH_2); 2.81 (s, 3H, 2-CH_3), 4.02 (s, 3H, N^+CH_3); (t, *J* = 7.5 Hz, 2H, N^+CH_2); [7.40 (s, 1H); 7.70 (s, 1H)] (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 11.1 (C-2-CH_3); 14.0 (decyl-CH_3); 22.6, 26.4, 29.0, 29.2, 29.3, 29.4, 29.8, 31.8 (decyl-CH_2); 36.3 (N^+CH_3); 49.1 (N^+CH_2); 120.9, 123.1 (C-4 and C-5); 143.8 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 237 ([C_{10}dmim] $^+$, 100%); ES^- *m/z* (% rel. intensity): 79 (Br^-, 90%).

N,N-Butylmethylpyrrolidinium bromide, [C_4mpyrrol]Br

White crystalline solid is obtained (87% yield).

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.78 (t, *J* = 7.3 Hz, 3H, butyl-CH_3); 1.24 (m, 2H, butyl-CH_2); 1.57 (m, 2H, butyl-CH_2); 2.10 (s, 4H, 3-4 CH_2); 3.08 (s, 3H, N^+CH_3); 3.46 (t, *J* = 8.4 Hz, 2H, N^+CH_2), 3.63 (s, 4H, 2-5 N^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.24 (butyl-CH_3); 19.25 (butyl-CH_2); 21.2 (4-3 CH_2), 25.5 (butyl-CH_2); 48.22 (N^+CH_3); 63.5 (N^+CH_2); 64.0 (5-2 N^+CH_2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 142.1 ([C_4mpyrrol] $^+$, 100%), 365.1 ({[C_4mpyrrol]$_2$Br}$^+$, 10%).

N,N-Octylmethylpyrrolidinium bromide, [C_8mpyrrol]Br

White crystalline solid is obtained (79% yield).

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.88 (t, *J* = 6.6 Hz, 3H, octyl-CH_3); 1.27-1.39 (m, 10H, octyl-$(CH_2)_5$); 1.76 (m, 2H, octyl-CH_2); 2.31 (s, 4H, 3-4 CH_2); 3.29 (s, 3H, N^+CH_3); 3.65 (t, *J* = 8.1 Hz, 2H, N^+CH_2), 3.84-3.88 (d, J= 12.6 Hz, 4H, 2-5 N^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.7 (octyl-CH_3); 21.3 (4-3 CH_2), 22.2, 23.7, 26.0, 28.6, 28.8, 31.2 (octyl-CH_2); 48.3 (N^+CH_3); 63.8 (N^+CH_2); 64.1 (5-2 N^+CH_2).

Electrospray MS: ES^+ *m/z* (% rel. intensity): 198 ([C_8mpyrrol] $^+$, 100%); ES^- *m/z* (% rel. intensity): 79 (Br^-, 90%).

General procedure for synthesis of bis(trifluoromethanesulfonyl) imide anion ionic liquids:

A solution of lithium bis(trifluoromethanesulfonyl) imide (1.2 eq) in deionised water (25 cm^3) was prepared. To this was added slowly a solution of halide precursor (1 eq) in deionised water (25 cm^3) with stirring. The mixture was left for 4 h. The reaction mixture forms a biphasic system, where the bottom phase was the ionic liquid. Dichloromethane was added to extract the viscous ionic liquid from the aqueous phase and washed with deionised water (6 x 100 cm^3). The solvent was removed under *vacuum* at 50 ºC and the resulting colourless liquid was dried under high vacuum.

3-Butyl-1-methylimidazolium bis(trifluoromethanesulfonyl) imide,$[C_4mim][(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (94% yield).

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.95 (t, J = 7.3 Hz, 3H, butyl-CH_3); 1.35 (m, 2H, butyl-CH_2); 1.84 (m, 2H, butyl-CH_2); 3.93 (s, 3H, N^+CH_3); 4.16 (t, J = 7.35 Hz, 2H, N^+CH_2); 7.30 (s, 2H, 4,5-H); 8.72 (s, 1H, 2-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.2 (butyl-CH_3); 19.3 (butyl-CH_2); 31.9 (butyl-CH_2); 36.4 (N^+CH_3); 50.0 (N^+CH_2); 122.1, 123.7 (C-4 and C-5); 136.2 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 139 ($[C_4mim]^+$, 100%), 558 ($\{[C_4mim]_2[(CF_3SO_2)_2N]\}^+$, 12%).

3-Hexyl-1-methylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_6mim][(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (95% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.86 (t, J = 6.8 Hz, 3H, hexyl-CH_3); 1.25-1.33 (m, 6H, hexyl-$(CH_2)_3$); 1.84 (m, 2H, hexyl-CH_2); 3.91 (s, 3H, N^+CH_3); 4.13 (t, J = 7.5 Hz, 2H, N^+CH_2); 7.31 (d, J = 2.1 Hz, 2H, 4,5-H); 8.69 (s, 1H, 2-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.7 (hexyl-CH_3); 22.1, 25.7, 25.7, 29.9, 30.9 (hexyl-CH_2); 36.2 (N^+CH_3); 50.1 (N^+CH_2); 117.6-121.9 (CF_3); 122.2, 123.7 (C-4 and C-5); 135.8 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 186.77 ($[C_6dmim]^+$, 100%), 613.78 ($\{[C_6mim]_2[(CF_3SO_2)_2N]\}^+$, 95%). Elemental analysis: Calculated (%): C 32.2, H 4.6, N 9.4; Results (%): C 31.4, H 4.2, N 9.1

3-Octyl-1-methylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_8mim][(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (97 % yield).

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.79 (t, J = 6.6 Hz, 3H, octyl-CH_3); 1.26-1.31 (m, 10H, octyl-$(CH_2)_5$); 1.86 (m, 2H, octyl-CH_2); 3.95 (s, 3H, N^+CH_3); 4.16 (t, J = 7.5, 2H, N^+CH_2); [7.27 (s, 1H); 7.29 (s, 1H)] (4,5-H); 8.79 (s, 1H, 2-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 14.0 (octyl-CH_3); 22.5, 26.1, 28.8, 28.9, 30.0, 31.6 (octyl-CH_2); 36.4 (N^+CH_3); 50.3 (N^+CH_2); 122.0, 123.5 (C-4 and C-5); 136.2 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 195.1 ($[C8mim]^+$, 100%), 670.1 ($\{[C8mim]_2[(CF_3SO_2)_2N]\}^+$, 12). Elemental analysis: Calculated (%): C 35.4, H 4.8, N 8.8; Results (%): C 35.4, H 4.8, N 9.1.

3-Decyl-1-methylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_{10}mim][(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (90% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.86 (t, J = 6.6 Hz, 3H, decyl-CH_3); 1.24-1.30 (m, 14H, decyl-$(CH_2)_7$); 1.84 (m, 2H, decyl-CH_2); 3.92 (s, 3H, N^+CH_3); 4.14 (t, J = 7.5, 2H, N^+CH_2); [7.30 (d, J= 1.6 Hz, 1H); 7.32 (d, J= 1.6 Hz, 1H)] (4,5-H); 8.71 (s, 1H, 2-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 14.0 (decyl-CH_3); 22.6, 26.1, 28.8, 29.1, 29.2, 29.3, 30.0, 31.8 (decyl-CH_2); 36.2 (N^+CH_3); 50.2 (N^+CH_2); 117.6-121.9 (CF_3); 122.2, 123.7 (C-4 and C-5); 135.9 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 223.16 ($[C_{10}mim]^+$, 100%), 726.40 ($\{[C_{10}mim]_2[(CF_3SO_2)_2N]\}^+$, 25%). ES^- *m/z* (% rel. intensity): 280.11 ($[(CF_3SO_2)_2N]^-$, 10%). Elemental analysis: Calculated (%): C 38.2, H 5.4 , N 8.4; Results (%): C 38.2, H 5.4, N 8.1.

3-Ethyl-1, 2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_2dmim][(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (93% yield).

^{1}H-NMR (500 MHz, d_6-Acetone): δ/ppm = 1.49 (t, J = 7.32 Hz, 3H, ethyl-CH_3); 2.85 (s, 3H, 2-CH_3), 3.96 (s, 3H, N^+CH_3); 4.34 (q, J = 7.5 Hz, 2H, N^+CH_2); [7.61 (d, J= 1.2 Hz, 1H); 7.65 (d, J= 1.2 Hz, 1H)] (4,5-H). ^{13}C-NMR (125 MHz, d_6-Acetone): δ/ppm = 10.6(C-2-CH_3); 16.2 (ethyl-CH_3); 36.5 (N^+CH_3); 45.3 (N^+CH_2); 117.6-121.8 (CF_3); 122.3, 124.5 (C-4 and C-5); 146.5 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 125.06 ($[C_2dmim]^+$, 100%), ES^- *m/z* (% rel. intensity): 279.91 ($[(CF_3SO_2)_2N]^-$, 3.2%). Elemental analysis: Calculated (%): C 26.7, H 3.2, N 10.4; Results (%): C 26.8, H 3.2, N 10.2

3-Butyl-1, 2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_4dmim][(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (98% yield).

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.95 (t, J = 7.5 Hz, 3H, butyl-CH_3); 1.36 (m, 2H, butyl-CH_2); 1.76 (m, 2H, butyl-CH_2); 2.59 (s, 3H, 2-CH_3), 3.79 (s, 3H, N^+CH_3); 4.34 (t, J = 7.5 Hz, 2H, N^+CH_2); [7.16 (d, J= 2.1 Hz, 1H); 7.19 (d, J= 2.1 Hz, 1H)] (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 9.7 (2-CH_3); 13.3 (butyl-CH_3); 19.5, 31.4 (butyl-CH_2); 35.4 (N^+CH_3); 48.7 (N^+CH_2); 120.8, 122.5 (C-4 and C-5); 146.5 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 153.0 ($[C_4dmim]^+$, 100%), 585.9 ($[C_4dmim]_2[(CF_3SO_2)_2N]^+$, 10%). Elemental analysis: Calculated (%): C 30.5, H 3.9, N 9.7; Results (%): C 30.5, H 4.2, N 9.6.

3-Hexyl-1, 2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_6dmim][(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (95% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.85 (t, J = 6.7 Hz, 3H, hexyl-CH_3); 1.29 (m, 6H, hexyl-$(CH_2)_3$); 1.74 (m, 2H, hexyl-CH_2); 2.55 (s, 3H, 2-CH_3), 3.75 (s, 3H, N^+CH_3); 4.00 (t, J = 7.5 Hz, 2H, N^+CH_2); [7.15 (d, J= 2.1 Hz ,1H); 7.17 (d, J= 2.1 Hz, 1H)] (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 9.4 (hexyl-CH_3); 13.7 (C-2-CH_3); 22.2, 25.8, 29.4, 30.9 (hexyl-CH_2); 35.1 (N^+CH_3); 48.7 (N^+CH_2); 121.8-117.7 (CF_3); 120.7, 122.4 (C-4 and C-5); 143.6 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 186.77 ($[C_6dmim]^+$, 100%). ES^- *m/z* (% rel. intensity): 280.11 ($[(CF_3SO_2)_2N]^-$, 100%). Elemental analysis: Calculated (%): C 33.8, H 4.6, N 9.1; Results (%): C 34.1, H 4.5, N 9.2

3-Octyl-1, 2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_8dmim][(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (90.0% yield).

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.87 (t, J = 6.6 Hz, 3H, octyl-CH_3); 1.26-1.32 (m, 10H, octyl-$(CH_2)_5$); 1.79 (m, 2H, octyl-CH_2); 2.61 (s, 3H, 2-CH_3), 3.81 (s, 3H, N^+CH_3); 4.04 (t, J = 7.8 Hz, 2H, N^+CH_2); [7.15 (d, J= 2.1 Hz ,1H); 7.20 (d, J= 2.1 Hz, 1H)] (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 9.6 (C-2-CH_3); 14.0 (octyl-CH_3); 22.5, 26.3, 28.9, 28.9, 29.5, 31.6 (octyl-CH_2); 35.4 (N^+CH_3); 48.9 (N^+CH_2); 121.8-117.7 (CF_3); 120.7, 122.54 (C-4 and C-5); 143.6 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 208.9 ($[C_8dmim]^+$, 100%), 279.9 ($[(CF_3SO_2)_2N]^-$, 1.6%). Elemental analysis: Calculated (%): C 36.8, H 5.1, N 8.6; Results (%): C 37.0, H 4.9, N 8.5.

3-Decyl-1, 2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_{10}dmim][(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (92.0% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.86 (t, J = 6.7 Hz, 3H, decyl-CH_3); 1.24-1.32 (m, 14H, decyl-$(CH_2)_7$); 1.81 (m, 2H, decyl-CH_2); 2.81 (s, 3H, 2-CH_3), 4.02 (s, 3H, N^+CH_3); 4.17 (t, J = 7.5 Hz, 2H, N^+CH_2); [7.40 (d, J= 2.1 Hz ,1H); 7.70 (d, J= 2.1 Hz, 1H)] (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 11.1 (decyl-CH_3); 14.1 (decyl-CH_3); 22.6, 26.4, 29.0, 29.2, 29.3, 29.4, 29.8, 31.8 (decyl-CH_2); 36.3 (N^+CH_3); 49.0 (N^+CH_2); 121.8-117.7 (CF_3); 120.9, 123.1 (C-4 and C-5); 143.8 (C-2). Electrospray MS: ES^+ *m/z* (% rel. intensity): 237.19 ($[C_{10}dmim]^+$, 100%). ES^- *m/z* (% rel. intensity): 280.12 ($[(CF_3SO_2)_2N]^-$, 100%). Elemental analysis: Calculated (%): C 39.5, H 5.6, N 8.1; Results (%): C 39.5, H 5.7, N 8.1

N,N-Butylmethylpyrrolidinium bis(trifluoromethanesulfonyl) imide, $[C_4mpyrrol]$ $[(CF_3SO_2)_2N]$

Colourless viscous liquid obtained (84 % yield).

^{1}H-NMR (300 MHz, d_6-Acetone): δ/ppm = 0.99 (t, J = 7.2 Hz, 3H, butyl-CH_3); 1.44 (m, 2H, butyl-CH_2); 1.92 (m, 2H, butyl-CH_2); 2.33 (s, 4H, 3-4 CH_2); 3.28 (s, 3H, N^+CH_3); 3.56 (t, J = 8.1 Hz, 2H, N^+CH_2), 3.75

(s, 4H, 2-5 N^+CH_2). ^{13}C-NMR (75 MHz, d_6-Acetone): δ/ppm = 14.8 (butyl-CH_3); 21.4 (butyl-CH_2); 23.4 (4-3 CH_2), 27.3 (butyl-CH_2); 50.0 (N^+CH_3); 66.0 (N^+CH_2); 66.3 (5-2 N^+CH_2); 117.6-121.8 (CF_3). Electrospray MS: ES^+ *m/z* (% rel. intensity): 142.1 ($[C_4mpyrrol]^+$, 100%). ES^- *m/z* (% rel. intensity): 279.9 ($[(CF_3SO_2)_2N]^-$, 6.2%). Elemental analysis: Calculated (%): C 31.3, H 4.7, N 6.6. Results (%): C 31.5, H 4.2, N 6.4

N,N-Octylmethylpyrrolidinium bis(trifluoromethanesulfonyl) imide, $[C_8mpyrrol][(CF_3SO_2)_2N]$
Colourless viscous liquid obtained (85.0% yield).
^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.87 (t, *J* = 6.9 Hz, 3H, octyl-CH_3); 1.26-1.32 (m, 10H, octyl-$(CH_2)_5$); 1.73 (m, 2H, octyl-CH_2); 2.24 (s, 4H, 3-4 CH_2); 3.02 (s, 3H, N^+CH_3); 3.25 (t, *J* = 8.4 Hz, 2H, N^+CH_2), 3.50 (s, 4H, 2-5 N^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.8 (octyl-CH_3); 21.3 (4-3 CH_2); 22.4, 23.6, 26.0, 28.8, 28.7, 31.4 (octyl-CH_2); 48.2 (N^+CH_3); 64.4 (N^+CH_2); 64.7 (5-2 N^+CH_2); 117.6-121.8 (CF_3). Electrospray MS: ES^+ *m/z* (% rel. intensity): 198.2 ($[C_8mpyrrol]^+$, 100%), 592.0 ($\{[C_8mpyrrol]_2[(CF_3SO_2)_2N]\}^+$, 30%). Elemental analysis: Calculated (%): C 37.6, H 5.9, N 5.9; Results (%): C 37.8, H 5.5, N 5.8

Trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl) imide $[P_{66614}][(CF_3SO_2)_2N]$
Colourless viscous liquid obtained (95.0% yield).
^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.86 (t, *J* = 6.9 Hz, 3H, tetradecyl- CH_3); 0.88 (t, *J* = 6.4 Hz, 9H, hexyl-CH_2); 1.18-1.36 (m, 32H), 1.38-1.56 (m, 16H) (hexyl/tetradecyl-CH_2); 1.98-2.19 (m, 8H, P^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.91, 14.19 (hexyl- and tetradecyl-CH_3); 18.38, 19.00, 21.49, 21.55, 22.35, 22.77, 28.86, 29.34, 29.45, 29.57, 29.70, 29.74, 30.17, 30.36, 30.51, 30.70, 30.94, 32.01 (hexyl- and tetradecyl-CH_2); 120.00 (q, *J*CF = 320 Hz, CF_3). ^{31}P-NMR (121 MHz, d_1-Chloroform): δ/ppm = 34.97. Electrospray MS: ES^+ *m/z* (% rel. intensity): 483.5 ($[P_{66614}]^+$, 100%), 1247.0 ($\{[P_{66614}]_2[(CF_3SO_2)_2N]\}^+$, 10%). Elemental analysis: Calculated (%): C 53.3, H 8.9, N 1.8; Results (%): C 54.5, H 10.2, N 2.1

Synthesis of functionalised ionic liquids

Synthesis of ester and amide bromide: A solution of triethylamine (1.5 eq), hexan-1-ol or octan-1-ol or *N*-methyl-butylamine (1 eq) was prepared with dichloromethane (150 cm^3) and cooled down at -78 °C under a nitrogen atmosphere. Bromoacetyl bromide was added dropwise (1.5 eq). After stirring at -78 °C for 4 h the reaction mixture was allowed to warm up to -10 °C and quenched by addition of water (50 cm^3). The organic phase was washed with distilled water (3 x 50 cm^3), saturated ammonium chloride (3 x 50 cm^3), saturated sodium bicarbonate (3 x 50 cm^3) and brine (2 x 50 cm^3) then dried over magnesium sulfate,

filtered and solvents removed *via* rotary evaporation. The crude product was distilled to give a pale yellow oil. Acetamide product was extracted from the crude with hexane (3 x 50 cm^3) and filtered.

Hexylbromoacetate

Colourless liquid obtained (86.0% yield); Bp(3 mmHg): 90 ºC; ^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 4.17 (t, J = 6.7 Hz, 2H, CH_2O), 3.83 (s, 2H, CH_2Br), 1.66 (q, J = 6.74, 7.0 Hz, 2H, hexyl-CH_2), 1.38–1.25 (m, 6H, hexyl-$(CH_2)_3$), 0.89 (t, J = 6.8Hz, 3H, hexyl-CH_3); ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm= 167.2(CO), 66.4 (CH_2Br), 31.3, 28.3, 25.9, 25.6, 22.4(hexyl-CH_2), 13.9 (hexyl-CH_3).
Elemental analysis: Calculated (%): C 43.0, H 6.7; Results (%): C 42.6, H 6.8

Octylbromoacetate

Colourless liquid obtained (65.0% yield); Bp(3 mmHg): 120 ºC; ^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 4.15 (t, J = 6.7 Hz, 2H, CH_2O), 3.81 (s, 2H, CH_2Br), 1.64 (q, J = 6.7, 7.2 Hz, 2H, octyl-CH_2), 1.36–1.26 (m, 10H, octyl-$(CH_2)_5$), 0.86 (t, J = 6.6 Hz, 3H, octyl-CH_3). ; ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm= 167.3(CO), 66.4 (CH_2Br), 31.7, 29.1 (2xC), 28.4, 25.9, 25.7, 22.6 (octyl-CH_2), 14 (octyl-CH_3).
Elemental analysis: Calculated (%): C 47.8, H 7.6; Results (%): C 48.3, H 7.7

N-Butyl-*N*-methyl-2-bromoacetamide

Pale yellow oil obtained (68.0% yield) <u>*Denote both configurations</u>; ^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.91 (major, t, J = 7.3 Hz, 3H, butyl-CH_3) 0.95 (minor, t, J = 7.3 Hz, 3H, butyl-CH_3); 1.27-1.63* (m, 4H, butyl-CH_2); 2.93 (minor, s, 3H, NCH_3) 3.05 (major, s, 3H, NCH_3); 3.31 (minor, t, J = 7.6 Hz, 2H, NCH_2) 3.36 (major, t, J = 7.6 Hz, 2H, NCH_2); 3.84 (major, s, 2H, $BrCH_2$) 3.85 (minor, s, 2H, $BrCH_2$); ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 14.2 (minor) 14.3 (major) (butyl-CH_3); 20.3 (major) 20.4 (minor) (NCH_3); 26.3 (minor), 27.0 (major), 29.4 (major), 30.9 (minor) , 34.2 (minor), 36.5 (major)(butyl-CH_2); 48.5 (NCH_2); 51.2 (CH_2Br); 167.0 (major, CO) 167.1(minor, CO). Elemental analysis: Theoretical (%): C 40.4, H 6.7, N 6.7; Results (%): C 37.0, H 6.0, N 6.2

Synthesis of ester and amide IL-

3-Hexoxycarbonylmethyl-1,2-dimethylimidazolium bromide, [$C_6H_{13}OCOCH_2$dmim]Br

Yellow solid obtained (100% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.87 (t, J = 6.7 Hz, 3H, hexyl-CH_3); 1.34-1.28 (m, 6H, hexyl-$(CH_2)_3$); 1.65 (quintet, J = 6.6-7.1 Hz, 2H, hexyl-CH_2); 2.71 (s, 3H, 2-CH_3); 3.94 (s, 3H, N^+CH_3); 4.17 (t, J = 6.9 Hz, 2H, OCH_2); 5.41 (s, 2H, N^+CH_2); [7.58 (d, J = 2.1 Hz, 1H); 7.80 (d, J = 2.0 Hz, 1H)] (4,5-H).

^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 11.2 (2-CH_3); 13.9 (hexyl-CH_3); 22.4, 25.3, 28.3, 31.2 (hexyl-CH_2); 50.0 (OCH_2); 36.0 (N^+CH_3); 67. 0 (N^+CH_2); 122.3, 122.9(C-4 and C-5); 145.6 (C-2); 166.3 (CO). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 239.16 ($[C_6H_{13}OCOCH_2dmim]^+$, 100%), 559.27 ($\{[C_6H_{13}OCOCH_2dmim]_2Br\}^+$, 10%). ES^- *m/z* (% rel. intensity): 80.91 (Br^-, 100%).

N-Hexoxycarbonylmethyl-*N*-methylpyrrolidinium bromide, $[C_6H_{13}OCOCH_2mpyrrol]Br$

Yellow solid obtained (99.0% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.89 (t, *J* = 6.7 Hz, 3H, hexyl-CH_3); 1.36-1.30 (m, 6H, hexyl-$(CH_2)_3$); 1.67 (quintet, *J* = 6.5-7.4 Hz, 2H, hexyl-CH_2); 2.32-2.26 (m, 4H, 3-4 CH_2); 3.28 (s, 3H, N^+CH_3); 3.80-3,73 (m, 4H, 2-5 N^+CH_2); 4.22 (t, *J* = 6.8 Hz, 2H, OCH_2); 4.29 (s, 2H, N^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.9 (hexyl-CH_3); 21.3 (3-4 CH_2); 22.4, 25.2, 28.2, 31.2 (hexyl-CH_2); 49.0 (N^+CH_3); 62.1 (OCH_2); 65.2 (5-2 N^+CH_2); 66.7 (N^+CH_2); 165.4 (CO). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 228.19 ($[C_6H_{13}OCOCH_2mpyrrol]^+$, 100%). ES^- *m/z* (% rel. intensity): 80.91 (Br^- ,100%).

3-Octoxycarbonylmethyl-1,2-dimethylimidazolium bromide, $[C_8H_{17}OCOCH_2dmim]Br$

Yellow solid obtained (73.1%)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.87 (t, *J* = 6.0 Hz, 3H, octyl -CH_3); 1.29-1.26 (m, 10H, octyl -$(CH_2)_5$); 1.66 (quintet, *J* = 6.9-6.8 Hz, 2H, octyl-CH_2); 2.74 (s, 3H, 2-CH_3); 3.94 (s, 3H, N^+CH_3); 4.18 (t, *J* = 6.9 Hz, 2H, OCH_2); 5.42 (s, 2H, N^+CH_2); [7.52 (d, *J* = 2.1 Hz, 1H), 7.79 (d, *J* = 2.1 Hz, 1H)] (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 11.2 (2-CH_3); 14.1 (octyl-CH_3); 22.6, 25.7, 28.3, 29.1 (2xC) 31.7 (octyl -CH_2); 36.0 (N^+CH_3); 50.1 (OCH_2); 67. 0 (N^+CH_2); 122.2, 122.9 (C-4 and C-5); 142.7 (C-2); 166.2 (CO). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 266.20 ($[C_8H_{17}OCOCH_2dmim]^+$, 100%), 613.36 ($\{[C_8H_{17}OCOCH_2dmim]_2Br\}^+$, 10%). ES^- *m/z* (% rel. intensity): 80.91 (Br^- ,100%).

N-Octoxycarbonylmethyl-*N*-methylpyrrolidinium bromide, $[C_8H_{17}OCOCH_2mpyrrol]Br$

Yellow solid obtained (99.5% yields)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.86 (t, *J* = 6.7 Hz, 3H, octyl-CH_3); 1.24-1.26 (m, 10H, octyl-$(CH_2)_5$); 1.63 (quintet, *J* = 6.7-7.0 Hz, 2H, octyl-CH_2); 2.20-2.34 (m, 4H, 3-4 CH_2); 3.46 (s, 3H, N^+CH_3); 4.08-4.17 (m, 4H, 2-5 N^+CH_2)(*J* = 7.1 Hz, 2H, OCH_2); 5.01 (s, 2H, N^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 14.0 (octyl-CH_3); 21.3 (3-4 CH_2); 22.5, 25.6, 28.2, 29.0 (2xC), 31.7 (octyl-CH_2); 49.0 (N^+CH_3); 62.1 (OCH_2); 65.2 (5-2 N^+CH_2); 66.7 (N^+CH_2); 165.2 (CO). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 256.22 ($[C_8H_{17}OCOCH_2mpyrrol]^+$, 100%). ES^+ *m/z* (% rel. intensity): (Br^-, 100%).

3-(*N*-butyl-*N*-methylcarbamoylmethyl)-1,2-dimethylimidazolium bromide,

$[C_4H_9CH_3NCOCH_2dmim]Br$

Brown viscous liquid obtained (50.0% yield)

Denote both configurations ^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.91 (major, t, J = 7.3 Hz, 3H, butyl -CH_3) 0.99 (minor, t, J = 7.3 Hz, 3H, butyl-CH_3); 1.23-1.45 (m, 2H, butyl-CH_2); 1.51 (major, m, 2H, butyl-CH_2) 1.66 (minor, m, 2H, butyl-CH_2); 2.72 (major, s, 3H, 2-CH_3) 2.71 (minor, s, 3H, 2-CH_3); 3.21 (major, s, 3H, NCH_3) 2.94 (minor, s, 3H, NCH_3); 3.35 (t, J = 7.5 Hz, 2H, NCH_2) 3.48 (minor, t, J = 7.6 Hz, 2H, NCH_2); 3.88 (major, s, 3H, N^+CH_3) 3.86 (minor, s, 3H, N^+CH_3); 5.74 (major, s, 2H, N^+CH_2) 5.66 (minor, s, 2H, N^+CH_2); 7.29 (major, dd, J = 2.0 Hz, 1H) 7.32 (minor, dd, J = 2.0 Hz, 1H), 7.68 (major, dd, J = 2.0 Hz, 1H) 7.61 (minor, dd, J = 2.0 Hz, 1H) (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 11.17 (2-CH_3); 13.7 (butyl-CH_3); 20.0 (NCH_3); 29.1, 30.1 (butyl-CH_2); 36.7 (N^+CH_3); 48.7 (NCH_2); 51.2 (N^+CH_2); 121.7, 124.5 (C-4* and C-5*); 138.5 (C-2); 169.7 (major, CO) 169.1(minor, CO). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 224.17 ($[C_4H_9CH_3NCOCH_2dmim]^+$, 100%). ES^- *m/z* (% rel. intensity): 80.91 (Br^-, 100%).

N'-(*N*-butyl-*N*-methylcarbamoylmethyl)-*N'*-methylpyrrolidinium bromide, $[C_4H_9CH_3NCOCH_2mpyrrol]Br$

Brown viscous liquid obtained (76.0% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.91 (major, t, J = 7.3 Hz, 3H, butyl-CH_3); 0.95 (minor, t, J = 7.3 Hz, 3H, butyl-CH_3); 1.41-1.17 (m, 2H*, butyl-CH_2); 1.48 (major, m, 2H, butyl-CH_2); 1.61 (minor, m, 2H, butyl-CH_2); 2.16-2.33 (m, 4H*, 3-4 CH_2); 2.91 (minor, 3H, NCH_3); 3.13 (major, 3H, NCH_3); 3.32 (major, J = 7.1 Hz, 2H, NCH_2); 3.46-3.39 (m, minor (2H, NCH_2), 3H*, N^+CH_3) ; 4.07* (m, 4H, 2-5 N^+CH2); 5.10 (minor, s, 2H, N^+CH_2), 5.17 (major, s, 2H, N^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.7 (butyl-CH_3); 20.0* (4-3 CH_2); 21.4 (major, NCH_3); 23.7 (minor, NCH_3); 29.1 (major), 30.4 (minor) 33.6 (minor) , 35.2(major) (butyl-CH_2); 48.11* (N^+CH_3); 63.3 (major, N^+CH_2) 63.0 (minor, N^+CH_2); 65.52 (major, 2-5 N^+CH_2) 65.66 (minor, 2-5 N^+CH_2); 163.2 (minor, CO); 163.4 (major, CO). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 213.19 ($[C_4H_9CH_3NCOCH_2mpyrrol]^+$, 100%).$ES^-$ *m/z* (% rel. intensity): 80.91 (Br^-, 100%).

Metathesis of ester and amide precursors, $[cation][(CF_3SO_2)_2N]$

3-Hexoxycarbonylmethyl-1,2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide,

$[C_6H_{13}OCOCH_2dmim][(CF_3SO_2)_2N]$

Yellow viscous liquid obtained (67.0% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.89 (t, J = 6.7 Hz, 3H, hexyl-CH_3); 1.30 (m, 6H, hexyl-$(CH_2)_3$); 1.67 (m, 2H, hexyl-CH_2); 2.56 (s, 3H, 2-CH_3); 3.82 (s, 3H, N^+CH_3); 4.20 (t, J = 6.7 Hz, 2H, OCH_2); 4.92 (s, 2H, N^+CH_2); 722 (d, J = 2.2 Hz, 1H), 7.24 (d, J = 2.2 Hz, 1H) (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 9.9 (2-CH_3); 13.9 (hexyl-CH_3); 22.4, 25.3, 28.2, 31.2 (hexyl-CH_2); 35.5 (N^+CH_3); 49.3 (OCH_2); 67.2 (N^+CH_2); 117.6-121.8 (CF_3); 122.3, 122.4(C-4 and C-5); 145.5 (C-2); 165.7 (CO). Electrospray mass spectrum: ES$^+$ *m/z* (% rel. intensity): 239.16 ($[C_6H_{13}OCOCH_2mim]^+$, 100%). ES$^-$ *m/z* (% rel. intensity): 758.26 ($\{[C_6H_{13}OCOCH_2min]_2[(CF_3SO_2)_2N]\}^+$, 20%). Elemental analysis: Calculated (%): C 34.7, H 4.4, N 8.1; Results (%): C 34.6, H 4.4, N 8.1

3-Octoxycarbonylmethyl-1,2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide, $[C_8H_{17}OCOCH_2dmim][(CF_3SO_2)_2N]$

Yellow viscous liquid obtained (85.0% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.87 (t, J = 6.2 Hz, 3H, octyl -CH_3); 1.26-1.29 (m, 10H, octyl -$(CH_2)_5$); 1.65 (m, 2H, octyl-CH_2); 2.53 (s, 3H, 2-CH_3); 3.79 (s, 3H, N^+CH_3); 4.18 (t, J = 6.9 Hz, 2H, OCH_2); 4.9 (s, 2H, N^+CH_2); 7. 23 (d, J = 221 Hz, 1H), 7.24 (d, J = 2.2 Hz, 1H) (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 9.7 (2-CH_3); 14.1 (octyl-CH_3); 22.6, 25.6, 28.2, 29.0 (2xC) 31.7 (octyl -CH_2); 35.4 (N^+CH_3); 49.2 (OCH_2); 67.2 (N^+CH_2); 117.6-121.8 (CF_3); 122.3 (C-4 and C-5); 145.4 (C-2); 165.7 (CO). Electrospray mass spectrum: ES$^+$ *m/z* (% rel. intensity): 267.20 ($[C_8H_{17}OCOCH_2dmim]^+$, 100%), 814.34 ($\{[C_8H_{17}OCOCH_2min]_2[(CF_3SO_2)_2N]\}^+$, 20%). ES$^-$ *m/z* (% rel. intensity): 279.9 ($[(CF_3SO_2)_2N]^-$, 100%) Elemental analysis: Calculated (%): C 37.4, H 4.9, N 7.8; Results (%): C 37.8, H 5.2, N 7.4

N-Hexoxycarbonylmethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide, $[C_6H_{13}OCOCH_2mpyrrol][(CF_3SO_2)_2N]$

Faint yellow viscous liquid obtained (85.0% yield)

^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.89 (t, J = 6.7 Hz, 3H, hexyl-CH_3); 1.30-1.34 (m, 6H, hexyl-$(CH_2)_3$); 1.66 (m, 2H, hexyl-CH_2); 2.25-2.32 (m, 4H, 3-4 CH_2); 3.27 (s, 3H, N^+CH_3); 3,79- 3.83 (m, 4H, 2-5 N^+CH_2); 4.21 (t, J = 6.8 Hz, 2H, OCH_2); 4.26 (s, 2H, N^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.9 (hexyl-CH_3); 21.5 (3-4 CH_2); 22.4, 25.2, 28.1, 31.2 (hexyl-CH_2); 49.6 (N^+CH_3); 62.4 (OCH_2); 65.8 (5-2 N^+CH_2); 67.2 (N^+CH_2); 117.6-121.9 (CF_3); 164.5 (CO). Electrospray mass spectrum: ES$^+$ *m/z* (% rel. intensity): 228.18 ($[C_6H_{13}OCOCH_2mpyrrol]^+$, 100%), 736.30 ($\{[C_6H_{13}OCOCH_2mpyrrol]_2[(CF_3SO_2)_2N]\}^+$, 20%). ES$^-$ *m/z* (% rel. intensity): 279.90 ($[(CF_3SO_2)_2N]$, 100%) Elemental analysis: Calculated (%): C 35.4, H 5.1, N 5.5; Results (%): C 36.1, H 6.4, N 5.1

N-Octoxycarbonylmethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide,
$[C_8H_{17}OCOCH_2mpyrrol][(CF_3SO_2)_2N]$
Yellow viscous liquid obtained (80.0% yield)
^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.87 (t, J = 6.7 Hz, 3H, octyl-CH_3); 1.29-1.26 (m, 10H, octyl-$(CH_2)_5$); 1.65 (m, 2H, octyl-CH_2); 2.25-2.31 (m, 4H, 3-4 CH_2); 3.27 (s, 3H, N^+CH_3); 3.72-3.83 (m, 4H, 2-5 N^+CH_2) ; 4.21 (J = 6.9 Hz, 2H, OCH_2); 4.28 (s, 2H, N^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 14.2 (octyl-CH_3); 21.7 (3-4 CH_2); 22.4, 25.7, 28.3, 29.2 (2xC), 31.9 (octyl-CH_2); 49.7 (N^+CH_3); 62.4 (OCH_2); 65.9 (5-2 N^+CH_2); 67.3 (N^+CH_2); 117.8-122.0 (CF_3); 164.7 (CO). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 256.21 ($[C_8H_{17}OCOCH_2mpyrrol]^+$, 100%), 792.37 ($\{[C_8H_{17}OCOCH_2mpyrrol]_2[(CF_3SO_2)_2N]\}^+$, 15%). ES^- *m/z* (% rel. intensity): 279.9 ($[(CF_3SO_2)_2N]^-$, 100%) Elemental analysis: Calculated (%): C 35.4, H 5.1, N 5.5; Results (%): C 36.1, H 6.4, N 5.1

3-(*N*-butyl-*N*-methylcarbamoylmethyl)-1,2-dimethylimidazolium bis(trifluoromethanesulfonyl) imide,
$[C_4H_9CH_3NCOCH_2dmim][(CF_3SO_2)_2N]$
Brown viscous liquid obtained (75.0% yield) <u>*Denote both configurations</u>
^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.92 (major, t, J = 7.3 Hz, 3H, butyl -CH_3) 0.99 (minor, t, J = 7.2 Hz, 3H, butyl -CH_3); 1.23-1.68 (m, 4H*, butyl-CH_2); 2.71 (s*, 3H, 2-CH_3); 3.07 (major, s, 3H, NCH_3) 2.96 (minor, s, 3H, NCH_3); 3.33 (minor, t, J = 7.4 Hz, 2H, NCH_2) 3.38 (major, t, J = 6.5 Hz, 2H, NCH_2); 3.79 (major, s, 3H, N^+CH_3) 3.80 (minor, s, 3H, N^+CH_3); 5.06 (major, s, 2H, N^+CH_2) 5.07 (minor, s, 2H, N^+CH_2); 7.13 (m*, 1H), 7.19 (m*, 1H) (4,5-H). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 10.0 (*N^+CH_3); 13.7* (butyl-CH_3); 19.8 (minor, NCH_3), 19.9 (major, NCH_3); 29.0(major), 30.3 (minor), 33.8* (butyl-CH_2); 34.3 (minor, N^+CH_3) 35.4 (major, N^+CH_3); 49.1 (minor, NCH_2) 48.4 (major, NCH_2); 50.0 (*N^+CH_2); 117.6-118.6 (CF_3); 121.5-122.7 (C-4* and C-5*); 137.8 (C-2); 163.4 (*CO). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 224.17 ($[C_4H_9CH_3NCOCH_2dmim]^+$, 100%). ES^- *m/z* (% rel. intensity): 279.91 ($[(CF_3SO_2)_2N]^-$, 100%); Elemental analysis: Calculated (%): C 33.3, H 4.4, N 11.1; Results (%): C 33.8, H 4.3, N 10.1

N'-(*N*-butyl-*N*-methylcarbamoylmethyl)-*N'*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide
$[C_4H_9CH_3NCOCH_2mpyrrol][(CF_3SO_2)_2N]$
Brown viscous liquid obtained (85.0% yield) <u>*Denote both configurations</u>
^{1}H-NMR (300 MHz, d_1-Chloroform): δ/ppm = 0.93 (major, t, J = 7.3 Hz, 3H, butyl-CH_3); 0.95 (minor, t, J = 7.2 Hz, 3H, butyl-CH_3); 1.24-158 (m*, 4H, butyl-$(CH_2)_2$); 2.17-2.34 (m, 4H*, 3-4 CH_2); 2.94 (minor, 3H, NCH_3); 2.96 (major, 3H, NCH_3); 3.07 (minor, s, 3H, N^+CH_3), 3.29 (major s, 3H*, N^+CH_3); 3.23 (major, J = 7.6 Hz, 2H, NCH_2); 3.29 (major s, 3H*, N^+CH_3); 3.36 (major, t, J = 7.6 Hz, 2H, NCH_2); 3.69-3.91 (m*, 4H,

2-5 N^+CH_2); 4.27 (minor, s, 2H, N^+CH_2), 4.35 (major, s, 2H, N^+CH_2). ^{13}C-NMR (75 MHz, d_1-Chloroform): δ/ppm = 13.7 (minor, butyl-CH_3) 13.6 (major, butyl-CH_3); 19.7 (minor, 4-3 CH_2), 19.9 (major, 4-3 CH_2); 21.5 (major, NCH_3); 21.4 (minor, NCH_3); 28.9 (major), 30.1 (minor) 33.5 (minor), 34.3 (major) (butyl-CH_2); 48.1 (minor, N^+CH_3), 49.6 (major, N^+CH_3); 63.0 (minor, N^+CH_2), 63.1 (major, N^+CH_2); 65.9 (major, 2-5 N^+CH_2), 66.0 (minor, 2-5N^+CH_2); 117.6-118.6 (CF_3); 162.5 (CO). Electrospray mass spectrum: ES^+ *m/z* (% rel. intensity): 213.19 ($[C_4H_9CH_3NCOCH_2mpyrrol]^+$, 100%). ES^- *m/z* (% rel. intensity): 279.91 ($[(CF_3SO_2)_2N]^-$, 100%). Elemental analysis: Calculated (%): C 34.1, H 5.1, N 8.5; Results (%): C 34.7, H 5.4, N 7.7

Growth and biotransformation procedures

Source of micro-organism:

P. putida UV4 was kindly provided by Professor D.R. Boyd of the School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, N. Ireland.

Growth of *P. putida* UV4 in shack-flask cultures:

In these experiments the medium used contained 0.96 g L^{-1} KH_2PO_4, 1.23 g L^{-1} K_2HPO_4, 3.00 g L^{-1} NH_4Cl, 0.40 g L^{-1} $MgSO_4.7H_2O$ and 1.9 cm^3 (trace elements solution) L^{-1}._Components excluding the trace elements were dissolved in distilled water and the pH was adjusted to pH 7.0 with either potassium hydroxide solution (2 M) or hydrochloric acid (1 M) prior to sterilisation. The trace elements solution was sterilised separately and added to the sterilised medium in aseptic conditions._The trace elements solution was contained 50 g Na_2EDTA, 2.20 g $ZnSO_4.7H_2O$, 5.54 g $CaCl_2$, 5.06 g $MnCl_2.4H_2O$, 5.00 g $FeSO_4.7H_2O$, 1.10 g $(NH_4)_6Mo_7O_{24}.4H_2O$, 1.57 g $CuSO_4.5H_2O$ and 1.61 g $CoCl_2.6H_2O$ per litre of distilled water. The Na_2EDTA was dissolved prior to the addition of other components in distilled water by adjusting the pH to a value of 6.0 with potassium hydroxide (2 M). The other components were dissolved sequentially in the above order. The pH of the solution was adjusted to 6.0 with the potassium hydroxide solution prior to sterilisation._All cultures were grown at 30 ºC on a L.H.E. vari-speed orbital shaker, at 150 rpm. *P. putida* UV4 was grown on sodium pyruvate (5.0 g L^{-1}) as carbon and energy source.

Growth of micro-organisms on large scale:

P. putida UV4 was grown on the same medium. Although, the carbon and energy source used was then D-glucose (5.0 g L^{-1}). The concentration of phosphate was increased to 6.85 g KH_2PO_4 L^{-1}, for *P. putida* UV4.

General biotransformation procedure:

In all cases *P. putida* UV4 cells were grown in 2 L shake-flasks with 495 cm^3 of growth medium. These cell cultures were harvested in late exponential phase to perform the biotransformation. 50 mM of phosphate buffer at pH 7.2 and 2.5 g L^{-1} of carbon source were added in the neat medium prior biotransformation. The time-course experiments were performed with the volume of the neat medium of 100 cm^3. During biotransformation the flasks were sealed with a Suba-Seal to prevent loss of substrate._The cell density during biotransformation was dependent up on the type of organisms. The dry cell concentrations were within a narrow range of 0.5 to 0.8 g L^{-1} dcw. The biotransformations were conducted under batch conditions; therefore chlorobenzene was added at the start of the biotransformation at 1 cm^3 per litre of culture medium.

Isolation of the cis-dihydrodiols:

Biotransfomations on halobenzenes (0.50 cm3) were performed in 500 cm3 (x3) shake flasks containing 200 cm3 of freshly grown *P. putida* UV4 prior to addition of phosphate buffer (pH 7.2) and 5 g L-1 carbon source and energy source as described above. The reaction mixture was carried out for 24 h at 30 ºC and 150 rpm. The mixture was centrifuged prior to extraction of metabolite with ethyl acetate (50 cm3 x 5). The mother liquor was concentrated and purified by flash chromatography (20%:80% ethyl acetate:hexane) yielding to only the *cis*-(1*S*,2*S*)-1,2-dihydroxy-3-halocyclohexa-3,5-diene.[a]

[a.] Enzymatic and chemoenzymatic synthesis and stereochemical assignment of *cis*-dihydrodiol derivatives of monosubstituted benzenes, Derek R. Boyd, Narain D. Sharma, Breige Byrne, Mark V. Hand, John F. Malone, Gary N. Sheldrake, John Blacker and Howard Dalton, *J. Chem. Soc., Perkin Trans. 1* , 1998, 1935-1944.

***P. putida* UV4 catalysed biotransformation processes- supporting data:**

	Initial reaction rate – mM h^{-1}	Conversion 6 h - %
P. putida UV4	0.47 ± 0.01	36.8 ± 0.6
$[C_8dmim][NTf_2]$	2.10 ± 0.06	47.8 ± 0.2
$[C_4mpyrrol][NTf_2]$	N/O	N/O
$[C_8mpyrrol][NTf_2]$	0.56 ± 0.00	15.4 ± 0.0

Table S1: Biphasic biotransformation of chlorobenzene in the presence of pyrrolidinium based-ILs with *P. putida* UV4, 2.0% (V_{IL}/V_{aq}) IL, for OD_{600}= 0.9 or 0.35 g L^{-1} dcw. Calculated values show mean of duplicate samples.

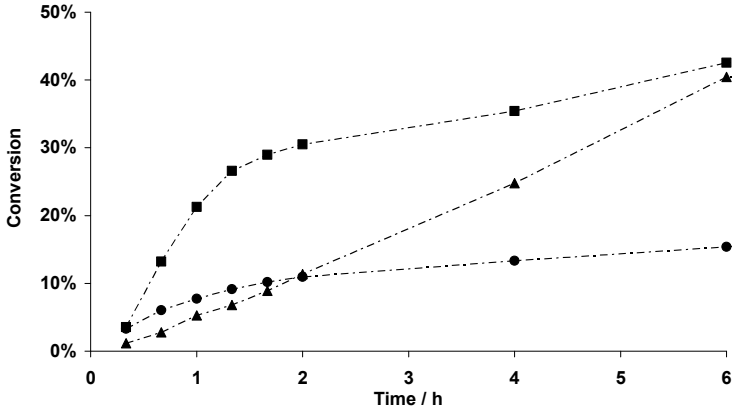

Figure S1: Biotransformation of chlorobenzene by *P. putida* UV4 in the presence of $[C_8mpyrrol][NTf_2]$. Conversion of 0.98 mmol chlorobenzene in a buffer pH 7.2, (▲) without IL and biphasic system volumetric ratio 2.0% (V_{IL}/V_{aq}) hydrophobic-IL (●) $[C_8mpyrrol][NTf_2]$ (■) $[C_8dmim][NTf_2]$. OD_{600}= 0.9 or 0.35 g L^{-1} dcw – Data points show mean of duplicate samples.

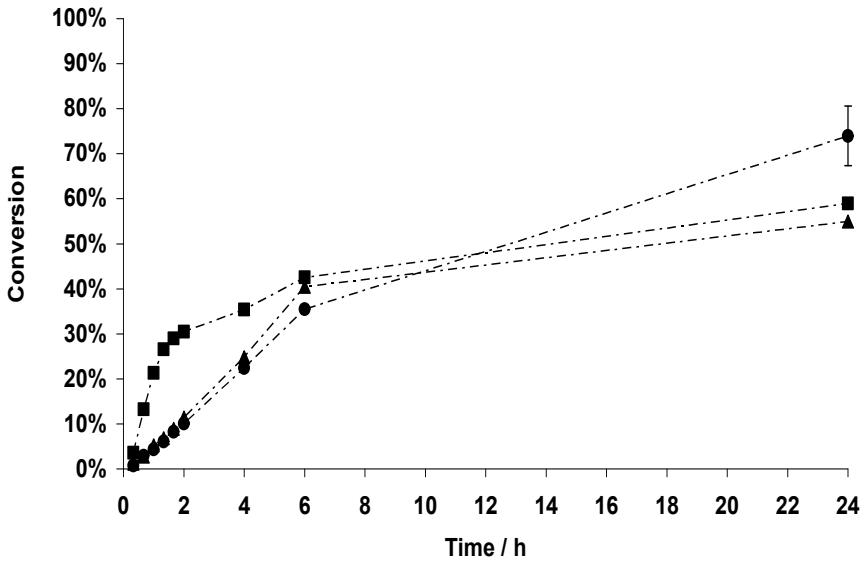

Figure S2: Biotransformation of chlorobenzene by *P. putida* UV4 in the presence $[P_{66614}][NTf_2]$. Conversion of 0.98 mmol chlorobenzene in a buffer (pH 7.2), (▲) without IL and biphasic system volumetric ratio 2.0% (V_{IL}/V_{aq}) hydrophobic-IL (●)$[P_{66614}][NTf_2]$ (■) $[C_8dmim][NTf_2]$. OD_{600}= 0.9 or 0.35 g L^{-1} dcw– Data points show mean of duplicate samples.

	Initial reaction rate – mM h^{-1}	Conversion 6 h - %
P. putida UV4	0.47 ± 0.01	36.8 ± 0.6
$[C_8dmim][NTf_2]$	2.10 ± 0.06	47.8 ± 0.2
$[P_{66614}][NTf_2]$	0.54 ± 0.03	35.5 ± 0.7

Table S2: Biphasic biotransformation of chlorobenzene in the presence of $[P_{66614}][NTf_2]$ with *P. putida* UV4, 2.0% (V_{IL}/V_{aq}) IL, for OD_{600}= 0.9 or 0.35 g L^{-1} dcw. Calculated values show mean of duplicate samples.

Ionic liquids solubility table:

	UV spectroscopy – mmol L^{-1} (cation)	IC – mmol L^{-1} (anion)
$[C_2mim][NTf_2]$	48.22 ± 0.20	51.64 ± 2.53
$[C_4mim][NTf_2]$	16.33 ± 0.18	17.77 ± 0.32
$[C_6mim][NTf_2]$	5.16 ± 0.11	5.57 ± 0.04
$[C_8mim][NTf_2]$	1.38 ± 0.02	1.67 ± 0.02
$[C_2dmim][NTf_2]$	32.18 ± 0.21	32.50 ± 0.41
$[C_4dmim][NTf_2]$	13.42 ± 0.04	12.42 ± 0.20
$[C_6dmim][NTf_2]$	3.94 ± 0.02	3.47 ± 0.06
$[C_8dmim][NTf_2]$	1.06 ± 0.01	1.38 ± 0.21

Table S3: Concentration at saturation of hydrophobic ionic liquids in water at 30ºC quantified with by two different analytical methods. Calculated values show mean of duplicate samples.

	Solubility in water - mmol L^{-1}
$[C_4mpyrrol][NTf_2]$	12.82 ± 0.86
$[C_8mpyrrol][NTf_2]$	0.92 ± 0.01

Table S4: $[C_nmpyrrol][NTf_2]$, solubility at saturation in pure water at 30ºC. Quantification method using ion chromatography, $[NTf_2]^-$. Calculated values show mean of duplicate samples.

	Density – g cm^{-3}	Viscosity - cPs
$[C_4H_9CH_3NCOCH_2dmim][NTf_2]$	1.3906	981.4
$[C_4H_9CH_3NCOCH_2mpyrrol][NTf_2]$	1.3714	414.2
$[C_6H_{13}OCOCH_2dmim][NTf_2]$	1.3609	299.1
$[C_8H_{17}OCOCH_2dmim][NTf_2]$	1.3177	340.7
$[C_6H_{13}OCOCH_2mpyrrol][NTf_2]$	1.3349	149.9
$[C_8H_{17}OCOCH_2mpyrrol][NTf_2]$	1.2881	252.8
$[C_8dmim][NTf_2]$	1.2938	114.2
$[C_8mpyrrol][NTf_2]$	1.2796	144

Table S5: Density and viscosity of novel ILs at 30 ºC

	Initial reaction rate – mM h^{-1}	Conversion 6 h - %
P. putida UV4	0.20 ± 0.02	33.4% ± 0.4%
$[C_8dmim][NTf_2]$	1.42 ± 0.11	67.6% ± 1.7%
$[C_6H_{13}OCOCH_2dmim][NTf_2]$	1.49 ± 0.05	67.2% ± 2.3%
$[C_8H_{17}OCOCH_2dmim][NTf_2]$	1.24 ± 0.23	60.1% ± 5.8%

Table S6: Biphasic biotransformation of chlorobenzene, 0.98 mmol, in the presence of ester-IL, 0.15% (V_{IL}/V_{aq}) IL, by *P. putida* UV4. Influence of ester side chains on imidazolium-based ILs, 0.78 g L^{-1} dcw, on the conversion of substrate – Data points show mean of duplicate samples.

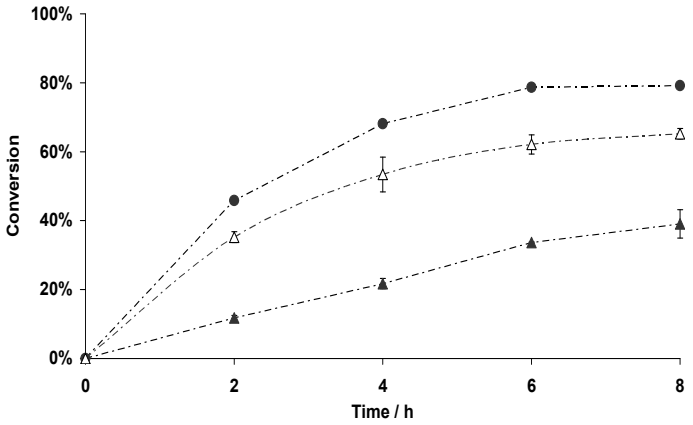

Figure S3: Effect of [C_8mpyrrol]Br & [C_8dmim]Br on the biotransformation of 0.98 mmol of chlorobenzene (pH 7.2) by *P. putida* UV4. Symbols (▲) Without inhibitor, (Δ) 4 mM [C_8mpyrrol]Br and (●) 2.4 mM [C_8dmim]Br. OD_{600}= 1.8 or 0.70 g L^{-1} dcw. Data points show mean of duplicate samples.

Inhibition of oxygen consumption.

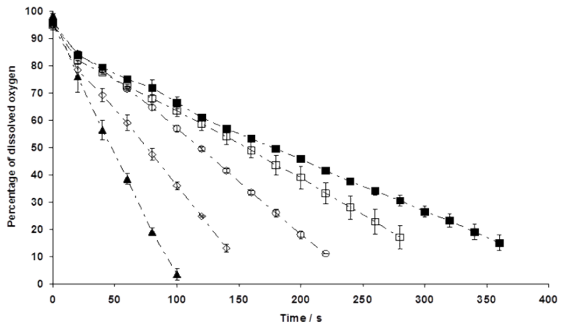

Figure 3a: Inhibition of oxygen consumption of *P. putida* UV4 by sodium azide. Symbol: (▲) Without inhibitor, Variation of the concentration of sodium azide symbols: (◊) 4.0, (○) 7.9, (□) 11.9 and (■) 15.5 mM. OD_{600}: 1.6 or 0.62 g L^{-1} dcw. Data points show mean of duplicate samples.

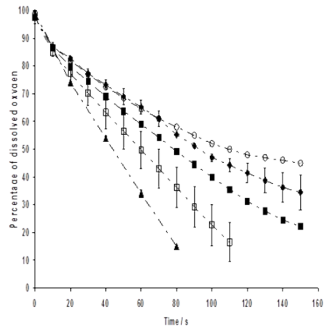

Figure 3b: Inhibition of oxygen consumption of *P. putida* UV4 by potassium cyanide. Symbol: (▲) Without inhibitor, Variation of the concentration of potassium cyanide symbols: (□) 0.78, (■) 2.4, (♦) 3.9 and (○) 4.7 mM. OD_{600}: 1.7 or 0.66 g L^{-1} dcw. Data points show mean of duplicate samples.

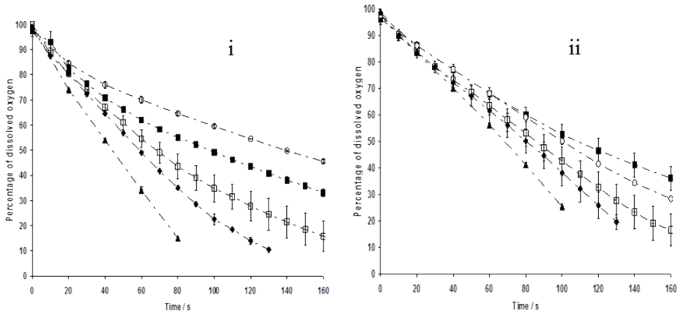

Figure 3.c: Inhibition of oxygen consumption of *P. putida* UV4 by [C_8dmim]Br & [C_8mpyrrol]Br. Symbol: (▲) Without inhibitor, i) Variation of the concentration of [C_8dmim]Br symbols: (♦) 2, (□) 4, (■) 8 and (○) 12 mM. ii) Variation of the concentration of [C_8mpyrrol]Br symbols: (♦) 4, (□) 8, (■) 10 and (○) 12 mM. OD_{600}: 1.7 or 0.66 g L^{-1} dcw. Data points show mean of duplicate samples.

Graphical determination of K_i

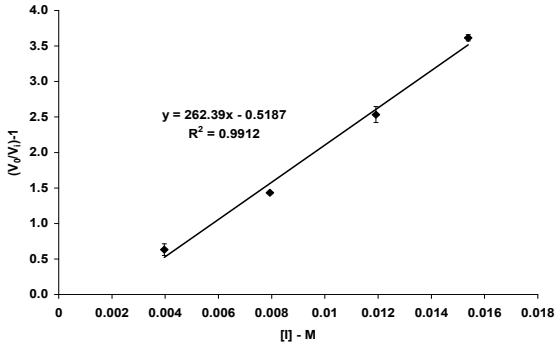

Figure E.1: Determination of $1/K_{i(app)}$ for sodium azide. *P. putida* UV4, OD_{600}: 1.6 or 0.62 g/L dcw. Data points show mean of duplicate samples.

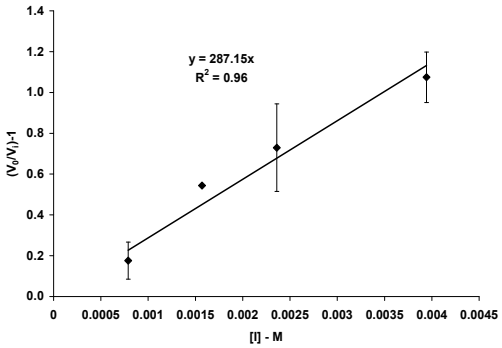

Figure E.2: Determination of $1/K_{i(app)}$ for potassium cyanide. *P. putida* UV4, OD_{600}: 1.7 or 0.66 g/L dcw. Data points show mean of duplicate samples.

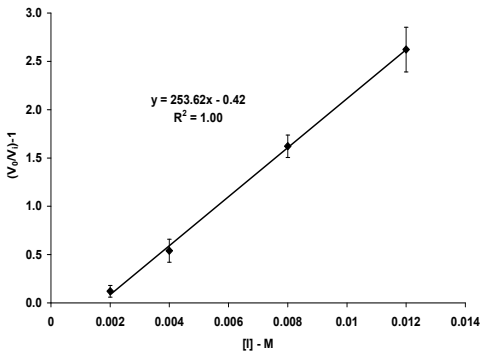

Figure E.3: Determination of $1/K_{i(app)}$ for $[C_8dmim]Br$. *P. putida* UV4, OD_{600}: 1.7 or 0.66 g/L dcw. Data points show mean of duplicate samples.

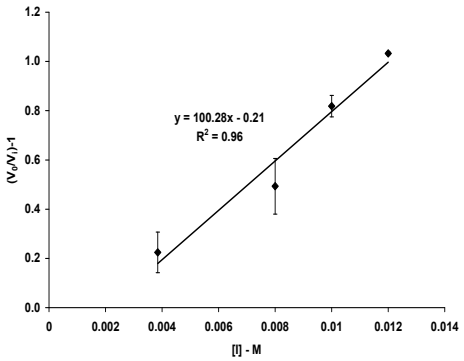

Figure E.4: Determination of $1/K_{i(app)}$ for [C_8mpyrrol]Br. *P. putida* UV4, OD_{600}: 1.7 or 0.66 g/L dcw. Data points show mean of duplicate samples.